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*Keywords*: Sulphate reducing bacteria, Sulphide, Groundwater.

## Update notice

The original report, dated December 2010, was found to contain both factual and editorial errors which have been corrected in this updated version. The corrected factual errors are presented below.

### Updated 2013-01

| Location | Original text | Corrected text |
|---|---|---|
| Page 213 | Delos A, Trinchero P, Dentz M, Pitkänen P, Richard L, Molinero J, 2010. Quantitative assessment of deep gas migration in Fennoscandian sites. SKB-XXX, draft version. Svensk Kärnbränslehantering AB. | Delos A, Trinchero P, Richard L, Molinero J, Dentz M, Pitkänen P, 2010. Quantitative assessment of deep gas migration in Fennoscandian sites. SKB R-10-61, Svensk Kärnbränslehantering AB. |

# Abstract

Sulphide concentrations in groundwater play a key role in the long-term reliability of the metal canisters containing the radioactive waste within a disposal facility for nuclear waste. This is because sulphide in the groundwaters circulating in the vicinity of the deposition tunnels can react with copper in the canisters causing corrosion and therefore reducing their expected lifetime; in a worst case scenario erosion of the bentonite buffer material will expose the canister more rapidly to the fracture groundwater.

Sulphide in the groundwater is predominantly microbially produced and thereby controlled by the content of oxidised sulphur sources, organics (carbon sources), reductants (mainly Fe(II), DOC, $H_2$ and $CH_4$), and also flow and mixing of different groundwater types. In addition, achieved saturation in respect to amorphous Fe-monosulphide will control the possible maximum values and will also limit the $Fe^{2+}$ and $S^{2-}$ values in the groundwater.

The aim of this report is to assess realistic, representative and reliable sulphide groundwater concentrations at present conditions in Forsmark and also to evaluate possible changes during different climatic conditions covering the repository operation period (some tens to hundreds of years), post closure conditions (some thousand of years) and the proceeding temperate period (some tens of thousands of years) which may be extended due to enhanced greenhouse effects etc. It is expected that this period will be followed by the onset of the next glaciation during which periglacial (permafrost), glacial and postglacial conditions may succeed each other.

To achieve these aims, an evaluation is performed of all the sulphide-related data reported from the Forsmark site investigations /Laaksoharju et al. 2008/ and later monitoring campaigns, all of which are stored in the Sicada database. This evaluation shows that values from the Complete Chemical Characterisation (CCC) sampling are usually lower than those measured during the monitoring phase. When both CCC and monitoring values are available from one borehole section two values are used, one representing each of the sampling methods. When time series are measured in the monitoring sections, in most cases the sulphide values are higher in the downhole tubing and in the borehole section compared with groundwater from the surrounding fractures. The routinely carried out removal of five borehole section water volumes prior to monitoring are in most cases inadequate to obtain representative samples from the bedrock fractures, i.e. without elevated sulphide due to contamination from the initial stagnant water from the borehole section. It is, however, assumed that the two groundwater samples from the same water conducting structures, i.e. the sample from the monitoring and the sample from the CCC sampling, the latter usually showing lower sulphide, spans the interval of representative sulphide values in the formation water.

For most of the CCC and monitoring sections the last sample in the time series is suggested as representing the ‘best possible’ value. It is worth noting that the plug flow calculations have proven to be very useful in order to judge the water volumes needed to be pumped at each monitored section before obtaining a sample sufficiently representative of the fracture groundwater.

Practically all sulphide concentrations at Forsmark are $\leq 0.013$ mmol/L (~0.4 mg/L). There is, however, a probability that for some deposition location in the repository the surrounding groundwaters may have sulphide concentrations as high as 0.12 mmol/L (~4 mg/L). In order to estimate canister corrosion rates in the SR-Site during a full glacial cycle, it is recommended that the observed distribution of sulphide in groundwaters at Forsmark during the present temperate conditions should be used. Furthermore, it should be noted that the present sulphide concentrations have been sampled after a recent period of possible intrusion of marine sulphate-rich waters.

# Sammanfattning

Mängden sulfid i grundvattnet har central betydelse för kopparkapslarnas livslängd i ett förvar för använt kärnbränsle. Sulfiden skulle kunna reagera med kopparn och därmed minska kapslarnas livslängd. Sulfid i grundvattnet produceras i huvudsak via microbiella reaktioner (sulfatreduktion) och är därför relaterad till mängden sulfat, organiskt material (som kolkälla), samt tillgängliga reduktanter (t.ex Fe(II), DOC, $H_2$ och $CH_4$). Mängden löst sulfid i grundvattnet kommer att begränsas genom mättnad med avseende på amorf Fe-monosulfid, vilket också medför att mängden löst Fe(II) och sulfid är relaterade till varandra.

Syfte med föreliggande rapport är att ange realistiska och trovärdiga sulfidvärden för de olika grundvattentyperna i Forsmark under nuvarande förhållanden. Dessa har stor betydelse i ett scenario där bufferten eroderas bort och kapseln exponeras för sulfid i grundvattnet. De aktuella sulfidvärdena används sedan för att blicka framåt och förutsäga troliga sulfidhalter under olika framtida perioder såsom: Öppet förvar (tio till hundra år), efter stängningen (några tusentals år), och den påföljande tempererade perioden (kanske tiotusen år). Den sistnämnda perioden kan bli längre beroende på växthuseffekten. Efter de temperarade perioderna kommer nästa glaciation som startar med permafrost och övergår i glaciala förhållanden med påföljande deglaciation.

För att uppnå syftet med rapporten har det gjorts en förnyad genomgång av de sulfidrelaterade parametrarna som redovisades i /Laaksoharju et al. 2008/ samt en noggrann genomgång av alla data från den senare grundvattenmoniteringen till och med 2009. All data har inhämtats från SKBs databas Sicada. Sulfidvärdena från den kompletta kemiska karakteriseringen (CCC) är vanligtvis påtagligt mycket lägre än de från moniteringsprogrammet. Från vissa sektioner finns analyser både från CCC och den senare moniteringen tillgängliga från samma vattenförande struktur i ett och samma borhål, och i dessa fall visar moniteringsvärdena med något enstaka undantag betydligt högre värden än de som erhållits vid CCC-provtagningen. Det kan emellertid antas att sulfidhalterna i den vattenförande strukturen representeras av spannet mellan CCC provet och moniteringsprovet. Under hösten 2009 gjordes en mer omfattande provtagning i samband med moniteringen, där en tidsserie om 5 prover (motsvarande 5 sektionsvolymer från borrhållet) analyserades. I de flesta fall visade de första proven (representerande volymen som stått i kontakt med utrustningen och själva borrhålssektionen) de högsta sulfidvärdena. När pumpningen fortsatte sjönk sulfidhalterna men stabiliserades vanligtvis inte . Detta innebär att de 5 sektionsvolymer som pumpades bort var för lite för att erhålla stabila värden som representerar grundvatten i sprickorna i berget. För de flesta borrhålssektionerna valdes ändå det sista provet i tidsserien som användbart eftersom det kan betraktas som ett maximivärde. Det bör noteras att hydrauliska ”pluggflödes” beräkningar för de provtagna sektionerna visade bra överstämmelse med de erhållna resultaten vilket innebär att denna typ av beräkningar kan vara till stor hjälp inför kommande provtagningar när det gäller att planera hur många sektionsvolymer som behöver pumpas bort för att få representativa prover. Praktiskt taget alla sulfidhalter i grundvattnet i Forsmark visar värden ≤ 0.013 mmol/L (~0.4 mg/L). Det finns emellertid en möjlighet att grundvattnet i närheten av vissa deponeringshål, under någon period, kommer att ha högre koncentrationer (upp till 0.12 mmol/L (~4 mg/L)). För att uppskatta korrosionshastigheter för kapslarna under en hel glacial-cykel rekommenderas den statistiska fördelningen av de utvalda sulfidhalterna under nuvarande förhållanden. Det bör i detta perspektiv påpekas att de nuvarande sulfidhalterna har uppmätts efter en period av intrusion av marint vatten (Littorina perioden) och att sulfathalten i grundvattnet därför får betraktas som relativt hög.

# Contents

**Appendix 2**

# 1 Introduction

## 1.1 Background

This report is part of the SR-Site safety assessment /SKB 2011/ for a repository in Forsmark based on the KBS-3 concept, cf. Figure 1-1. The final purpose is to provide a groundwater sulphide data set for use in the long term safety assessment modelling, and in this respect the present report constitutes a background report to SR-Site's Data Report /SKB 2010a/. A similar dataset with sulphide groundwater data will be presented for the Laxemar site in a separate report /SKB 2010b/.

In the safety assessment perspective for nuclear waste disposal, sulphide concentrations in groundwater play a key role in the long-term stability of the copper canisters containing the waste. Sulphide in the fracture groundwaters circulating in the vicinity of the deposition tunnels can react with the copper in the canisters causing corrosion and therefore reducing their expected lifetime. As long as the bentonite buffer remains intact, sulphide formed by SRB (Sulphate-reducing bacteria) in the groundwater at the boundary between the rock and the compacted bentonite buffer only reaches the container by diffusion with very little or no sulphate reduction taking place in the bentonite matrix /King et al. 1999, Pedersen 2010/, although sulphide will react with available Fe on its way through the bentonite. However, rapid access to the canisters can result from erosion of the bentonite buffer material along water-conducting fractures intersecting the disposal borehole.

The chemical reaction of the copper corrosion process can be described as:

$$2Cu(s) + HS^{-} + H^{+} \leftrightarrow Cu_2S(s) + H_2(aq) \qquad 1\text{-}1$$

In the presence of sulphate and SRB, the hydrogen produced will be converted to additional sulphide according to:

$$\tfrac{1}{4}\, SO_4^{2-} + H_2(aq) + \tfrac{1}{4}\, H^{+} \rightarrow \tfrac{1}{4}\, HS^{-} + H_2O(l) \qquad 1\text{-}2$$

so that the overall reaction becomes:

$$2Cu(s) + 0.25\, SO_4^{2-} + 0.75\, HS^{-} + 1.25\, H^{+} \rightarrow Cu_2S(s) + H_2O(l) \qquad 1\text{-}3$$

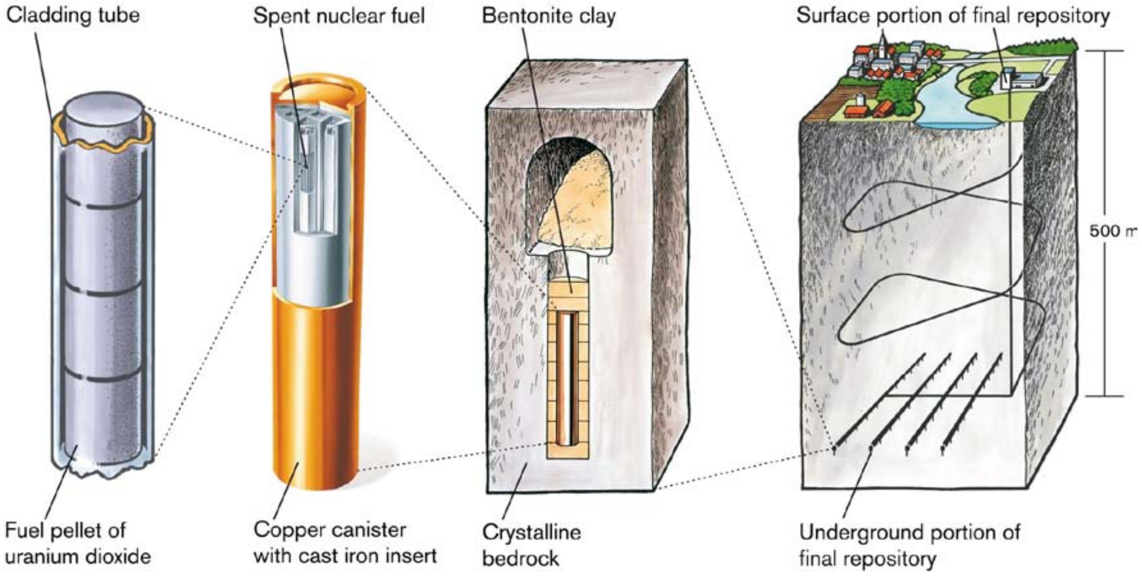


***Figure 1-1.*** *The KBS-3 concept for a repository for spent nuclear fuel in crystalline bedrock cf. /Gunnarsson et al. 2006/.*

Within the SR-Site project there is a need to judge if present day sulphide data selected for the Forsmark site are realistic, representative and reliable /SKB 2011/. In this context, 'representative' refers to a selected sulphide value that satisfies a number of criteria which reflect the complexity of the systems being studied, for example, taking into account the hydrogeochemistry, hydrogeology and fracture geometry of the sampled borehole section, and indirectly microbial effects. In addition, the potential influence of the downhole isolation and sampling equipment as potential sources of contamination has also played a major role.

Not only do the sulphide concentrations at present need to be defined, but the expected changes during a glacial cycle are also required in order to evaluate the extent of the corrosion of the canisters over long time periods. In order to estimate the changes in sulphide concentrations, it is necessary to have a good understanding of the processes behind sulphide production (e.g. by sulphate reduction). Because the temperature in the repository (outside the canisters) is not expected to exceed 100°C, the production of sulphide can only proceed through microbial processes. Therefore, it is important to understand the conditions and limiting factors for microbial sulphate reduction based on, for example, the available amounts of sulphate, organic carbon and reactive gases such as hydrogen and methane. Of importance is also the contents of Fe(II) in the groundwaters because the saturation of amorphous monosulphide will provide an upper limit for the the content of sulphide and ferrous iron in the groundwater.

## 1.2 Aim and scope

The aim of this report is to provide dependable sulphide groundwater concentrations for present day conditions at the Forsmark site and to comment on their associated uncertainties for the SR-Site safety assessment analyses.

Also included in this report are proposed changes (or lack of change) in values for different future time periods covering open repository conditions (some tens to hundreds of years), post closure conditions (some thousands of years) and the proceeding temperate period (some tens of thousands of years) which may be extended due to enhanced greenhouse effects etc. This is followed by the onset of the next glaciation (e.g. permafrost), glacial conditions and finally postglacial conditions.

Sulphide in the groundwater is microbially produced and thereby controlled by the content of sulphate, organics (carbon sources), reductants (mainly Fe(II), DOC, $H_2$ and $CH_4$), and also flow and mixing of different groundwater types. In addition, achieved saturation with respect to amorphous Fe-monosulphide will control the possible maximum values and will also bind the $Fe^{2+}$ and $S^{2-}$ values in the groundwater. Each of these factors will be addressed emphasising their potential effect on sulphide predictability.

To achieve these aims, an evaluation was performed of all the sulphide-related data reported from the Forsmark site investigations /Laaksoharju et al. 2008/ and later monitoring campaigns, all of which are stored in the Sicada database. This present report includes all the groundwater data from Forsmark where sulphide has been analysed and extracted from Sicada. From this dataset a reduced set of representative sulphide groundwater concentrations has been selected for Forsmark that can be used in subsequent modelling of canister corrosion within the SR-Site during "undisturbed" temperate periods. For other possible future conditions expected during different climatic periods of the repository evolution, data on sulphide concentrations are provided based on judgement of known processes and their expected extent during these varied conditions.

Data from other sites are sometimes used to support arguments made, for example in Figure 5-10, but only Forsmark data have been evaluated in this work. For site intercomparison purposes, the data from Laxemar is analysed in /SKB 2010b/.

It was discovered from the preinvestigation studies at the Äspö Hard Rock Laboratory (HRL) that long delays between drilling boreholes and the subsequent Complete Chemical Characterisation (CCC) investigations (i.e. time gaps of approximately four months to one year) resulted in high sulphide concentrations in CCC samples, cf. Section 3.1.5. A thorough discussion on conceptual and representativity uncertainties of the selected sulphide data are an important part of this work, both for the temperate periods based on present available data at Forsmark, and for other climatic periods where the data are mainly based on conceptual models (cf. Chapter 3 and 4).

## 1.3 Report structure

This study represents the integration of several disciplines which are interdependent and complex, and the report has been structured to systematically introduce each discipline and discuss the interrelationships between them. Some repetition between chapters is inevitable but generally this is considered to facilitate the reader.

The introduction to the study is detailed in Chapter 1 under background, aim and scope, report structure and finally an outline of the hydrogeochemical background to the Forsmark site emphasising groundwater evolution, composition and redox conditions. Chapter 2 introduces the major processes contributing to the production of sulphide in groundwaters involving microbial activity and water/rock interaction sources.

A critical part of the present study has been to establish and explain the sampling uncertainties surrounding the different methods used for groundwater sampling and analysis. Sampling methods may, to a varying extent, result in the interaction of hydrogeochemistry, hydrogeology, microbiology, downhole equipment materials and sample extraction rates and time. These are addressed in Chapter 3 and are discussed in relation to field studies carried out at Laxemar and Äspö. Information discussed ranges from: a) the recently completed Forsmark site investigations to overlapping and later monitoring programmes on selected borehole sections, b) a detailed *in situ* study in one borehole section at Laxemar, and c) observations from Äspö. Based on these studies, together with expert judgement from experience gained during the Forsmark and Laxemar site investigations, Chapter 4 details the selection criteria of 'representative' sulphide values for the Forsmark site safety case calculations. A thorough documentation of the selection procedure is presented in Appendix 1 and diagrams produced to visualise the sensitive changes in sulphide chemistry that occurred during sampling of the groundwater time series data are given in Appendix 2.

To put the selected sulphide values into a broader perspective, Chapter 5 provides an overview of present day hydrogeochemical conditions at Forsmark. The seven major groundwater types are introduced and then systematically the different chemical processes relevant to sulphide production are described and discussed. When it comes to gases (methane, carbon dioxide and hydrogen) the number of analyses available from Forsmark is relatvely small and therefore results from Laxemar and Olkiluoto have been included for comparison. Also evaluated is the correlation of sulphide with hydrogeological parameters. A comprehensive literature study of sulphate production rates in different hydrogeological environments has been carried out and presented in Appendix 3 and a short summary included in Chapter 5.

Finally, using present day conditions as a baseline, Chapter 6 outlines in tabular form expected changes during future climatric conditions and their potential influence on sulphide production.

The main conclusions as bullets are presented in Chapter 7, the acknowledgements in Chapter 8 and references in Chapter 9.

There is a necessity to explain the units used in the report. For sulphide and other groundwater compositions given in the tables (Appendix 1), in the scatter plots (Appendix 2) and in Table 4.1 (which represents data direct from Sicada), 'mg/L' has been retained. However, in order to facilitate comparison of different concentrations of sulphur compounds, mmol/L has been preferred over the previously used mg/L. Generally, it takes 1 methane or DOC + 1 sulphate to produce 1 molecule of sulphide. When referring to a specific section in a borehole, the mid elevation of this section is given in metres above sea level e.g KFM02A:–495 masl.

## 1.4 Hydrogeochemical background of the Forsmark site

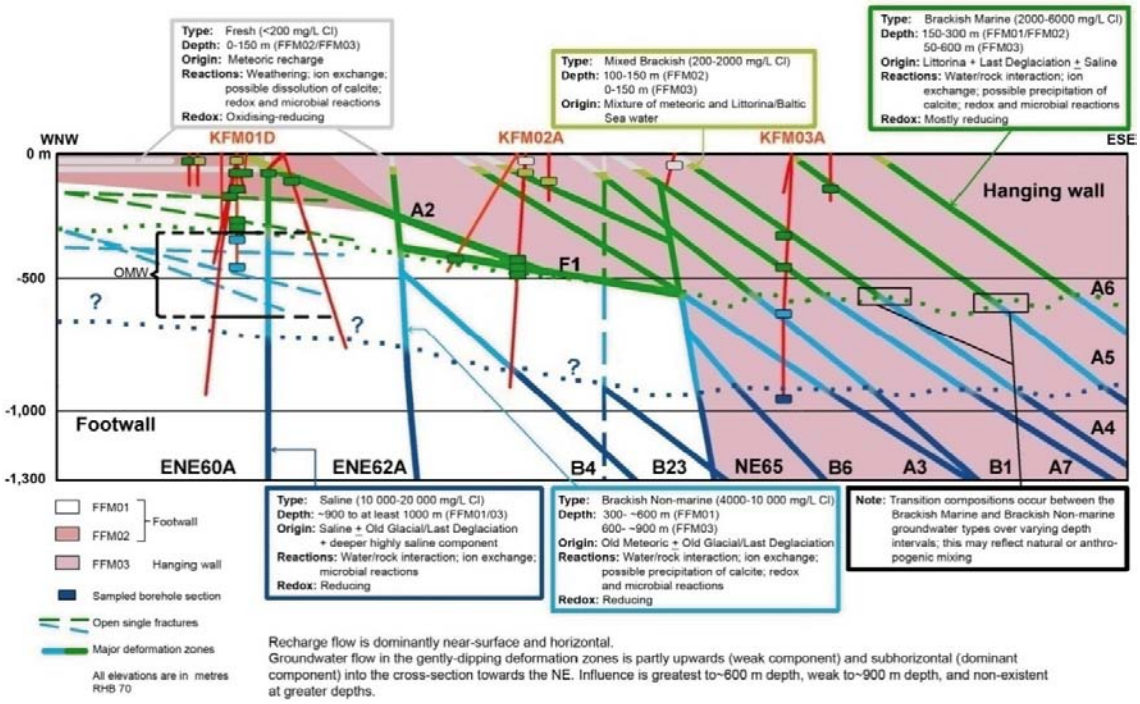
### 1.4.1 Groundwater evolution

During the site investigation at Forsmark, explorative analyses and modelling of groundwater chemistry data measured in samples from cored boreholes, percussion boreholes, shallow soil boreholes and rock matrix porewaters were used to evaluate the hydrogeochemical conditions at the site /Laaksoharju et al. 2008/.

The three major groundwater types indentified were; Fresh water (< 200 mg/L Cl), Brackish Marine (2,000 to 6,000 mg/L Cl and Mg > 100 mg/L) and Brackish to Saline Non-marine groundwater with Cl between 4,000 to 16,000 mg/L and Mg < 25 mg/L. Mixing between these three groups occurred in several of the sampled sections and mixing between fresh and brackish waters with Cl in the interval 200 to 2,000 mg/L are labelled "Mixed Brackish". Mixing between Brackish Non-marine and Brackish to Saline Non-marine groundwaters are called Transition type. The distribution of these groundwater types are shown in the conceptual model in Figure 1-2. At the very end of the site investigation programme it was discovered that some sections had groundwaters with very low $\delta^{18}O$ (< −13.0‰ V-SMOW) which, if detected earlier in the investigations, would had resulted in a fourth water type called Brackish Glacial. This groundwater type was particularly obvious at relatively shallow depths (200 to 300 m) in boreholes KFM10A and KFM12A /Smellie et al. 2008/. Significant components of glacial water were also observed at depth below 900 metres in borehole KFM03A.

Several groundwater types which are now present in the bedrock can be associated with past climatic events in the late Pleistocene, including interglaciations, glaciations, deglaciations, and associated changes in the shoreline in connection with marine transgressions and regressions. Among these, the last glaciation and post glacial period are the most important for the groundwater development in the Fennoscandian shield, especially in terms of land uplift and shore-level displacement as well as the development of the Baltic Basin.

The post glacial development reveals that, when the continental ice melted and retreated from the Forsmark area around 8800 BC, glacial meltwater was hydraulically injected under considerable head pressure into the bedrock. The exact penetration depth is unknown, but, according to results of hydrogeological modelling, depths exceeding several hundred metres are possible. Since the deglaciation of the Forsmark region coincided with the end of the Yoldia period, there are no signs of Yoldia Sea water in the bedrock. The Ancylus Lake (8800 to 7500 BC) was lacustrine and developed after the deglaciation. This period was followed by the brackish Littorina Sea (7500 BC to present).



**Type:** Fresh (<200 mg/L Cl)
**Depth:** 0-150 m (FFM02/FFM03)
**Origin:** Meteoric recharge
**Reactions:** Weathering; ion exchange; possible dissolution of calcite; redox and microbial reactions
**Redox:** Oxidising-reducing

**Type:** Mixed Brackish (200-2000 mg/L Cl)
**Depth:** 100-150 m (FFM02)
0-150 m (FFM03)
**Origin:** Mixture of meteoric and Littorina/Baltic Sea water

**Type:** Brackish Marine (2000-6000 mg/L Cl)
**Depth:** 150-300 m (FFM01/FFM02)
50-600 m (FFM03)
**Origin:** Littorina + Last Deglaciation ± Saline
**Reactions:** Water/rock interaction; ion exchange; possible precipitation of calcite; redox and microbial reactions
**Redox:** Mostly reducing

**Type:** Saline (10 000-20 000 mg/L Cl)
**Depth:** ~900 to at least 1000 m (FFM01/03)
**Origin:** Saline ± Old Glacial/Last Deglaciation + deeper highly saline component
**Reactions:** Water/rock interaction; ion exchange; microbial reactions
**Redox:** Reducing

**Type:** Brackish Non-marine (4000-10 000 mg/L Cl)
**Depth:** 300- ~600 m (FFM01)
600- ~900 m (FFM03)
**Origin:** Old Meteoric ± Old Glacial/Last Deglaciation
**Reactions:** Water/rock interaction; ion exchange; possible precipitation of calcite; redox and microbial reactions
**Redox:** Reducing

**Note:** Transition compositions occur between the Brackish Marine and Brackish Non-marine groundwater types over varying depth intervals; this may reflect natural or anthropogenic mixing

Recharge flow is dominantly near-surface and horizontal.
Groundwater flow in the gently-dipping deformation zones is partly upwards (weak component) and subhorizontal (dominant component) into the cross-section towards the NE. Influence is greatest to~600 m depth, weak to~900 m depth, and non-existent at greater depths.

***Figure 1-2.*** *WNW-ESE 2D cross-section through the central part of the Forsmark candidate area showing the groundwater types and their properties (salinity, origin, major reactions and redox conditions). The footwall (FFM01 and FFM02) and hanging wall (FFM03) bedrock segments are indicated, separated by the gently dipping deformation zones ZFMA2 and ZFMF1 (abbreviated to A2 and F1), and the steeply dipping deformation zone ZFMNE0065. The dotted lines in different colours crossing the section represent the approximate depths of penetration of (or extrapolation of) the major groundwater types along hydraulically-active fracture zones. (Cross-section length = 6,790 metres) /Laaksoharju et al. 2008/.*

During the Littorina Sea stage, the salinity was considerably higher than in the Baltic Sea at present, reaching a maximum of about 15‰ in the period 4000 to 3000 BC. Dense brackish seawater from the Littorina Sea penetrated the bedrock, resulting in a density intrusion that affected the groundwater in the more conductive parts of the bedrock. When the first parts of the Forsmark region subsequently emerged from the sea, starting ca. 500 years BC, recharge of meteoric water formed a freshwater layer on top of the saline water because of its lower density. As a result of the flat topography of the Forsmark area and of the short time period elapsed since the area emerged from the sea, the out-flushing of saline water has been limited, and consequently a freshwater layer still remains at shallow depth.

Past Quaternary evolution has affected the groundwater chemistry at Forsmark, but this is not restricted to post glacial time since there is groundwater and porewater evidence that indicates a pre-Pleistocene warm-climate derived meteoric water component. The hydrochemistry of the Forsmark area cannot be explained without recognising this older component. The present groundwaters therefore are a result of mixing and reactions over a long period of geological time. The interfaces between different water types are not sharp but reflect the variability in the structural-hydraulic properties of the site.

### 1.4.2 Groundwater composition

Groundwaters in the uppermost 20–200 m of the bedrock display a wide chemical variability with Cl concentrations in the range 200–2,000 mg/L suggesting the influence of both fresh meteorioc water and brackish marine water (i.e. Baltic Sea water and Littorina Sea relicts). Furthermore, a sharp decrease in tritium and $^{14}C$ contents at about 100–150 m depth indicate that these shallow groundwaters have short residence times that are in the order of a few hundred years to only a few decades.

At depths greater than about 200 m, the water composition is indicative of a brackish marine water with Cl concentrations in the range 2,000 to 6,000 mg/L and with a clear Littorina component, as indicated by significant concentrations of Mg and the ratio of Br to Cl concentrations. This groundwater type is recognised down to 600 to 700 m depth in the transmissive, gently dipping fracture zones in the south-eastern part of the investigated area, whereas the penetration depth in the repository target volume, where the frequency of water-conducting fractures is lower, it is restricted to about 300 m. Below these depths, the water composition indicates brackish to saline non-marine groundwaters (i.e. absence of Littorina influence), reflecting processes which have occurred prior to the intrusion of the Littorina Sea waters. These deep waters further show an increase in calcium with depth, which is a well recognised trend and indicative of water/rock interactions that occur under increasingly low flow to stagnant groundwater conditions with increasing depth.

### 1.4.3 Redox conditions

Based on the information from the CCC sampling, the following description of the redox system was presented in /Laaksoharju et al. 2008/ and detailed in /Gimeno et al. 2008/.

According to data analyses and modelling of the redox system, reducing conditions currently prevail at depths greater than about 20 m. Most of the Eh values determined in brackish groundwaters (at depths between 110 and 646 m) seem to be controlled by the occurrence of an amorphous iron oxyhydroxide with higher solubility than a truly crystalline phase. This indicates that the iron system is disturbed (cf. discussion below), which is also supported by mineralogical investigations that identified the presence of fine-grained amorphous to poorly crystalline oxyhydroxides now evolving towards more crystalline phases. Dissolved sulphide concentrations, linked to the activity of sulphate-reducing bacteria (SRB), are systematically low, possibly due to the precipitation of amorphous Fe(II)-monosulphides (based on saturation indices), At depths greater than 600 m, the sulphide concentrations increase, which is consistent with a decrease in $Fe^{2+}$. The iron system at these depths seems to be limited by crystalline oxides, mainly hematite.

The presence of goethite (FeOOH) in some hydraulically active fractures and fracture zones (mainly within the major gently dipping deformation zone ZFMA2/ZFMF1) in the upper part of the bedrock, indicates circulation of oxidising fluids during some period in the past (potentially Quaternary). However, the presence of pyrite in the same zones suggests that the circulation of oxidising fluids has been concentrated along channels in which different redox micro environments may have been formed. Furthermore, mobilisation as well as deposition of uranium, which maybe the result of changes in redox conditions during the last 1 Ma in the upper 150 m of the bedrock, is indicated by U-series decay analyses (USD) of fracture coatings.

Analyses of the current redox system at Forsmark have consistently indicated that sampling (or drilling-induced) perturbations may have altered the original redox conditions of the hydrochemical system. Examples include oxygen intrusion and precipitation of amorphous iron oxyhydroxides, as indicated by the colloidal composition /Laaksoharju et al. 2008/ and mineralogical determinations. Additionally, there could have been modification of the original Eh and/or alkalinity by drilling waters which suggests that the increase in dissolved uranium contents or changes in sulphide contents could partly have been caused by one or more of these disturbances.

Despite these potential disturbances, the buffer capacity of the system maintains a noticeable reducing character. Concerning the potential redox buffering capacity of the fracture system it is concluded that previous oxidising episodes have not been intense enough to exhaust the reducing capacity of fracture filling minerals, which are still present in the shallow system (e.g. chlorite and pyrite).

Analyses of gas dissolved in groundwater at Forsmark (cf. Section 5.4) have shown that, while the gas content increases with depth, the groundwaters are far from being oversaturated. The major gas components are nitrogen and helium. Methane has also been detected, but generally in small amounts (with one exception less than 0.012 mmol/L) and currently it is not known whether it is of biogenic or non-biogenic origin.

# 2 Sulphide related processes

## 2.1 Microbial sulphide producing processes

### 2.1.1 Metabolism

Sulphate-reducing prokaryotes (organisms lacking cell nucleus), such as Bacteria and Archaea, play a key role in marine and brackish systems for the terminal oxidation of organic material to $CO_2$ /Muyzer and Stams 2008/ and have been isolated from shallow and deep groundwaters in the Fennoscandian shield (e.g. /Pedersen et al. 2008/). The metabolic pathway of sulphate reduction, using either $H_2$ or an organic energy source, is known for Archaea and Bacteria. Hydrogen sulphide, here used to indicate the species $H_2S$, $HS^-$, and $S^{2-}$, is produced in the enzymatic reduction of sulphate ($SO_4^{2-}$), sulphite ($SO_3^{2-}$), and thiosulphate ($S_2O_3^{2-}$). Few Archaea and Bacteria can also reduce elemental sulphur to hydrogen sulphide. A more recently discovered pathway involves the disproportionation of elemental sulphur, thiosulphate, and sulphite /Finster et al. 1998/. This process, which is akin to fermentation, splits a partially oxidised sulphur species into a reduced (hydrogen sulphide) and an oxidised component (sulphate). A third, generally minor pathway of hydrogen sulphide production, is catalysed by fermenting bacteria that degrade sulphur-containing organic molecules (i.e.proteins or amino acids) and release hydrogen sulphide. However, these bacteria do not employ a dissimilatory pathway and the amount of hydrogen sulphide produced is generally small compared to this pathway.

The reduction process involves multiple enzymatically catalysed steps and requires prior activation of the sulphate molecule before it can be reduced. Sulphate is thus activated by the enzyme ATP sulphurylase to form adenosine phosphosulphate (APS), which is subsequently reduced in two steps by; 1) the adenosine phosphosulphate reductase (APSR) to bisulphite ($HSO_3^-$), and 2) the dissimilatory sulphite reductase (DSR) to hydrogen sulphide.

### 2.1.2 Energy and carbon sources

Sulphate-reducing bacteria (SRB) conserve energy by ATP (adenosine triphosphate) synthesis through transmembral proton dislocation. The electrons for the reduction of sulphate are transported by membrane-associated cytochromes. Sulphate-reducing prokaryotes can use a large variety of electron donors ranging from $H_2$ over short-chain fatty acids (lactate, formate, propionate, butyrate) to aromatic compounds (benzene, benzoate) to alkanols, alkanoic acids and alkanes /Muyzer and Stams 2008/. The rates of sulphide production in many aquatic systems are therefore critically dependent on the rates of production of the potential electron donors in preceding fermentation reactions. Several SRB are known to be autotrophic and to utilise $H_2$ and $CO_2$ (e.g. most notable being the various *Desulfovibrio* species).

Sulphate-reducing prokaryotes can also be involved in the corrosion of metallic iron (e.g. /Dinh et al. 2004/). Both direct and indirect iron corrosion mechanisms have been proposed, the most common explanation being an indirect corrosion process called “hydrogen embrittlement” that occurs as a result of the oxidation of metallic iron with hydrogen sulphide (produced by microbiological sulphate reduction) according to the reaction: $Fe + H_2S$ à $FeS + H_2$. The ready consumption of the $H_2$ by sulphate-reducing bacteria drives this reaction. Waters with high concentrations of biodegradable organics may, therefore, promote the corrosion of iron. Sulphate-reducing prokaryotes may also be directly involved in corrosion, i.e. a cell surface active cytochrome may serve as an electron shuttle and participate in the electron transport from metallic iron to reduce protons to $H_2$. The oxidation of $H_2$, in turn, drives the reduction of sulphate /Dinh et al. 2004/.

An important process for sulphate reduction is the anaerobic reduction of sulphate by methane. Most existing evidence suggests that this process is catalysed by a syntrophic anaerobic consortium of methane-oxidising Archaea that transfer a reactive intermediate (possibly methanethiol) to the sulphate-reducing partner /Knittel and Boetius 2009/. In this case the sulphate reducers live off the product from the methane-oxidisers. In the marine environment, this process oxidises globally up to 95% of all methane formed biogenically in the marine subsurface.

Despite their name, sulphate-reducing bacteria neither are exclusively dependent on sulphate or other dissolved sulphur compounds, nor are they always obligate anaerobic bacteria. Some SRB, e.g. several *Desulfovibrio* species and *Desulfobulbus propionicus*, can use nitrate ($NO_3^-$ ) as an alternative electron acceptor, and reduce $NO_3^-$ to $NH_4^+$ /Widdel and Pfennig 1982/. Few sulphur bacteria even have been shown to perform oxygen respiration. However, aerobic respiration does not support growth and is probably a means of removing $O_2$ when it is present in an environment otherwise suitable for growth of sulphate-reducing bacteria /Madigan et al. 2000/. Reduction of iron(III) has rarely been observed for sulphate reducers. Growth occurred only when iron(III) was present in chelated form /Lovley et al. 1993/. In non-chelated form, reduction of iron(III) was detected on ferrihydrite for *Desulfotalea psychrophila*, but no growth was observed /Knoblauch et al. 1999/.

### 2.1.3 Adaptations

Sulphate-reducing bacteria have been isolated from a wide range of physical and chemical environments /Rabus et al. 2000/. Psychrophilic (grow at low temperatures i.e. < 15°C) and a range of mesophilic (growth optimum in temperature range of 25–45°C), and thermophilic (growth optimum at high temperatures 45–80°C) sulphate-reducing Bacteria and Archaea have been isolated and show the broad temperature tolerance of this group of microorganisms /Rabus et al. 2000/. Sulphate reducers are also known from acidic (e.g., acid mine drainage environments) and alkalic lakes /Rabus et al. 2000/. High pressures are also not known to limit sulphate reducers as indicated by their activity in the deep marine biosphere environments several thousand metres below the sea surface /D'Hondt et al. 2004/. Sulphate-reducing bacteria occur in environments of low permeability, but also in systems of slow flow such as fine-grained sand aquifers. It is generally poorly understood whether sulphate-reducing bacteria are mainly associated with solid surfaces or free-living. In systems with low permeability, SRB are likely to be associated with particles and rely on the molecular diffusion of substrate to the cell. In flowing systems, the bacteria are also likely to be free living as indicated by successful enrichments from pumped groundwater /Pedersen et al. 2008/. Sulphate-reducing bacteria have been found often attached to mineral or other solid surfaces and are part of biofilms /Pedersen et al. 1996, Santegoeds et al. 1999/. It is important to emphasise that in any given environment, the proportion between free living and surface attached bacteria, for example in deep groundwaters, is generally poorly established. The greatest restriction to sulphate-reducing microbial activity is the presence of consistently high concentrations of molecular oxygen, since reactive oxygen species such as peroxide and superoxide can damage or destroy reactive centres and redox-sensitive proteins. At concentrations of oxygen of less than 1 μM, activity of sulphate reducers was sustained and oxygen may even have been used as an alternative electron acceptor /Krekeler et al. 1997/.

### 2.1.4 Ecology, growth requirements, viruses

Since most sulphate reducers are anaerobic heterotrophs, their activity relies on the concomitant production of suitable low molecular weight organic electron donors that can be taken up across the cell membrane and are needed for energy conservation. In most aquatic settings, the rate of sulphate reduction is, therefore, limited by the availability of suitable electron donors and many SRB therefore live in intimate syntrophic associations with fermenting bacteria or with other electrondonor producing partners /Plugge et al. 2002, Harmsen et al. 1993/. Sulphate reduction is thought to be limited when electron donor or acceptor concentrations fall below the so-called thermodynamic energy threshold. Below this threshold, the energy required for ATP synthesis can no longer be provided at the ambient concentrations of either sulphate or electron donor /Hoehler et al. 1998/. The sulphate concentration dependent rate limitation only occurs at very low sulphate concentrations. Pure culture experiments have indicated half saturation concentrations as low as 0.5 μg/L, where half saturation constants of natural communities appear to be higherat 0.5–1 mg/L /Pallud and Van Cappellen 2006/.

### 2.1.5 Methods to analyse microbial populations

There are many microbiological methods in use for the analysis of sulphide producing processes. The most common method involves bacterial enrichments and most probable number (MPN) counting. Common nucleic acid based methods include 16S-rDNA/rRNA- or functional gene based fingerprinting methods to assess microbial community composition, or microarray based gene sequence analyses /Muyzer and Stams 2008/. Generally, these molecular methods cannot be used to quantify microbial population size, but they offer assessments of spatial or temporal changes in microbial community composition. As a functionally well defined group, sulphate-reducing bacteria have been studied by sequencing part of the 16S region of ribosomal DNA, or the functional genes dissimilatory sulphite reductase (DSR) and adenosine phosphosulphate reductase (APR) /Meyer and Kuever 2007, Loy et al. 2002/.

Direct quantification of active sulphate reducing populations is currently performed using fluorescent *in situ* hybridisation (FISH) of 16S rRNA-based oligonucleotide probes /Amann and Ludwig 2000/ and by using quantitative PCR (Polymerase Chain Reaction) of functional genes /Leloup et al. 2009/. A range of primers and probes is available for sulphate-reducing bacteria; however, it is generally recommended to combine quantification with the creation of a 16S rDNA clone library or a 16S pyrosequence library to obtain broad sequence information for a particular environment.

Direct measurements of sulphate reduction rates require the application of radiolabelled $^{35}$S-sulphate for direct determination of sulphate reduction rates /Fossing 1995/. This method, which allows quantification of sulphate reduction rates to as low as 10 pmol per cm$^3$ per day, is the most direct method for detection of active sulphate reduction. The method has been extensively used to study the deep marine subsurface /D'Hondt et al. 2004/ and the compacted bentonite buffer /Masurat et al. 2010/.

A classic method for the identification of biologically catalysed sulphate reduction is to use the mass dependent fractionation of the stable $^{32}$S and $^{34}$S isotopes during sulphate reduction. In the process of sulphate reduction, hydrogen sulphide becomes enriched in the light sulphur isotope $^{32}$S and leaves the residual sulphate enriched in the isotope $^{34}$S /Detmers et al. 2001/. The degree of enrichment is both species dependent and a function of the relative rates of electron donor and acceptor transport into the bacterial cell. Fractionations may vary between 4 and 70‰ relative to the isotope composition of sulphate /Detmers et al. 2001/.

Microbiological analyses of Forsmark groundwaters were carried out using the most probable number (MPN) method to determine nitrate, manganese, iron, and sulphate- reducing bacteria, as well as autotrophic and heterotrophic acetogens, and autotrophic and heterotrophic methanogens. More recently, nucleic acid methods based on 16S rRNA sequencing were applied, but have not been published to date.

## 2.2 Water-rock reactions

The reduction of sulphate to sulphide in natural systems may occur both inorganically (thermochemical sulphate reduction, TSR) and bacterially mediated (bacterial sulphate reduction, BSR) but in mutually exclusive thermal regimes; TSR at temperatures higher than 100–140°C and BSR at lower temperatures (e.g. /Machel 2001/ and references therein). Thus, the presence of dissolved sulphide in low temperature aqueous environments is undoubtedly related to SRB activity. However, additional factors other than SRB activity, and mainly related to the iron system, may participate in the control of dissolved sulphide contents in low temperature groundwaters.

Different inorganic, kinetically fast reactions that may play important roles in the control of dissolved sulphide contents in reducing groundwaters is the precipitation of ferrous sulphide and the inorganic reductive dissolution of iron (or manganese) oxyhydroxides by the dissolved sulphide.

Ferrous sulphide formation in low temperature environments is intimately linked to the activity of sulphate-reducing bacteria (SRB) as a source of $H_2S$. It is a potentially important process as it can control dissolved sulphide (and iron) concentrations, limiting their mobility in anaerobic aquifers. The "amorphous" iron monosulphide (more properly termed disordered mackinawite or nanocrystalline mackinawite; cf. /Gimeno et al. 2009/ and references therein) is the first phase to precipitate in most natural aqueous environments because it is the most soluble of the ferrous sulphide phases, according to the reaction:

$$\mathrm{Fe^{2+} + H_2S \rightarrow FeS + 2H^+} \qquad 2\text{-}1$$

Its precipitation rate is very fast compared to other sulphides and the nanocrystalline character of this first precipitate /Wolthers et al. 2003, 2005, Rickard 2006/ may induce the formation of colloidal phases. Recrystallisation (ripening) towards more ordered, crystalline mackinawite is also a fast process that can affect the composition of the surrounding waters, which would quickly re-equilibrate with respect to this less soluble and more crystalline mackinawite /Chen and Liu 2005/.

Apart from SRB activity, a source of iron is needed in order to surpass the IAP (Ion Activity Product) of the amorphous monosulphides, allowing their precipitation. The relative importance of these two factors (SRB activity and iron availability) would give rise to waters with high dissolved sulphide contents (if there is no source of iron) or low sulphide contents in spite of the SRB activity (if the amorphous ferrous monosulphides precipitate).

The activity of iron reducing bacteria (IRB) may serve as a source of Fe(II) but the reductive dissolution of iron oxyhydroxides by $H_2S$ may also provide both an additional source of Fe(II) and an additional sink of dissolved sulphide. The inorganic reductive dissolution of iron oxyhydroxides by the dissolved sulphide (sulphidisation of iron minerals), proceeds via the oxidation of dissolved sulphide at the mineral surface (e.g. according to /Pyzik and Sommer 1981, Yao and Millero 1996, Poulton et al. 2004/:

$$H_2S + 2FeOOH + 4H^+ \rightarrow S^0 + 2Fe^{2+} + 4H_2O \qquad 2\text{-}2$$

This reaction promotes the release of Fe(II) to solution and its subsequent reaction with additional dissolved sulphide to produce FeS according to reaction (1). The extent to which iron minerals are able to control dissolved sulphide contents depends on the reactivity and abundance of the particular minerals present. Iron minerals display a wide variability in terms of their reactivity towards dissolved sulphide, ranging from reactive Fe(III)-oxyhydroxides (with very fast kinetics) to essentially unreactive Fe-silicates (/Gimeno et al. 2009/ and references therein).

Similarly, dissolved sulphides may quickly react with manganese oxides (if present) according to /Yao and Millero 1993/:

$$H_2S + MnO_2 \rightarrow S^0 + Mn^{2+} + 2OH^- \qquad 2\text{-}3$$

$$H_2S + 4MnO_2 + 2H_2O \rightarrow SO_4^{2-} + 4Mn^{2+} + 4OH^- \qquad 2\text{-}4$$

Thus, the availability of iron (e.g. hematite) and manganese oxyhydroxides in the fracture fillings may play an important role in the buffering of the dissolved sulphide in groundwaters and this potential role would merit further study.

# 3 Sampling uncertainties

## 3.1 Different methods for groundwater sampling and analysis

The groundwater data in the Sicada database originate from groundwaters sampled under quite different conditions in terms of possible influence from drilling, hydraulic tests and other activities /Smellie et al. 2008/. Furthermore, they are sampled in different ways which may severely influence the results of certain parameters (e.g. trace elements such as Cu, Mo, As and Cr and the lanthanides). This may also be the case for elements involved in microbial or inorganic redox reactions, for example, Fe(II)/Fe(III), S(−II)/S(VI) and Mn(II)/Mn(IV). Below are described the sequence of borehole activities carried out and the different sampling techniques, together with their possible influence on the sulphide system in particular.

Section 3.1.4 describes the introduction of a modified monitoring approach in the Autumn of 2009 which implied thorough cleaning of stand pipes and collection of sample series (five samples) from 13 borehole sections. Subsequent estimation of the contributions of initial borehole section water to the samples /cf.Section 3.1.5/ support the hypothesis that portions of the residual initial borehole section stagnant water is contributing to anomalously high sulphide concentrations in the samples.

### 3.1.1 Investigation sequence in cored boreholes

During the site investigations in Forsmark, bedrock groundwater samples for sulphide analyses were mainly collected by two different methods, *Complete Chemical Characterisation (CCC)* soon after borehole completion, and subsequent regular periodic *Monitoring Sampling*. No early sulphide data were obtained from packed-off borehole sections in percussion boreholes, only from selected sections during the later monitoring sampling programme. The following discussion concerns the cored borehole investigations and methods.

Microbial production of sulphide is probably affected by borehole activities /Hallbeck and Pedersen 2008a, b, c/. Especially heavy pumping or conditions causing mixing of groundwaters from different aquifers may disturb or promote microbial activity. Therefore, it is necessary to consider also the sequence of borehole events that have preceeded each sampling occasion. Important to mention in this context is the rigorous demands on cleaning the downhole equipment prior to use and on the correct choice of lubricants, especially for activities early in the sequence before the CCC sampling programme commenced. The bioaccessibility of all chemical products used were thoroughly addressed.

In general, the different geoscientific investigation activities carried out in the core drilled boreholes within the Forsmark site investigation were conducted in the following order:

*Drilling and contemporaneous mammoth pumping*. For a 1,000 m long SKB type telescopic cored borehole, typically about 1,000 $m^3$ drilling water (spiked with uranine as tracer) was consumed and about twice the volume (2,000 $m^3$) was discharged from the borehole during mammoth pumping from the uppermost 100 m of the borehole of greatest diameter at a flow rate between 20–50 L/min. The pipe string and the drilling crown were steam cleaned before use and the drilling water supply tubeline was scanned with UV-ligth for sterilisation. However, total sterile conditions are unrealistic to expect and possible major impacts are: 1) Decrease in microbial activity in the groundwater due to the heavy pumping /Hallbeck and Pedersen 2008a, b, c/. 2) Introduction of foreign microbe populations and/or microbial remains by the drilling water or downhole equipment. 3) Extensive mixing of waters from different aquifers during pumping may, given some time, promote microbial activity and therefore sulphide production.

*Additional pumping (if required ) to remove the remaining drilling water from the borehole.* A routine problem encountered in most boreholes and borehole sections in Forsmark was to obtain a sufficiently low drilling water content in the groundwater samples and additional pumping was often necessary. The extra volumes removed prior to sampling varied from a few cubic metres to a few thousand cubic metres pumped from packed-off sections or entire boreholes, respectively. This pumping and mixing may have influenced microbial activity and therefore sulphide production.

*Different downhole activities (BIPS (Borehole Image Processing System), geophysical loggings, flow logging etc).* Of these, only differential flow logging involves pumping and discharge of water. However, mixing of waters in the water column takes place when different equipment is lowered and raised in the borehole. To minimise possible contamination (completely sterile conditions are not expected), the different logging equipment was cleaned before use, using steam or 70% ethanol depending on the type of equipment. Except for the possible disturbance of microbial activity by pumping during differential flow logging, these downhole activities should have little impact on sulphide concentrations besides some effects from limited mixing of water and possible minor introduction of foreign microbes into the borehole from other sources.

*Complete Chemical Characterisation (CCC) /SKB 2001/ using the special SKB mobile chemistry units.* This involves equipment comprising an integrated system for: 1) Sealing off the borehole section by inflatable packers and pumping of groundwater from the section. 2) Sampling of pumped groundwater as well as sampling *in situ* in the section to obtain groundwater samples at maintained pressure. 3) On-line long term measurements of chemical and physical parameters at the ground surface and downhole (cf. Section 3.1.2 for more details).

*Hydraulic injection tests (only in selected boreholes and borehole sections).* A total water volume in the order of 100 mL to 4,000 L (generally less than 500 L) is injected into each borehole section (i.e. at 20 m and 5 m section lengths) during the tests. The injected water is spiked with uranine to the same concentration as the flushing water (i.e. 0.2 mg/L). This activity is, almost without exception, conducted after the CCC sampling. A notable exception, however, is one of the deepest boreholes investigated (KFM07A) where it was concluded that the redox conditions had been changed to positive values as an immediate result of these tests. Additional effects may include mixing of waters and the introduction of foreign microbes by the injected water or associated with the downhole equipment.

*Groundwater flow measurements (only in selected boreholes and borehole sections).* A tracer is injected into the groundwater in the borehole section at a high concentration and thus the added water volume is very small. This activity should have little or no impact on sulphide concentrations besides the influence from mixing of water and possible introduction of foreign microbes to the borehole. However, the use of uranine as a tracer may prevent determination of the drilling water content.

*Installation of stationary monitoring equipment* for groundwater level monitoring, groundwater sampling as well as groundwater flow measurements in packed-off borehole sections. A maximum of ten borehole sections for groundwater level monitoring were isolated using a straddle packer system, and two of these sections were instrumented for groundwater sampling and flow measurements. The installation of the downhole equipment is followed by clean-up pumping to obtain a stable groundwater composition in the stand pipes and tubing. If the standard procedure for this pumping is used, the resulting water in the tubing and stand pipes will represent a groundwater mixture from water-yielding fractures along the entire borehole. (cf. Section 3.1.3 for more details of the equipment used).

*Hydrochemical monitoring of selected borehole sections (i.e. sampling twice per year /SKB 2007/).* Generally, one or two sections in each core drilled borehole are included in the monitoring programme. (cf. Section 3.1.3 for more details).

*Monitoring of groundwater flow using the tracer dilution technique.* A tracer is added to the groundwater in the borehole section (i.e. the same borehole section sampled in the hydrochemical programme) at a high concentration. Because the injected volume is very small and is performed after the hydrochemical sampling each Autumn, this activity should have little impact on sulphide concentrations apart from the possible introduction of foreign microbes to the borehole. However, the use of uranine as a tracer may prevent determination of the drilling water content. A significant increase in sulphide concentration was observed in most borehole sections between the first sampling campaign (CCC) and the later monitoring programme. This increase may be related to the time lapse between the two sampling campaigns and/or the different sampling methods involved. The former may be important since there are strong indications of increased microbial activity with time in the stagnant groundwater present in the borehole between sampling periods and in the development of biofilm on the rock surfaces. The two sampling methods, together with possible contamination sources and other differences in methodology that may be relevant to the sulphide issue, are discussed in Sections 3.1.2 and 3.1.3 below.

Table 3-1 provides a summary of the sampling conditions which characterise the CCC and monitoring programmes.

**Table 3-1. Summary of sampling conditions characterising the CCC and monitoring programmes.**

| Condition | CCC sampling | Monitoring sampling |
|---|---|---|
| Frequency. | On one occasion. | Twice each year. |
| Time between completion of drilling and sampling. | 1–2 months. | From 4 months to several years delay before the first sampling occasion. |
| Typical borehole settling/stabilised period prior to pump start*. | In the order of 3–14 days. | 4–6 months. |
| Typical exchanged volume prior to first sample/sampling. | Water channel volume in the 1,000 m long umbilical hose**= 25 L. | 3–5 borehole section volumes (according to plug flow calculations in May 2010; cf. Appendix 1) |
| Section volume/section + tube volume. | 15–20 L / 40–45 L. | 12–40 L / 18–63 L. |
| Sample water flow rate. | 10–250 mL/min. | 20–300 mL/min (is dependent of the hydraulic transmissivity of the borehole section and therefore a low flow rate during CCC implies a low flow rate also during monitoring sampling). |
| Main difference from contamination aspects. | The groundwater is always flowing through the equipment during operation and the equipment is removed when not in use. | Stationary equipment in borehole section and close to stagnant groundwater present in the complex monitoring system for several months between sampling occasions. |
| Number of time-series samples taken during continuous pumping. | 6 or more. | 1 (5 in series Oct 2009 and May 2010***). |

* If clean-up pumping is performed in the borehole section to be investigated using the CCC equipment as an initial measure to lower the drilling water content there will be no settling/resting period.

** Furthermore, the removed volume from the borehole section will amount to a 1–4 $m^3$.

***Time series from May 2010 are only used as supporting data, cf. Appendix 1.

### 3.1.2 Complete Hydrochemical Characterisation (CCC)

The equipment for CCC consists of a hose unit with facilities for lowering and raising the approximately 1,000 m long umbilical hose carrying the downhole units which consist of: 1) Upper and lower packers used to isolate a predetermined borehole section. 2) Downhole piston pump controlled by a pump unit at the ground surface 3) Probe for *in situ* measurements of pH, Eh, pressure and water temperature. 4) Downhole sampler for collecting *in situ* samples at maintained pressure. The investigations are performed in one borehole section at a time using downhole equipment which has been internally rinsed and filled with deareated and deionised water before use and where the outside of the equipment is cleaned/wiped using 70% ethanol when being lowered into the borehole. Despite this cleaning, sterile conditions are not expected to prevail and foreign microbes may be introduced by the equipment.

Prior to sampling, the sample water is first pumped through the downhole units and further through the Tecalan tube housed in the umbilical hose to the ground surface where sample portions are collected for sulphide (and other components) analyses. All contact surfaces are either composed of polyamide or high quality stainless steel, and lubricants (generally Teflon spray but also vaseline) are used sparsely on O-rings in valves and other different types of connections.

During the site investigations in Forsmark, the CCC sampling campaign generally was performed between one and two months after drilling of the borehole was completed. The lengths of the packed-off borehole sections were around 7 m with some exceptions which could be both shorter and longer (5–21 m). The volume of the borehole sections was in the order of 0.3 to 1.0 L but depends on section length and configuration of the downhole equipment, and the water-conducting part of the approximately 1.000 long umbilical tube adds an additional 25 L. The pumping flow rate was between 10 to 250 mL/min depending of water yield and the pumping periods were a minimum of three weeks, however, pumping was often prolonged due to unacceptably high drilling water contents. Generally, two samples per week were collected and all were analysed for sulphide. Duplicate samples were collected in Winkler bottles and immediately conserved with sodium hydroxide and zinc acetate in the field. The analytical method for sulphide Swedish Standard SIS 02 81 15 /SIS 1976/ was based on /Grasshoff and Chan 1971/ and the analyses were conducted by two reliable certified laboratories.

Advantages with the CCC sampling method as used during the PLU site investigations:

- Shorter contact time between the sampled water and equipment compared to monitoring sampling where stationary, long term borehole installations are used.
- The advanced equipment is specially designed to minimise contamination risks and other disturbances.
- Collection of sample time series including at least six samples during continuous pumping permits judgement concerning the stability of the groundwater composition and especially the sulphide concentration.
- Investigation activities involving injection of water (injection tests and groundwater flow measurements) had not been performed in the borehole prior to the CCC campaign.
- The boreholes are relatively new and quite recently filled with groundwater from the bedrock fractures, and the rock surfaces of the borehole may still still be fresh.

Disadvantages with the CCC sampling method as used during the PLU site investigations:

- Of all the borehole activities that may disturb or promote microbial production of sulphide, the actual drilling combined with heavy mammoth pumping and the use of drilling water is probably the most serious cause of perturbation. Removal of large water volumes (i.e. during drilling procedures and subsequent clean up pumping) shortly before the sampling campaign may decrease the microbial sulphide production according to /Hallbeck and Pedersen 2008a, b, c/.
- In common with most downhole activities, the lowering of the CCC equipment into the borehole may cause mixing of different water types and may also introduce foreign microbes despite the rigorous cleaning and sterilisation procedures.
- Diffusion of oxygen (from the air) into the water-conducting part of the approximately 1,000 m long umbilical hose, or subsequently through connections and tubing in the sample water line, may change the redox conditions and cause oxidation of sulphide. Such conditions, however, have proved to be irrelevant if negative Eh values are measured in the flow through cell at the surface. An amorphous black precipitation on the outside of the downhole equipment has been observed when raising it from the borehole on two or three occasions in Forsmark. However, no occurrence of black precipitation in the sampled groundwater has been noticed.

### 3.1.3 Hydrochemical monitoring in boreholes

Regular hydrochemical monitoring in packed-off borehole sections requires the installation of stationary and long term downhole equipment. This equipment includes a packer system dividing the borehole into a maximum of ten sections for groundwater level monitoring. Each borehole section is connected by tubing to a stand pipe (ø 34/23.5 mm) in the wider upper part of the telescopic borehole. This stand pipe includes a pressure transducer for groundwater pressure monitoring. A maximum of two sections are also connected to a second larger diameter stand pipe (ø 66/53.5 mm) for chemical sampling and groundwater flow measurements. The different materials in contact with the water sample are listed in Table 3-2.

**Table 3-2. Equipment details and material.**

| Detail | Material |
|---|---|
| Water stand pipe | PEHD (High density polyethene) in the upper pipes and stainless steel in the bottom pipe. |
| Tubing | Tecalane (polyamide) |
| Casing rubber | Polyuerethane |
| Connection pipes and supporting frame | Stainless steel |
| Dummy | PEHD |
| Other details | Tape, pump, filter (polyamide yarn) |

***Figure 3-1.*** *Lowering of sampling equipment in the wide diameter water stand pipe in order to pump water from the connected borehole section. From the bottom; filters, small inflatable packer and pump.*

The large diameter stand pipes allow lowering of a pump connected to a 50 µm filter (polyamide) and a mini packer for isolating the stand pipe from the atmosphere (cf. Figure 3-1). In order to collect samples, pumping is conducted in the closed stand pipe. When the pressure decreases, groundwater from the connected borehole section is sucked into the stand pipe and pumped to the ground surface.

The packed-off borehole sections that were included in the monitoring programme in Forsmark varied in length between 9 m and 31 m. Dummies (PEHD) were installed in all the sections to reduce the section volumes and facilitate exchange of water in the sections. The section volumes varied between 12 and 40 litres and the total volumes including tubing between the stand pipe and borehole section amounted to between 18 and 62 litres.

Before pumping sample water from the connected borehole section the pump was always rinsed by pumped water from the upper part of the stand pipe for a few minutes. The pumping flow rate used for water exchange and sampling amounted to between 20 and 300 L/ min depending on the hydraulic transmissivity of the borehole section. The sample treatment and analytical method used were identical to the ones previously described for CCC. (Note: When the borehole section being monitored is the same as that sampled earlier during CCC, the pump rates used are similar as they are both determined by the same bedrock with the same hydraulic properties).

The major advantage with the monitoring method as used during the PLU site investigations and subsequent monitoring phase is that:

- It provides the possibility to verify the major groundwater chemistry over long periods of time.
- The same equipment can be used for several purposes, i.e. continuous groundwater pressure registrations, groundwater sampling for chemical analyses and groundwater flow measurements.

For more delicate hydrochemical studies such as trace element analyses, and also involving redox sensitive elements such as Fe(II) , Mn(II) and S(−II), there are, however, several problems as described below:

- Long contact time between groundwater and the stationary borehole equipment.
- Generally, only one sample is collected at each sampling occasion (i.e. Spring and Autumn). The sample is collected after removing at least three but generally five section volumes of groundwater.
- The stand pipes, the tubing connecting each stand pipe to the corresponding borehole section, and probably also the sections themselves, contain after some time a dirty, smelling stagnant water with a high microbe content and high TOC and sulphide concentrations /Rosdahl et al. 2010, Nilsson et al. 2010/, all of which may contaminate the samples. The only way to minimise contamination is to ensure a sufficient exchange of groundwater into the borehole section before sampling.
- The need to remove large volumes of water from the borehole section in order to prevent contamination from stagnant water initially present in the borehole section, or in the stand pipe, may affect a large bedrock volume with one or more sources of groundwater from different aquifers. This may result in questionable representativity of the sampled water due to mixing which, in turn, may also impact on the sulphide concentration.
- The equipment constitutes a complex system and the contribution from trapped stagnant water to the samples from the borehole section or from tubing may be difficult to avoid, inspite of long pumping periods and removal of large water volumes before sampling.
- A pump connected to a 50 µm filter has to be lowered through the dirty water to the bottom of the stand pipe in order to sample the connected borehole section. However, the pump is rinsed first with this water to avoid contamination from the previously sampled borehole. During sampling, therefore, the filter will most probably catch solid dirt that may contaminate subsequently collected samples.
- The lowering and raising of equipment in the two stand pipes connected to each circulation section creates pressure differences and water movements that probably propagate down to the borehole section being sampled. The sounding of the groundwater level each month in the narrow stand pipe for pressure measurements is a frequently repeated activity that in the long run may impact on conditions in the borehole section.
- Remains from dead insects and vegetation and even mice are often present on top of the packers sealing off the stand pipes. It is not unreasonable to believe that some of these materials reach the water in the stand pipes when the packers are released and lifted to the surface. Furthermore, transport of this material further down to the borehole section by gravity is likely to occur.

### 3.1.4 Hydrochemical monitoring performance in the Autumn of 2009

Uncertainties concerning the sulphide concentrations in the Forsmark bedrock groundwaters still remained after completion of the site investigations in 2007 and one additional year of routine monitoring. Therefore, additional efforts were made in the Autumn of 2009 in 13 out of the 33 borehole sections included in the monitoring programme in order to improve the sampling and avoid some of the disadvantages listed above /Nilsson et al. 2010/. This section describes these measures and Section 3.1.5 presents estimations of the amount of initial stagnant section water contributing to the samples. Furthermore, the observed correlation between the decrease in sulphide concentration and estimated initial section water contribution to each sample in nine sample series is discussed.

The measures taken were:

- Additional cleaning and complete exchange of water in the stand pipes in contact with the groundwater samples, followed by the minimum removal of three section volumes of water in the borehole sections. This was to ensure that after the cleaning and pumping procedures, each stand pipe contained groundwater only from its connected borehole section and not a mixture representing the entire borehole.
- The borehole sections were allowed to settle for one to two weeks prior to sampling in order to minimise the increased turbidity caused by vigorous cleaning resulting in the transport of dislodged dirt particles of varying type, precipitates and/or microbes to the water in the stand pipes and/or borehole sections.
- Sample time series, including five samples from each borehole section, where collected during continuous pumping when; a) one tube volume, b) one section volume, c) two section volumes, d) three section volumes, and finally e) five section volumes, where removed from the borehole sections.
- Estimations of the contribution from the initial section water to each sample in the time series were conducted using simple plug flow calculations (cf. Section 3.1.5).

As expected, the resulting sulphide data from the Autumn monitoring campaign generally show decreasing trends within each sample time series. The concentrations do not quite reach stable values and there is an obvious need for longer pumping periods (cf. discussion on residual borehole section water below). In addition, despite the cleaning efforts, the final sulphide values generally verify the concentrations obtained from the previous monitoring data and not the very low concentrations from the initial CCC programme.

Importantly, a connection between pump stops and irregularities in the sulphide data trends was observed. This indicates the existence of a flow/pressure dependent contamination source, i.e. either; a) stagnant water high in sulphide present in the borehole section or tubing contributes more to the sample water when the pumping has stopped, and/or b) the microbes in the borehole section respond quickly with increased activity when the pump is stopped, and again section water contributes more when the drawdown in the section decreases. Typical sulphide trends with and without pump stops are presented in Figure 3-2 and 3-3. The effect of pump stops has been reported earlier from the MICROBE project at the Äspö HRL (Hard Rock Laboratory). In contrast to the monitored borehole sections in Forsmark, the volume of the investigated borehole section in this case was reduced to a minimum (30+60 mL dead volume) and the conclusions were different, cf. Section 3.2.3 and /Hallbeck and Pedersen 2008c/.

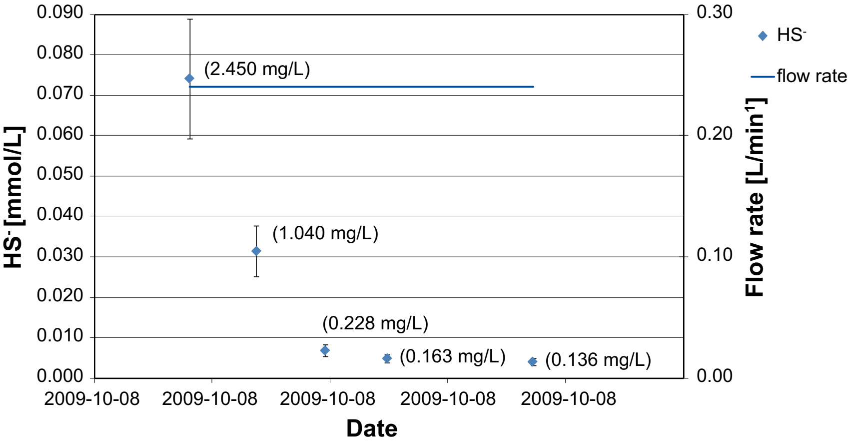


***Figure 3-2.** Decreasing sulphide concentration trend (mmol/L) in sample time series collected in KFM01D: −252.5 masl, together with the measured pumping flow rate. The concentrations in mg/L are given to each data point. The error bars represent the measurement uncertainty ± 25% (2σ).*

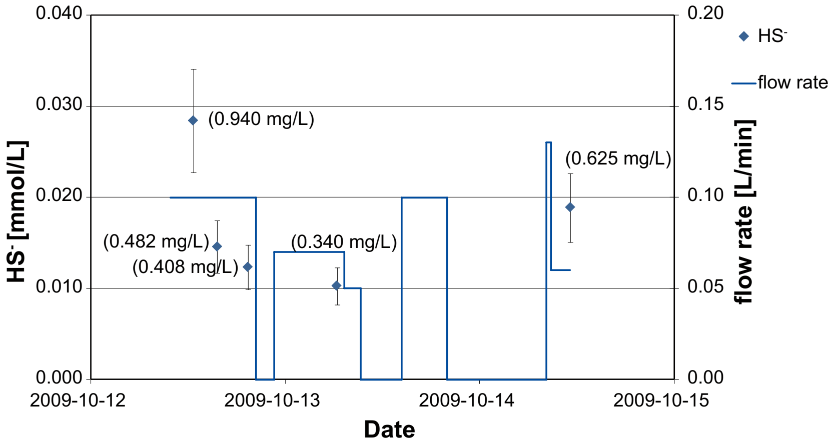


***Figure 3-3.*** *Sudden increase in an otherwise decreasing sulphide concentration trend (mmol/L) in sample time series collected in KFM08D: −662.5 masl, together with the measured pumping flow rate indicating three pump stops, the most prolonged and important being the final one. The concentrations in mg/L are given to each data point. The error bars represent the measurement uncertainty of ± 25% (2σ).*

### 3.1.5 Plug flow estimation of the contributions of initial borehole section stagnant water to the samples

One possible reason for the observed enhanced sulphide concentrations with time is the contribution to the samples from the initial stagnant water present in the borehole section prior to pump start. These residual section waters may contain high sulphide concentrations reflecting changes in borehole conditions with time. This hypothesis was tested by estimating the percentage of borehole section water in each sample in the sample time series and comparing these with the corresponding sulphide concentrations.

Groundwater samples should ideally consist of 100% formation groundwater directly from the water bearing fractures in the adjacent bedrock in order to be fully representative. To which extent this condition is fulfilled, if three to five section volumes are removed from the borehole section prior to sampling, depends on the distribution and hydraulic transmissivity of the flow anomalies influencing the borehole section (cf. Figure 3-4). For example, a single water bearing fracture (**A** and **B**) with high hydraulic transmissivity, located in the upper/nearest part of the borehole section close to the outlet from the section is favourable, since the water volume in the part of the borehole section beneath the fracture will stay trapped regardless of the removal of water from the section (i.e. it is a dead volume). If, on the other hand, there are several fractures in the section (**C** and **D**), borehole water between the fractures will contribute to the sample until formation water from the last fracture reaches the outlet. In this case there is a good possibility that some residual water will remain in the borehole section when sampling commences and can be expected also in the final samples .

Simple plug flow calculations /Nilsson et al. 2010/ were made in order to estimate the percentage contribution of the initial borehole section water to each sample in nine time series samples (i.e. nine borehole sections without pump stops during the sampling sequence) and the results were compared to the sulphide concentrations in the samples.

Selected examples from two of the nine borehole sections both in borehole KFM02A, representing one favourable (KFM02A:−495 masl) and one unfavourable borehole section (KFM02A:−418 masl) from a water exchange point of view, are given in in Figures 3-5 to 3-7. The contribution from formation water to the total pumped flow is displayed in Figure 3-5 and the travel time in hours before a certain flow anomaly was contributing is given above each bar. From Figures 3-5 and 3-6 it may be concluded that the first sample from borehole section KFM02A:−495masl, was collected before any contribution of formation water took place and therefore consisted of 100% initial borehole section stagnant water. The dominating anomaly (6) should begin to influence the pumped water after about 1½ hours and give almost full contribution to the total flow after about 2.5–3 hours. This coincides in time with a pronounced reduction in sulphide concentration.

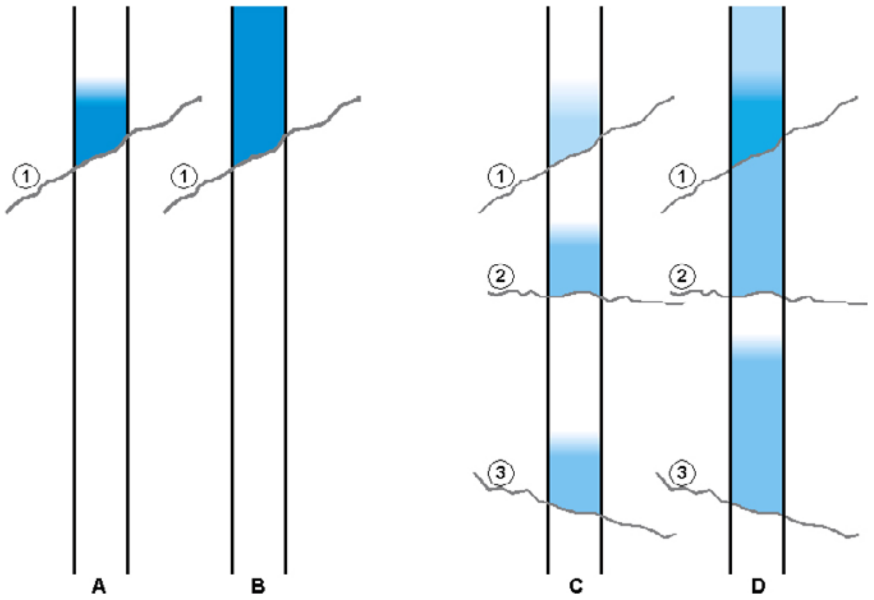


***Figure 3-4.*** *The colour strength illustrates the amount of new formation groundwater in a borehole section during pumping. A and B show a situation with one water yielding fracture. Shortly after pump start (A) the water from the only fracture has not reached the outlet from the section. After a certain time (B), all the water leaving the section is formation water. C and D show a situation with three fractures yielding similar contributions to the total flow. Shortly after pump start (C), no formation water has reached the outlet from the section. After a certain time (D), corresponding to situation B, formation water from fracture 1) has reached the outlet and formation water from fracture 2 has passed fracture 1. Formation water from fracture 3 has not yet reached fracture 2 and the water at the outlet from the borehole is still a mixture between formation water and initial section water since fractures 2) and 3) are not yet contributing.*

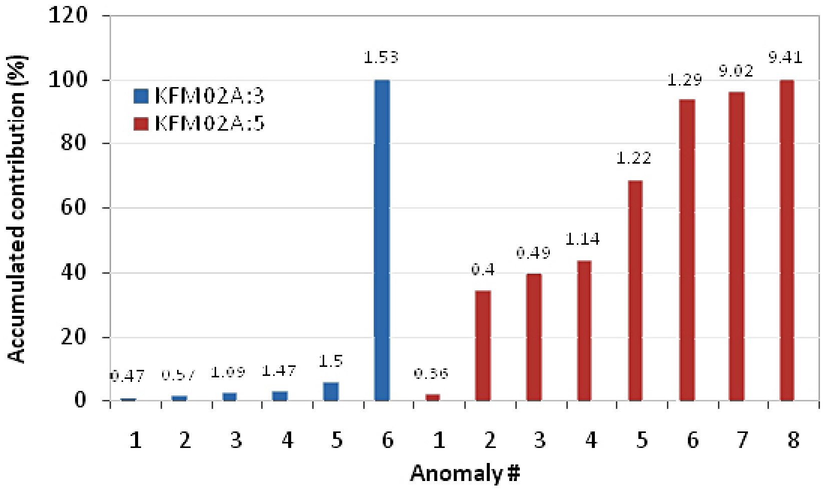


***Figure 3-5.*** *Accumulated contribution (in % of total flow) of formation water from an increasing number of flow anomalies for borehole KFM02A and borehole sections #3 (−495 masl) and #5(−418 masl). Each contributing anomaly (1–6 and 1–8) represents an increase in depth of each flow anomaly from the top of the borehole section. The calculated travel time (in hours) is given above each bar.*

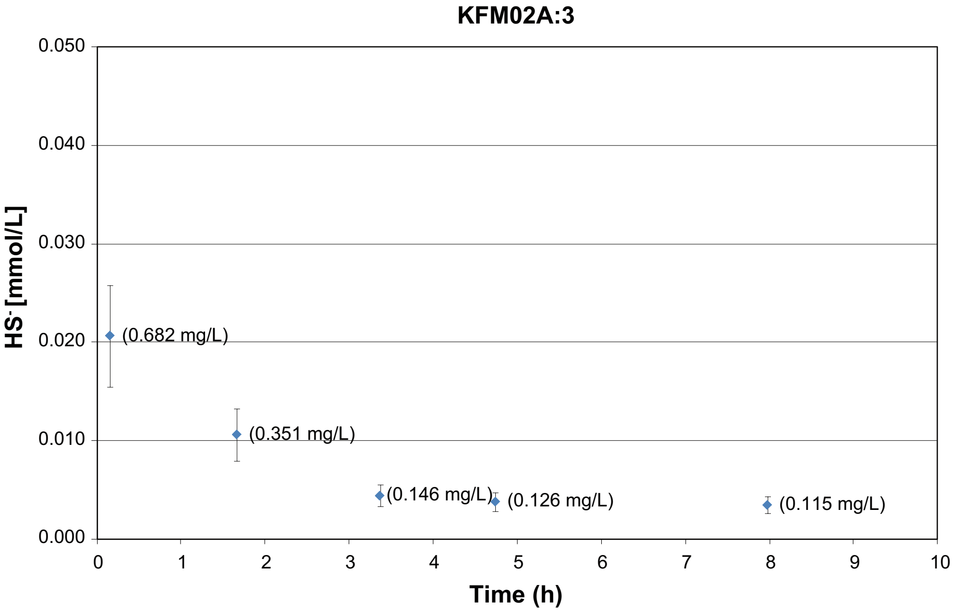


*Figure 3-6. Sulphide concentrations in sample time series from borehole section KFM02A: −495 masl. Time from pump start to sampling is reduced by the travel time from the top of the borehole section to ground surface. The concentrations in mg/L are given to each data point. The error bars represent the measurement uncertainty ± 25% (2σ).*

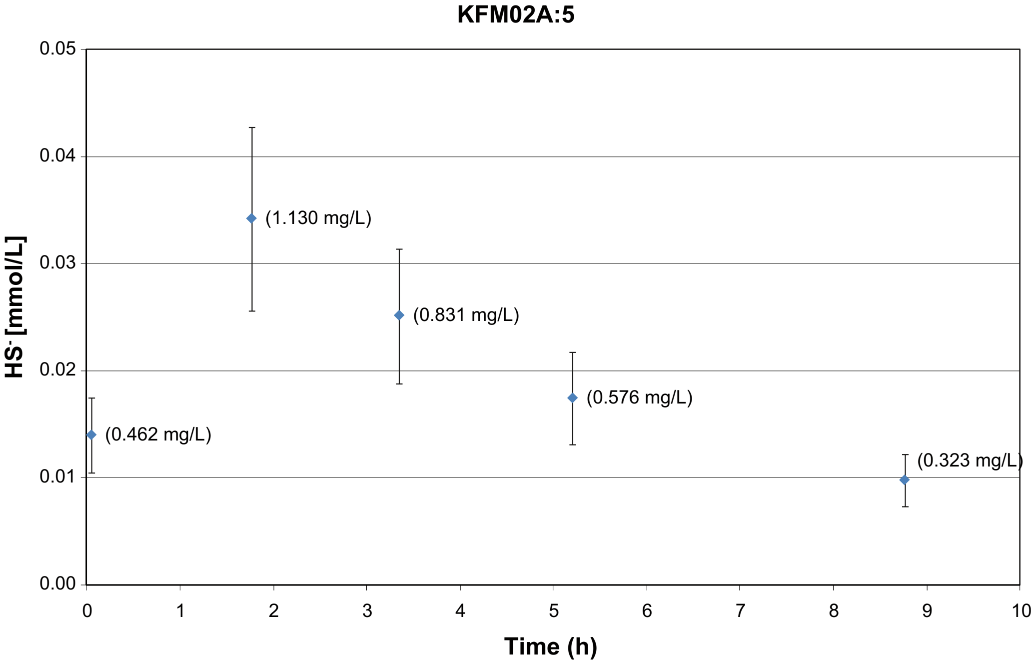


*Figure 3-7. Sulphide concentrations in sample time series from borehole section KFM02A:−418 masl. Time from pump start to sampling is reduced for the travel time from the top of the borehole section to ground surface. The concentrations in mg/L are given to each data point. The error bars represent the measurement uncertainty ± 25% (2σ).*

Comparison of the Figures 3-5 and 3-7 reveals that, when the first sample from section KFM02A: −418 masl, was collected, a certain amount of the water originated from the tubing between the borehole section and ground surface. Furthermore, since the water from anomaly 7 never contributed during the sampling, the final sample contained approximately 7% of the initial borehole section stagnant water. The sulphide trend in Figure 3-7 remains quite steep and it is obvious that more water should have been removed in order to obtain representative samples.

Taking into account all possible errors in the calculations, a comparison between the nine sulphide concentration trends and the corresponding calculated admixture of formation water, supports the hypothesis that residual initial borehole section stagnant water is causing enhanced sulphide concentrations. Generally, the different sulphide trends (i.e. speed of decrease), correspond quite well to the increases of formation groundwater contribution (or decreases of initial borehole section stagnant water contribution). Furthermore, stable low concentrations coincided with a favourable geometric situation in the borehole, i.e. the samples contain close to 100% formation groundwater from the start. Pump stops occurred in the remaining four borehole sections which prevented estimations of section water contribution and caused irregular trends due to sudden increases in concentrations. The last sample in the sample series from borehole KFM01D at −343 masl, showed an increased sulphide concentration most probably due to a documented hydraulic connection to the borehole section above. The different cases are commented on for each borehole section in Appendix 1.

The borehole sections showing the highest sulphide concentration in the final sample coincide with those sections where the contributing initial borehole section stagnant water remains significant.

### 3.1.6 Other experience and observations

The two described sampling methods have been used in other SKB projects and also under somewhat different conditions from the ones accounted for above.

The CCC method was used already during the pre-investigation phase within the Äspö Hard Rock Laboratory project from 1986–1990 /Smellie and Laaksoharju 1992/ with similar equipment. Unlike the present programme in Forsmark, the time delay for the CCC between the drilling and the hydrochemical investigation campaign was between four months and a year. The sulphide concentrations encountered were often relatively high and could be correlated to the long delay before the sampling occasion. Samples with sulphide concentrations exceeding 1 mg/L (and a few concentrations as high as 7 mg/L) were measured in boreholes some eight months after being drilled.

In the SFR-extension project, from 2007–2009 groundwater samples were collected from several recently drilled boreholes using the same type of stationary borehole equipment as in the ongoing monitoring programme at the Forsmark site. In contrast, the sampling (i.e. sample time series from each borehole section) took place shortly after drilling (about two months). The measured sulphide concentrations were generally stable and well below 0.02 mg/L. However, one borehole section was sampled repeatedly in November 2008 as well as in March 2009 /Thur and Nilsson 2009/. In this case the sulphide concentrations amounted initially to 0.022 mg/L in November and then showed higher values, but with a decreasing trend (0.110, 0.105 and 0.077 mg/L), in the sample time series from March.

## 3.2 Potential implications from observations at Laxemar and Äspö

### 3.2.1 Sulphate-reducing bacteria at Äspö

The presence of sulphate-reducing bacteria in Forsmark, Laxemar and Äspö and the SRB activity in Äspö at 450 m depth has been reported in /Hallbeck and Pedersen 2008a, b, c, Rosdahl et al. 2010/. The study on groundwater viruses /Eydal et al. 2009/ also indicates that SRB are ubiquitous in the Äspö groundwaters.

### 3.2.2 In situ studies to investigate sulphide production processes in groundwaters at Äspö and Laxemar

In order to better understand the variations in sulphide contents (and especially the very high values) obtained during the monitoring sampling at Laxemar and Forsmark, one borehole from the Laxemar area (KLX06) was selected to study the variation in sulphide during a longer period of continuous sampling (up to 145 section volumes). During this period, 13 samples were analysed and after a pause of two and a half months the sampling was repeated again when only 7 borehole section volumes were pumped and 4 samples were analysed, cf. Figure 3-8. The two sampling series show identical behaviour with the highest sulphide contents present in the first section volume, i.e. where the water is exposed to both the fracture walls and the downhole equipment. With continued pumping, the sulphide contents decreased significantly but stable values were measured only first after 60 borehole section volumes of water were removed.

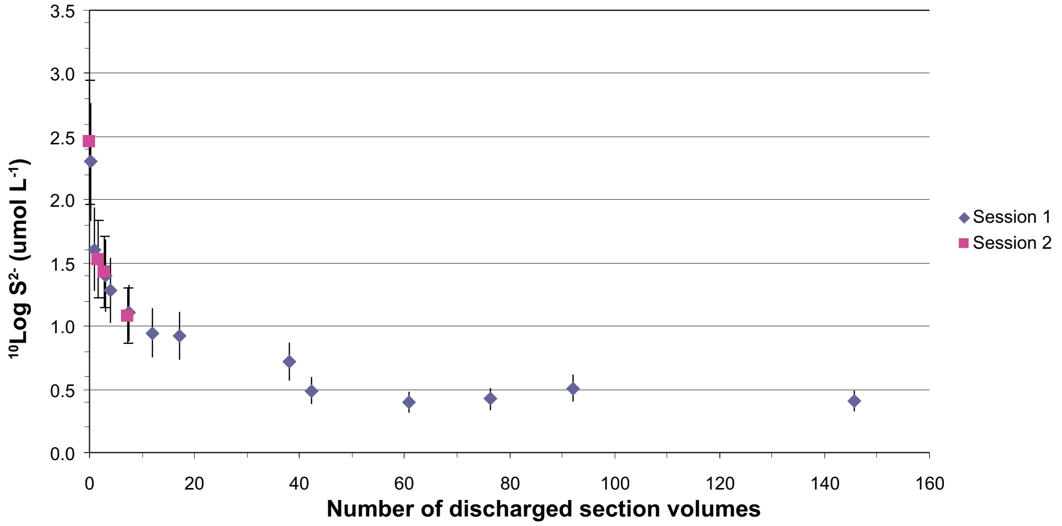


***Figure 3-8.*** *Sulphide contents in groundwaters from KLX06:−475 masl versus number of pumped borehole section volumes removed. First time series,blue symbols (2009-02-09 to 2009-02-23) was extended to 145 pumped borehole section volumes removed. Second time series, pink symbols, started after 2.5 months and comprise only 7 pumped borehole section volumes removed. The error bars represent the measurement uncertainty at ± 25% (2σ).*

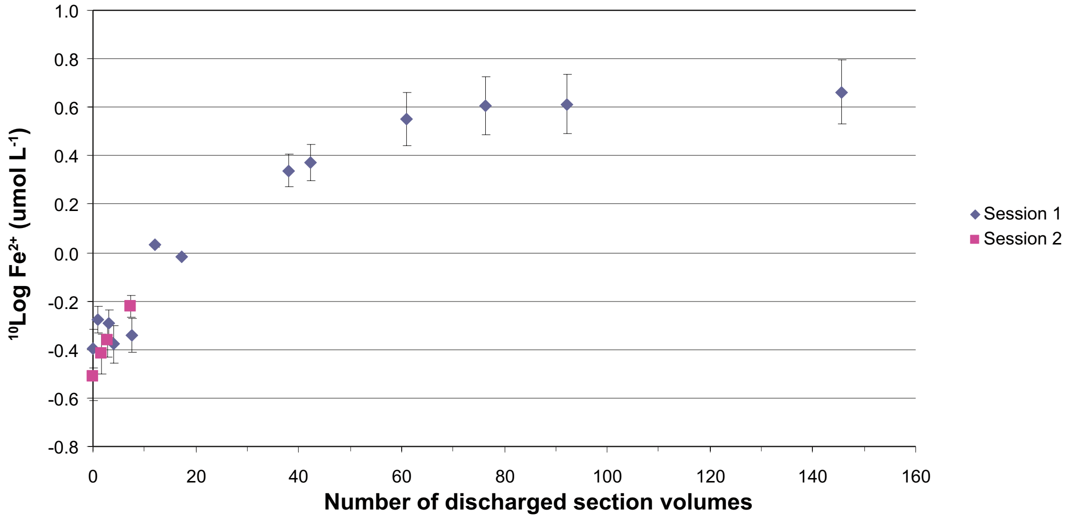


***Figure 3-9.*** *Fe$^{2+}$contents in groundwaters from KLX06:−475 masl versus number of pumped borehole section volumes. Time series (2009-02-09 to 2009-02-23) was extended to 145 pumped borehole section volumes. The error bars represent the measurement uncertainty ± 25% (2σ).*

Analyses from two boreholes at Äspö (KAS03 and KAS09) drilled during 1988 and 1989 were also included in the study. Aging of equipment (from the early 1990´s) and long water exposure times of the borehole walls have been suggested as a possible trigger to sulphide production. In both boreholes the equipment was subsequently removed and the nature of the corrosion and the black amorphous precipitate covering the downhole parts could be observed /Rosdahl et al. 2010/. Some unrealistically high values of sulphide and DOC (> 100 mg/L) were measured and attributed to the addition of partly solid material passing through the filter. This is in line with the observations of turbid samples where particulate sulphide may be included in the analyses.

Important observations and lessons learned during the project are:

- In KLX06 the entire groundwater chemistry differs in the first samples collected in the time series. The reason for more dilute water in the first samples may be due to a leakage in a standpipe connection or a connection in one of the tubes leading to the test section. Since the water pressure is higher in the uppermost section than in the tested section, such a leakage may transport shallow water to the test section via the tubes.
- From the long time series in KLX06 it is evident that only after 60 section volumes have been removed does the water reach stable sulphide values; this is also reflected by Fe. When repeating the sampling after several months an identical decrease in sulphide was detected, cf. Figures 3-8 and 3-9. Only four samples were taken during this sampling event and it is obvious from the plot that stable values were not achieved. As discussed in Section 3.1.4, the extent of the pumping required is section-specific and different volumes may need to be removed to achieve stable values that are representative of the fracture groundwater. It is worth noting that the plug flow calculation on the section sampled in KLX06, corresponds very well with the obtained results, in agreement with the Forsmark results, cf. Section 3.1.4.
- The section sampled in KLX06 is especially unfavourable from the water exchange point of view since the dominating flow anomaly is located in the middle of the borehole and a second anomaly, with very low hydraulic transmissivity, is present close to the bottom. This geometry explains the extremely slow stabilisation of the sulphide concentration.
- The study confirms earlier indications from borehole sampling that the aging of the borehole and borehole equipment makes it increasingly more difficult to obtain reliable values of especially trace and redox sensitive elements. This study, together with the results from the time series measurements at Forsmark, shows that a time series of 5 borehole section volumes removed by pumping can be assumed to be far too low in many cases to obtain reliable sulphide values from the fracture groundwaters.

### 3.2.3 The MICROBE project

A methodology for the determination of microbial process rates was developed and tested under open and closed controlled conditions in a circulation system situated 447 m underground at the MICROBE site at the Äspö HRL /Hallbeck and Pedersen 2008c/. The site includes three core drilled boreholes, each one intersecting a water yielding fracture that was packed-off in a 20-cm section with metal-free, inflatable packers. The section in the borehole denoted KFJ0052F01 was used for the described experiment. A circulating system connected to the borehole section allowed groundwater from the fracture to be pumped through four flow cells in the laboratory and then back to the borehole section again under maintained *in situ* conditions. The volume of the borehole section itself was only 30+60 mL (volume included in the circulation and dead volume close to the inflated rubber part of the packers and not included in the circulation, respectively). The section volume was minimised by a dummy made of PEEK (Polyetheretherketone). The total circulation system constituted a volume between 1,057 and 5,000 mL (minimised and maximised expansion vessel, respectively).

Sampling for sulphide determinations was conducted first under open condition, during 140 days. The sample water was collected almost immediately in the flow line from the borehole section, but after the pump. Duplicate samples for sulphide analyses were collected and the sample volume was about 2×120 mL. Before sampling the circulation was flushed with 2,000 mL of formation groundwater from the fracture system. Since the sulphide concentration varied significantly during the first 60 days, more frequent sampling was performed between day 80 and 105 in order to analyse whether the fluctuations were correlated with the sampling frequency. The sampling continued under closed conditions from day 140 to day 230 where the volume of the expansion vessel was used for repeated microbe determinations as well as acetate and sulphide analyses.

From the experiment in the borehole KJ0052F01 it was observed that the concentrations of sulphide seemed very sensitive to the sampling procedure which is also the experience from the monitoring programme in Forsmark. Frequent sampling and flushing in the open circulation configuration, in contact with the intersected fracture, lowered the sulphide concentration while less frequent sampling due to weekends increased the concentration. In the closed configuration without possible supply of formation water, on the other hand, the sulphide concentration increased with time. Several possible explanations were suggested: 1) Sulphide production is going on in some descrete fractures but not in others and flushing may cause dilution of the produced sulphide in the groundwater. 2) Production of sulphide by SRB may be sensitive to flushing for similar reasons, as their sources of energy may become diluted. 3) Most of the groundwaters contained dissolved Fe(II) and precipitation of solid iron sulphide may be induced by the mixing of groundwater caused by flushing and pumping. The increase in sulphide concentration observed in the closed mode is in the last case consistent with the absence of iron oxide minerals. In contrast to the presented views in this report regarding the Forsmark data, the conclusion from the MICROBE experiment, concerning sulphide concentrations, was that the low concentrations generally found during flushing or pumping as well as from the CCC method during the site investigations are artefacts and that the high values represent a more accurate concentration in the groundwaters.

# 4 Evaluation of the sulphide data from Forsmark

## 4.1 Introduction

The evaluation of the Forsmark dataset intends to establish as close as possible the natural, undisturbed groundwater sulphide contents. This considers not only the measured sulphide contents, but also the amount and variation of the reductant species, i.e. mainly Fe and DOC, but Mn (as a further redox indicator) and $HCO_3$ (as a further indicator of microbial sulphate reduction) also have been used.

Because of the large amount of information contained in Chapter 3, Sections 4.2 and 4.3 have been introduced to facilitate the reader by briefly summarising some of the background information relating to the evaluation of the sulphide data, i.e. the data sources available, a brief mention of some of the sampling difficulties involved, and a short summary of the sampling strategy.

## 4.2 Data sources and availability

The evaluation discussed below is based on the dataset extracted and delivered from Sicada (Sicada-09-185) which includes *all* the groundwater samples from percussion and cored boreholes analysed for sulphide from Forsmark. Sampling series sulphide trends from the monitoring performance in Spring 2010 have been used as supporting data in Appendix 1 (Sicada-10-126).

Two sources of sulphide data are available; 1) Complete Chemical Characterisation (CCC) data from cored boreholes of the site characterisation programme (i.e. Forsmark Extended 2.3 data freeze /Laaksoharju et al. 2008/) that includes the earlier established categorisation of the samples based on groundwater type and major ion chemistry, and 2) data from the monitoring of selected borehole sections in percussion and cored boreholes initiated at different times during and following the site characterisation programme up to November 2009. Figure 4-1 shows sulphide content (with analytical error bars) versus elevation for the entire Forsmark dataset.

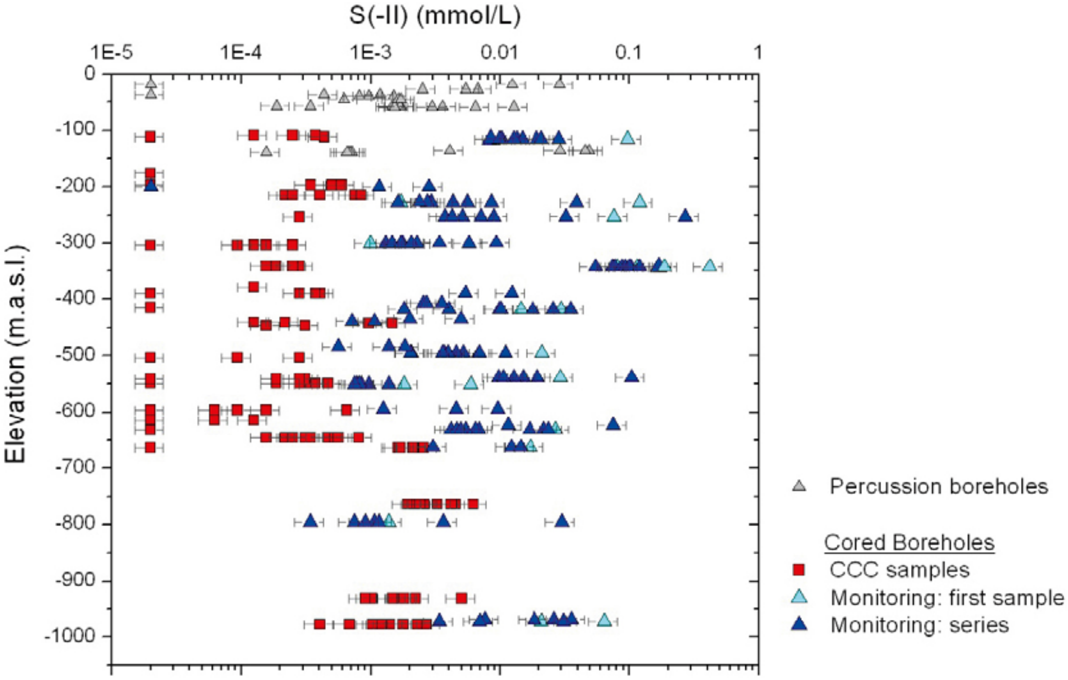


***Figure 4-1.*** *Sulphide versus elevation from cored and percussion boreholes. Data below the detection limit of the analyses (2σ i.e. 0.006 mg/L or 0.19 µmol/L) are shown in this diagram at $2\cdot10^{-5}$ mmol/L.*

It is important to note that detection levels for sulphide have varied during the site investigations from 0.002 to 0.006 mg/L but during some periods a "reporting limit" of 0.03 mg/L (equal to 10σ) has been used when the measured values are included in the data base.

The overall quality of the Forsmark groundwater samples has been categorised already as 1–5 (i.e. highest to lowest quality) for the hydrogeochemical site descriptive modelling /Smellie et al. 2008/ and will not be repeated here, but it is important to note that these criteria relate mostly to major ions and the important environmental isotopes. Because of the increased sensitivity of many minor elements to drilling and sampling procedures, sometimes their element values may either be missing or obviously wrong when compared to the rest of the data. This refers mainly to the redox sensitive elements (e.g. $S^{2-}$, Fe and Mn), which are of special importance for the SR-Site safety case. This is, for example, the case with the two sections from boreholes KFM04A sampled with CCC. These where categorised as Category 3 (suitable for modelling purposes) based on major ions, but their high Fe and Mn contents, together with the problematic Eh measurements in these sections, makes their sulphate content unreliable and consequently no sulphide values where selected from these sections.

The sulphide values recorded during the CCC sampling are generally low compared with those measured when monitoring has been carried out subsequently in the same sections. However, because different sampling techniques have been employed on these occasions, introducing contrasting types of disturbances and uncertainties (cf. Chapter 3 for details), evaluating the "true" sulphide values is therefore a very difficult task.

## 4.3 Analytical uncertainties

The inclusion of analytical uncertainties in plots and diagrams are often requested and these are included in the sulphide plots in Figure 4-1 above and 4-3 below and are also commented upon in the foot note of Table 4-1. It is important to keep in mind that the sampling uncertainties are generally much larger than the reported analytical uncertainties and therefore the analytical uncertainties are not included in all diagrams in Chapter 5 as it may give a false picture of the reliability of the values.

## 4.4 Sampling strategy

Only cored boreholes have been sampled in the CCC programme, whilst both cored and percussion boreholes form part of the monitoring programme. Sampling in all boreholes is carried out in packed-off borehole sections.

The differences between the two sampling methods are described in detail in Chapter 3. When considering the output of data from the two contrasting types of sampling campaigns it is important to remember that: 1) Sampling in the CCC programme has been conducted normally on a single occasion in a cored borehole section where there is usually a long time series of data extending over some weeks. 2) Sampling in the monitoring programme in most cases has been conducted at several occasions from the same cored borehole section (usually periodically after at least six months or more and using the same permanently installed equipment) and where the time-series data can vary from a single value to, in some cases, a series of values extending over some days (this includes 5 samples collected in the Autumn of 2009), but never to the same extent as the CCC programme.

In some cases the selected monitoring sections coincide, at least closely with those sampled earlier for CCC, thus providing the possibility to compare sulphide values over even longer time intervals. It is important in this context to note that when the borehole section being monitored is the same as that sampled earlier during CCC, the pump rates used are similar as they are both determined by the same bedrock with the same hydraulic properties.

With respect to the percussion boreholes, ten borehole sections from ten different boreholes have been monitored chemically using packed-off sections which are generally less than 15 m in length (normally around 10 m). Sampling has been carried out following the initial removal of at least 5 borehole section volumes of water in order to access suitable formation groundwater quality, and normally one sample is taken on a yearly basis. For most percussion boreholes there are data from three or four such sampling occasions included in the dataset. Seven of the monitored sections show moderate (HFM21, HFM 27 and HFM 32) or high (HFM01, HFM02, HFM15 and HFM19) instability in terms of major ion groundwater chemistry; stable conditions characterise HFM04, HFM 13 and HFM 16. The instability in the groundwater chemistry is due to the interference between the packed-off section being sampled and the fresh water/brackish marine water boundary, and may reflect seasonal variations and/or pumping activities in the sampled borehole section and/or in nearby boreholes.

## 4.5 Selection criteria

Because some borehole sections have been sampled and analysed for sulphide more often than others, a bias would be introduced if all sulphide data deemed as representative were selected to be used in SR-Site. In order to avoid this bias, the approach has been to select a single groundwater sample (with a sulphide value) that can be assumed to be representative for a given section. When time-series data during sampling are available, variations of the reductant species, together with sulphide, can be carefully assessed to provide some insight into presently active sulphide-producing microbial conditions and/or degrees of anthropogenic contamination from pumping/sampling activities.

Evaluation and selection of groundwater samples with respect to the representativity of the sulphide values are based on:

- The stability of the major ion and isotope groundwater chemistry throughout the sampling period. For the CCC samples this is already judged from the earlier categorisation (cf. Smellie et al. 2008) and in these samples the contamination of drilling fluid is one important parameter in that evaluation. For the monitoring samples, in contrast, the potential portions of drilling fluid in many cases cannot be evaluated due to the use of uranine introduced earlier as part of the hydraulic tracer test programme which has been conducted in, or nearby, the same borehole section being monitored .
- The charge balance should be less than ± 5%. A large difference in charge balance indicates that something is seriously wrong with the analytical or the sampling programmes.
- The samples should not show supersaturation in respect of amorphous monosulphide. It is assumed that the precipitation of amorphous monosulphide is very rapid and a groundwater showing significant supersaturation of this phase cannot exist. It therefore indicates a serious analytical error in either the sulphide or ferrous iron analyses, or both.
- The combined variation of one or more of $S^{2-}$, $Fe^{2+}$, $Mn^{2+}$, DOC, $HCO_3^-$ and $SO_4^{2-}$ in the time series may also be an important criteria. Concerning the CCC samples, these elements usually show stable values in the time series measurements for the Category 1–3 samples (a few exceptions occur and are commented upon in the text below). For the monitoring samples, however, the situation is quite different and time series samples measured during the Autumn of 2009 in particular, generally show systematic trends in the behaviour of these elements. The rationale behind these trends are thoroughly discussed in Chapter 3 and will not be repeated here. Generally, the lowest sulphide values are selected which usually correspond to the lowest DOC and $HCO_3^-$ values and also that there is a general stabilising trend towards lower values with increased time series.

Detailed documentation of this evaluation and the chosen sulphide values to be used in the modelling exercises are presented in Appendix 1 in table format. These tables include the total range of $S^{2-}$, $Fe^{2+}$, $Mn^{2+}$ and DOC and the values for the selected sample are also recorded. In addition, time-series data of these elements comprising three or more values in a single sampling sequence (or over longer time periods from the same borehole section) have been recorded with respect to increasing, decreasing or absence of compositional trends with time. Information on groundwater type, chloride content and stability of the major ion chemistry, and the rationale behind the choice of sulphide values, is also given.

## 4.6 Evaluation

### 4.6.1 Cored boreholes

#### *Introduction*

Based on the derived dataset, a graphical framework has been produced to visualise the sensitive changes in chemistry that occurred during sampling of the groundwater time series data, thus leading to a better understanding of the processes involved. The parameters that have been plotted against time (i.e. sampling date) for each of the selected borehole sections sampled are listed in Table 4-1 and described below, and the complete set of plots are included in Appendix 2.

The parameters in question are: $S^{2-}$(mg/L), $Fe^{2+}$ (mg/L), Mn (mg/L), FeS (amorphous) Saturation Index, Cl (mg/L), Mixing Proportion (%), $SO_4$ (mg/L), $\delta S^{34}$ (% CDT), Mg (mg/L), $HCO_3$ (mg/L), DOC (mg/L), Calcite Saturation Index, and pH.

When both CCC sampling and monitoring data are available from the same water conducting structure these are shown also in the same diagrams. It can be seen that, in some sections, the major ion groundwater chemistry is perfectly stable (e.g. KFM02A: −418 m and −496 masl) whereas in others the groundwater has changed significantly between the CCC sampling and the start of the monitoring programme (e.g. KFM 08D: −540.63/−538.06 masl), cf. Figure 4-2. The effect of such changes on the redox sensitive elements is difficult to elucidate.

#### *CCC data*

The initial evaluation step is based on the assumption that groundwaters already judged from the site investigations to be representative from an analysis of the major ions and the important environmental isotopes, would also include the minor elements (e.g. $S^{2-}$, Fe and Mn). Most of the selected CCC sulphide values therefore correspond to groundwater samples previously selected as being representative (i.e. Category 1–3). Sulphide contents for Category 1–2 groundwaters tend to be low, ranging from below detection to 0.063 mg/L (0.002 mmol/L) and Category 3 groundwaters mainly from below detection to 0.3 mg/L (0.009 mmol/L) with most samples below 0.07 mg/L (0.002 mmol/L). Exceptions are one sample from KFM01D and one from KFM06A which record 0.287 and 0.368 mg/L respectively. In one case (KFM03A) where no sulphide value is available, an alternative complete analysis from the same time series which includes a sulphide value was substituted. Because most of the CCC sulphide values are generally low in concentration and reasonably stable during the sampling period, this is considered acceptable.

#### *Monitoring data*

For the monitoring data, the groundwater major ions and isotopes are sometimes unstable when each different sampling occasion is compared, and they may also differ from earlier representative CCC sampling in the same borehole section (if present). In addition, there are less time series sulphide data from each sampling occasion (sometimes only one value) and the values are also generally much higher; mainly 0.003–0.03 mmol/L ( 0.1–1 mg/L) with anomalous outliers at 0.12 mmol/L (3.84 mg/L) and 0.42 mmol/L (13.40 mg/L) and more unstable during the actual period of sampling compared to the CCC data. Allocating a ‘representative’ sulphide value is therefore a difficult task especially when only one sample is analysed at each sampling occasion. In several favourable cases from the monitoring samples (less so from the CCC samples), there are adequate time-series data to show a clear and systematic time-dependent inverse relationship during sampling between sulphide (decreasing with time) and ferrous iron (increasing with time). Other time-series data show opposite trends indicating the unpredictable perturbation effects influencing the borehole sections being sampled. Systematic changes in DOC/TOC, sulphate and bicarbonate are less common but are indicated in some samples. Collectively, these observations probably reflect the differences in microbial processes taking place in the downhole tubings and monitoring sections compared with the processes ongoing in the bedrock fractures.

Corrosion effects may result in anomalously high Fe and Mn, for example as noted in borehole KFM04A: −302.75 masl and borehole KFM10A: −299.83 masl. In contrast, the salinity can be quite stable, showing that these changes are not the product of short-circuiting during monitoring when

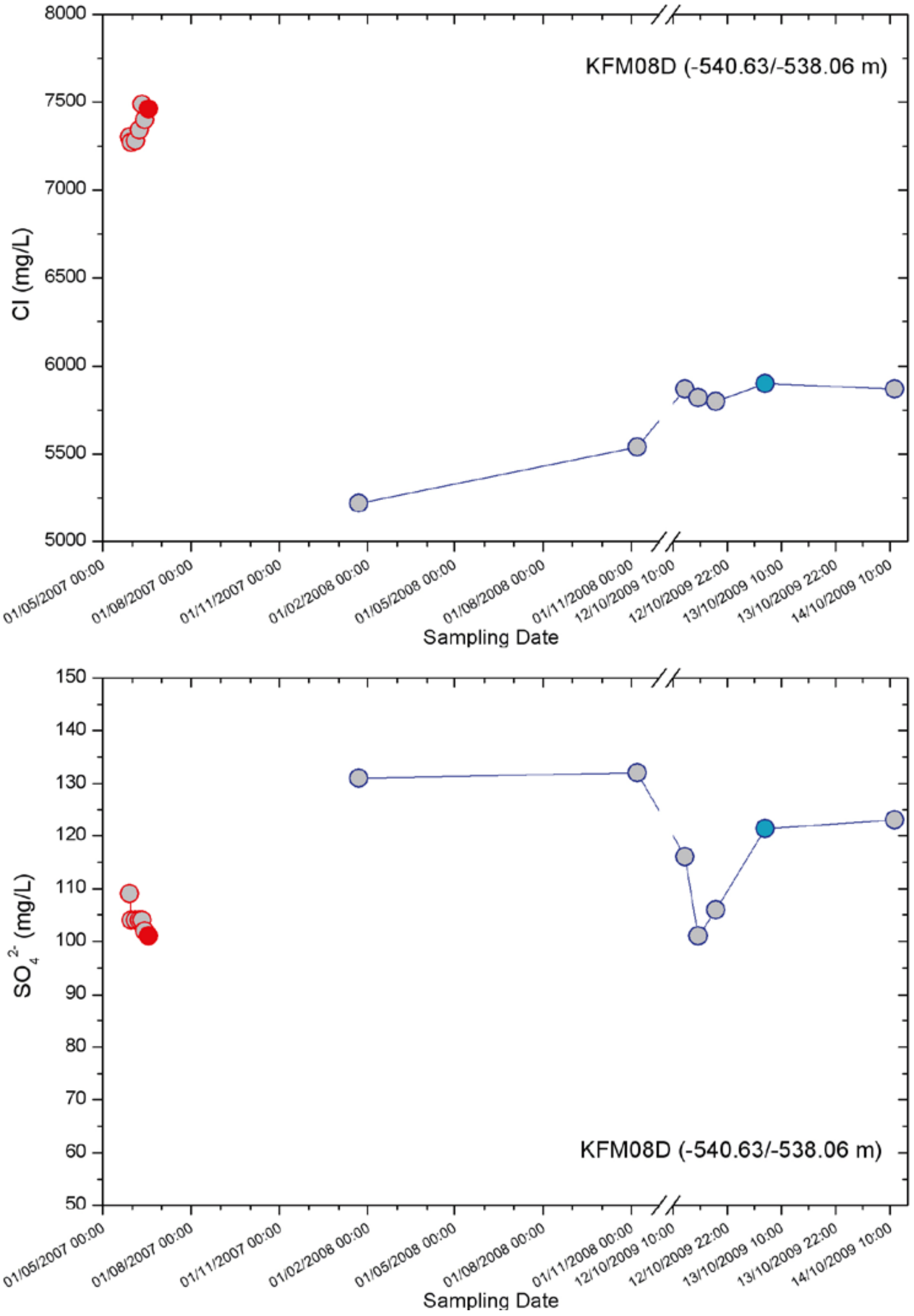


***Figure 4-2.*** *Chloride( upper) and sulphate (lower) contents versus time in borehole KFM 8D: −540.63/ −538.06 masl. The red circles refer to the CCC sampling campaign and the blue circles to the monitoring programme. The respective infilled circles denote the sample chosen as the 'best choice' value. Similar plots for each section are included in Appendix 2.*

portions of other groundwater types can be systematically pulled into the sampling section resulting in mixing. However due to the very high Fe contents no sulphide values have been chosen from these sections.

Examples exist where hydraulic responses are recorded in nearby borehole sections when monitoring is in progress. In this case there is a larger risk of mixing of different groundwaters which may of course affect the composition of the redox sensitive elements. Examples where the monitoring sections are in contact with interconnected water-conducting fractures include KFM01D: −343 masl (cf. Appendix 2).

In KFM01A: −116 masl the monitoring was influenced by the drilling of KFM01D and possibly KFM01B resulting in flushing water and shallow water contamination. In KFM08D:−538 masl and −662 masl a tube between the two sections was found to be leaking, resulting in 40% of water from the upper section in the samples from the deep section and 4% of water from the deep section in samples from the upper section.

The final sulphide value of the time-series data showing a systematic decrease in sulphide, which is a major trend of importance for this evaluation, is selected as being the 'best possible' representative sample available. There are enough data to indicate that, with continued time-series sampling, the sulphide contents probably will continue to decrease, possibly approaching similarly low values to those recorded from many of the CCC sampling occasions (e.g. KFM08A: −550.5 masl). In some cases, however, the final time-series sample shows a sharp increase in sulphide (e.g. KFM08D: −538 masl). This, and other anomalies may be explained by faulty equipment, in this case by an unscheduled pump stop, and therefore the previous value (i.e. the lowest) in the time series is taken as the 'best possible'.

When adequate data are available for both CCC samples and later monitoring samples from the same borehole section, and there are higher values for the monitoring samples which is the normal case, two values have been selected from these sections; one from the CCC sample (corresponding to the earlier selected representative and categorised sample) and one value selected from the monitoring.

### 4.6.2 Percussion boreholes

The sulphide data set from the percussion boreholes presents a special problem, for example, there are no original values compatible with the CCC from the cored boreholes available, and no time-series data have been collected. As mentioned above, most of the percussion borehole sections (seven out of ten) show instability concerning major ion chemistry. This underlines the dynamic situation in the upper bedrock which facilitates groundwaters of different origin and composition to mix and react, possibly enhancing microbial activity and thus sulphide production.

Because information from the upper approximately 150 metres of bedrock, based on the cored boreholes, is very limited, the sulphide data from the percussion boreholes are nevertheless included. Furthermore, these sulphide data provide useful input on the fresh groundwaters which are restricted to the upper approximately 50 metres of the bedrock.

Selected samples/values for the sulphides systematically refer to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time in the borehole, the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion. The variation of sulphide content with time is shown in Figure 4-3 where the initial sample collected for each borehole section is denoted by an arrow. In general, most borehole sections show only a small to negligible variation in sulphide with time (HFM01, HFM02, HFM04, HFM13, HFM16, HFM27), two show an increase (HFM21 and HFM32), and HFM15 shows no systematic trend. HFM19 is shown as an open symbol indicating that no sulphide value has been selected. This borehole section is characterised by very high Fe(II) and Mn(II) values together with high sulphide$^{-}$ and that the calculated saturation index for monosulphide shows significant supersaturation. Consequently, this sample is no longer considered in the evaluation.

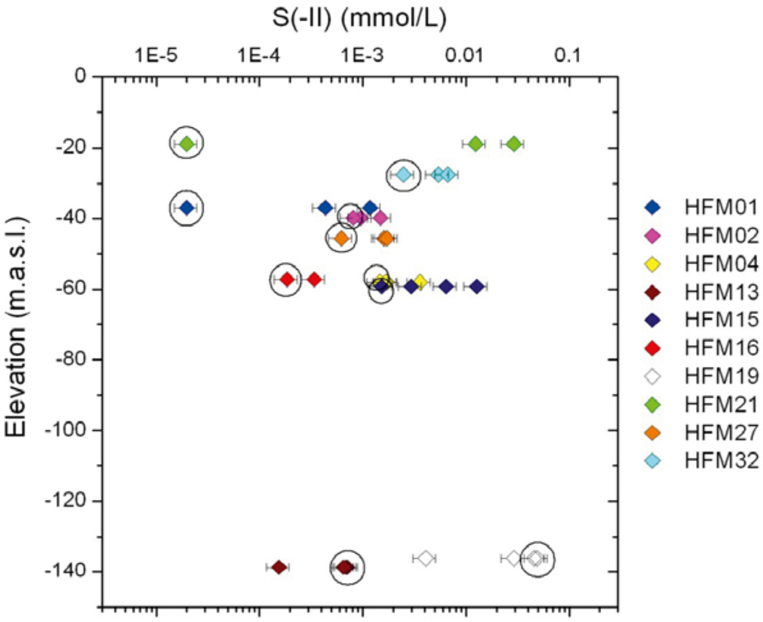


***Figure 4-3.*** *Sulphide values versus elevation for monitoring samples from percussion boreholes. The initial sample collected for each borehole section is encircled. Data below the detection limit of the analyses are shown in this diagram at 2·10$^{-5}$ mmol/L.*

## 4.7 Recommendations

The values from the CCC sampling are usually lower than those measured during the monitoring phase. When both CCC and monitoring values are available from one borehole section two values are used, one representing each of the sampling methods.

When time series are measured in the monitoring sections, in most cases the sulphide values are higher in the downhole tubes and in the borehole section compared with groundwater from the surrounding fractures. The removal of five borehole section water volumes are in most cases not enough to guarantee stable sulphide values. For most of the sections, the last sample in the time series is suggested as representing the ‘best possible’ value.

For the percussion boreholes only monitoring values without time series are available; one sample is taken at each sampling occasion, usually every Autumn over a period of 3 or 4 years. Selected samples/values for the sulphides systematically refer to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time in the borehole the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity on the boreholes walls.

The finally selected samples and values of key parameters are shown in Table 4-1.

In the following Chapter 5: “Overview of Forsmark data for present day conditions”, only the selected samples shown in Table 4-1 are considered.

**Table 4-1. Sulphide and related parameters of the selected samples from the CCC sampling and the monitoring sections.**

| Borehole | Sample-number | Sample type | Elev. m.a.s.l. | $S^{2-}$ mg/L | Fe mg/L | Cl mg/L | $SO_4$ mg/L | Mg mg/L | $HCO_3$ mg/L | Mn mg/L | DOC mg/L | $S^{34}$ ($SO_4$) ‰ CDT | $CO_2$ml/L | $CH_4$ ml/L | $H_2$ ul/L | SRB cells/mL | ATP fmol/mL | siFeS (am) | siCalcite | Trans. (m$^2$/s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HFM01 | 12757 | Monit | −37.02 | < 0.006 | 0.805 | 739.0 | 180.0 | 29.0 | 425.0 | 0.160 | 9.5 | 15.2 | | | | | | | 0.26 | |
| HFM02 | 12006 | Monit | −39.91 | 0.026 | 0.417 | 396.0 | 83.7 | 20.9 | 407.0 | 0.127 | 9.8 | 17.9 | | | | | | −1.03 | 0.42 | |
| HFM04 | 12003 | Monit | −57.92 | 0.047 | 0.348 | 56.3 | 44.8 | 7.6 | 390.0 | 0.080 | 8.3 | 13.4 | | | | | | −0.89 | 0.05 | |
| HFM13 | 12009 | Monit | −138.63 | 0.023 | 3.110 | 5,020.0 | 476.0 | 198.0 | 124.0 | 2.150 | 2.2 | 21.1 | | | | | | −0.93 | 0.33 | |
| HFM15 | 12007 | Monit | −59.11 | 0.206 | 1.020 | 406.0 | 104.0 | 15.2 | 471.0 | 0.467 | 13.0 | 27.8 | | | | | | −0.19 | 0.27 | |
| HFM16 | 12379 | Monit | −57.18 | 0.011 | 0.356 | 187.0 | 101.0 | 9.0 | 446.0 | 0.090 | 13.0 | 12.4 | | | | | | −1.53 | 0.17 | |
| HFM21 | 12758 | Monit | −18.82 | < 0.006 | 1.020 | 241.0 | 105.0 | 19.7 | 450.0 | 0.190 | 7.6 | 9.4 | | | | | | | 0.43 | |
| HFM27 | 12506 | Monit | −45.60 | 0.020 | 2.640 | 2,660.0 | 347.0 | 125.0 | 247.0 | 0.847 | 4.6 | 25.9 | | | | | | −1.03 | 0.35 | |
| HFM32 | 12518 | Monit | −27.46 | 0.080 | 3.570 | 3,970.0 | 374.0 | 173.0 | 195.0 | 0.919 | 3.5 | 28.3 | | | | | | −0.62 | −0.01 | |
| KFM01A | 4538 | CCC | −111.74 | 0.014 | 0.790 | 4,562.8 | 315.7 | 142.0 | 61.5 | 0.691 | 1.5 | 25.5 | | | | 1.20 | | −1.33 | 0.22 | 6.20 E−08 |
| KFM01A | 16512 | Monit | −115.79 | 0.313 | 0.488 | 3,970.0 | 306.0 | 120.0 | 95.3 | 0.737 | 2.1 | 25.5 | | | | | | −0.12 | 0.45 | 6.20 E−08 |
| KFM01A | 4724 | CCC | −176.26 | < 0.030 | 0.515 | 5,329.5 | 547.0 | 204.0 | 99.5 | 1.020 | 2.3 | 25.6 | 1.19 | 0.12 | 5.4 | 0.20 | | | 0.20 | |
| KFM01D | 12366 | CCC | −253.31 | 0.009 | 2.480 | 3,890.0 | 279.0 | 101.0 | 131.0 | 0.584 | 4.1 | | | | | | | −1.12 | 0.51 | 2.90 E−07 |
| KFM01D | 16527 | Monit | −252.53 | 0.136 | 1.450 | 4,180.0 | 167.0 | 56.7 | 29.8 | 0.488 | 3.0 | 23.4 | | | | | | −0.15 | −0.08 | 2.90 E−07 |
| KFM01D | 12316 | CCC | −341.93 | 0.009 | 1.360 | 5,160.0 | 78.6 | 13.7 | 21.5 | 0.171 | 2.3 | 33.8 | 0.2 | 0.14 | < 2.8 | 7.00 | 142,000 | −0.85 | 0.46 | 1.30 E−07 |
| KFM01D | 16519 | Monit | −343.03 | 3.850 | 0.139 | 4,570.0 | 104.0 | 33.7 | 39.6 | 0.190 | 2.9 | 41.7 | | | | | | −0.02 | 0.15 | 1.30 E−07 |
| KFM01D | 12343 | CCC | −446.86 | 0.010 | 0.729 | 5,960.0 | 31.1 | 10.9 | 17.1 | 0.088 | 11.0 | 24.0 | 0.04 | 4.60 | < 3.4 | 13,000 | 233,000 | −0.88 | 0.65 | 1.70 E−08 |
| KFM02A | 8100 | CCC | −108.85 | 0.008 | 1.370 | 642.0 | 89.6 | 31.0 | 354.0 | 0.254 | 11.0 | 20.8 | | | | | | −1.34 | 0.38 | 2.20 E−05 |
| KFM02A | 8272 | CCC | −414.81 | < 0.002 | 0.736 | 5,380.0 | 434.0 | 198.0 | 93.4 | 1.810 | < 1.0 | 26.0 | | | | | | | 0.00 | 1.61 E−07 |
| KFM02A | 16577 | Monit | −417.80 | 0.323 | 0.537 | 5,460.0 | 412.0 | 199.0 | 101.0 | 1.920 | 1.8 | 23.0 | | | | | | 0.13 | 0.44 | 1.51 E−06 |
| KFM02A | 8016 | CCC | −503.47 | 0.009 | 1.700 | 5,410.0 | 498.0 | 226.0 | 126.0 | 2.160 | 2.1 | 24.9 | 4.00 | 0.04 | 199.0 | 1.40 | | −2.16 | −0.12 | 4.75 E−06 |
| KFM02A | 16572 | Monit | −494.97 | 0.115 | 1.960 | 5,520.0 | 485.0 | 241.0 | 127.0 | 2.120 | 2.0 | 24.2 | | | | | | −0.36 | 0.32 | 4.72 E−09 |
| KFM02B | 12900 | Monit | −407.05 | 0.081 | 2.820 | 5,580.0 | 430.0 | 222.0 | 114.0 | 2.250 | 1.7 | 24.6 | | | | | | −0.63 | 0.15 | 8.20 E−06 |
| KFM02B | 12898 | Monit | −483.83 | 0.018 | 4.430 | 5,550.0 | 506.0 | 244.0 | 134.0 | 2.220 | 2.3 | 24.7 | | | | | | −1.30 | −0.02 | 4.50 E−05 |
| KFM03A | 8011 | CCC | −379.06 | 0.004 | 0.714 | 5,440.0 | 515.0 | 224.0 | 99.6 | 1.140 | 1.3 | | | | | | | −2.28 | 0.19 | 5.56 E−05 |
| KFM03A | 8017 | CCC | −440.79 | 0.007 | 0.905 | 5,430.0 | 472.0 | 202.0 | 91.8 | 1.170 | 1.2 | 25.4 | | | | | | | 0.40 | 1.28 E−09 |
| KFM03A | 8284 | CCC | −442.34 | 0.047 | 1.070 | 5,330.0 | 511.0 | 216.0 | 93.7 | 1.250 | | 25.7 | 1.50 | 0.03 | 213.0 | 17.00 | 555,000 | −1.13 | 0.15 | 6.65 E−06 |
| KFM03A | 8271 | CCC | −631.91 | < −0.002 | 0.273 | 5,440.0 | 193.0 | 53.1 | 22.8 | 0.318 | 1.3 | 27.6 | 0.57 | 0.07 | < 2.7 | 30.00 | 45,700 | | −0.20 | 2.56 E−06 |
| KFM03A | 16609 | Monit | −631.10 | 0.158 | 0.650 | 5,750.0 | 197.0 | 62.8 | 22.6 | 0.414 | 1.3 | 25.9 | | | | | | −0.43 | −0.06 | 2.56 E−06 |

| | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KFM03A | 8281 | CCC | −930.50 | 0.058 | 0.086 | 8,560.0 | 73.9 | 17.6 | 9.9 | 0.114 | 1.5 | 27.3 | 0.16 | 0.06 | 44.0 | 500.00 | 242,000 | −2.00 | −0.27 | 3.79 E−07 |
| KFM03A | 8152 | CCC | −977.66 | 0.033 | 0.034 | 9,690.0 | 46.7 | 8.1 | 6.9 | 0.009 | 1.4 | 29.6 | 0.03 | 0.05 | < 3.8 | 24.00 | | −2.06 | 0.05 | 5.57 E−09 |
| KFM03A | 16582 | Monit | −969.13 | 0.109 | 0.269 | 10,500.0 | 44.0 | 9.8 | 6.4 | 0.038 | < 1.0 | 31.2 | | | | | | −0.95 | −0.28 | 2.24 E−07 |
| KFM06A | 8809 | CCC | −303.24 | < 0.002 | 0.900 | 4,560.0 | 151.0 | 71.2 | 45.7 | 0.578 | < 1.0 | 27.5 | 0.67 | 0.02 | 430 | 0.40 | 9,540 | | 0.00 | 1.00 E−06 |
| KFM06A | 12399 | Monit | −298.54 | 0.108 | 2.330 | 4,620.0 | 186.0 | 81.8 | 60.9 | 0.820 | 2.0 | 28.0 | | | | | | −0.32 | 0.11 | 1.40 E−09 |
| KFM06A | 12398 | Monit | −622.78 | 0.368 | 0.892 | 6,200.0 | 115.0 | 31.8 | 24.0 | 0.461 | 1.8 | 29.8 | | | | | | −0.91 | 0.88 | 3.30 E−07 |
| KFM06A | 8785 | CCC | −645.95 | 0.018 | 0.038 | 7,080.0 | 35.5 | 3.9 | 5.7 | 0.082 | 1.6 | 38.4 | 0.00 | 0.09 | −3.2 | 0.20 | 3,700 | −0.40 | −0.07 | 2.70 E−08 |
| KFM07A | 8843 | CCC | −763.62 | 0.062 | 0.277 | 14,400.0 | 103.0 | 21.5 | 7.4 | 0.141 | 2.0 | 22.8 | −4.8 | 0.04 | < 4.8 | < 0.20 | 5,120 | −0.83 | 0.29 | |
| KFM07A | 16613 | Monit | −795.22 | 0.029 | 0.076 | 14,400.0 | 108.0 | 25.0 | 17.4 | 0.127 | 2.6 | 24.0 | | | | | | | 1.13 | |
| KFM08A | 16557 | Monit | −227.79 | 0.138 | 1.350 | 4,490.0 | 81.1 | 44.4 | 85.0 | 0.590 | 2.5 | 36.4 | | | | | | 0.06 | 0.70 | 2.20 E−009 |
| KFM08A | 12000 | CCC | −549.16 | 0.012 | 0.676 | 6,100.0 | 91.5 | 14.1 | 10.4 | 0.191 | < 1.0 | 29.1 | 0.08 | 0.03 | −4.3 | 500.00 | 3,810 | −1.14 | 0.14 | 1.90 E−006 |
| KFM08A | 16567 | Monit | −550.55 | 0.024 | 0.302 | 6,270.0 | 85.1 | 15.3 | 14.2 | 0.162 | < 1.0 | 30.2 | | | | | | −1.18 | 0.22 | 1.90 E−006 |
| KFM08D | 12818 | CCC | −540.63 | < 0.006 | 0.004 | 7,460.0 | 101.0 | 4.9 | 7.0 | 0.050 | < 1.0 | 31.6 | | | | 13.00 | 7,350 | | 0.27 | 2.10 E−007 |
| KFM08D | 16546 | Monit | −538.06 | 0.340 | < 0.1 | 5,900.0 | 121.3 | 22.7 | 14.1 | 0.163 | 1.5 | | | | | | | | 0.47 | 1.70 E−009 |
| KFM08D | 12776 | CCC | −664.06 | 0.068 | 0.114 | 8,160.0 | 156.0 | 8.5 | 9.1 | 0.073 | < 1.0 | 26.6 | | | | | | −1.20 | 0.18 | 2.40 E−008 |
| KFM08D | 16560 | Monit | −662.55 | 0.391 | 0.015 | 6,920.0 | 121.0 | 15.0 | 15.8 | 0.081 | 1.4 | 29.9 | | | | | | −0.67 | 1.04 | 2.40 E−008 |
| KFM09A | 12243 | CCC | −614.01 | 0.004 | 0.130 | 14,800.0 | 118.0 | 17.7 | 6.7 | 0.107 | 1.3 | 27.0 | | | | | | −2.29 | 0.30 | |
| KFM10A | 12552 | CCC | −214.77 | 0.027 | 1.010 | 4,050.0 | 215.0 | 29.6 | 20.5 | 0.186 | 2.0 | 25.2 | | | | 500.00 | 12,163 | −0.43 | 0.36 | 3.40 E−008 |
| KFM11A | 12703 | CCC | −389.68 | < 0.006 | < 0.2 | 4,550.0 | 213.0 | 25.1 | 8.4 | 0.098 | 2.5 | | | | | 140.00 | | | −0.48 | 4.40 E−008 |
| KFM11A | 12829 | Monit | −389.62 | 0.172 | 0.534 | 4,400.0 | 244.0 | 37.9 | 15.8 | 0.193 | 1.9 | 25.9 | | | | | | −0.10 | 0.09 | 4.40 E−008 |
| KFM12A | 16118 | Monit | −226.74 | 0.076 | 0.255 | 3,610.0 | 98.6 | 46.3 | 58.5 | 0.575 | < 1.0 | 29.5 | | | | | | −1.70 | −0.14 | |
| KFM12A | 12792 | CCC | −439.26 | 0.034 | 0.268 | 6,130.0 | 381.0 | 94.1 | 58.9 | 0.859 | 1.1 | 26.1 | | | | | | −1.57 | 0.43 | |

Note that the gas and SRB and ATP values given in *italics* are imported from a sample in the same time series.

The analytical uncertainties differs for the different elements; Main elements (e.g $Cl^-$ , $HCO_3^{\ -}$, $SO_4^{2-}$ ) are in the 5–10% interval; Minor elements like S(−II), Fe(II) and Mn(II), 12–20% interval; Gas analyses 30–100% interval depending on concentration; Stable isotope analyses for sulpur ± 0.4 (1σ) ‰

# 5 Overview of Forsmark data for present day conditions

## 5.1 Introduction

This chapter discusses the variation of certain factors of importance for sulphide production. Because some of the elements described vary between the different groundwater types, the plots have been colour coded according to the subdivision described below:

**Fresh (Light Grey colour code ⬜)**

***Water type:*** Fresh (< 200 mg/L Cl; < 1.0 g/L TDS); Mainly meteoric in origin, i.e. Na(Ca)-$HCO_3(SO_4)$ in type, $\delta^{18}O = -12.0$ to $-10.5$‰ V-SMOW.

**Mixed Brackish (Light Green colour code 🟩), Not a specific groundwater type)**

Waters of mixed Fresh ± Brackish Glacial (± Brackish Marine) origin (200–2,000 mg/L Cl; 1.0–3.5 g/L TDS); it is usually sampled at 20–150 m depth and may be the result of natural and/or anthropogenic mixing during drilling activities and sampling.

**Brackish Glacial (Dark orange colour code 🟧)**

***Water type:*** Brackish Glacial (200–10,000 mg/L Cl; < 1.0–18 g/L TDS; $\delta^{18}O \leq -13.0$‰ V-SMOW). Last Deglaciation meltwater + Brackish Non-marine or Brackish Marine to Saline component; Ca-Na-Cl ($SO_4$); Mg < 25 mg/L; $\delta^{18}O < -13.0$‰ V-SMOW.

**Brackish Marine (Green colour code 🟩)**

***Water type:*** Brackish Marine (2,000–6,000 mg/L Cl; 3.5–10 g/L TDS; Mg > 100 mg/L); variable Littorina Sea component (± modern Baltic Sea) + Last Deglaciation meltwater ± Brackish Non-marine to Saline component; Na-Ca-Mg-Cl-$SO_4$; $\delta^{18}O > -13.0$‰ V-SMOW.

**Transition water samples (Turquoise code 🟦), Not a specific water type**

Transition type representing a mixture of Brackish Glacial and/or Brackish Non-marine groundwaters with a variable component of Brackish Marine. These waters range from 2,000–10,000 mg/L Cl and from 25–100 mg/L Mg; $\delta^{18}O > -13.0$‰ V-SMOW. They may be the result of natural and/or anthropogenic mixing during drilling activities and sampling.

**Brackish Non-marine (Medium blue colour code 🟦)**

***Water type:*** Brackish Non-marine (3,000–10,000 mg/L Cl; 5–18 g/L TDS; Mg < 25 mg/L); Old Meteoric ± Old Glacial ± Last Deglaciation meltwater ± Saline component, i.e. Na-Ca-Cl ($SO_4$) in type, $\delta^{18}O > -13.0$‰ V-SMOW.

**Saline (Medium lilac colour code 🟪)**

***Water type:*** Saline (10,000–20,000 mg/L Cl; 18–35 g/L TDS); Old Meteoric ± Old Glacial ± Last Deglaciation meltwater ± Highly saline component, i.e. Ca-Na-Cl ($SO_4$) in type, $\delta^{18}O = -13.0$ to $-10.0$‰ V-SMOW.

This subdivision is extended compared with the one used for the site modelling of Forsmark to distinguish the brackish-glacial groundwater. During the stage of the Forsmark investigation when the different major groundwater types were established, there were no groundwaters identified with exceptionally low $\delta^{18}O$. However, when the site investigation proceeded a small number of borehole sections showed this groundwater type /Smellie et al. 2008/.

Note: In order to facilitate comparison of different concentrations of sulphur compounds, mmol/L have been preferred over the previously used mg/L. Generally it takes 1 methane or DOC + 1 sulphate to produce 1 molecule of sulphide.

## 5.2 The sulphur system

The available sulphur sources for interaction with the bedrock aquifers comprise, for example, dissolved species in groundwaters or precipitates along fracture walls or in wall rock adjacent to flowing fractures. The different oxidation states of the sulphur compounds together with the available sources of organic materials (e.g. reductants and carbon sources), and finally the supply of gases (e.g. methane and carbon dioxide) that can contribute to microbial activity, provide the framework for sulphide production in the bedrock groundwater system. In this section, the different sulphur sources are discussed.

### 5.2.1 Sulphate concentrations in groundwater

In general, sulphate constitutes the largest sulphur pool in bedrock groundwaters and may have very different origins depending on the groundwater history. The main sources in fresh waters are usually the result of atmospheric deposition and oxidation of sulphides or dissolution of possible sulphates in the overburden. Deeper in the bedrock fracture system pyrite is relatively common, but only very minor amounts of sulphate minerals have been observed (no gypsum but a few grains of barite) /Sandström et al. 2008/. Water of marine origin (e.g. Baltic Sea and Littorina Sea at Forsmark) initially carries elevated sulphate contents with a specific isotopic signature when entering the bedrock or the overlying sediments. However, subsequently this content may be lowered to various degrees due to microbially mediated sulphate reduction thus modifing the sulphur isotope signatures (generally enriched in $^{34}$S) in the remaining sulphate. Brackish and saline waters at greater depths characterised by long residence times in the bedrock have sulphate contents of mixed origins, such as marine sources, interactions with solid phases (e.g. dissolution of sulphate-bearing minerals), or sulphate from very old brine waters (potentially of sedimentary origin). The sulphate contents may also be modified by permafrost freeze-out processes (i.e. formation and dissociation of mirabilite).

Figure 5-1 gives an overall picture of the variation in sulphate content in the different groundwaters at Forsmark versus elevation. Only the selected samples from CCC and monitoring sampling, respectively, are shown in the plots. It is evident that the brackish marine waters have the highest sulphate contents, whereas fresh waters, and brackish to saline non-marine types are dominated by relatively low sulphate contents (with one exception below 1.5 mmol/L). Transition type waters show variable sulphate from just below 1 to 4 mmol/L depending on the size of the marine component in these water samples. Because the main source of sulphate is marine and mainly associated with the brackish marine water of Littorina type which is mostly restricted down to about 500–650 m depth, the sulphate content in the deeper samples is generally low.

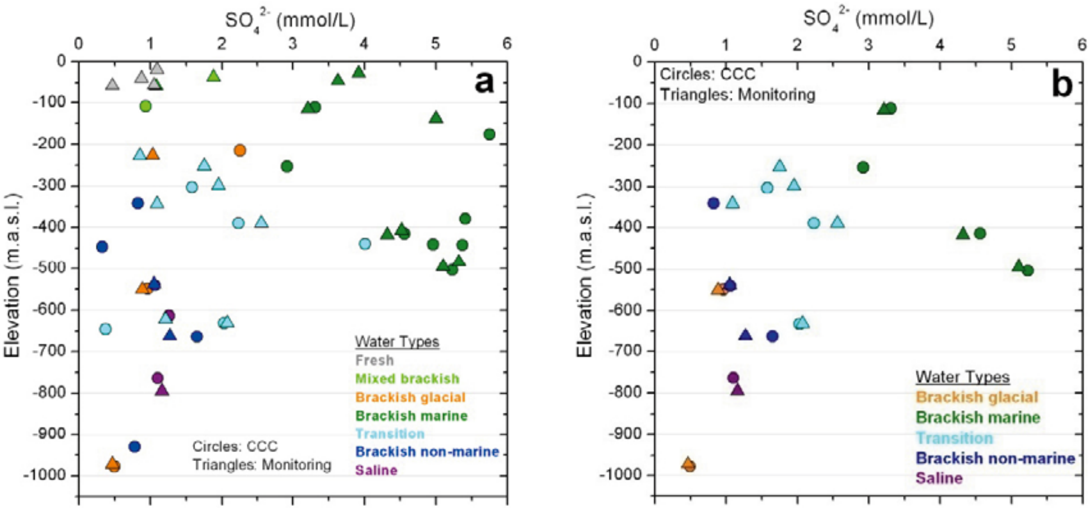


*Figure 5-1. (a) $SO_4$ in groundwaters from percussion and cored boreholes from CCC and monitoring sampling versus elevation (masl).(b) Only CCC and monitoring samples from the same water conducting structure are shown in order to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period. Note that in some borehole sections there has been a change in groundwater type from the CCC to the monitoring stage suggesting increased mixing of groundwaters.*

When comparing CCC samples with later monitoring results from the same water conducting structures it can be concluded that the changes in sulphate contents with time are relatively small and non-systematic. A minor increase in some of the non-marine or transition type groundwaters is observed due to an increasing inflow of brackish marine waters (also supported by slightly higher Mg in the same samples), or *vice-versa*. An increase in a non-marine component in the monitoring samples coupled with a decrease in the sulphate content is exemplified in section KFM01D:−253 masl.

Considering the relatively high sulphate contents compared with the measured sulphide values, it is doubtful that any lowering of sulphate due to ongoing sulphate reduction to sulphide within the section volume can be detected with accuracy.

### $\delta^{34}$S in sulphate

Stable sulphur isotope ratios, expressed as $\delta^{34}$S CDT (Canyon Diablo Troilite), can be used not only to trace the origin of the sulphur sources for the sulphate but also processes such as biogenic sulphur reduction modifying the isotope ratios. Sulphur isotopes were determined in sulphate from surface waters and groundwaters during the site investigation and reported in /Tröjbom and Söderbäck 2006/ (shallow waters) and /Smellie et al. 2008/ (groundwaters). The evaluation of possible origins of sulphur ($SO_4$) in the surface water system showed that atmospheric deposition and oxidation of sulphides in the soil cover constitute the most important sources, together with marine sulphate /Tröjbom and Söderbäck 2006/. The sulphate contents in the surface waters are, however, generally low (~1 mmol/L).

For the groundwater in the bedrock it is evident that the major input of sulphur is associated with the brackish marine components (Figure 5-1). However, the $\delta^{34}$S CDT show values clearly exceeding the marine values of approximately +21‰ CDT (Figure 5-2) /Clark and Fritz 1997/ which is a strong indication of modification by sulphate reduction in these waters. Because sulphate reduction during closed conditions produces enrichment of the heavier isotope $^{34}$S in the sulphate, in such cases $\delta^{34}S_{(SO4)}$ is expected to correlate inversely with the sulphate content. Most of the brackish marine waters show relatively homogeneous $\delta^{34}S_{(SO4)}$ values around 26‰ CDT irrespective of sulphate content (Figure 5-3), which may instead be interpreted as an influence of sulphate reduction during open to partly closed conditions. However, the reduction may have taken place already in the marine bottom sediment before intrusion into the bedrock. It is important also to note that none of the brackish marine waters have preserved their original marine $SO_4$/Cl ratio (~ 0.052 mol). This may be partly due to mixing with other waters but is mostly by sulphate reduction as suggested by the $\delta^{34}S_{(SO4)}$ signature. Ongoing sulphate reduction is documented and sulphate-reducing bacteria were identified at depths greater than 320 m in all but one of the boreholes sampled for microbes /Hallbeck and Pedersen 2008a/.

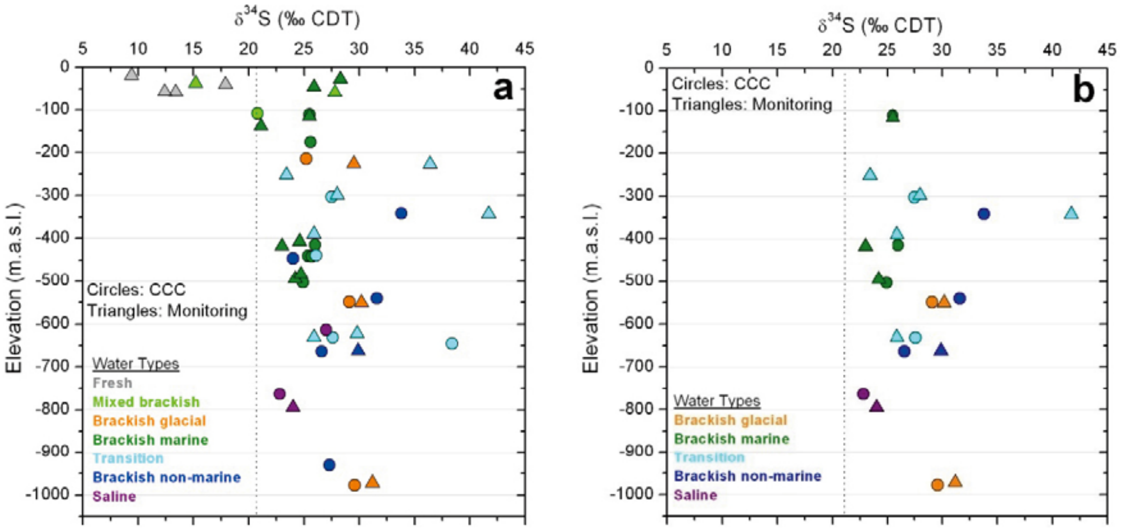


***Figure 5-2.*** *(a)$\delta^{34}S_{(SO4)}$ in groundwaters from percussion and cored boreholes from CCC and monitoring sampling versus elevation (masl). (b) Only CCC and monitoring samples from the same water conducting structure are shown to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period. Note that in some borehole sections there has been a change in groundwater type from the CCC to the monitoring stage suggesting increased mixing of groundwaters.*

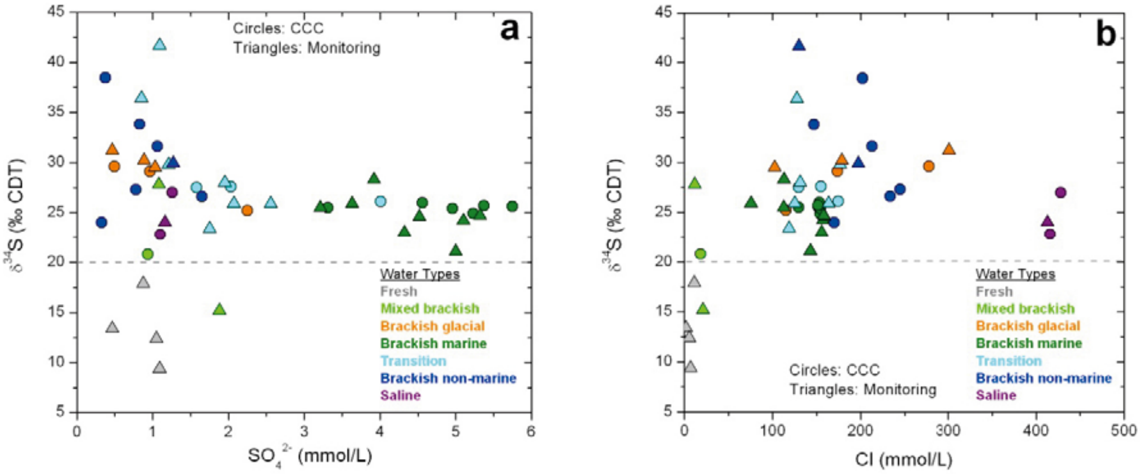


***Figure 5-3.*** *$\delta^{34}S_{(SO4)}$ in groundwaters from percussion and cored boreholes from CCC (circles) and monitoring (triangles)versus sulphate content (a) and chloride (b).*

The brackish to saline non-marine waters show generally low sulphate contents and high $\delta^{34}S_{(SO4)}$ values (≥ 26‰ CDT) (Figure 5-3). As discussed above, this is a strong indication of modification caused by sulphate reduction. No major additional sulphur source in these groundwaters can be identified, which means that the bedrock aquifer at depth in Forsmark represents a low sulphate environment. This is also supported by the fracture mineralogy which shows very little evidence of sulphate minerals (cf. below).

The possibility of residual higher sulphate concentrations in glacial meltwater, for example caused by locally precipitated sulphate minerals (gypsum and mirabilite) produced as a result of permafrost and later dissolved by intruding meltwater, is not supported by the sulphate content in the brackish glacial waters (cf. Figure 5-1). On the other hand, the $\delta^{34}S_{(SO4)}$ values are quite high in these waters indicating a decrease of the sulphate content by microbial sulphate reducion, making the interpretation of the original sulphate contents difficult to estimate. However, the brackish glacial waters do not deviate from the trend observed in the non-marine and transition type groundwaters, so there are no reasons to assume a significant addition of sulphate by the glacial meltwater.

### 5.2.2 Solid sulphates and sulphides

The totally dominating sulphur mineral in the fracture system is pyrite /Sandström et al. 2008/. Sulphur isotope analyses of fracture coating pyrite support a biogenic origin potentially suggesting that pyrite is a young phase (i.e. Palaeozoic or younger). Most analysed pyrites show $\delta^{34}$S values between +5 and +31.5‰ (CDT) (Figure 5-4), compared to $\delta^{34}$S values typically close to 0‰ CDT (Canyon Diablo Troilite) for hydrothermal/magmatic pyrite, e.g. /Hoefs 2004/. The large variation (even within a single sampled fracture surface) and especially the positive values (i.e. greater than 20‰ CDT) are interpreted as a result of Rayleigh fractionation in a closed system, cf. /Hoefs 2004/ where sulphate enriched in $^{34}$S has been reduced during the oxidation of organic matter by microbial or thermochemical processes. This large variation and the lack of any depth trend support *in situ* microbial activity. Detailed studies reported in /Sandström et al. 2008/ indicate, however, that most of the observed pyrite shows a clear association with the Palaeozoic generation of fracture mineralisations, and also is associated with very small amounts of galena. Because the total system is heterogeneous, it is highly likely that alternative processes which represent a more open system have influenced sulphate reduction in other parts of the bedrock fracture geometry.

Concerning a possible sulphate phase such as gypsum, or barite, only a few microscopic grains of the latter have been identified. Gypsum is not identified in any fractures from Forsmark but it can of course be easily over looked during the drillcore mapping, for example if mixed with calcite. However, if present, it should most probably have resulted in an addition of sulphate to the brackish non-marine and saline groundwaters (as indicated in Laxemar /Laaksoharju et al. 2009/) but this is not the case, supporting the thesis that gypsum is not present in the bedrock/groundwater system at Forsmark.

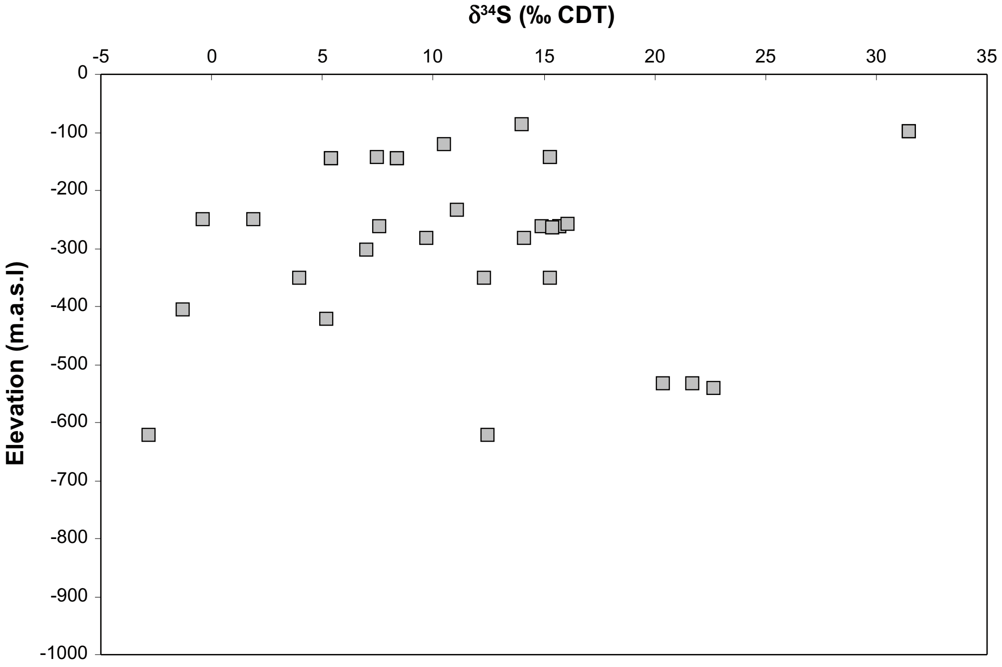


***Figure 5-4.*** *$\delta^{34}$S values versus depth (elevation) of pyrite in fractures. Analytical errors are within the size of the symbols (from /Sandström et al. 2008/).*

### 5.2.3 Sulphide in groundwaters

Chapter 3 has addressed in detail the problems associated with the derivation of reliable sulphide contents during groundwater sampling. Nevertheless, from present measured values it has been possible to extract sulphide data that have been very useful in the interpretation of the borehole sections sampled because they give the most probable intervals for naturally occurring sulphide values. CCC data and monitoring data are compared and described below in terms of their compositional variation and depth trends, and potential correlation with the different groundwater types.

The sulphide values measured in the groundwaters during CCC and subsequent monitoring show, as pointed out in Section 4.4, a large variation, and the possible reasons for this are discussed in Chapter 3 and 4. The increased values in the monitoring samples are very prominent down to a depth of about 650 m. In contrast, all but two sulphide values measured during CCC show values about or below $3 \times 10^{-4}$ mmol/L down to this depth. For the monitoring samples, all values are higher than $5 \times 10^{-4}$ mmol/L and all but three are even higher than $2 \times 10^{-3}$ mmol/L). At depths below 650 m all four CCC samples show values between $1 \times 10^{-3}$ and $2.1 \times 10^{-3}$ mmol/L. Two monitoring samples in the elevation interval −750 to −1,000 masl show values similar to CCC samples in the same depth interval. Very few samples are available at these depths but the general trend is that the sulphide values measured during CCC increases with depth, whereas the monitoring samples show usually enriched but variable contents throughout with no visible trend.

Because the sulphide values span three orders of magnitude the values are displayed in logarithmic scale for the two diagrams in Figure 5-5. In total, eight samples are below the detection limit of $1.9 \times 10^{-4}$ and $6 \times 10^{-5}$ mmol/L. In order to be able to show these in the logarithmic diagram, the values corresponding to the actual detection limit have been chosen; two are monitoring samples from percussion boreholes (HFM01 and HFM21), and the remainder are CCC samples from KFM01A:−177 m (where a reporting limit of 0.0009 mmol/L (0.03 mg/L) sulphide was applied) KFM02A: − 414 masl, KFM03:−632 masl, KFM6A:−303 masl, KFM08D−540 masl and KFM11A −389 masl. This means that very low sulphide values are found in samples down to −632 masl.

It is not possible to find any correlation between groundwater type and sulphide values.

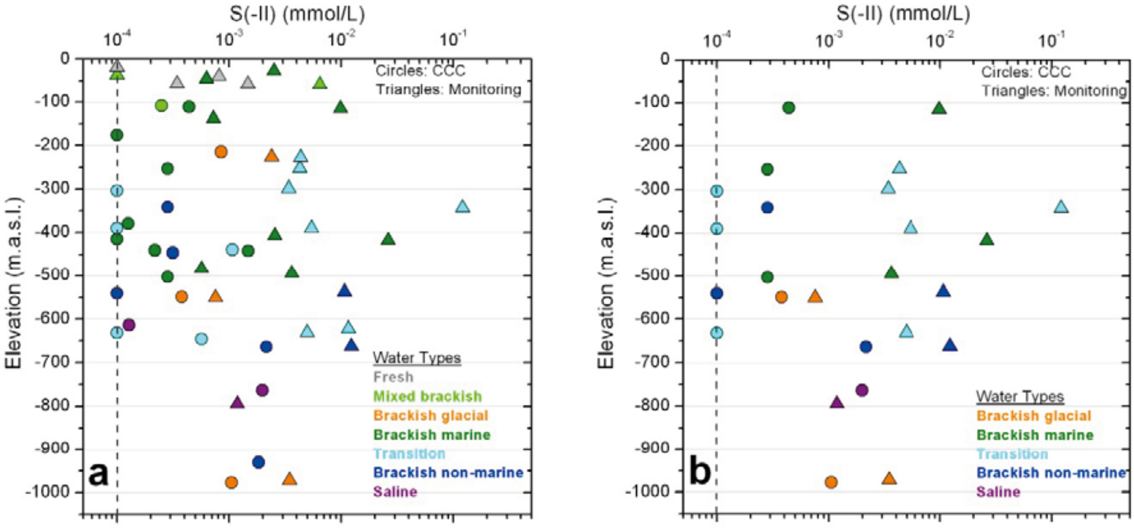


***Figure 5-5.*** *(a) Dissolved S(−II) in groundwaters from percussion and cored boreholes from CCC and monitoring sampling versus elevation (masl). (b) Only CCC and monitoring samples from the same water conducting structure are shown in order to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period. Note that in some borehole sections there has been a change from the CCC to the monitoring stage suggesting increased mixing of groundwaters. Data below the detection limit of the analyses are shown in this diagram at $10^{-4}$ mmol/L, i.e. at 0.003 mg/L.*

As commented above, the sulphide contents measured and shown in Figure 5-5 span at least three orders of magnitude, with the CCC samples usually on the lower side and the monitoring samples on the higher side, some showing very high values. Uncertainties involved in the monitoring sampling programme include the possibility of an anthropogenic increase in sulphide production associated with the downhole equipment and the exposed borehole walls, and the resulting sulphide content in the water is is in turn related to the different borehole section volumes of water (cf. Chapter 3). Based on these uncertainties, it can be concluded that, in many cases, the volume of water pumped before the last sample collected (usually the one selected as most representative) has not been sufficient to remove all the contaminated water from the borehole section sampled (cf. the plug flow calculations in Section 3.1.4 and also the experience from the sulphide monitoring project /Rosdahl et al. 2010/).

Calculation of the saturation indices for amorphous FeS (Figure 5-6b) show that ten monitoring samples and one CCC sample are at, or close to saturation in respect of FeS(am). Two important observations are evident; a) in samples at or close to saturation, the measured $Fe^{2+}$ and $S^{2-}$ values in a single sample are interconnected, and b) the solubility of FeS(am) consequently sets an upper limit for these species in the groundwater. Actual precipitation of FeS(am) has not been possible to demonstrate, but an opportunity to study this will take place during 2010/2011 when downhole monitoring equipment will be removed from some of the boreholes at Laxemar, and possible precipitates on this equipment will be investigated. Unfortunately, at the moment nothing similar is planned for Forsmark. If precipitation of FeS is observed to have taken place, it means that more sulphide than the contents measured in the water have been produced during a certain time interval. If effective enough, this process should in such cases have resulted in a significant lowering of the sulphate content combined with increased $\delta^{34}S$ values in a specific water volume, for example the sampled borehole section.

### 5.2.4 Concluding remarks

Because sulphate is needed for microbial sulphide production, the sulphate sources are of interest. At Forsmark these are related to the surface water (oxidation of sulphides in the soil and leaching of marine sediments) and to brackish marine waters (present Baltic or the Littorina type), whereas the deeper non-marine waters are low in sulphate and an easily dissolvable sulphate phase in the fractures has not been identified /Sandström et al. 2008/. The amount of sulphate contributed by the marine waters is by far the largest source and because the inflow of present marine water is, and will be restricted for a long period of time, the main contribution is the Littorina Sea water.

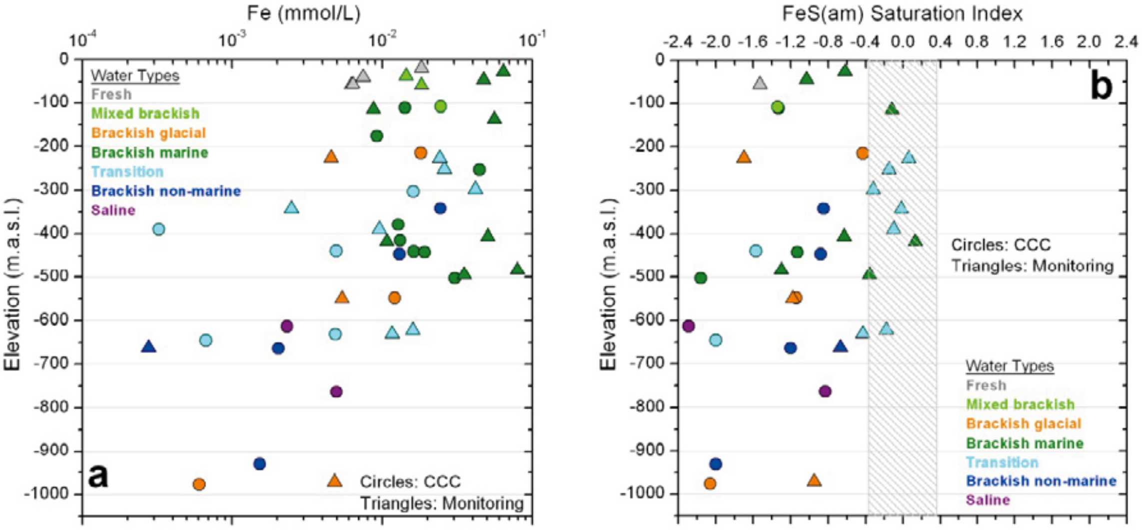


***Figure 5-6.*** *(a) Dissolved Fe in groundwaters from percussion and cored boreholes from the CCC and monitoring sampling programmes versus elevation (masl). (b) Saturation index for amorphous monosulphide versus elevation.*

Evidence from minerals and groundwater analyses at Forsmark show that microbial sulphate reduction has been active in the bedrock since at least the Palaeozoic onwards.

The recorded sulphide values measured during CCC and the monitoring programmes show large variations (at least three orders of magnitude) with the CCC samples generally characterised by lower values than from the monitoring when samples from the same borehole section can be compared. These differences are significant down to 650 m depth. However, taking into account only the CCC samples there is an increase in sulphide below 650 m which is not evident in the monitoring samples. Time series measurements during the monitoring programme show in most cases decreasing sulphide values, i.e. the pumped volumes have not been large enough to ensure stable values representing the bedrock fracture groundwaters. On the other hand, very low sulphide values were measured during the CCC sampling and it is possible that some of these are due to artefacts from the drilling and heavy pumping carried out in the boreholes.

Saturation in respect of FeS(am) is reached for many monitoring samples but only for one CCC sample. In samples at or close to saturation, the measured $Fe^{2+}$ and $S^{2-}$ values in a single sample are interconnected and consequently the solubility of FeS(am) sets an upper limit for these species in the groundwater.

## 5.3 Organic carbon

Organic materials in the groundwaters have been analysed and are presented either as TOC (Total Organic Carbon) or as DOC (Dissolved Organic Carbon) if filtered through a 0.4 µm filter before being analysed. In a number of samples both TOC and DOC have been analysed (Figure 5-7), and these generally show a good correlation which implies that almost all organic carbon is present as molecules less than 0.4 µm in size. However, the analyses of organic matter in deep groundwaters is a complicated task for sampling and analytical reasons, and obtained results need to be interpreted with caution.

### 5.3.1 Concentrations

The DOC values at depth are expected to be close to the detection limit 0.1 mmol/L (1 mg/L) but generally the more dependable CCC values at depths greater than 100 m still vary between 0.1 to 0.4 mmol/L (1 and 5 mg/L) with a few exceptions where the values are even higher (Figure 5-8a). This observation was commented upon in /Laaksoharju et al. 2008/. The reason for these slightly increased values (also found in Laxemar and elsewhere in the Nordic sites, cf. /SKB 2010c/) is not known. Contamination during drilling/sampling, new routines for cleaning the equipment, natural

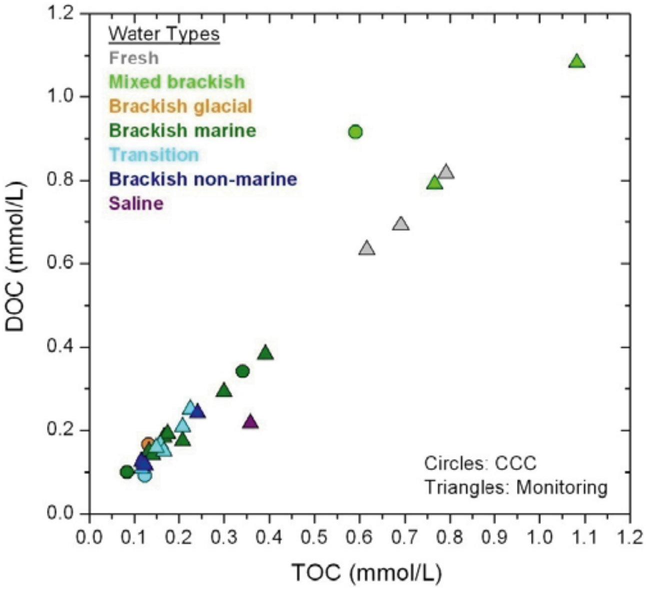


***Figure 5-7.*** *Dissolved organic carbon (DOC) plotted versus total organic carbon (TOC) for the Forsmark groundwaters.*

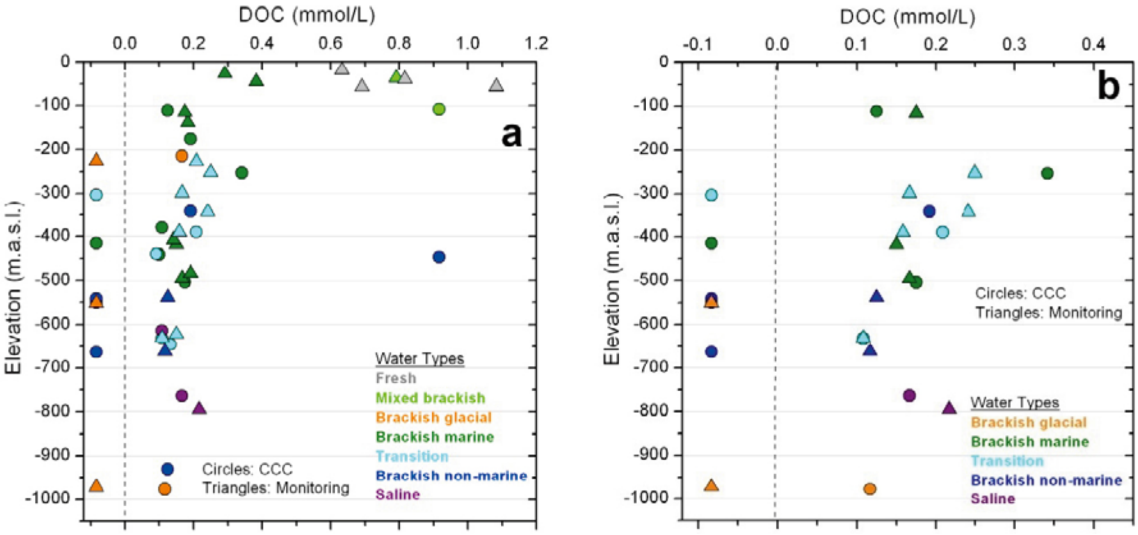


***Figure 5-8.*** *(a) DOC in groundwaters from percussion and cored boreholes from CCC and monitoring sampling versus elevation (masl). (b) Only CCC and monitoring samples from the same water conducting structure are shown to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period. Note that in some borehole sections there has been a change in groundwater type from the CCC to the monitoring stage suggesting increased mixing of groundwaters. Note also the different DOC scales in the two plots.*

sources such as asphaltite, cf. /Sandström et al. 2006/, Littorina Sea etc have been discussed. It was hoped that additional data from the monitoring programme would help to clarify the long term behaviour of DOC, but this has not materialised. In this context it has been noted also (e.g. Figure 5-8) that saline groundwaters of old age (> 700–800 m depth) tend to have enhanced DOC contents which so far have not been satisfactorily explained.

In this light, it can be concluded that there are no major differences between the values obtained during the CCC and the monitoring sampling programmes. When looking at the plots with only the pairs ( i.e. CCC and monitoring values from the same conductive structures; Figure 5-8b), no systematic change can be seen. Of the twelve sections measured, seven of the monitoring values exceed those of the CCC samples, in three CCC samples the values exceed those of the monitoring samples, and in two sections both sampling occasions gave the same results. In many cases the first sample from the monitoring section is higher in DOC due to microbial activity in the borehole section itself, and in some sections a correlation with sulphide can be observed (e.g. KFM08A:−228 masl in Figure 5-9).

### 5.3.2 Stable isotopes

In nine different borehole sections organic material was collected for carbon isotope analysis during the site investigations (CCC sampling). This included $^{14}C$ (pmC) in order to provide some age contraints on the material and $\delta^{13}C$ to give information on the origin of the organic material (Table 5-1). Three samples of brackish marine groundwaters have been analysed for carbon isotopes in the organic material yielding $^{14}C_{(org)}$ values of 45 to 53 pmC supporting a postglacial origin for the brackish marine (Littorina) groundwater. These results are qualitatively in accordance with ages of about 5,000 to 6,000 years covering the period of maximum salinity during the Littorina stage (4500 to 3000 BC), and is based on the assumption that the organic material has not incorporated any carbon after recharge. An additional sample of brackish marine water (KFM10A) shows unrealistically high $^{14}C$ values, indicating contamination of young carbon. This is also the case for samples from KFM06A, KFM08A and KFM01D which are groundwaters of brackish non-marine or brackish glacial types. This means that they are clearly older than the brackish marine (Littorina type) groundwaters; however, this is not supported by the organic material which indicates ages younger or similar to the Littorina groundwater. The $\delta^{13}C$ values are generally low (−21 to −30‰ PDB with one exception), possibly indicating a terrestrial rather than a marine origin /Faure and Mensing 2005/ supporting the possibility of some contamination.

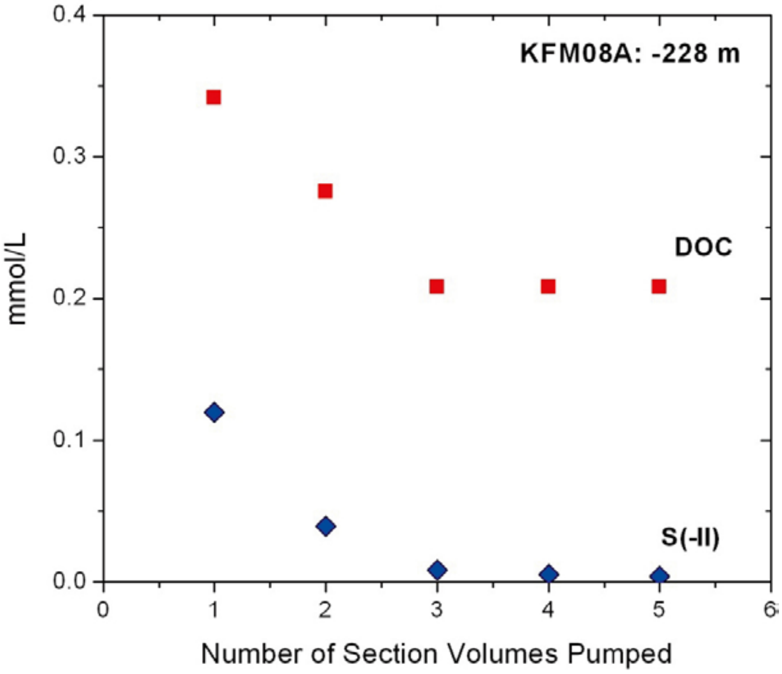


***Figure 5-9.*** *Dissolved organic carbon (DOC) and sulphide (mmol/L) in time series from KFM08A:−228 m.a.s.l.*

**Table 5-1. Carbon isotope analyses of organic material from groundwaters at Forsmark. Data from the CCC samples.**

| Borehole | Elevation (masl) | pmC (%) | $\delta^{13}$C (‰ PDB) | Groundwater type |
|---|---|---|---|---|
| KFM02A | −108.86 | 89.3 | −26.7 | Mixed brackish |
| KFM01A | −111.75 | 53.2 | −28.3 | Brackish marine |
| KFM01A | −176.27 | 46.4 | −27.4 | Brackish marine |
| KFM02A | −503.34 | 45.1 | −9.1 | Brackish marine |
| KFM10A | −328.08 | 93.1 | −30.3 | Brackish marine |
| KFM06A | −301.99 | 70.1 | −26.6 | Transition type |
| KFM06A | −645.34 | 68.2 | −21.3 | Brackish non-marine |
| KFM08A | −546.42 | 62.4 | −25.4 | Brackish glacial |
| KFM01D | −443.17 | 47.7 | −25 | Brackish non-marine |

## 5.4 Hydrogen, methane and carbon dioxide

As stated earlier in the report, the amount of sulphide not only depends on sources such as dissolved sulphate and available sulphate- and sulphide-bearing minerals, but also on the presence of reductants which includes methane and hydrogen; carbon dioxide is also included here because it can provide a food source for potential bacterial activity and is therefore relevant to the discussion.

In general, relatively few analyses of $H_2$, $CH_4$ and $CO_2$ are available from the Forsmark site and unfortunately there are no time series data and no monitoring data. Additional data from the Olkiluoto site in Finland and from the Laxemar/Simpearp/Äspö sites in Sweden are included therefore for comparison and discussion purposes. The values are given as mmol disolved gas per litre of groundwater. The Forsmark gas analyses have earlier been reported by /Hallbeck and Pedersen 2008a/ and the Laxemar Simpevarp analyses have been reported in /Hallbeck and Pedersen 2008c/. The laboratory reports < 20% measurement uncertainty for the analyses and separation of the gases from the water. However, based on repeated sampling and analyses for the Swedish samples, the uncertainty is estimated to 30–100% depending on the concentration of the gas component.

### 5.4.1 Methane

At Forsmark all methane values are between $10^{-3}$ to $10^{-2}$ mmol/L with one exception; KFM01D: −445 masl shows a methane value of about $2\times10^{-1}$ mmol/L (cf. Figure 5-10a). No significant trend with depth or with groundwater type can be seen. This is similar to the Laxemar/Simpevarp/Äspö sites, (Figure 5-10b), where almost all data plot between $10^{-3}$ to $10^{-2}$ mmol/L. However, the highest values (> $10^{-2}$ mmol/L) all relate to Laxemar but appear to be independent of groundwater type and depth.

The Olkiluoto data, in contrast, clearly show an increasing methane trend with depth (Figure 5-10c), especially from close to the bedrock surface to about −500 masl where values, despite showing a degree of scattering down to about −350 masl, increase systematically from about $10^{-2}$ to 10 mmol/L. From about −500 to −650 masl the methane content remains quite constant at about 10 mmol/L, but shows even slightly more increased values at depth below −750 masl. This clear trend shows also a well defined change in groundater type with increasing depth (Figure 5-10c).

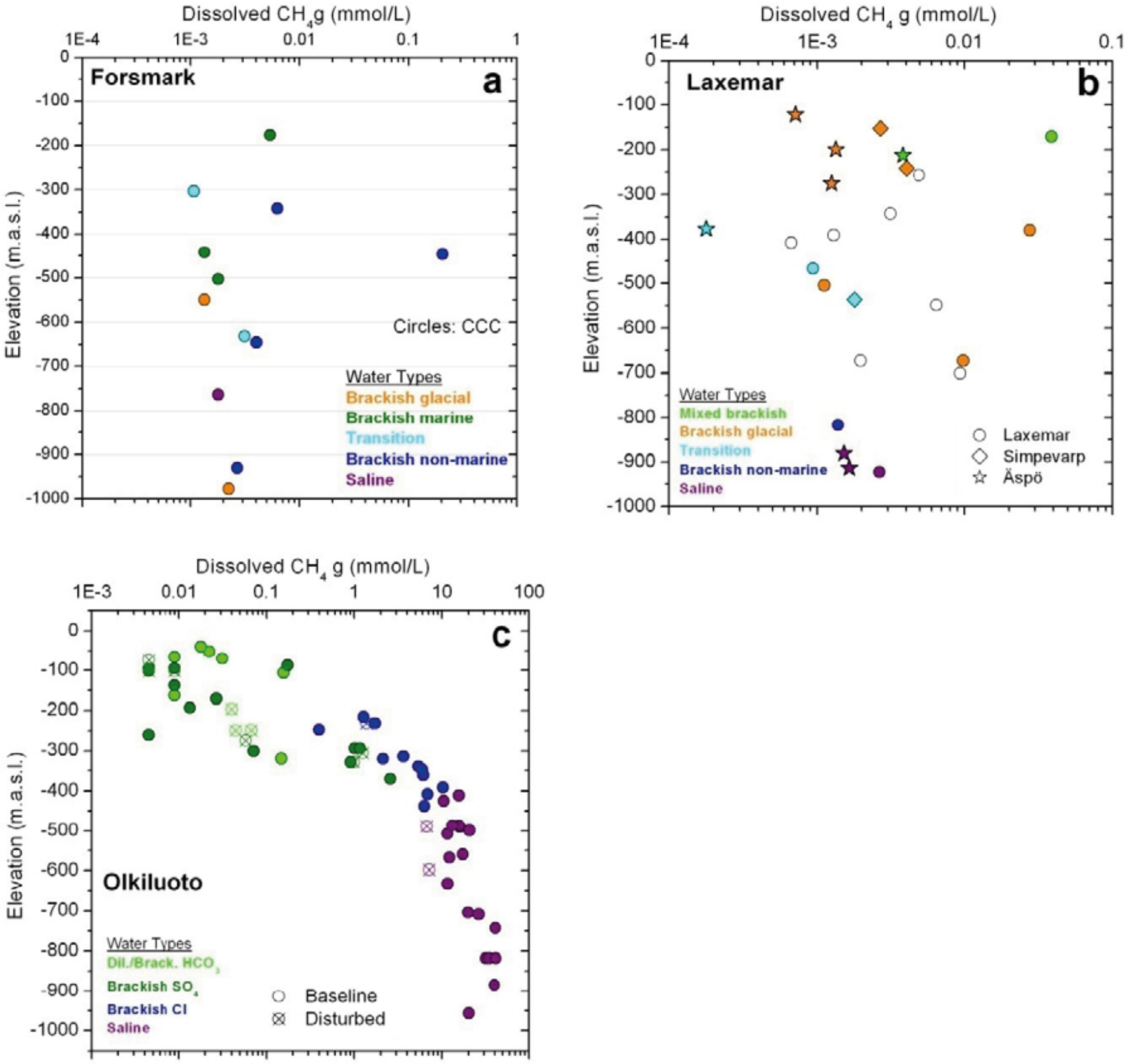


*Figure 5-10.* *Methane concentrations (dissolved gas) in groundwaters from: a) Forsmark, b) Laxemar/Simpevarp/Äspö, and c) Olkiluoto.*

### 5.4.2 Hydrogen

More than half of the Forsmark data (Figure 5-11a), are at or close to the detection limit of $2\times10^{-5}$ mmol/L; the remaining 5 groundwater samples representing depths from −170 masl to −950 masl show hydrogen values from $2\times10^{-4}$ to $2\times10^{-2}$ mmol/L.

Most of the groundwaters from the Laxemar/Simpevarp/Äspö sites (Figure 5-11b), plot at or close to detection. The remaining five groundwaters, three from Laxemar and two from Simpevarp, show values between $2\times10^{-3}$ and $9\times10^{-3}$ mmol/L.

The groundwaters at Olkiluoto (Figure 5-11c and d) show a scattered distribution, but nevertheless an increase in hydrogen from $4.5\times10^{-5}$ to 1 mmol/kg is suggested with increasing depth (i.e. −100 to −900 masl).

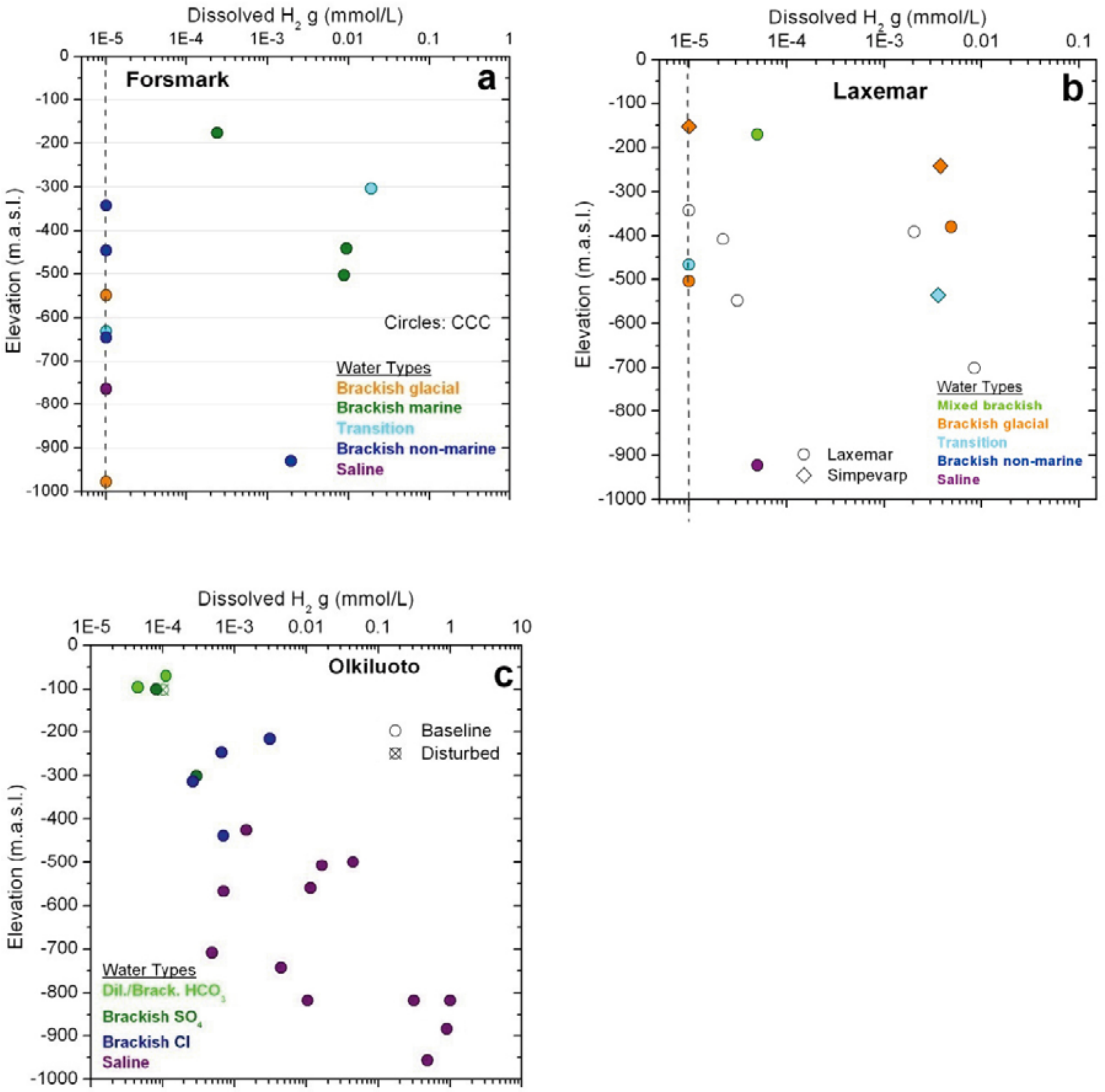


***Figure 5-11.*** *Hydrogen concentrations (dissolved gas) in groundwaters from: a) Forsmark, b) Laxemar/Simpevarp/Äspö, and c) Olkiluoto.*

### 5.4.3 Carbon dioxide

Despite the Forsmark data (Figure 5-12a) showing a large scatter in carbon dioxide content from $5\times10^{-4}$ to $2\times10^{-1}$ mmol/L, there is a weak indication that it decreases with increasing depth. The highest values are found in the brackish marine waters and characteristically indicate a product of bacterial activity often associated with these marine groundwaters.

For the Laxemar/Simpevarp/Äspö site (Figure 5-12b) most carbon dioxide data from the depth interval sampled (between −100 to −950 masl) plot within the range of $10^{-2}$ to $10^{-1}$ mmol/L. One Äspö sample at −212 masl records the highest value at $2\times10^{-1}$ mmol/L, and a group of four samples (mostly Laxemar) at intermediate depths of about −400 to −550 masl show the lowest values from $3\times10^{-3}$ to $6\times10^{-3}$ mmol/L. This group of four represent brackish glacial (with one transition) groundwater types generally not associated with bacterial activity.

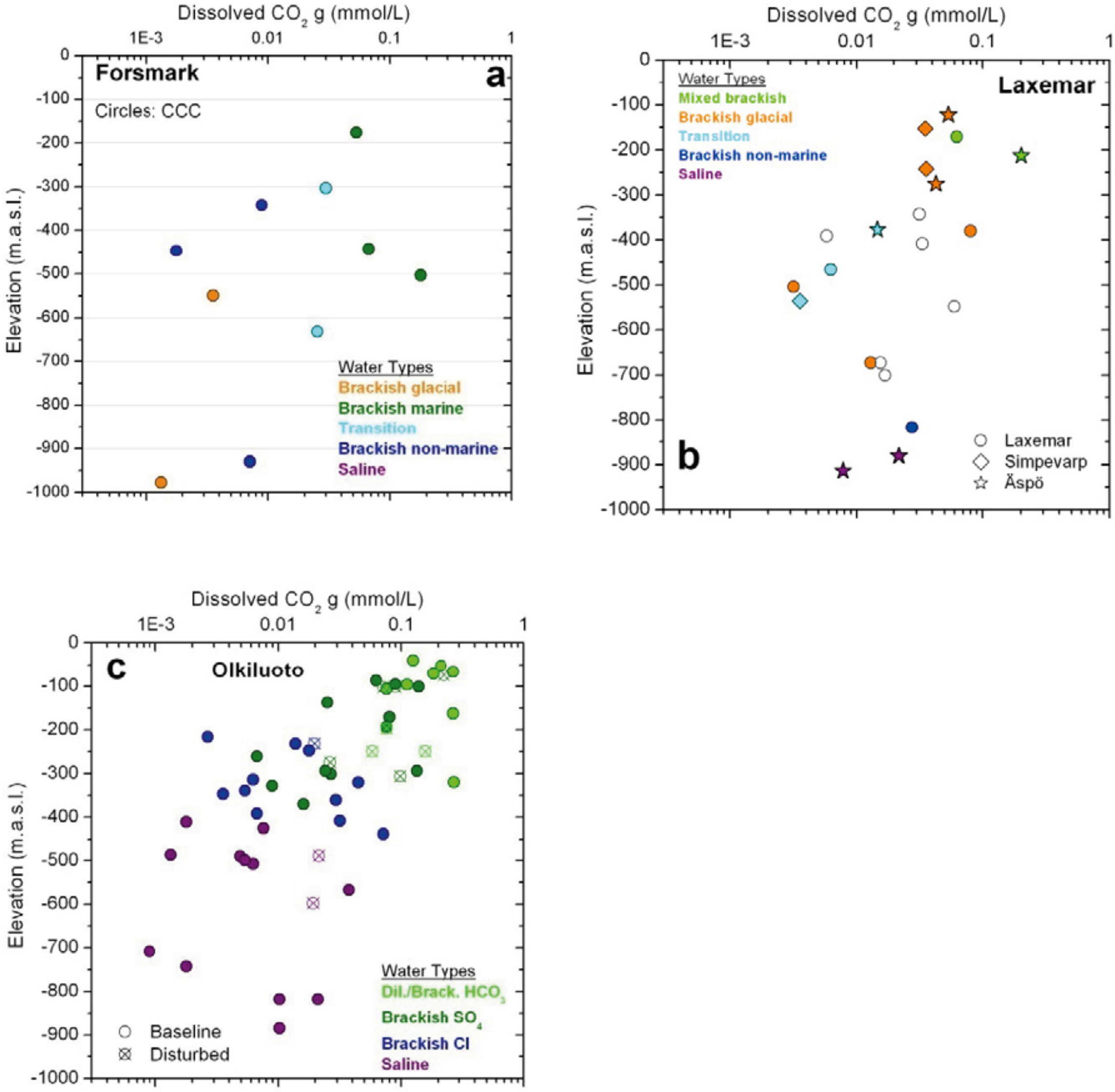


***Figure 5-12.** Carbon dioxide concentrations (dissolved gas) in groundwaters from: a) Forsmark, b) Laxemar/Simpevarp/Äspö, and c) Olkiluoto.*

At Olkiluoto (Figure 5-12c and d) the upper 350 m of bedrock has the largest spread and highest carbon dioxide values, the latter associated mainly with the dilute, brackish bicarbonate groundwater types (and some of the brackish sulphate types) associated with bacterial activity. From −400 masl to the maximum depths sampled, there is a sharp decrease in carbon dioxide to less than $5\times10^{-2}$ mmol/L with many values at or near detection limit; this depth interval is dominated by the deeper saline groundwaters.

### 5.4.4 General comments

The analyses of gas dissolved in groundwater at Forsmark and Laxemar/Simpevarp/Äspö generally show a lack of strong depth trends, especially for methane and hydrogen. At Olkiluoto the increase in methane with depth suggests a deep input of abiogenic methane, and the two highest outlier values at intermediate depths may represent biogenic sources. The decrease in hydrogen with depth observed at Olkiluoto is not shown in the data sets from Forsmark and Laxemar/Äspö/Simpevarp. On the other hand, the number of analyses are much less in the Swedish data set and many of the values are below detection limit. An overall decrease of carbon dioxide with depth is indicated at all sites. The Swedish observations are best compared with and supported by the Olkiluoto site, which shows close hydrochemical similarities with Forsmark.

## 5.5 Sulphate reducing bacteria (SRB) and adenosine-tri-phosphate (ATP)

Data of total cell counts, ATP concentrations, and most probable number (MPN) for sulphate-reducing bacteria (SRB), exist for 15 samples out of the 373 samples, cf. Figure 5-14. Comparison of the SRB cell numbers estimated with the MPN technique with the total numbers of directly measured cells indicate that SRB contributed generally less than 4.8% to the total bacterial cell numbers. These numbers are comparable to estimates with the same method from other sulphate-reducing environments. Compared to studies that used molecular methods, however, the relative proportion of SRB to the total bacterial community determined here is relatively low. For example, in a deep marine biosphere study with active bacterial sulphate reduction, /Leloup et al. 2009/ estimated, based on real-time PCR of the functional gene dsrAB (which shows how active the SRB are), that sulphate reducers comprised up to 22% of the total bacterial community. The lower numbers in Forsmark groundwaters could be due to selective enrichment of bacteria adapted to high substrate concentrations (i.e. more electron donors than in the natural environment favour some SRB) in the medium chosen in the MPN method. Counts of SRB in sample #12354 (KFM01D:−446 masl) are unusually high (13,000 cells/mL) compared with the rest of the samples, which suggests different environmental conditions of this sample compared to the remaining samples. This interpretation is also in accordance with the high DOC and ATP levels in this sample and suggests an active community of heterotrophic sulphate reducers. Nitrate-reducing bacteria (NRB) and both autotrophic and heterotrophic acetogenic bacteria were also unusually abundant in this sample. SRB numbers were also significant in three other samples (500 cells/mL), but here they only made up 1% of the total cell counts.

As discussed in the Forsmark report /Hallbeck and Pedersen 2008a/ prolonged pumping could have affected sulphide concentrations and bacterial cell numbers so that a significant uncertainty is associated with the cell counts. Overall, DOC concentrations, dissolved sulphate and sulphide concentrations, and stable sulphur isotope composition of sulphate, were poorly correlated with cell numbers of SRB. This may be partly due to the fact that dissolved sulphide was buffered by iron (II) leading to the removal of sulphide as iron sulphide /Hallbeck and Pedersen 2008a/. In support of this, counts of iron-reducing bacteria (IRB) were elevated in some samples with higher counts of sulphate-reducing bacteria. An alternative explanation could be that sulphate-reducing activity was suppressed in the environment due to the co-existence of heterotrophic nitrate-reducing bacteria, or that the sulphate-reducing bacteria enriched by the MPN method also possessed the ability to reduce nitrate or nitrite. In support of this, cell counts of NRB were the highest in the same samples that had high counts of SRB. In the absence of supporting phylogenetic information, it is not clear whether the same organisms

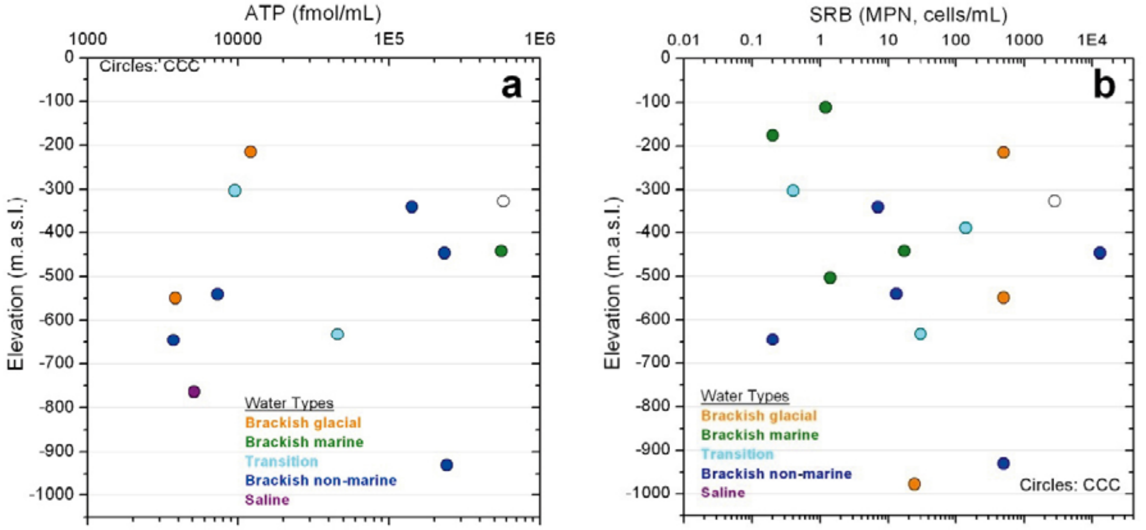


*Figure: 5-13. ATP production (a) and most probable numbers of SRB (b) versus depth for groundwaters at Forsmark. Note that these plots only show the CCC data set.*

were enriched with these two electron acceptors. The very low levels of nitrate and nitrite may thus be attributed to the consumption of these electron acceptors to their energy thresholds. A third explanation for the lack of correlation with sulphide levels may be that chemolithotrophic, nitrate-reducing bacteria catalyse the oxidation of sulphide by reduction of nitrate to $N_2$ /Greene et al. 2004/. However, based on the existing data set it is not clear if this pathway that is used in many oil reservoirs for sulphide remediation is active in the groundwaters at Forsmark.

With respect to distribution, there was no significant correlation between MPN counts of sulphate reducers and borehole length or to borehole location. However, higher counts of SRB were only found below 300 m borehole length in groundwaters with magnesium concentrations of less than 25 mg/L, but with high chloride concentrations. This suggests that SRB were largely derived from brackish glacial or mixed glacial brackish/old meteoric water types, but not necessarily from groundwaters of brackish marine origin.

## 5.6 Correlation of sulphide and sulphide related parameters with transmissivity

To see if high dissolved sulphide concentrations were related to any hydrogeological parameter, the transmissivity and natural flow were plotted against sulphide concentration. As can be seen in Figure 5-14 there is no clear relationship between dissolved sulphide concentration and any of these hydrogeological parameters.

The analysis revealed that, in those depths where the highest sulphide values are recorded, the transmissivity is generally higher than the mean of the borehole, though not all the transmissive zones are enriched in dissolved sulphide (cf. Figure 5-15 and 5-16), and not all the sulphide-enriched groundwaters are associated with high transmissivity zones.

In some cases when the transmissivity is higher the natural flow is also higher, and therefore sometimes high sulphide values coincide with high flow (e.g. borehole KFM02A; Figure 5-15). In other cases, however, some highly transmissive zones (either enriched or not in dissolved sulphide) do not have any flow at all (e.g. borehole KFM03A; Figure 5-16).

Similar conclusions can be obtained from the counting of fractures were no relationship has been observed between the amount of dissolved sulphide and the number of open fractures.

## 5.7 Sulphide reduction rates

Sulphate reduction rates (SRR) in sedimentary and crystalline aquifers have been reviewed and some SRR calculations have been performed for the Laxemar and Forsmark groundwater systems (Figure 5-17), cf. Appendix 3 for details.

In deep and long residence time groundwaters from sedimentary aquifers, the SRR are extremely low, as low as those observed in deep highly oligotrophic subseafloor marine settings. The main control of such SRR is the low availability of suitable, surface-derived organic matter. In crystalline aquifer systems, where the availability of this type of organic matter is much more limited, SRR must be equal to (or even lower than) those in deep sedimentary aquifers. Thus:

- The estimated SRR for groundwaters at repository level with residence times of 3,000–15,000 years are between $10^{-4}$ and $10^{-5}$ mM/year (the lower value being the most probable, as the higher one corresponds to Littorina-enriched groundwaters from Olkiluoto, inside the range of values for deep sedimentary aquifers.
- In deeper (600–1,000 m depth) and longer residence time groundwaters from Laxemar and Forsmark, the SRR would be of the order of $10^{-6}$–$10^{-8}$ mM/year (Appendix 3), in agreement with the few available values in crystalline systems at these depths, and lower than the values for deep sedimentary aquifers (Figure 5-17).

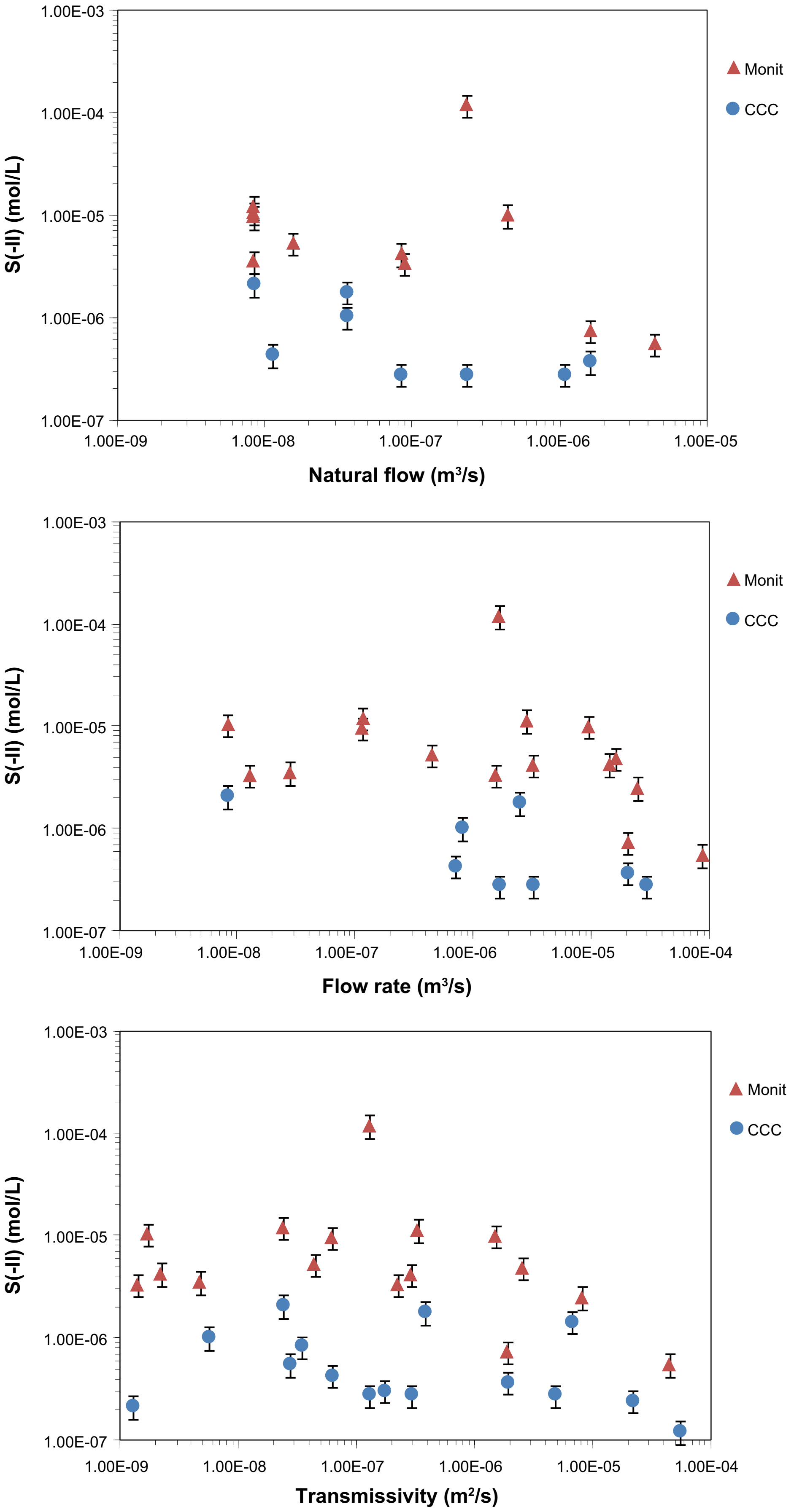


***Figure 5-14.*** *Natural flow, flow rate $Q_1$ and transmissivity plotted against dissolved sulphide concentrations (with ± 25% error bars) in Forsmark boreholes.*

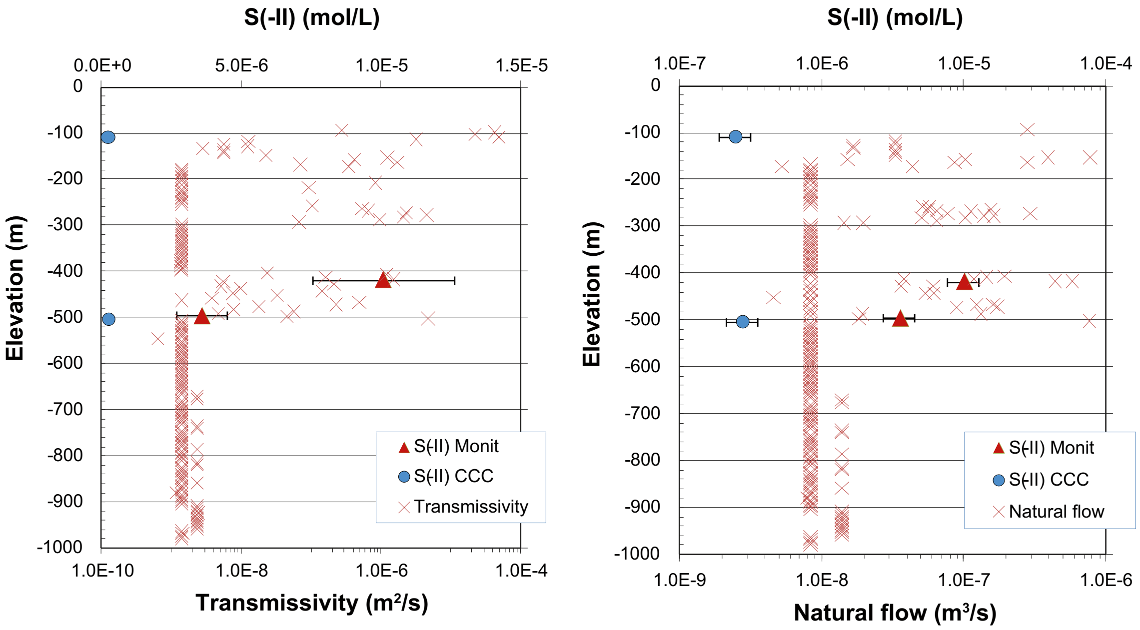


***Figure 5-15.*** *Dissolved sulphide concentration (with ± 25% error bars), transmissivity and flow plotted against elevation for the Forsmark KFM02A borehole.*

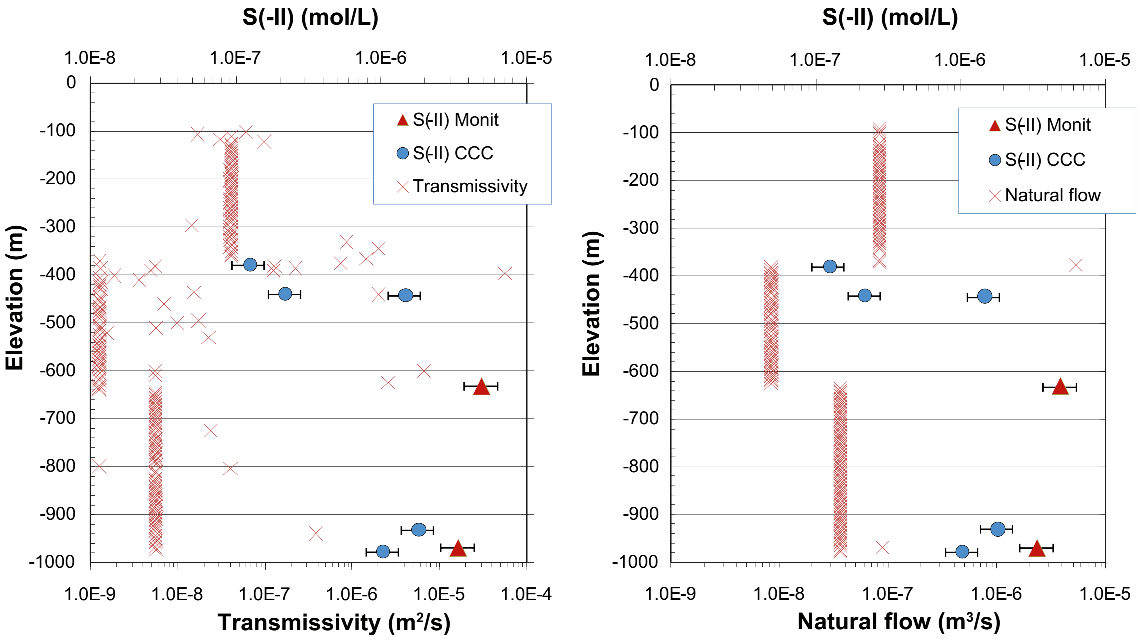


***Figure 5-16.*** *Dissolved sulphide concentration (with ± 25% error bars), transmissivity and flow plotted against elevation for the Forsmark KFM03A borehole.*

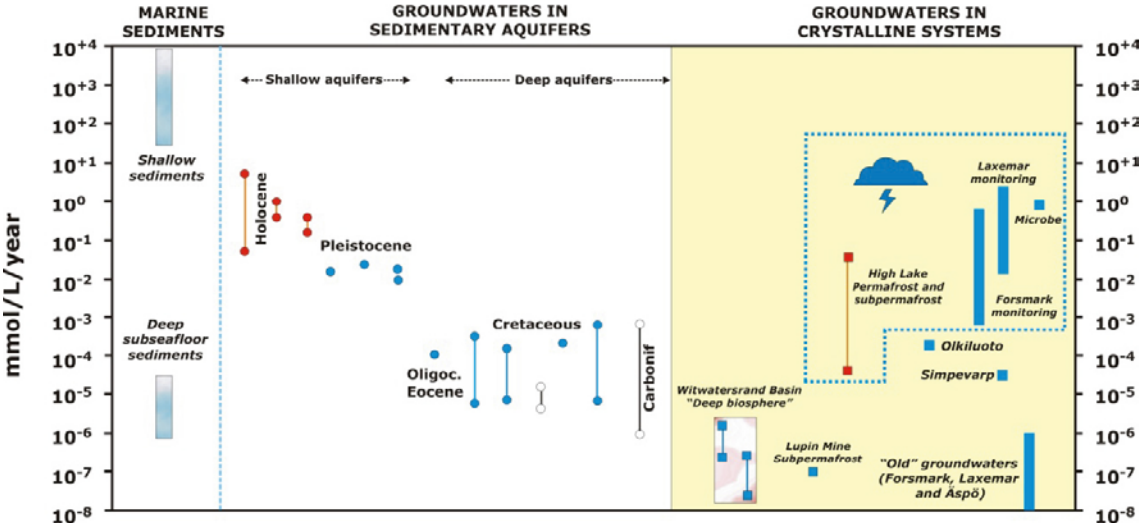


***Figure 5-17.** Compilation of published sulphate reduction rates (the sources of information are listed in Figure 1:Appendix3) including those values calculated in this study (Littorina-enriched groundwaters from Olkiluoto; brackish non-marine groundwaters from Simpevarp at 250–500 m depth; and old, deep (> 600 m depth) saline groundwaters from Forsmark, Laxemar and Äspö). Conflictive or unrealistic rates are included in the dotted area.*

Autotrophic metabolisms, based on deep-sourced $H_2$ and $CH_4$, may participate in the control of sulphate reduction rates in crystalline systems. This type of microbial activity is limited by the flux of $H_2$ and $CH_4$ and, with the presently available data on these fluxes, SRR would be in the range from $10^{-6}$ to $10^{-8}$ mM/year. These values are compatible with independent calculations based on dissolved sulphide contents in old deep groundwaters from Laxemar and Forsmark and in agreement with the few data found in the literature (Appendix 3).

The presence of dissolved Fe(II) sources, mainly iron oxhydroxides, exerts a major control on the dissolved sulphide produced by the SRB activity. In absence of these Fe(II) sources, local accumulation of dissolved sulphide occurs in some points of the groundwater systems. At low SRR typical of pristine conditions in deep sedimentary and crystalline systems, build up of meaningful concentrations of dissolved sulphide would need long periods of time. In any case, more detailed data on the spatial variability of Fe(II) mineral sources would be necessary to estimate the "buffering" capacity for dissolved sulphide at repository levels.

In this context, the SRR obtained from the dissolved sulphide "peaks" during the monitoring programme or in experimental setups in crystalline systems (e.g. the MICROBE experiment; Figure 5-17) are too high to be considered representative of the pristine conditions. SRR as high as those obtained in the monitoring programme are only observed in shallow aquifers enriched in organic matter. This fact, as well as other lines of evidence, supports an enhancement of SRB activity by additional, human-induced sources of organic matter.

Sulphate reducing bacteria have been identified in the Forsmark and Laxemar groundwater systems but their amounts (as most probable numbers, MPN) are not homogeneously distributed with depth. SRB data do not show any clear trend with respect to the amounts of dissolved sulphate and no significant correlations exist with respect to DOC, TOC and hydrogen (cf. references in Appendix 3). Thus, factors conditioning the presence and distribution of SRB, the size of their populations and the distribution of SRR in a more detailed level in the sites, are still poorly known.

The ultimate limiting factor on the rate of sulphate reduction is not necessarily the amounts of electron donor and sulphate (cf. references in Appendix 3). Energy availability (ΔG) constitutes a primary control on the distribution and rate of microbial sulphate reduction in nature that needs to be evaluated in the studied systems.

# 6 Sulphide during future climatic conditions

Not only present conditions (in terms of sulphide concentrations) need to be evaluated in SR-Site, but also the possibility of significant changes in sulphide during alternative climatic conditions. The various scenarios in SR-Site address the following periods;

- Open conditions (building and operation of the repository).
- Temperate climatic conditions following sealing of the repository, which includes groundwater interaction with the large amounts of backfill material (mainly bentonite at repository level).
- Periglacial climatic conditions: A cold period with permafrost formation preventing groundwater intrusion and circulation and possibly increasing concentrations of, for example, methane.
- Glaciation/deglaciation: It is expected that the glaciation period will be relatively stable in terms of hydrogeology, whereas the short periods of glacial advance and deglaciation are dramatic with strongly enhanced hydraulic gradients and intrusion of dilute meltwater to great depths in highly transmissive bedrock, and also into lower transmissive bedrock at shallower levels where it may be better preserved.
- A glaciation will probably be followed by a stadial with fresh to brackish "lake" conditions, characterised by stable and low flow conditions.
- This might be followed by the transgression of a brackish sea stadium, leading to density intrusion of brackish marine waters.

The possible evolution of sulphide concentrations and other pertinent parameters, such as DOC, sulphate ($SO_4^{2-}$) and gases (e.g. $H_2$ and $CH_4$), is presented in Table 6-1 below for all the climatic periods expected to influence repository evolution. The information in the table is based on the hydrogeological analyses made within SR-Site, which shows that the conditions influencing repository depths will change from drawdown/upconing circulation during repository operation, to the following post closure sequence of hydraulic conditions:

- Increasing depth of recharge/discharge of groundwaters during uplift under temperate conditions.
- Period of hydraulic inactivity where continuous permafrost exists, but this may be accompanied by the possibility of a deeper, horizontal flow determined by the presence of taliks.
- Period of penetrating glacial meltwater under high hydraulic pressure gradients.
- Submergence under fresh/brackish lake systems where hydraulic gradients are low and the main groundwater flow is upwards.
- Submergence under brackish marine transgressions where downward flow is dominant and density driven.

The parameters that will have greatest influence on the sulphide production are DOC, $H_2$ $CH_4$ and $SO_4$, and the estimated risk of increase in these parameters is summarised in Table 6-1.

From the arguments and uncertainties presented in the table above, and the uncertainties discussed in all sections of this report, it may be concluded that sulphide concentrations in groundwaters, including the potential input from methane and hydrogen, and the uncertain contribution from "natural" DOC and bentonite organic carbon, will be at levels found at present in the Forsmark site, or lower, during a complete glacial cycle. Naturally, for any given deposition location, oscillations in sulphide levels may take place. During the operational phase and during a marine transgression, the overall sulphide levels are expected to increase but these periods are relatively short compared with the temperate, perigacial and glacial periods. In addition, the sulphide concentrations in general are expected to decrease during the glacial periods.

**Table 6-1. Estimated increases/decreases in sulphide and sulphide-related parameters for SR-Site during future periods with different climates.**

| Period | DOC | $CH_4$ and $H_2$ | $SO_4^{2-}$ | $S^{2-}$ |
|---|---|---|---|---|
| Open repository | The organic content may increase during the operational phase due to drawdown, but also due to activities in the repository (e.g. diesel spills and fumes, the use of different organic materials etc) and due to biofilm forming on the tunnel walls. Even more importantly, the bentonite contains relatively high amounts of organic material which could increase the DOC values in the backfill porewaters /Hallbeck 2010/. | Drawdown may enhance the intrusion of biogenic methane from the near surface environment (e.g. lake or sea sediments). This will depend on the flow paths during open repository conditions.<br>A decrease of methane and hydrogen in other parts of the rock around the repository could be induced by the drawdown of meteoric waters expected to have low $H_2$ and $CH_4$. concentrations.<br>There may also be degassing into the repository tunnels which will induce, at least localised, a decrease in the groundwater gas concentrations. | An increase of sulphate could be induced either by drawdown of Baltic Sea waters or by an enhanced circulation of groundwaters with a large Littorina component.<br>A decrease of sulphate in other parts of the bedrock around the repository could be induced by the drawdown of meteoric waters expected to have low $SO_4^{2-}$ concentrations.<br>Increase in $SO_4^{2-}$ due to oxidation of pyrite in the host rock ⁄Baertschi 1991/ is expected to give only a minor contribution. | Potentially an increase due to availablility of DOC and $SO_4^{2-}$, especially in the backfill. To which extent the organic matter from bentonite will be available for breakdown and sulphide production is, however, difficult to discern /Hallbeck 2010/.<br>The sulphide values in the groundwaters may be similar in range as those from the monitoring boreholes.<br>Saturation in respect of amorphous Fe(II) monosulphide will prevent the values becoming much higher.<br>The Fe values are not expected to decrease during the open repository phase although some oxidation of Fe(II) may take place close to the tunnel walls. |
| Temperate climate | The bentonite in the backfill contains relatively high amounts of organic material and, if soluble, would increase the DOC values in the backfill porewaters /Hallbeck 2010/. Similar increases would also occur during the initial period of the first temperate phase following repository closure. The DOC values will return eventually to similar levels found prior to repository construction. | Corrosion of steel will produce substantial amounts of $H_2$. | A long period of infiltration of waters of meteoric origin would result in groundwaters with lower sulphate concentrations. | In the backfill waters, possibly some increase of sulphide will occur during the initial period of the first temperate phase following repository closure, if the large organic content in the bentonite is suitable for sulphate reduction. Other stray materials are minor in comparison /Hallbeck 2010/. $H_2$ from steel corrosion may be used by SRB to produce sulphide, but this would react with the Fe(II) resulting from the corrosion, and no net increase of sulphide by this mechanism is expected.<br>For groundwaters, probably no significant changes when compared with the situation existing before repository construction. $H_2$ produced by steel corrosion in the repository might diffuse into the surrounding rock mass and be used by SRB to increase sulphide in groundwaters at some distance from the repository. |

| Period | DOC | $CH_4$ and $H_2$ | $SO_4^{2-}$ | $S^{2-}$ |
|---|---|---|---|---|
| Periglacial | Probably no changes from the situation existing before repository construction.<br>Introduction of DOC from the surface is reduced due to the lower hydraulic conductivity of permafrost layers (either continuous or discontinuous). | Gases could be trapped due to the reduced permeability of frozen ground under periods of continuous permafrost. However, in Forsmark the flow of gases is considered too low to achieve significant accumulation /Delos et al. 2010/. | Above, within and closely below the permafrost layers, freeze- out of salts may locally concentrate sulphate-forming minerals such as mirabilite and/or gypsum. However, an important source of sulphate, the Baltic Sea, will be far away from the Forsmark site during periglacial periods.<br>For most of the rock volume no significant changes are expected when compared with the situation during the preceding temperate period. | Possibly a localised increase in sulphide concentrations will occur in favourable environments.<br>However, as the availability of DOC and gases is not expected to increase subtantially, the sulphide values generally will be at similar levels or lower than those found during the preceding temperate period. |
| Glacial | Probably no major changes.<br>Subglacial meltwaters will probably have some DOC which could infiltrate to relatively great depths during the advance and retreat of an ice-sheet. This would change the DOC fconcentrations at depth.<br>However, most probably these dilute meltwaters will decrease the DOC in large parts of the rock volume. | Probably no significant changes from the situation existing before repository construction.<br>It is to be expected that glacial meltwaters do not have high concentrations of dissolved methane or hydrogen gas. Therefore, infiltration to great depths of these waters would decrease the levels of these gases in the groundwaters. On the other hand, the meltwater may contain dissolved oxygen which may decrease the amounts of dissolved sulphide. | It is to be expected that glacial meltwaters will not have high concentrations of sulphate. Therefore, infiltration to great depths of these waters would then decrease the overall sulphate levels in the groundwaters. | There are few arguments supporting significant microbial sulphide production beneath glaciers. However, /Wadham et al. 2004/ report stable isotope evidence for microbial sulphate reduction at the bed of an Arctic glacier, cf. also /Hallbeck 2009/<br>A decrease in sulphide is to be expected in rock volumes where substantial inflow of glacial meltwaters has occurred, given the low concentrations of sulphate, gases and probably decreased DOC levels. |
| Submerged: Meltwater/ freshwater | Stable groundwater conditions with no addition of DOC; probably no major changes compared with the glacial period. | Stable groundwater conditions with no addition of gases; probably no major changes compared with the glacial period. | Stable groundwater conditions with no addition of sulphate; probably no major changes compared with the glacial period. | Stable groundwater conditions; probably no major changes in sulphide production compared with the glacial period. |
| Submerged: Marine transgression | An increase in DOC due to seawater intrusion can be expected. It is not known to what extent this DOC infiltrates together with the marine waters without being first consumed through diverse microbial processes. | Similar to the levels found during temperate conditions prior to repository construction.<br>Drawdown may enhance the intrusion of methane from sea sediments.<br>As in the case of DOC, it is not clear how far the marine waters can infiltrate. | Increase in sulphate due to seawater intrusion. | Expected increase in sulphide production and concentrations as compared with the glacial and meltwater lake periods.<br>Similar to the sulphide concentrations measured at present, that is, analogous to the temperate period. |

As discussed in Section 5.2.3, practically all sulphide concentrations at Forsmark are ≤ 0.013 mmol/L (0.4 mg/L). There is, however, a probability that for some deposition holes the surrounding groundwaters have sulphide concentrations as high as 0.12 mmol/L (~4 mg/L). In order to estimate canister corrosion rates in the SR-Site during a full glacial cycle, it is recommended that the observed distribution of sulphide in groundwaters at Forsmark during the present temperate conditions should be used. It should be noted that the present sulphide concentrations have been sampled after a recent period of possible intrusion of marine sulphate-rich waters. For estimating the canister corrosion in the SR-Site there are at present no arguments to rule out that high sulphide concentrations during a time period at a given deposition hole in the repository will be averaged with other periods with low sulphide concentrations. Therefore, it must be pessimistically assumed that the fraction of canisters affected with groundwaters with sulphide concentrations as high as 0.12 mmol/L will be influenced by this sulphide concentration during the total assessment period of one million years.

# 7 Conclusions

The problem with identifying reliable sulphide values was recognised at an early stage in the Forsmark site investigations (PLU) when the large variation between CCC and monitoring samples was observed, and also the very large variation within the monitoring time series.

The selection of “best possible” values has been handled accordingly: 1) For the CCC samples, the assumption is that groundwaters already judged from the site investigations to be representative from an analysis of the major ions and the important environmental isotopes, would also include the minor elements like Fe, DOC, and $S^{2-}$. Most of the selected CCC sulphide values therefore correspond to groundwater samples previously selected as being representative (i.e. Categories 1–3). 2) For the monitoring samples, in most cases during the time series measurements the sulphide values are higher in the downhole tubes and in the borehole section compared with formation groundwaters from the surrounding fractures. The routine removal of 5 borehole section water volumes is, in most cases, inadequate to guarantee stable sulphide values. Therefore, for most of the sections, the last sample in the time series is suggested as best representing the the fracture groundwater value. However, even when only considering these “best possible” values during the monitoring programme and the CCC, there are still large variations (in many cases more than one order of magnitude) with the CCC samples generally characterised by lower values than those from the monitoring when samples from the same borehole section can be compared. These differences are significant down to 650 m depth. However, taking into account only the CCC samples, there is an increase in sulphide below about 650 m which is not evident in the monitoring samples.

As mentioned above, time series measurements recorded during the monitoring programme show in most cases decreasing sulphide values, i.e. the pumped volumes have not been large enough to ensure stable values representing the bedrock fracture groundwaters. However, in sections where the monitoring values seems to have levelled out, there is still a discrepancy between this value and the lower CCC sulphide value. This either means that: a) the last groundwater sample from the borehole section sampled still has not reached 100% formation groundwater and sulphide would decrease further with additional pumping over a longer period of time, or, b) the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, c) it may be almost impossible to avoid minor contamination to the monitoring samples from the section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, d) differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

It can, however, be assumed that the two selected groundwater samples from the same water conducting structures, i.e. the “best possible” sample from the monitoring and the sample from the CCC sampling, the latter usually showing lower sulphide, spans the interval of representative sulphide values in the formation water.

Saturation in respect of FeS(am) is achieved for many monitoring samples but only for one CCC sample. In samples at or close to saturation, the measured $Fe^{2+}$ and $S^{2-}$ values in a single sample are interdependent and consequently the solubility of FeS(am) sets an upper limit for these species in the groundwater.

It is worth noting that the plug flow calculations performed for the monitored sections are very useful in order to judge the volumes of water needed to be pumped at each section before obtaining a suitable sample representing the fracture groundwater. This means that for future sampling campaigns these plug flow calculations provide a powerful means to improve (by knowing) the individual sampling schemes for each borehole section.

The plot below (Figure 7-1) compares the sulphide values from the earlier SR-Can report and the present selected distribution for the SR-Site Forsmark. Practically all sulphide concentrations at Forsmark are $\leq 0.013$ mmol/L (0.4 mg/L). There is, however, a probability that for some deposition holes the surrounding groundwaters have sulphide concentrations as high as 0.12 mmol/L (~4 mg/L).

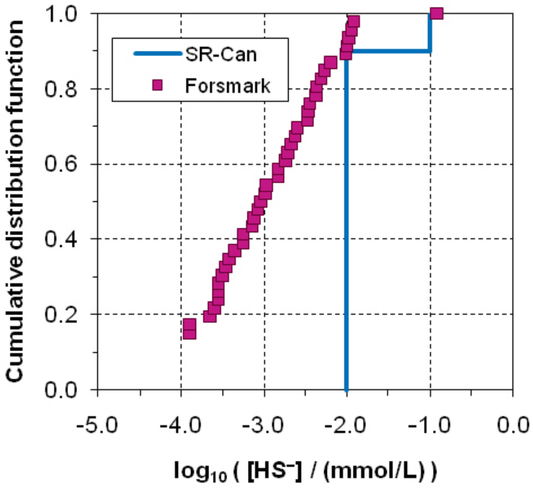


***Figure 7-1.*** *Cumulative distribution curve showing the selected sulphide values for goundwaters to be used for Forsmark in the SR-Site. The blue curve shows the values used in the earlier performed safety assesment (SR-Can). The distribution function describes the probability that a sulphide concentration will be found to be less than or equal to a given value. The data show, for example, that the probability of finding a sulphide value ≤ 0.001 mM is ≈50%.*

In order to estimate canister corrosion rates in the SR-Site during a full glacial cycle, it is recommended that the observed distribution of sulphide in groundwaters at Forsmark during the present temperate conditions should be used. Because there are no sufficient arguments at present showing that sulphide concentrations will be time-averaged, the calculations of canister corrosion rates have to assume pessimistically that the fraction of deposition holes influenced by high sulphide concentrations will be affected during the full glacial cycle.

# 8 Acknowledgements

Birgitta Kalinowski and Ignasi Puigdomenech, SKB, are acknowleged for providing important improvements to the microbiological sections and for input to Sections 1 and 6. Petteri Pitkänen, Posiva, kindly provided gas and sulphide analyses from the Olkiluoto site in Finland.

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# Appendix 1

## Tables

This appendix contains tables reviewing the $S^{2-}$, $Fe^{2+}$, $Mn^{2+}$ and DOC/TOC contents for all the analyses from percussion and cored boreholes in Forsmark where sulphide has been analysed. Groundwater type and chloride content are also given.

Data from two different types of sampling are used: a) Complete Chemical Characterisation (CCC) data from cored boreholes of the site characterisation programme (i.e. Forsmark Extended 2.3 data freeze /Laaksoharju et al. 2008/) that includes the earlier established categorisation of the samples, and b) data from the monitoring of selected borehole sections in percussion and cored boreholes initiated at different times during and following the site characterisation programme up to the Autumn of 2009. For some of the monitored boreholes, additional time series data became available after the deadline (in the Spring of 2010) to provide input to the safety assessment calculations and therefore, for interest, plots and a description of these extended time series data trends is included for the relevant boreholes (KFM01A, KFM01D, KFM02A, KFM03A, KFM07A, KFM08A, KFM08D and KFM10A). In the description, implications from Section 3.1.4 are discussed for each borehole section and the concepts *section water* and *formation water* have been used for initial stagnant water present in the borehole section prior to pumping/sampling and groundwater entering the borehole section via the fracture system in the bedrock due to pumping/sampling, respectively.

Comparing these two latest sampling periods show that generally the sulphide trends were repeated and the final values were supported by the 2010 data. However, the sulphide concentrations in the samples have proved to be very sensitive to small differences in the sampling procedures and the modified performance in 2010 may explain the few divergences. In 2010 a high-pressure cleansing device and simultaneous pumping were used for cleaning the stand pipes prior to sampling. This procedure implies only a limited removal of water from the borehole section compared to the large volumes removed during the clean-up pumping (103–360 L) that was performed in the Autumn of 2009. Because of this, the procedure was not expected to affect the groundwater conditions in the borehole section and therefore the time between cleaning and pump start (settling period) was not specified and varied between 6–47 days. In retrospect, it seems plausible that pressure effects in the stand pipes probably propagate down to the connected borehole sections. Another difference is the pumping flow rates which were generally lower in 2010 than in 2009. Either of these events, or a combination of both, may have caused the differences between the two time-series sulphide concentration trends observed in a few borehole sections. When possible, conditions such as different pumping methods or flow rates, short settling times and pump stops are commented on when relevant for each borehole section in the following documentation.

Some of the CCC and monitoring sections correspond to each other (the same water conducting fracture is sampled) and in such cases the corresponding section is referred to in the heading of the table.

It is also commented upon if the major ion chemistry has been stable during the sampling period, and for the monitoring samples corresponding to a CCC sampled section, it is recorded if the water chemistry deviates from the earlier sampled CCC values.

Concerning the measured sulphide values given, it is important to note that detection levels for sulphide have varied during the site investigations from 0.002 to 0.006 mg/L but during some periods a "reporting limit" of 0.03 mg/L (equal to 10σ) has been used when the measured values are included in the data base.

The iron content (mainly $Fe^{2+}$) is obtained by using ICP to measure the total Fe content and using spectrophotometry to measure Fe(tot) and Fe(II). There is usually a good correlation between all three values. The values for Fe(ICP) are chosen in the present study because these are measured for almost all samples and constitute, therefore, the largest data set.

The organic content is given as DOC (analysed for most of the samples) and its correlation with TOC (if analysed) is noted. The groundwater sample for TOC (Total organic Carbon) is not filtered and the sample for DOC (Dissolved Organic Carbon) is filtered through a 0.4 um disposable filter. The samples are stored immediately in the freezer and transported to the laboratory in isolated bags with cooling blocks. The analytical method used includes: A) Acidification to remove inorganic carbon and volatile organic carbon. B) UV-oxidation to convert all the carbon present to carbon dioxide which is flushed through scrubber tubes to remove chlorine gas and water vapour. C) Detection and quantification using an Infrared Detector.

### HFM01

**Monitoring section:** 33.5 to 45.5 m

Elevation sec mid:

–37.02 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during three occasions: 2007-04-10, 2007-19-23 and 2008-10-07. | First value is selected because of increasing instability with time resulting in a less suitable sample for the sample depth. |
| Groundwater type. | Na-Ca-Cl-$HCO_3$ type.<br>Cl varies between 739 to 1,400 mg/L. | Mixed brackish groundwater type.<br>Unstable major ion chemistry indicated by, e.g. the variable Cl range. | Selected sample: #12757 (2007-04-10); 739 mg/L Cl. |
| $S^{2-}$ | Below detection limit (0.006) to 0.038 mg/L. | Values increase systematically with time. | < 0.006 mg/L |
| Fe | 0.622 to 0.805 (Fe mg/L) | Good correlation between Fe, Fe(tot) and Fe(II).<br>Values decrease systematically with time. | 0.805 mg/L |
| Mn | 0.158 to 0.311 mg/L | No systematic time change. | 0.160 mg/L |
| DOC | 9.5 to 7.9 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 9.5 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

**Note:** This borehole section corresponds to a well connected fracture zone with high transmissivity and responses caused by drilling and pumping activities in for example KFM01D, may have influenced the groundwater composition.

### HFM02

**Monitoring section:** 38.0 to 48.0 m

Elevation sec mid:

–39.91 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during four occasions: 2005-11-09, 2006-10-17, 2007-10-23 and 2008-10-07. | First value selected because of overall instability with time resulting in an increased marine (e.g. Mg) signature. |
| Groundwater type. | Na-Ca-Cl-$HCO_3$ type.<br>Cl varies between 396 to 2,140 mg/L. | Mixed brackish groundwater type.<br>Unstable major ion chemistry indicated by varying proportions of marine water content. | Selected sample: #12006 (2005-11-09); 396 mg/L Cl. |
| $S^{2-}$ | 0.026 to 0.048 mg/L | No systematic time change. | 0.026 mg/L |
| Fe | 0.417 to 1.74 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 0.417 mg/L |
| Mn | 0.127 to 0.577 mg/L | No systematic time change. | 0.127 mg/L |
| DOC | 7.1 to 9.8 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 9.8 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

**Note**: This borehole section corresponds to a well connected fracture zone with high transmissivity and responses caused by drilling and pumping activities in for example KFM01D, may have influenced the groundwater composition.

### HFM04

**Monitoring section:** 58.0 to 66.0 m

Elevation sec mid:

–57.92 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during four occasions: 2005-11-07, 2006-10-31, 2007-11-01 and 2008-09-30. | Overall stability with time and first value selected. |
| Groundwater type. | Na-(Ca)-$HCO_3$-(Cl) type.<br>Cl varies between 56.3 to 64.6 mg/L. | Fresh groundwater type.<br>Stable major ion chemistry. | Selected sample: #12003 (2005-11-07); 56.3 mg/L Cl. |
| $S^{2-}$ | 0.047 to 0.115 mg/L | Values increase systematically for the first 3 sampling occasions. | 0.047 mg/L |
| Fe | 0.337 to 0.393 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 0.348 mg/L |
| Mn | 0.078 to 0.082 mg/L | No systematic time change. | 0.080 mg/L |
| DOC | 8.3 to 9.2 mg/L | Good correlation between DOC and TOC.<br>No significant time change. | 8.3 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### HFM13

**Monitoring section:** 159.0 to 173.0 m

Elevation sec mid:

–138.63 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during four occasions: 2005-11-09, 2006-10-24, 2007-10-17 and 2008-09-30. | Overall stability with time and first value selected. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 4,960 to 5,280 mg/L. | Brackish marine groundwater type.<br>Largely stable major ion chemistry. | Selected sample: #12009 (2005-11-09); 5,020 mg/L Cl. |
| $S^{2-}$ | 0.005 to 0.023 mg/L | Three out of four values are within the range of 0.021 to 0.023 mg/L.<br>No systematic time change. | 0.023 mg/L |
| Fe | 3.110 to 3.67 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>An increase with time is indicated. | 3.110 mg/L |
| Mn | 2.15 to 2.55 mg/L | An increase with time is indicated. | 2.15 mg/L |
| DOC | 1.8 to 2.3 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 2.2 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### HFM15

**Monitoring section:** 85.0 to 95.0 m

Elevation sec mid:

–59.11 masl

| | **Groundwater chemistry** | **Comment** | **Selected sample/value*** |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during four occasions: 2005-11-09, 2006-10-24, 2007-10-17 and 2008-10-28. | First value selected because of overall instability with time resulting in groundwaters with and without a marine component. |
| Groundwater type. | Na-(Ca)-Cl- $HCO_3$ type.<br>Cl varies between 406.0 to 2,250.0 mg/L. | Mixed brackish groundwater type.<br>Unstable major ion chemistry, e.g. first and last sampling occasions show similar chemistry (406–503 mg/L Cl) compared to the other two (1,710–2,250 mg/L). | Selected sample: #12007 (2005-11-09); 406 mg/L Cl. |
| $S^{2-}$ | 0.049 to 0.409 mg/L | First and last samples show highest values (0.206 and 0.409 mg/L).<br>Values decrease systematically for the first 3 sampling occasions (0.206–0.049 mg/L). | 0.206 mg/L |
| Fe | 0.643 to 2.81 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>First and last samples show lowest values (0.617 and 1.23 mg/L).<br>Values increase systematically for the first 3 sampling occasions. | 1.020 mg/L |
| Mn | 0.239 to 0.833 mg/L | First and last samples show lowest values (0.239 and 0.467 mg/L).<br>No systematic time change. | 0.467 mg/L |
| DOC | 5.7 to 13.0 mg/L | Good correlation between DOC and TOC. First and last samples show the highest values (12.0 and 13.0 mg/L). | 13.0 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

## HFM16

**Monitoring section:** 54.0 to 67.0 m
Elevation sec mid:
–57.18 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during 3 occasions: 2006-10-06, 2007-10-23 and 2008-10-17. | Overall stability with time and first value selected. |
| Groundwater type. | Na-(Ca)-$HCO_3$-(Cl)-($SO_4$) type.<br>Cl varies between 145.0 to 187.0 mg/L. | Fresh groundwater type. | Selected sample: #12379 (2006-10-06); 187 mg/L Cl. |
| $S^{2-}$ | 0.006 to 0.011 mg/L | Overall low sulphide values.<br>Values decrease with time. | 0.011 mg/L |
| Fe | 0.347 to 0.359 mg/L | Fe(tot) and Fe(II) are higher (0.595 and 0.594 mg/L) than the Fe measured with ICP in the selected sample.<br>In the two other samples the correlation between the three Fe values is good. | 0.356 mg/L |
| Mn | 0.074 to 0.090 mg/L | No systematic time change. | 0.090 mg/L |
| DOC | 13.0 to 17.0 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 13.0 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

## HFM19

**Monitoring section:** 168.0 to 182.0 m
Elevation sec mid:
–136.09 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during four occasions: 2005-11-09, 2006-10-25, 2007-10-17 and 2008-10-28. | No value has been selected due to unrealistically high Fe, Mn and $S^{2-}$ at each sampling occasion, indicating sampling or analytical problems. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 3,360 to 5,330 mg/L. | Brackish marine groundwater type.<br>The two last sampling occasions show increased components of meteoric water over marine (Littorina) type. | |
| $S^{2-}$ | 0.131 to 1.570 mg/L. | The two first samples show typical Littorina type water judged to be representative for this section, and also record the highest sulphide values (1.46 and 1.57 mg/L).<br>Values decrease systematically with time. | |
| Fe | 3.66 to 5.4 mg/L. | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | |
| Mn | 1.29 to 1.93 mg/L. | No systematic time change. | |
| DOC | 35.7 to 2.7 mg/L | The first sample showed high DOC (35.7 mg/L) and TOC (40.3 mg/L) due to contamination? The other samples show DOC values between 2.7 and 5.8 mg/L and a lack of correlation between DOC and TOC.<br>DOC values decrease systematically with time. | |

### HFM21

**Monitoring section:** 22.0 to 32.0 m

Elevation sec mid:

–18.82 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during three occasions: 2007-04-10, 2007-10-23 and 2008-10-22. | First value selected because of some instability indicated by a small marine input in the second sample. |
| Groundwater type. | Na-(Ca)-$HCO_3$-Cl-($SO_4$) type.<br>Cl varies between 241.0 to 355.0 mg/L. | Largely fresh groundwater type.<br>Some instability generally indicated by small but variable portions of brackish marine groundwater type. | Selected sample: #12758 (2007-04-10); 241.0 mg/L Cl. |
| $S^{2-}$ | Below 0.006 (detection limit) to 0.931 mg/L. | Values increase systematically with time. | Below 0.006 mg/L |
| Fe | 0.526 to 1.020 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Values decrease systematically with time. | 1.020 mg/L |
| Mn | 0.143 to 0.193 mg/L | No systematic time change. | 0.190 mg/L |
| DOC | 7.6 to 10.0 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 7.6 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### HFM27

**Monitoring section:** 46.0 to 58.0 m

Elevation sec mid:

–45.60 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during three occasions: 2006-10-17, 2007-10-26 and 2008-10-17. | First value selected because of some instability indicated by an increase in meteoric input in the last sample. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 2,250.0 to 2,990.0 mg/L. | Brackish marine groundwater type.<br>Somewhat unstable major ion chemistry with time. | Selected sample: #12506 (2006-10-17); 2,660.0 mg/L Cl. |
| $S^{2-}$ | Between 0.02 to 0.055 mg/L. | Values increase weakly but systematically with time. | 0.020 mg/L |
| Fe | 2.260 to 2.900 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 2.640 mg/L |
| Mn | 0.695 to 0.896 mg/L | No systematic time change. | 0.847mg/L |
| DOC | 4.6 to 5.4 mg/L | Relatively good correlation between DOC and TOC.<br>Values increase systematically with time. | 4.6 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion

### HFM32

**Monitoring section:** 26.0 to 31.0 m

Elevation sec mid:

–27.46 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during three occasions: 2006-10-30, 2007-11-12 and 2008-10-14. | First value selected because of sample instability, i.e. a variable marine signature. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 290.0 to 3,970.0 mg/L. | Brackish marine type.<br>Some instability in the major ion chemistry during the monitoring period. | Selected sample: #12518 (2006-10-30); 3,970 mg/L Cl. |
| $S^{2-}$ | Between 0.08 to 0.214 mg/L. | Values increase systematically with time. | 0.08 mg/L |
| Fe | 2.63 to 3.57 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 3.57 mg/L |
| Mn | 0.644 to 0.919 mg/L | No systematic time change. | 0.919 mg/L |
| DOC | 3.5 to 70.0 mg/L | Relatively good correlation between DOC and TOC.<br>No systematic time change. | 3.5 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### KFM01A

**CCC section:** 110.10 m to 120.77 m. (Corresponds to the monitoring section 109.0 to 130.0 m).

Elevation sec mid:

–111.74 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples. | Samples collected during one occasion: 2003-01-22 to 2003-02-24. | The selected value is the last sample collected in the time series corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 4,078 to 4,567 mg/L. | Brackish marine groundwater type. | Selected sample: #4538 (Category 2*, 2003-02-24); 4,563 mg/L Cl. |
| $S^{2-}$ | Below detection limit of 0.03 but a measured value of 0.014 mg/L was obtained for the last sample. | No systematic time change. | 0.014 mg/L |
| Fe | 1.61 to 0.790 mg/L (measured by ICP). | Good correlation between Fe(tot) and Fe(II). These values are generally about 0.2 mg/L higher than Fe values measured by ICP.<br>Last 4 recorded values decrease systematically with time. | 0.0790 mg/L |
| Mn | 0.691 to 0.729 mg/L | No systematic time change. | 0.691 mg/L |
| DOC | 1.5 to 4.6 mg/L | No TOC measured.<br>DOC values recorded<br>Values decrease systematically with time. | 1.5 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM01A

**Monitoring section** 109.0 to 130.0 m. (Corresponds to the CCC section 110.10m to 120.77 m).
Elevation sec mid:
–115.79 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 10 samples. | Samples collected during five occasions: 2005-11-09, 2006-10-09, 2008-05-21 to 2008-05-29 (2 samples), and 2008-10-03 to 2009-10-06 (5 samples).<br>The final sampling occasion comprised a single day time series of five samples. | The selected value represents the final sample taken from the last time series occasion which showed good major ion stability. |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 3,900 to 4,050 mg/L. | Brackish marine groundwater type.<br>Compared with the CCC sampling, the monitoring period gave a somewhat lower Cl content, slightly higher $HCO_3$ and $d^{18}O$ and showed minor instability. This was probably due to a connection with a nearby highly conductive system. | Selected sample: #16512 (2009-10-06); 3,970 mg/L Cl. |
| $S^{2-}$ | 0.269 to 3.11 mg/L | The 5 samples of the final sampling occasion show values decreasing systematically with time (3.110–0.313 mg/L). | 0.313 mg/L |
| Fe | 0.170 to 0.546 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Final 5 samples show Fe values increasing systematically with time. | 0.488 mg/L |
| Mn | 0.478 to 0.791 mg/L | No systematic time change. | 0.737 mg/L |
| DOC | 2.1 to 34.0 mg/L | Relatively good correlation between DOC and TOC.<br>Final 5 samples show values decreasing systematically with time. | 2.1 mg/L |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance were that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*), and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional Spring time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-1.

The 2010 time-series sulphide trend fits well with the trend obtained in 2009. Also the 2010 sulphide data decrease rapidly and level out to values (0.269–0.335 mg/L) closely similar to the sulphide value chosen as ‘representative’ for the safety case calculations (0.313 mg/L). The indicated small displacement between the two steep curves is within the error in the volume determination (the volume is calculated from flow rate and time). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible and specific for each section, b) the chosen ‘representative’ 2009 sulphide value for the safety case calculations, in this specific case, has been supported, and c) there is still a discrepancy between this value and the much lower CCC sulphide value (0.014 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% formation groundwater and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the monitoring samples from the section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

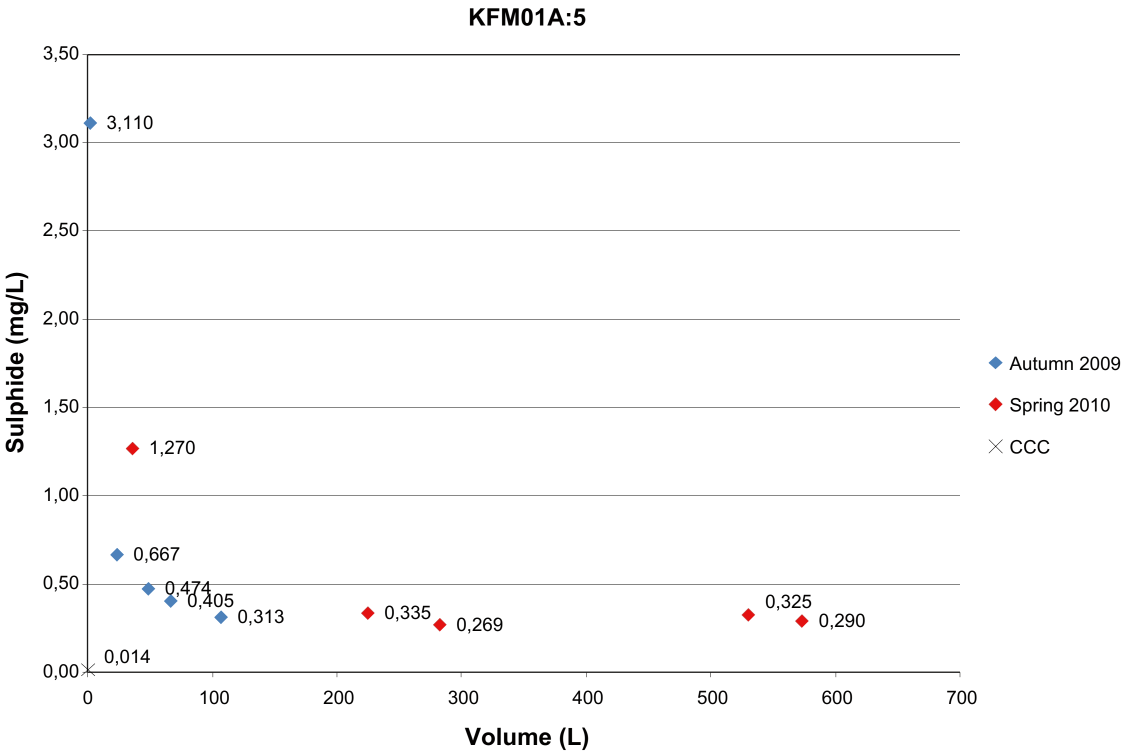


***Figure A1-1.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM01A (–115.79 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

### KFM01A

**CCC section:** 176.80 to 183.90 m
Elevation sec mid:
–176.26 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 9 samples. | Samples collected during one sampling occasion from 2003-03-03 to 2003-03-31. | The selected value represents the last sample collected to correspond to the Category 2* sample deemed most representative |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 5,041.0 to 5,329.5 mg/L. | Brackish marine (Littorina) groundwater type<br>Overall stable major ion chemistry. | Selected sample: #4724 (Category 2*, 2003-03-31); 5,329.5 mg/L Cl. |
| $S^{2-}$ | Below 0.03 mg/L (detection limit). | No systematic time change. | < 0.03 mg/L |
| Fe | 0.512 to 1.590 mg/L | Relatively good correlation between Fe, Fe(tot) and Fe(II).<br>Apart from the initial sample, values generally decrease systematically with time, especially Fe(II). | 0.515 mg/L |
| Mn | 0.966 to 1.020 mg/L | No systematic time change until the final 4 samples which show a weak systematic increase. | 1.020 mg/L |
| DOC | 1.1 to 4.1 mg/L | TOC not analysed.<br>No systematic time change in DOC until the final 4 samples which show a weak systematic decrease. | 2.3 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedaxure of representative sample selection.

### KFM01D

**CCC section** 314.5 to 319.5 m. (Corresponds to monitoring section 311 to 321 m).
Elevation sec mid:
–253.31 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 1 sample. | Sample collected from 2006-08-22. | The selected value corresponds to the Category 3* sample deemed most representative |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl at 3,890 mg/L. | Brackish marine groundwater type.<br>Sampled in a low conductive section. | Selected sample: #12366 (Category 3*, 2006-08-22); 3,890 mg/L Cl. |
| $S^{2-}$ | 0.009 mg/L | No systematic time change. | 0.009 mg/L |
| Fe | 2.480 mg/L | Fe(tot) and Fe(II) not measured.<br>No systematic time change. | 2.480 mg/L |
| Mn | 0.584 mg/L | No systematic time change. | 0.584 mg/L |
| DOC | 4.1 mg/L | TOC is also 4.1 mg/L.<br>No systematic time change. | 4.1 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM01D

**Monitoring section:** 311.00 to 321.00 m. (Corresponds to the CCC section 314.5 to 319.5 m).
Elevation sec mid:
–252.53 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 8 samples. | Samples collected during four occasions: 2007-04-18, 2008-05-29, 2008-10-03, and 2009-10-08 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | The selected value represents the final sample taken from the last time series occasion which showed some instability in the major ion chemistry. |
| Groundwater type | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 3,680 to 4,310 mg/L. | Transition groundwater type.<br>Brackish marine groundwater evolving to a brackish non-marine type with time.<br>Differs from the CCC sample by having slightly higher Cl, but lower Mg, $HCO_3$ and $SO_4$. | Selected sample: #16527 (2009-10-08); 4,180 mg/L Cl. |
| $S^{2-}$ | 0.120 to 2.45 mg/L | Final 5 samples show values decreasing systematically with time (2.450–0.136 mg/L). | 0.136 mg/L |
| Fe | 0.226 to 3.23 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 1.450 mg/L |
| Mn | 0.421 to 0.956 mg/L | No systematic time change. | 0.488 mg/L |
| DOC | 1.8 to 8.1 mg/L | Good correlation with TOC except for a few values.<br>Final 4 samples show a systematic increase in DOC with time. | 3.0 mg/L |

### Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance was that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*), and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-2.

The 2010 time-series sulphide trend fits well with the trend obtained in 2009. Also the 2010 sulphide data decrease rapidly and level out to values (0.139–0.144 mg/L) closely similar to the sulphide value chosen as 'representative' for the safety case calculations (0.136 mg/L). If the second data point is omitted, the indicated small displacement between the two steep curves is well within the error in the volume determination (the volume is calculated from flow rate and time). The deviation from the trend by the second data point is possibly due to occasional contamination from stagnant water somewhere in the equipment or from the borehole section stagnant water, but may also be an indication of a larger displacement similar to the ones observed in both sections of KFM02A (cf. Figures A1-4 and A1-5). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible and specific for each section, b) the chosen 'representative' 2009 sulphide value for the safety case calculations, in this specific case, has been supported, and c) there is still a discrepancy between this value and the much lower CCC sulphide value (0.009 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% formation groundwater and sulphide would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the monitoring samples from the section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

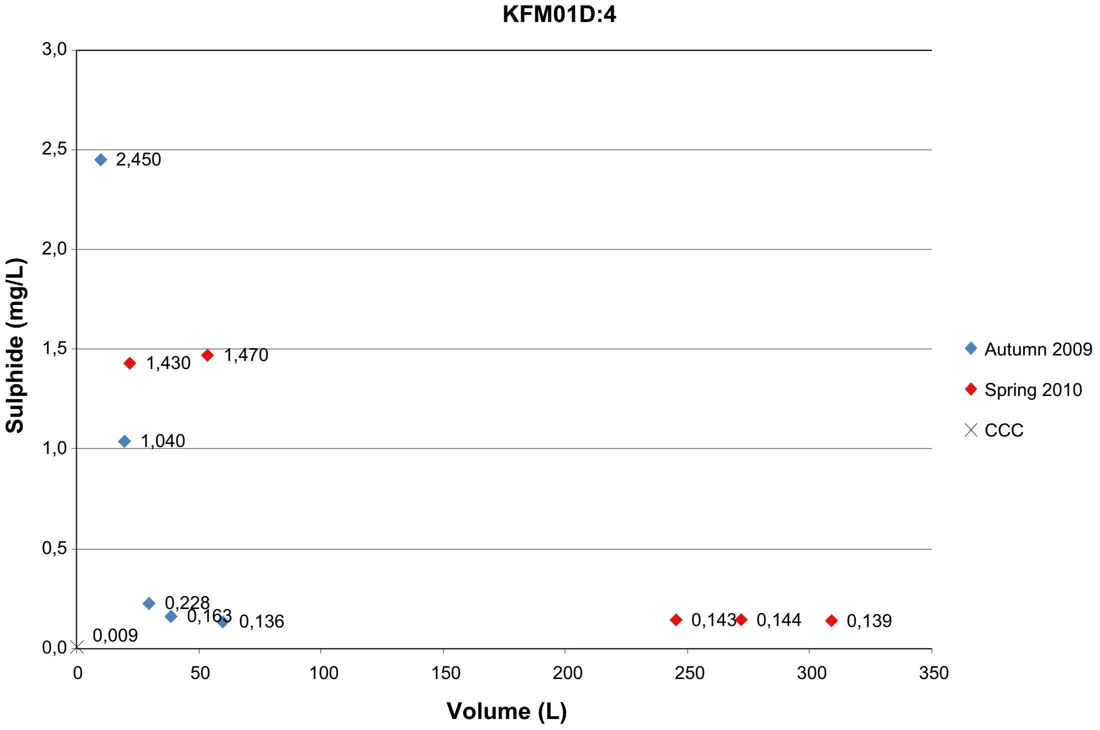


***Figure A1-2.** Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM01D (–252.53 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

## KFM01D

**CCC section:** 428.50 to 435.64 m. (corresponds to monitoring section 429.0 to 438.0 m).
Elevation sec mid:
–341.93 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 6 samples. | Samples collected during one occasion: 2006-06-12 to 2006-07-03. | The selected value represents the fourth sample collected in the stable time series to correspond to the Category 2* sample deemed most representative.<br>**Note:** Gas and microbe data imported from sample 12326. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 4,940 to 5,460 mg/L. | Brackish non-marine groundwater type. | Selected sample: #12316 (Category 2*, 2006-06-26); 5,160 mg/L Cl. |
| $S^{2-}$ | 0.005 to 0.009 mg/L | No systematic time change. | 0.009 mg/L |
| Fe | 0.894 to 1.930 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Apart from the third sample, values generally increase with time. | 1.360 mg/L |
| Mn | 0.165 to 0.329 mg/L | Apart from the final sample, values generally decrease with time. | 0.171 mg/L |
| DOC | 2.3 to 3.7 mg/L | Good correlation with the only TOC value measured.<br>No systematic time change. | 2.3 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM01D

**Monitoring section:** 429.00 to 438.00 m. (Corresponds to CCC section 428.50 to 435.64 m).
Elevation sec mid:
–343.03 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 15 samples.<br>Four samples have no major ion data; all 15 samples have $S^{2-}$ values. | Samples collected during six occasions: 2007-04-23, 2008-01-30 to 2008-01-31 (3 samples), 2008-05-29, 2008-10-02, 2009-05-19 (4 samples) and 2009-10-07 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | The selected value represents the final value taken from the last sampling time series occasion which showed good major ion stability. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 3,760 to 4,640 mg/L. | Brackish non-marine groundwater type.<br>Section shows instability in major ion chemistry during the monitoring period indicating variable marine components.<br>Compared with the CCC sample, more brackish marine water has intruded.<br>Last sampling series stable and approaching the CCC sampling results.<br>Hydraulic responses are recorded in the section above when sampling in the actual monitoring section. | Selected sample: #16519 (2009-10-07); 4,570 mg/L Cl. |
| $S^{2-}$ | 1.77 to 13.4 mg/L | No systematic time change. | 3.85 mg/L |
| Fe | 0.041 to 0.583 mg/L | Good correlation between Fe, Fe(tot) and Fe(II) when measured.<br>No systematic time change. | 0.139 mg/L |
| Mn | 0.162 to 0.570 mg/L | No systematic time change. | 0.190 mg/L |
| DOC | 2.9 to 21.0 mg/L | TOC values correspond relatively close to the DOC values.<br>Final 5 samples show a systematic decrease in TOC/DOC with time. | 2.9 mg/L |

### Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance was that 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100 formation water*), and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-3.

Although it is difficult to compare the 2009 time-series and the 2010 time-series sulphide trends due to different pumping methods used, high concentration levels of sulphide are common for both trends. From pressure responses recorded by the Hydro Monitoring System (HMS) during sampling it was concluded that there is a connection between this borehole section and the section above (i.e. the borehole section located in between the two monitored ones). The connection is probably via the fracture system in the bedrock and not due to leaking equipment since the response is somewhat delayed. It is likely that the initial decrease and then increase in the sulphide concentration trend obtained in 2009 is an effect of this connection. After some time, the lowering of the pressure in the section during pumping most probably causes an increased contribution of section stagnant water with high sulphide content from the section above. Consequently, the sulphide concentration increases in the samples. In order to prevent the intrusion of more shallow section water from this source, contemporaneous pumping in both sections was used in the Spring sampling in 2010. It is, however, difficult to maintain a suitable pressure balance and therefore varying contributions of section water from the upper section to the samples may explain the irregular sulphide trend in 2010. In spite of the irregularities, the 2010 sulphide data decrease rapidly and seem to level out (1.920–2.710 mg/L) i.e. lower than the sulphide value chosen as 'representative' for the safety case calculations (3.850 mg/L) and also somewhat lower than all the data from 2009. These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is interrupted if stagnant section water from the borehole above or below the pumped section contributes to the samples, b) the conservative choice of the last and somewhat elevated sulphide value as the 'representative' 2009 sulphide value for the safety case calculations was

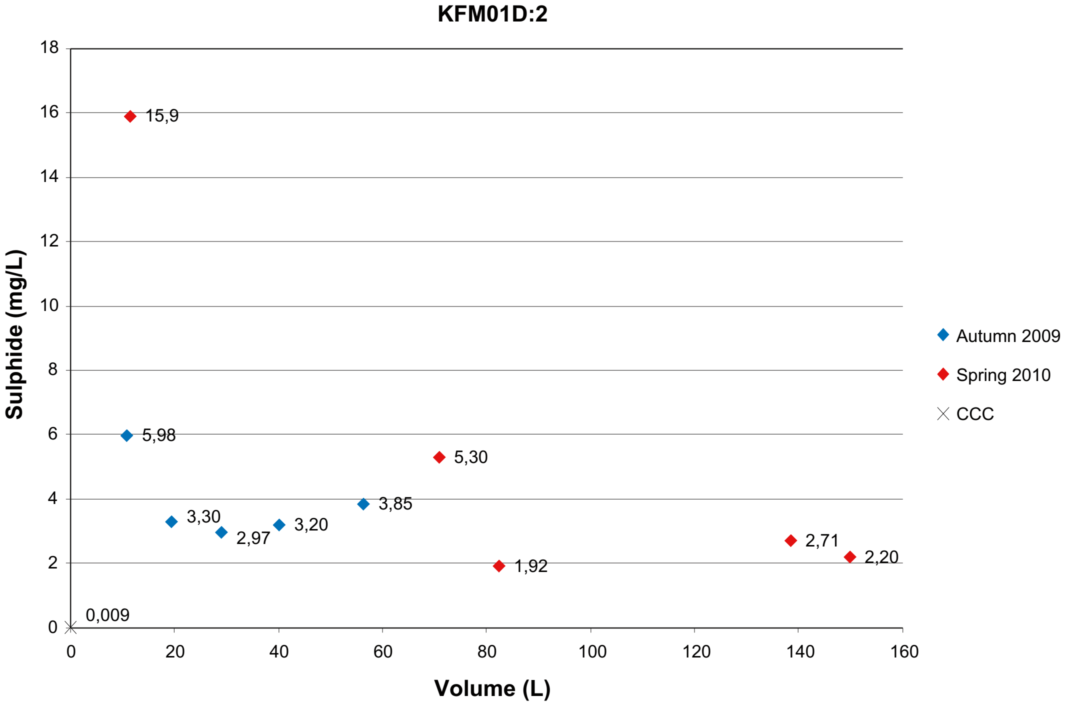


***Figure A1-3.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM01D (–343.03 masl). A different pumping method was used 2010, see below. Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

due to the complexity of the situation and, in this specific case, it is most probably too high, c) there is a large discrepancy between the monitoring values and the much lower CCC sulphide value (0.009 mg/L). Probably, all monitoring samples collected from this borehole section are contaminated by section water from the section itself and/or, more especially the section above, and this is one reason for the generally higher sulphide concentrations compared to other borehole sections. A further contributing factor may be the resulting mixing of brackish non-marine water and shallower water with a somewhat more marine character which may favour microbial activity and sulphide production.

### KFM01D

**CCC section:** 568.00 to 575.14 m
Elevation sec mid:
–446.86 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during one occasion: 2006-07-13 to 2006-07-30. | The selected value represents the first sample collected in the time series to correspond to the Category 1* sample deemed most representative.<br>**Note:** Gas and microbe data imported from sample 12354. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 5,800.0 to 5,960.0 mg/L. | Brackish non-marine groundwater type.<br>Stable major ion chemistry | Selected sample: #12343 (Category 1*, 2006-07-13); 5,960 mg/L Cl. |
| $S^{2-}$ | Below 0.005 to 0.010 mg/L. | No systematic time change. | 0.010 mg/L |
| Fe | 0.729 to 1.240 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Values increasing systematically with time. | 0.729 mg/L |
| Mn | 0.083 to 1.113 mg/L | No systematic time change. | 0.088 mg/L |
| DOC | 6.9 to 11.0 mg/L | Only one TOC value was analysed and correlates with the DOC value.<br>No systematic time change. | 11.0 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM02A

**CCC section:** 106.50 to 126.50 m
Elevation sec mid:
–108.85 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 3 samples. | Sampled during one occasion: 2003-11-07 to 2003-11-18. | The selected value represents the final sample collected in the time series to correspond to the Category 3* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl-$HCO_3$ type.<br>Cl varies between 584.0 to 642.0 mg/L. | Mixed brackish groundwater type.<br>Relatively fresh water with a brackish marine component and small instability indicated by a weak increase in Cl with time. | Selected sample: #8100 (Category 3*, 2003-11-18); 642.0 mg/L Cl. |
| $S^{2-}$ | 0.004 to 0.012 mg/L | No systematic time change. | 0.008 mg/L |
| Fe | 1.020 to 1.370 mg/L | Fe(II) not measured.<br>Fe values increasing systematically with time. | 1.370 mg/L |
| Mn | 0.254 to 0.295 mg/L | No systematic time change. | 0.254 mg/L |
| DOC | 11.0 to 14.0 mg/L | TOC measured only in the selected sample (7.1 mg/L).<br>No systematic time change. | 11.0 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM02A

**CCC section:** 413.50 to 433.50 m. (Corresponds to monitoring section 411.0 m to 442.0 m).
Elevation sec mid:
–414.81 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected on one occasion: 2004-02-05 to 2004-02-23. | The selected value represents the final sample collected in the stable time series to correspond to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,380 to 5,420 mg/L. | Brackish marine groundwater type.<br>Stable major ion chemistry. | Selected sample: #8272 (Category 2*, 2004-02-23); 5,380 mg/L Cl. |
| $S^{2-}$ | Below detection limit (0.002 mg/L). | No systematic time change. | < 0.002 mg/L |
| Fe | Measured on the two last samples: 0.736 o 0.742 mg/L. | Fe tot and Fe(II) were measured for all samples. Fe (II) is 0.02 to 0.05 lower than Fe tot.<br>Good correlation between Fe and Fe tot.<br>Fe(tot) values decreasing systematically with time. | 0.736 mg/L |
| Mn | 1.81 and 1.88 mg/L | No systematic time change. | 1.81 mg/L |
| DOC | Below detection limit (1.0) to 1.5 mg/L. | TOC not measured.<br>Decrease of DOC with time is indicated. | < 1.0 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM02A

**Monitoring section:** 411.0 m to 442.0 m. (Corresponds to CCC section 413.50 to 433.50 m).
Elevation sec mid:
–417.80 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 9 samples. | Samples collected during five occasions: 2005-11-04, 2006-10-10, 2008-05-29, 2008-10-01 to 2009-10-27 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | The selected value represents the final sample collected in the stable time series. |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,380 to 5,590 mg/L. | Brackish marine type.<br>Stable major ion chemistry showing good correlation with the CCC sampling. | Selected sample: #16577 (2009-10-27); 5,460 mg/L Cl. |
| $S^{2-}$ | 0.058 to 1.13 mg/L | Final four values from the last sampling occasion show a systematic decrease with time (1.130–0.323 mg/L). | 0.323 mg/L |
| Fe | 0.127 to 1.64 mg/L | Good correlation between Fe, Fe(tot) and Fe(II) when measured.<br>No systematic time change. | 0.537 mg/L |
| Mn | 1.840 to 1.920 mg/L | No systematic time change. | 1.920 mg/L |
| DOC | 1.2 to 2.3 mg/L | TOC with relatively good correlation with DOC values.<br>No systematic time change. | 1.8 mg/L |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance was that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*), and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-4.

This borehole section presents a rather unfavourable flow anomaly distribution from water exchange aspects with several flow anomalies distributed along the entire section. Therefore, the 2009 time-series sulphide trend did not level out and the volume removed in 2010 was about five times as large. The 2010 time series sulphide trend shows some resemblance to the trend obtained in 2009, however, the displacement between the two steep curves exceeds 100 L. This may be due to the different flow rates of 0.3 L/min and 0.2 L/min used in 2009 and 2010, respectively. At a higher flow rate, the flow may be more turbulent which makes the exchange of section water more efficient compared to a lower flow rate associated with a more laminar flow. Another possible cause may be that the settling period after high-pressure clensing of the stand pipe was too short to overcome possible perturbation effects in the borehole section. This is suggested by the observation that the shortest settling periods (6 and 7 days compared to 13 or more) coincide with the two borehole sections, both in borehole KFM02A, showing the most clear curve displacements. The 2010 sulphide data level out to lower values (0.165–0.189 mg/L) compared to the sulphide value chosen as 'representative' for the safety case calculations (0.323 mg/L). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible, b) the chosen 'representative' 2009

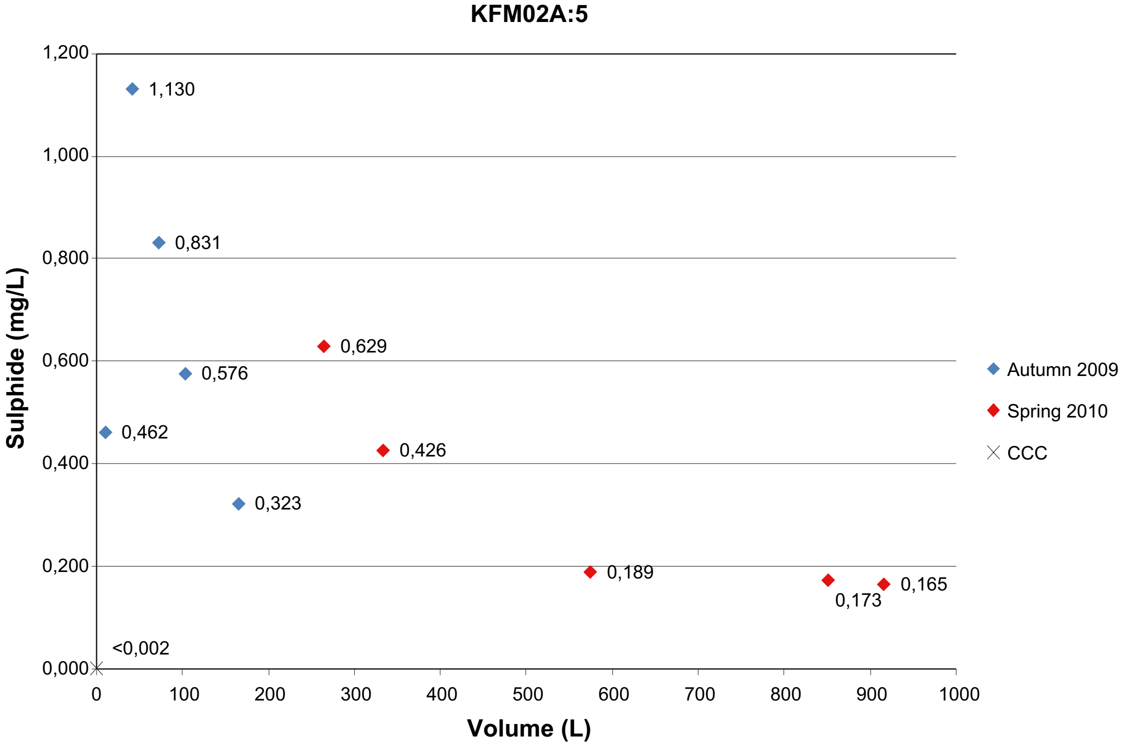


***Figure A1-4.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM02A (–417.80 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

sulphide value for the safety case calculations, in this specific case, is somewhat too high which was expected since the trend from 2009 did not level out, and c) there is still a discrepancy between the 2010 data and the much lower CCC sulphide value (< 0.002 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% of formation groundwater (i.e. some residual section stagnant water still present) and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the monitoring samples from the section water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

### KFM02A

**Monitoring section:** 490.0 m to 518.0 m. (Corresponds to CCC section 509.0 m to 516.08 m).
Elevation sec mid:
–494.97 masl

| | **Groundwater chemistry** | **Comment** | **Selected sample/value** |
|---|---|---|---|
| Number of samples. | 11 samples. | Samples collected during six occasions: 2005-11-07, 2006-06-20, 2006-10-18, 2007-10-30, 2008-05-29, 2008-10-01 and 2009-10-26 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | The selected value represents the final sample collected in the stable time series. |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,370 to 5,570 mg/L. | Brackish marine groundwater type.<br>Stable major ion chemistry showing good correlation with the CCC sampling. | Selected sample: #16572 (2009-10-26); 5,520 mg/L Cl. |
| $S^{2-}$ | 0.065 to 0.682 mg/L | Last sampling time series occasion shows a systematic decrease with time (0.682–0.115 mg/L). | 0.115 mg/L |
| Fe | 1.730 to 3.190 mg/L | Good correlation between Fe, Fe(tot) and Fe(II) when measured.<br>Final four Fe values from the last sampling time series occasion show a systematic decrease with time. | 1.960 mg/L |
| Mn | 2.060 to 2.440 mg/L | No systematic time change. | 2.120 mg/L |
| DOC | 1.5 to 2.4 mg/L | TOC with relatively good correlation with DOC values.<br>During the last time series sampling occasion a small decrease in TOC (partly also DOC) with time was indicated. | 2.0 mg/L |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance was that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*), and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-5.

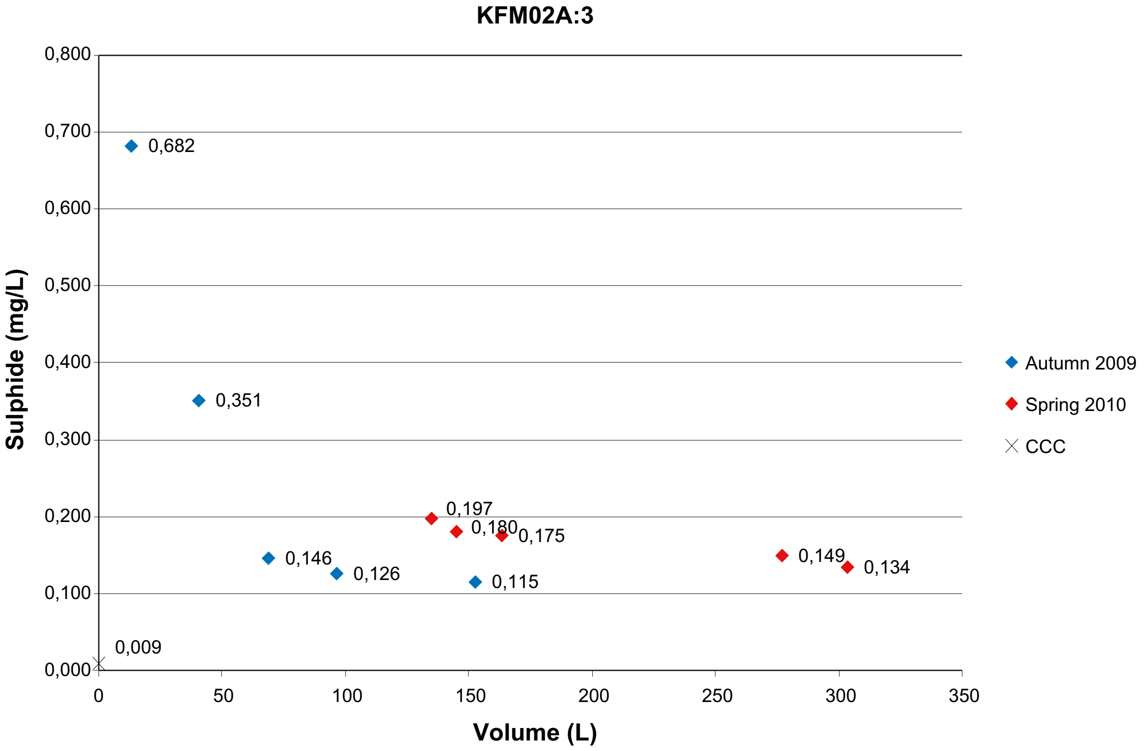


***Figure A1-5.** Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM02A (–494.97 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

This borehole section is quite favourable from water exchange aspects since a very dominating flow anomaly is located in the bottom of the section and the five additional shallow anomalies have low hydraulic transmissivities. The 2010 time-series sulphide trend resembles the trend obtained in 2009 but there is also a displacement between the two steep curves which exceeds 100 L (cf. Figure A1-4). This displacement may be due to the different flow rates of 0.3 L/min and 0.1 L/min used in 2009 and 2010, respectively. At a higher flow rate, the flow may be more turbulent which makes the exchange of section water more efficient compared to a lower flow rate associated with a more laminar flow. Another possible cause may be that the settling period after high-pressure clensing of the stand pipe was too short to overcome possible perturbation effects in the borehole section. This is suggested from the observation that the shortest settling periods (6 and 7 days compared to 13 or more) coincide with the two borehole sections, both in borehole KFM02A, showing the most clear curve displacements. The 2010 sulphide data do not quite level out and the values are somewhat higher (0.175–0.134 mg/L) compared to the sulphide value chosen as 'representative' for the safety case calculations (0.115 mg/L). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible, b) the chosen 'representative' 2009 sulphide value for the safety case calculations, in this specific case, has been supported, and c) there is still a discrepancy between the monitoring data and the much lower CCC sulphide value (0.009 mg/L). This means either that the sample time-series have still not reached 100% formation groundwater and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the monitoring samples from section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

### KFM02A

**CCC section:** 509.0 m to 516.08 m. (Corresponds to the monitoring section 490 to 518 m).

Elevation sec mid:

–503.47 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 8 samples. | Samples collected during one occasion: 2003-09-04 to 2003-10-20. | The selected sample represents the final sample collected in the stable time series to correspond to the Category 3* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,400 to 5,460 mg/L. | Brackish marine groundwater type.<br>Stable major ion chemistry. | Selected sample #8016 (Category 3*, 2003-10-20); 5,410 mg/L Cl. |
| $S^{2-}$ | 0.009 mg/L to below detection limit. | No systematic time change. | 0.009 mg/L |
| Fe | 1.080 to 1.910 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 1.700 mg/L |
| Mn | 2.140 to 2.170mg/L | No systematic time change. | 2.160 mg/L |
| DOC | 2.1 to 2.5 mg/L<br>DOC measured only for six samples. | TOC not measured.<br>No systematic time change. | 2.1 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM02B

**Monitoring section:** 410.00 to 431.00 m

Elevation sec mid:

–407.05 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during 3 sampling occasions: 2007-10-30, 2008-05-29 and 2008-10-01. | First sample is selected simply because of increasing instability with time resulting in a less suitable sample for the sample depth. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 5,470 to 5,580 mg/L. | Brackish marine (Littorina) groundwater type.<br>Stable groundwater chemistry. | Selected sample: #12900 (2007-10-30); 5,580 mg/L Cl. |
| $S^{2-}$ | 0.081 to 0.113 mg/L | No systematic time change. | 0.081 mg/L |
| Fe | 2.450 to 2.820 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change for Fe(tot) and Fe(II); Fe shows a systematic decrease. | 2.820 mg/L |
| Mn | 2.250 to 2.260 mg/L | No systematic time change. | 2.250 mg/L |
| DOC | 1.6 to 1.7 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 1.7 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### KFM02B

**Monitoring section:** 491.00 to 506.00 m
Elevation sec mid:
–483.83 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected from 2007-10-30, 2008-05-29 and 2008-10-01. | First value selected. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 5,420 to 5,550 mg/L. | Brackish marine groundwater of Littorina type.<br>Stable groundwater chemistry. | Selected sample: #12898 , (2007-10-30); 5,550 mg/L Cl. |
| $S^{2-}$ | 0.018 to 0.059 mg/L | No systematic time change. | 0.018 mg/L |
| Fe | 4.43 to 4.48 mg/L | Fe(tot) and Fe(II) slightly lower (3.65 and 3.66 respectively) than in the selected sample.<br>Otherwise good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 4.430 mg/L |
| Mn | 2.220 to 2.270 mg/L | No systematic time change. | 2.220 mg/L |
| DOC | 2.1 to 2.3 mg/L | Good correlation between DOC and TOC.<br>No systematic time change. | 2.3 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### KFM03A

**CCC section:** 386.00 to 391.00 m
Elevation sec mid:
–379.06 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during at 2 occasions: 2003-09-23 to 2003-10-02. | The selected sample represents the second sample collected, corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 5,420 to 5,440 mg/L. | Brackish marine (Littorina) groundwater type. | Selected sample: #8011 (Category 2*, 2003-10-02); 5,440 mg/L Cl. |
| $S^{2-}$ | 0.004 mg/L in both samples. | No systematic time change. | 0.004 mg/L |
| Fe | 0.518 to 0.714 mg/L | Fe(II) slightly lower (0.45 to 0.558 mg/L respectively) than Fe(tot) and Fe(II).<br>No systematic time change. | 0.714 mg/L |
| Mn | 1.140 mg/L in both samples. | No systematic time change. | 1.140 mg/L |
| DOC | 1.3 to 1.4 mg/L | TOC was not analysed.<br>No systematic time change. | 1.3 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM03A

**CCC section:** 448.00 to 453.00 m
Elevation sec mid:
–440.79 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during 1 occasion: 2003-10-17 to 2003-10-24. | The selected sample represents the second sample collected, corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 5,380 to 5,430 mg/L. | Brackish marine (Littorina) groundwater type.<br>Stable major ion chemistry. | Selected sample: #8017 (Category 2*, 2003-10-24); 5,430 mg/L Cl. |
| $S^{2-}$ | 0.004 to 0.007 mg/L | No systematic time change. | 0.007 mg/L |
| Fe | 0.736 to 0.905 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 0.905 mg/L |
| Mn | 1.140 to 1.170 mg/L | No systematic time change. | 1.170 mg/L |
| DOC | 1.2 mg/L | Only one DOC value and TOC is not analysed.<br>No systematic time change. | 1.2 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM03A

**CCC section:** 448.50 to 455.62 m
Elevation sec mid:
–442.34 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during 1 occasion: 2004-04-15 to 2004-04-27. | The selected sample represents the second sample collected, corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 5,330 to 5,440 mg/L. | Brackish marine (Littorina) groundwater type. | Selected sample #8284 (Category 2*, 2004-04-27), 5,330 mg/L Cl. |
| $S^{2-}$ | 0.031 to 0.047 mg/L | No systematic time change. | 0.047 mg/L |
| Fe | 1.070 to 1.180 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 1.070 mg/L |
| Mn | 1.250 to 1.270 mg/L | No systematic time change. | 1.250 mg/L |
| DOC | | DOC and TOC were not analysed.<br>No systematic time change. | |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM03A

**CCC section:** 639.0 to 646.12 m (Corresponds to the monitoring section 633.5 to 650.0 m).
Elevation sec mid:
–631.91 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during 1 occasion: 2004-02-06 to 2004-02-20. | The selected sample represents the second sample collected, corresponding to the Category T2*. In reality sample #8273 Category 2 was originally considered but there was no sulphide value. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between 5,380 to 5,470 mg/L. | Transition groundwater type. | Selected sample #8271 (best choice in the category T2* time series, 2004-02-20), 5,440 mg/L Cl. |
| $S^{2-}$ | Below detection limit (0.002 mg/L). | No systematic time change. | < 0.002 mg/L. |
| Fe | 0.273 to 0.457 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Apart from the initial sample, the remaining three samples show a systematic decrease with time. | 0.273 mg/L |
| Mn | 0.318 to 0.339 mg/L | Apart from the initial sample, the remaining three samples show a systematic decrease with time. | 0.318 mg/L |
| DOC | 1.3 to 2.3 mg/L | TOC not analysed.<br>The three DOC values show a systematic decrease with time. | 1.3 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

**KFM03A**

**Monitoring section:** 633.5 to 650.0 m. (Corresponds to the CCC sampling 639.0 to 646.12 m).
Elevation sec mid:
–631.10 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 10 samples. | Samples collected during 6 occasions: 2005-06-23, 2005-11-07, 2006-10-24, 2007-10-15, 2008-10-24, and 2009-11-03 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | The selected sample represents the final sample collected in the stable time series. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 5,570 to 5,770 mg/L. | Brackish non-marine groundwater type, with a component of brackish marine type (transition type).<br>The major ion chemistry is largely stable during the monitoring period.<br>Small variations in Mg indicate variations in the marine component.<br>Good major chemistry and correlation between CCC and the monitoring samples. | Selected sample: #16609 (2009-11-03), 5,750 mg/L Cl. |
| $S^{2-}$ | 0.133 to 0.865 mg/L | Both the combined 2005-11-07 to 2008-10-24 period and the single day sampling period in 2009-11-03 show a systematic decrease in sulphide with time (0.701–0.147 mg/L and 0.865–0.158 mg/L respectively). | 0.158 mg/L |
| Fe | 0.299 to 0.981 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>The combined 2005-11-07 to 2008-10-24 sampling period shows a systematic decrease with time.<br>The single day sampling period in 2009-11-03 shows no systematic time change. | 0.650 mg/L |
| Mn | 0.385 to 0.511 mg/L | No systematic time change | 0.414 mg/L |
| DOC | Below detection limit (1.0) to 2.0 mg/L. | Correlation with TOC.<br>The combined 2005-11-07 to 2008-10-24 sampling period shows a weak decrease with time.<br>The single day sampling period in 2009-11-03 shows no systematic time change. | 1.3 mg/L |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance was that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*); and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-6.

The flow anomaly distribution in this borehole section is quite favourable from water exchange aspects since the two detected flow anomalies have very different hydraulic transmissivities and the dominating flow anomaly is located below the minor anomaly. The 2010 time-series sulphide trend fits in very well with the trend obtained in 2009. Also, the 2010 sulphide data decrease rapidly and level out to values (0.189–0.197 mg/L) similar to the sulphide value chosen as 'representative' for the safety case calculations (0.158 mg/L). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible and specific for each section, b) the chosen 'representative' 2009 sulphide value for the safety case calculations, in this specific case, is supported,

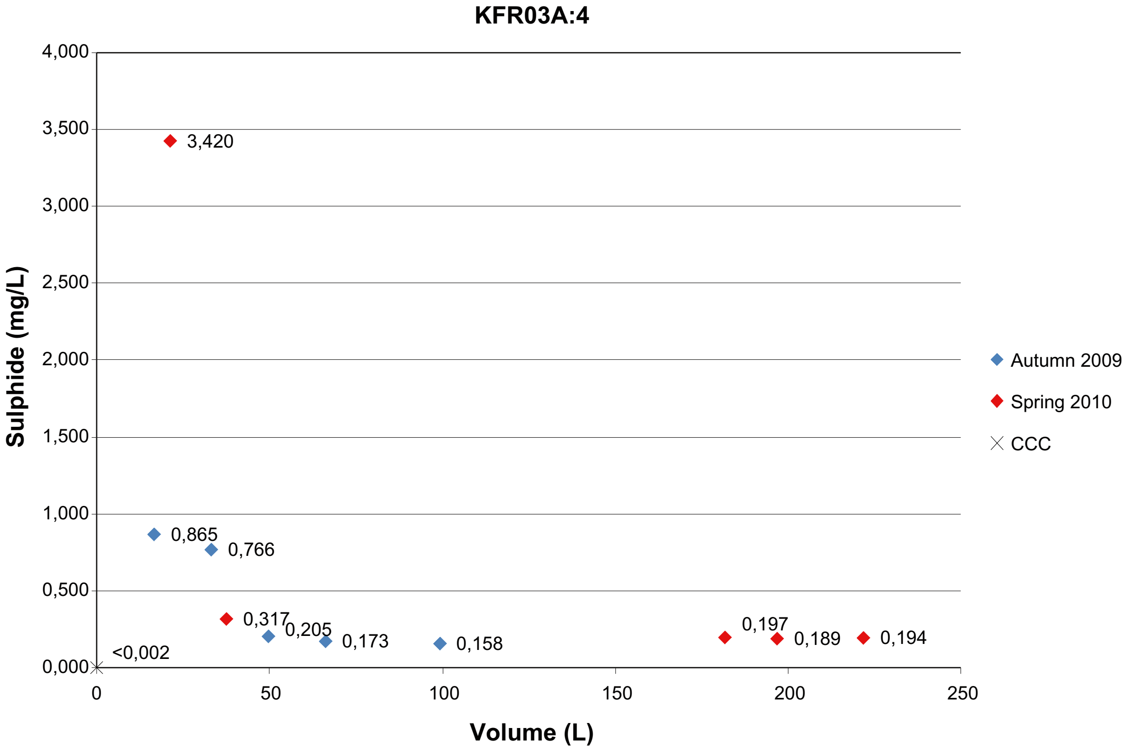


***Figure A1-6.** Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM03A (–631.10 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

and c) there is still a discrepancy between the monitoring data and the much lower CCC sulphide value (< 0.002 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% formation groundwater and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the monitoring samples from the section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

### KFM03A

**CCC section:** 939.50 to 946.62 m

Elevation sec mid:

–930.50 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples. | Samples collected during 1 occasion: 2004-03-03 to 2004-03-29. | Last sample in the time series was selected corresponding to the Category 3* sample deemed most representative. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 7,560 to 8,560 mg/L. | Brackish non-marine groundwater type. | Selected sample: #8281 (Category 3*, 2004-03-29); 8,560 mg/L Cl. |
| $S^{2-}$ | 0.029 to 0.161 mg/L | No systematic time change. | 0.058 mg/L |
| Fe | 0.086 to 1.260 mg/L | Relatively good correlation between Fe, Fe(tot) and Fe(II).<br>Excluding the initial sample, there is a general decrease with time. | 0.086 mg/L |
| Mn | 0.112 to 0.214 mg/L | Excluding the initial sample, there is a general decrease with time. | 0.114 mg/L |
| DOC | 1.5 to 5.7 mg/L | Apart from one, all samples are below 3 mg/L DOC. The sample with highest DOC also has the highest Fe value. TOC was not analysed.<br>Excluding the initial sample, there is a general decrease with time. | 1.5 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM03A

**CCC section:** 980.0 to 1,001.19 m. (Corresponds to section 969.0 to 994.5 m).

Elevation sec mid:

–977.66 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 8 samples. | Samples collected during 1 occasion: 2003-11-06 to 2003-12-08. | Last sample in the time series was selected corresponding to the Category 3* sample deemed most representative. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 10,000 to 9,690 mg/L. | Brackish glacial groundwater type. | Selected sample #8152 (Category 3*, 2003-12-08), 9,690 mg/L Cl. |
| $S^{2-}$ | 0.013 to 0.087 mg/L | There is a systematic decrease with time for the first 5 samples (0.056 to 0.029 mg/L). | 0.033 mg/L |
| Fe | Below 0.02 to 0.040 mg/L. | Good correlation between Fe, Fe(tot) and Fe(II).<br>There is a general decrease with time during the total sampling period. | 0.034 mg/L |
| Mn | 0.009 to 0.0427 mg/L | There is a general decrease with time during the total sampling period. | 0.009 mg/L |
| DOC | 1.1 to 1.6 mg/L | TOC not analysed.<br>No systematic time change. | 1.4 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM03A

**Monitoring section:** 969.5 to 994.5 m. (Corresponds to CCC section 980.0 to 1,001.19 m).
Elevation sec mid:
–969.13 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 9 samples. | Samples collected during 5 occasions: 2005-11-07, 2006-10-25, 2007-10-15, 2008-11-07, and 2009-11-04 to 2009-11-06 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | The selected sample represents the final sample collected in the stable time series. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 10,100 to 10,500 mg/L. | Brackish glacial groundwater type.<br>Stable major ion chemistry and good correlation with the CCC section despite slightly higher Cl and lower d$^{18}$O. | Selected sample: #16582; 2009-11-06); 10,500 mg/L Cl. |
| $S^{2-}$ | 0.109 to 2.060 mg/L | Both the combined 2005-11-07 to 2008-10-15 period and the single day sampling period in 2009-11-04 show a systematic decrease in sulphide with time (0.838–0.245 mg/L and 2.060–0.109 mg/L respectively). | 0.109 mg/L |
| Fe | 0.204 to 1.090 mg/L | Good correlation between Fe, Fe(tot) and Fe(II) when measured.<br>The combined 2005-11-07 to 2008-10-15 period shows a systematic decrease in Fe, but the single day sampling period in 2009-11-04 shows no systematic time change. | 0.269 mg/L |
| Mn | 0.038 to 0.089 mg/L | No systematic time change. | 0.038 mg/L |
| DOC | Less than 1.0 to 13.0 mg/L. | DOC and TOC analysed for all samples.<br>The combined 2005-11-07 to 2008-10-15 period shows no clear systematic decrease, but the single day sampling period in 2009-11-04 shows a systematic decrease in TOC/DOC. | < 1.0 mg/L (detection limit). |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance was that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*); and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-7.

The 2010 time-series sulphide trend fits in well with the trend obtained in 2009 except for the starting point. This may be due to an occasionally more contaminated first sample or, possibly, there is a displacement between the steep curves similar to both sections of KFM02A. However, the difference in flow rate between the two occasions was rather limited (0.061 L/min compared to 0.090 L/min in 2009) and the settling period was not very short (16 days). The 2010 sulphide data decrease rapidly and level out to values (0.100–0.105 mg/L) closely similar to the sulphide value chosen as 'representative' for the safety case calculations (0.109 mg/L). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible and specific for each section, b) the chosen 'representative' 2009 sulphide value for the safety case calculations, in this specific case, has been supported, and c) there is still a discrepancy between the monitoring values and the lower CCC sulphide value (0.033 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% formation groundwater and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried

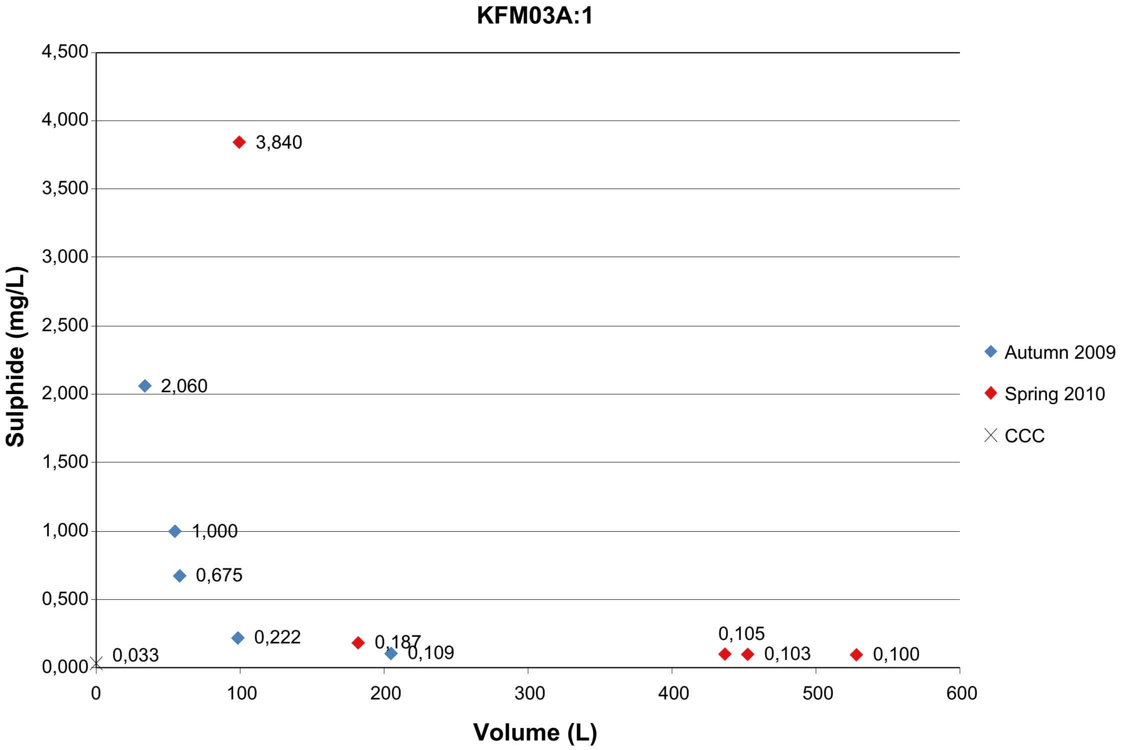


***Figure A1-7.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM03A (–969.13 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the monitoring samples from the section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

### KFM04A

**CCC section:** 230.50 to 237.64 m
Elevation sec mid:
–196.86 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 6 samples. | Samples collected during one occasion: 2004-01-16 to 2004-02-12. | |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,480 to 5,680 mg/L. | Brackish marine (Littorina) groundwater type. | Due to disturbances (equipment, corrosion) and anomalously high Fe- and Mn contents, no sample was selected. (Note: Category 3* for major ion chemistry). |
| $S^{2-}$ | Below 0.002 to 0.019 mg/L. | Decreasing values with time. | |
| Fe | 1.98 to 7.05 mg/L | Fe(tot) and Fe(II) are lower compared with Fe (ICP) in the samples with highest values .<br>Fe (ICP) shows a systematic decrease with time. | |
| Mn | 2.58 to 2.82 mg/L | No systematic variation with time. | |
| DOC | 1.7 to 3.0 mg/L | TOC not analysed.<br>Values show an overall decrease with time. | |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM04A

**Monitoring section:** 230.0 to 245.0 m
Elevation sec mid:
–199.83 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected from 2007-04-11 to 2008-10-06. | |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,850 to 5,980 mg/L. | Brackish marine (Littorina) groundwater type. | Due to disturbances and anomalously high Fe and Mn contents, no sample was selected as suitable. |
| $S^{2-}$ | Below 0.006 to 0.09 mg/L. | Values show a systematic increase with time. | |
| Fe | 1.99 to 2.33 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | |
| Mn | 3.15 to 3.39 mg/L | No systematic time change. | |
| DOC | 1.3 to 1.7 mg/L | Good correlation with TOC.<br>Values indicate a decrease with time. | |

### KFM04A

**CCC section:** 354.0 to 361.13 m
Elevation sec mid:
–302.75 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during one occasion: 2004-04-20 to 2004-05-10. | |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 5,610 to 5,780 mg/L. | Brackish marine (Littorina) groundwater type. | Due to disturbances (equipment, corrosion) and anomalously high Fe- and Mn contents, no sample was selected. (Category 3* for major ion chemistry). |
| $S^{2-}$ | Below 0.004 to 0.008 mg/L. | No systematic time change. | |
| Fe | 2.13 to 2.34 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Values show a systematic decrease with time. | |
| Mn | 1.31 to 1.58 mg/L | Values show a systematic decrease with time. | |
| DOC | 1.7 to 3.0 mg/L | TOC not analysed.<br>Values show an overall decrease with time. | |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM05A

**CCC section:** 712.55 to 722.02 m

Elevation sec mid:

–596.30 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 6 samples. | Samples collected during one occasion: 2004-09-24 to 2004-10-18. | |
| Groundwater type. | Na-Ca-Cl-$SO_4$ type.<br>Cl varies between 4,490 to 4,600 mg/L. | Brackish marine (Littorina) groundwater type. | No value selected due to short circuiting, other disturbances and an anomalously high Fe-content (Category 5*). |
| $S^{2-}$ | Less than 0.002 to 0.021 mg/L. | Weak systematic decrease with time. | |
| Fe | 13.1 to 15.9 mg/L | Fe(tot) (2.81–3.8) and Fe(II) (3.60–3.82) are lower than Fe (ICP).<br>No systematic time change. | |
| Mn | 1.47 to 1.56 mg/L | No systematic time change. | |
| DOC | 4.2 to 6.5 mg/L | TOC analysed in one sample (4.8).<br>No systematic time change. | |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM06A

**CCC section:** 353.50 to 360.62 m. (Corresponds to monitoring section 341.0 to 362.0 m).

Elevation sec mid:

–303.24 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples | Samples collected during one occasion: 2005-02-15 to 2005-03-07. | Last sample in the time series was selected corresponding to the Category 3* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl-($SO_4$) type.<br>Cl varies between, 4,560 to 4,710 mg/L. | Transition type groundwater. | Selected sample: #8809 (Category 3*, 2005-03-07); 4,560 mg/L Cl. |
| $S^{2-}$ | Less than 0.002 to 0.003 mg/L. | No systematic time change. | < 0.002 mg/L. |
| Fe | 0.733 to 1.21 mg/L | Relatively good correlation between Fe, Fe(tot) and Fe(II).<br>Excluding the initial two samples, there is a systematic decrease with time. | 0.900 mg/L |
| Mn | 0.56 to 0.905 mg/L | Excluding the initial two samples, there is a systematic decrease with time. | 0.578 mg/L |
| DOC | Less than 1.0 to 2.4 mg/L. | TOC not analysed.<br>Excluding the initial two samples, there is a weak decrease with time. | < 1.0 mg/L. |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM06A

**Monitoring section:** 341.00 to 362.00 m. (Corresponds to CCC section 353.50 to 360.62 m).
Elevation sec mid:
–298.54 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during two occasions: 2006-10-09 and 2008-10-17. | First value selected. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl is identical in both samples at 4,620 mg/L. | Transition groundwater type.<br>Brackish marine groundwater with a portion of brackish non-marine type.<br>Major ion chemistry of the monitoring section generally corresponds with the CCC section. | |
| $S^{2-}$ | 0.108 to 0.298 mg/L | No systematic time change. | 0.108 mg/L |
| Fe | 1.420 to 2.330 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 2.330 mg/L |
| Mn | 0.541 to 0.820 mg/L | No systematic time change. | 0.820 mg/L |
| DOC | 1.5 to 2.0 mg/L | TOC correlates with DOC.<br>No systematic time change. | 2.0 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### KFM06A

**Monitoring section:** 738.00 to 748.00 m
Elevation sec mid:
–622.78 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during two occasions: 2006-10-09 and 2008-10-17. | First value also has a more complete chemistry. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 6,200 to 6,420 mg/L. | Transition groundwater type.<br>The two samples suggest a fairly stable major ion chemistry. | Selected sample: #12398 (2006-10-09); 6,200 mg/L Cl. |
| $S^{2-}$ | 0.368 to 2.410 mg/L | No systematic time change. | 0.368 mg/L |
| Fe | 0.892 to 0.167 mg/L | Only Fe(tot) and Fe(II) analysed in selected sample.<br>No systematic time change. | 0.892 mg/L |
| Mn | 0.417 to 0.461 mg/L | No systematic time change. | 0.461 mg/L |
| DOC | 1.8 mg/L. | DOC and TOC only analysed in selected sample. Good correlation.<br>No systematic time change. | 1.8 mg/L. |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

## KFM06A

**CCC section:** 768.00 to 775.12 m
Elevation sec mid:
–645.95 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 9 samples. | Samples collected during one occasion: 2004-12-14 to 2005-01-31. | Last sample in the time series was selected corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 6,730 to 7,150 mg/L. | Brackish non-marine groundwater type. | Selected sample: #8785 (Category 2*, 2005-01-31); 7,080 mg/L Cl. |
| $S^{2-}$ | 0.005to 0.026 mg/L | No systematic time change. | 0.018 mg/L |
| Fe | 0.0376 to 1.660 mg/L | Relatively good correlation between Fe, Fe(tot) and Fe(II).<br>Generally a decrease in time apart from the final two samples. | 0.0376 mg/L |
| Mn | 0.082 to 0.271 mg/L | A systematic decrease in time apart from the final two samples. | 0.082 mg/L |
| DOC | 1.3 to 1.7 mg/L | TOC not analysed.<br>No systematic time change. | 1.6 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM06C

**Monitoring section:** 531.00 to 540.00 m
Elevation sec mid:
–434.84 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during two occasions: 2006-10-10 and 2008-10-17. | No value collected because impossible to judge representativity. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 4,790 to 4, 830 mg/L. | Brackish marine groundwater type with a portion of brackish non-marine type (i.e. transition type).<br>Stable major ion chemistry but impossible to judge whether samples are representative, e.g. very high drilling water content. | |
| $S^{2-}$ | 0.064 to 0.159 mg/L | No systematic time change. | |
| Fe | 0.824 to 0.843 mg/L | Only Fe(tot) and Fe(II) analysed in selected sample. Both showed good agreement. | |
| Mn | 0.849 to 0.874 mg/L | | |
| DOC | 1.6 mg/L. | DOC and TOC only analysed in the first sample.<br>Good correlation. | |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### KFM07A

**CCC section:** 848.00 to 1,001.55 m. (Corresponds to the monitoring section 962.0 to 972.0 m).

Elevation sec mid:

–763.62 masl

| | **Groundwater chemistry** | **Comment** | **Selected sample/value** |
|---|---|---|---|
| Number of samples. | 10 samples. | Samples collected during one occasion: 2005-03-22 to 2005-04-25. | Second value in the time series was selected corresponding to the Category 3* sample deemed most representative.<br>**Note:** Gas and microbe data imported from sample #8879. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 14,100 to 14,800 mg/L. | Saline groundwater type.<br>Small variation in major ion chemistry (e.g. Cl, $^{18}$O). | Selected sample: #8843 (Category 3*, 2005-03-24); 14,400 mg/L Cl. |
| $S^{2-}$ | 0.062 to 0.199 mg/L | No systematic time change. | 0.062 mg/L |
| Fe | Less than 0.2 to 0.424 mg/L. | Good correlation between Fe, Fe(tot) and Fe(II).<br>Excluding the third sample, there is a systematic decrease with time. | 0.277 mg/L |
| Mn | 0.127 to 0.145 mg/L | No systematic time change. | 0.141 mg/L |
| DOC | Less than 1.0 to 2.0 mg/L. | TOC not analysed.<br>No systematic time change. | 2.0 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM07A

**Monitoring section:** 962.0 to 972.0 m. (Corresponds to the hydraulic conductive section in the CCC sampled interval 848.00 to 1,001.55 m).

Elevation sec mid:

–795.22 masl

| | **Groundwater chemistry** | **Comment** | **Selected sample/value** |
|---|---|---|---|
| Number of samples. | 8 samples. | Samples collected during four occasions: 2007-03-20, 2007-10-26, 2008-10-29, and 2009-11-04 to 2009-11-05 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | Last value in the final time series was selected. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 14,100 to 15,000 mg/L. | Saline groundwater type.<br>Stable major ions during the monitoring period and good correlation with previous CCC sampling.<br>Slightly lower d$^{18}$O in the time series of five monitoring sample. | Selected sample: #16613 (2009-11-05); 14,400 mg/L Cl. |
| $S^{2-}$ | 0.011 to 0.116 mg/L | No systematic time change. | 0.029 mg/L |
| Fe | Less than 0.004 to 0.202 mg/L. | Good correlation between Fe, Fe(tot) and Fe(II) for the five samples analysed.<br>No systematic time change. | 0.076mg/L |
| Mn | 0.00022 to 1.77 mg/L | No systematic time change. | 0.127 mg/L |
| DOC | Less than 1.0 to 47.0 mg/L. | Relatively good correlation with TOC.<br>No systematic time change. | 2.6 mg/L |

### Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance were that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*): and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-8.

A counter-pressure was applied when pumping in this section, at both occasions, to prevent release of gas which obstructed the pumping. Because of this, the flow rates were very low and varied considerably during the pumping periods (0.08–0.13 mL/min), and as a consequence the volume calculations were uncertain. The indicated curve displacement may also be an effect of the clensing procedure used in 2010. However, the same low sulphide concentration level is common for both monitoring time-series trends and also for the CCC time series data. The 2010 sulphide data trend decreases rapidly from 0.281 mg/L to 0.059 mg/L but does not level out, although the sulphide value chosen as 'representative' for the safety case calculations (0.029 mg/L) is quite close. These results underline three important observations: a) the sulphide concentration trend is very sensitive to pumping and sampling methods, b) the chosen 'representative' 2009 sulphide value for the safety case calculations, in this specific case, is somewhat lower but within an acceptable concentration range, and c) there is a small discrepancy between this value and the CCC sulphide value, however, this time the CCC value is somewhat higher (0.062 mg/L) and agrees well with the 2010 data.

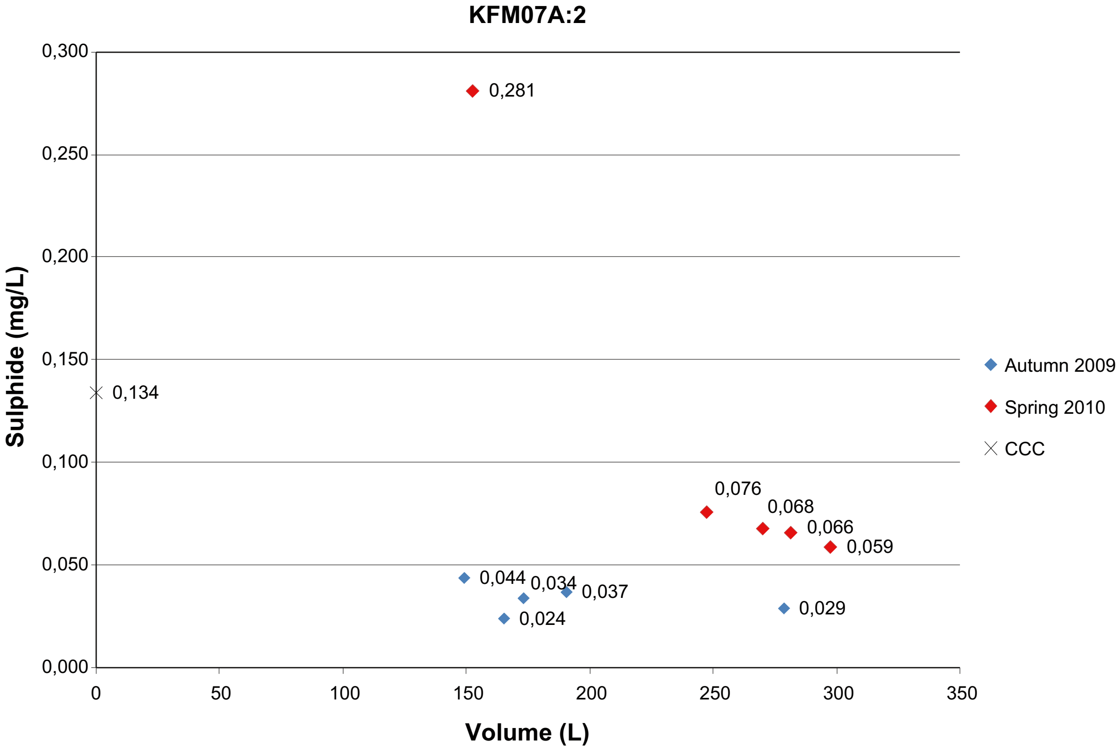


***Figure A1-8.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM07A (–795.22 masl). A counter-pressure was applied when pumping in order to prevent gas release. Two different pumping methods were used (see description below) and several pump stops occurred in 2009. Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

### KFM08A

**Monitoring section:** 265.00 to 280.00 m.
Elevation sec mid:
–227.79 masl.

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 9 samples. | Samples collected during three occasions: 2008-01-22, 2008-10-22 and 2009-10-21 (5 samples). | Last value in the final time series is selected.<br>Successive decrease in Cl contents during the monitoring period with no levelling out. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 4,410 to 5,880 mg/L. | Brackish glacial groundwater type.<br>Includes an increasing marine component during monitoring.<br>A decrease in salinity and slight increase in marine and glacial components occur during the entire monitoring period. | Selected sample: #16557 (2009-10-21); 4,490 mg/L Cl. |
| $S^{2-}$ | 0.052 to 3.84 mg/L | First time series of three samples show no systematic time change. Second and last time series of five samples show a systematic decrease with time (3.840–0.138 mg/L). | 0.138 mg/L |
| Fe | 0.169 to 1.370 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>First time series of three samples and last time series of five samples show a systematic increase in Fe with time. | 1.350 mg/L |
| Mn | 0.153 to 0.590 mg/L | First time series of three samples and last time series of five samples show a systematic increase in with time. | 0.590 mg/L |
| DOC | 2.0 to 4.1 mg/L | DOC and TOC from six analysed samples.<br>First time series of three samples and last time series of five samples show a weak systematic decrease in DOC/TOC with time. | 2.5 mg/L |

### KFM08A

**CCC section:** 683.50 to 690.64 m. (Corresponds to the monitoring section 684.00 to 694.00 m).
Elevation sec mid:
–549.16 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 12 samples. | Samples collected during one occasion: 2005-09-13 to 2005-10-31. | Last value in the time series was selected corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 6,010 to 6,190 mg/L. | Brackish glacial groundwater type. | Selected sample: #12000 (Category 2*, 2005-10-31); 6,100 mg/L Cl. |
| $S^{2-}$ | Less than 0.002 to 0.015 mg/L. | No systematic time change. | 0.012 mg/L |
| Fe | Less than 0.2 to 0.676 mg/L. | Good correlation between Fe, Fe(tot) and Fe(II) .<br>Excluding the initial three samples, there is a systematic increase in Fe and Fe(tot) with time. | 0.676 mg/L |
| Mn | 0.179 to 0.248 mg/L | No systematic time change. | 0.191 mg/L |
| DOC | Less than 1.0 to 2.6 mg/L. | TOC not analysed except for one sample (less than 1.0 mg/L).<br>No systematic time change. | < 1.0 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

**KFM08A**

**Monitoring section** 684.00 to 694.00 m. (Corresponds to CCC section 683.50 to 690.64 m).
Elevation sec mid:
–550.55 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 8 samples. | Samples collected during three occasions: 2008-01-22 (2 samples), and 2008-10-28 to 2009-10-20 (5 samples).<br>The last sampling occasion comprised a single day time series of five samples. | Last value was selected in the final sampling occasion. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 6,070 to 6,350 mg/L. | Brackish glacial groundwater type.<br>Stable major ion chemistry and good correlation with the chemistry sampled in the CCC section. | Selected sample: #16567 (2009-10-20); 6,270 mg/L Cl. |
| $S^{2-}$ | 0.024 to 0.19 mg/L | First two sampling occasions show no systematic time change.<br>On the last sampling occasion the five samples show a systematic decrease with time (0.058–0.024 mg/L). | 0.024 mg/L |
| Fe | Less than 0.1 to 0.445 mg/L. | Fe(tot) and Fe(II) measured in three samples show a good correlation.<br>First two sampling occasions show no systematic time change.<br>On the last occasion the five samples show a systematic increase in Fe with time, and suggested also for Fe(tot) and Fe(II). | 0.302 mg/L |
| Mn | 0.0336 to 0.172 mg/L. | No systematic time change. | 0.162 mg/L |
| DOC | Less than 1.0 to 1.7 mg/L. | TOC correlates with DOC.<br>On the last occasion the five samples show a weak overall decrease in DOC/TOC with time. | < 1.0 mg/L |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance were that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*): and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-9.

The water exchange conditions in this borehole section are very favourable since the single flow anomaly, detected close to the outlet from the section, will contribute to the flow very soon after pump start. The 2010 time-series sulphide trend fits in well with the trend obtained in 2009. The first sample in the 2010 sulphide data trend is elevated but the remaining four samples level out to values (0.047–0.073 mg/L) closely similar to the sulphide value chosen as 'representative' for the safety case calculations (0.024 mg/L). The indicated small displacement between the two steep curves is within the error in the volume determination (the volume is calculated from flow rate and time). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible and specific for each section, b) the chosen 'representative' 2009 sulphide value for the safety case calculations, in this specific case, is somewhat lower but within an acceptable concentration range, and c) there is still a minor discrepancy between the monitoring data and the lower CCC sulphide value (0.012 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% formation groundwater and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contamination to the

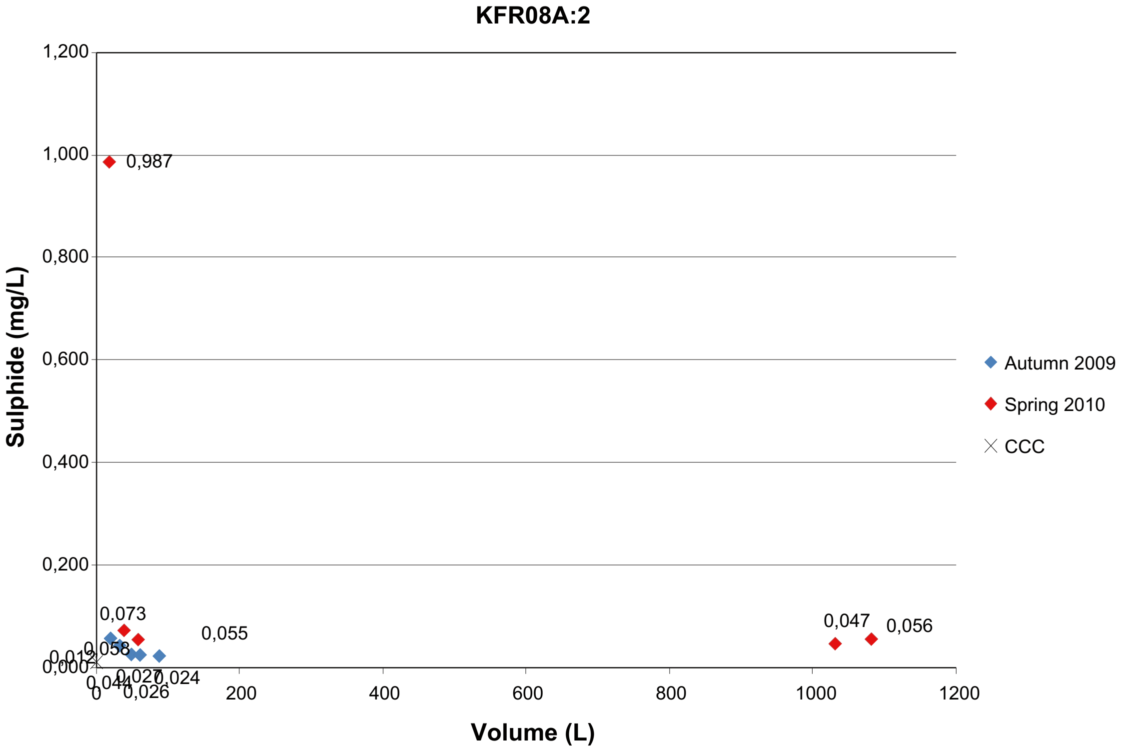


***Figure A1-9.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM08A (–550.55 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

monitoring samples from the section water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

### KFM08D

**CCC section** 669.70 to 676.84 m. (Corresponds to the monitoring section 660.00 to 680.00 m).
Elevation sec mid:
–540.63 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples. | Samples collected during one occasion: 2007-05-29 to 2007-06-18. | Last value in the time series was selected corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 7,270 to 7,460 mg/L. | Brackish non-marine groundwater type. | Selected sample: #12818 (Category 2*; 2007-06-18); 7,460 mg/L Cl. |
| $S^{2-}$ | Less than 0.006 to 0.01 mg/L. | No systematic time change. | < 0.006 mg/L. |
| Fe | 0.004 to 0.589 mg/L | Good correlation between Fe, Fe(tot) and Fe(II) .<br>Fe, Fe(tot) and Fe(II) values decrease systematically with time. | 0.004 mg/L |
| Mn | 0.050 to 0.107 mg/L | Values decrease systematically with time. | 0.050 mg/L |
| DOC | Less than 1.0 to 1.1 mg/L. | TOC in selected sample < 1.0 mg/L.<br>No systematic time change. | < 1.0 mg/L. |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM08D

**Monitoring section** 660.00 to 680.00 m. (Corresponds to the CCC sampled section 669.70 to 676.84 m).
Elevation sec mid:
–538.06 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples. | Samples collected during three occasions: 2008-01-22, 2008-11-07 and 2009-10-14.<br>The last sampling occasion comprises a single day time series of five samples. | Second last value was selected in the final sampling occasion. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl varies between 5,220 to 5,900 mg/L, i.e. significantly lower than in the CCC samples. | Brackish non-marine groundwater type.<br>Slight increase in the Cl content during the monitoring period, but more importantly a large decrease compared with the CCC sample. Mg is slightly higher in the monitoring samples (cf. 4.41 for explanation).<br>Although this monitoring section is not representative, they do indicate a change in major ion chemistry during pumping etc, resulting in a change of groundwater type.<br>Short circuiting to shallower levels? | Selected sample: #16546 (2009-10-13); 5,900 mg/L Cl. |
| $S^{2-}$ | 0.312 to 3.33 mg/L | Excluding the earlier first two samples and the final sample because of technical reasons (pump stop), the values decrease systematically with time (0.940–0.340 mg/L). | 0.340 mg/L |
| Fe | Less than 0.1 to 0.138 mg/L. | Fe(tot) and Fe(II) measured for three samples with relatively good correlation with Fe .<br>The first three samples of the last sampling occasion indicate an increase in Fe with time. | < 0.1 mg/L. |
| Mn | 0.116 to 0.239 mg/L | The first three samples of the last sampling occasion increase systematically with time. | 0.163 mg/L |
| DOC | 1.5 to 6.4 mg/L | Good correlation with TOC.<br>Excluding the earlier first two samples and the final sample, the values decrease systematically with time. | 1.5 mg/L |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance were that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*): and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-10.

The 2010 time-series sulphide trend forms a continuation to that obtained in 2009. The anomalous last data point in the sulphide trend in 2009 (0.625 mg/L) coincides with a preceding pump failure which most probably caused a remixing with section water and thus an increased sulphide concentration in the sample. The 2010 sulphide data level out to lower concentrations (0.106–0.119 mg/L) compared to the sulphide value chosen as 'representative' for the safety case calculations (0.340 mg/L). These results underline three important observations: a) the decreasing sulphide concentration trend with pumped

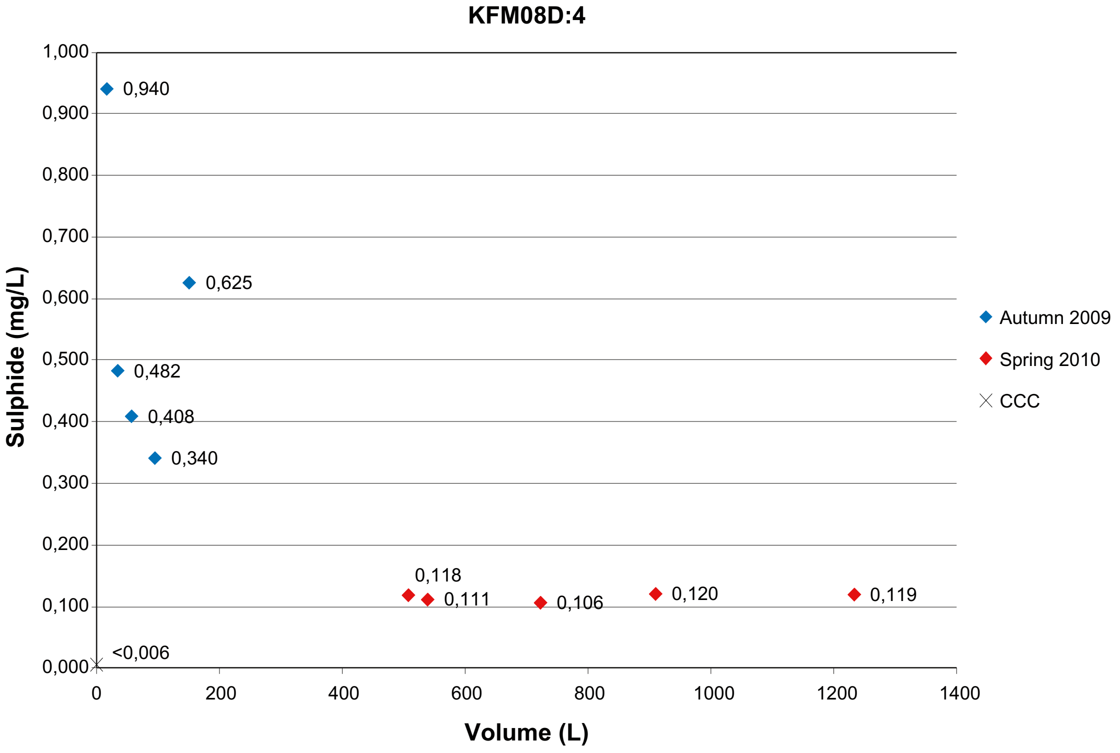


***Figure A1-10.** Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM08D (–538.06 masl). Also shown is the CCC sulphide value chosen as this monitoring section overlaps that of the CCC sampling in the same borehole section.*

volume is reproducible and specific for each section, b) the chosen ‘representative’ 2009 sulphide value for the safety case calculations, in this specific case, is too high, and c) there is still a discrepancy between the higher monitoring data and the much lower CCC sulphide value (< 0.006 mg/L). This either means that the last groundwater sample from the borehole section sampled in 2010 still has not reached 100% formation groundwater and the sulphide concentration would decrease further with additional pumping over a longer period of time, or, the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, it may be almost impossible to avoid minor contribution to the monitoring samples from section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

## KFM08D

**CCC section** 828.4 to 835.4 m. (Corresponds to monitoring section 825.0 to 835.0 m).
Elevation sec mid:
–664.06 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples. | Samples collected during one occasion: 2007-04-09 to 2007-04-30. | Last value in the time series was selected corresponding to the Category 3* sample deemed most representative. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 7,910 to 8,160 mg/L. | Brackish non-marine groundwater type.<br>Major ion chemistry shows a weak increase in Cl and decrease in Mg with time. | Selected sample: #12776 (Category 3*; 2007-04-30); 8,160 mg/L Cl. |
| $S^{2-}$ | Less than 0.006 to 0.068 mg/L. | No systematic time change. | 0.068 mg/L |
| Fe | Less than 0.04 to 0.114 mg/L. | Fe(tot) and Fe(II) have a relatively good correlation with Fe (ICP).<br>Fe, Fe(tot) and Fe(II) values increase systematically with time. | 0.114 mg/L |
| Mn | 0.073 to 0.094 mg/L | Apart from the fourth sample, values decrease systematically with time. | 0.073 mg/L |
| DOC | Less than 1.0 to 2.6 mg/L. | TOC (1.0) only measured for the selected sample.<br>DOC values decrease systematically with time. | < 1.0 mg/L. |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

## KFM08D

**Monitoring section** 825.0 to 835.0 m. (Corresponds to the CCC section 828.4 to 835.4 m).
Elevation sec mid:
–662.55 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 5 samples. | Samples collected during two occasions: 2008-11-11 and 2009-10-23.<br>The second and last sampling occasion comprises a single day time series of four samples. | The second last sample has been chosen because of a pump strop during the final sampling occasion. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 5,880 to 6,920 mg/L. | Brackish non-marine groundwater type.<br>Instability and an increase in major ion chemistry during the monitoring period but even more importantly a large decrease compared with the CCC samples.<br>Although this monitoring section is not representative, it does indicate a change in major ion chemistry during pumping etc, resulting in a change of groundwater type to a distinctly less saline groundwater with a weak glacial signature (cf. Section 4.41 for explanation).<br>Short-circuiting to shallower levels? | Selected sample #16560 (2009-10-21); 6,920 mg/L Cl. |
| $S^{2-}$ | 0.097 to 0.548 mg/L. | The first three samples of the second and last sampling occasion decrease systematically with time (0.548–0.391 mg/L). | 0.391 mg/L. |
| Fe | Less than 0.100 to 0.746 mg/L. | Fe(tot) and Fe(II) measured in three samples where they show good correlation with Fe (ICP).<br>In the last sampling occasion Fe shows a systematic increase. | 0.015 mg/L. |
| Mn | 0.023 to 0.266 mg/L. | In the last sampling occasion there is a systematic increase. | 0.081 mg/L. |
| DOC | 1.4 to 2.9 mg/L. | TOC correlates relatively well with DOC.<br>No systematic time change. | 1.4 mg/L. |

### KFM09A

**CCC section:** 785.10 to 792.24 m
Elevation sec mid:
–614.01 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 4 samples. | Samples collected during one occasion: 2006-04-20 to 2006-05-02. | Third value in the time series was selected corresponding to the Category 2* sample deemed most representative.<br>Represents also the most complete series available. |
| Groundwater type. | Ca-Na-Cl type.<br>Cl varies between 14,200 to 14,800 mg/L. | Saline groundwater type.<br>Significant glacial component (–13.30‰ V-SMOW). | Selected sample #12243 (Category 2*, 2006-04-27); 14,800 mg/L Cl. |
| $S^{2-}$ | Below detection limit (0.002 mg/L) to 0.004 mg/L. | No systematic time change. | 0.004 mg/L |
| Fe | 0.107 to 0.175 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>Last three samples indicate a decrease in Fe. | 0.130 mg/L |
| Mn | 0.103 to 0.110 mg/L | No systematic time change. | 0.107 mg/L |
| DOC | Below detection limit (1.0 mg/L) to 1.5 mg/L. | TOC not analysed.<br>Last three samples indicate a decrease. | 1.3 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM10A

**CCC section:** 298.00 to 305.14 m
Elevation sec mid:
–214.77 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 5 samples. | Samples collected during one occasion: 2006-011-13 to 2006-11-26. | Last value in the time series was selected corresponding to the Category 2* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 3,880 to 4,050 mg/L. | Brackish glacial groundwater type.<br>Small marine component present. | Selected sample: #12552 (Category 2*, 2006-11-26); 4,050 mg/L Cl. |
| $S^{2-}$ | 0.007 to 0.027 mg/L | No systematic time change. | 0.027 mg/L |
| Fe | 1.010 to 3.810 mg/L | Relatively good correlation between Fe, Fe(tot) and Fe(II).<br>Apart from the first sample, Fe, Fe(tot) and Fe(II) values decrease systematically with time. | 1.010 mg/L |
| Mn | 0.183 to 0.367 mg/L. | Apart from the first sample, values decrease systematically with time. | 0.186 mg/L |
| DOC | 1.5 to 8.0 mg/L | TOC not analysed except for the last sample in the time series (1.6 mg/L).<br>General decrease in DOC with time. | 2.0 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM10A

**Monitoring section:** 430.0 to 440.0 m
Elevation sec mid:
–299.83 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 8 samples. | Samples collected during four occasions: 2007-04-17, 2007-10-17, 2008-09-30 and 2009-10-09 (5 samples).<br>The last sampling occasion comprises a single day time series of five samples. | No sample was selected due to anomalously high Fe content, and also high Mn. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 4,900 to 5,570 mg/L. | Brackish marine (Littorina) groundwater type.<br>Reasonably stable major ion chemistry during the monitoring. | |
| $S^{2-}$ | 0.032 to 0.183 mg/L | Last sampling occasion shows a systematic increase with time (0.032 to 0.066 mg/L). | |
| Fe | 6.71 to 12.5 mg/L<br>Note: anomalously high Fe values. | Relatively good correlation between Fe, Fe(tot) and Fe(II). Not analysed in three of the samples.<br>Last sampling occasion shows a systematic decrease in Fe with time | |
| Mn | 1.47 to 1.73 mg/L<br>Note: high Mn values. | No systematic time change. | |
| DOC | 1.8 to 3.2 mg/L | Relatively good correlation between DOC and TOC.<br>No systematic time change. | |

## Additional time series data from the Spring of 2010

As detailed in Section 3.1.4, special efforts were made in the Autumn sampling of 2009 in 13 out of the 33 borehole sections included in the monitoring programme to improve the sampling methodology. The main conclusions from the 2009 performance were that: 1) in many cases, the pumping period was too short to obtain representative groundwater samples (i.e. *100% formation water*): and 2) the estimated stagnant *section water* contribution to each sample (from plug flow calculations) showed a good correlation with the sulphide concentration. Due to experience from 2009, the volumes to be removed in order to get close to 100% *formation water* in the groundwater samples were estimated individually for each borehole section and this information was used in the Spring sampling of 2010. These additional time-series monitoring data, together with the earlier time-series data presented above for this section, are plotted in Figure A1-11.

The 2010 and the 2009 time-series sulphide data forms two different trends with few similarities except for the low concentration level which is common in both time-series trends. The increasing trend in 2009 might have been the result of changing flow distribution between the two flow anomalies present in the borehole section, resulting in an increasing mixture of initial *section water* from below. According to estimations (plug flow calculations), the dominating flow anomaly supplied the major part of the discharged water already when the first sample was taken and water from the second anomaly did not reach the outlet before the last sample was collected in 2009. This is also the situation when the first sample was collected in 2010. The 2010 time series sulphide data level out (0.049–0.057 mg/L) and could have justified a selection of a sulphide value of about 0.050 mg/L as 'representative' for the safety case calculations. These results underline two important observations: a) the decreasing sulphide concentration trend with pumped volume is reproducible but the specific geometric situation in each section needs to be considered, and b) with the current understanding, a 'representative' sulphide value of 0.050 mg/L could have been selected for the safety case calculations.

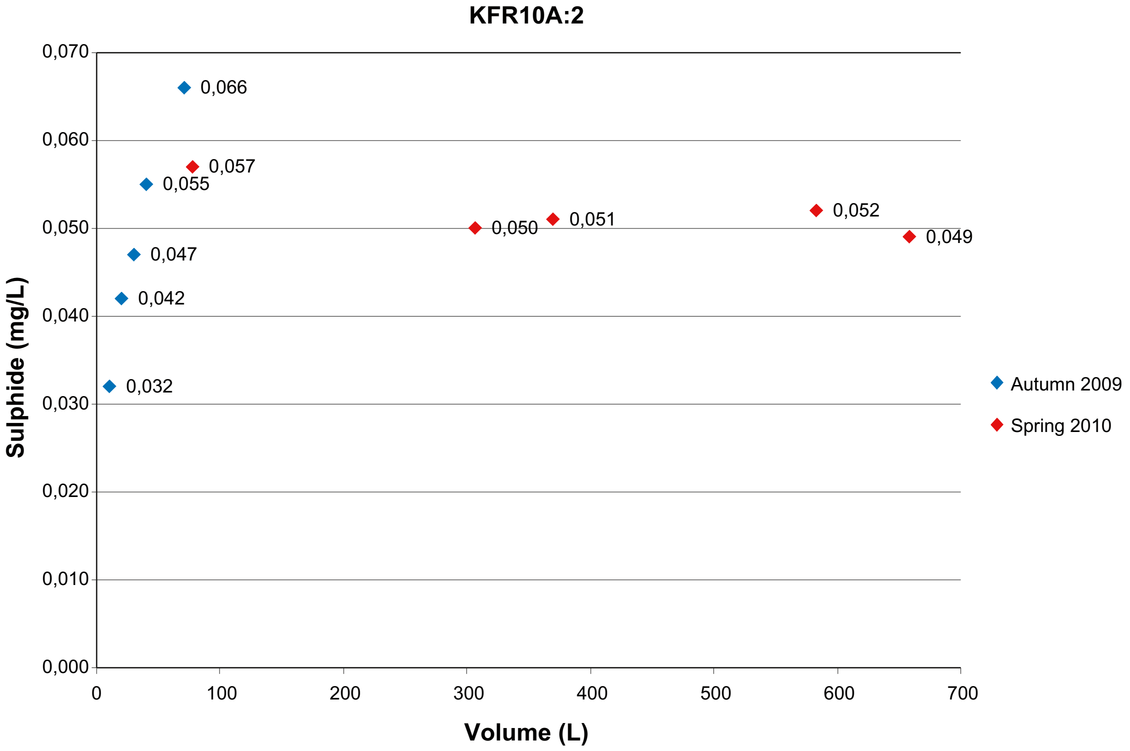


***Figure A1-11.*** *Comparison of time-series data from Autumn 2009 and Spring 2010 for monitoring section KFM10A (–299.83 masl).*

### KFM11A

**CCC section:** 447.5 to 454.64 m. (Corresponds to monitoring section 446.0 to 456.0 m).
Elevation sec mid:
–389.68 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 7 samples. | Samples collected during one occasion: 2007-02-19 to 2007-03-12. | First sample in the time series was selected corresponding to the Category 4* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 4,210 to 4,550 mg/L. | Transition groundwater type.<br>Brackish non-marine groundwater with a component of brackish marine groundwater.<br>Major ion chemistry shows a small but gradual decrease in Cl and increase in a marine component (i.e. Mg) during monitoring. | Selected sample: #12703; (2007-02-19; Category 4* due to unstable chemistry and relatively high drilling water content); 4,550 mg/L Cl. |
| $S^{2-}$ | Less than 0.006 to 0.013 mg/L. | Weak systematic increase with time. | < 0.006 mg/L |
| Fe | Less than 0.200 to 0.447 mg/L. | Good correlation between Fe (ICP), Fe(tot) and Fe(II).<br>No systematic time change. | < 0.200 mg/L |
| Mn | 0.098 to 0.123 mg/L | Weak systematic increase with time. | 0.098 mg/L |
| DOC | 1.0 to 2.5 mg/L | TOC measured in one sample showing good correlation with DOC.<br>No systematic time change. | 2.5 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

### KFM11A

**Monitoring section:** 446.0 to 456.0 m (Corresponds to the CCC section 447.5 to 454.64 m).
Elevation sec mid:
–389.62 masl

| | Groundwater chemistry | Comment | Selected sample/value* |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during two occasions: 2007-10-09 and 2008-10-06. | First value selected even though major ion chemistry is stable.* |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 4,400 to 4,410 mg/L. | Transition groundwater type.<br>Brackish non-marine groundwater with a component of brackish marine groundwater.<br>Little change in the major ion chemistry between the two sampling occasions, although a weak increase in a glacial component and a decrease in tritium are observed. | Selected sample:<br>#12829; (2007-10-09) 4,400 mg/L Cl. |
| $S^{2-}$ | 0.172 to 0.393 mg/L | No systematic time change. | 0.172 mg/L |
| Fe | Less than 0.254 to 0.534 mg/L. | Good correlation between Fe (ICP), Fe(tot) and Fe(II).<br>No systematic time change. | 0.534 mg/L |
| Mn | 0.140 to 0.193 mg/L | No systematic time change. | 0.193 mg/L |
| DOC | 1.3 to 1.9 mg/L | Good correlation with TOC.<br>No systematic time change. | 1.9 mg/L |

*Selected sample/value for sulphide systematically refers to the earliest sample taken following installation of the monitoring equipment. This is based on the assumption that with increased time the monitoring equipment may become contaminated by a continuous build-up of metal corrosion products and of bacterial activity, thus potentially influencing the measured groundwater sulphide contents at each successive sampling occasion.

### KFM11A

**Monitoring section:** 690.0 to 710.0 m.
Elevation sec mid:
–593.76 masl

| | Groundwater chemistry | Comment | Selected sample/value |
|---|---|---|---|
| Number of samples. | 3 samples. | Samples collected during 3 occasions: 2007-07-16, 2007-10-09 and 2008-10-06. | No value selected because of a continuous change in the major ion chemistry between the sampling occasions (i.e. increase in Cl with time), and also high tritium (varies from 1.5–3.5 TU). |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 5,360 to 6,700 mg/L. | Transition groundwater type.<br>Brackish non-marine groundwater with various components of brackish marine ground water.<br>Unstable section in the Singö deformation zone. | |
| $S^{2-}$ | 0.040 to 0.307 mg/L | Systematic increase with time. | |
| Fe | Less than 0.635 to 2.910 mg/L. | Good correlation between Fe (ICP), Fe(tot) and Fe(II).<br>Fe, Fe(tot) and Fe(II) values decrease systematically with time. | |
| Mn | 0.344 to 0.763 mg/L | No systematic time change. | |
| DOC | Less than 1.0 to 6.3 mg/L. | Good correlation with TOC.<br>Systematic decrease with time. | |

### KFM12A

**Monitoring section:** 270.00 to 280.00 m
Elevation sec mid:
–226.74 masl

| | **Groundwater chemistry** | **Comment** | **Selected sample/value** |
|---|---|---|---|
| Number of samples. | 1 sample. | Sample collected from 2008-10-07. | Chosen value represents a distinct glacial type with low tritium from a shallow bedrock location. |
| Groundwater type. | Na-Ca-Cl type.<br>Cl at 2,010 mg/L. | Brackish glacial groundwater type.<br>Mixed origin with a substantial glacial and weak marine component. | Selected sample:<br>#16118 (2008-10-07); 3,610 mg/L Cl. |
| $S^{2-}$ | 0.076 mg/L | No systematic time change. | 0.076 mg/L |
| Fe | 0.255 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 0.255 mg/L |
| Mn | 0.575 mg/L | No systematic time change. | 0.575 mg/L |
| DOC | Below detection limit (1.0 mg/L). | TOC (1.3 mg/L).<br>No systematic time change. | < 1.0 mg/L |

### KFM12A

**Sampled using the PLU hydraulic testing equipment**
**section:** 516.00 to 536.00 m
Elevation sec mid:
–439.26 masl

| | **Groundwater chemistry** | **Comment** | **Selected sample/value** |
|---|---|---|---|
| Number of samples. | 2 samples. | Samples collected during one occasion: 2007-05-15 to 2007-05-21. | Second value was selected corresponding to a Category 3* sample deemed most representative. |
| Groundwater type. | Na-Ca-Cl($SO_4$) type.<br>Cl varies between 6,130 to 6,190 mg/L Cl. | Transition groundwater type (i.e. brackish non-marine groundwater with a significant marine component).<br>Stable major ion chemistry. | Selected sample: #12792 (Category 3*, 2007-02-21); 6,130 mg/L Cl. |
| $S^{2-}$ | 0.023 to 0.034 mg/L | No systematic time change. | 0.034 mg/L |
| Fe | 0.250 to 0.268 mg/L | Good correlation between Fe, Fe(tot) and Fe(II).<br>No systematic time change. | 0.268 mg/L |
| Mn | 0.830 to 0.859 mg/L | No systematic time change. | 0.859 mg/L |
| DOC | 1.1to 1.9 mg/L | Only one TOC value (1.5 mg/L from the selected sample).<br>No systematic time change. | 1.1 mg/L |

* see documentation in /Smellie et al. 2008/ dealing with the evolution of the groundwater and describing the procedure of representative sample selection.

# Appendix 2

A number of diagrams have been produced to visualise the sensitive changes in chemistry that occurred during sampling of the groundwater time series data. The parameters that have been plotted against time (i.e. sampling date) for each of the selected borehole sections sampled are:

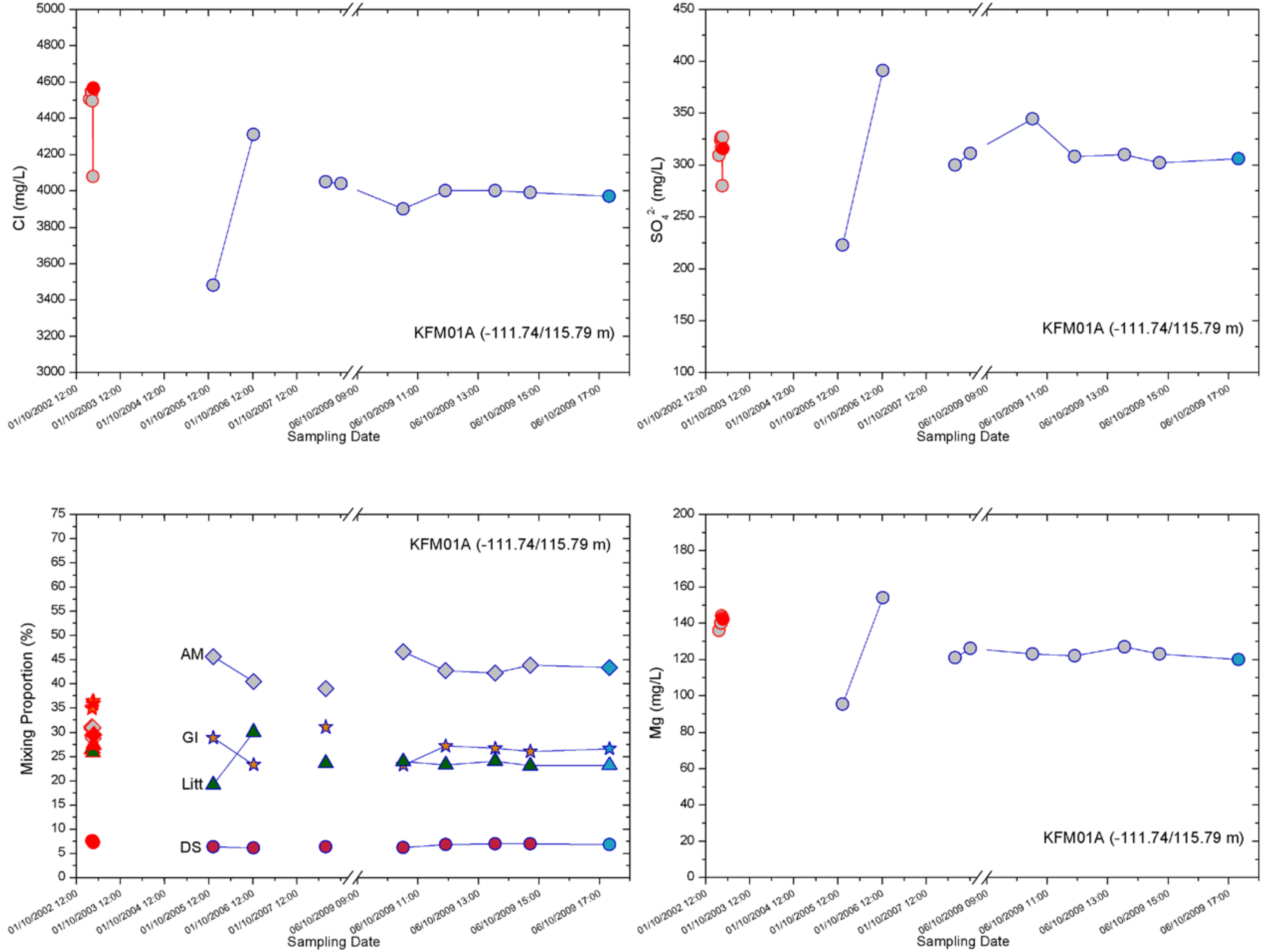
Cl (mg/L), Mixing Proportion (%), Mg (mg/L), $SO_4$ (mg/L), $S^{2-}$(mg/L), Fe(II) (mg/L), FeS (amorphous) Saturation Index, $\delta S^{34}$ (% CDT), $HCO_3$ (mg/L), Mn (mg/L), Calcite Saturation Index, and DOC (mg/L),

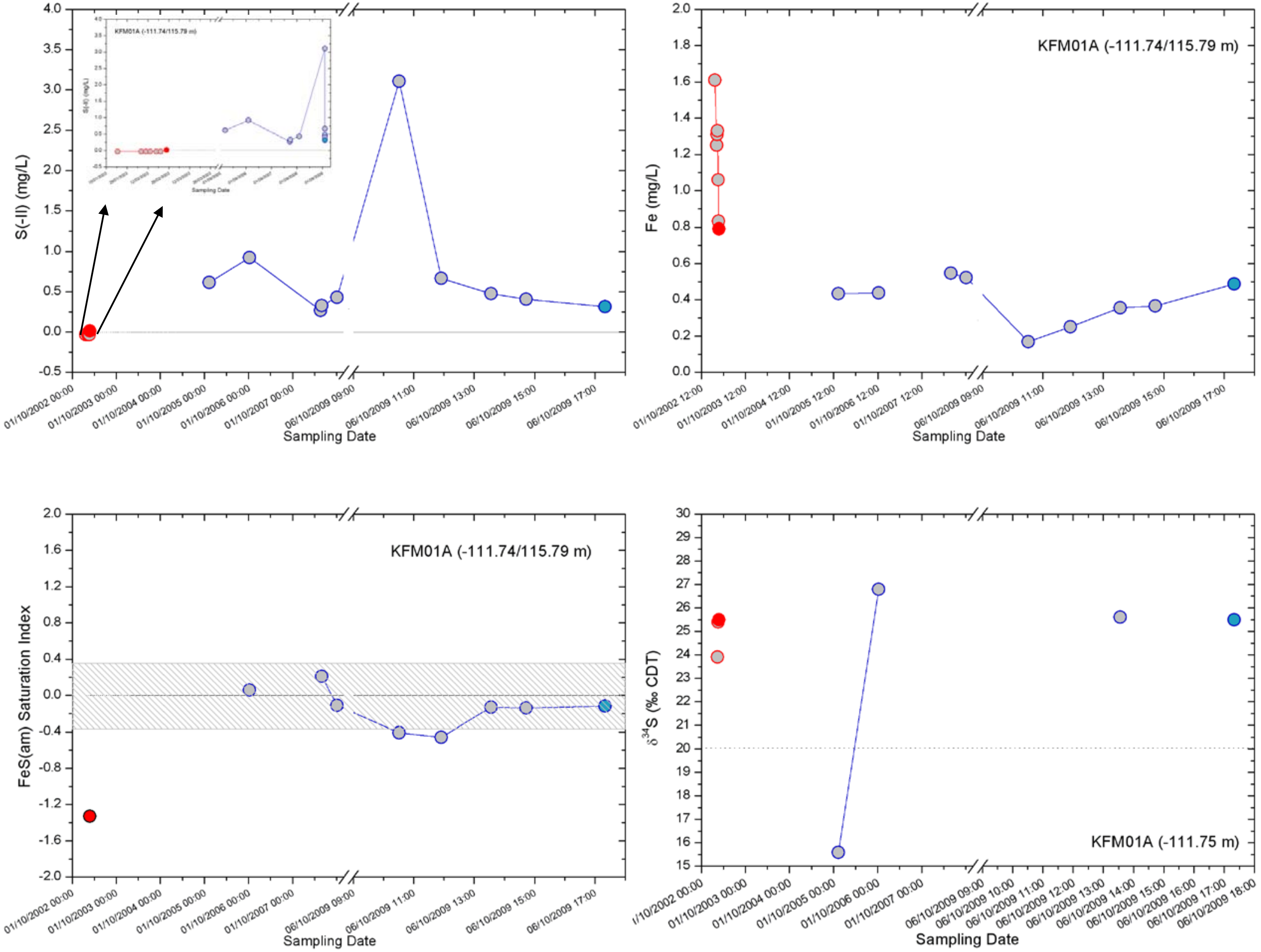
Red symbols refers to CCC (Complete Chemical Characterisation).

Blue symbols refers to monitoring samples.

In a number of sections both CCC and monitoring samples are available representing essentially the same conducting structure. In such cases the entire data set is included in the same plot (starting with the CCC campaign and continuing with the monitoring).

KFM01A (–111.75 / –115.79 m)
Eh = –195 mV




S(-II) (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
KFM01A (-111.74/115.79 m)
Sampling Date
01/10/2002 00:00
01/10/2003 00:00
01/10/2004 00:00
01/10/2005 00:00
01/10/2006 00:00
01/10/2007 00:00
06/10/2009 09:00
06/10/2009 11:00
06/10/2009 13:00
06/10/2009 15:00
06/10/2009 17:00
Fe (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
KFM01A (-111.74/115.79 m)
01/10/2002 12:00
01/10/2003 12:00
01/10/2004 12:00
01/10/2005 12:00
01/10/2006 12:00
01/10/2007 12:00
06/10/2009 09:00
06/10/2009 11:00
06/10/2009 13:00
06/10/2009 15:00
06/10/2009 17:00
Sampling Date
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
KFM01A (-111.74/115.79 m)
01/10/2002 00:00
01/10/2003 00:00
01/10/2004 00:00
01/10/2005 00:00
01/10/2006 00:00
01/10/2007 00:00
06/10/2009 09:00
06/10/2009 11:00
06/10/2009 13:00
06/10/2009 15:00
06/10/2009 17:00
Sampling Date
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
KFM01A (-111.75 m)
1/10/2002 00:00
01/10/2003 00:00
01/10/2004 00:00
01/10/2005 00:00
01/10/2006 00:00
01/10/2007 00:00
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06/10/2009 13:00
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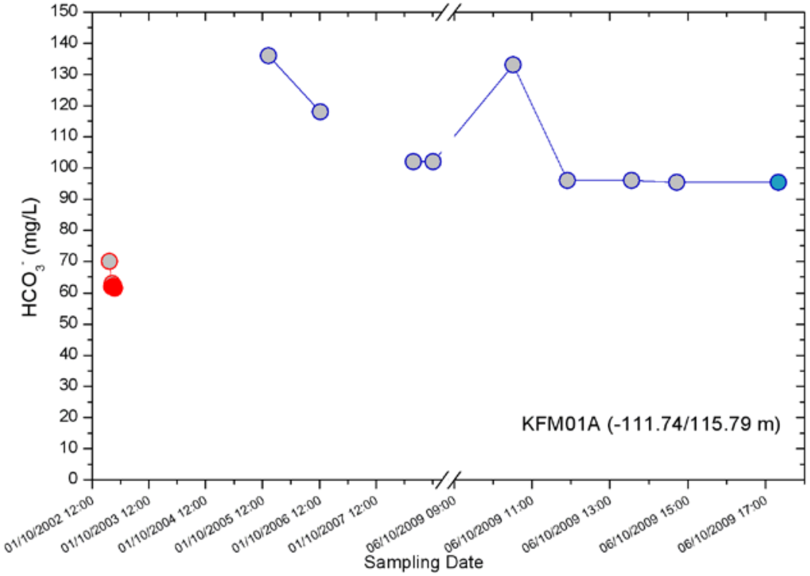
06/10/2009 15:00
06/10/2009 16:00
06/10/2009 17:00
06/10/2009 18:00
Sampling Date


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
$HCO_3^-$ (mg/L)
KFM01A (-111.74/115.79 m)
01/10/2002 12:00
01/10/2003 12:00
01/10/2004 12:00
01/10/2005 12:00
01/10/2006 12:00
01/10/2007 12:00
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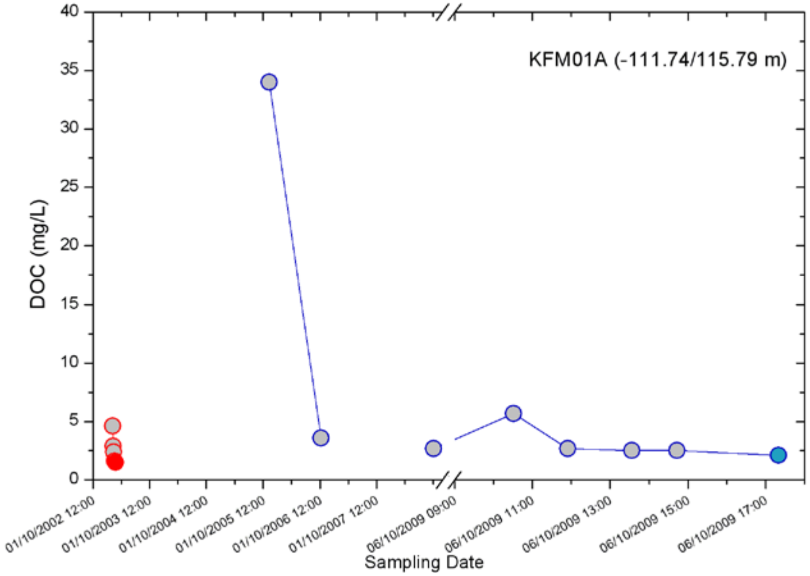
06/10/2009 17:00
Sampling Date


40
35
30
25
20
15
10
5
0
DOC (mg/L)
KFM01A (-111.74/115.79 m)
01/10/2002 12:00
01/10/2003 12:00
01/10/2004 12:00
01/10/2005 12:00
01/10/2006 12:00
01/10/2007 12:00
06/10/2009 09:00
06/10/2009 11:00
06/10/2009 13:00
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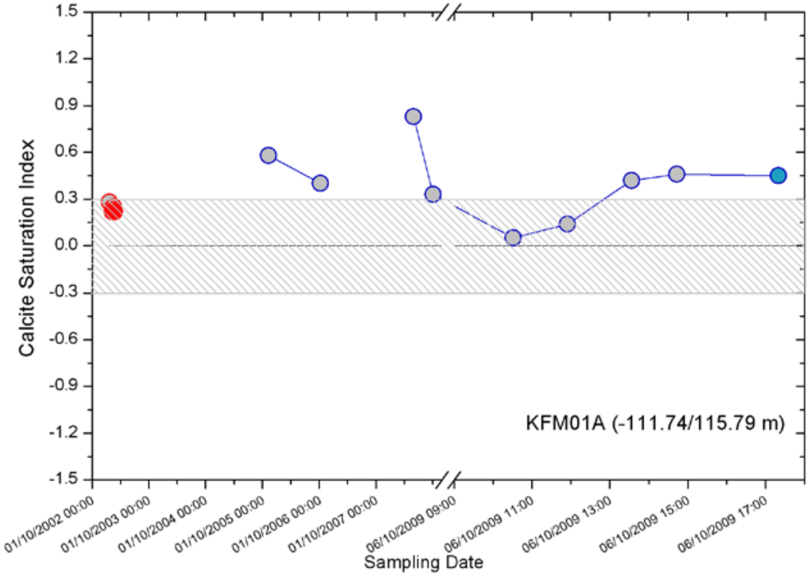
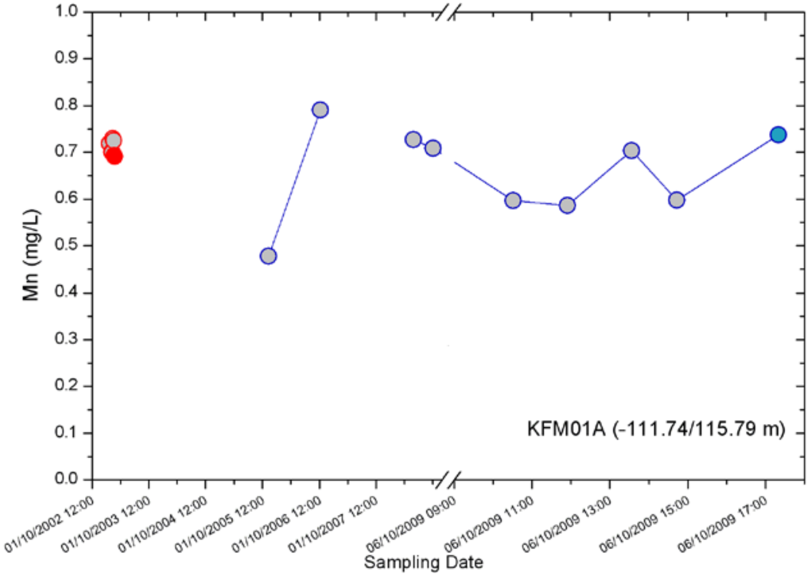
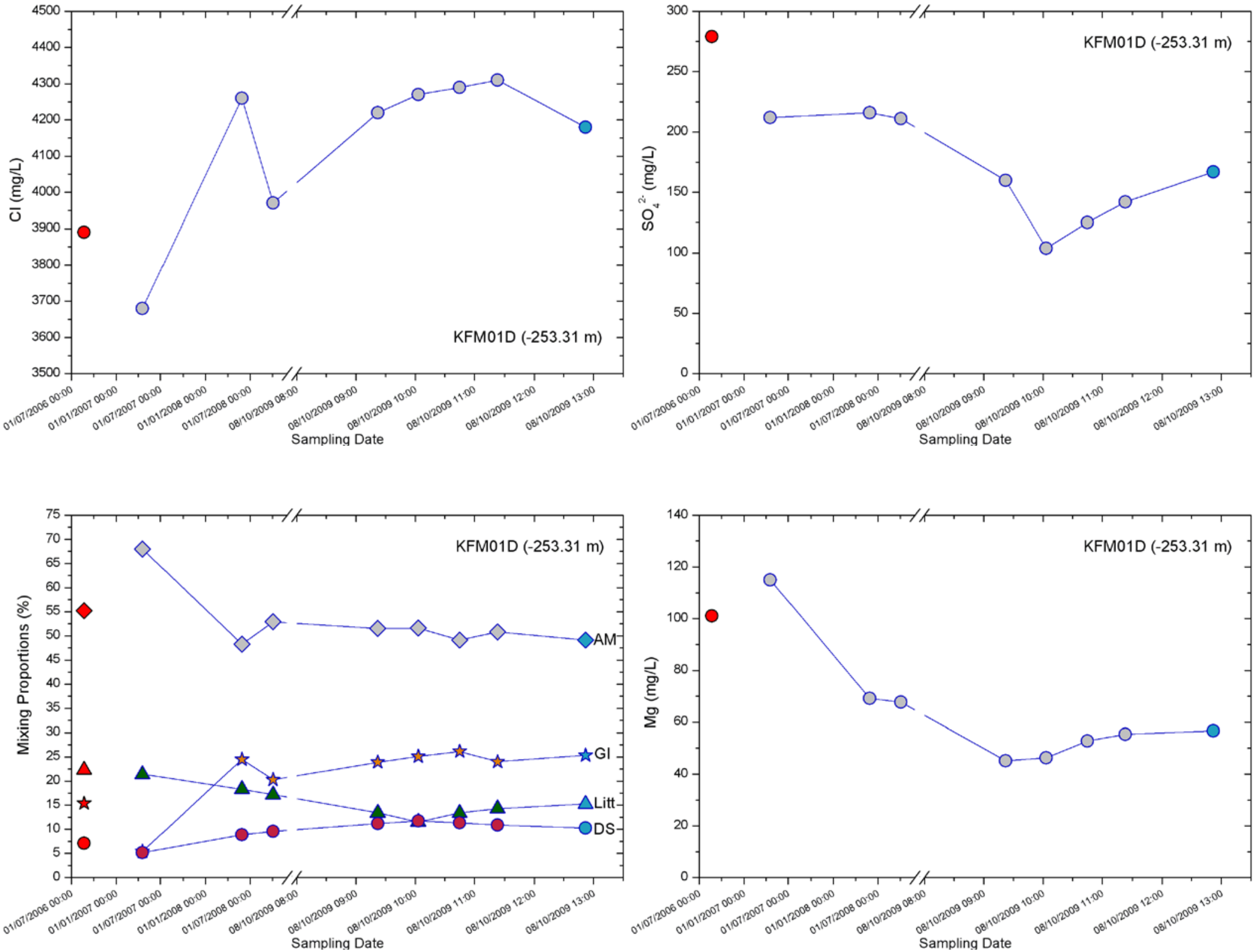
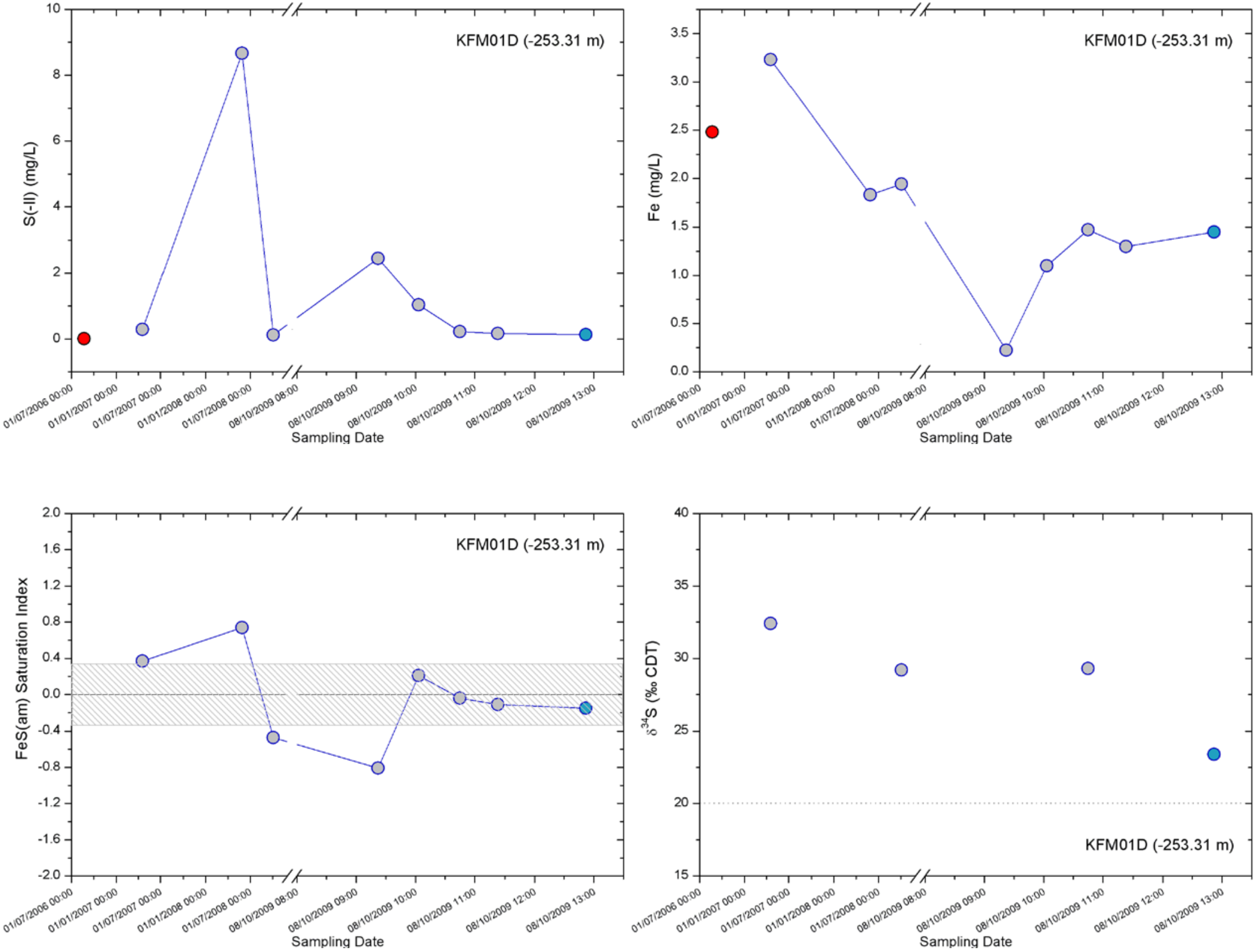
06/10/2009 17:00
Sampling Date

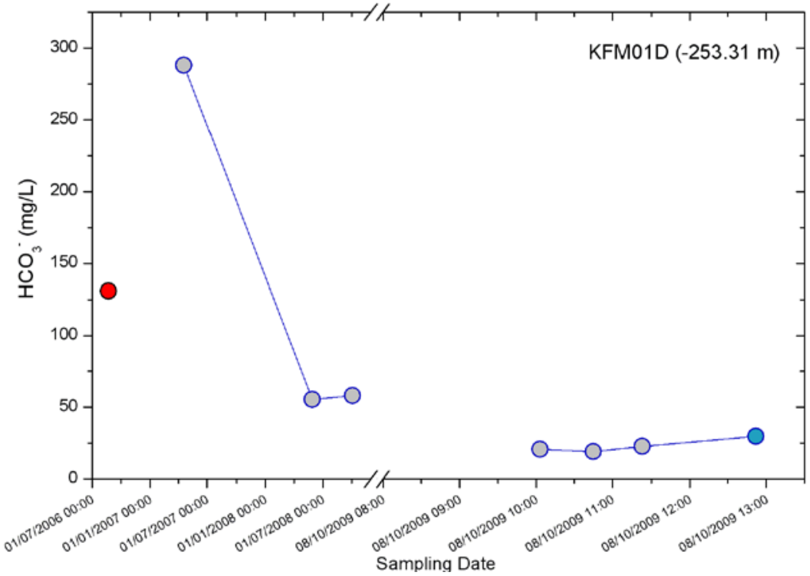

1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Calcite Saturation Index
KFM01A (-111.74/115.79 m)
01/10/2002 00:00
01/10/2003 00:00
01/10/2004 00:00
01/10/2005 00:00
01/10/2006 00:00
01/10/2007 00:00
06/10/2009 09:00
06/10/2009 11:00
06/10/2009 13:00
06/10/2009 15:00
06/10/2009 17:00
Sampling Date

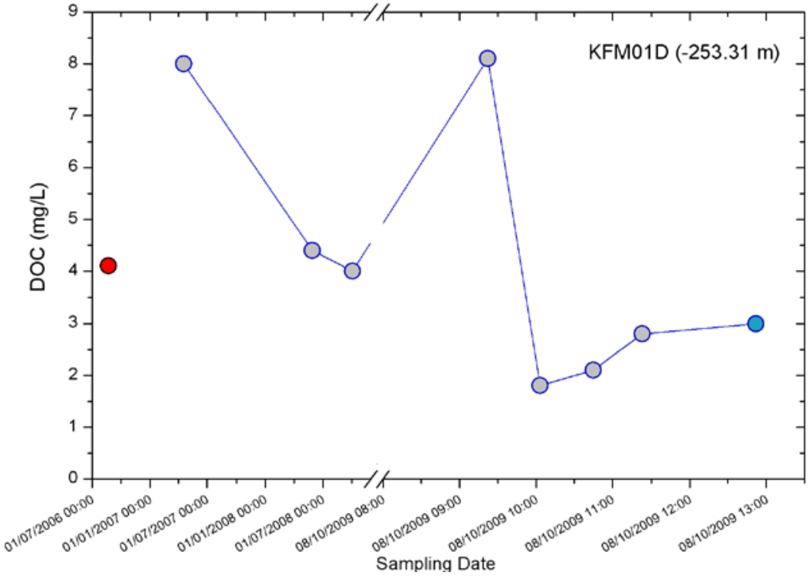

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Mn (mg/L)
KFM01A (-111.74/115.79 m)
01/10/2002 12:00
01/10/2003 12:00
01/10/2004 12:00
01/10/2005 12:00
01/10/2006 12:00
01/10/2007 12:00
06/10/2009 09:00
06/10/2009 11:00
06/10/2009 13:00
06/10/2009 15:00
06/10/2009 17:00
Sampling Date

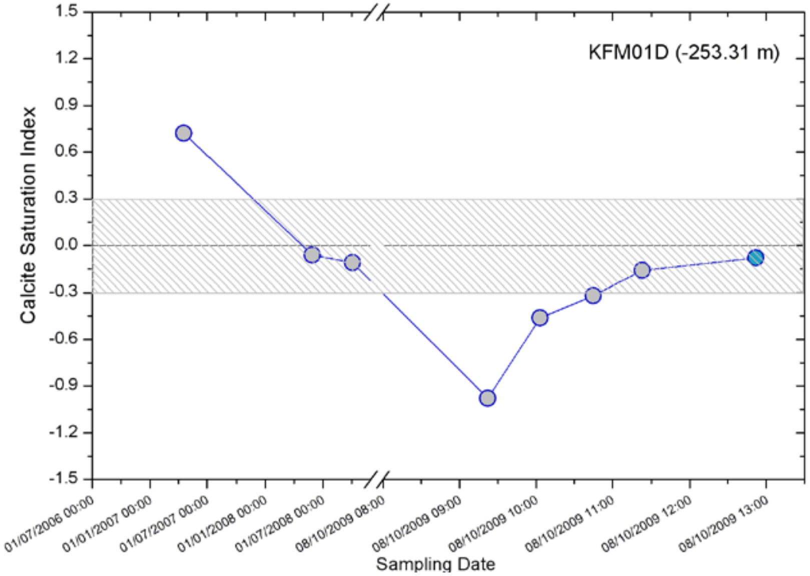
KFM01D (–253.31 / –252.53 m)

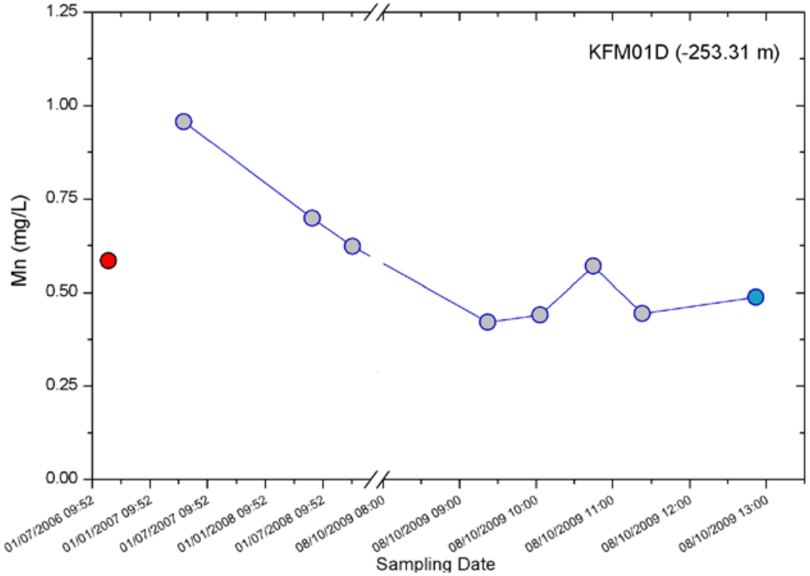



KFM01D (-253.31 m)
S(-II) (mg/L)
10
8
6
4
2
0
Fe (mg/L)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
$\delta^{34}S$ (‰ CDT)
40
35
30
25
20
15
01/07/2006 00:00
01/01/2007 00:00
01/07/2007 00:00
01/01/2008 00:00
01/07/2008 00:00
08/10/2009 08:00
08/10/2009 09:00
08/10/2009 10:00
08/10/2009 11:00
08/10/2009 12:00
08/10/2009 13:00
Sampling Date

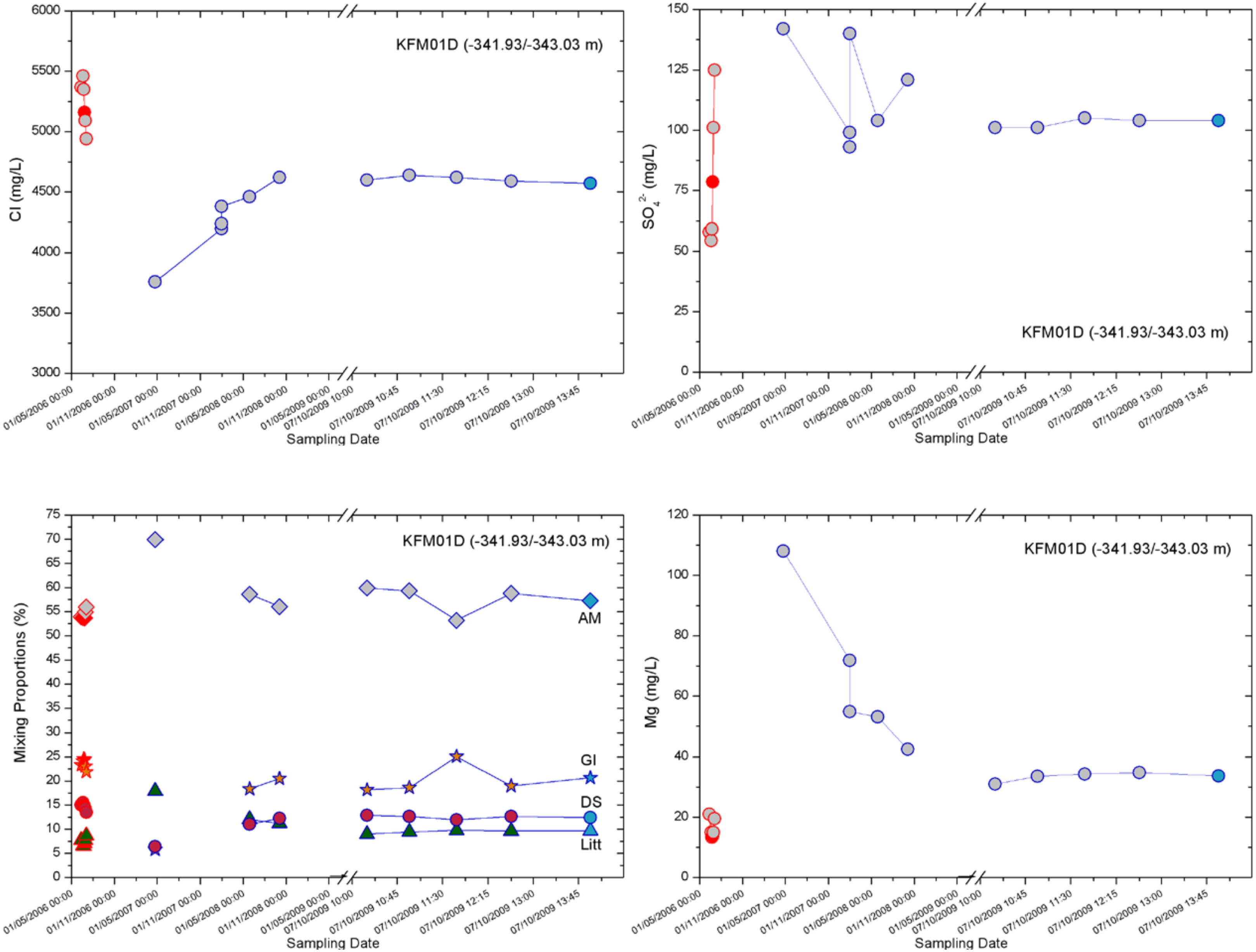

KFM01D (-253.31 m)
HCO$_3^-$ (mg/L)
0
50
100
150
200
250
300
Sampling Date
01/07/2006 00:00
01/01/2007 00:00
01/07/2007 00:00
01/01/2008 00:00
01/07/2008 00:00
08/10/2009 08:00
08/10/2009 09:00
08/10/2009 10:00
08/10/2009 11:00
08/10/2009 12:00
08/10/2009 13:00

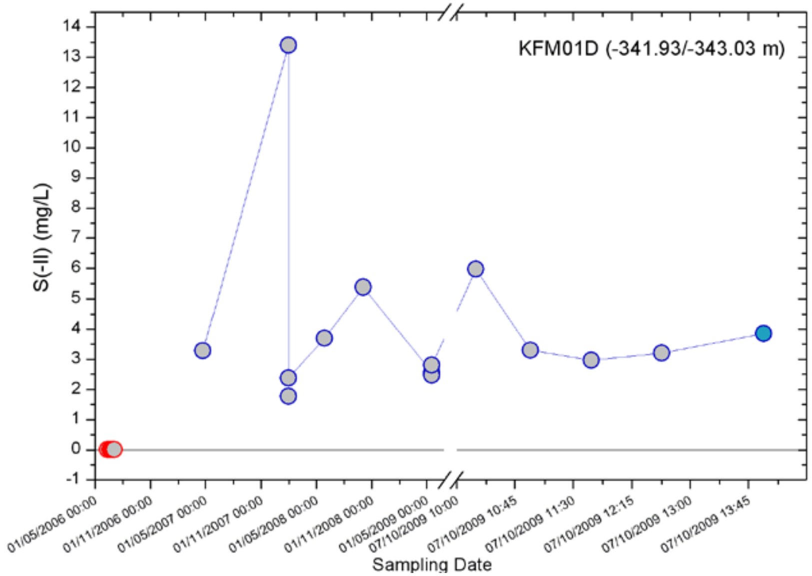

KFM01D (-253.31 m)
DOC (mg/L)
0
1
2
3
4
5
6
7
8
9
Sampling Date
01/07/2006 00:00
01/01/2007 00:00
01/07/2007 00:00
01/01/2008 00:00
01/07/2008 00:00
08/10/2009 08:00
08/10/2009 09:00
08/10/2009 10:00
08/10/2009 11:00
08/10/2009 12:00
08/10/2009 13:00

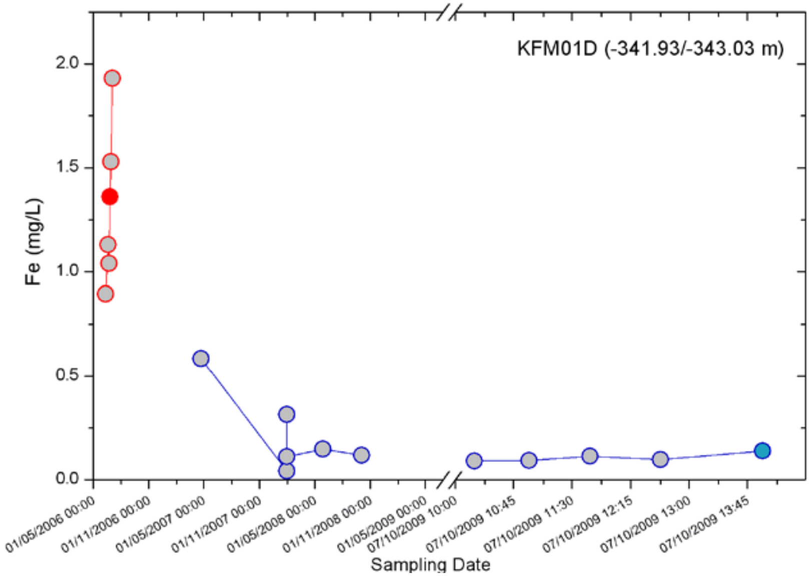

KFM01D (-253.31 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
Sampling Date
01/07/2006 00:00
01/01/2007 00:00
01/07/2007 00:00
01/01/2008 00:00
01/07/2008 00:00
08/10/2009 08:00
08/10/2009 09:00
08/10/2009 10:00
08/10/2009 11:00
08/10/2009 12:00
08/10/2009 13:00

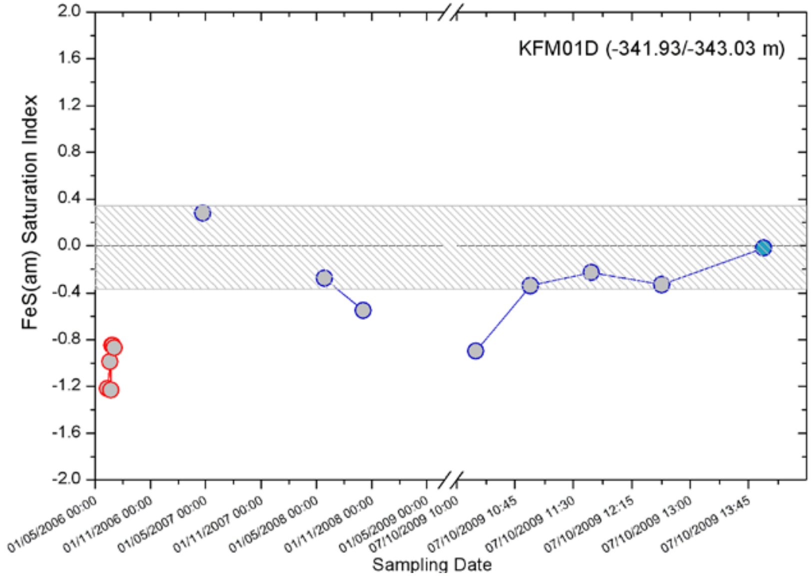

KFM01D (-253.31 m)
Mn (mg/L)
0.00
0.25
0.50
0.75
1.00
1.25
Sampling Date
01/07/2006 09:52
01/01/2007 09:52
01/07/2007 09:52
01/01/2008 09:52
01/07/2008 09:52
08/10/2009 08:00
08/10/2009 09:00
08/10/2009 10:00
08/10/2009 11:00
08/10/2009 12:00
08/10/2009 13:00

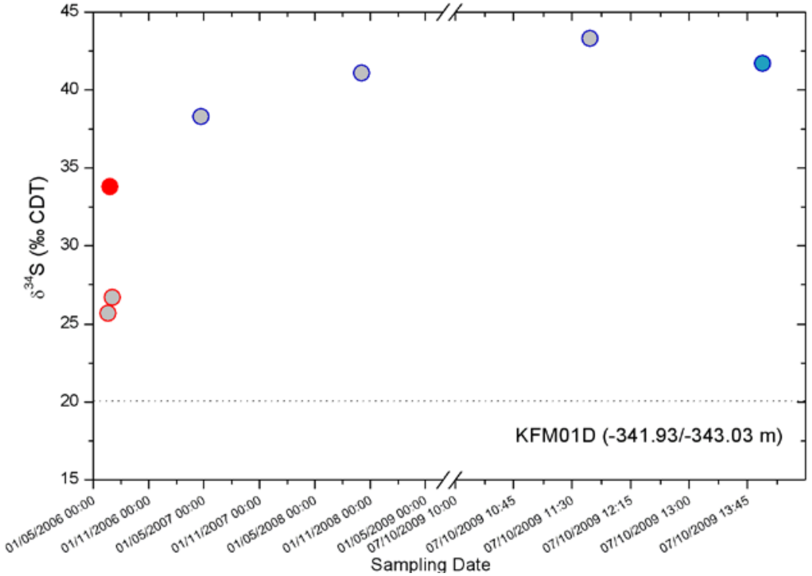
KFM01D (–341.93 / –343.03 m)
Eh = –263 mV

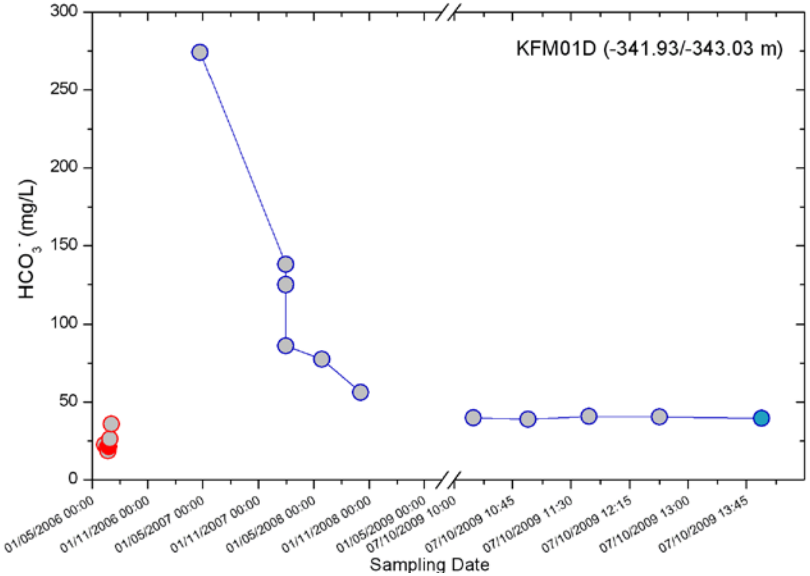


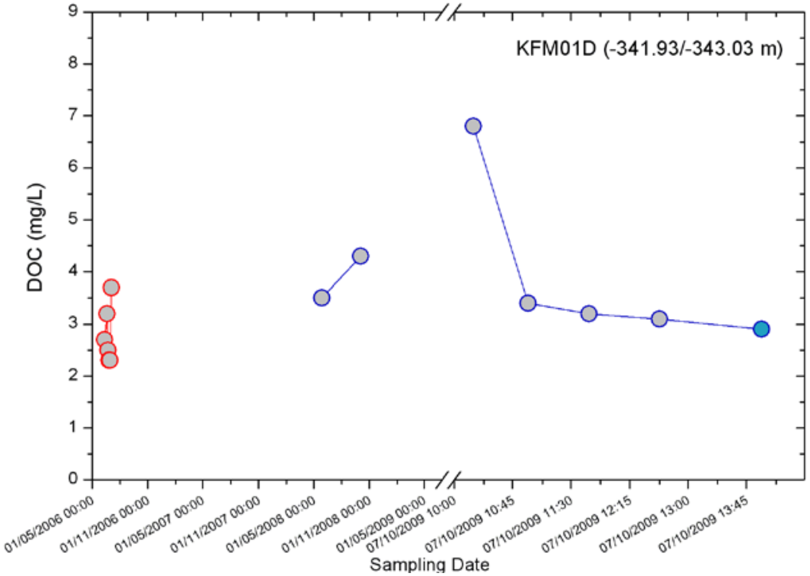

KFM01D (-341.93/-343.03 m)
S(-II) (mg/L)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45
Sampling Date

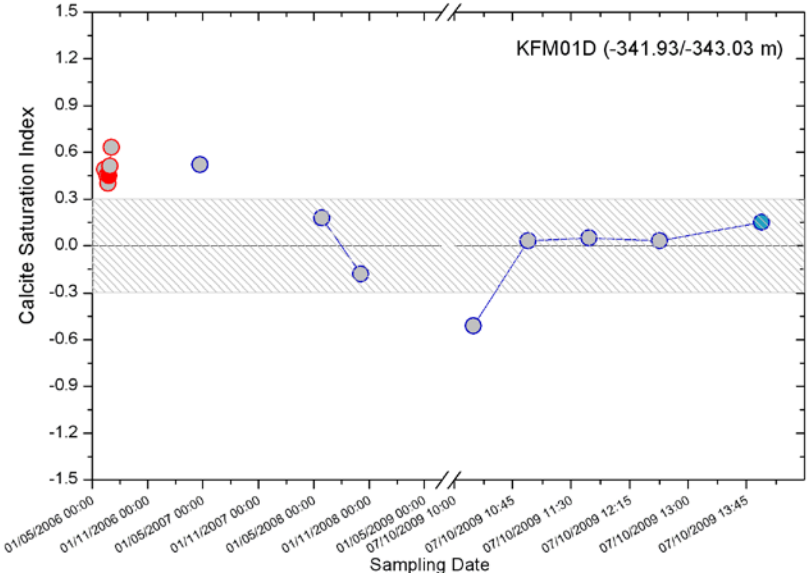

KFM01D (-341.93/-343.03 m)
Fe (mg/L)
2.0
1.5
1.0
0.5
0.0
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45
Sampling Date

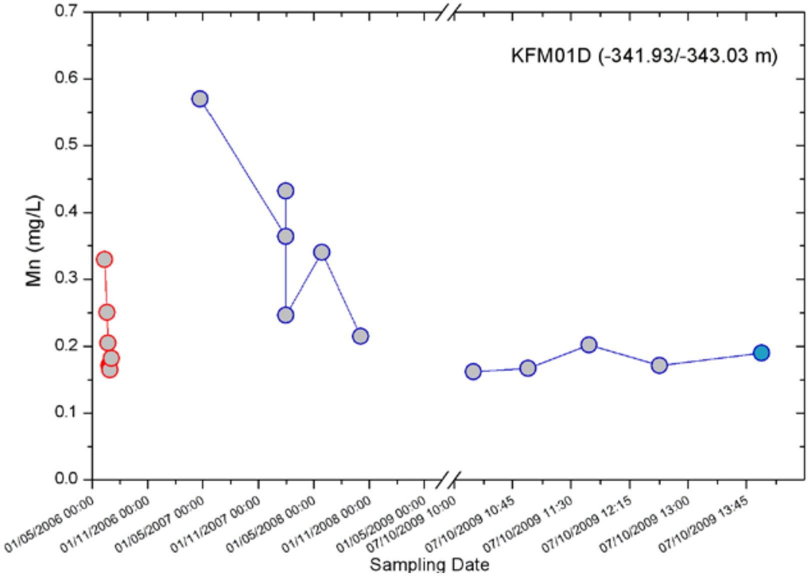

KFM01D (-341.93/-343.03 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45
Sampling Date


KFM01D (-341.93/-343.03 m)
$\delta^{34}$S (‰ CDT)
45
40
35
30
25
20
15
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45
Sampling Date

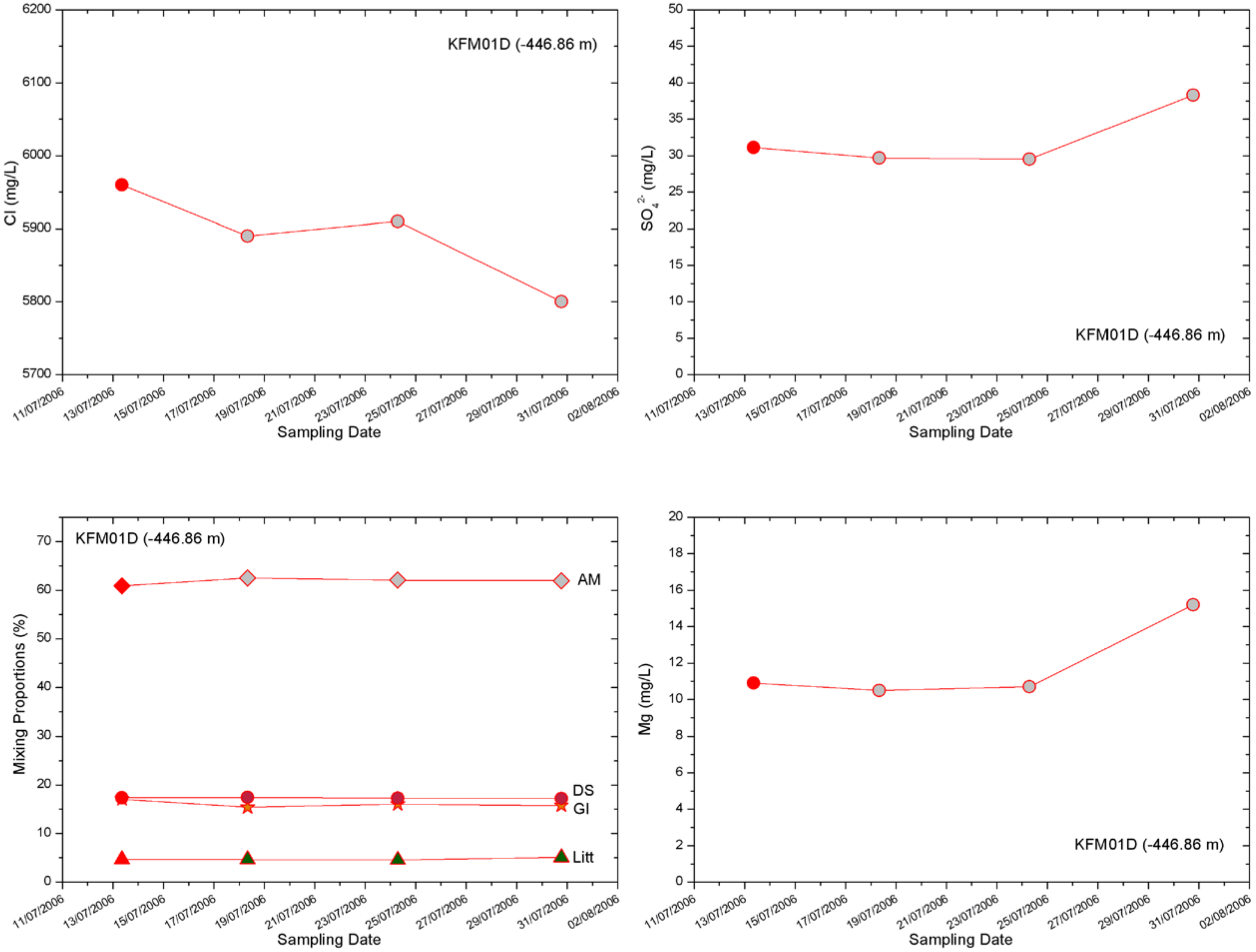

KFM01D (-341.93/-343.03 m)
HCO$_3^-$ (mg/L)
0
50
100
150
200
250
300
Sampling Date
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45

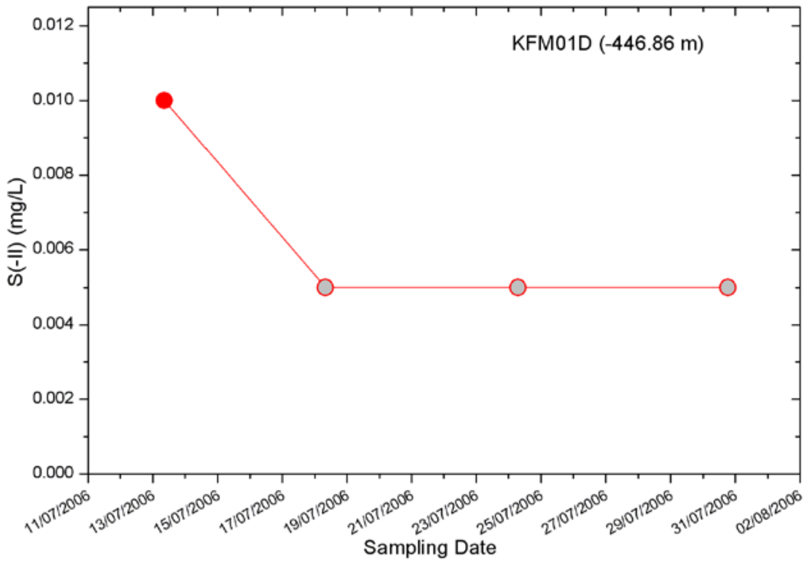

KFM01D (-341.93/-343.03 m)
DOC (mg/L)
0
1
2
3
4
5
6
7
8
9
Sampling Date
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45

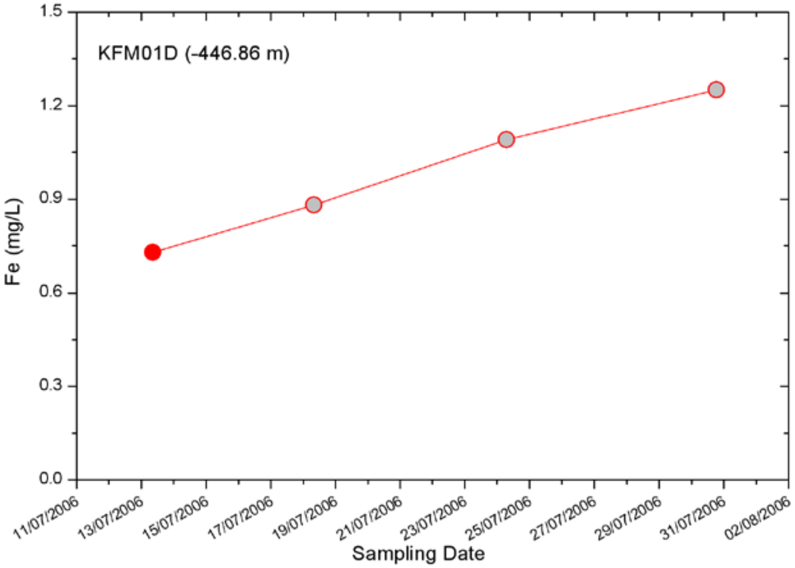

KFM01D (-341.93/-343.03 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Sampling Date
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45

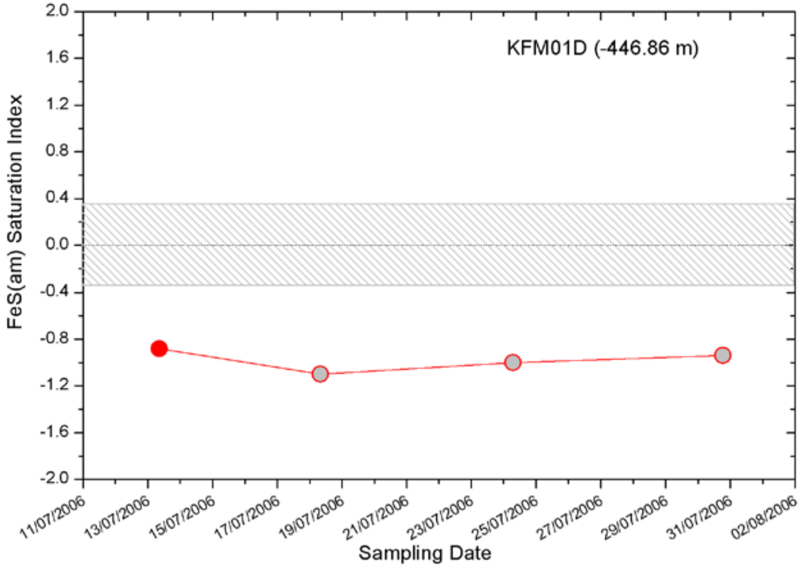

KFM01D (-341.93/-343.03 m)
Mn (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Sampling Date
01/05/2006 00:00
01/11/2006 00:00
01/05/2007 00:00
01/11/2007 00:00
01/05/2008 00:00
01/11/2008 00:00
01/05/2009 00:00
07/10/2009 10:00
07/10/2009 10:45
07/10/2009 11:30
07/10/2009 12:15
07/10/2009 13:00
07/10/2009 13:45

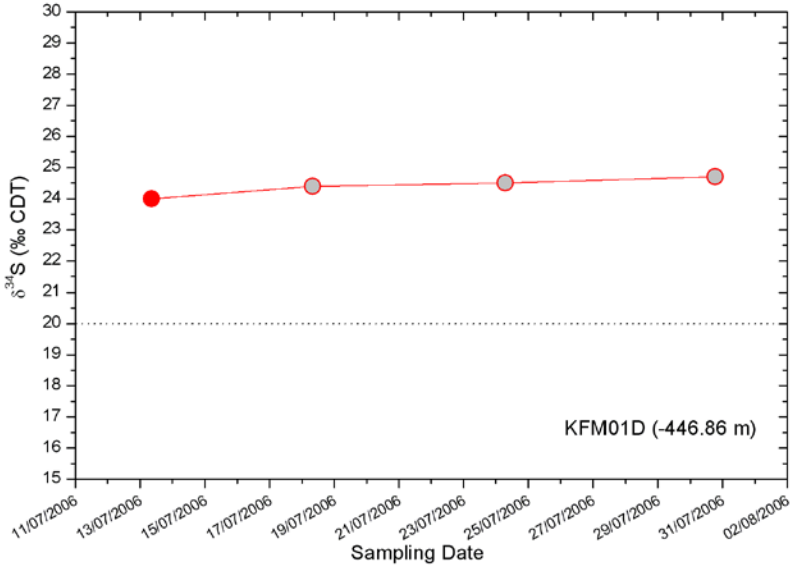
KFM01D (–446.86 m)
Eh = –260 mV

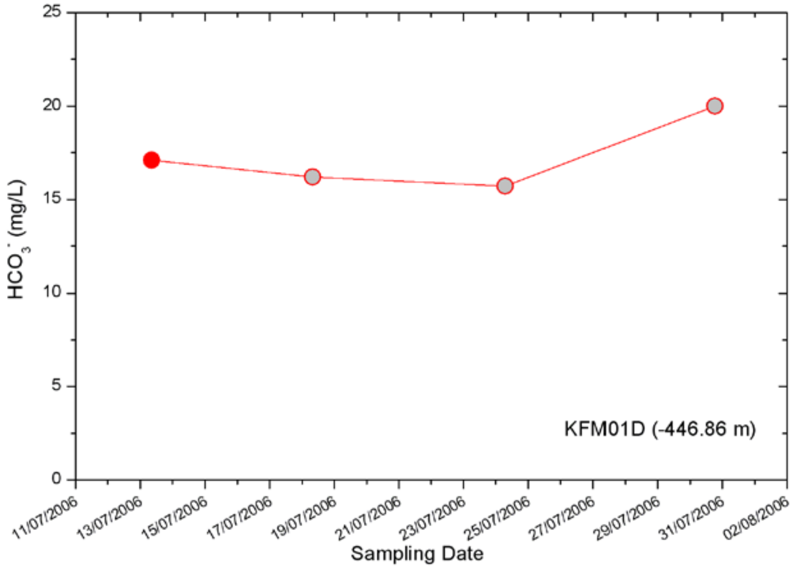


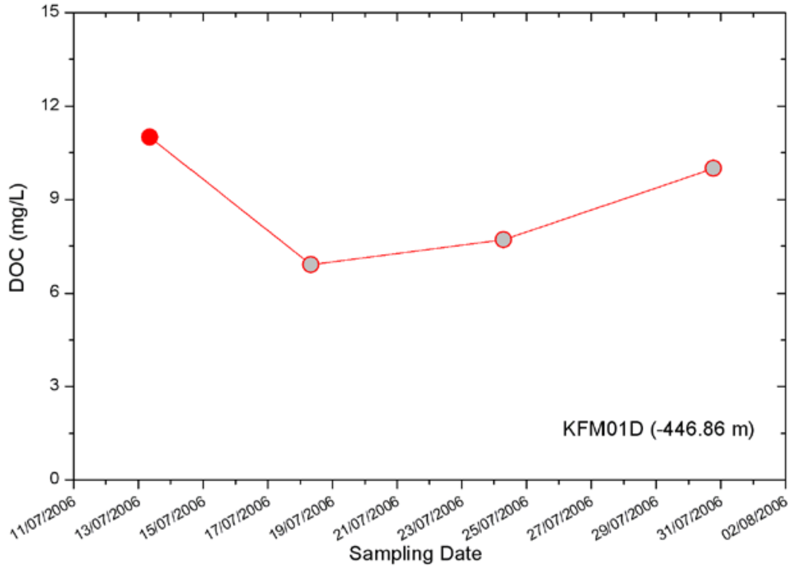

KFM01D (-446.86 m)
S(-II) (mg/L)
0.000
0.002
0.004
0.006
0.008
0.010
0.012
Sampling Date
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006

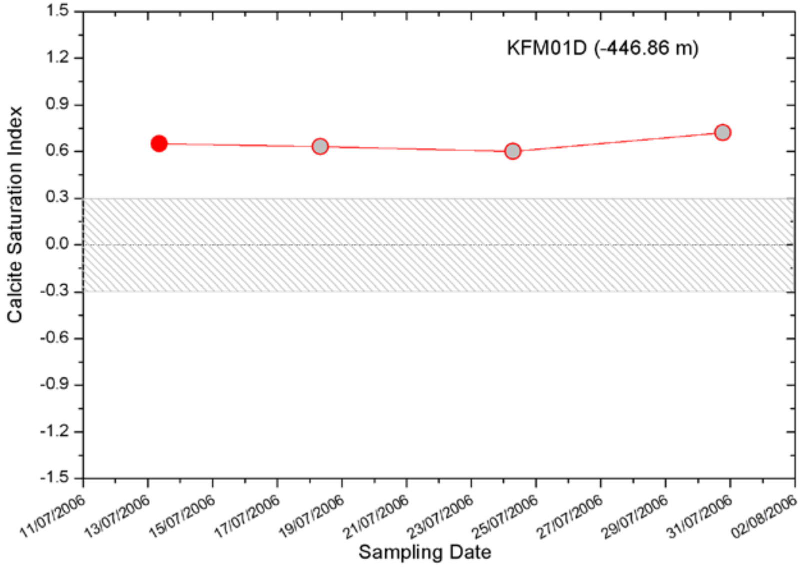

KFM01D (-446.86 m)
Fe (mg/L)
0.0
0.3
0.6
0.9
1.2
1.5
Sampling Date
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006

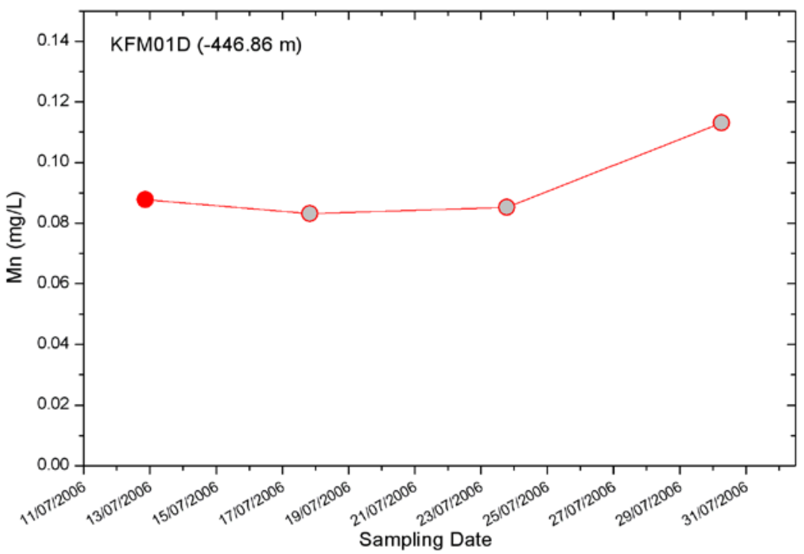

KFM01D (-446.86 m)
FeS(am) Saturation Index
-2.0
-1.6
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
1.6
2.0
Sampling Date
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006


KFM01D (-446.86 m)
δ34S (‰ CDT)
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
Sampling Date
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006

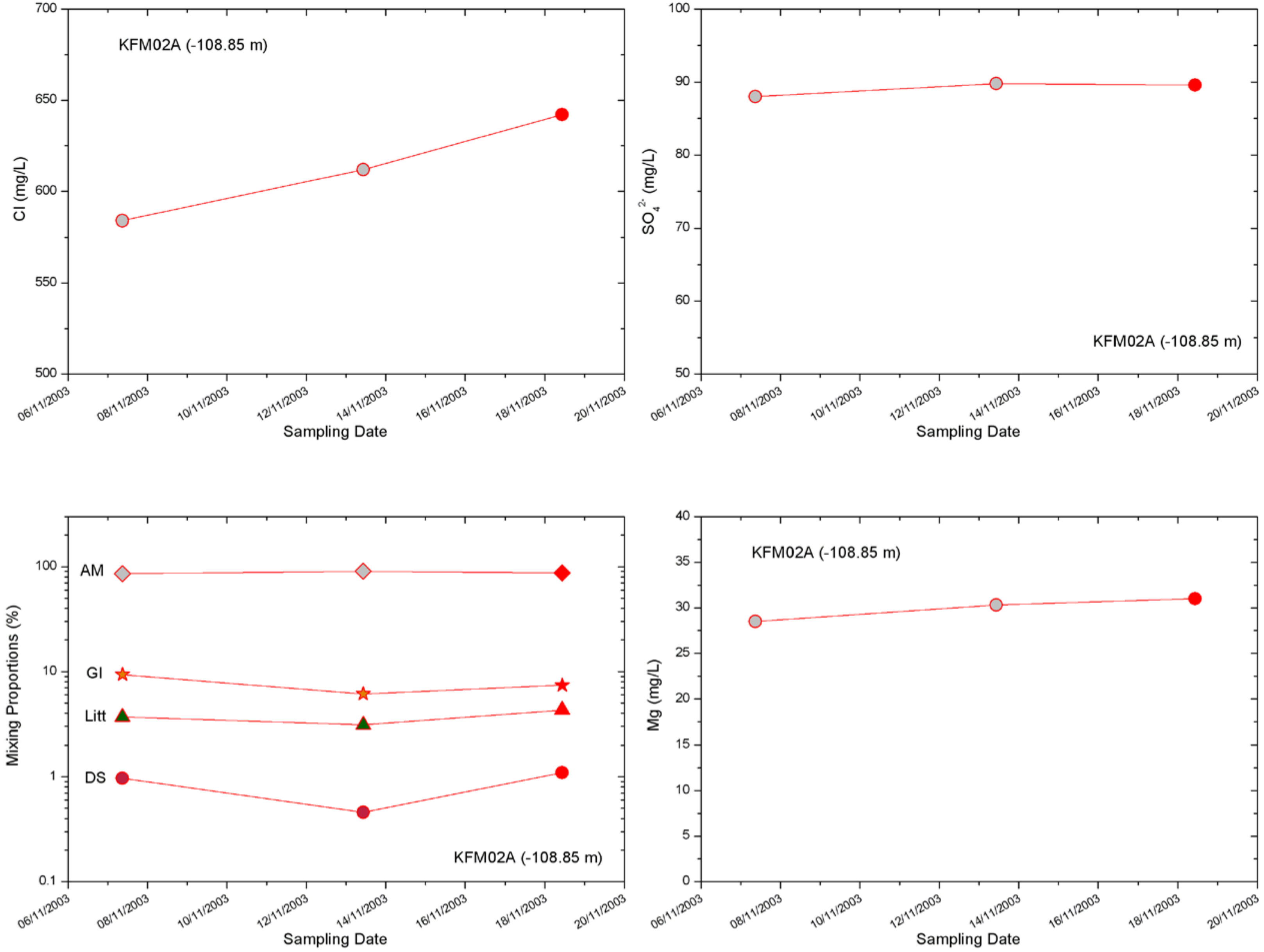

25
20
15
10
5
0
$HCO_3^-$ (mg/L)
KFM01D (-446.86 m)
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006
Sampling Date

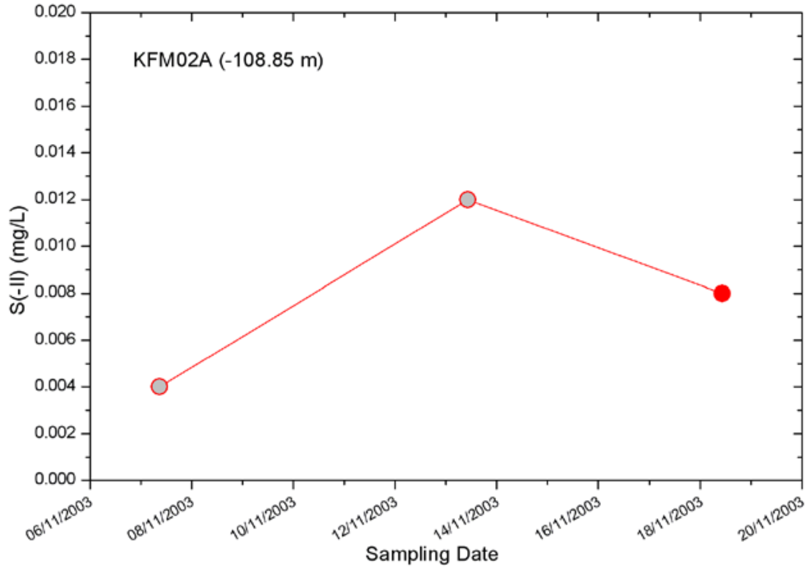

15
12
9
6
3
0
DOC (mg/L)
KFM01D (-446.86 m)
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006
Sampling Date

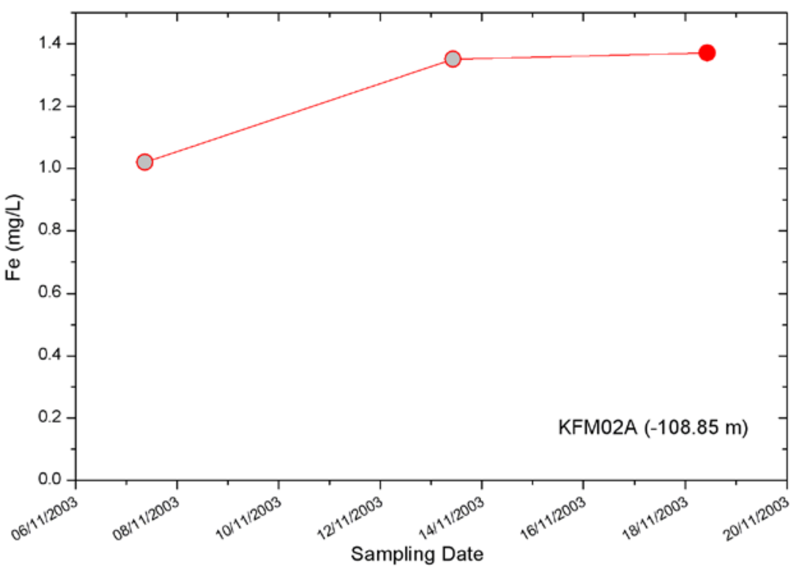

1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Calcite Saturation Index
KFM01D (-446.86 m)
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
02/08/2006
Sampling Date

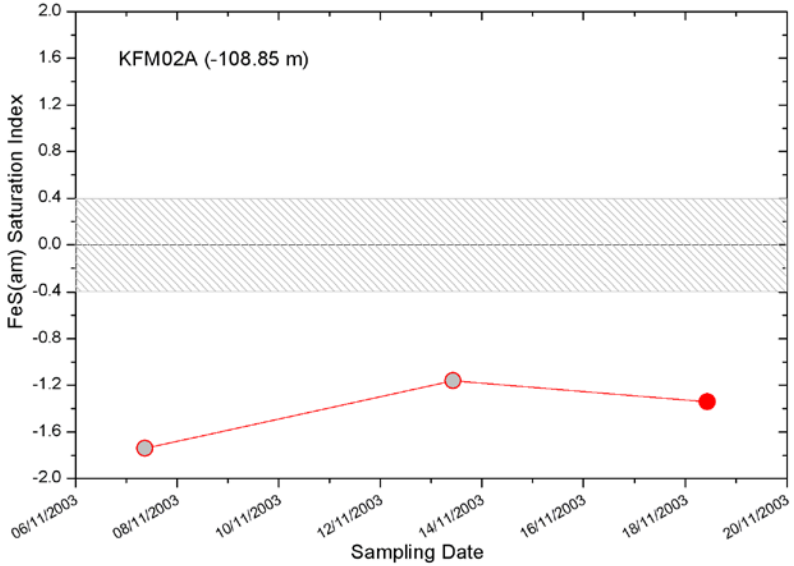

0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Mn (mg/L)
KFM01D (-446.86 m)
11/07/2006
13/07/2006
15/07/2006
17/07/2006
19/07/2006
21/07/2006
23/07/2006
25/07/2006
27/07/2006
29/07/2006
31/07/2006
Sampling Date

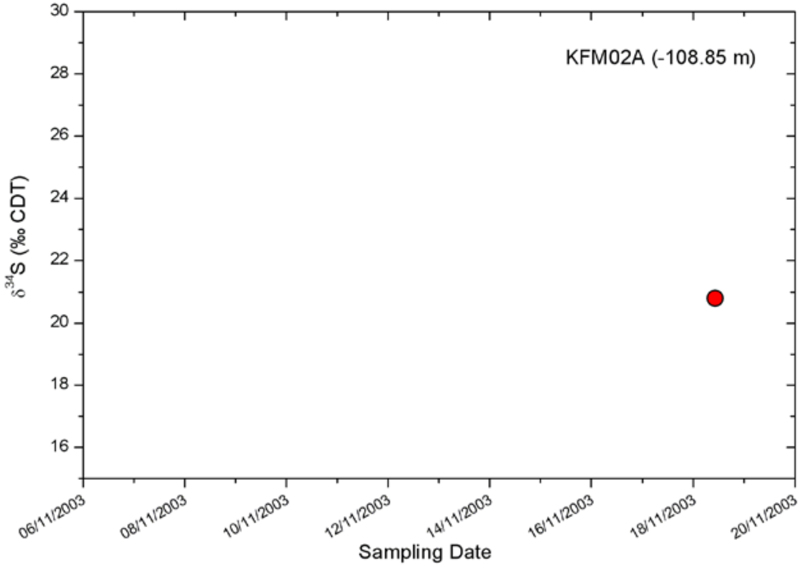
KFM02A (–108.85 m)

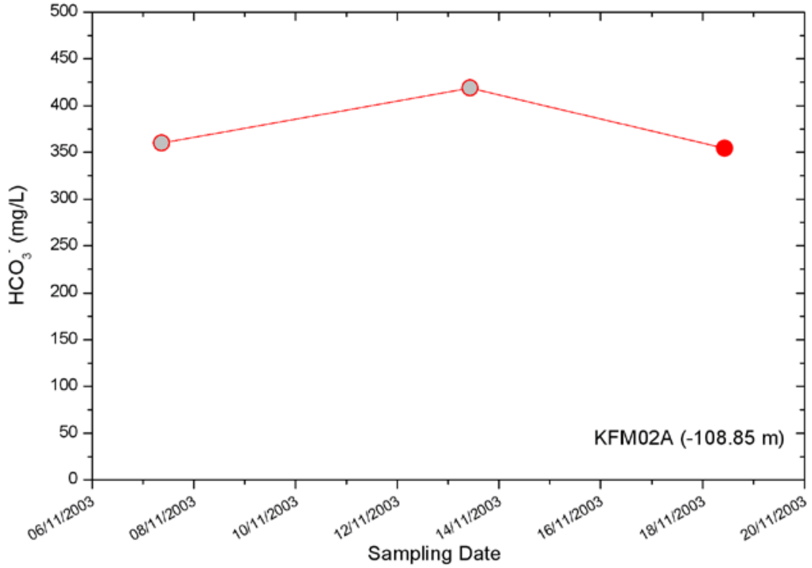


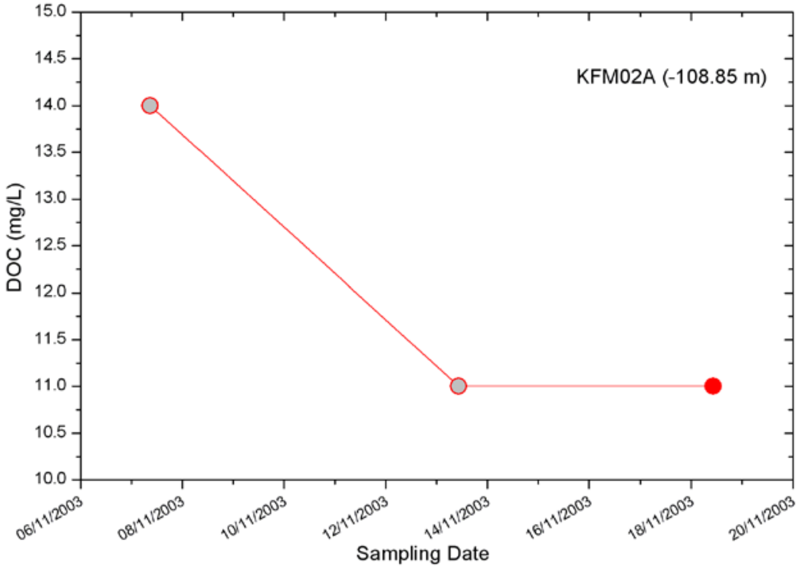

KFM02A (-108.85 m)
S(-II) (mg/L)
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

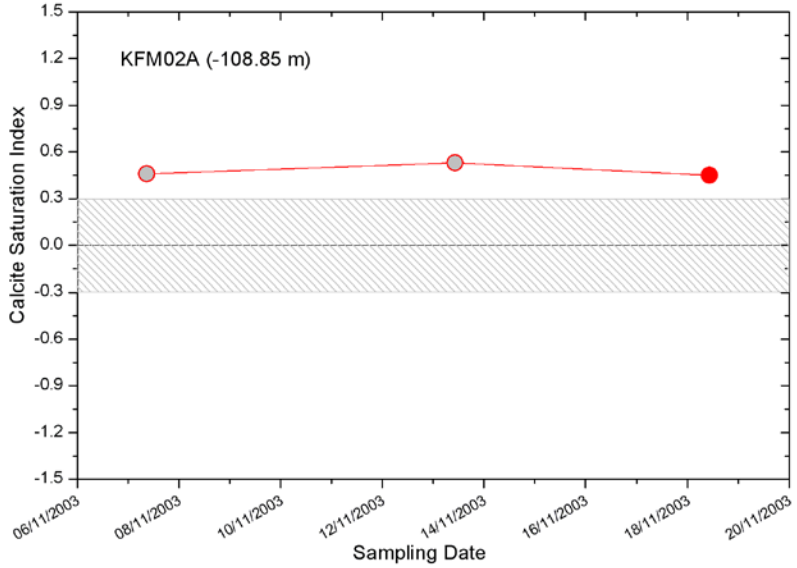

KFM02A (-108.85 m)
Fe (mg/L)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

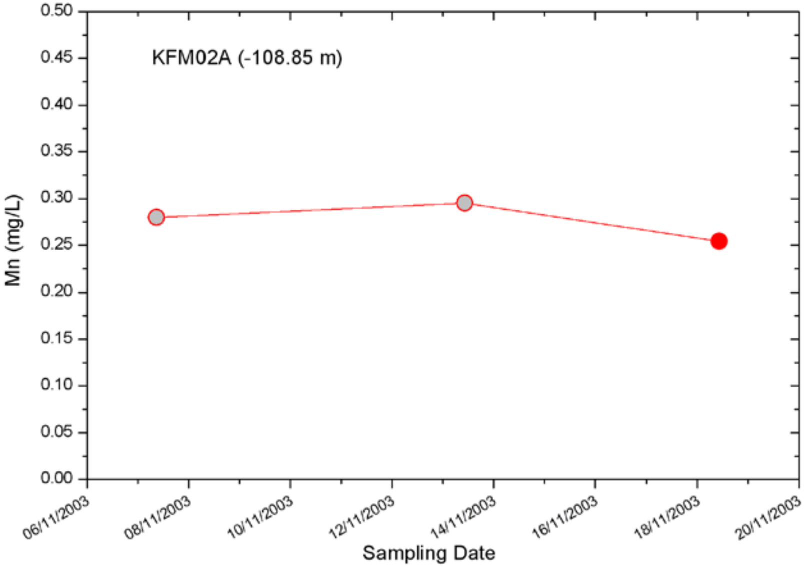

KFM02A (-108.85 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date


KFM02A (-108.85 m)
δ34S (‰ CDT)
30
28
26
24
22
20
18
16
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

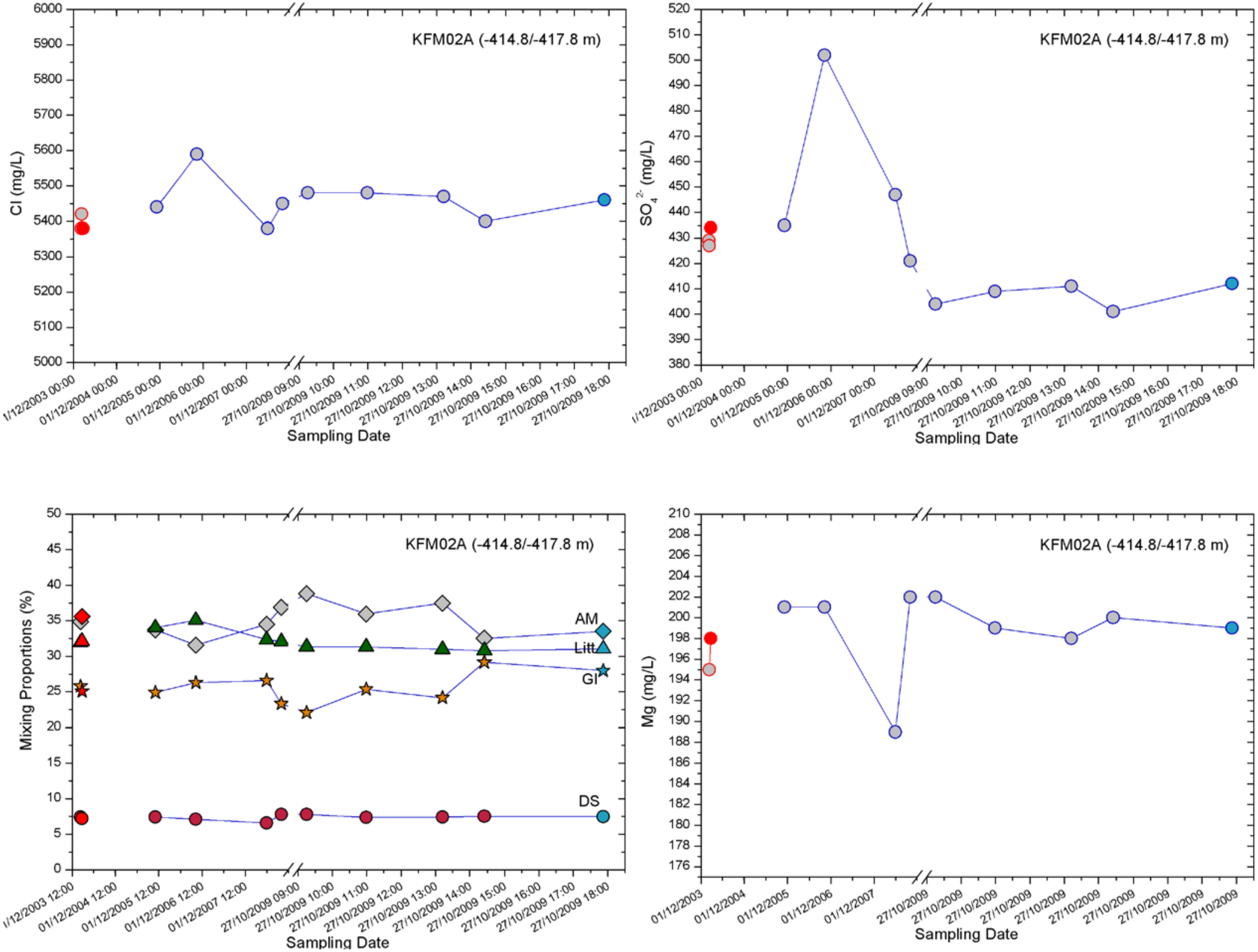

500
450
400
350
300
250
200
150
100
50
0
HCO$_3^-$ (mg/L)
KFM02A (-108.85 m)
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

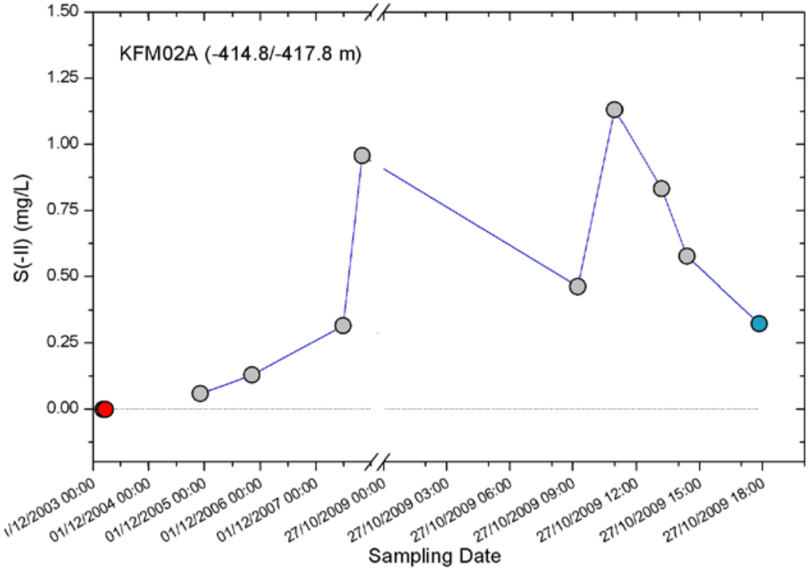

15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
DOC (mg/L)
KFM02A (-108.85 m)
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

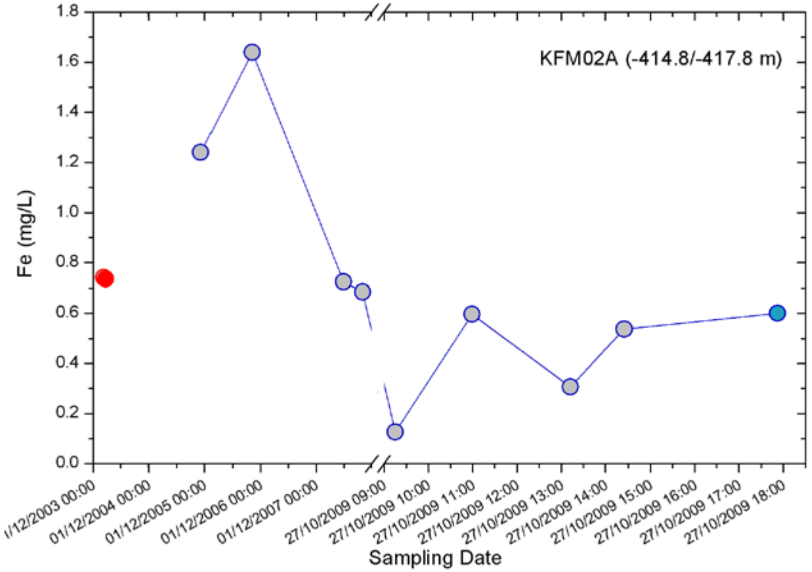

1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Calcite Saturation Index
KFM02A (-108.85 m)
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

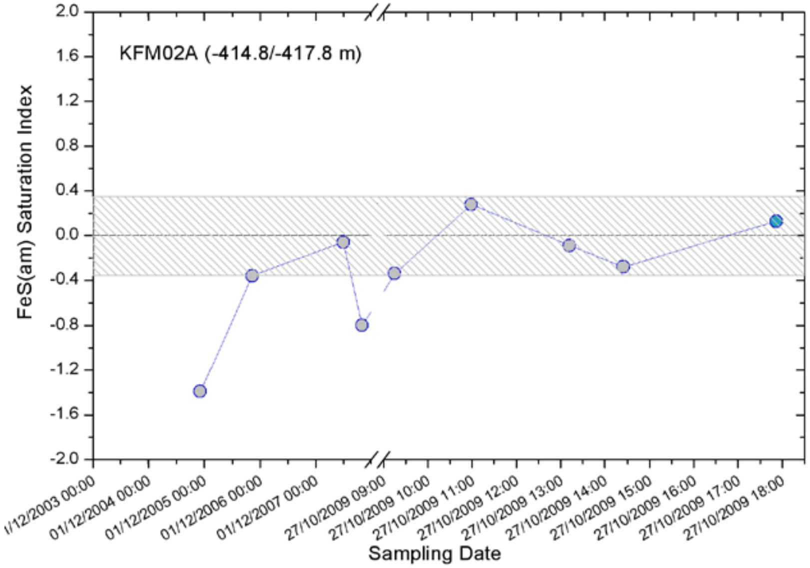

0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Mn (mg/L)
KFM02A (-108.85 m)
06/11/2003
08/11/2003
10/11/2003
12/11/2003
14/11/2003
16/11/2003
18/11/2003
20/11/2003
Sampling Date

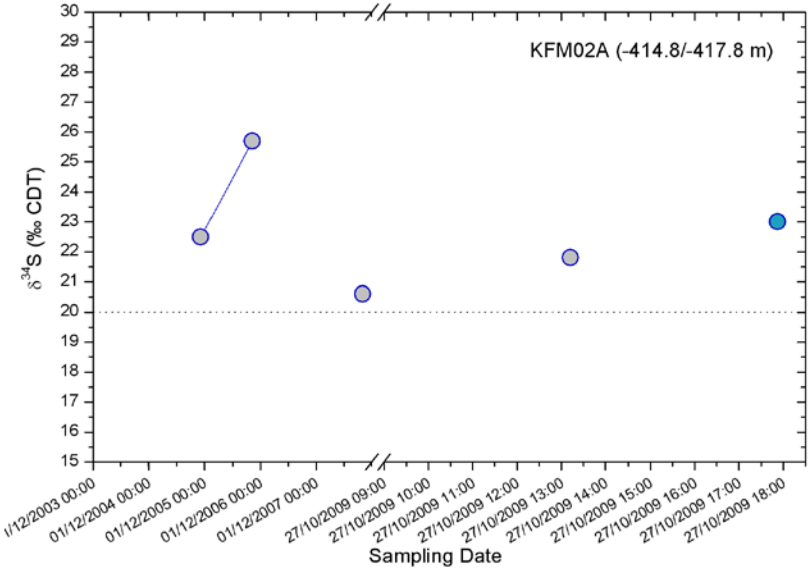
KFM02A (–414.81/–417.8 m)

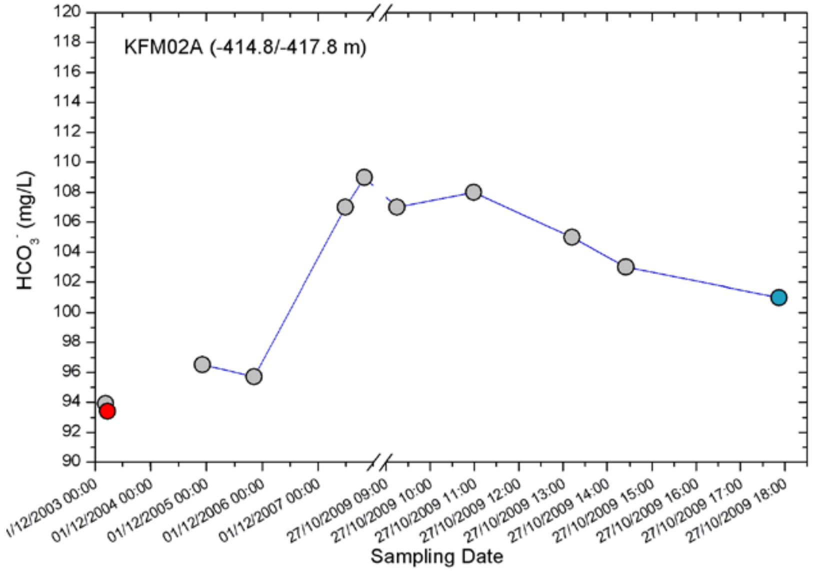


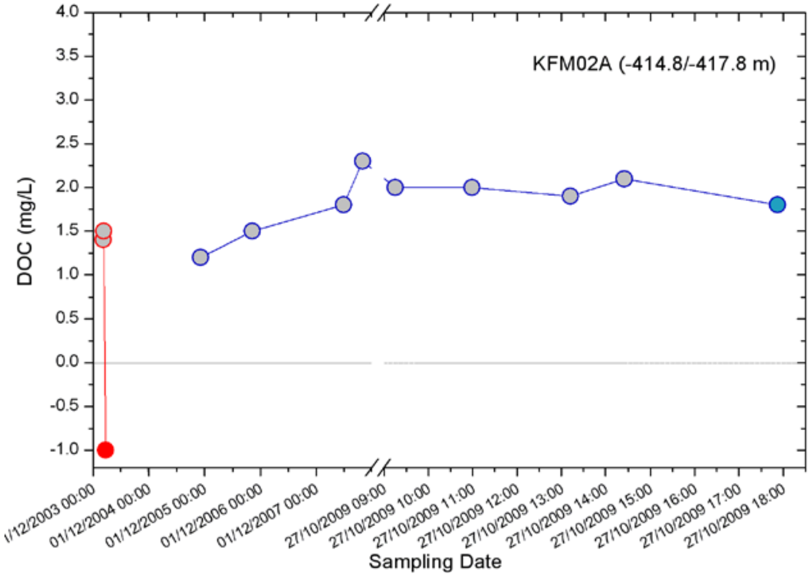

KFM02A (-414.8/-417.8 m)
S(-II) (mg/L)
1.50
1.25
1.00
0.75
0.50
0.25
0.00
Sampling Date
1/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 00:00
27/10/2009 03:00
27/10/2009 06:00
27/10/2009 09:00
27/10/2009 12:00
27/10/2009 15:00
27/10/2009 18:00

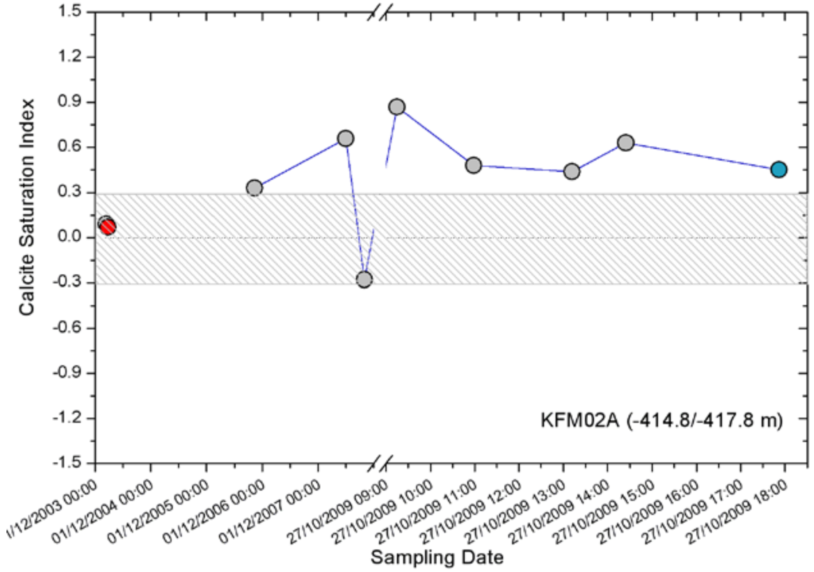

KFM02A (-414.8/-417.8 m)
Fe (mg/L)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Sampling Date
1/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00

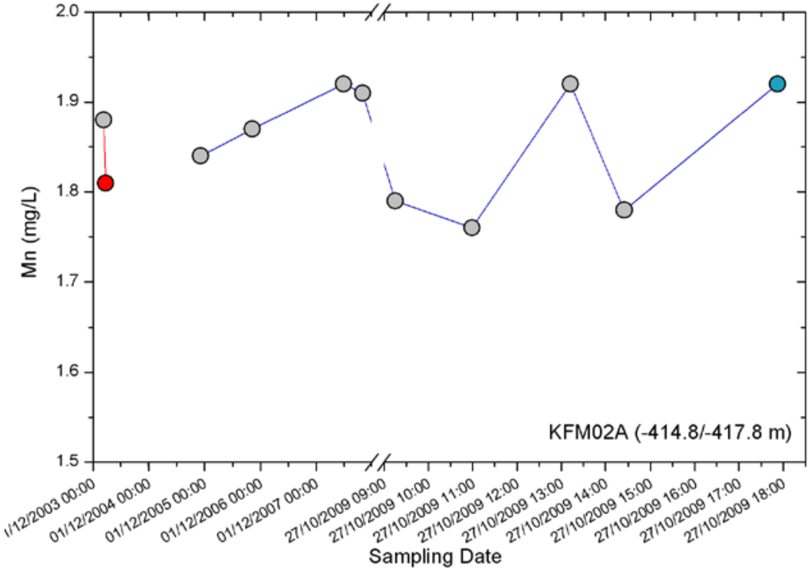

KFM02A (-414.8/-417.8 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
Sampling Date
1/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00


KFM02A (-414.8/-417.8 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
Sampling Date
1/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00

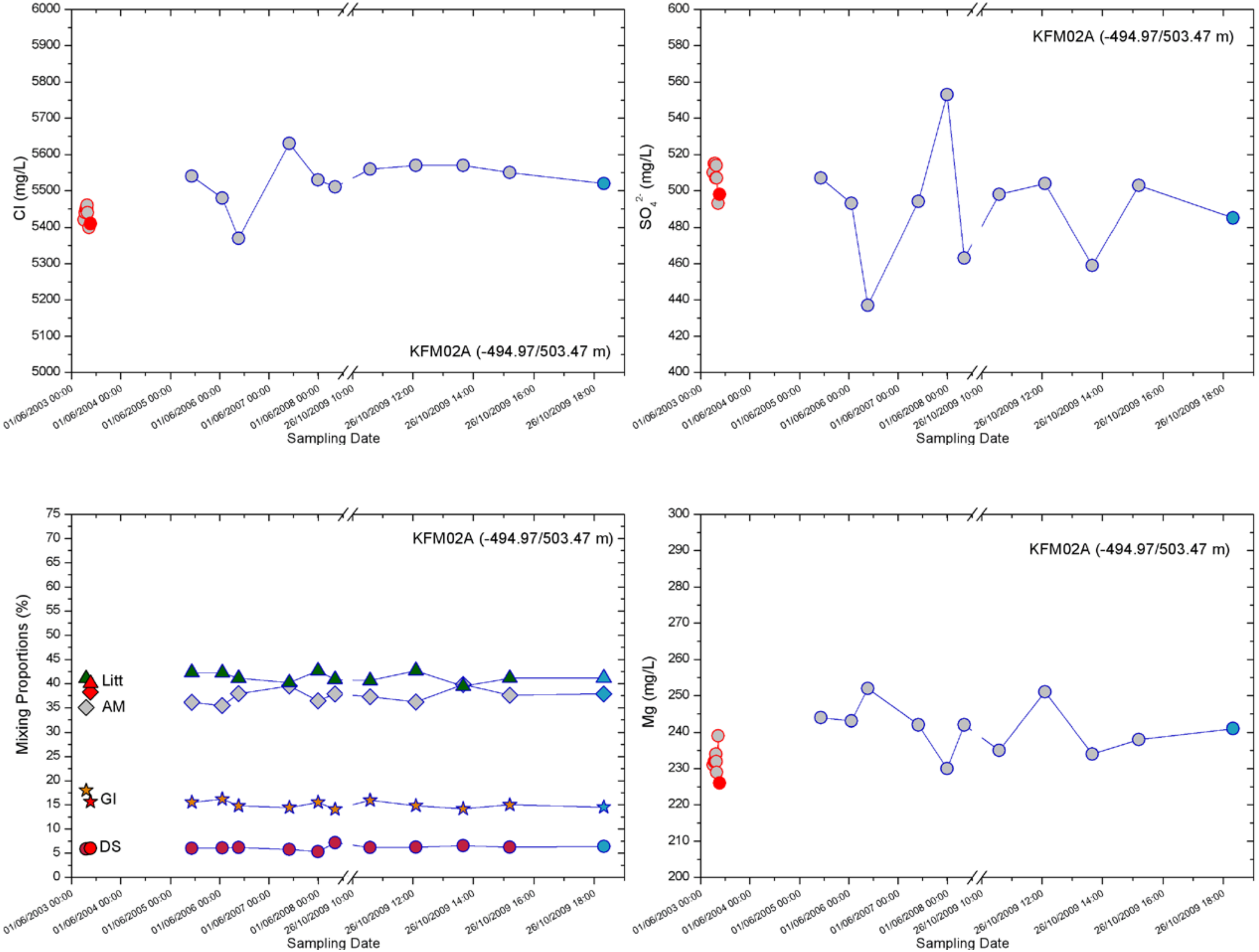

KFM02A (-414.8/-417.8 m)
$HCO_3^-$ (mg/L)
120
118
116
114
112
110
108
106
104
102
100
98
96
94
92
90
/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00
Sampling Date

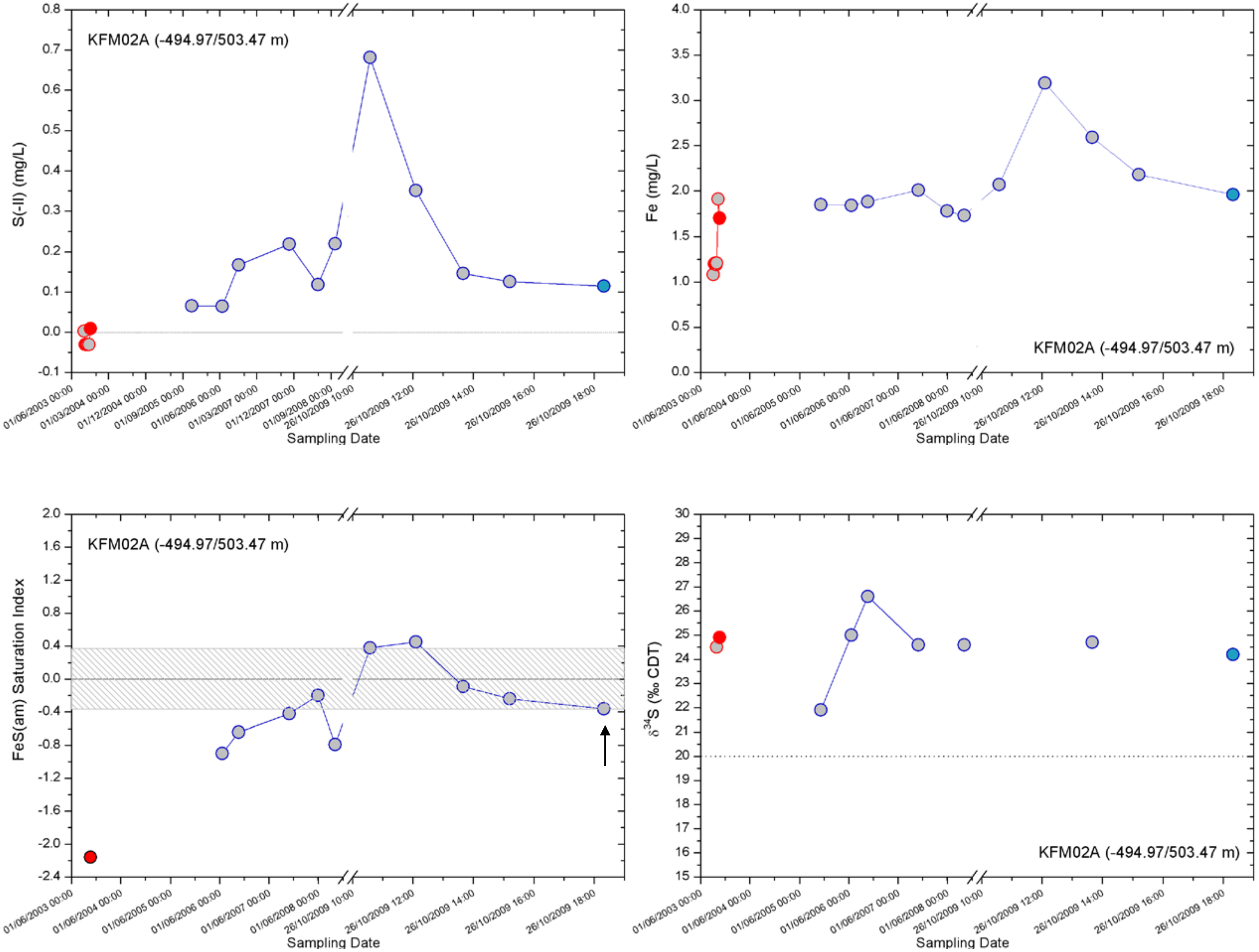

KFM02A (-414.8/-417.8 m)
DOC (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00
Sampling Date

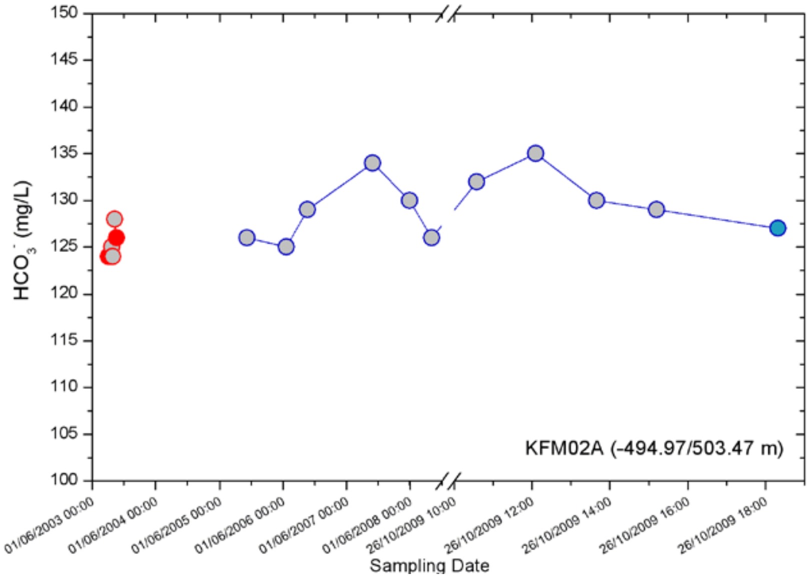

KFM02A (-414.8/-417.8 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00
Sampling Date

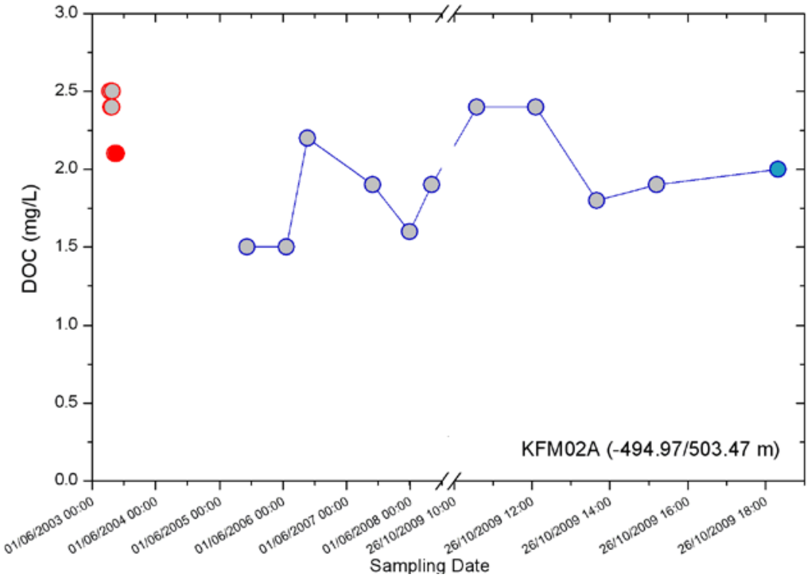

KFM02A (-414.8/-417.8 m)
Mn (mg/L)
2.0
1.9
1.8
1.7
1.6
1.5
/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
27/10/2009 09:00
27/10/2009 10:00
27/10/2009 11:00
27/10/2009 12:00
27/10/2009 13:00
27/10/2009 14:00
27/10/2009 15:00
27/10/2009 16:00
27/10/2009 17:00
27/10/2009 18:00
Sampling Date

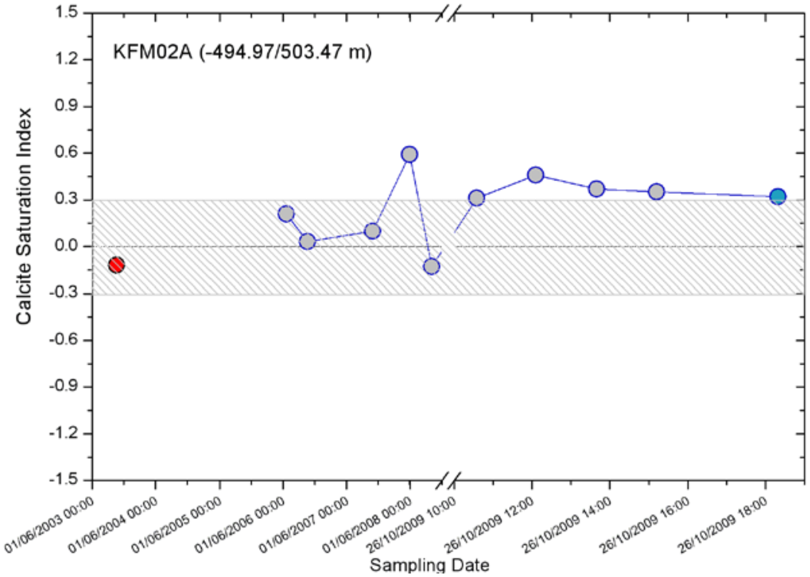
KFM02A (–494.97 / –503.47 m)
Eh = –143 mV)

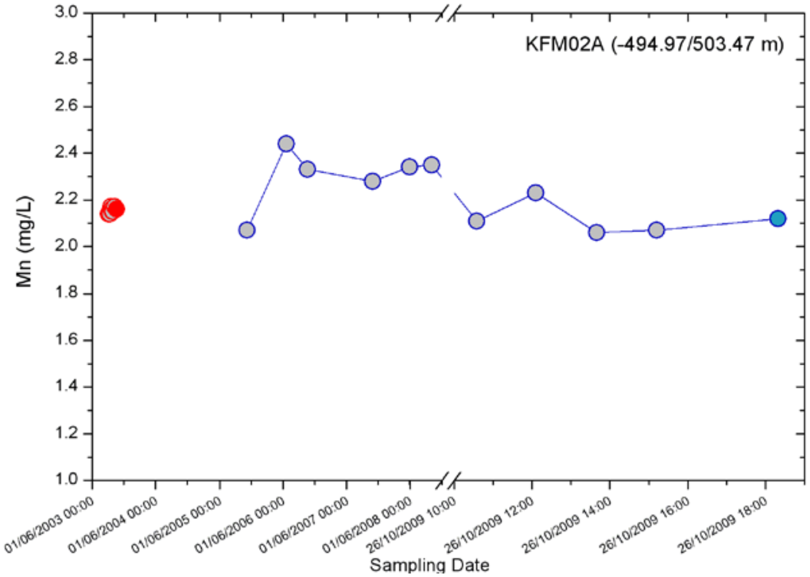



KFM02A (-494.97/503.47 m)
S(-II) (mg/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
01/06/2003 00:00
01/03/2004 00:00
01/12/2004 00:00
01/09/2005 00:00
01/06/2006 00:00
01/03/2007 00:00
01/12/2007 00:00
01/09/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date
Fe (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
KFM02A (-494.97/503.47 m)
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date
KFM02A (-494.97/503.47 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
KFM02A (-494.97/503.47 m)
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date

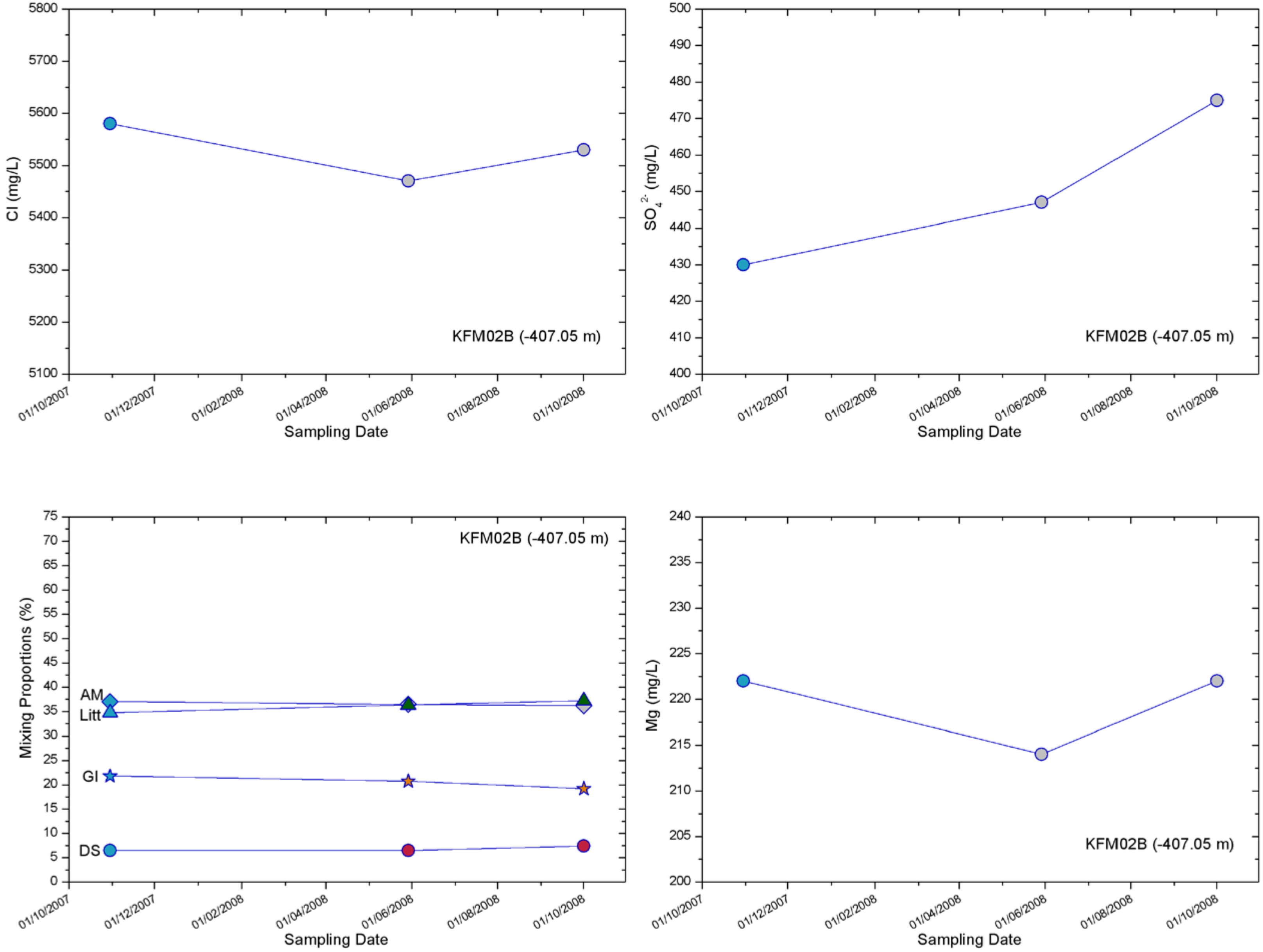

150
145
140
135
130
125
120
115
110
105
100
HCO$_3^-$ (mg/L)
KFM02A (-494.97/503.47 m)
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date

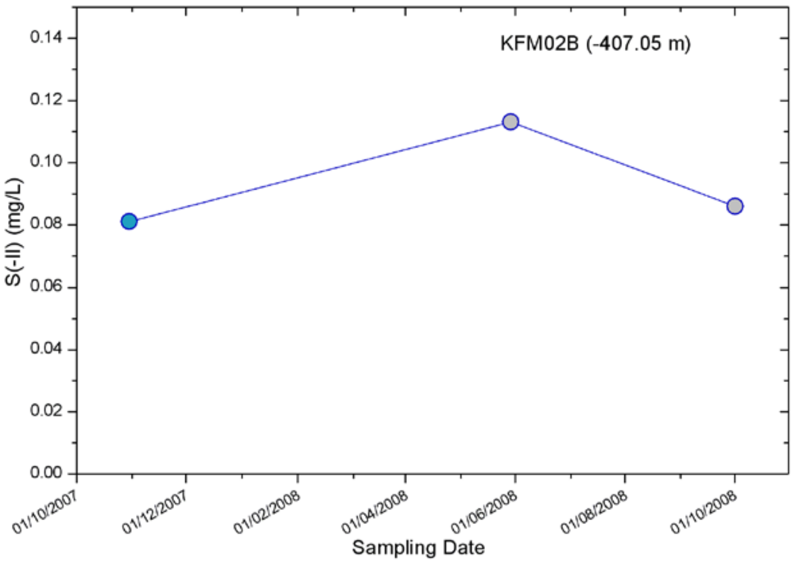

3.0
2.5
2.0
1.5
1.0
0.5
0.0
DOC (mg/L)
KFM02A (-494.97/503.47 m)
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date

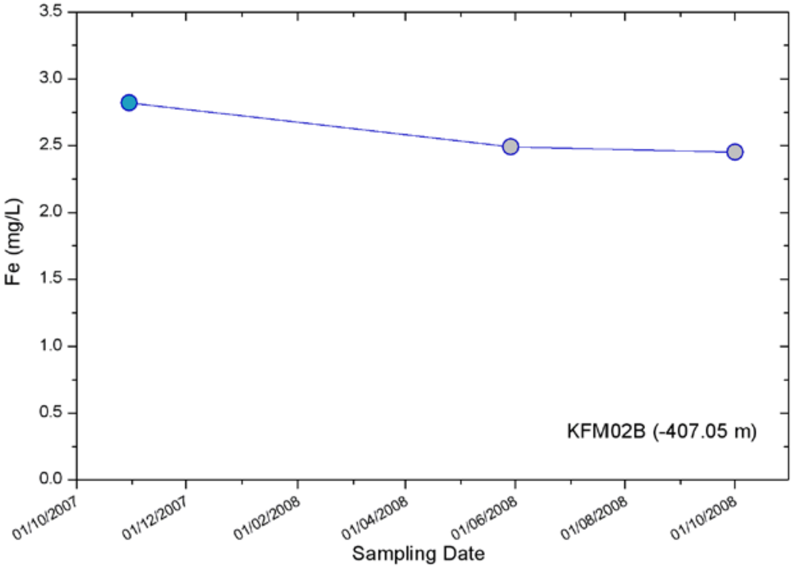

1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Calcite Saturation Index
KFM02A (-494.97/503.47 m)
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date

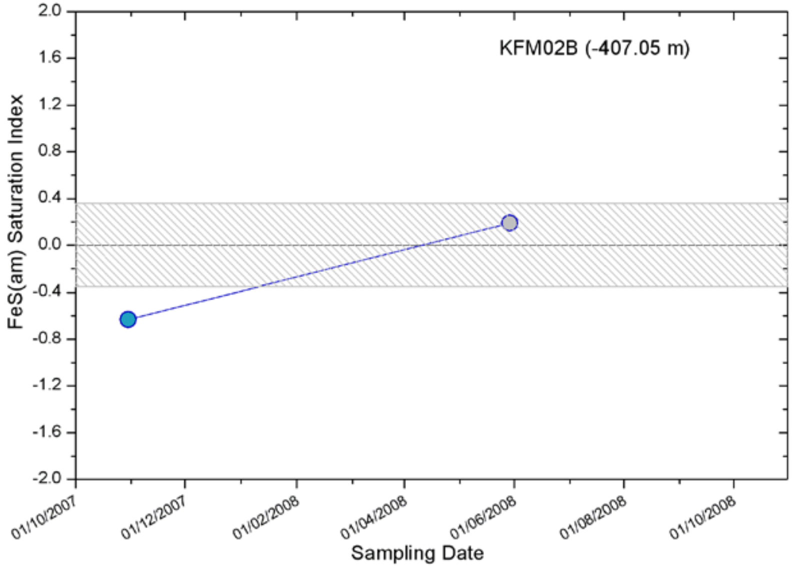

3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
Mn (mg/L)
KFM02A (-494.97/503.47 m)
01/06/2003 00:00
01/06/2004 00:00
01/06/2005 00:00
01/06/2006 00:00
01/06/2007 00:00
01/06/2008 00:00
26/10/2009 10:00
26/10/2009 12:00
26/10/2009 14:00
26/10/2009 16:00
26/10/2009 18:00
Sampling Date

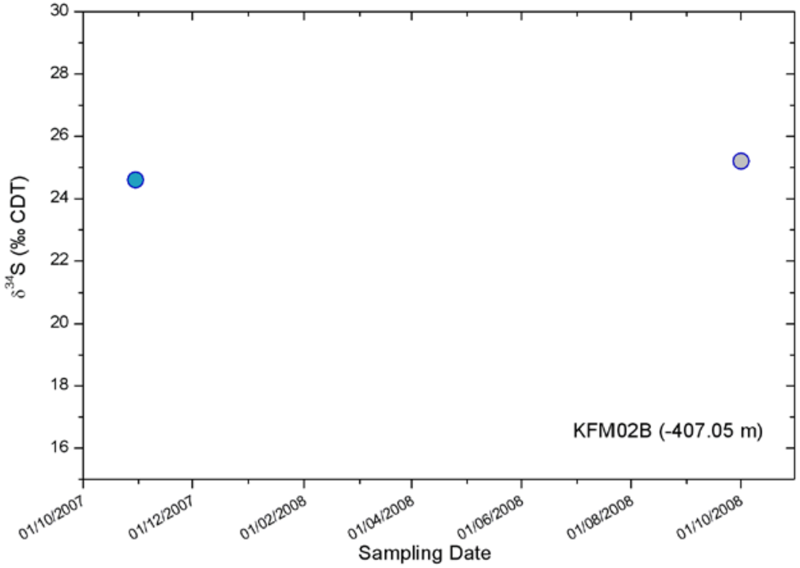
KFM02B (–407.05 m)

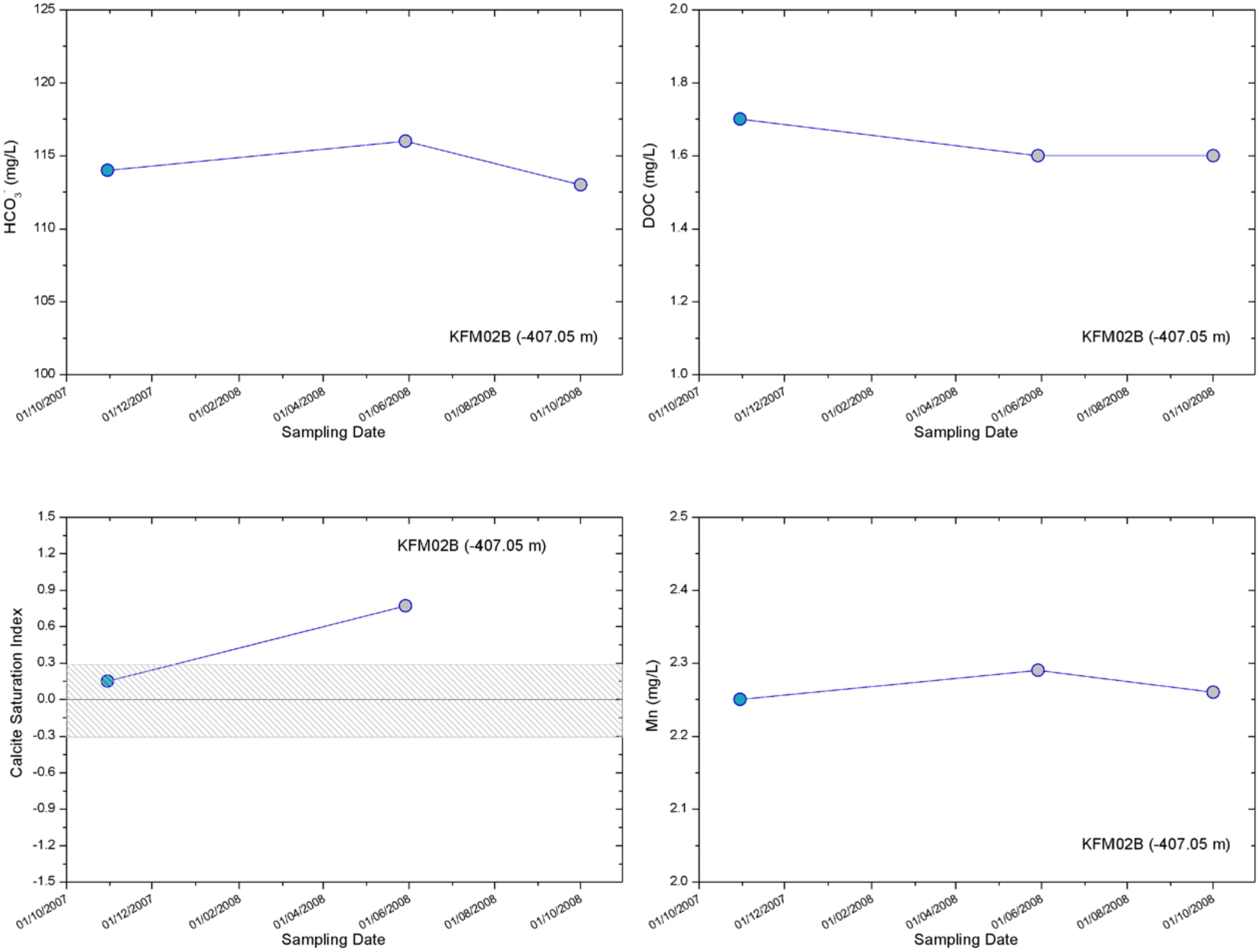



KFM02B (-407.05 m)
S(-II) (mg/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
Sampling Date
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008

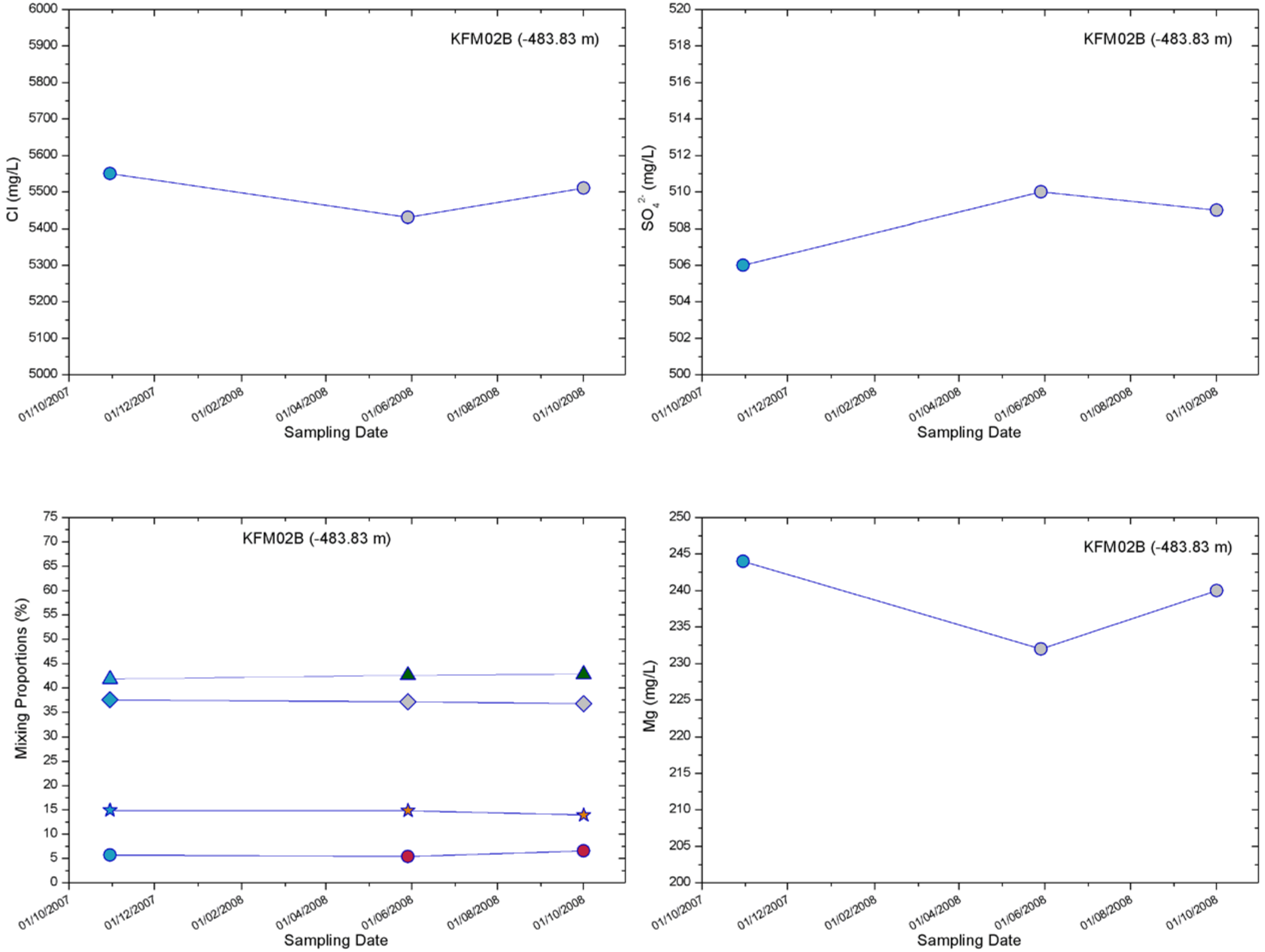

Fe (mg/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
KFM02B (-407.05 m)
Sampling Date
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008

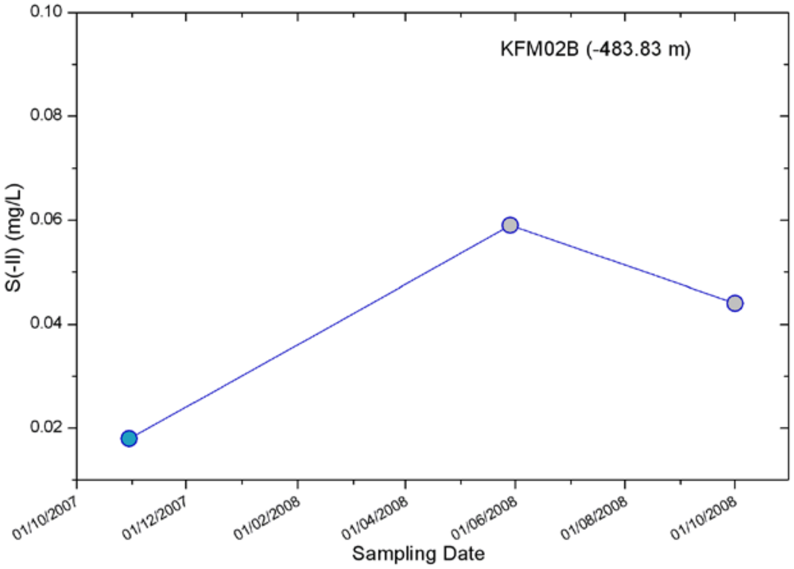

KFM02B (-407.05 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
Sampling Date
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008

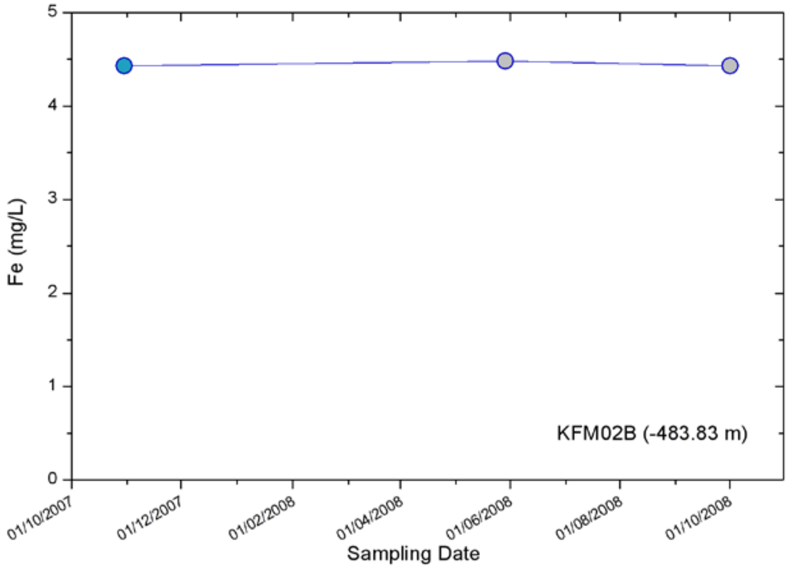

δ34S (‰ CDT)
16
18
20
22
24
26
28
30
KFM02B (-407.05 m)
Sampling Date
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008

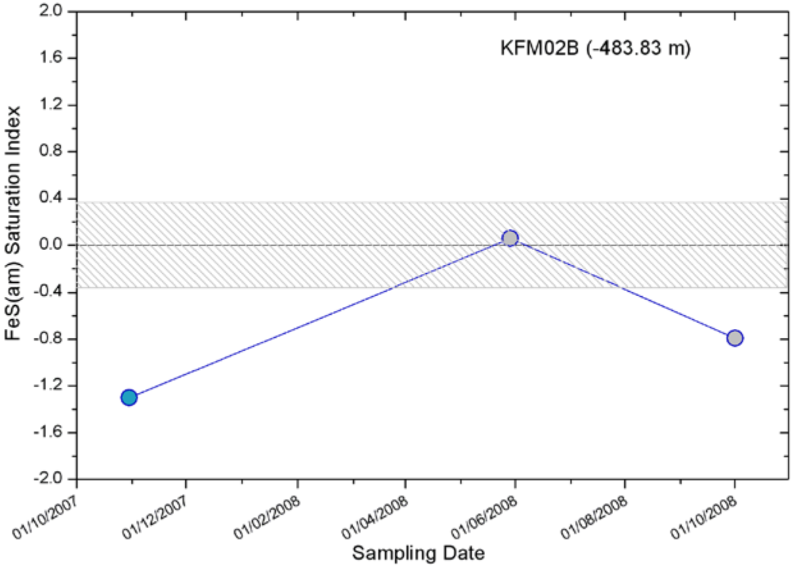

HCO3- (mg/L)
125
120
115
110
105
100
KFM02B (-407.05 m)
DOC (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
KFM02B (-407.05 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
KFM02B (-407.05 m)
Mn (mg/L)
2.5
2.4
2.3
2.2
2.1
2.0
KFM02B (-407.05 m)
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

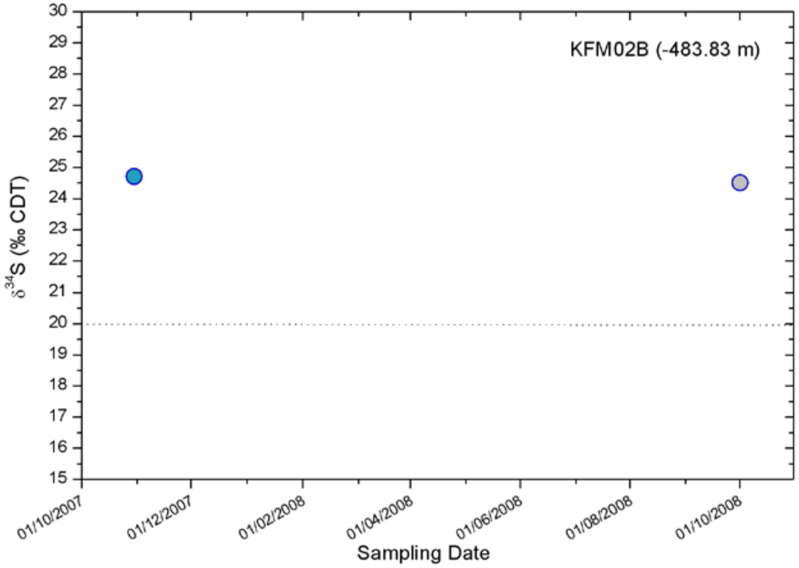
KFM02B (–483.83 m)

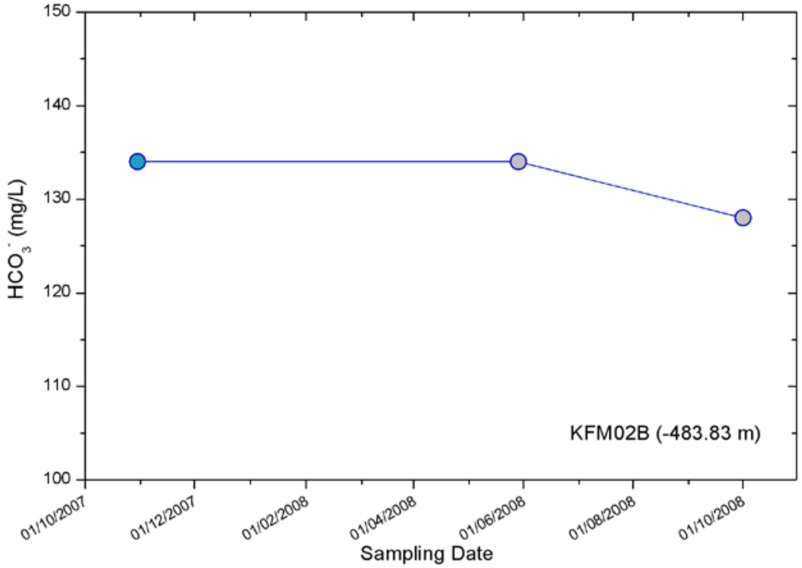


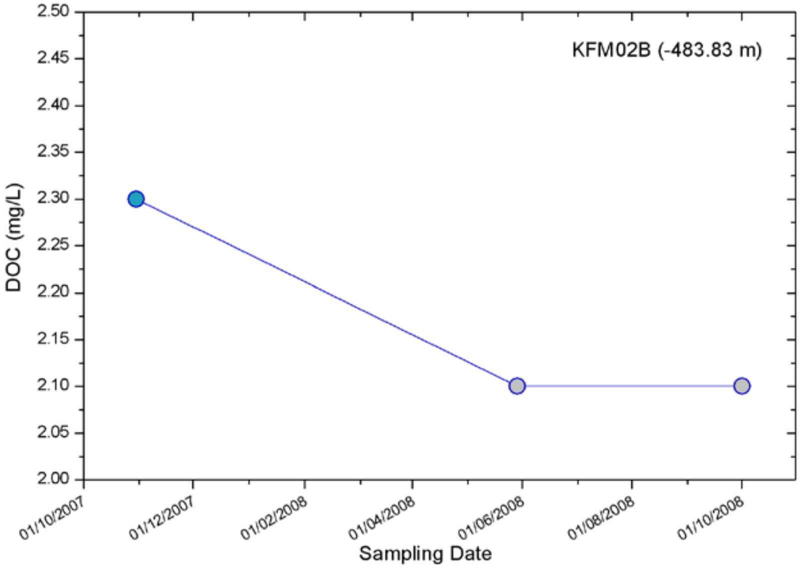

KFM02B (-483.83 m)
S(-II) (mg/L)
0.10
0.08
0.06
0.04
0.02
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

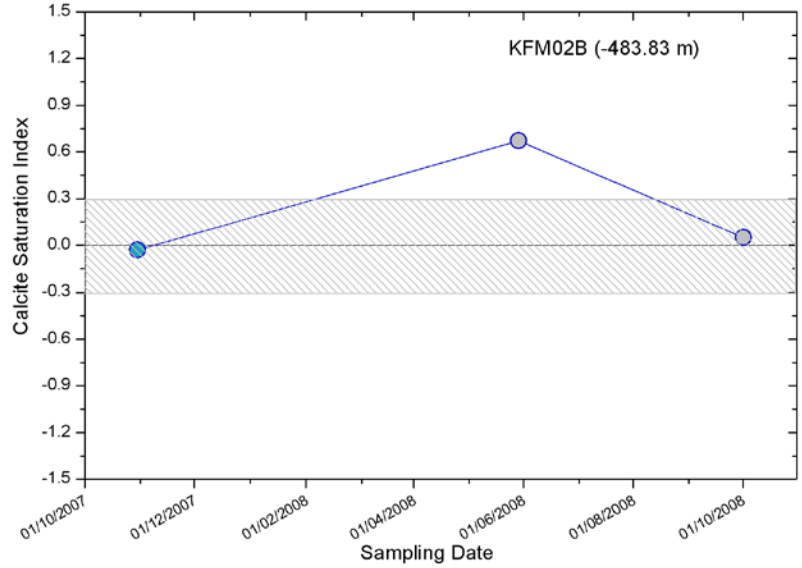

KFM02B (-483.83 m)
Fe (mg/L)
5
4
3
2
1
0
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

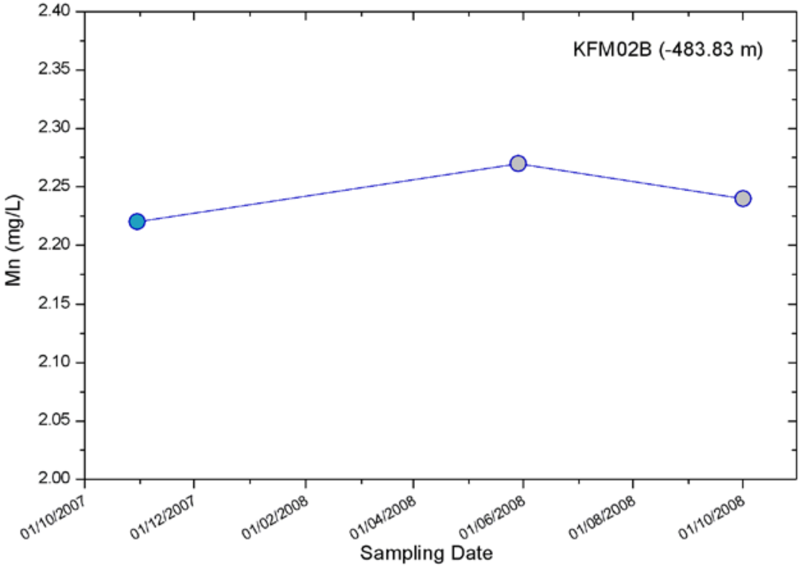

KFM02B (-483.83 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date


KFM02B (-483.83 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

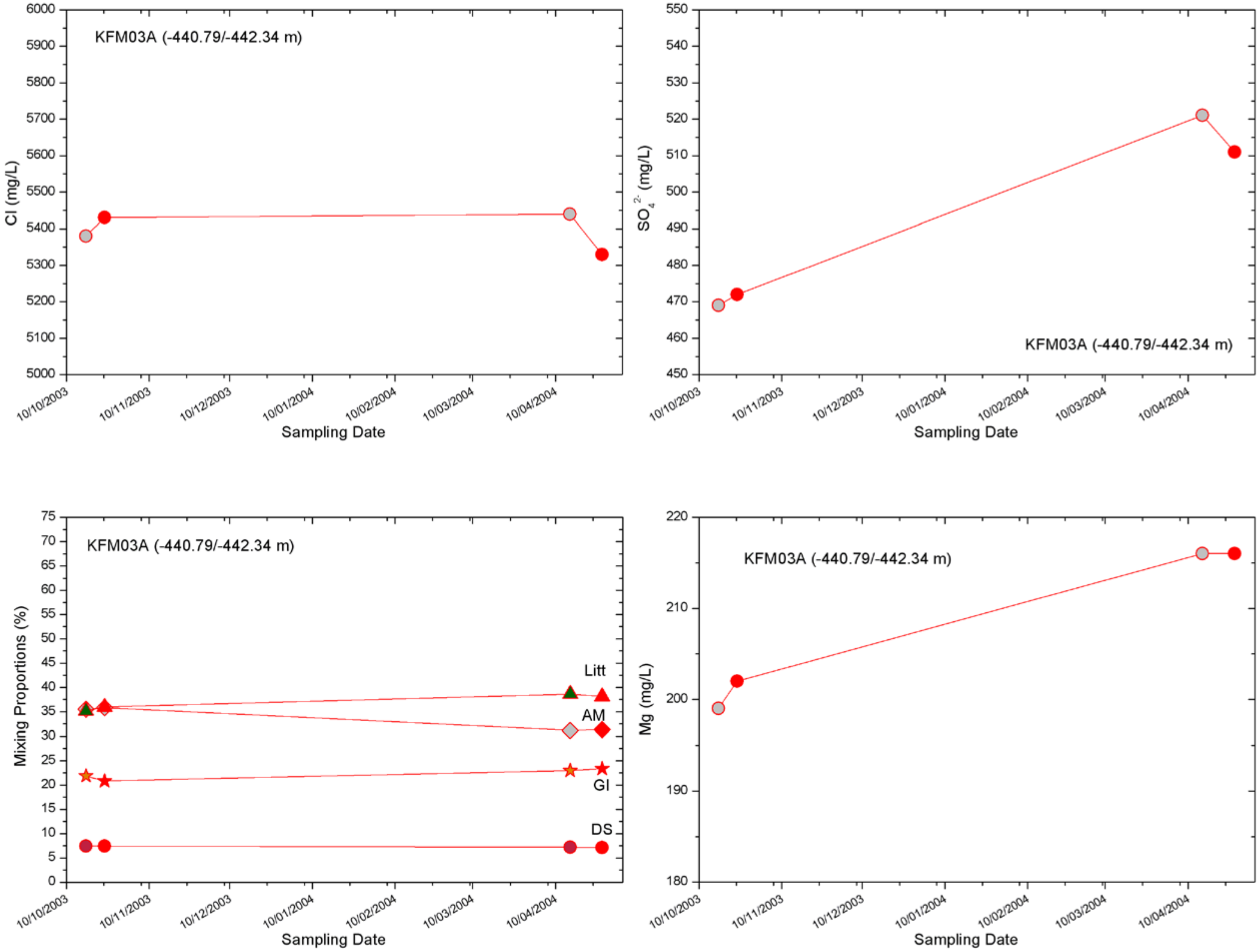

KFM02B (-483.83 m)
$HCO_3^-$ (mg/L)
150
140
130
120
110
100
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

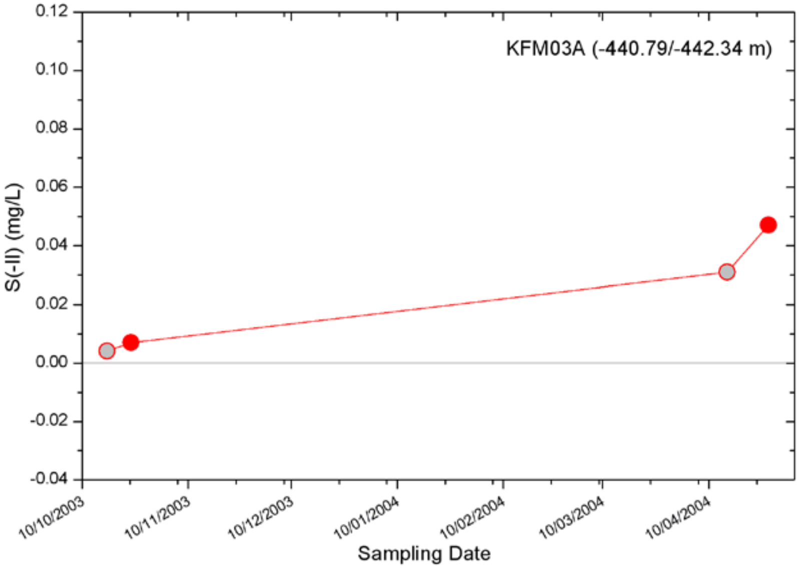

KFM02B (-483.83 m)
DOC (mg/L)
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

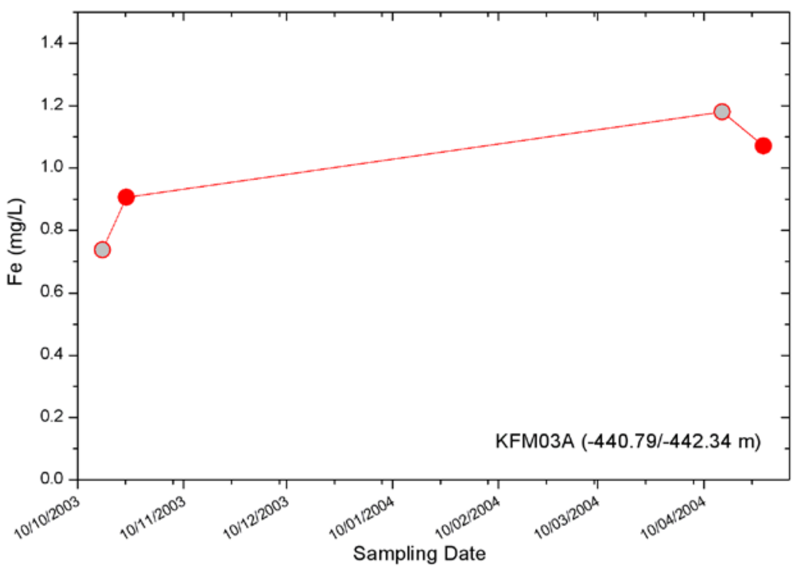

KFM02B (-483.83 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

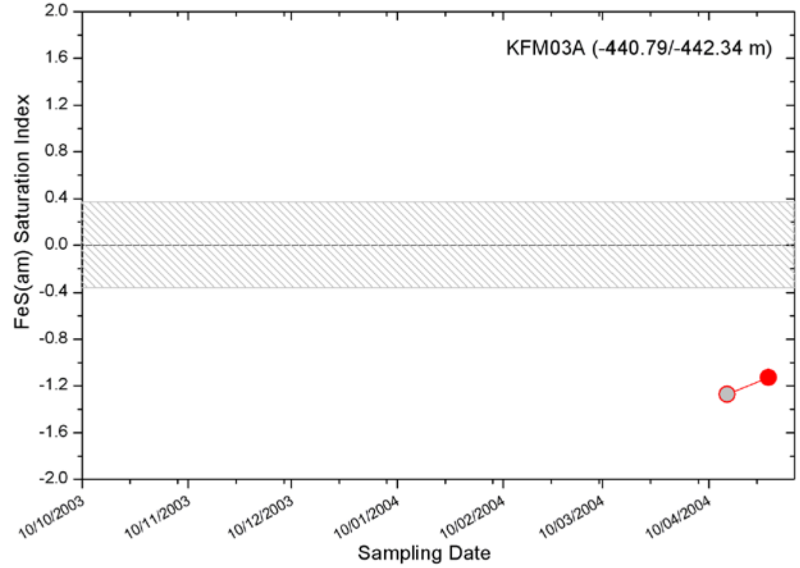

KFM02B (-483.83 m)
Mn (mg/L)
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
01/10/2007
01/12/2007
01/02/2008
01/04/2008
01/06/2008
01/08/2008
01/10/2008
Sampling Date

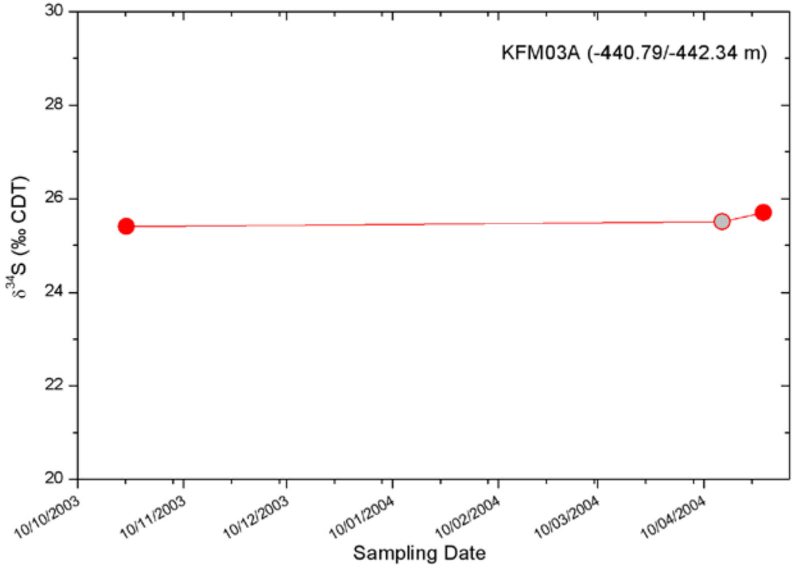
KFM03A (–440.79/–442.34 m)
Eh = –176 mV

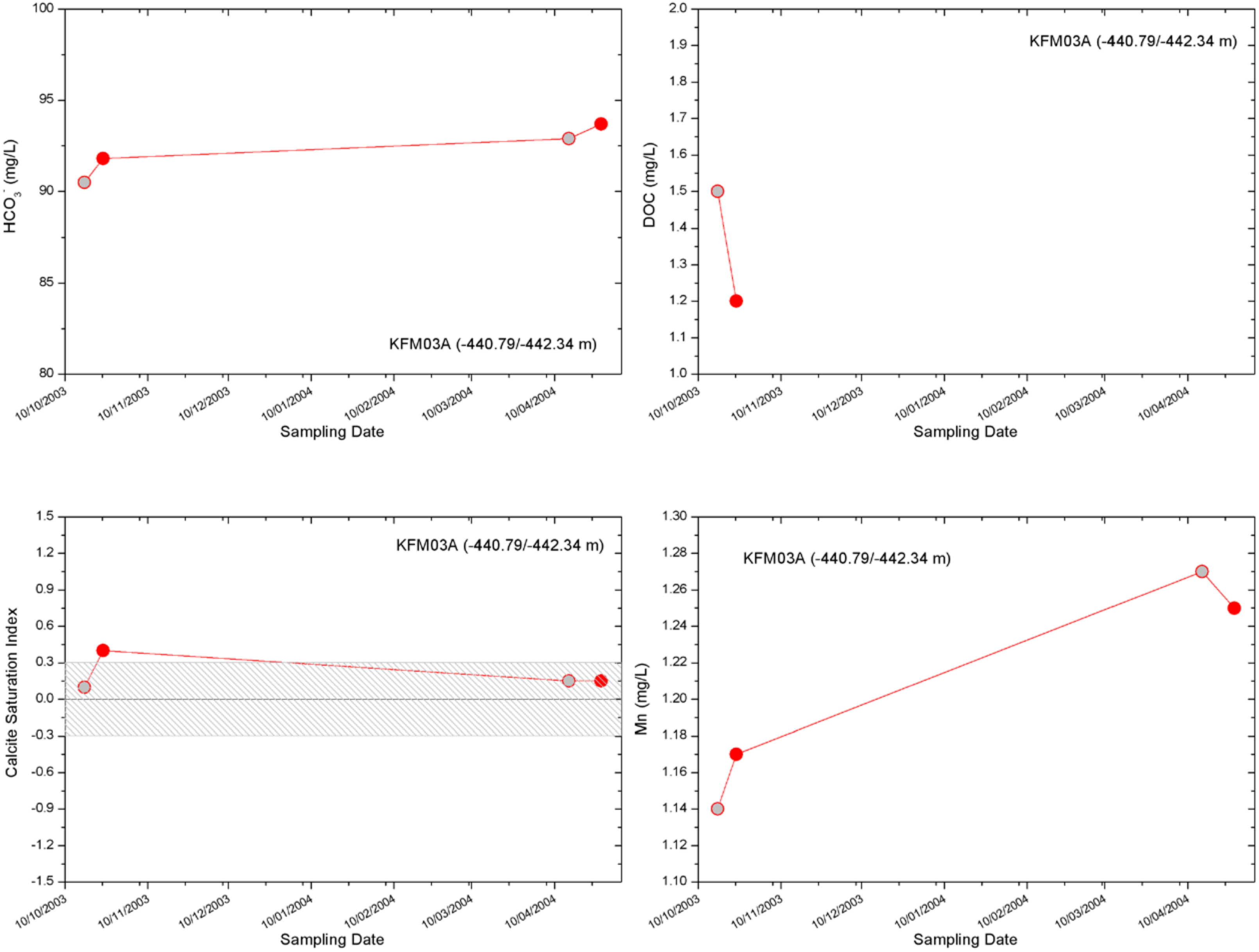



KFM03A (-440.79/-442.34 m)
S(-II) (mg/L)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
10/10/2003
10/11/2003
10/12/2003
10/01/2004
10/02/2004
10/03/2004
10/04/2004
Sampling Date

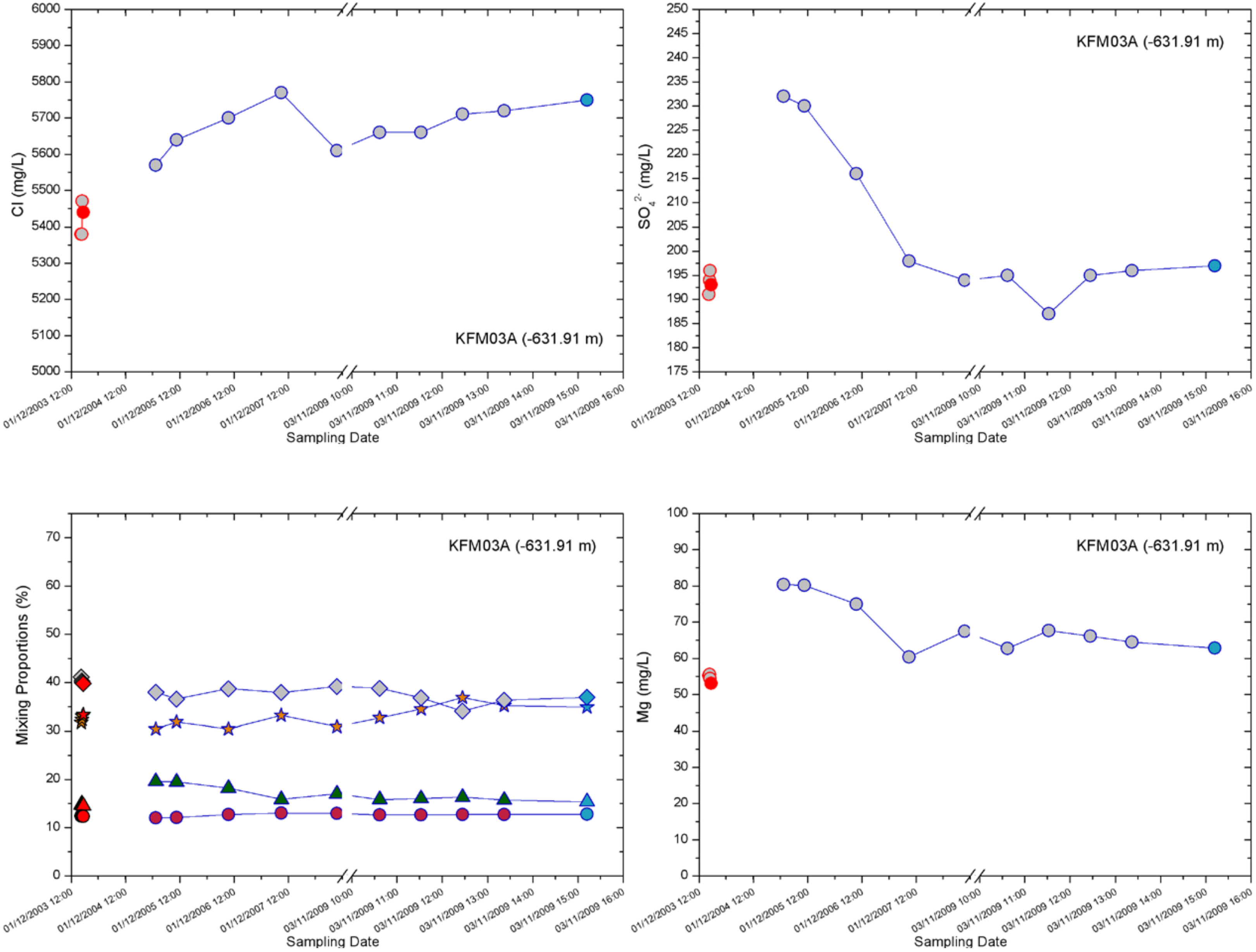

Fe (mg/L)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
KFM03A (-440.79/-442.34 m)
10/10/2003
10/11/2003
10/12/2003
10/01/2004
10/02/2004
10/03/2004
10/04/2004
Sampling Date

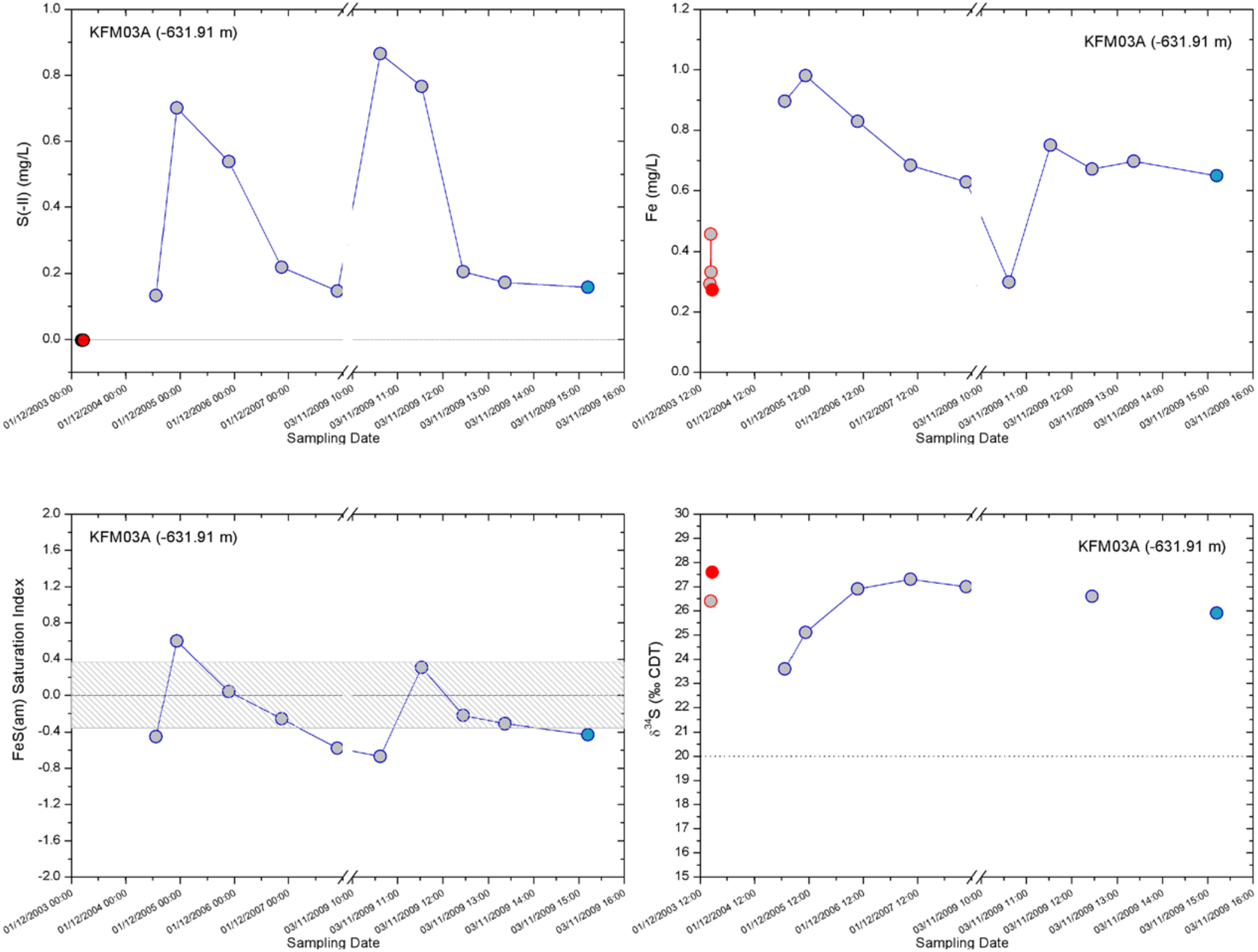

KFM03A (-440.79/-442.34 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
10/10/2003
10/11/2003
10/12/2003
10/01/2004
10/02/2004
10/03/2004
10/04/2004
Sampling Date

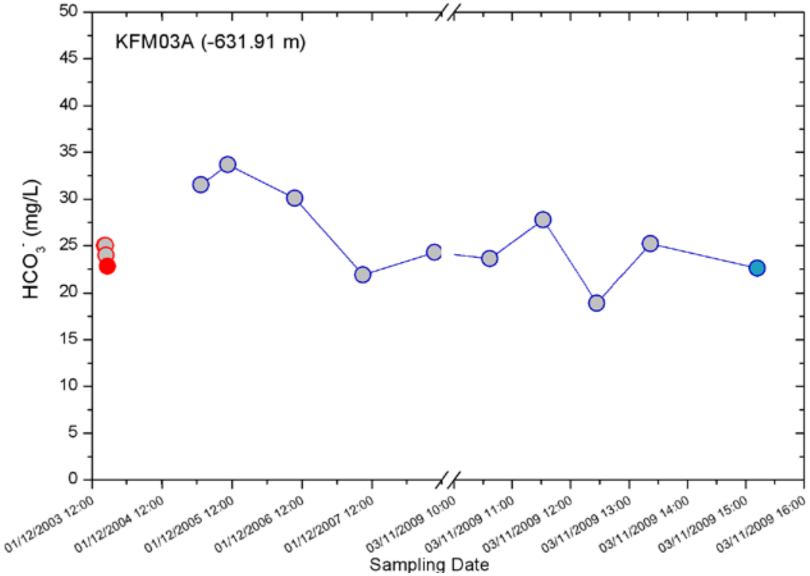

KFM03A (-440.79/-442.34 m)
δ34S (‰ CDT)
30
28
26
24
22
20
10/10/2003
10/11/2003
10/12/2003
10/01/2004
10/02/2004
10/03/2004
10/04/2004
Sampling Date

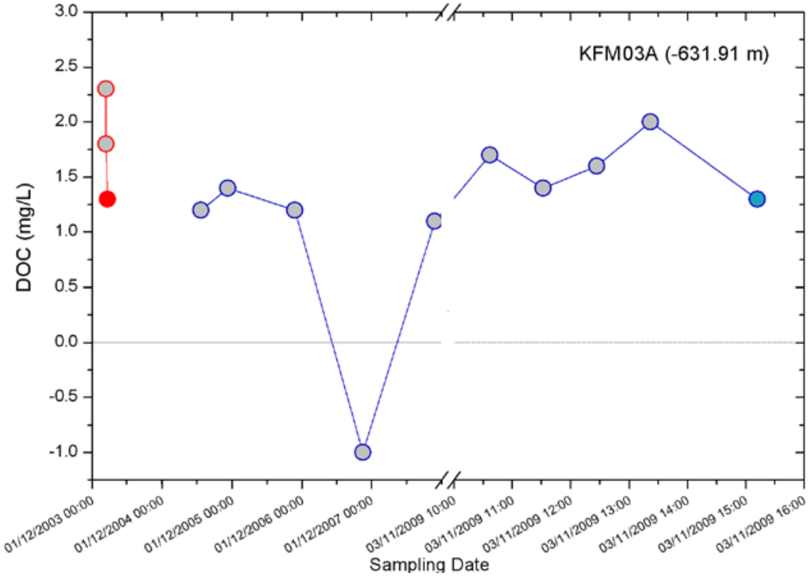

100
95
90
85
80
HCO$_3^-$ (mg/L)
KFM03A (-440.79/-442.34 m)
10/10/2003
10/11/2003
10/12/2003
10/01/2004
10/02/2004
10/03/2004
10/04/2004
Sampling Date
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
DOC (mg/L)
KFM03A (-440.79/-442.34 m)
Sampling Date
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Calcite Saturation Index
KFM03A (-440.79/-442.34 m)
Sampling Date
1.30
1.28
1.26
1.24
1.22
1.20
1.18
1.16
1.14
1.12
1.10
Mn (mg/L)
KFM03A (-440.79/-442.34 m)
Sampling Date

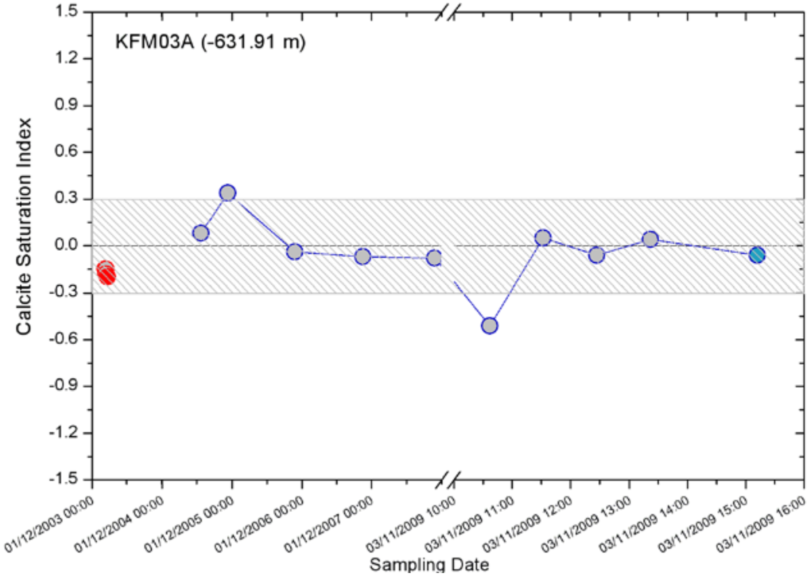
KFM03A (–631.91 m)
Eh = –196 mV

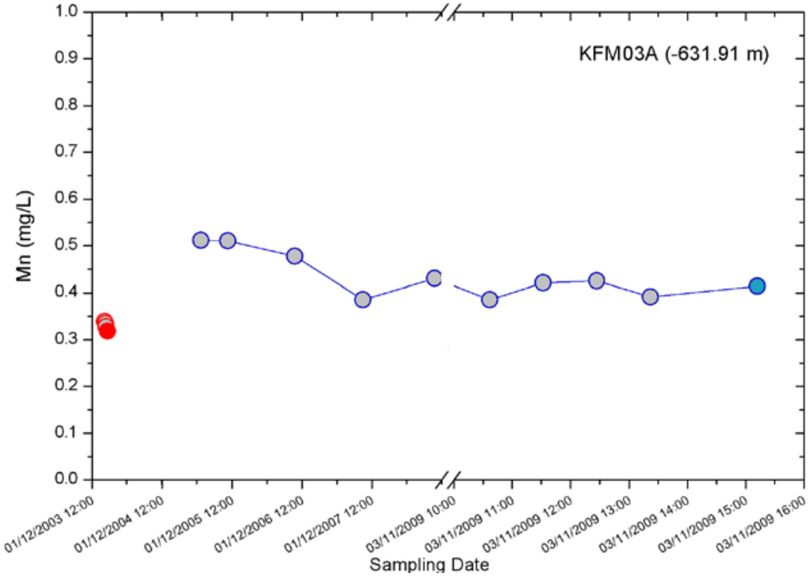



KFM03A (-631.91 m)
S(-II) (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
Fe (mg/L)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
$\delta^{34}$S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
Sampling Date
01/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
01/12/2003 12:00
01/12/2004 12:00
01/12/2005 12:00
01/12/2006 12:00
01/12/2007 12:00
03/11/2009 10:00
03/11/2009 11:00
03/11/2009 12:00
03/11/2009 13:00
03/11/2009 14:00
03/11/2009 15:00
03/11/2009 16:00

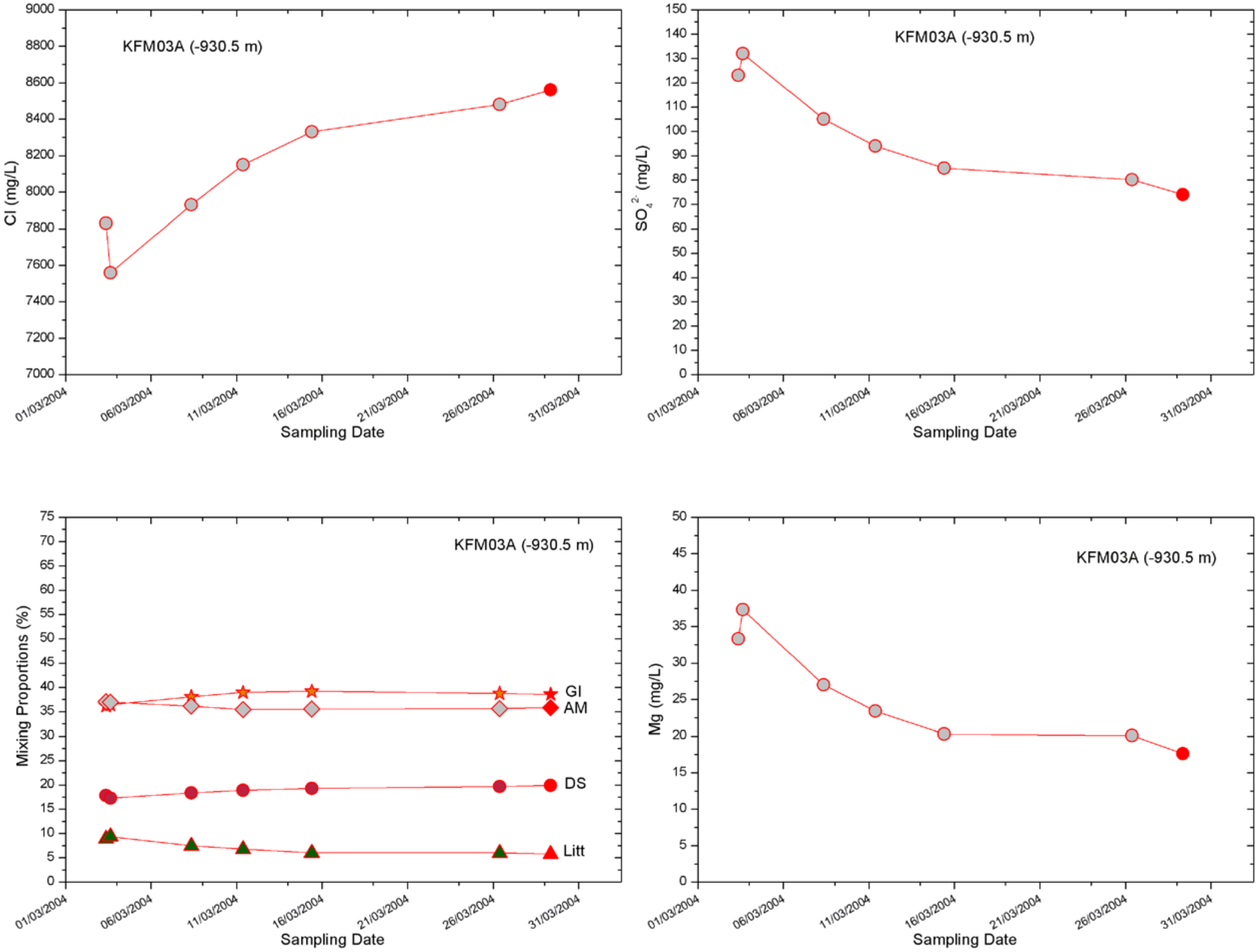

KFM03A (-631.91 m)
HCO$_3^-$ (mg/L)
50
45
40
35
30
25
20
15
10
5
0
01/12/2003 12:00
01/12/2004 12:00
01/12/2005 12:00
01/12/2006 12:00
01/12/2007 12:00
03/11/2009 10:00
03/11/2009 11:00
03/11/2009 12:00
03/11/2009 13:00
03/11/2009 14:00
03/11/2009 15:00
03/11/2009 16:00
Sampling Date

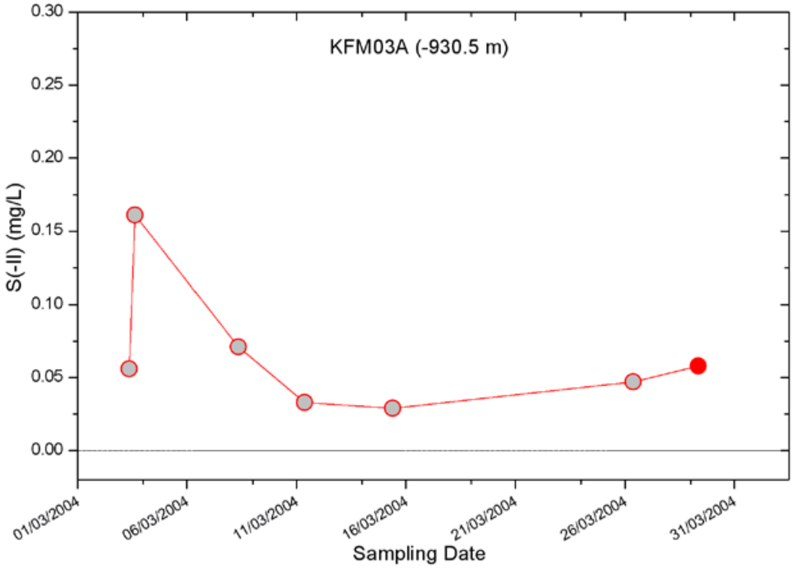

KFM03A (-631.91 m)
DOC (mg/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
01/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
03/11/2009 10:00
03/11/2009 11:00
03/11/2009 12:00
03/11/2009 13:00
03/11/2009 14:00
03/11/2009 15:00
03/11/2009 16:00
Sampling Date

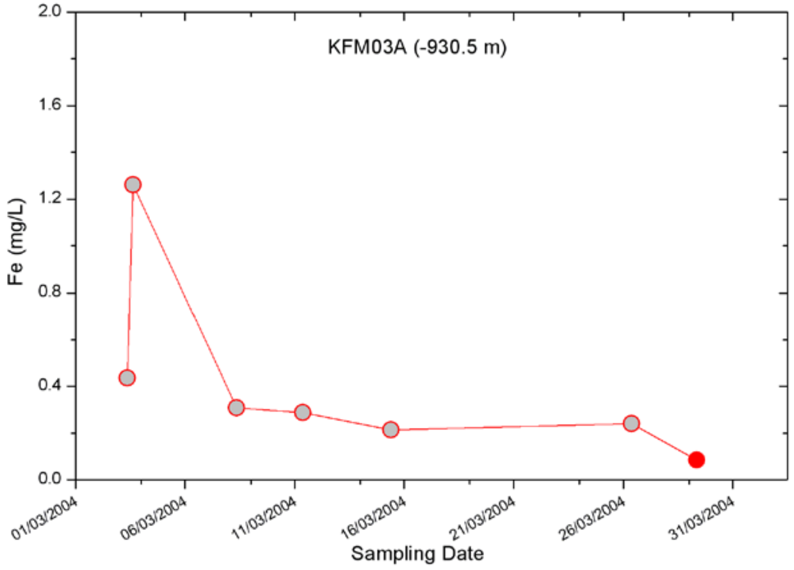

KFM03A (-631.91 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
01/12/2003 00:00
01/12/2004 00:00
01/12/2005 00:00
01/12/2006 00:00
01/12/2007 00:00
03/11/2009 10:00
03/11/2009 11:00
03/11/2009 12:00
03/11/2009 13:00
03/11/2009 14:00
03/11/2009 15:00
03/11/2009 16:00
Sampling Date

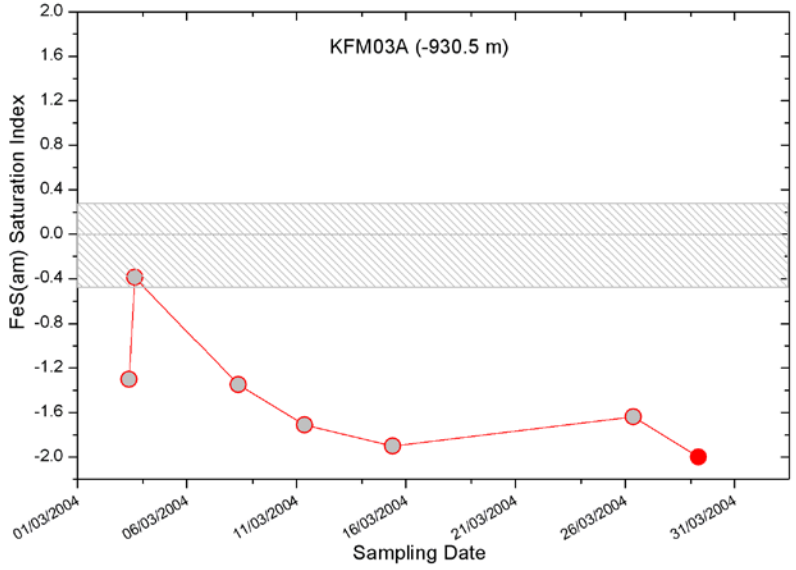

KFM03A (-631.91 m)
Mn (mg/L)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
01/12/2003 12:00
01/12/2004 12:00
01/12/2005 12:00
01/12/2006 12:00
01/12/2007 12:00
03/11/2009 10:00
03/11/2009 11:00
03/11/2009 12:00
03/11/2009 13:00
03/11/2009 14:00
03/11/2009 15:00
03/11/2009 16:00
Sampling Date

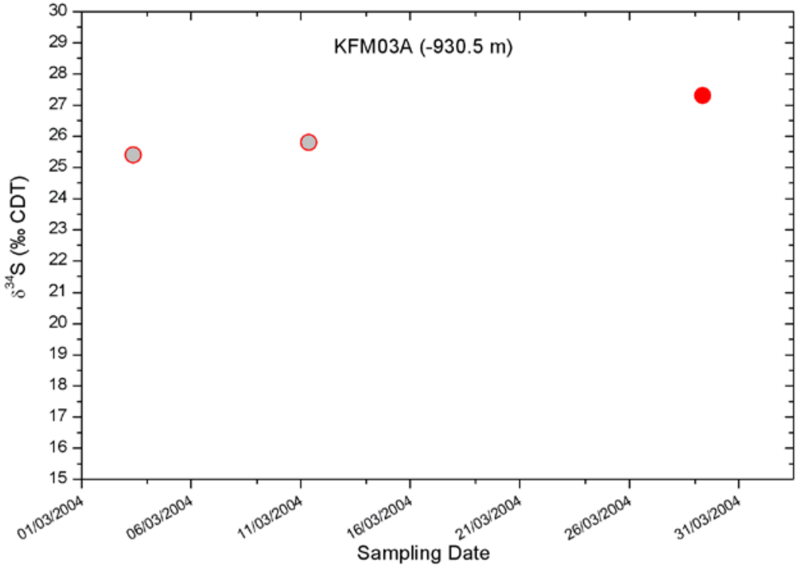
KFM03A (–930.5 m)
Eh = –245 mV

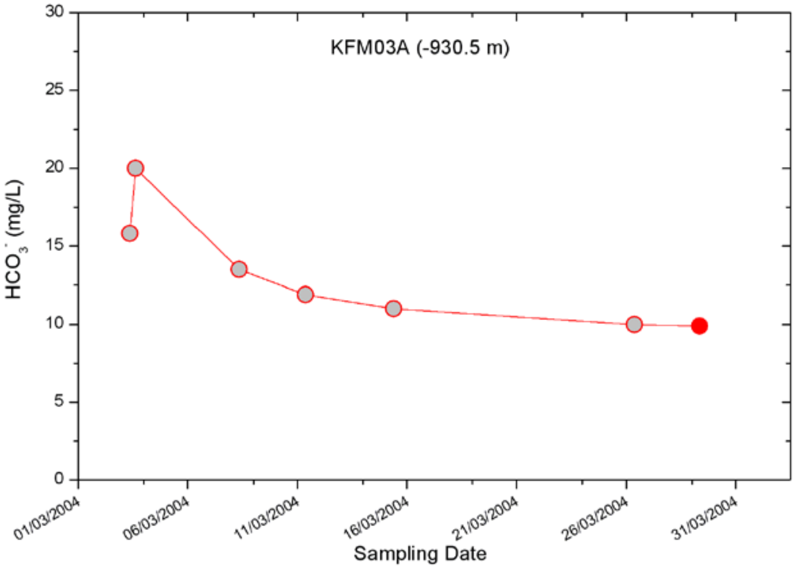


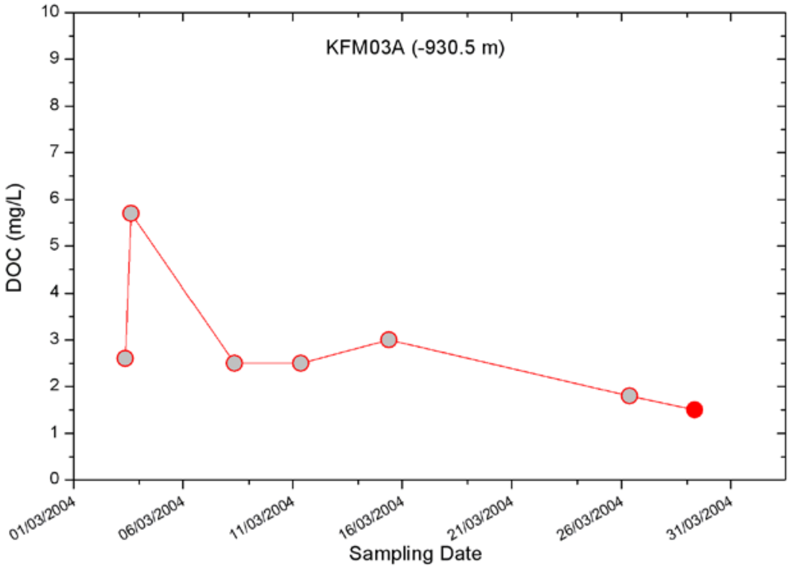

KFM03A (-930.5 m)
S(-II) (mg/L)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004
Sampling Date

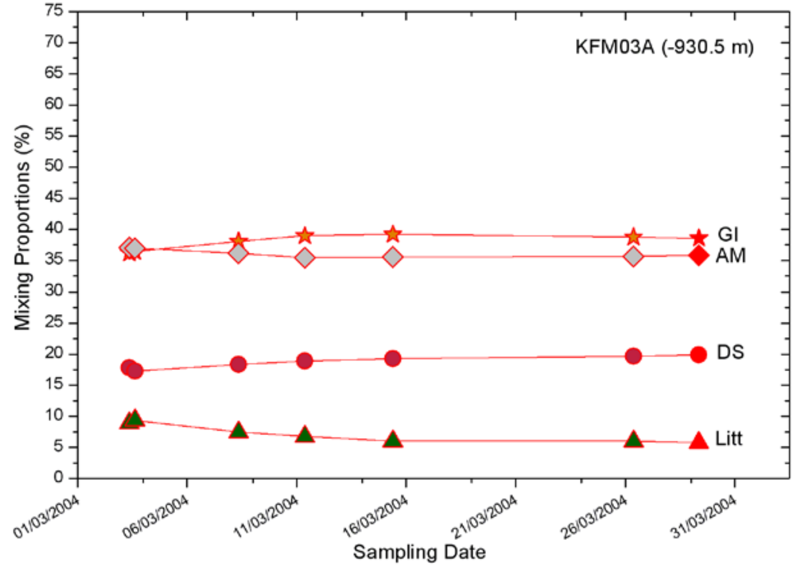

KFM03A (-930.5 m)
Fe (mg/L)
2.0
1.6
1.2
0.8
0.4
0.0
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004
Sampling Date

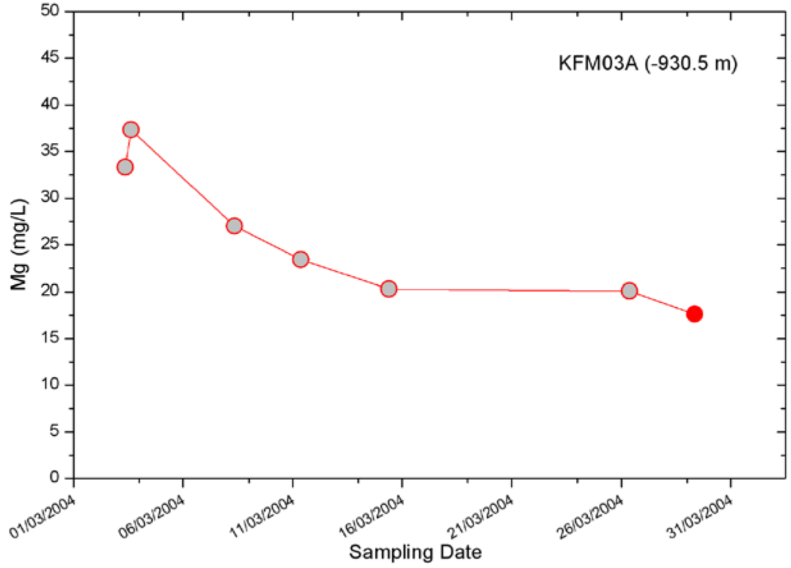

KFM03A (-930.5 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004
Sampling Date


KFM03A (-930.5 m)
$\delta^{34}S$ (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004
Sampling Date

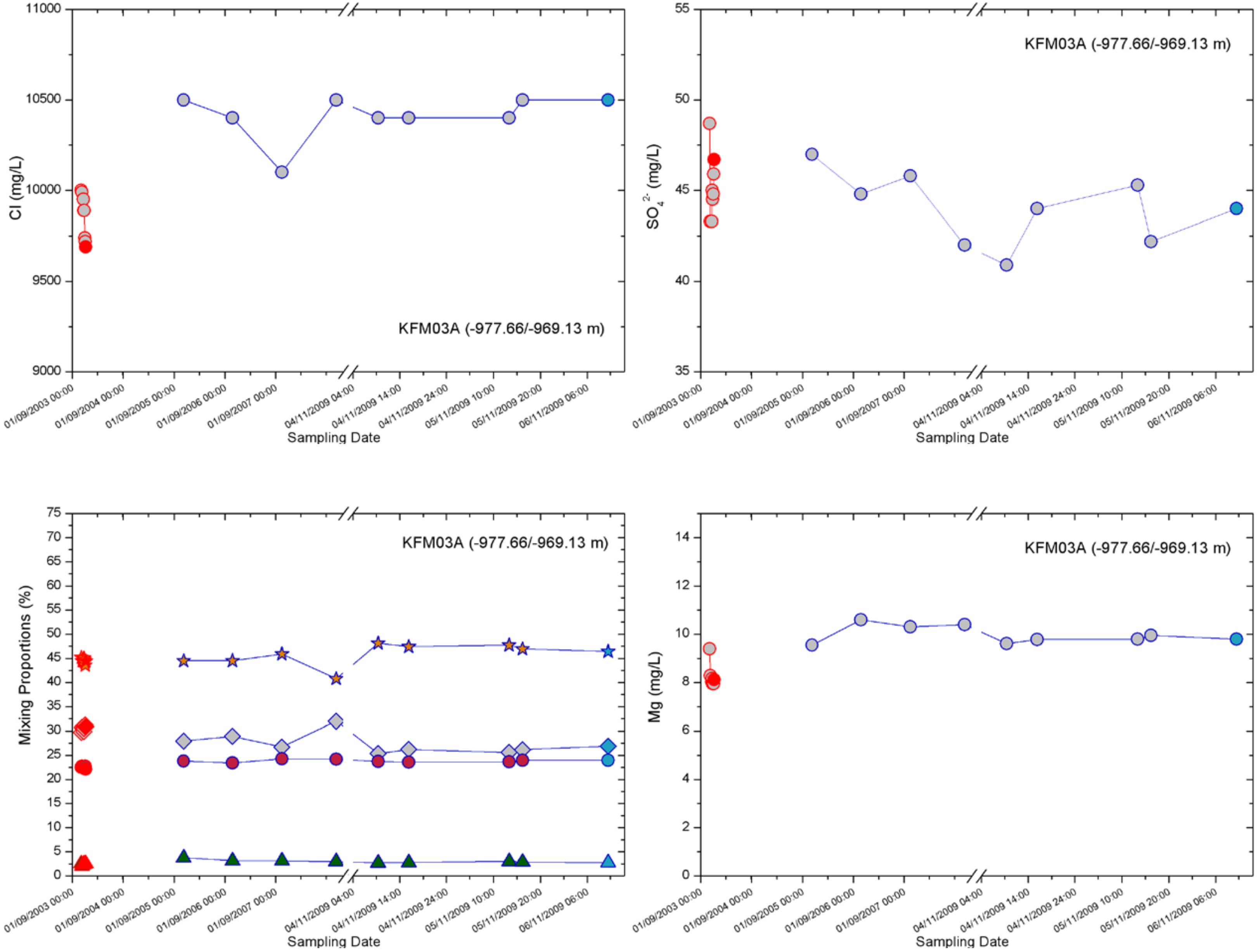

KFM03A (-930.5 m)
HCO$_3^-$ (mg/L)
0
5
10
15
20
25
30
Sampling Date
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004

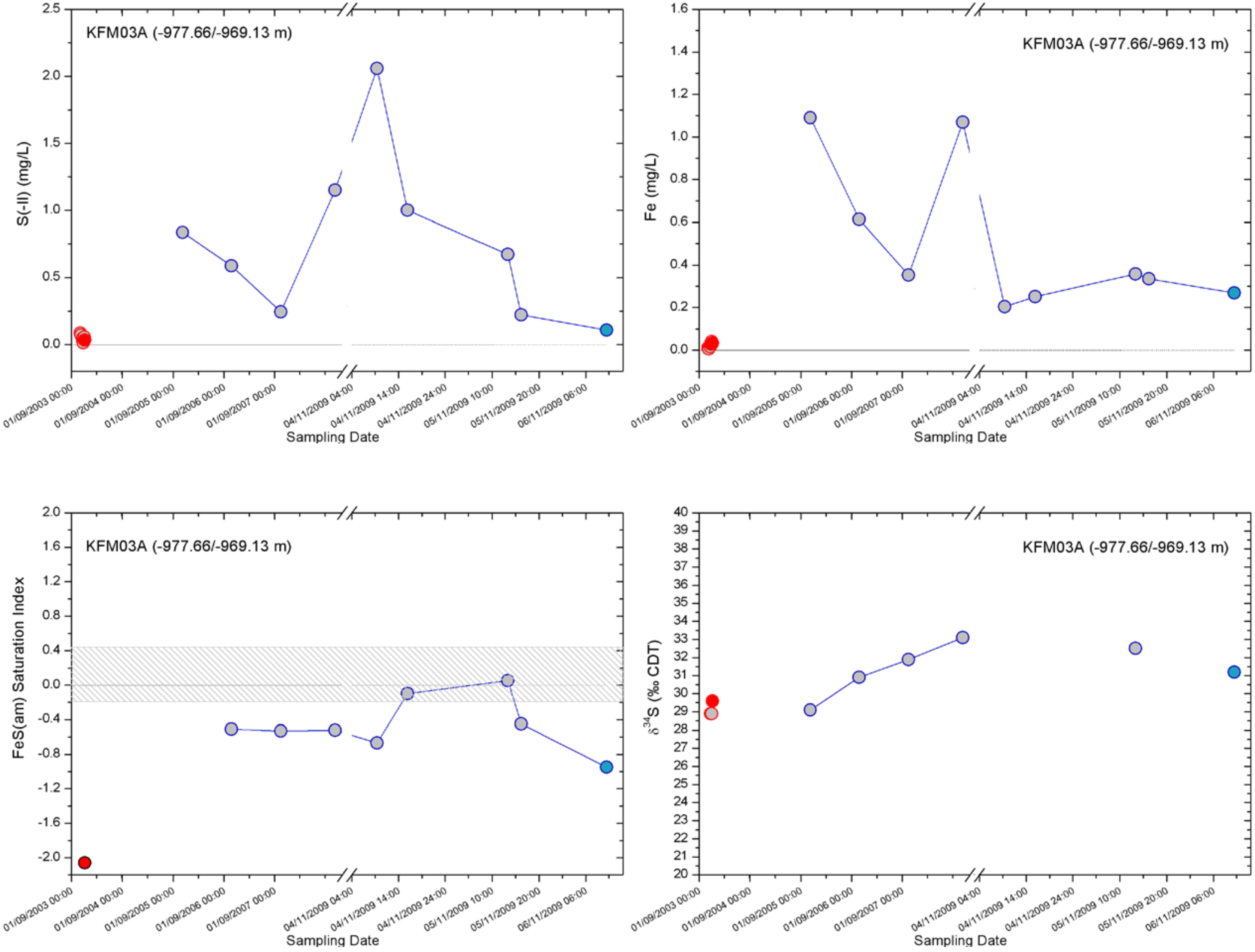

KFM03A (-930.5 m)
DOC (mg/L)
0
1
2
3
4
5
6
7
8
9
10
Sampling Date
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004

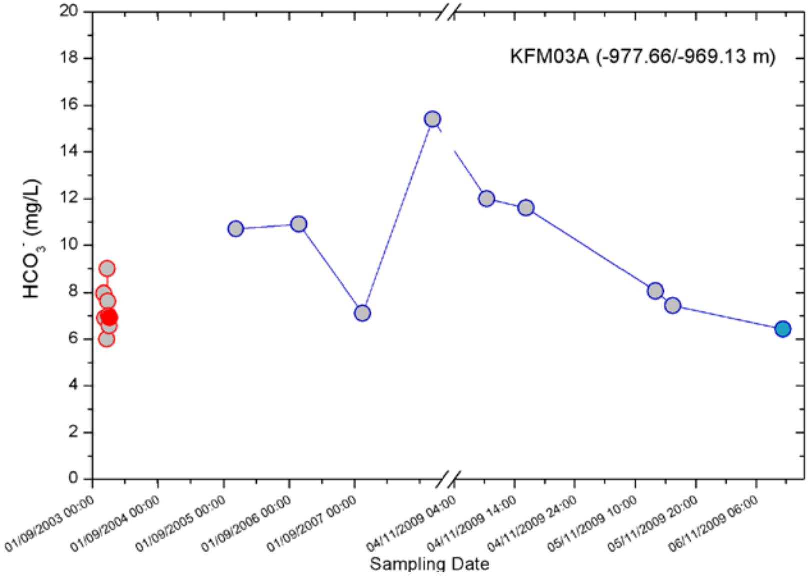

KFM03A (-930.5 m)
Mixing Proportions (%)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
GI
AM
DS
Litt
Sampling Date
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004

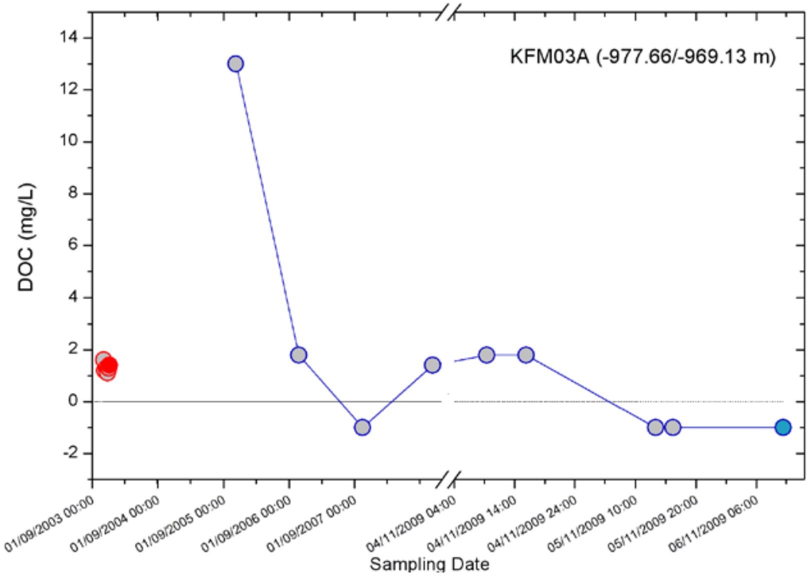

KFM03A (-930.5 m)
Mg (mg/L)
0
5
10
15
20
25
30
35
40
45
50
Sampling Date
01/03/2004
06/03/2004
11/03/2004
16/03/2004
21/03/2004
26/03/2004
31/03/2004

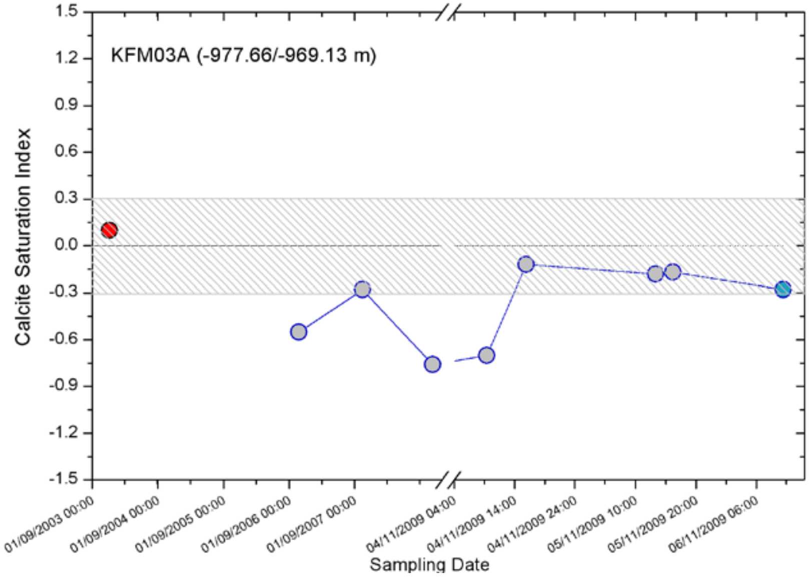
KFM03A (–977.66/–969.13 m)

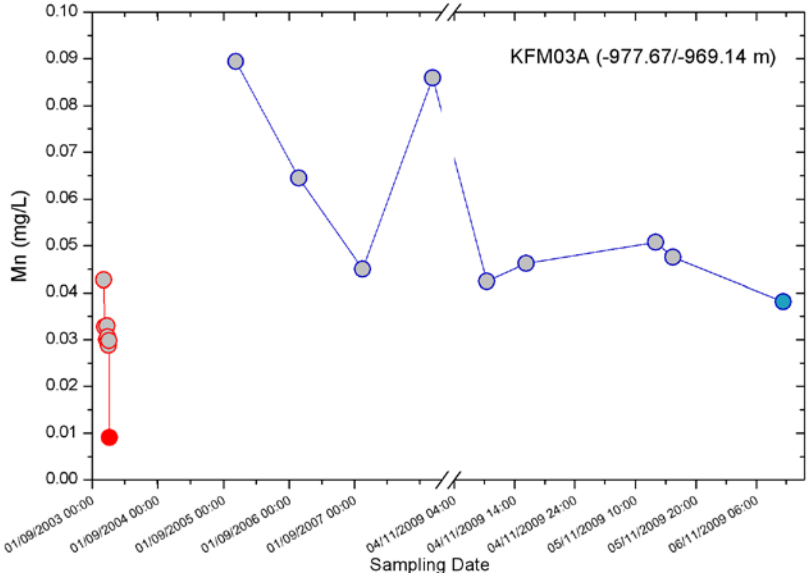



KFM03A (-977.66/-969.13 m)
S(-II) (mg/L)
0.0
0.5
1.0
1.5
2.0
2.5
Fe (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
FeS(am) Saturation Index
-2.0
-1.6
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
1.6
2.0
$\delta^{34}$S (‰ CDT)
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
01/09/2003 00:00
01/09/2004 00:00
01/09/2005 00:00
01/09/2006 00:00
01/09/2007 00:00
04/11/2009 04:00
04/11/2009 14:00
04/11/2009 24:00
05/11/2009 10:00
05/11/2009 20:00
06/11/2009 06:00
Sampling Date

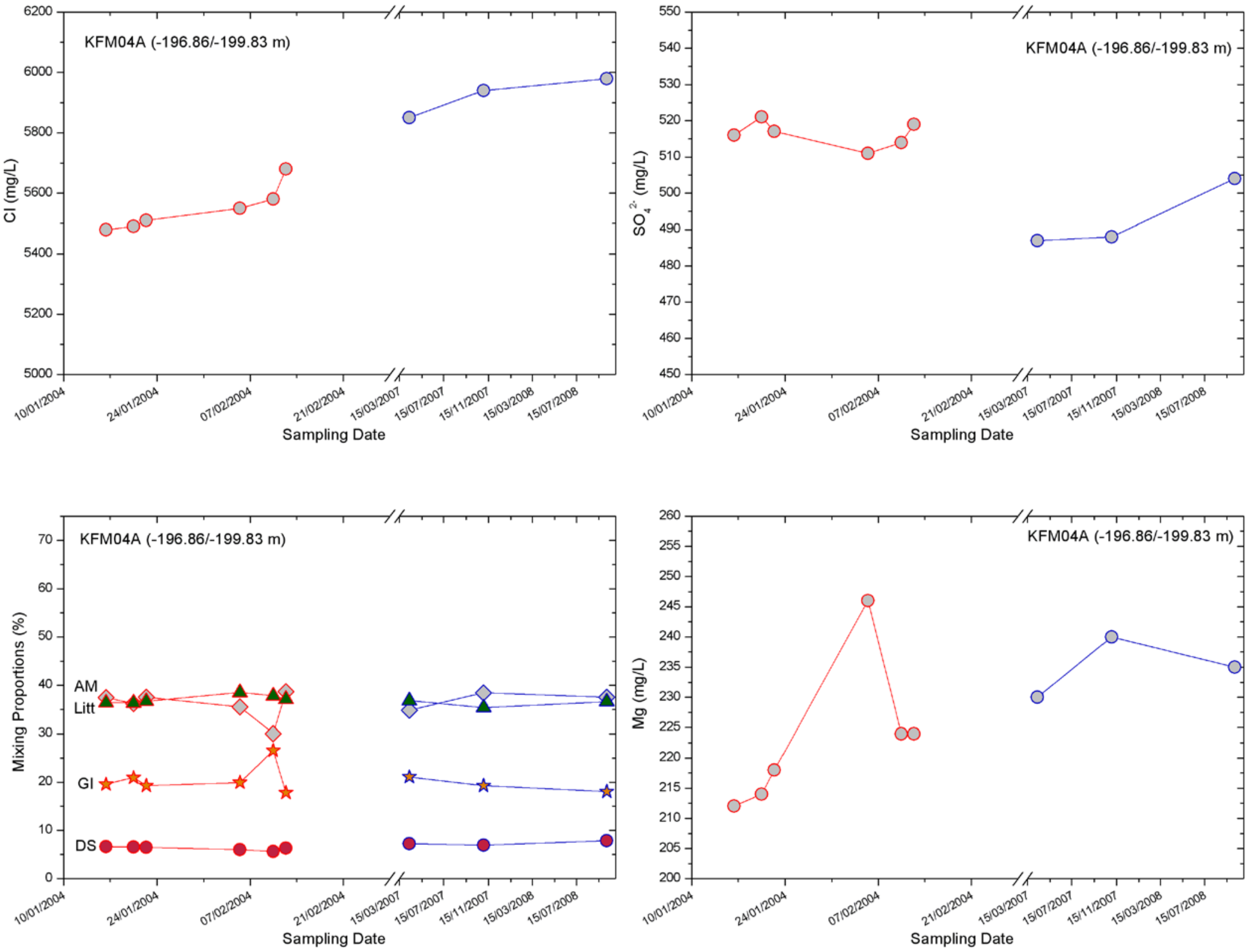

KFM03A (-977.66/-969.13 m)
HCO$_3^-$ (mg/L)
0
2
4
6
8
10
12
14
16
18
20
01/09/2003 00:00
01/09/2004 00:00
01/09/2005 00:00
01/09/2006 00:00
01/09/2007 00:00
04/11/2009 04:00
04/11/2009 14:00
04/11/2009 24:00
05/11/2009 10:00
05/11/2009 20:00
06/11/2009 06:00
Sampling Date

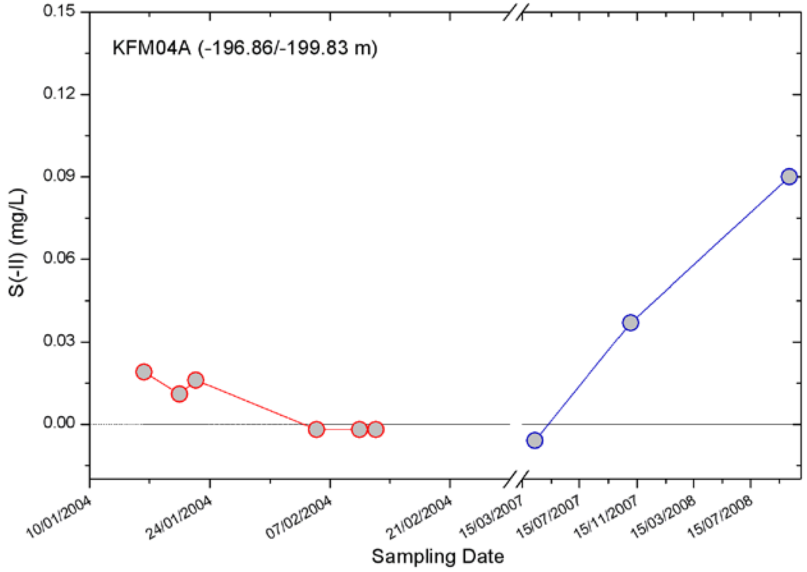

KFM03A (-977.66/-969.13 m)
DOC (mg/L)
-2
0
2
4
6
8
10
12
14
01/09/2003 00:00
01/09/2004 00:00
01/09/2005 00:00
01/09/2006 00:00
01/09/2007 00:00
04/11/2009 04:00
04/11/2009 14:00
04/11/2009 24:00
05/11/2009 10:00
05/11/2009 20:00
06/11/2009 06:00
Sampling Date

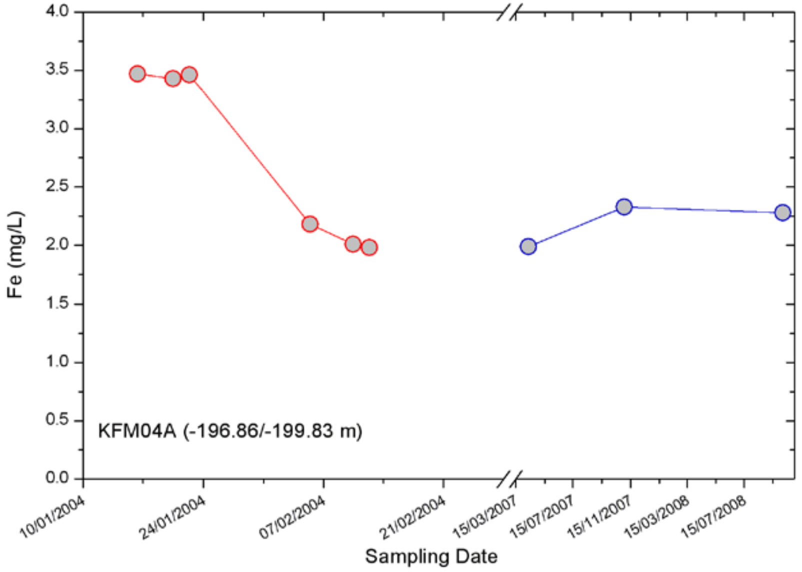

KFM03A (-977.66/-969.13 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
01/09/2003 00:00
01/09/2004 00:00
01/09/2005 00:00
01/09/2006 00:00
01/09/2007 00:00
04/11/2009 04:00
04/11/2009 14:00
04/11/2009 24:00
05/11/2009 10:00
05/11/2009 20:00
06/11/2009 06:00
Sampling Date

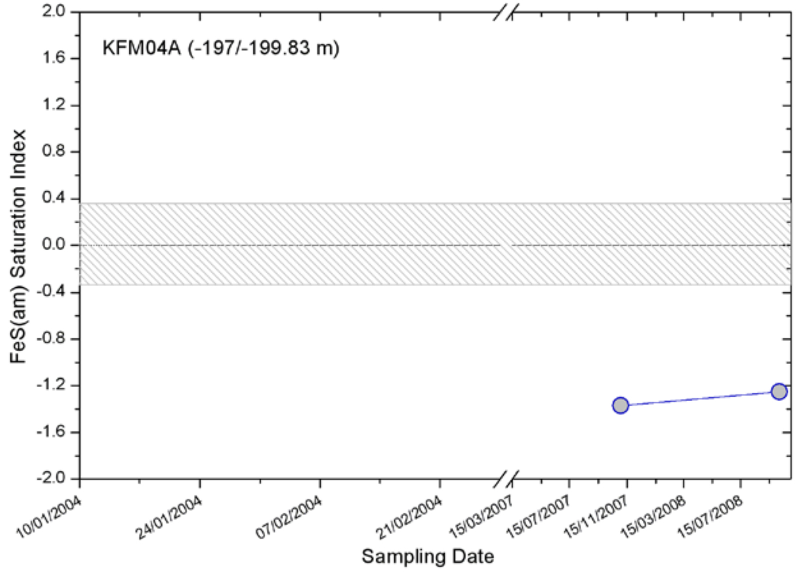

KFM03A (-977.67/-969.14 m)
Mn (mg/L)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
01/09/2003 00:00
01/09/2004 00:00
01/09/2005 00:00
01/09/2006 00:00
01/09/2007 00:00
04/11/2009 04:00
04/11/2009 14:00
04/11/2009 24:00
05/11/2009 10:00
05/11/2009 20:00
06/11/2009 06:00
Sampling Date

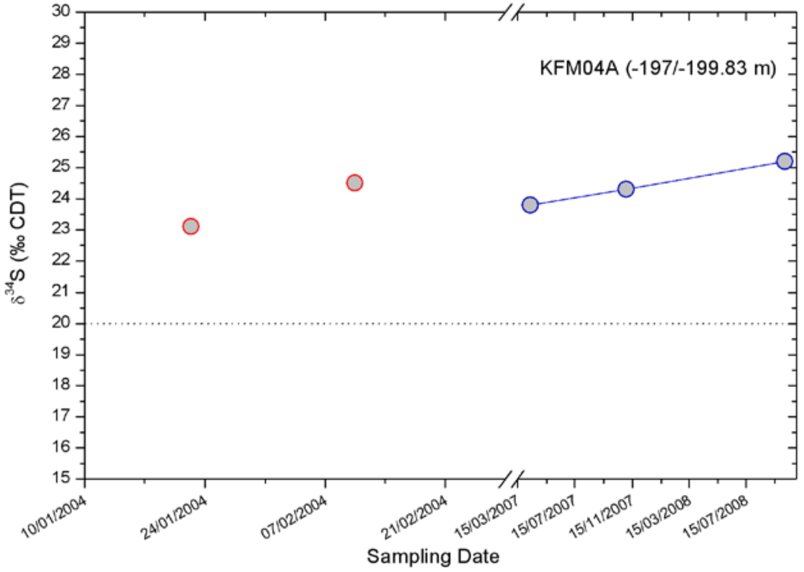
KFM04A (–196.86/–199.83 m)

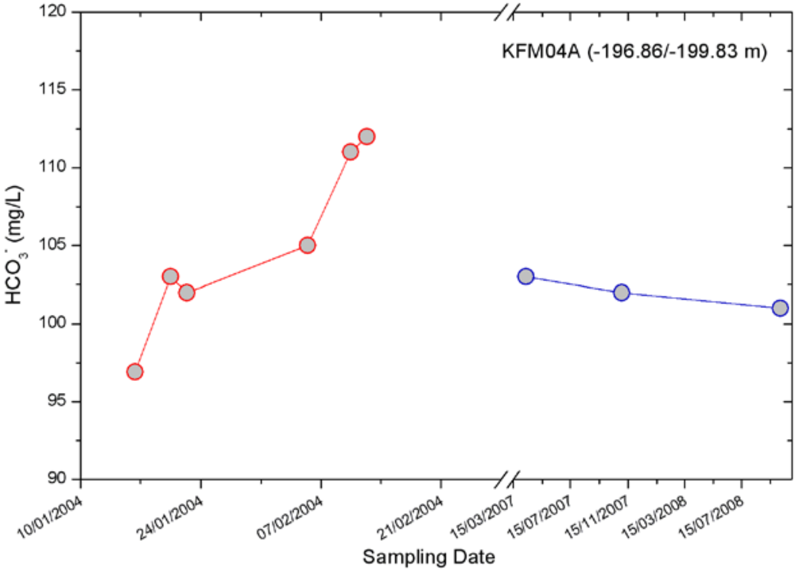


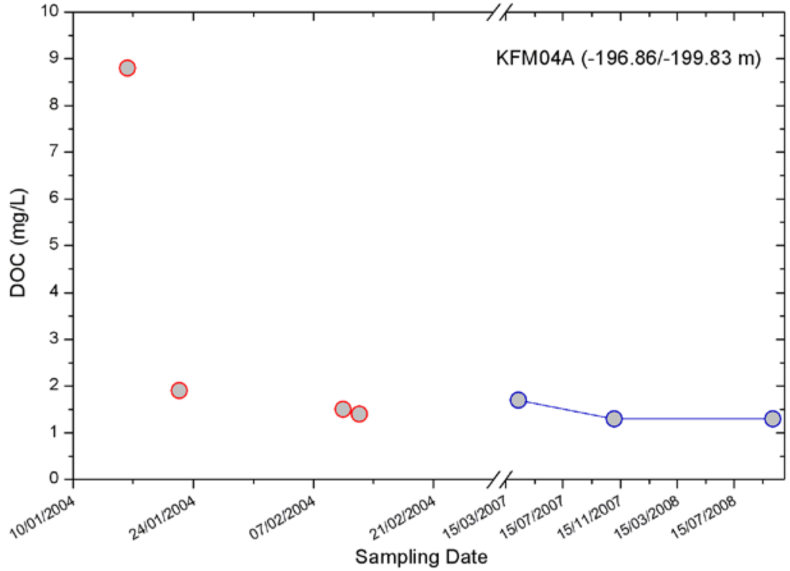

KFM04A (-196.86/-199.83 m)
S(-II) (mg/L)
0.15
0.12
0.09
0.06
0.03
0.00
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

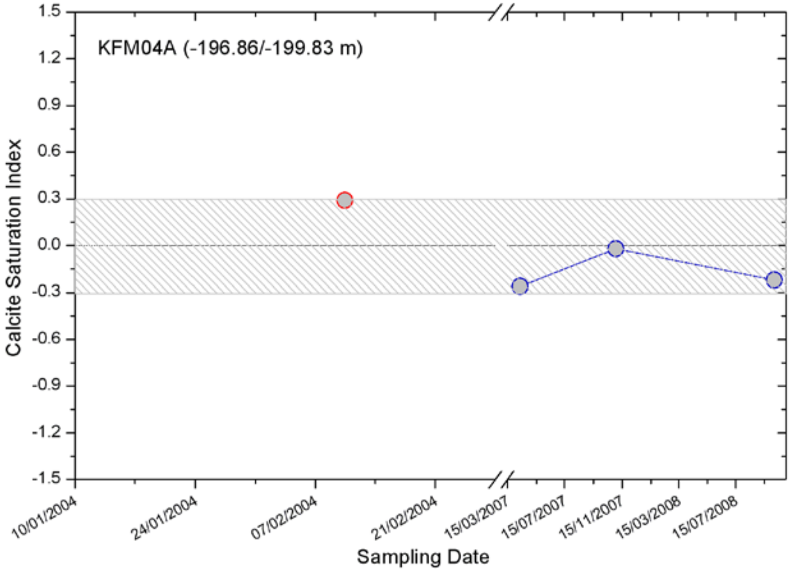

KFM04A (-196.86/-199.83 m)
Fe (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

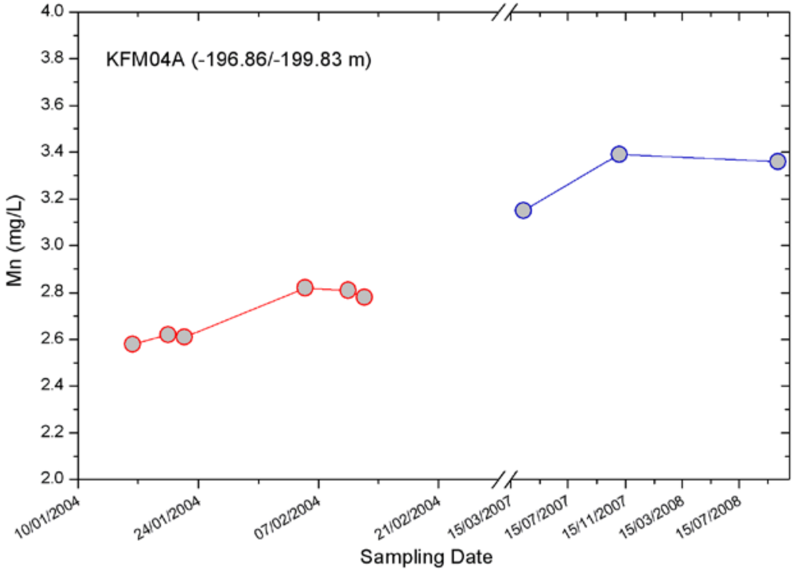

KFM04A (-197/-199.83 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date


KFM04A (-197/-199.83 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

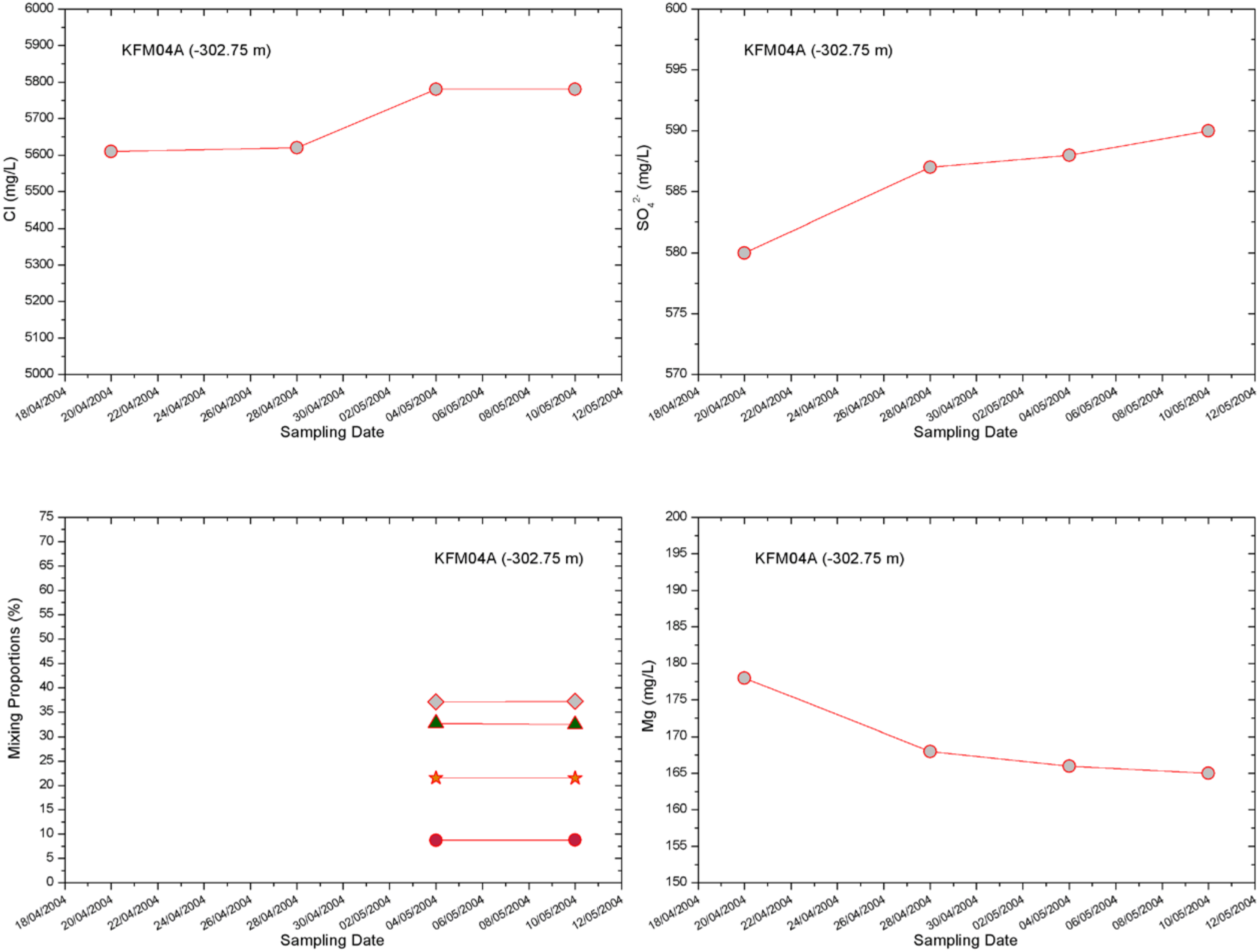

KFM04A (-196.86/-199.83 m)
HCO3- (mg/L)
120
115
110
105
100
95
90
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

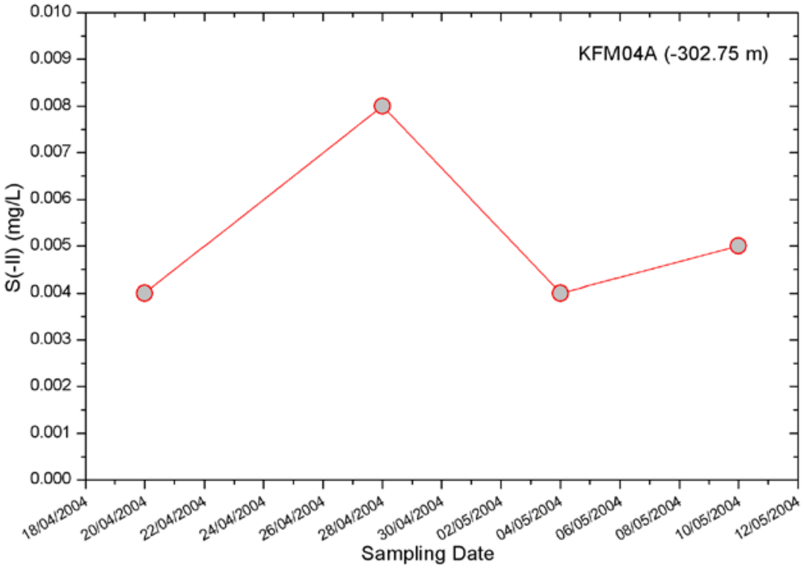

KFM04A (-196.86/-199.83 m)
DOC (mg/L)
10
9
8
7
6
5
4
3
2
1
0
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

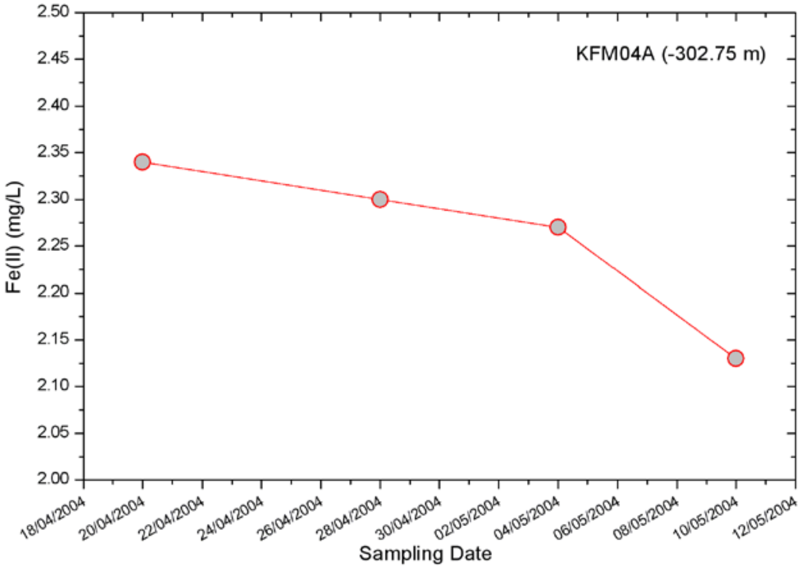

KFM04A (-196.86/-199.83 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

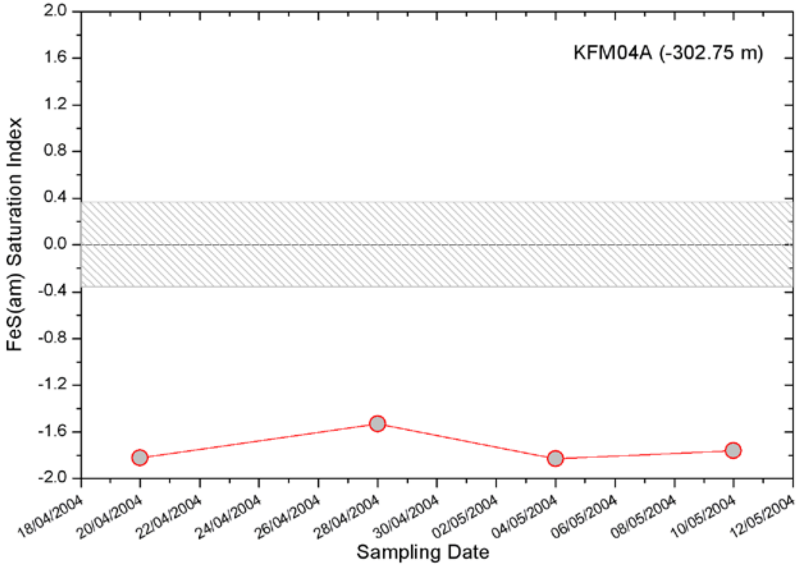

KFM04A (-196.86/-199.83 m)
Mn (mg/L)
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
10/01/2004
24/01/2004
07/02/2004
21/02/2004
15/03/2007
15/07/2007
15/11/2007
15/03/2008
15/07/2008
Sampling Date

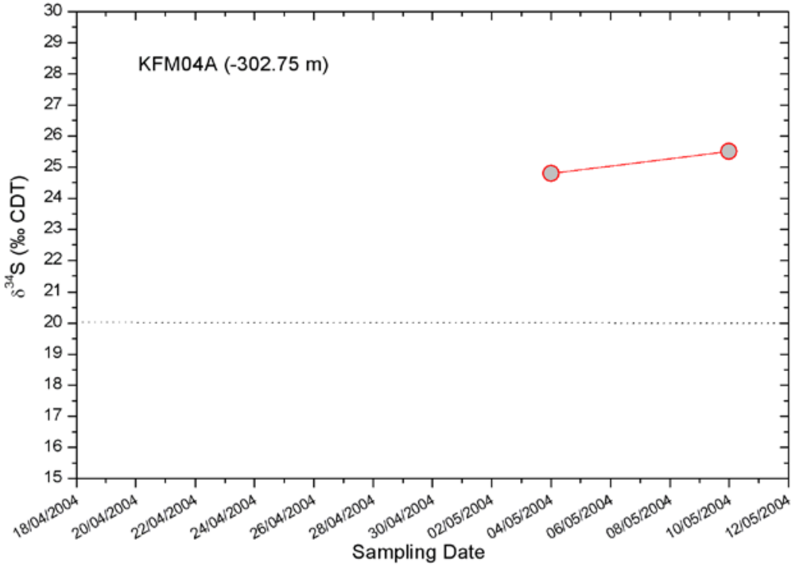
KFM04A (–302.75 m)

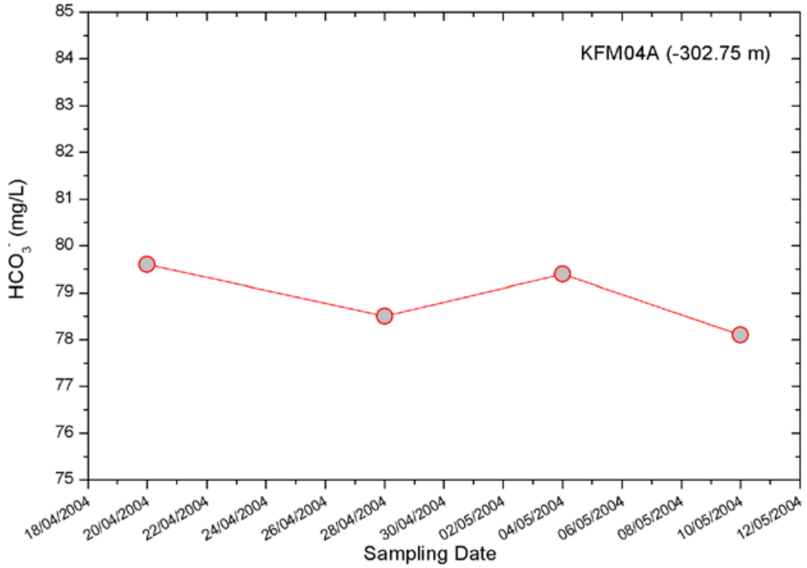


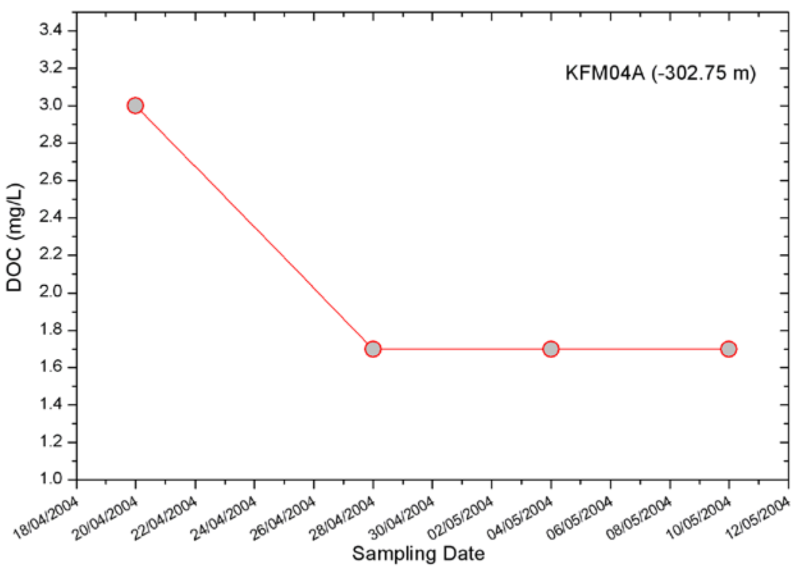

KFM04A (-302.75 m)
S(-II) (mg/L)
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date

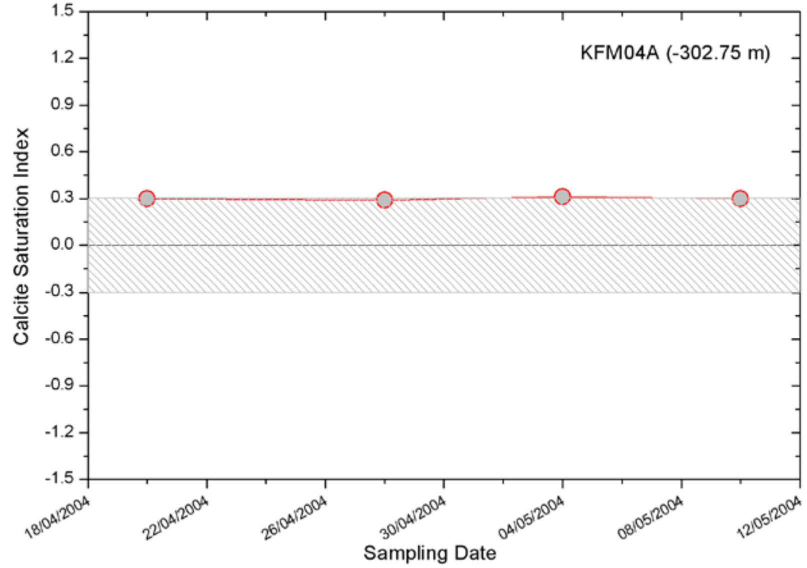

KFM04A (-302.75 m)
Fe(II) (mg/L)
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date

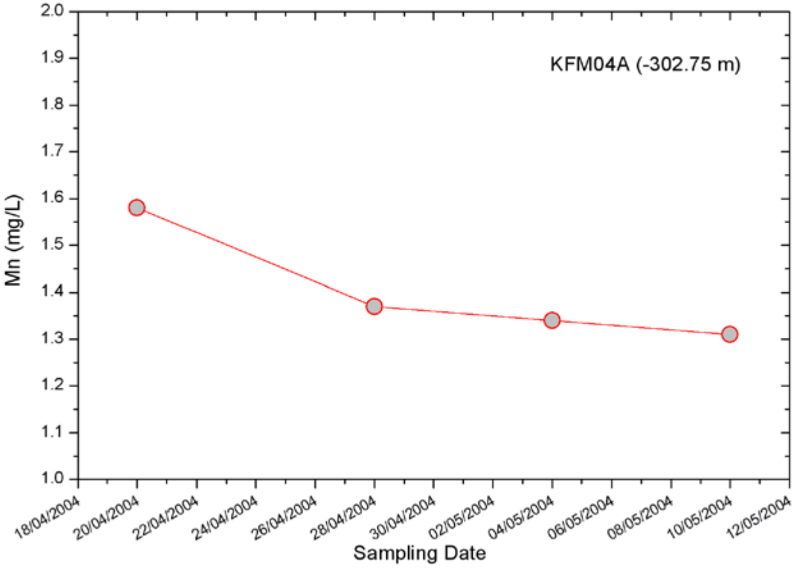

KFM04A (-302.75 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date


KFM04A (-302.75 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date

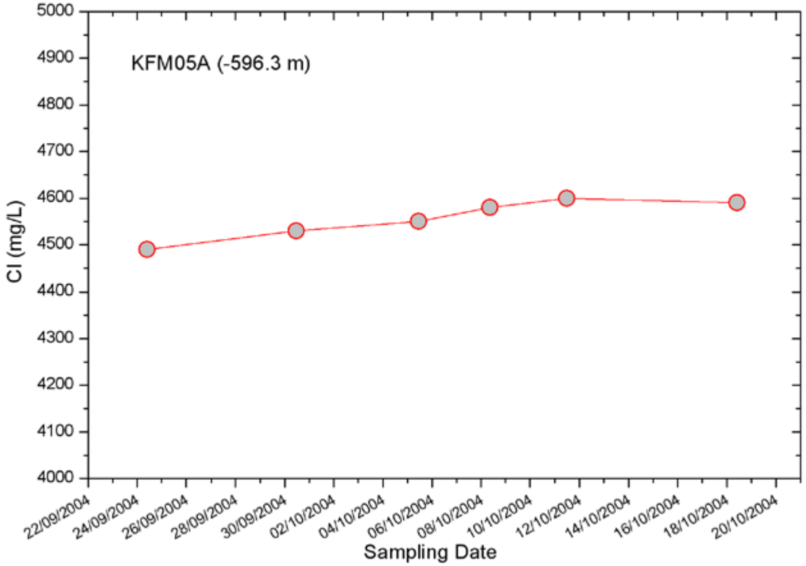

KFM04A (-302.75 m)
HCO3- (mg/L)
85
84
83
82
81
80
79
78
77
76
75
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date

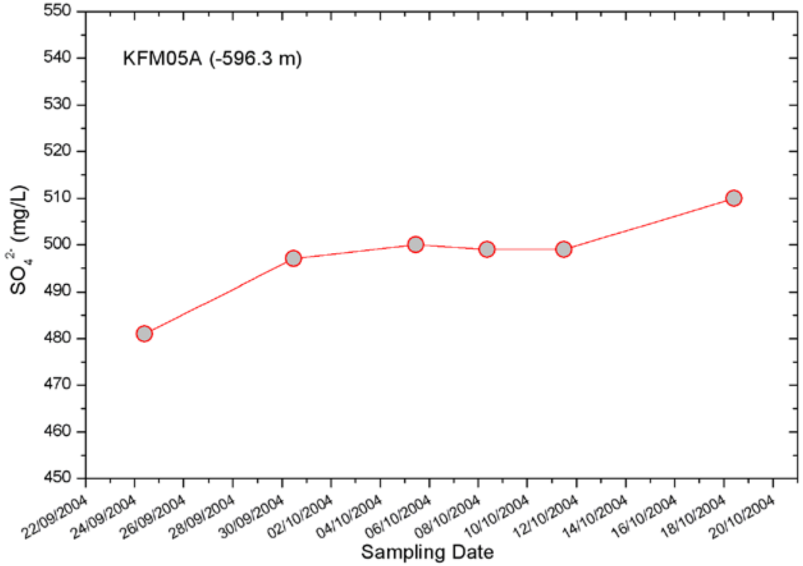

KFM04A (-302.75 m)
DOC (mg/L)
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date

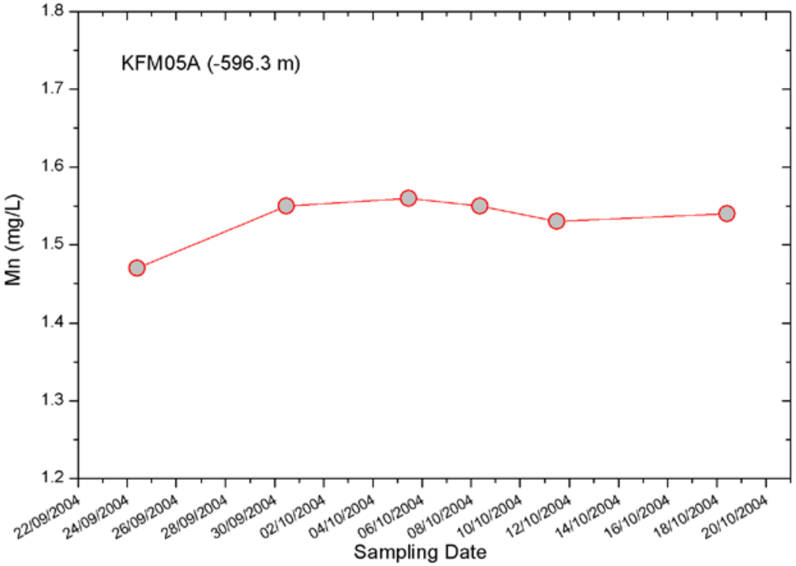

KFM04A (-302.75 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
18/04/2004
22/04/2004
26/04/2004
30/04/2004
04/05/2004
08/05/2004
12/05/2004
Sampling Date

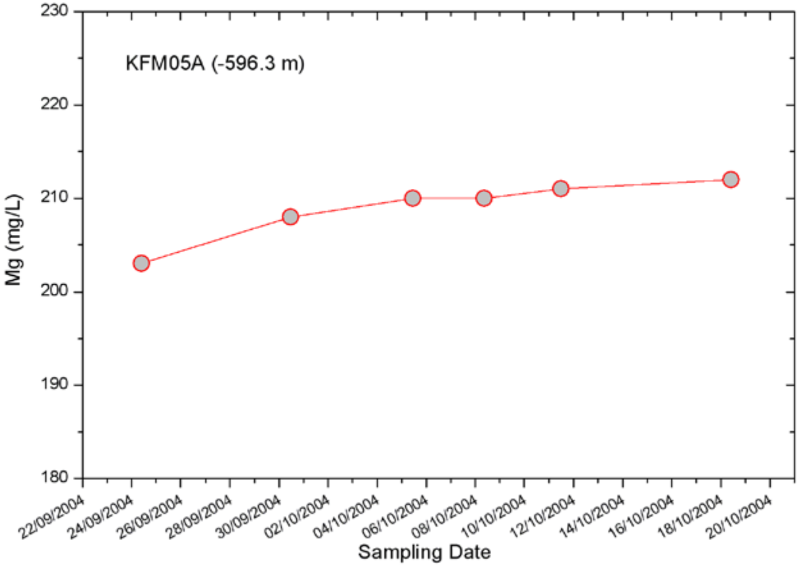

KFM04A (-302.75 m)
Mn (mg/L)
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
18/04/2004
20/04/2004
22/04/2004
24/04/2004
26/04/2004
28/04/2004
30/04/2004
02/05/2004
04/05/2004
06/05/2004
08/05/2004
10/05/2004
12/05/2004
Sampling Date

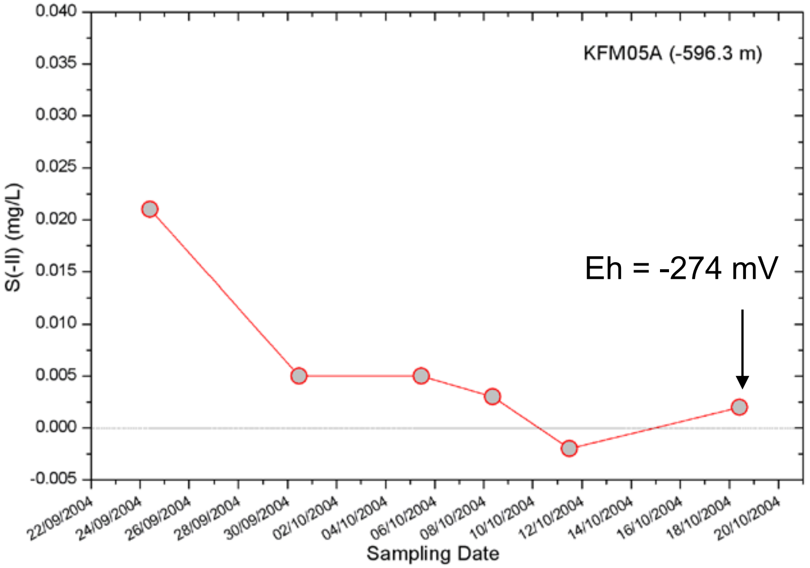
KFM05A (–596.3 m)

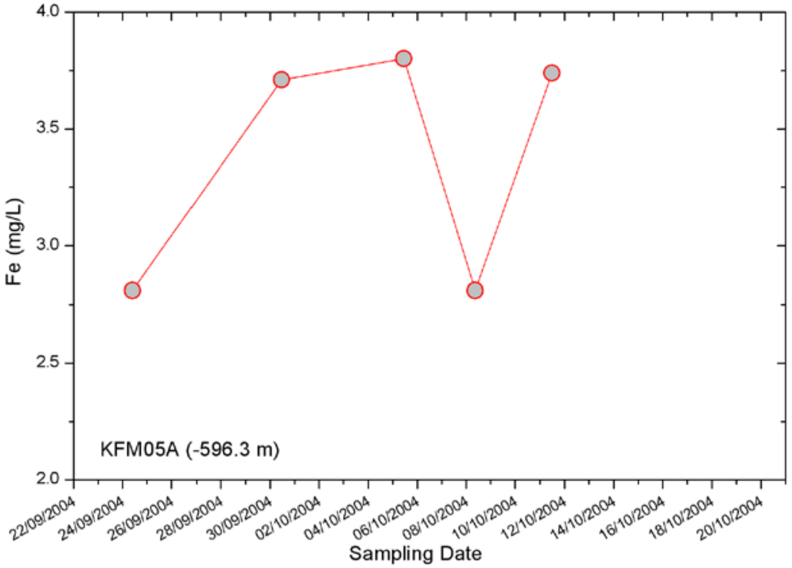


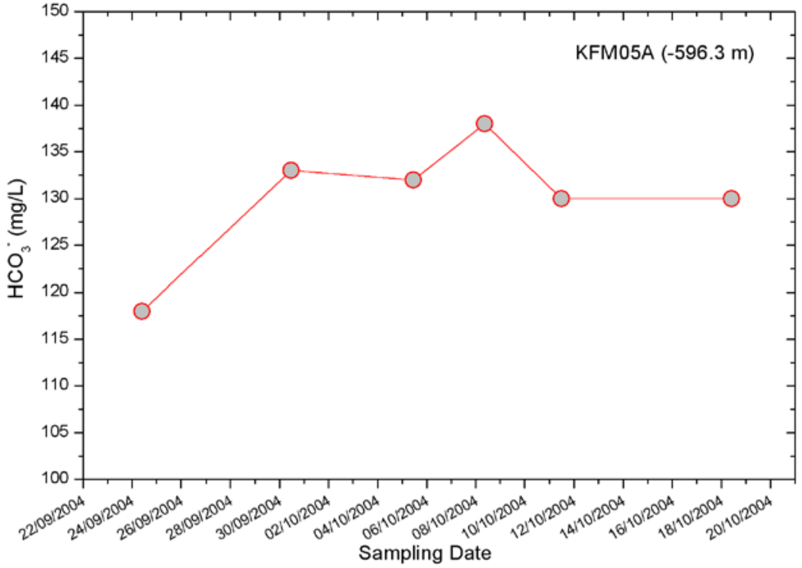


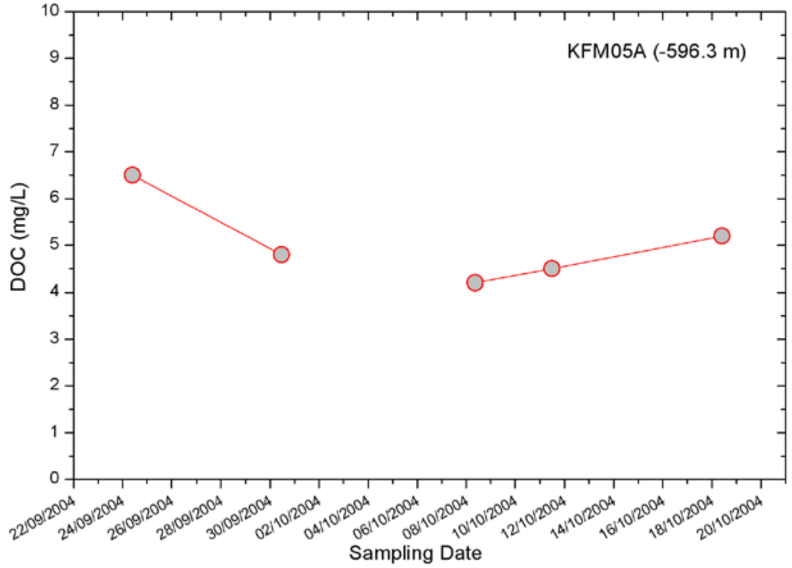




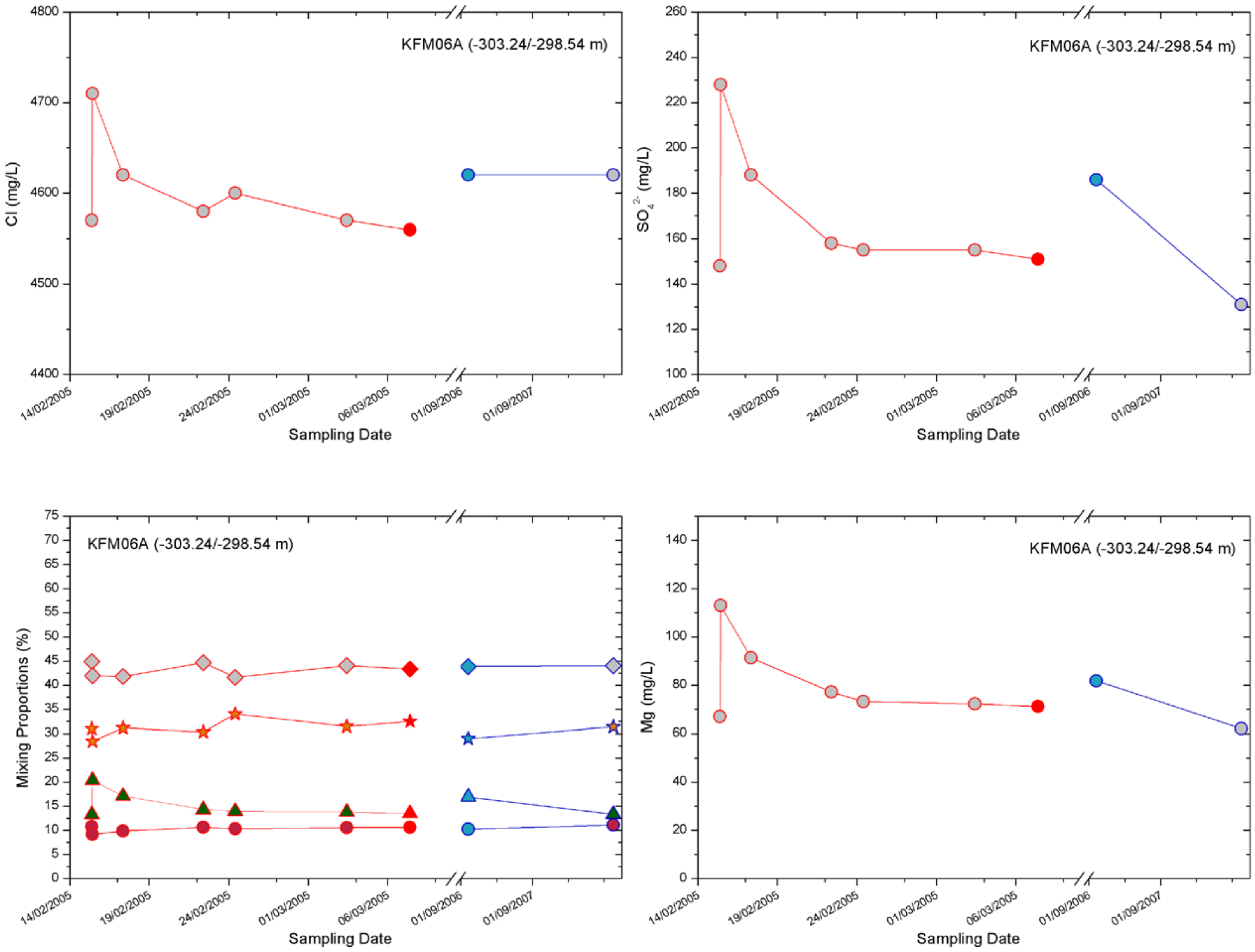

KFM05A (-596.3 m)
S(-II) (mg/L)
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
Eh = -274 mV
22/09/2004
24/09/2004
26/09/2004
28/09/2004
30/09/2004
02/10/2004
04/10/2004
06/10/2004
08/10/2004
10/10/2004
12/10/2004
14/10/2004
16/10/2004
18/10/2004
20/10/2004
Sampling Date

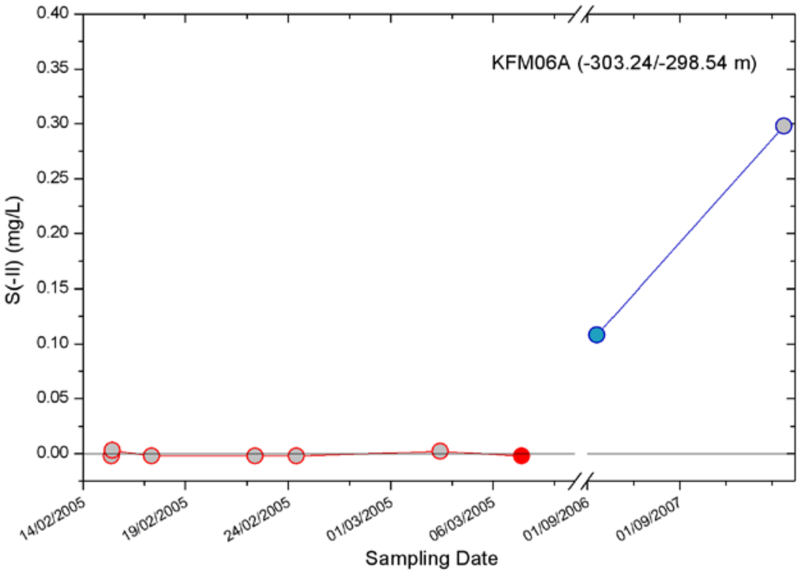

Fe (mg/L)
4.0
3.5
3.0
2.5
2.0
KFM05A (-596.3 m)
22/09/2004
24/09/2004
26/09/2004
28/09/2004
30/09/2004
02/10/2004
04/10/2004
06/10/2004
08/10/2004
10/10/2004
12/10/2004
14/10/2004
16/10/2004
18/10/2004
20/10/2004
Sampling Date

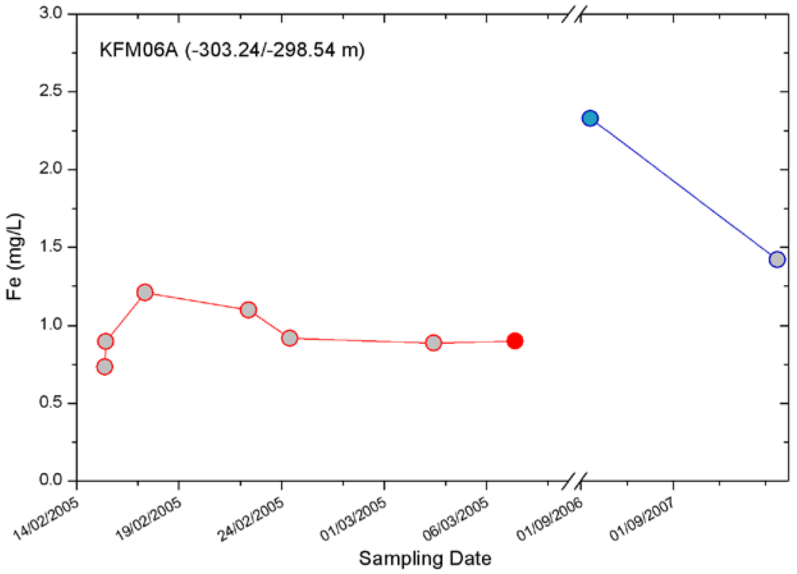

KFM05A (-596.3 m)
HCO3- (mg/L)
150
145
140
135
130
125
120
115
110
105
100
22/09/2004
24/09/2004
26/09/2004
28/09/2004
30/09/2004
02/10/2004
04/10/2004
06/10/2004
08/10/2004
10/10/2004
12/10/2004
14/10/2004
16/10/2004
18/10/2004
20/10/2004
Sampling Date

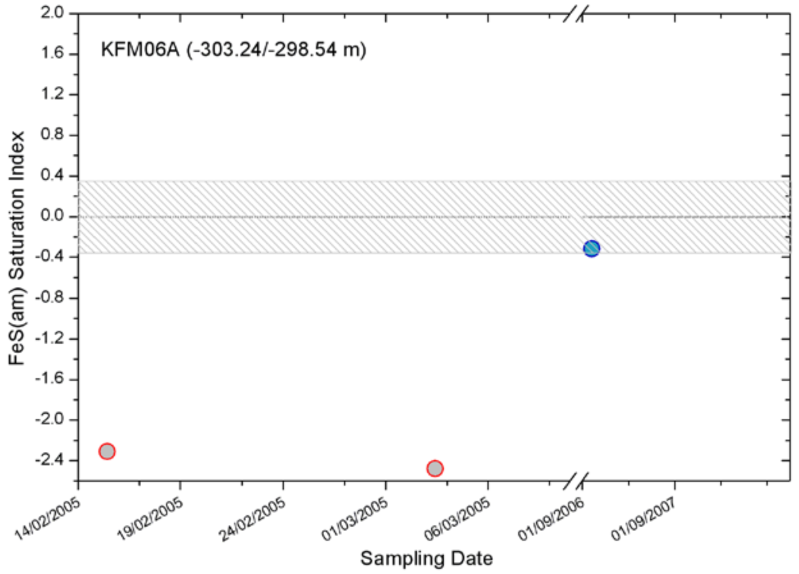

KFM05A (-596.3 m)
DOC (mg/L)
10
9
8
7
6
5
4
3
2
1
0
22/09/2004
24/09/2004
26/09/2004
28/09/2004
30/09/2004
02/10/2004
04/10/2004
06/10/2004
08/10/2004
10/10/2004
12/10/2004
14/10/2004
16/10/2004
18/10/2004
20/10/2004
Sampling Date

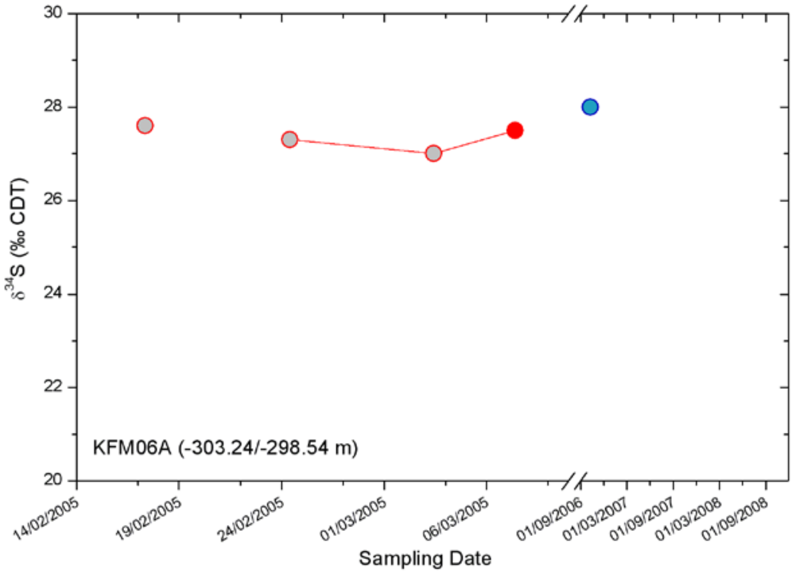
KFM06A (–303.24/–298.54 m)
Eh = –155 mV

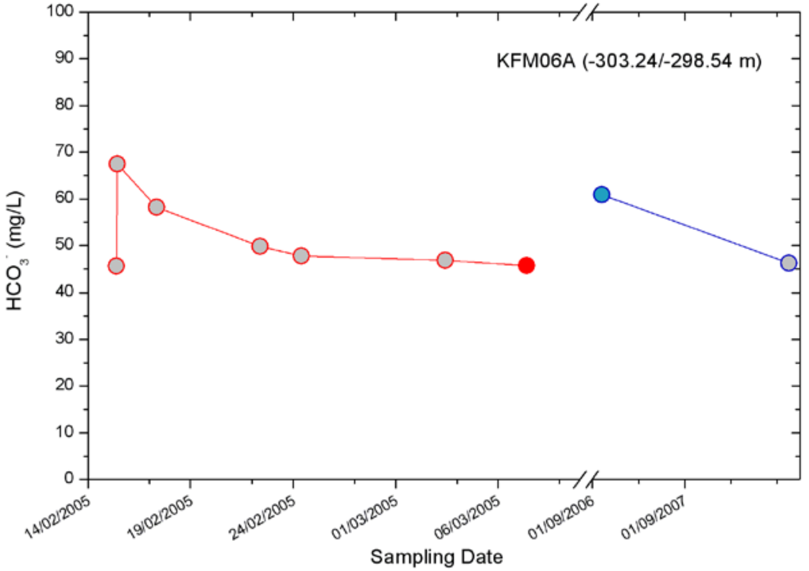


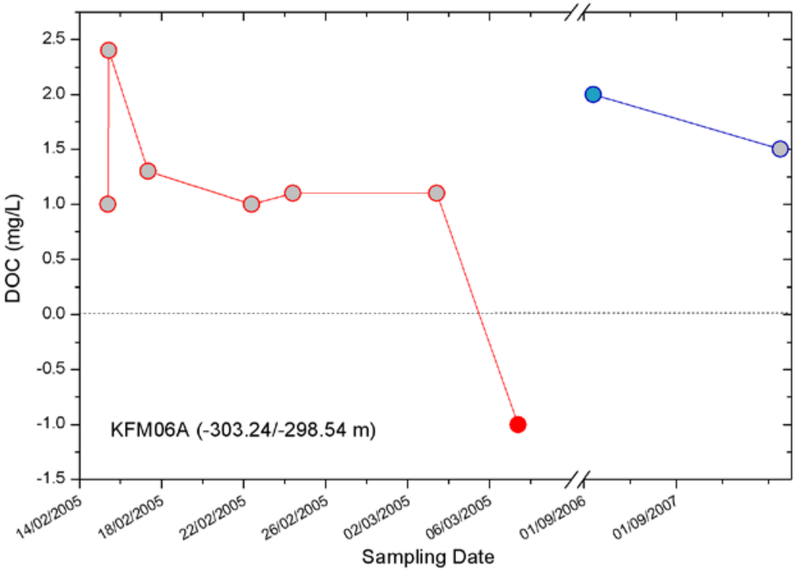

KFM06A (-303.24/-298.54 m)
S(-II) (mg/L)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date

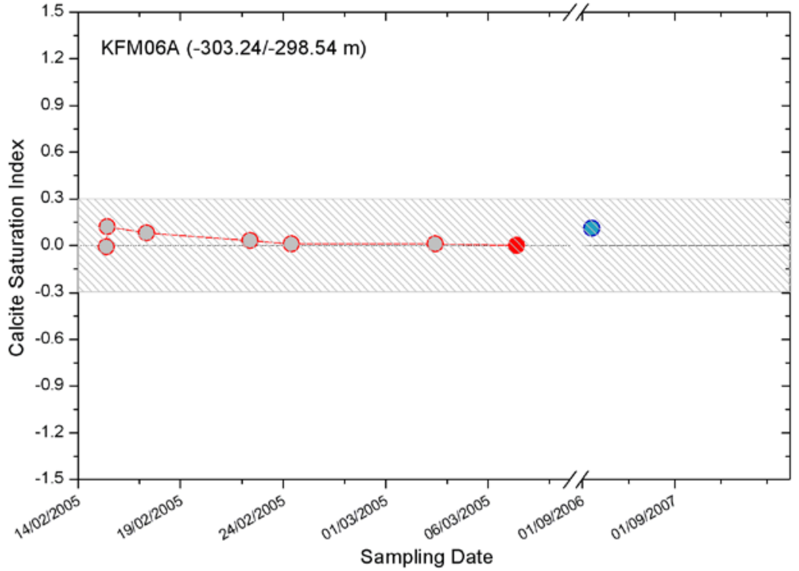

KFM06A (-303.24/-298.54 m)
Fe (mg/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date

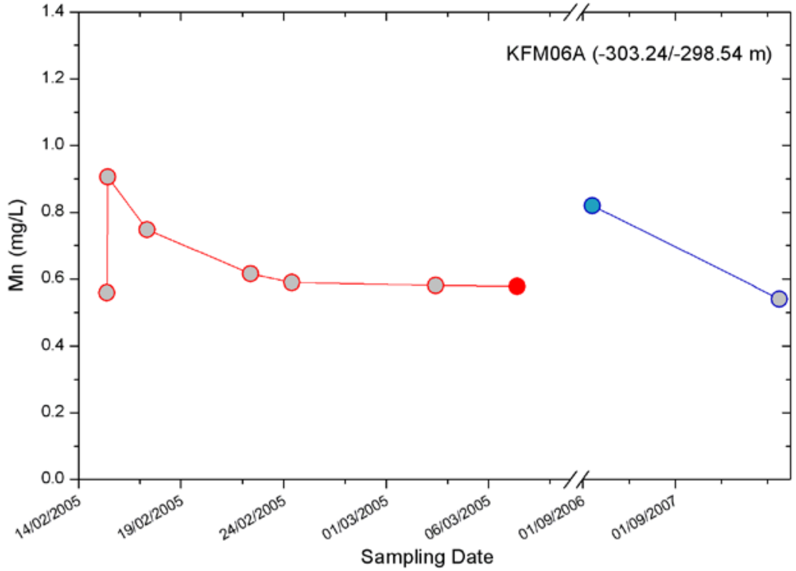

KFM06A (-303.24/-298.54 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date


KFM06A (-303.24/-298.54 m)
$\delta^{34}$S (‰ CDT)
30
28
26
24
22
20
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/03/2007
01/09/2007
01/03/2008
01/09/2008
Sampling Date

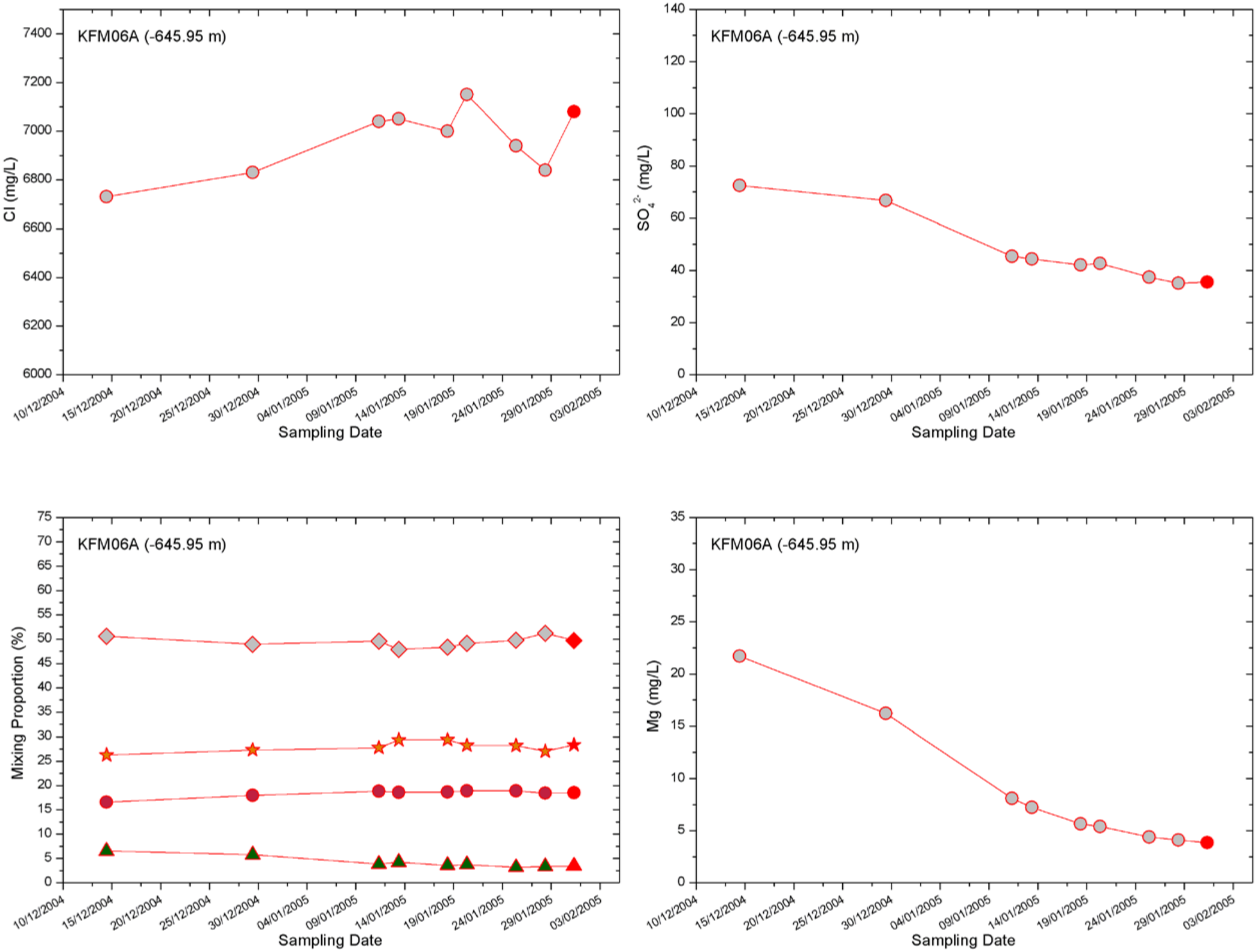

KFM06A (-303.24/-298.54 m)
$HCO_3^-$ (mg/L)
0
10
20
30
40
50
60
70
80
90
100
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date

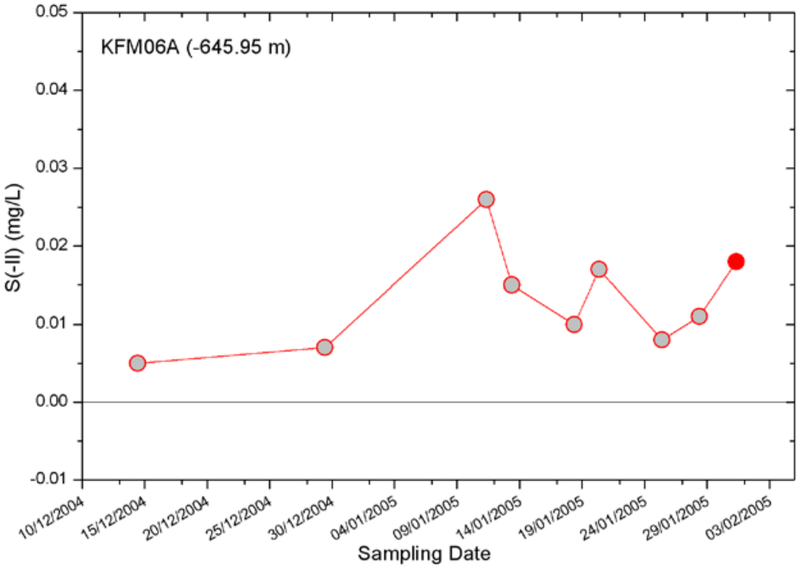

KFM06A (-303.24/-298.54 m)
DOC (mg/L)
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
14/02/2005
18/02/2005
22/02/2005
26/02/2005
02/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date

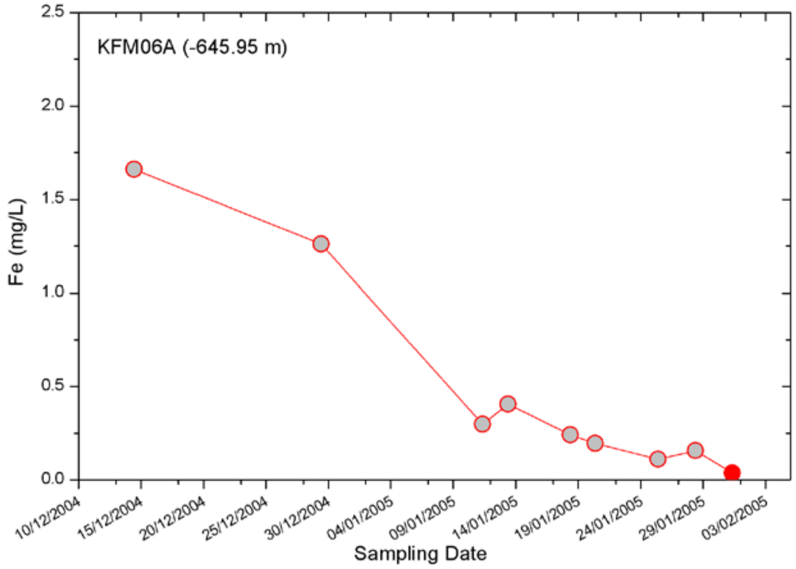

KFM06A (-303.24/-298.54 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date

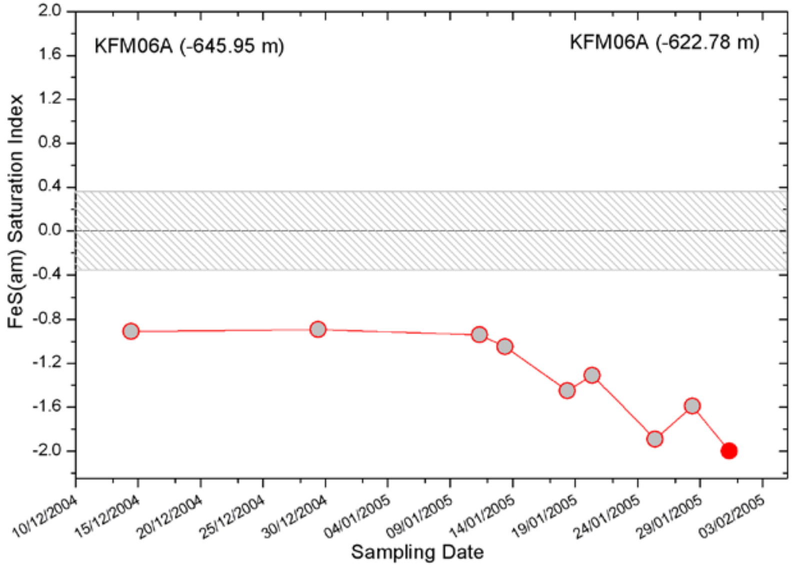

KFM06A (-303.24/-298.54 m)
Mn (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
14/02/2005
19/02/2005
24/02/2005
01/03/2005
06/03/2005
01/09/2006
01/09/2007
Sampling Date

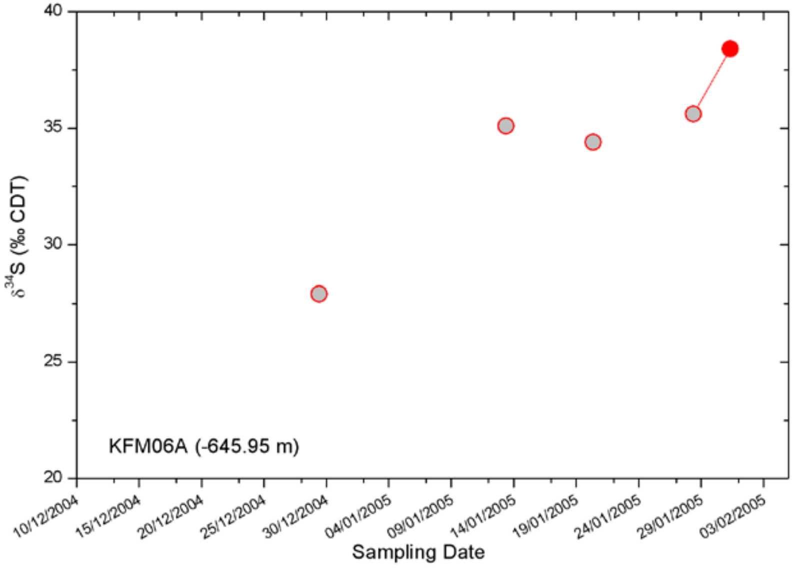
KFM06A (–645.95 m)

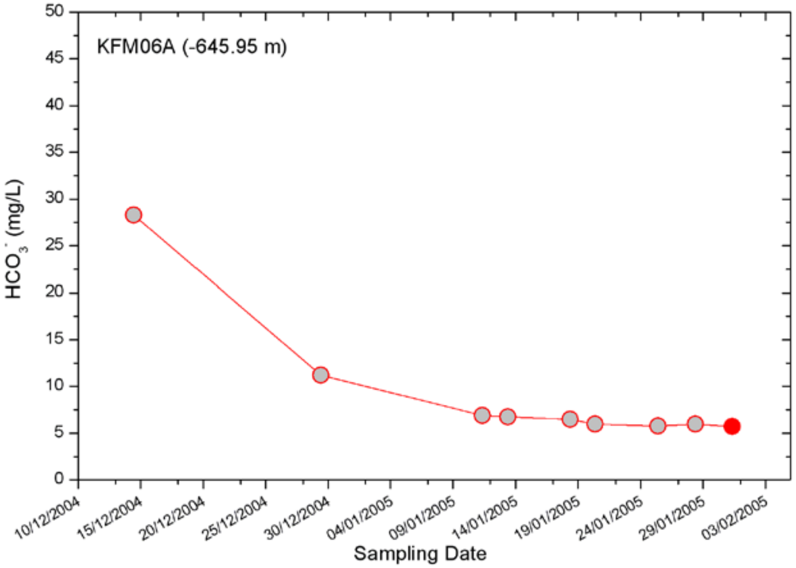


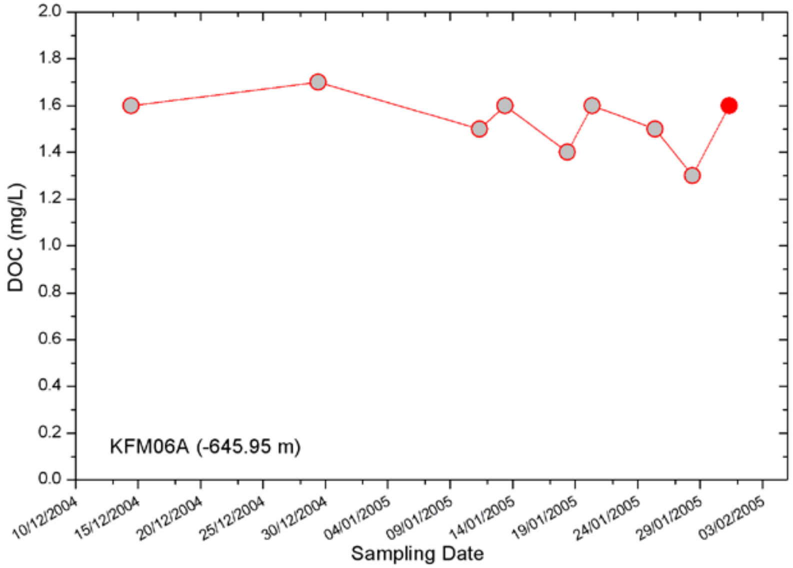

KFM06A (-645.95 m)
S(-II) (mg/L)
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005
Sampling Date

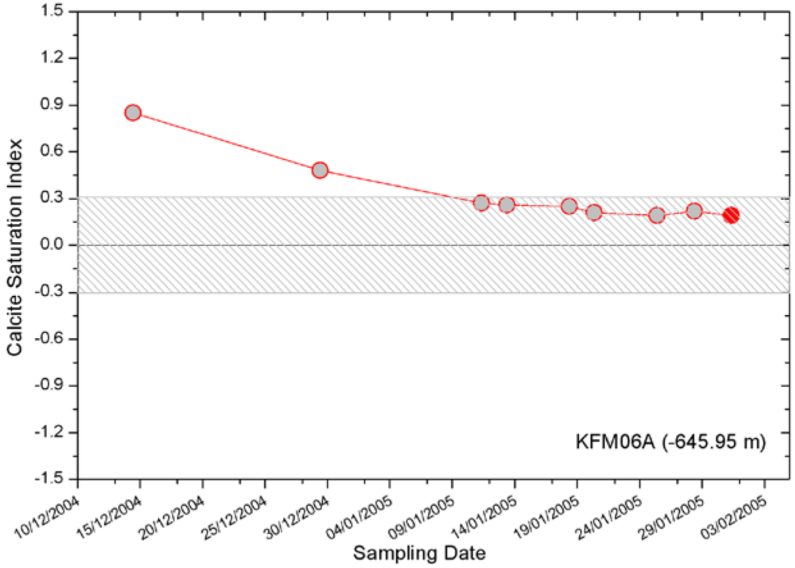

KFM06A (-645.95 m)
Fe (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005
Sampling Date

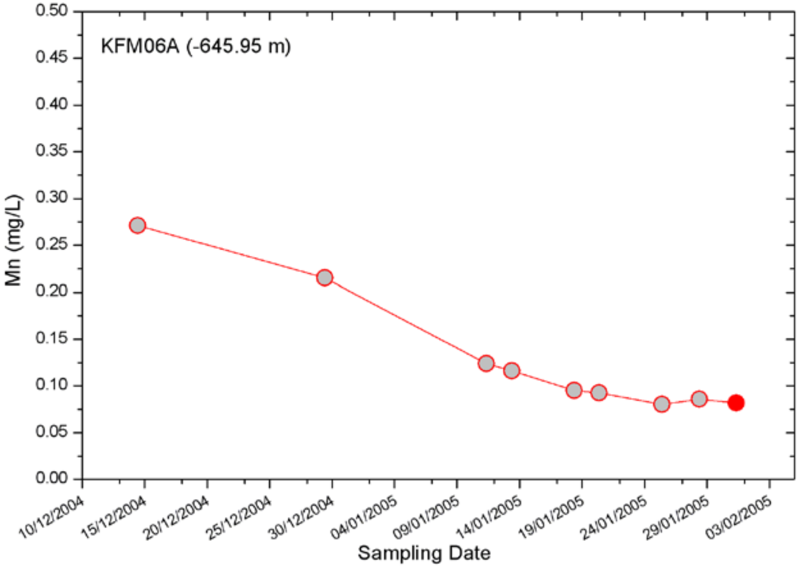

KFM06A (-645.95 m)
KFM06A (-622.78 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005
Sampling Date


KFM06A (-645.95 m)
δ³⁴S (‰ CDT)
40
35
30
25
20
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005
Sampling Date

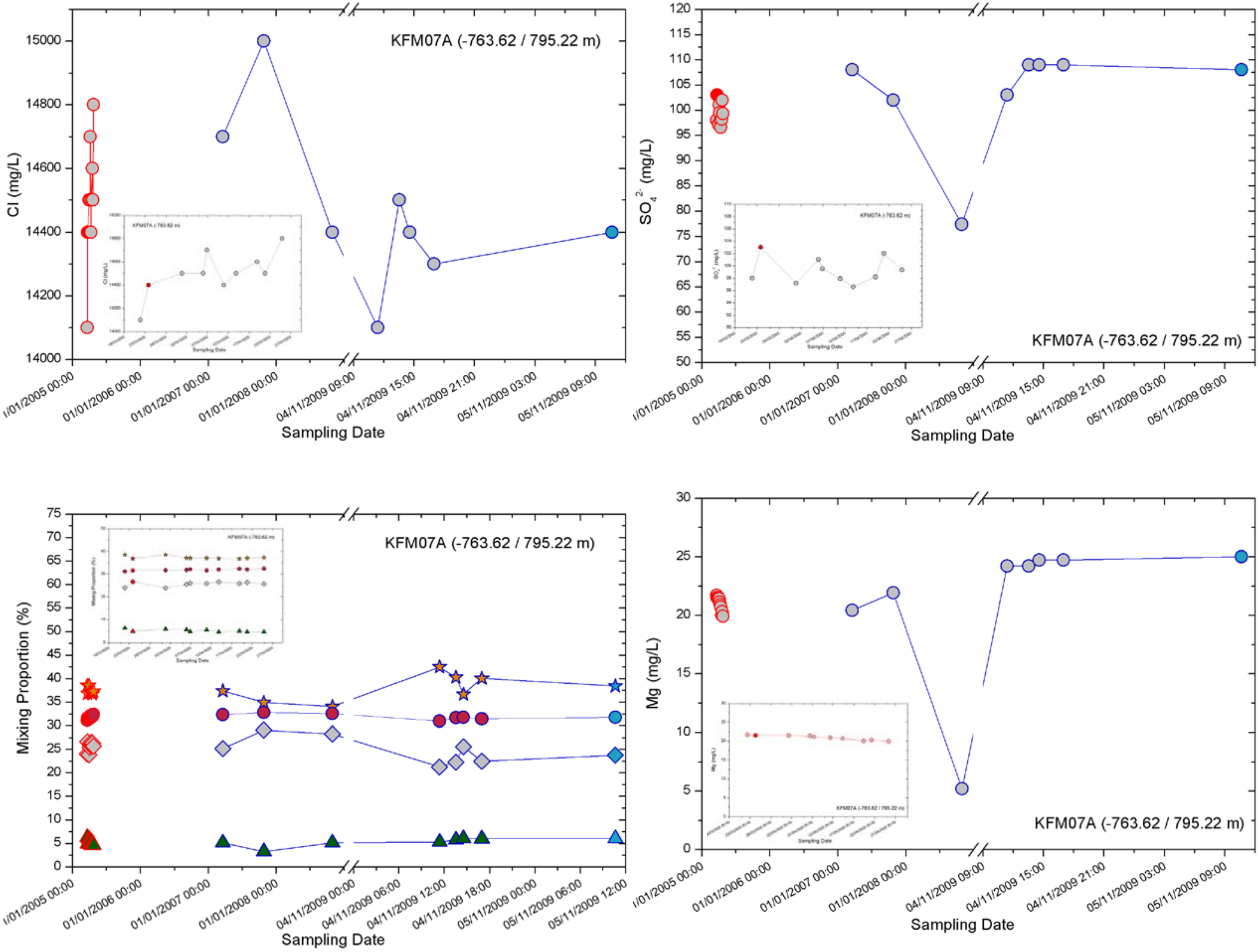

KFM06A (-645.95 m)
HCO$_3^-$ (mg/L)
0
5
10
15
20
25
30
35
40
45
50
Sampling Date
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005

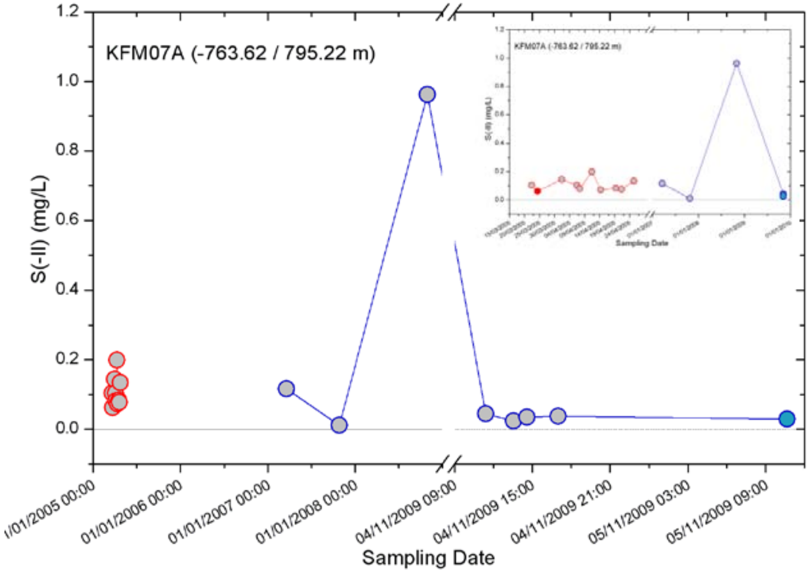

KFM06A (-645.95 m)
DOC (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Sampling Date
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005

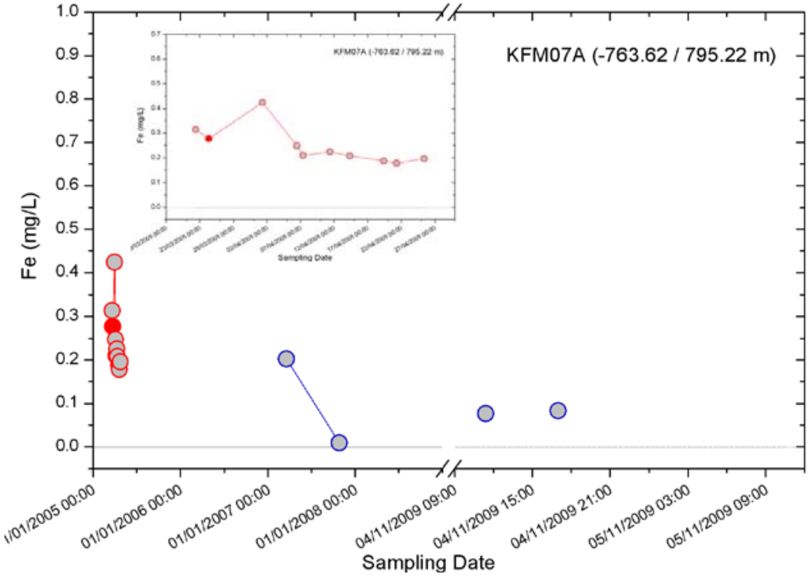

KFM06A (-645.95 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
Sampling Date
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005

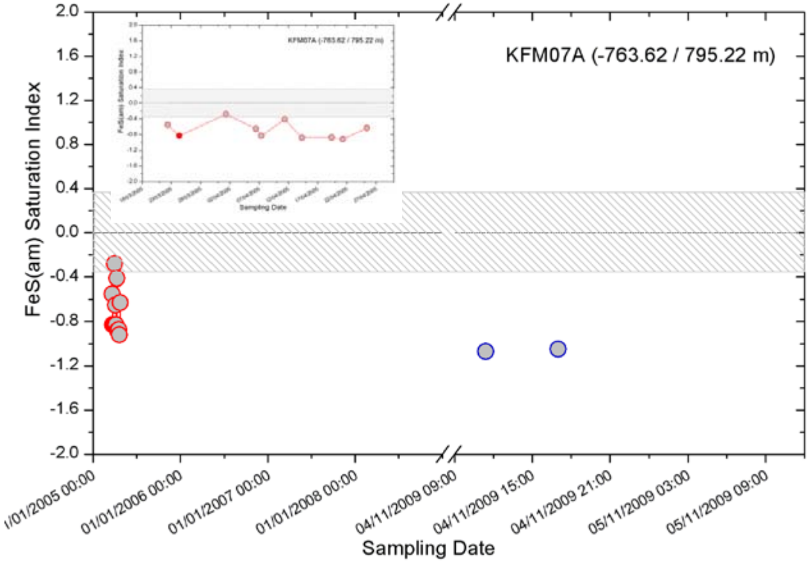

KFM06A (-645.95 m)
Mn (mg/L)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Sampling Date
10/12/2004
15/12/2004
20/12/2004
25/12/2004
30/12/2004
04/01/2005
09/01/2005
14/01/2005
19/01/2005
24/01/2005
29/01/2005
03/02/2005

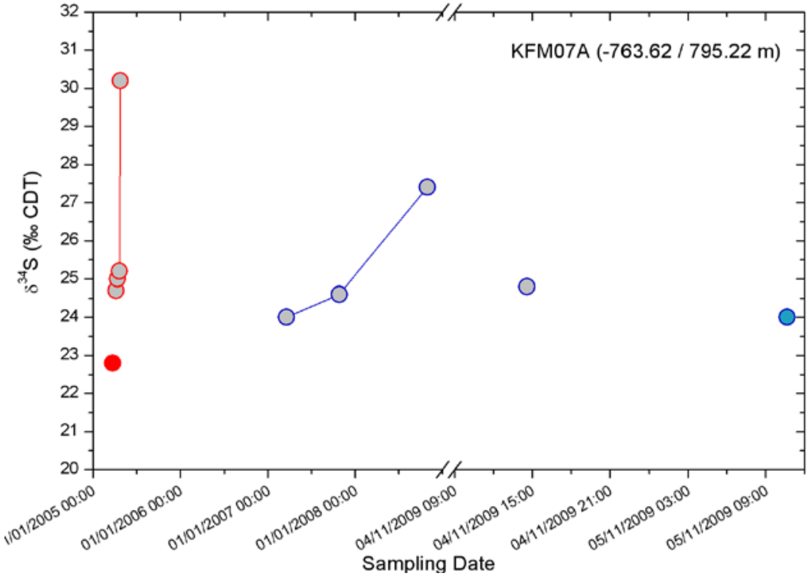
KFM07A (–763.62 / –795.22 m)

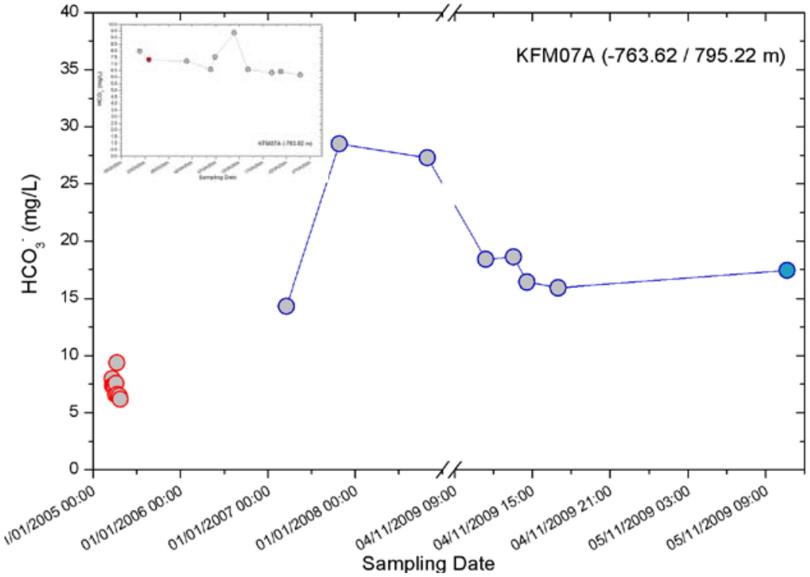


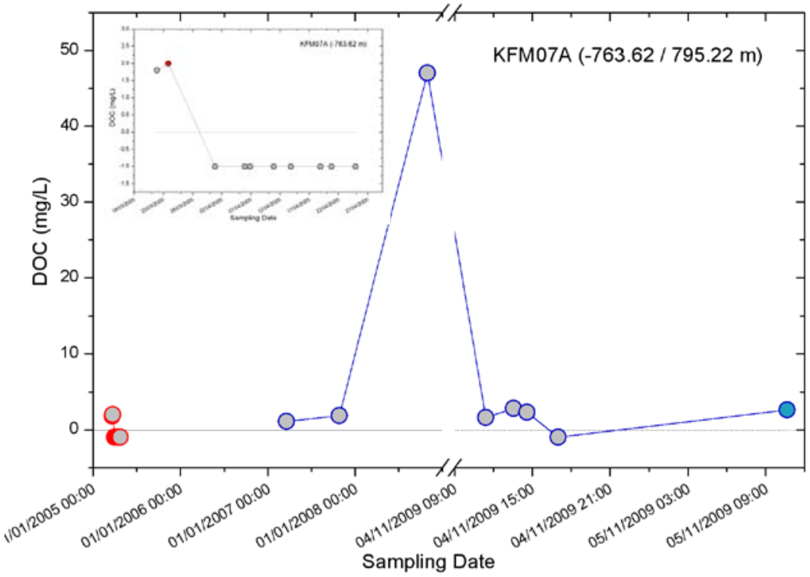

KFM07A (-763.62 / 795.22 m)
S(-II) (mg/L)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

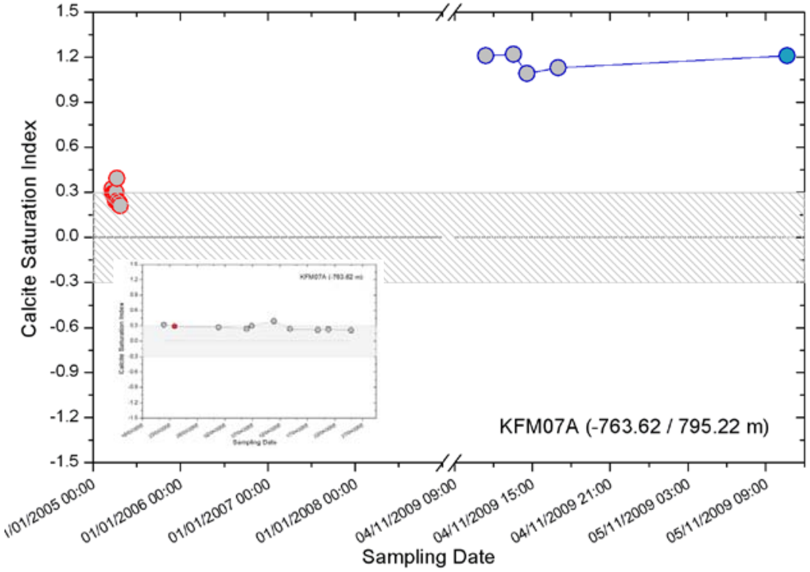

KFM07A (-763.62 / 795.22 m)
Fe (mg/L)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

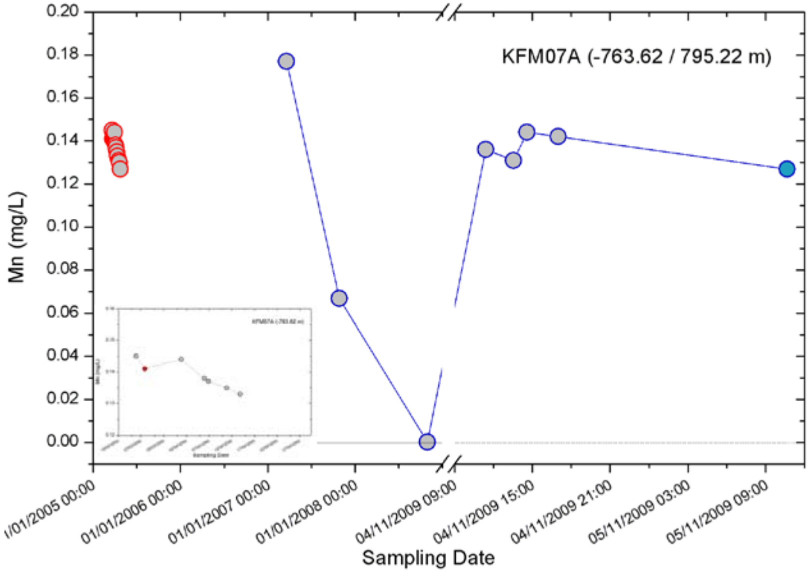

KFM07A (-763.62 / 795.22 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00


KFM07A (-763.62 / 795.22 m)
δ34S (‰ CDT)
32
31
30
29
28
27
26
25
24
23
22
21
20
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

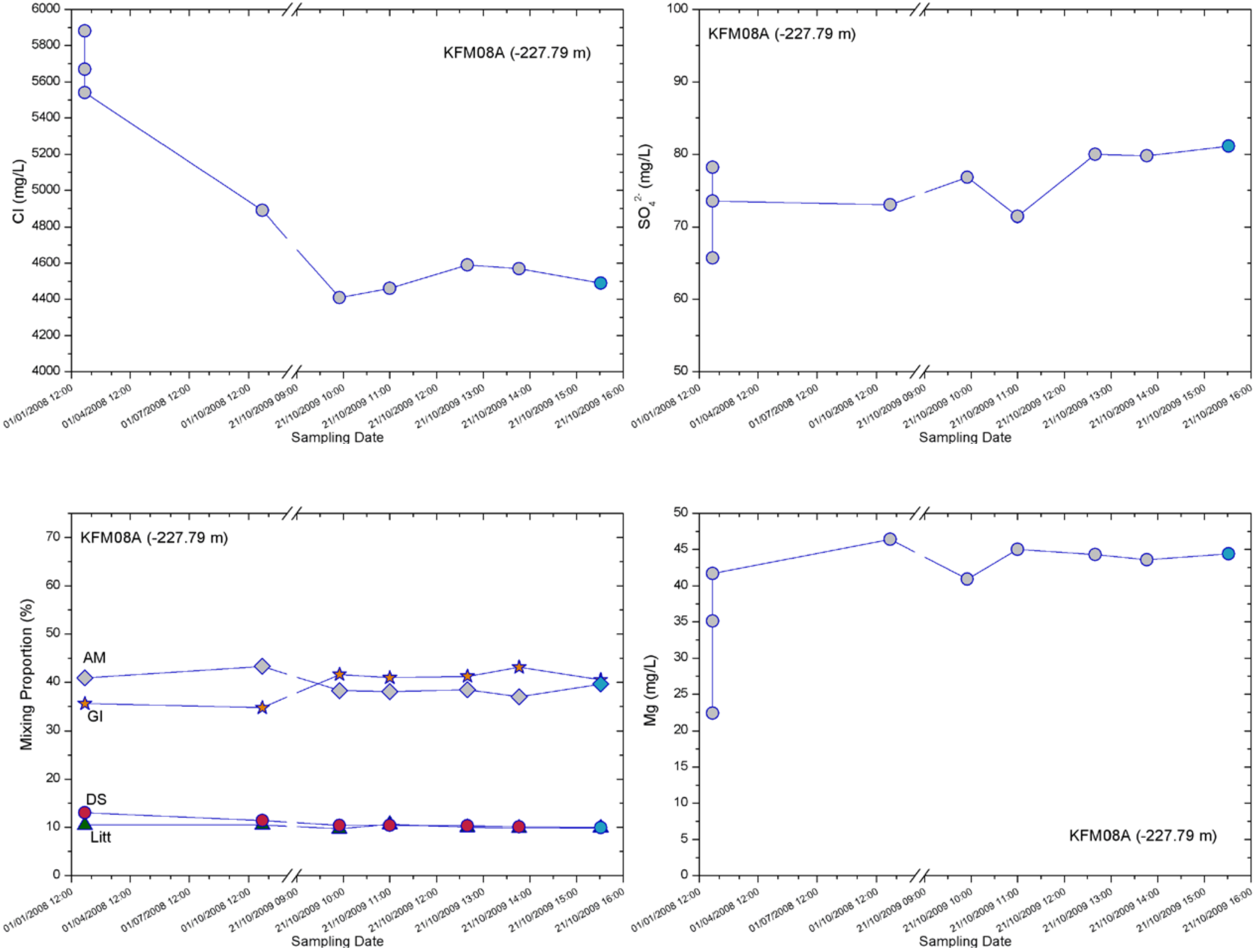

KFM07A (-763.62 / 795.22 m)
HCO$_3^-$ (mg/L)
0
5
10
15
20
25
30
35
40
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

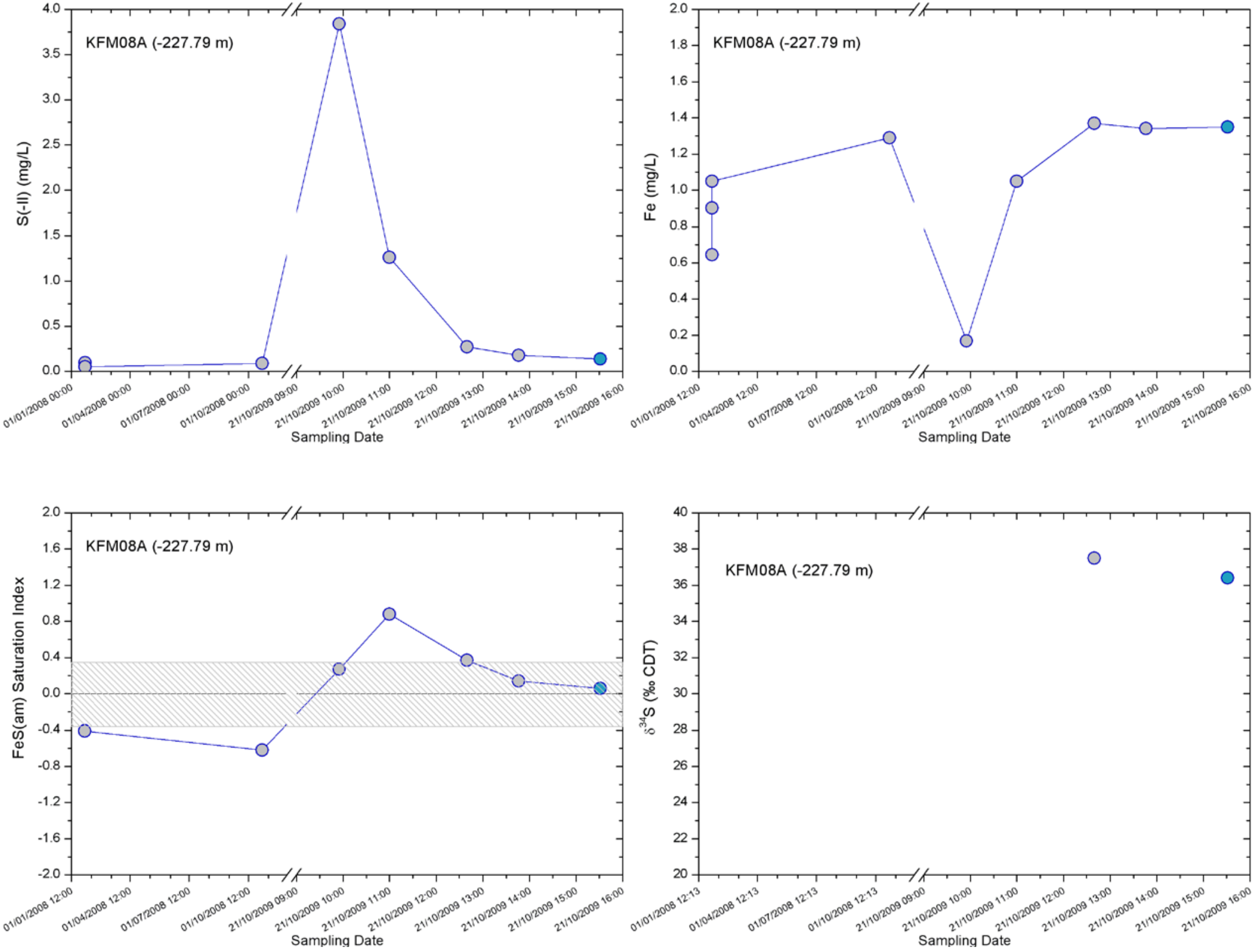

KFM07A (-763.62 / 795.22 m)
DOC (mg/L)
0
10
20
30
40
50
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

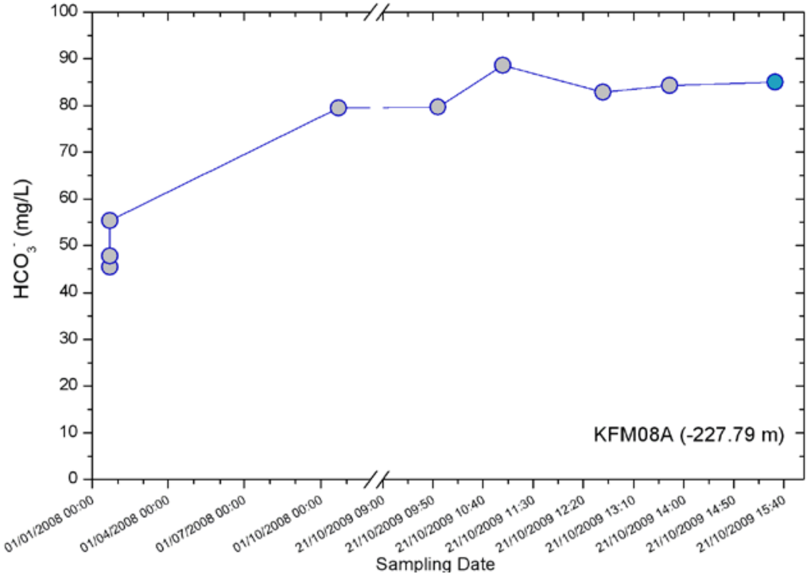

KFM07A (-763.62 / 795.22 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

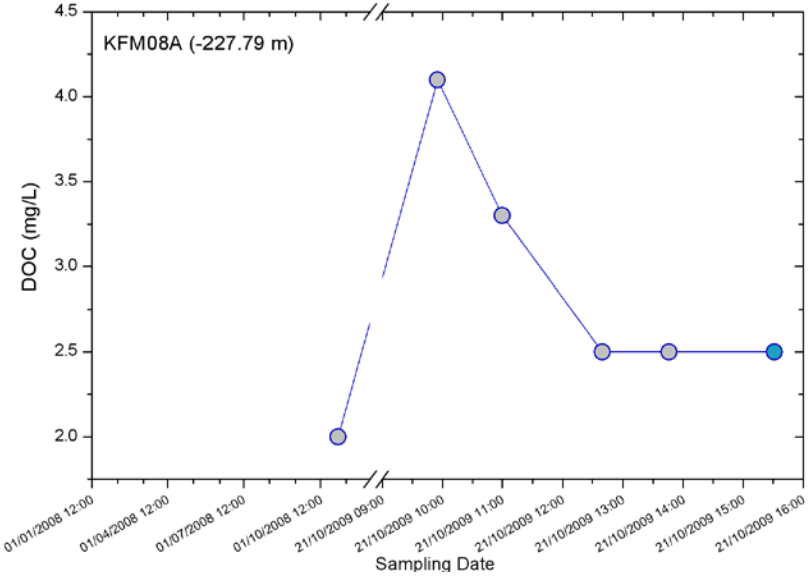

KFM07A (-763.62 / 795.22 m)
Mn (mg/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
Sampling Date
1/01/2005 00:00
01/01/2006 00:00
01/01/2007 00:00
01/01/2008 00:00
04/11/2009 09:00
04/11/2009 15:00
04/11/2009 21:00
05/11/2009 03:00
05/11/2009 09:00

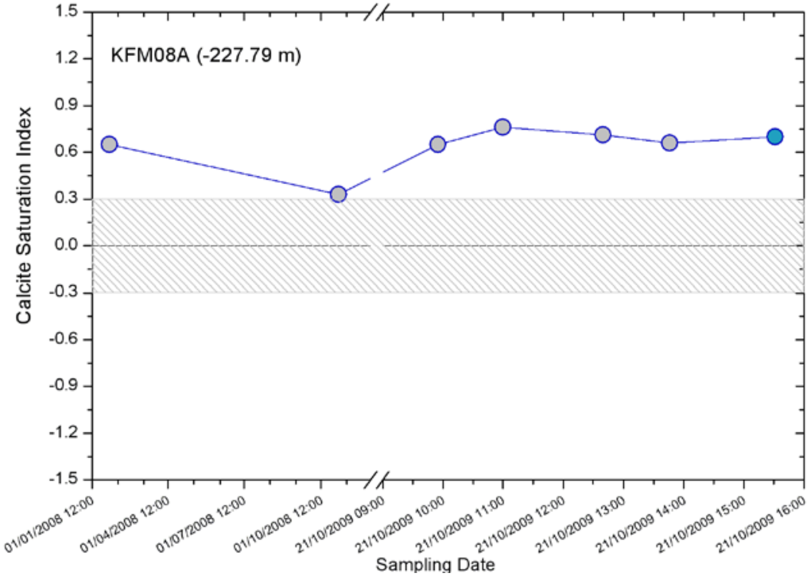
KFM08A (–227.79 m)

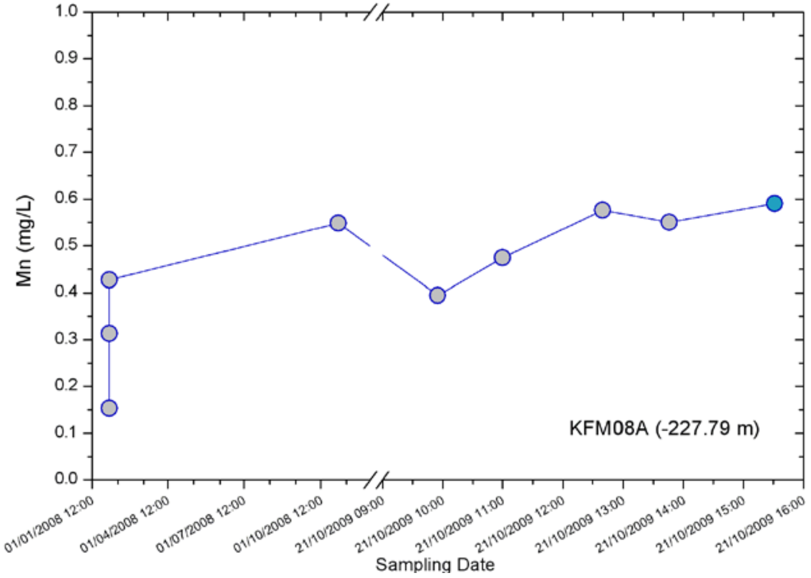



KFM08A (-227.79 m)
S(-II) (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
01/01/2008 00:00
01/04/2008 00:00
01/07/2008 00:00
01/10/2008 00:00
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00
Sampling Date
KFM08A (-227.79 m)
Fe (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
01/01/2008 12:00
01/04/2008 12:00
01/07/2008 12:00
01/10/2008 12:00
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00
Sampling Date
KFM08A (-227.79 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
01/01/2008 12:00
01/04/2008 12:00
01/07/2008 12:00
01/10/2008 12:00
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00
Sampling Date
KFM08A (-227.79 m)
δ34S (‰ CDT)
40
38
36
34
32
30
28
26
24
22
20
01/01/2008 12:13
01/04/2008 12:13
01/07/2008 12:13
01/10/2008 12:13
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00
Sampling Date

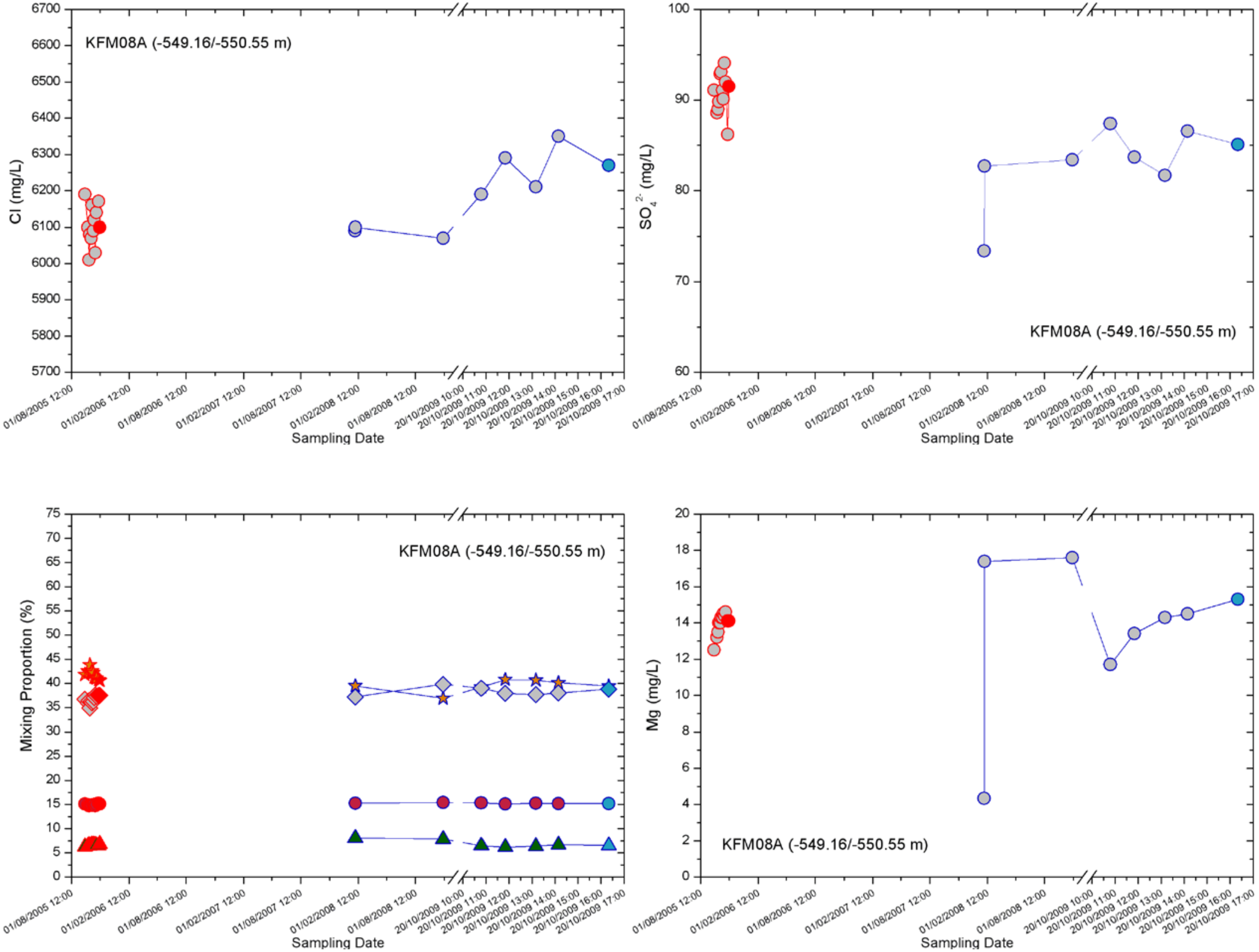

KFM08A (-227.79 m)
$HCO_3^-$ (mg/L)
0
10
20
30
40
50
60
70
80
90
100
Sampling Date
01/01/2008 00:00
01/04/2008 00:00
01/07/2008 00:00
01/10/2008 00:00
21/10/2009 09:00
21/10/2009 09:50
21/10/2009 10:40
21/10/2009 11:30
21/10/2009 12:20
21/10/2009 13:10
21/10/2009 14:00
21/10/2009 14:50
21/10/2009 15:40

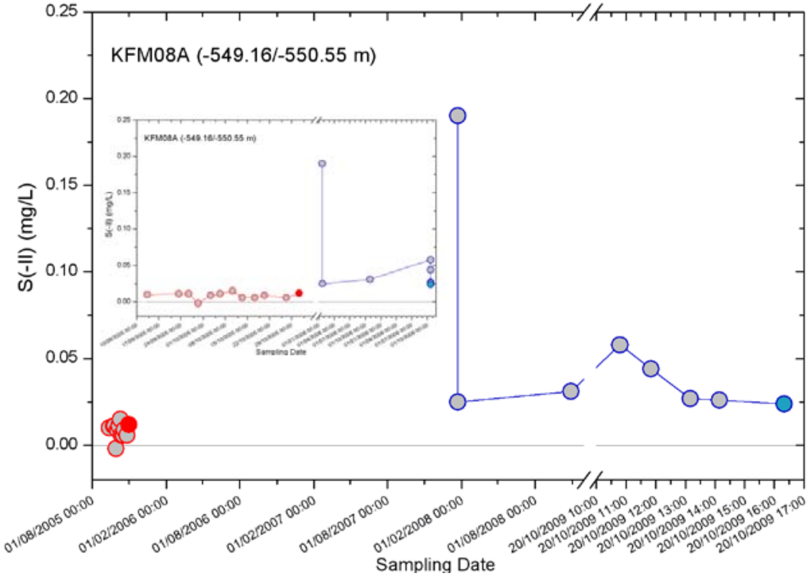

KFM08A (-227.79 m)
DOC (mg/L)
2.0
2.5
3.0
3.5
4.0
4.5
Sampling Date
01/01/2008 12:00
01/04/2008 12:00
01/07/2008 12:00
01/10/2008 12:00
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00

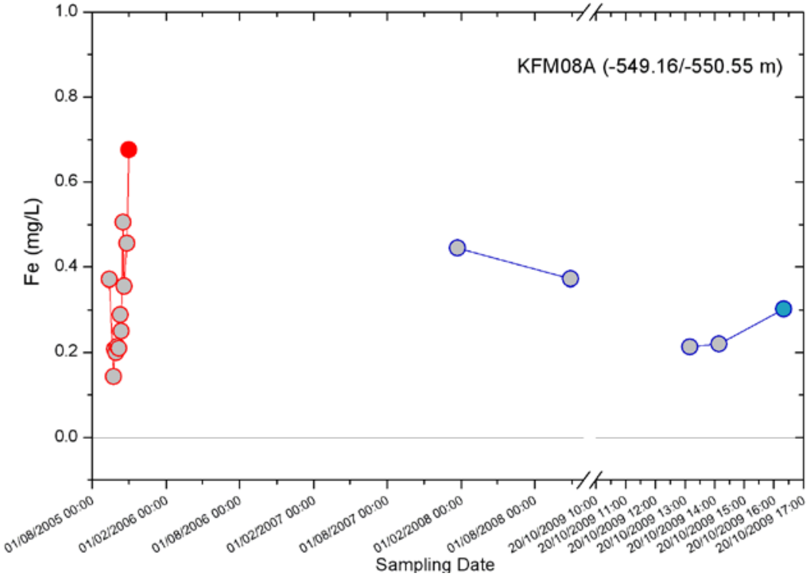

KFM08A (-227.79 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
Sampling Date
01/01/2008 12:00
01/04/2008 12:00
01/07/2008 12:00
01/10/2008 12:00
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00

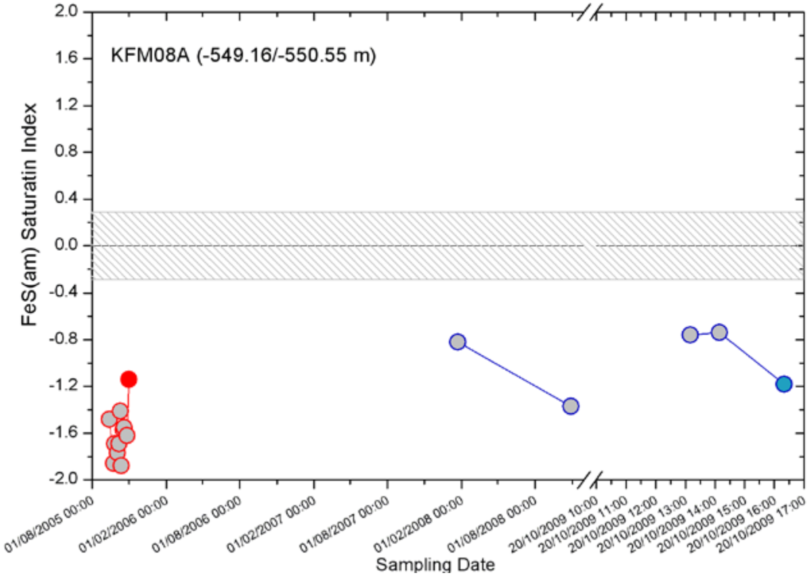

KFM08A (-227.79 m)
Mn (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Sampling Date
01/01/2008 12:00
01/04/2008 12:00
01/07/2008 12:00
01/10/2008 12:00
21/10/2009 09:00
21/10/2009 10:00
21/10/2009 11:00
21/10/2009 12:00
21/10/2009 13:00
21/10/2009 14:00
21/10/2009 15:00
21/10/2009 16:00

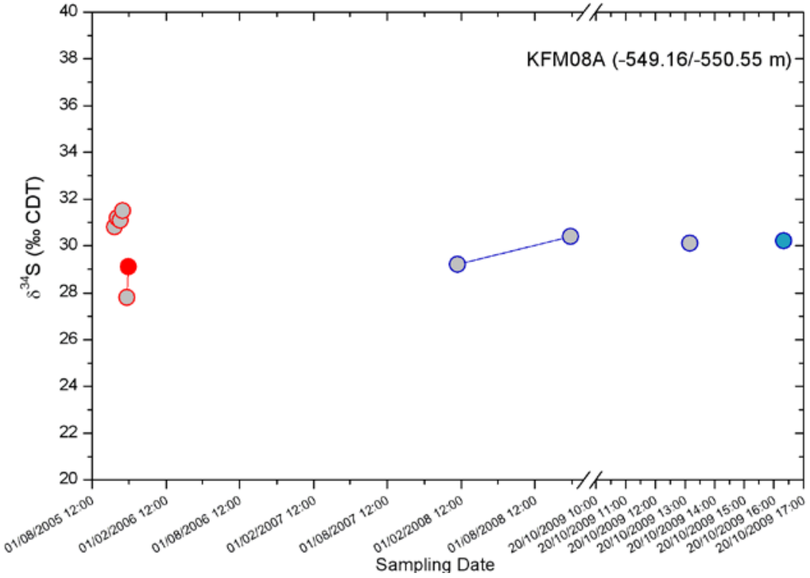
KFM08A (–549.16/–550.55 m)

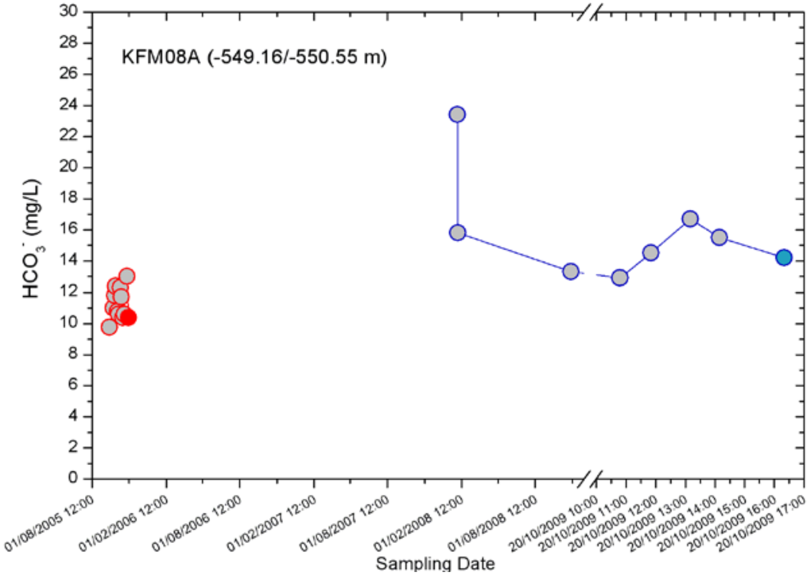


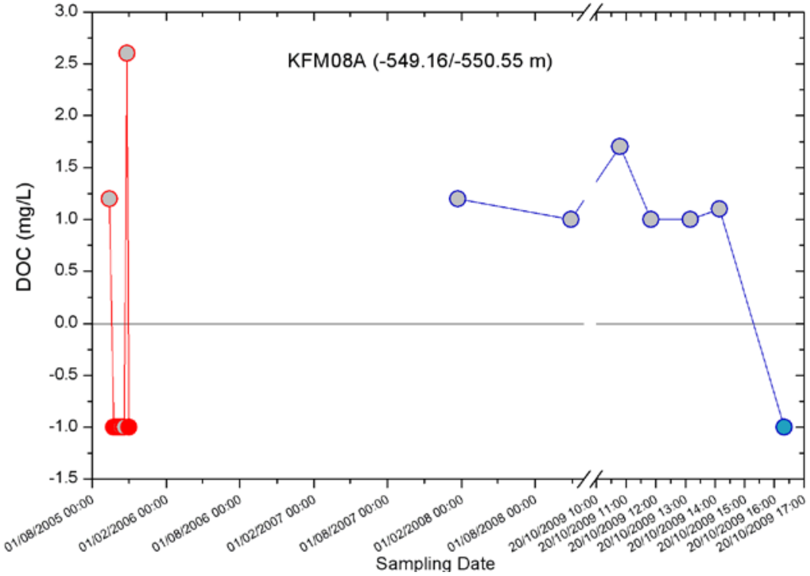

KFM08A (-549.16/-550.55 m)
S(-II) (mg/L)
0.25
0.20
0.15
0.10
0.05
0.00
Sampling Date
01/08/2005 00:00
01/02/2006 00:00
01/08/2006 00:00
01/02/2007 00:00
01/08/2007 00:00
01/02/2008 00:00
01/08/2008 00:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00
KFM08A (-549.16/-550.55 m)
S(-II) (mg/L)
Sampling Date

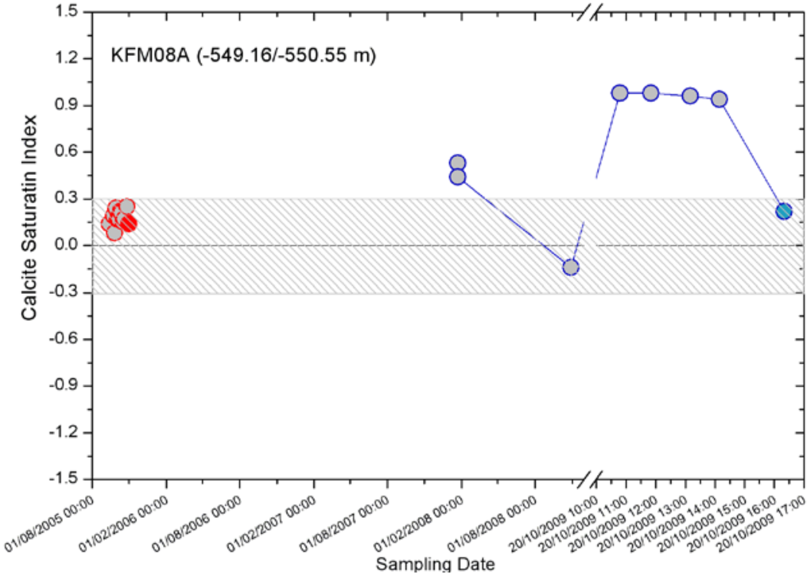

KFM08A (-549.16/-550.55 m)
Fe (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
Sampling Date
01/08/2005 00:00
01/02/2006 00:00
01/08/2006 00:00
01/02/2007 00:00
01/08/2007 00:00
01/02/2008 00:00
01/08/2008 00:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00

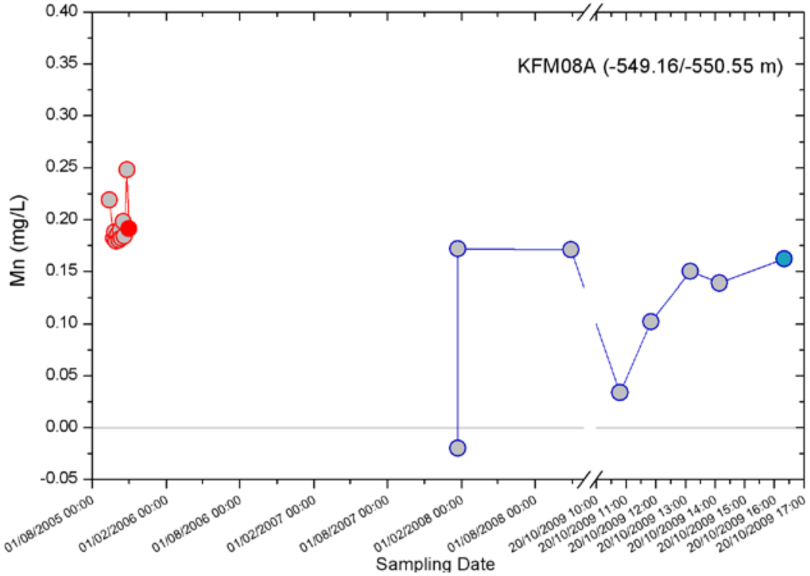

KFM08A (-549.16/-550.55 m)
FeS(am) Saturatin Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
Sampling Date
01/08/2005 00:00
01/02/2006 00:00
01/08/2006 00:00
01/02/2007 00:00
01/08/2007 00:00
01/02/2008 00:00
01/08/2008 00:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00


KFM08A (-549.16/-550.55 m)
δ34S (‰ CDT)
40
38
36
34
32
30
28
26
24
22
20
Sampling Date
01/08/2005 12:00
01/02/2006 12:00
01/08/2006 12:00
01/02/2007 12:00
01/08/2007 12:00
01/02/2008 12:00
01/08/2008 12:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00

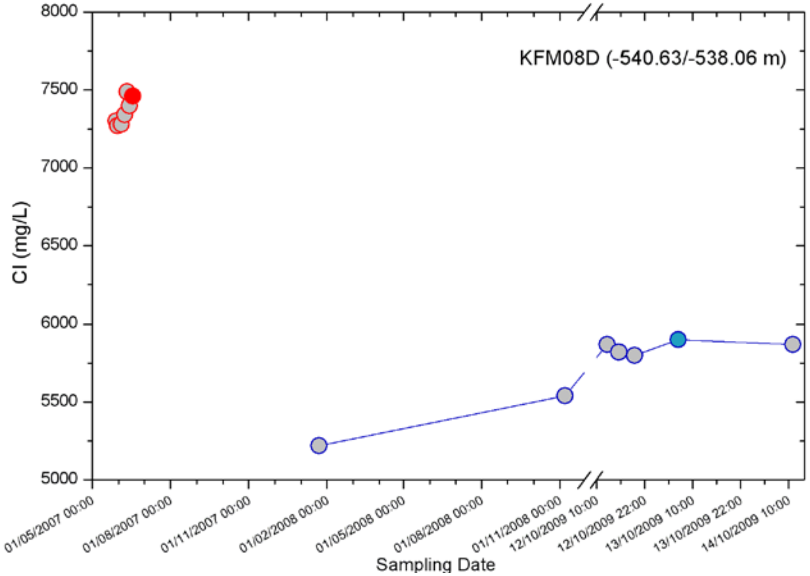

KFM08A (-549.16/-550.55 m)
HCO$_3^-$ (mg/L)
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
01/08/2005 12:00
01/02/2006 12:00
01/08/2006 12:00
01/02/2007 12:00
01/08/2007 12:00
01/02/2008 12:00
01/08/2008 12:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00
Sampling Date

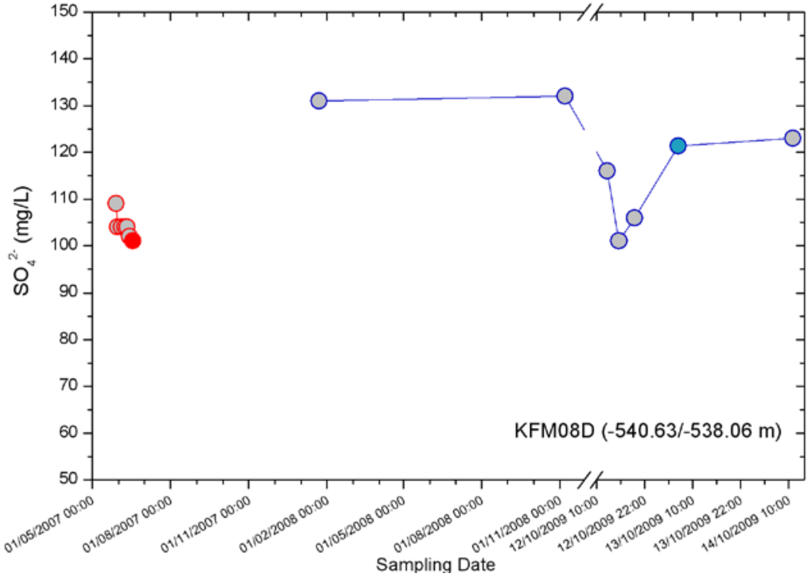

KFM08A (-549.16/-550.55 m)
DOC (mg/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
01/08/2005 00:00
01/02/2006 00:00
01/08/2006 00:00
01/02/2007 00:00
01/08/2007 00:00
01/02/2008 00:00
01/08/2008 00:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00
Sampling Date

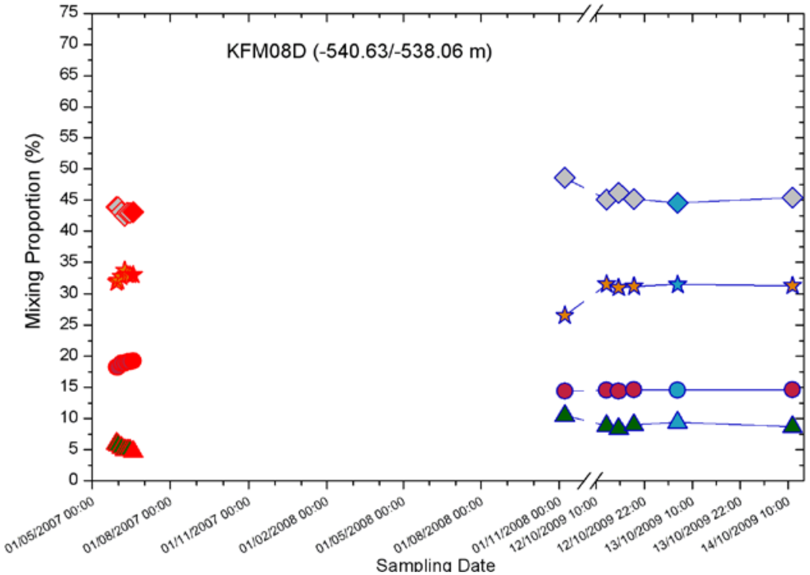

KFM08A (-549.16/-550.55 m)
Calcite Saturatin Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
01/08/2005 00:00
01/02/2006 00:00
01/08/2006 00:00
01/02/2007 00:00
01/08/2007 00:00
01/02/2008 00:00
01/08/2008 00:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00
Sampling Date

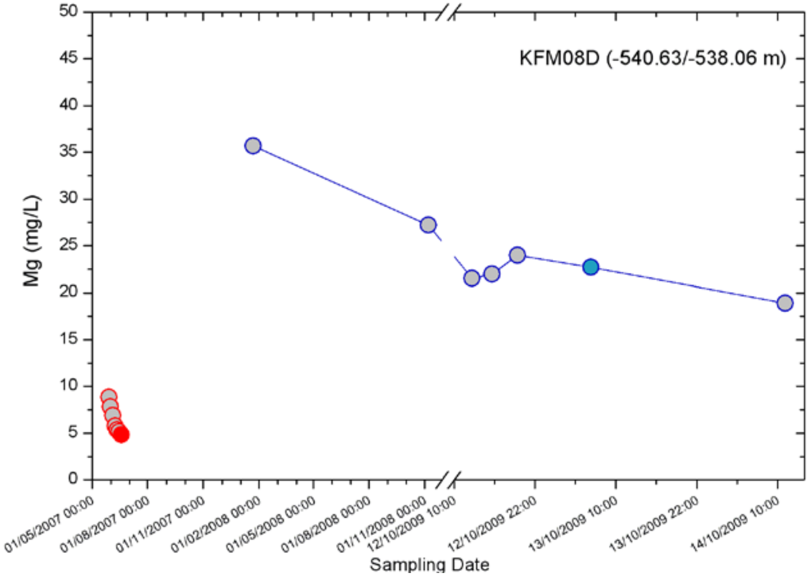

KFM08A (-549.16/-550.55 m)
Mn (mg/L)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
01/08/2005 00:00
01/02/2006 00:00
01/08/2006 00:00
01/02/2007 00:00
01/08/2007 00:00
01/02/2008 00:00
01/08/2008 00:00
20/10/2009 10:00
20/10/2009 11:00
20/10/2009 12:00
20/10/2009 13:00
20/10/2009 14:00
20/10/2009 15:00
20/10/2009 16:00
20/10/2009 17:00
Sampling Date

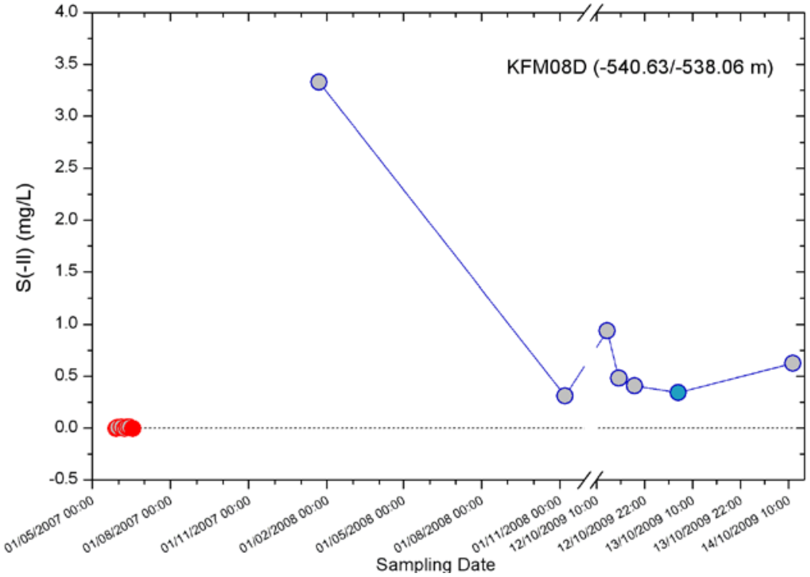
KFM08D (–540.63/–538.06 m)
Eh = –260 mV

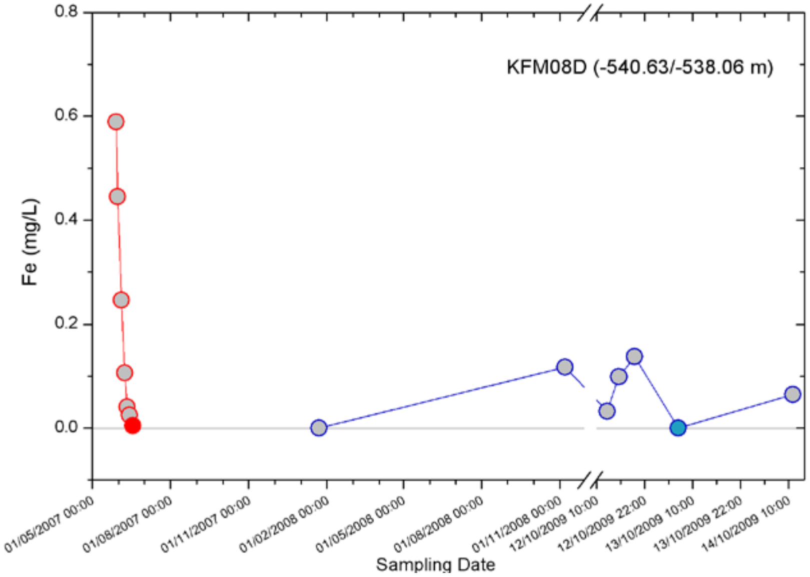


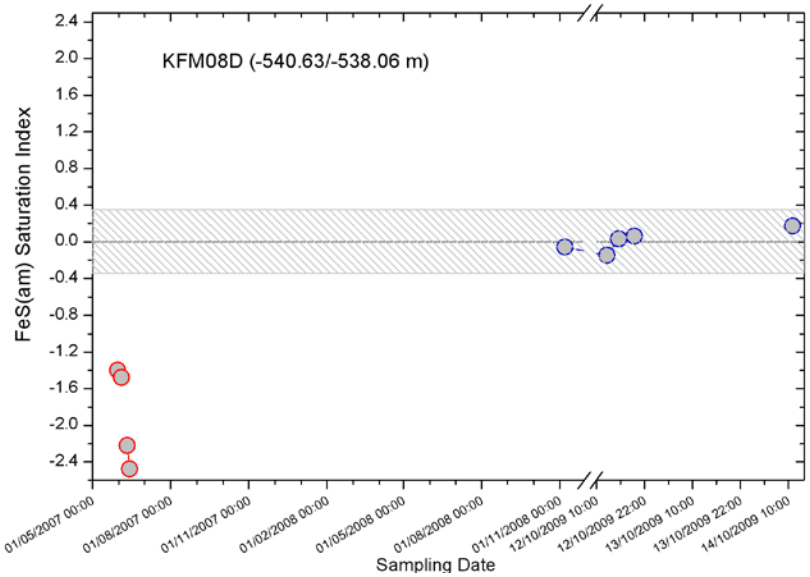


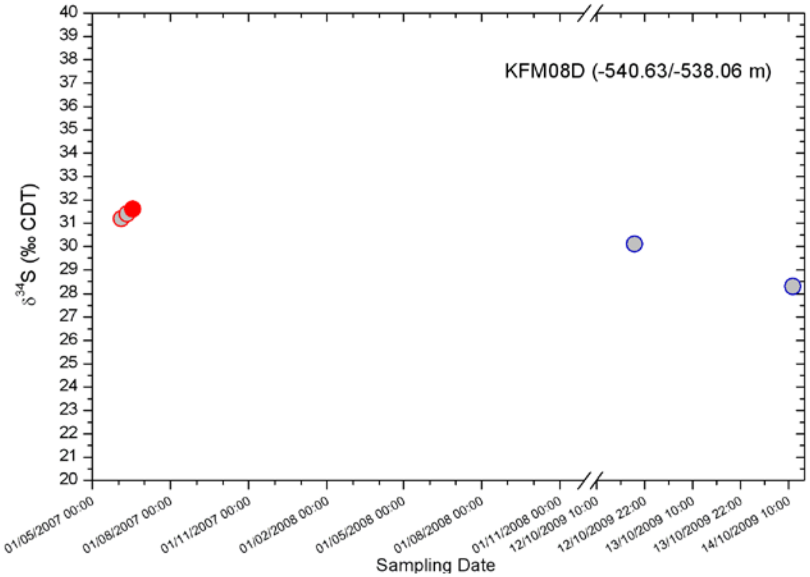


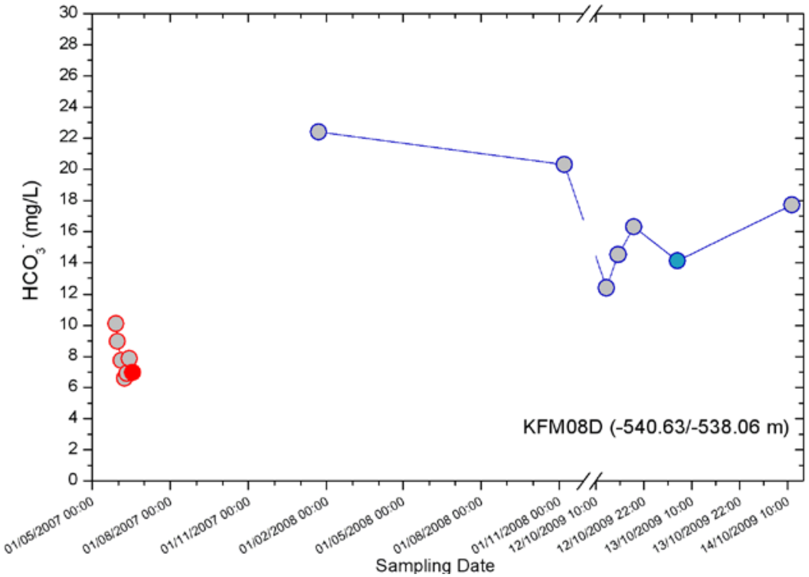


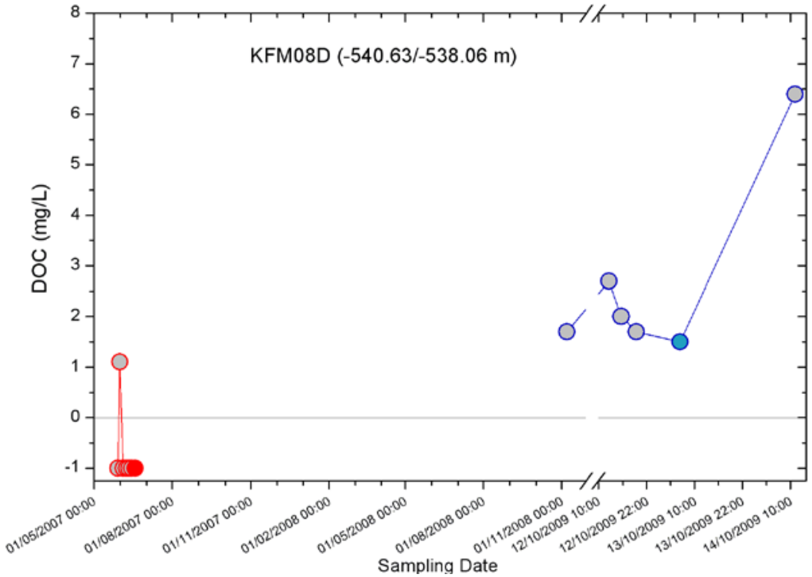

KFM08D (-540.63/-538.06 m)
S(-II) (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00
Sampling Date

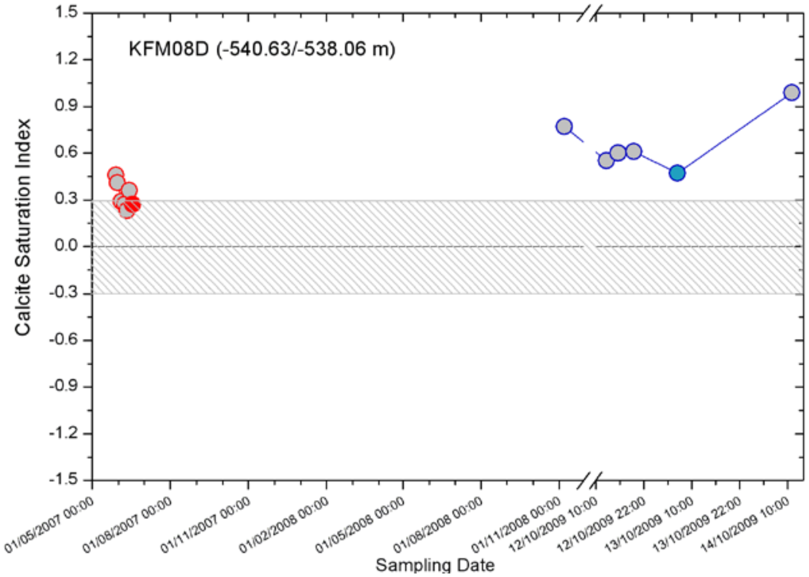

KFM08D (-540.63/-538.06 m)
Fe (mg/L)
0.8
0.6
0.4
0.2
0.0
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00
Sampling Date

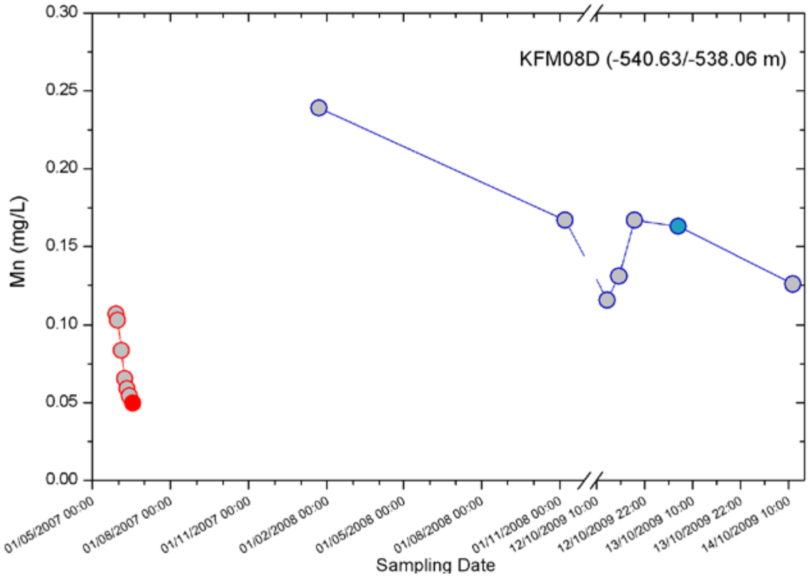

KFM08D (-540.63/-538.06 m)
FeS(am) Saturation Index
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00
Sampling Date


KFM08D (-540.63/-538.06 m)
δ34S (‰ CDT)
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00
Sampling Date

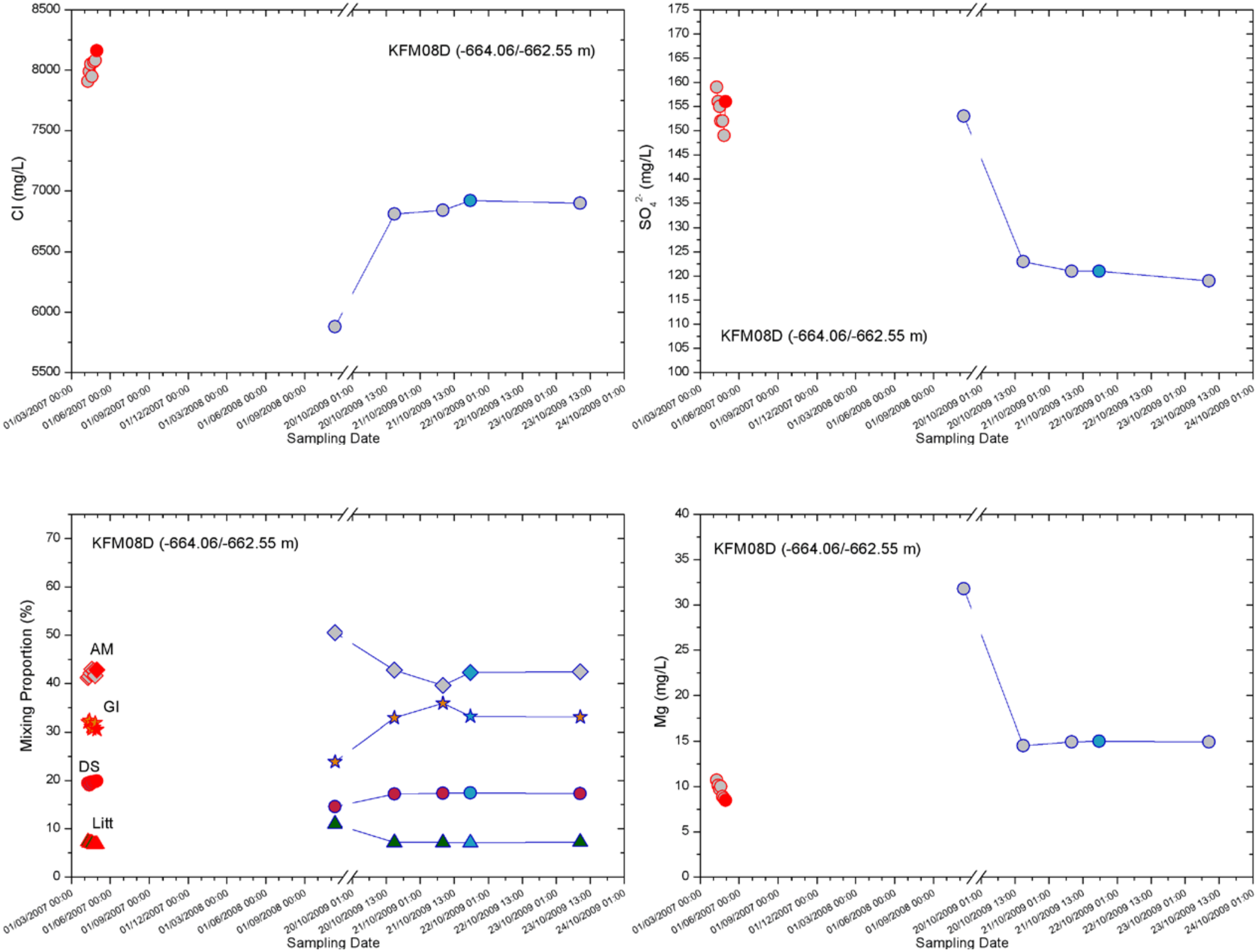

KFM08D (-540.63/-538.06 m)
HCO$_3^-$ (mg/L)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Sampling Date
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00

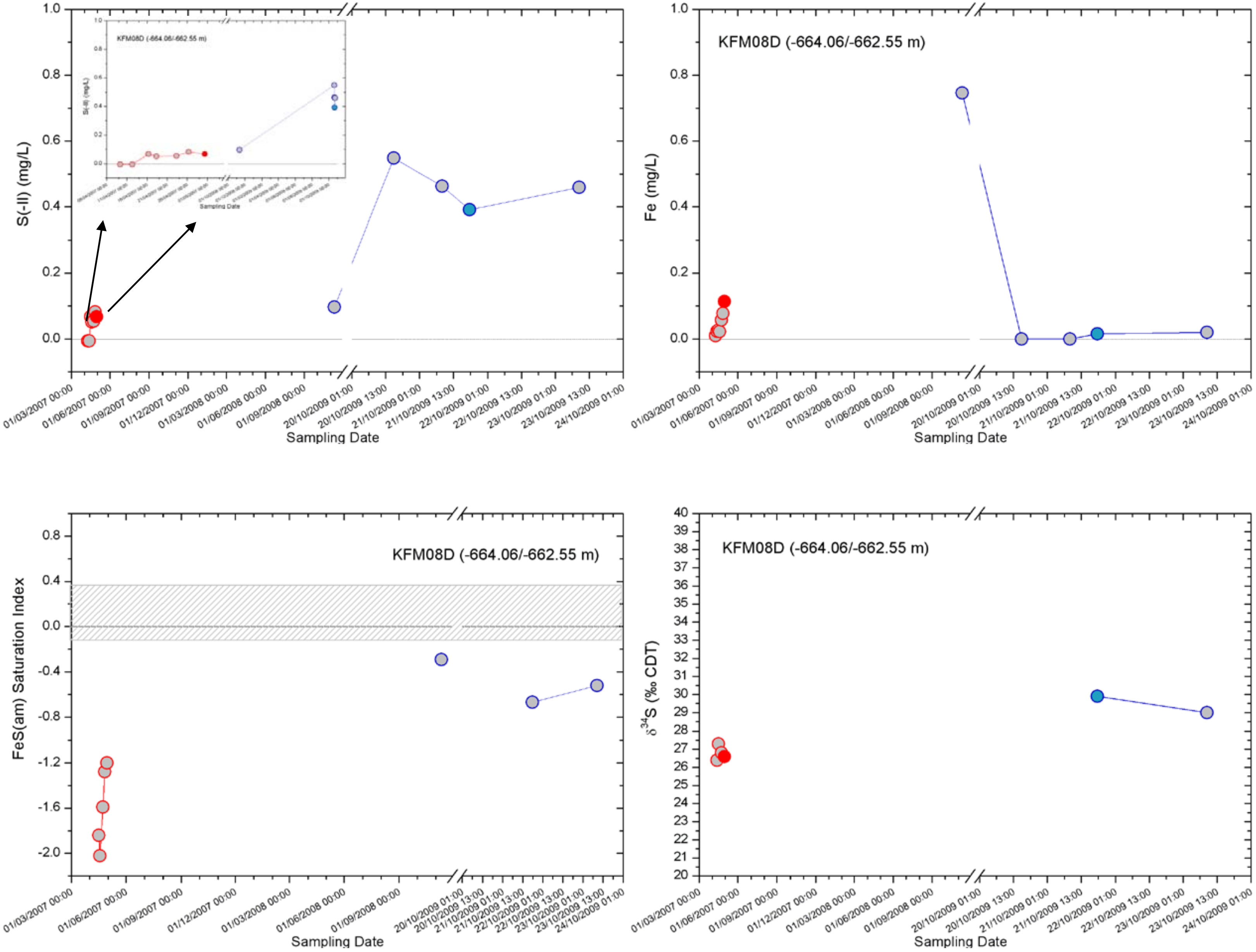

KFM08D (-540.63/-538.06 m)
DOC (mg/L)
-1
0
1
2
3
4
5
6
7
8
Sampling Date
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00

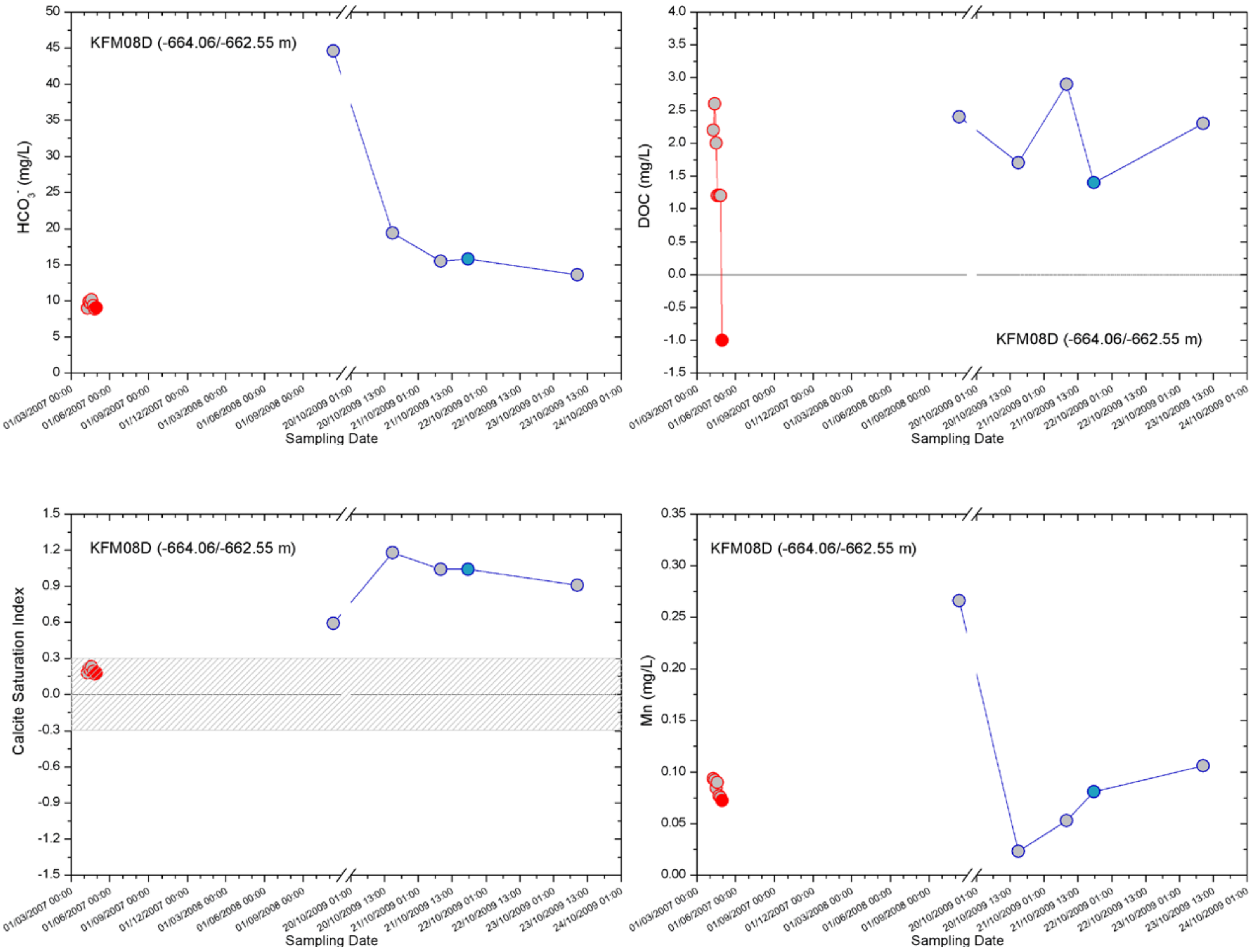

KFM08D (-540.63/-538.06 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
Sampling Date
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00


KFM08D (-540.63/-538.06 m)
Mn (mg/L)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Sampling Date
01/05/2007 00:00
01/08/2007 00:00
01/11/2007 00:00
01/02/2008 00:00
01/05/2008 00:00
01/08/2008 00:00
01/11/2008 00:00
12/10/2009 10:00
12/10/2009 22:00
13/10/2009 10:00
13/10/2009 22:00
14/10/2009 10:00

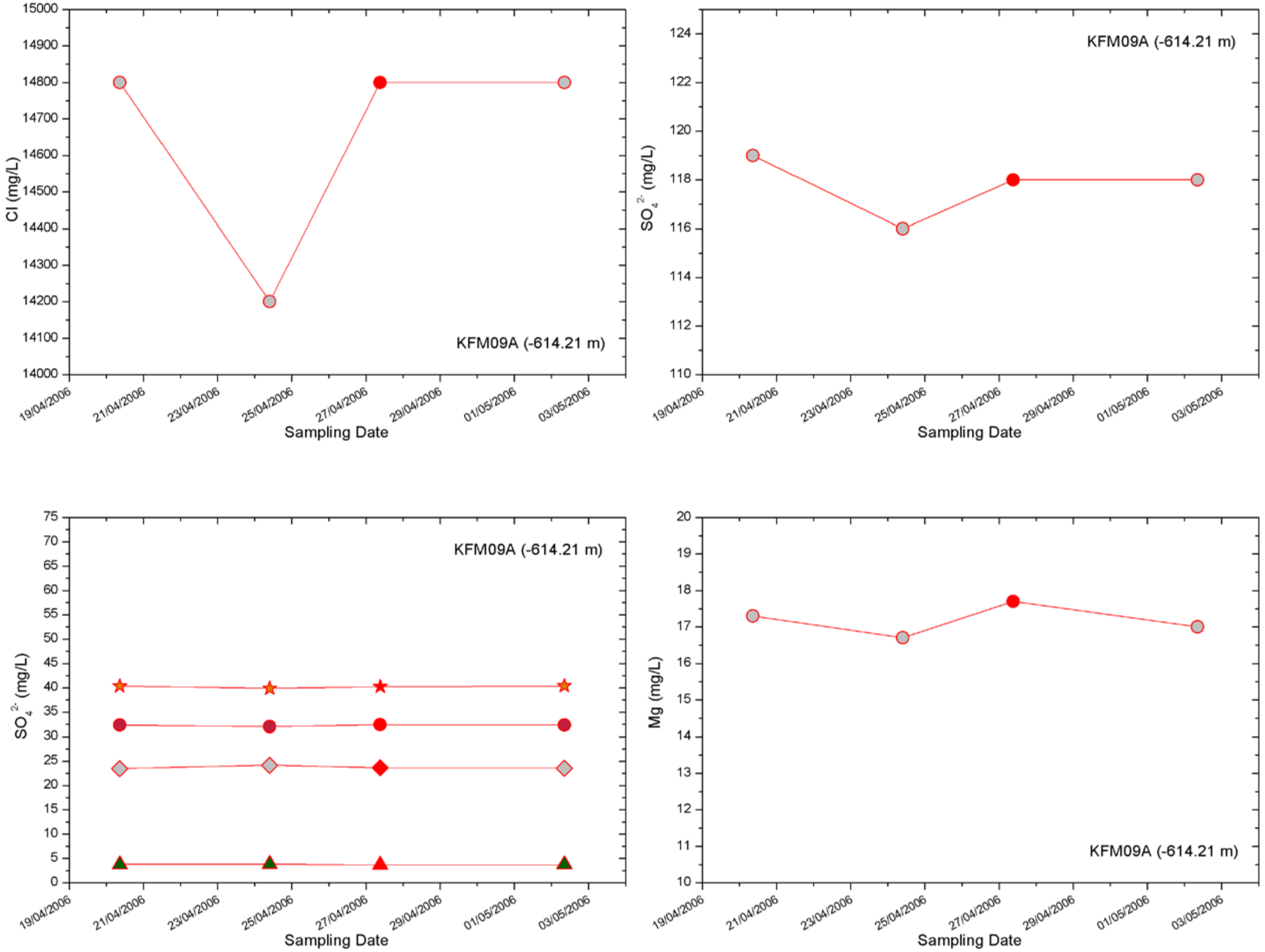
KFM08D (–664.06/–666.55 m)

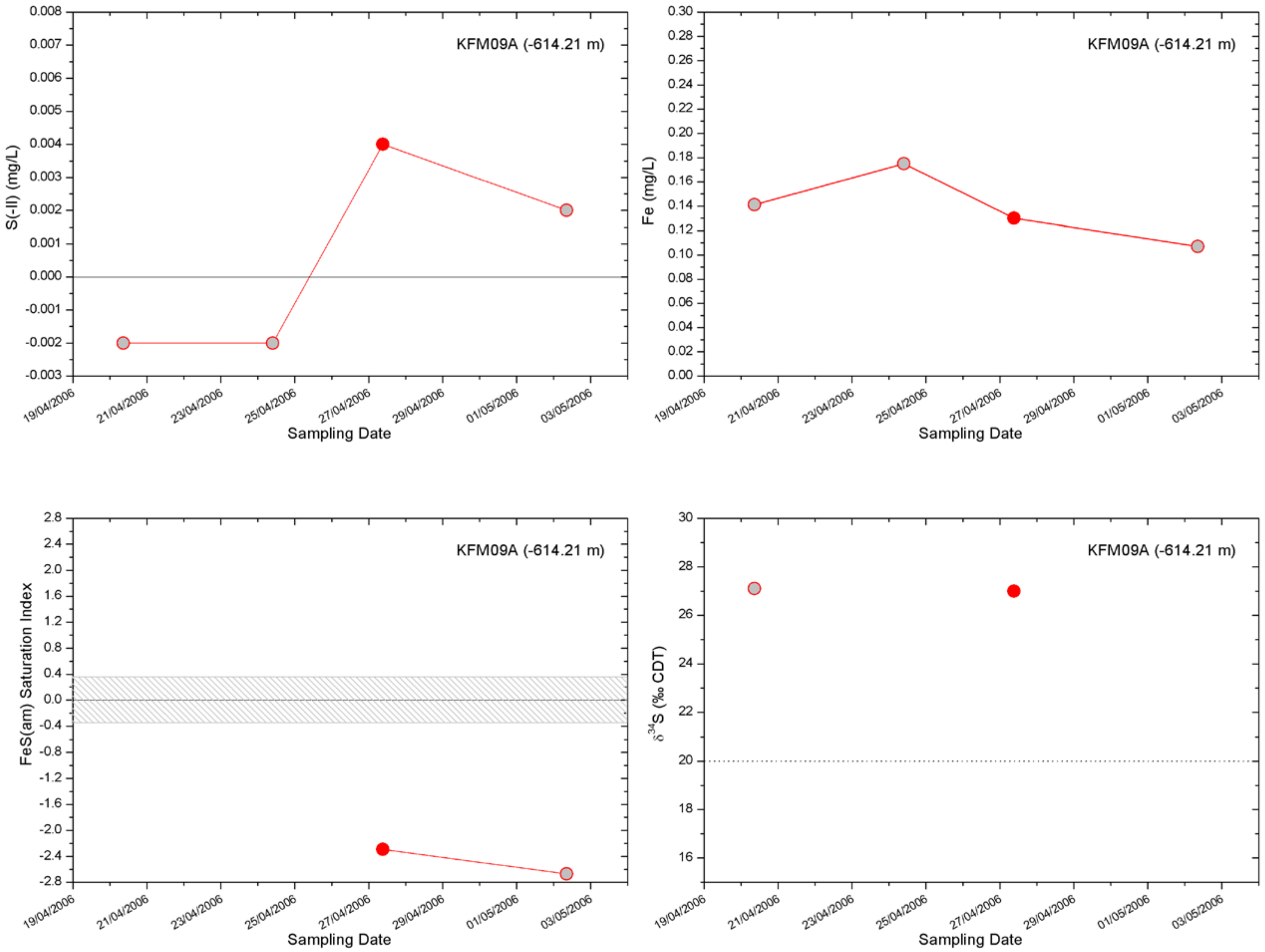


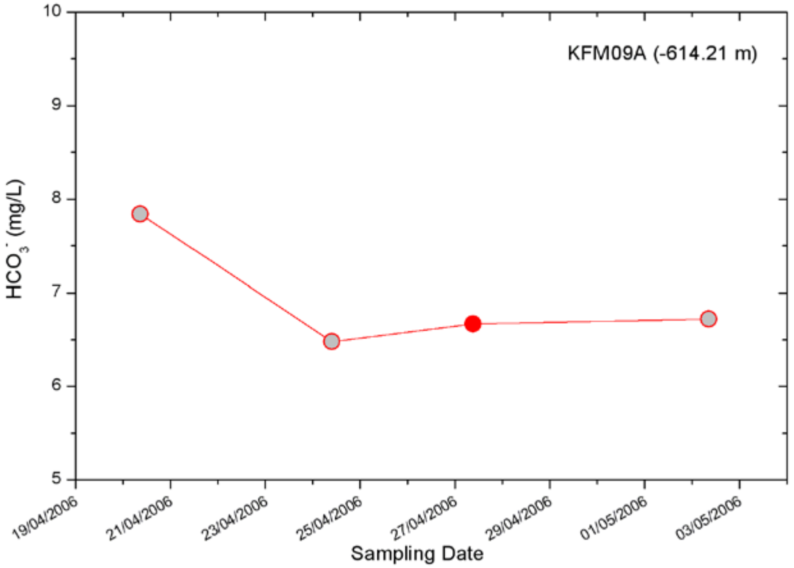

1.0
0.8
0.6
0.4
0.2
0.0
S(-II) (mg/L)
KFM08D (-664.06/-662.55 m)
S(-II) (mg/L)
Sampling Date
01/03/2007 00:00
01/06/2007 00:00
01/09/2007 00:00
01/12/2007 00:00
01/03/2008 00:00
01/06/2008 00:00
01/09/2008 00:00
20/10/2009 01:00
20/10/2009 13:00
21/10/2009 01:00
21/10/2009 13:00
22/10/2009 01:00
22/10/2009 13:00
23/10/2009 01:00
23/10/2009 13:00
24/10/2009 01:00
Sampling Date
Fe (mg/L)
KFM08D (-664.06/-662.55 m)
FeS(am) Saturation Index
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
KFM08D (-664.06/-662.55 m)
$\delta^{34}$S (‰ CDT)
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
KFM08D (-664.06/-662.55 m)

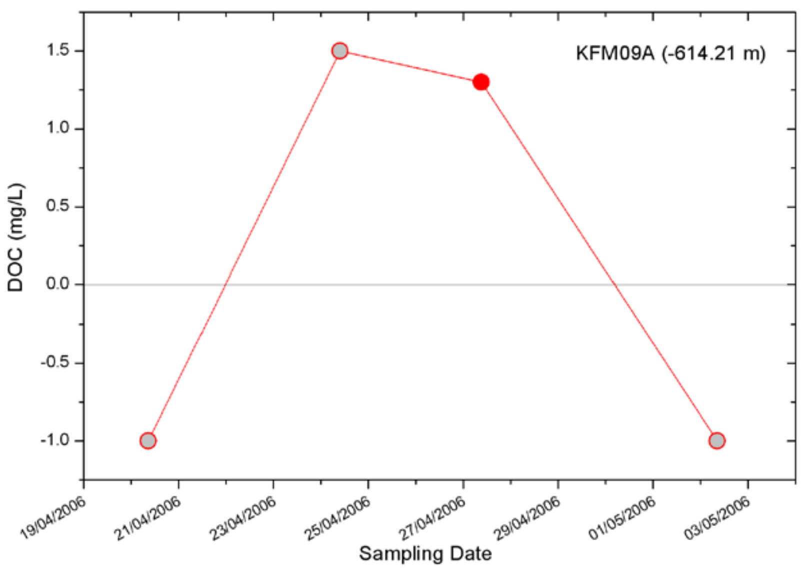

KFM08D (-664.06/-662.55 m)
HCO3- (mg/L)
0
5
10
15
20
25
30
35
40
45
50
DOC (mg/L)
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
Mn (mg/L)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
Sampling Date
01/03/2007 00:00
01/06/2007 00:00
01/09/2007 00:00
01/12/2007 00:00
01/03/2008 00:00
01/06/2008 00:00
01/09/2008 00:00
20/10/2009 01:00
20/10/2009 13:00
21/10/2009 01:00
21/10/2009 13:00
22/10/2009 01:00
22/10/2009 13:00
23/10/2009 01:00
23/10/2009 13:00
24/10/2009 01:00

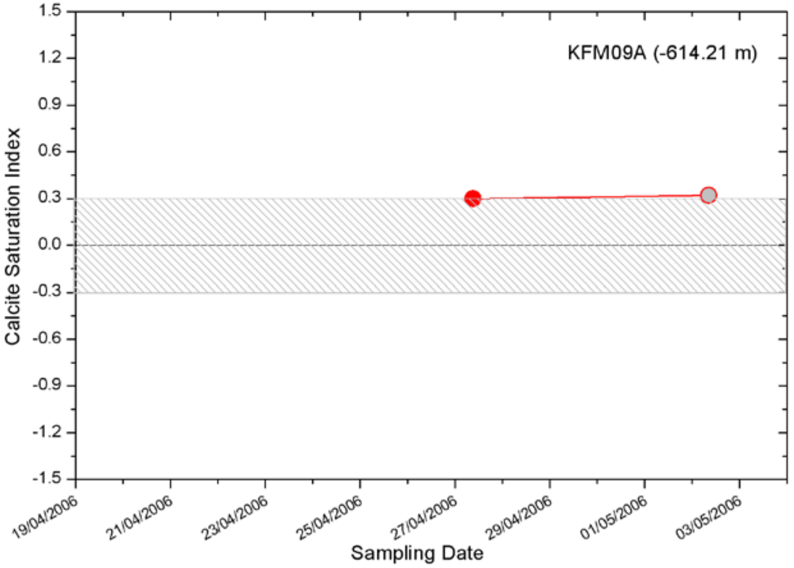
KFM09A (–614.21 m)

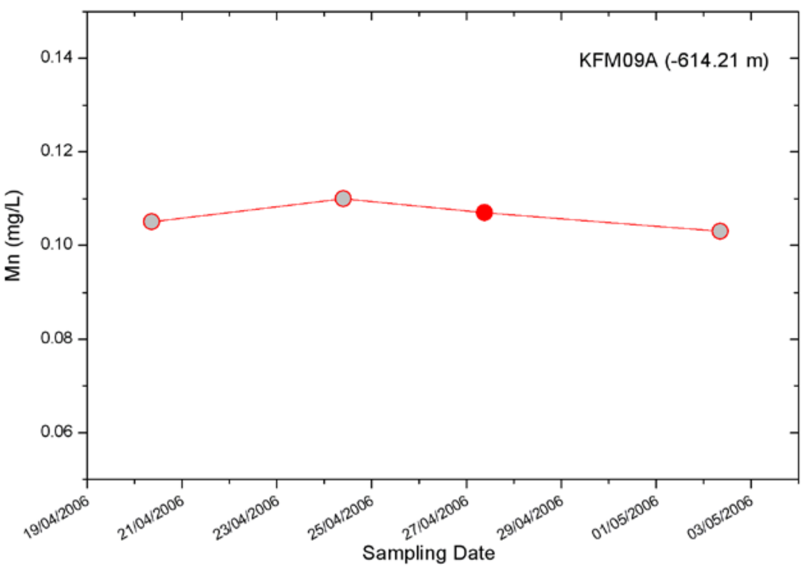



KFM09A (-614.21 m)
S(-II) (mg/L)
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
-0.002
-0.003
Sampling Date
19/04/2006
21/04/2006
23/04/2006
25/04/2006
27/04/2006
29/04/2006
01/05/2006
03/05/2006
KFM09A (-614.21 m)
Fe (mg/L)
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Sampling Date
KFM09A (-614.21 m)
FeS(am) Saturation Index
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
-2.8
Sampling Date
KFM09A (-614.21 m)
$\delta^{34}$S (‰ CDT)
30
28
26
24
22
20
18
16
Sampling Date

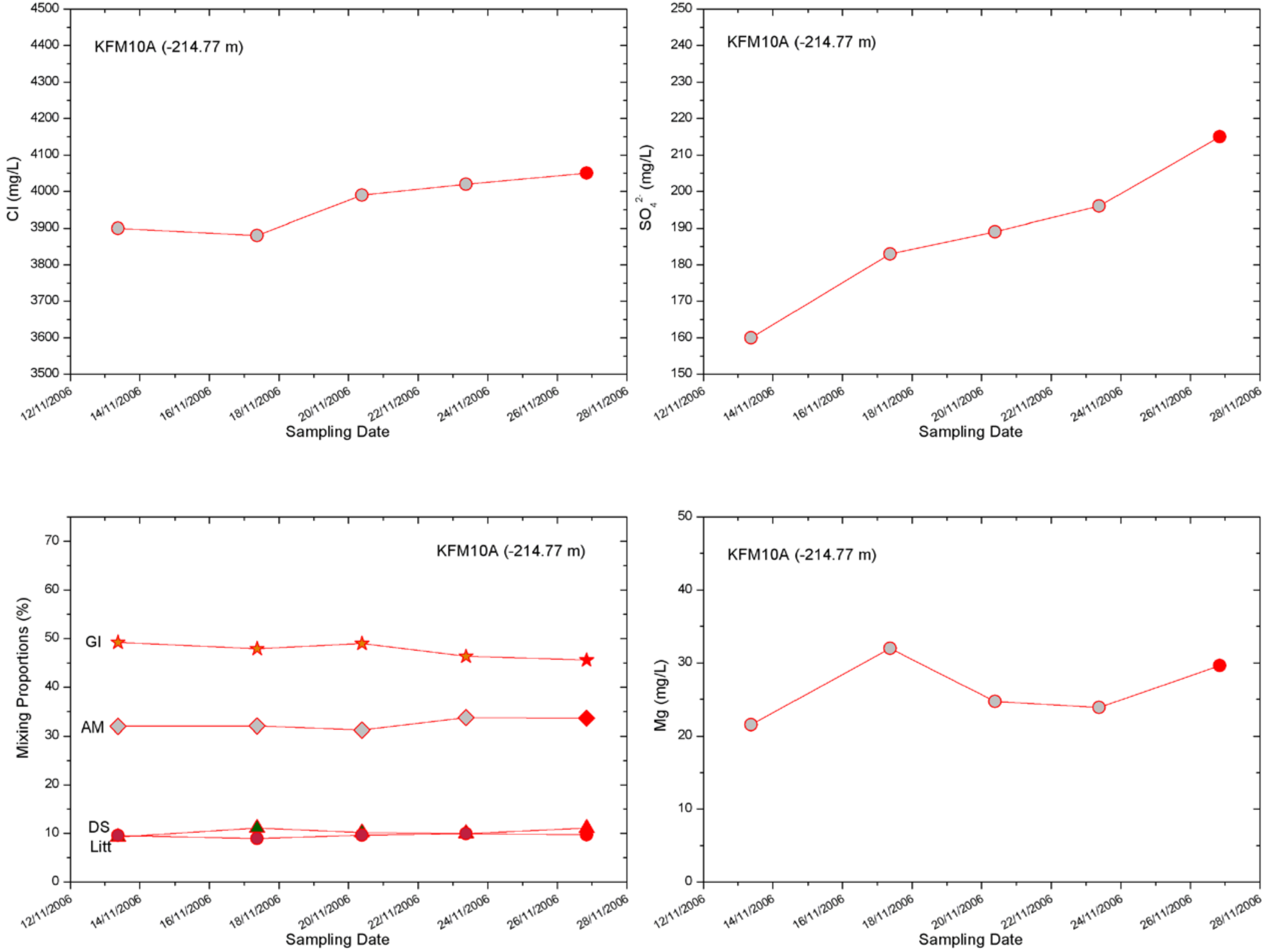

KFM09A (-614.21 m)
$HCO_3^-$ (mg/L)
10
9
8
7
6
5
19/04/2006
21/04/2006
23/04/2006
25/04/2006
27/04/2006
29/04/2006
01/05/2006
03/05/2006
Sampling Date

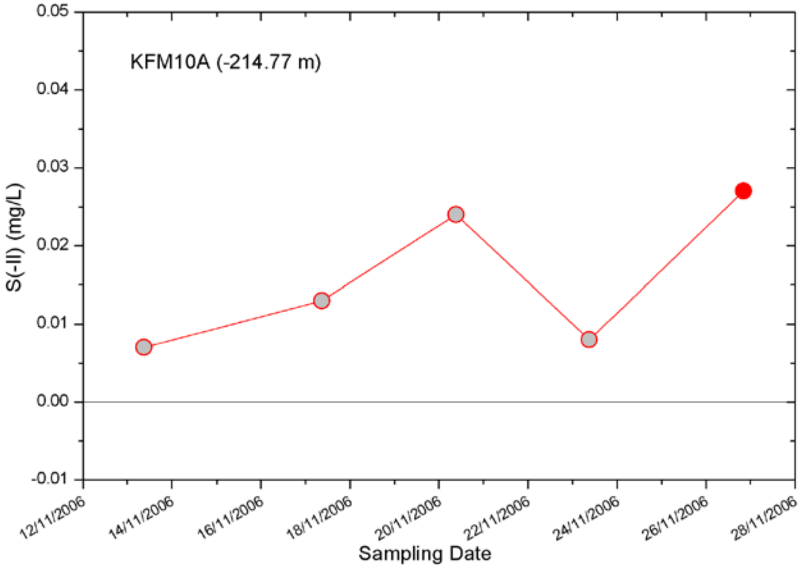

KFM09A (-614.21 m)
DOC (mg/L)
1.5
1.0
0.5
0.0
-0.5
-1.0
19/04/2006
21/04/2006
23/04/2006
25/04/2006
27/04/2006
29/04/2006
01/05/2006
03/05/2006
Sampling Date

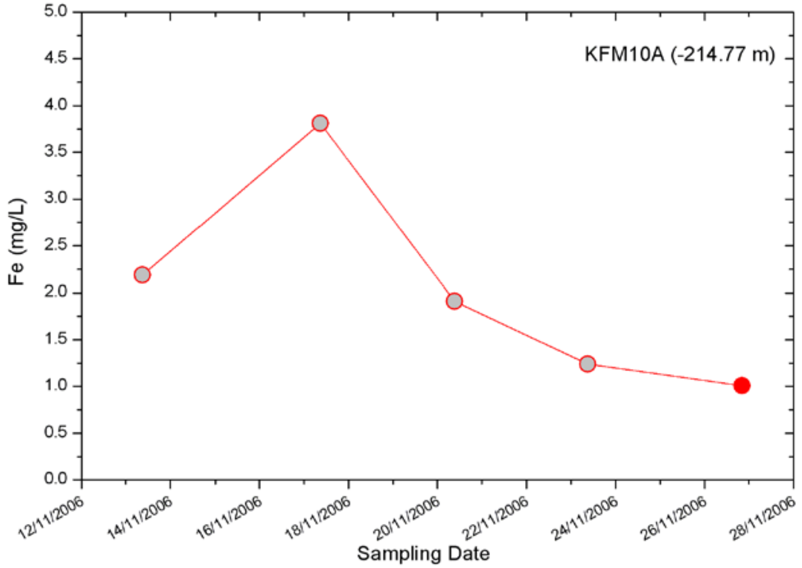

KFM09A (-614.21 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
19/04/2006
21/04/2006
23/04/2006
25/04/2006
27/04/2006
29/04/2006
01/05/2006
03/05/2006
Sampling Date

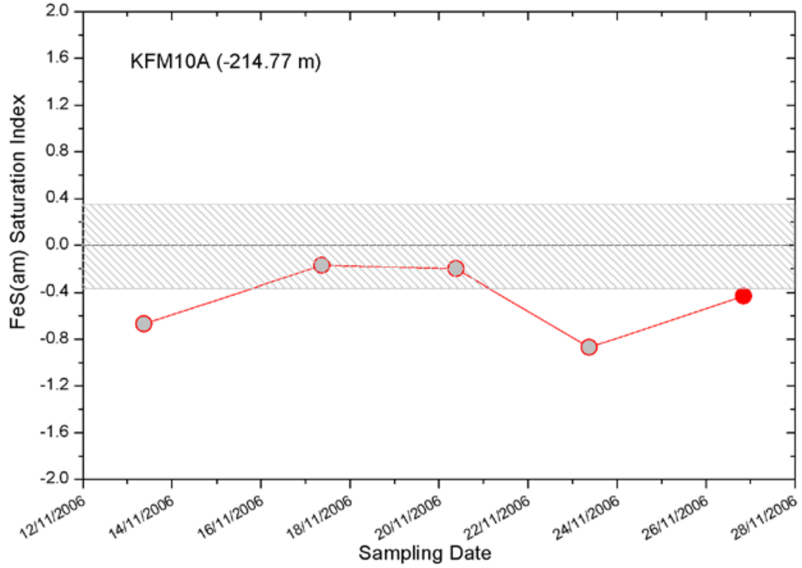

KFM09A (-614.21 m)
Mn (mg/L)
0.14
0.12
0.10
0.08
0.06
19/04/2006
21/04/2006
23/04/2006
25/04/2006
27/04/2006
29/04/2006
01/05/2006
03/05/2006
Sampling Date

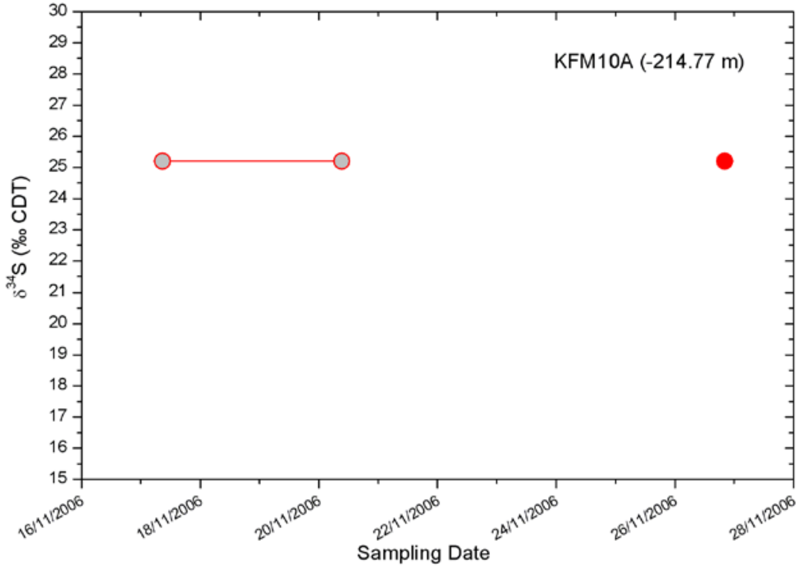
KFM10A (–214.77 m)
Eh = –281 mV

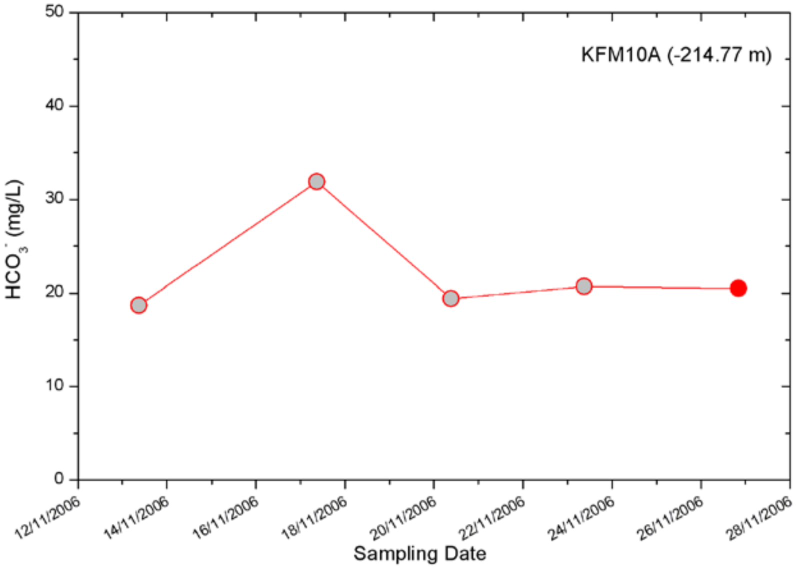


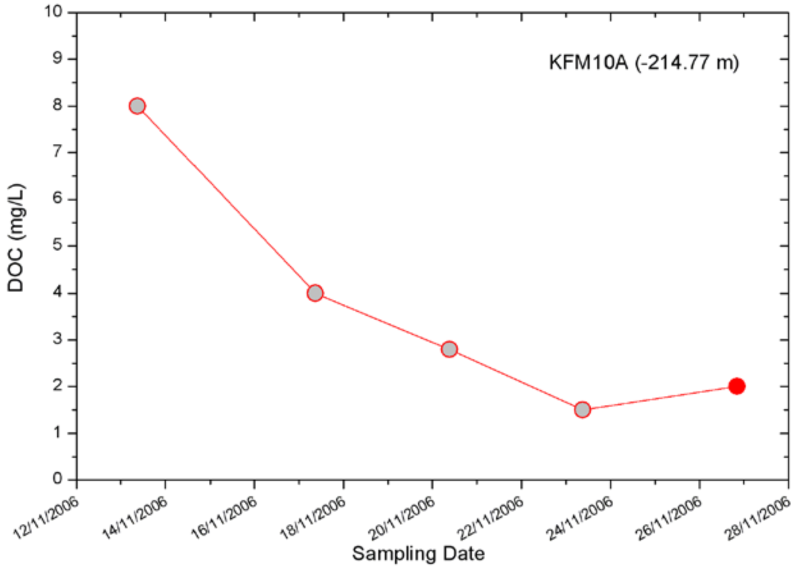

KFM10A (-214.77 m)
S(-II) (mg/L)
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

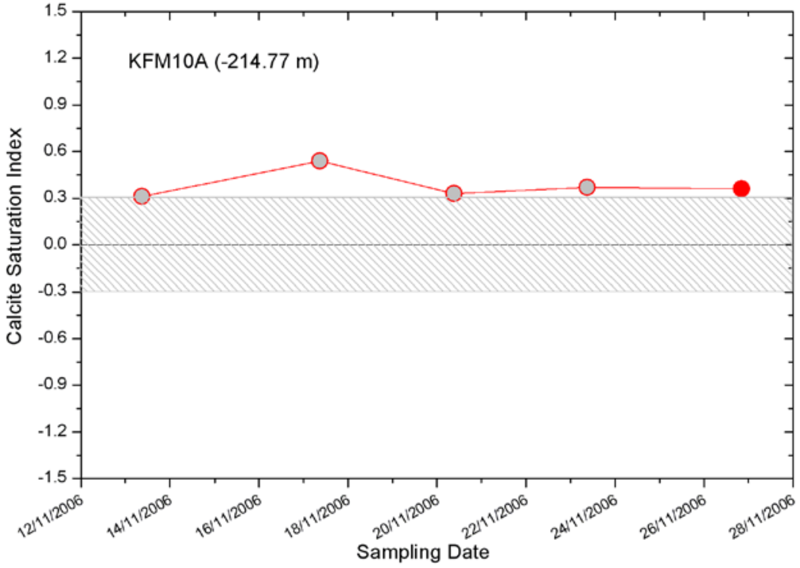

KFM10A (-214.77 m)
Fe (mg/L)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

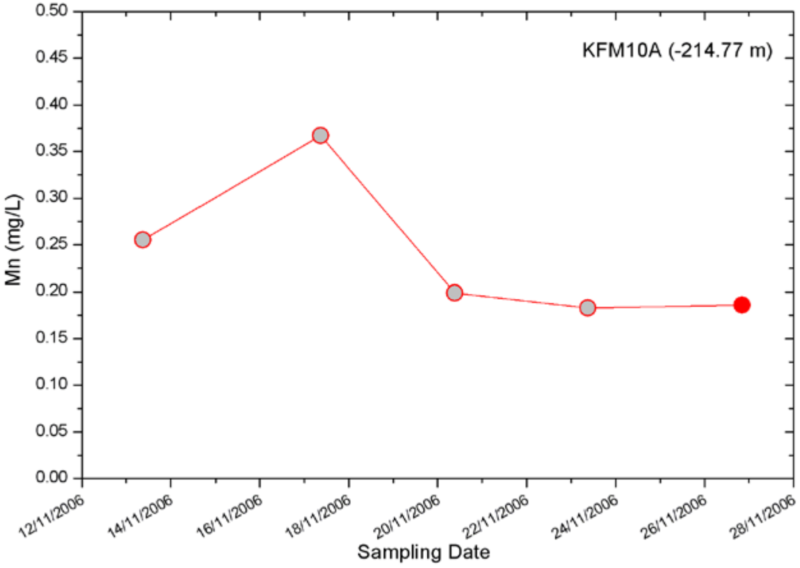

KFM10A (-214.77 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date


KFM10A (-214.77 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

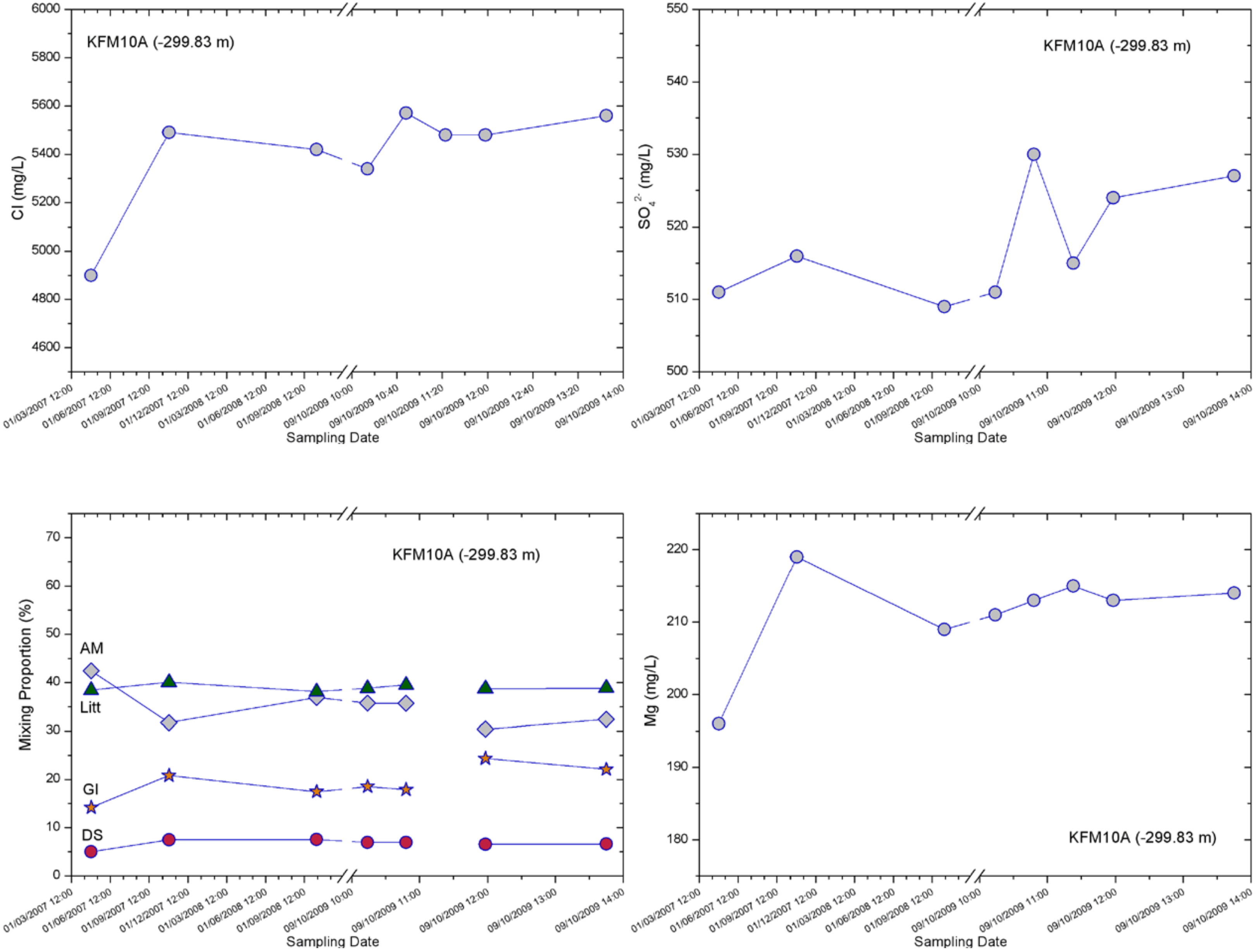

KFM10A (-214.77 m)
$HCO_3^-$ (mg/L)
0
10
20
30
40
50
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

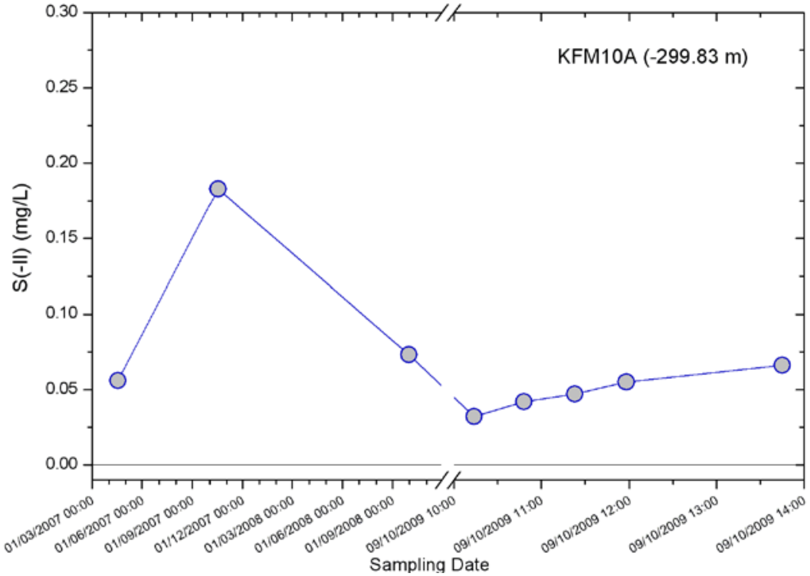

KFM10A (-214.77 m)
DOC (mg/L)
0
1
2
3
4
5
6
7
8
9
10
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

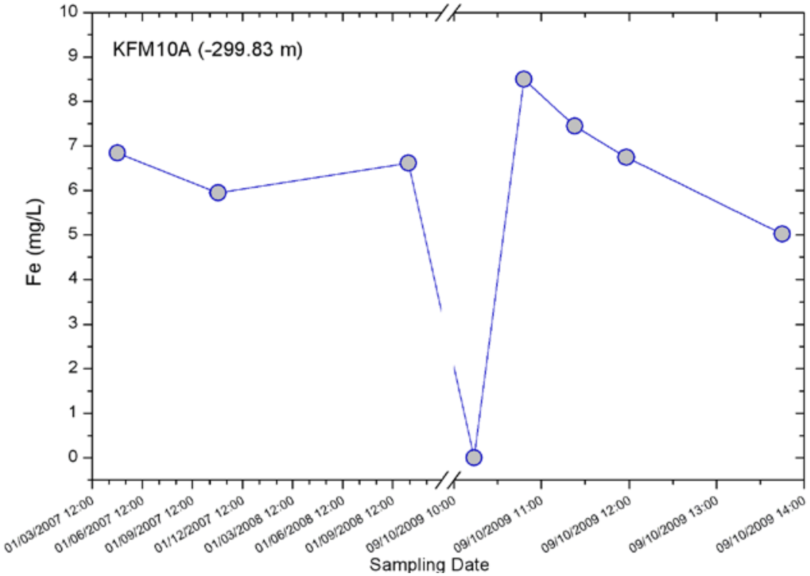

KFM10A (-214.77 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

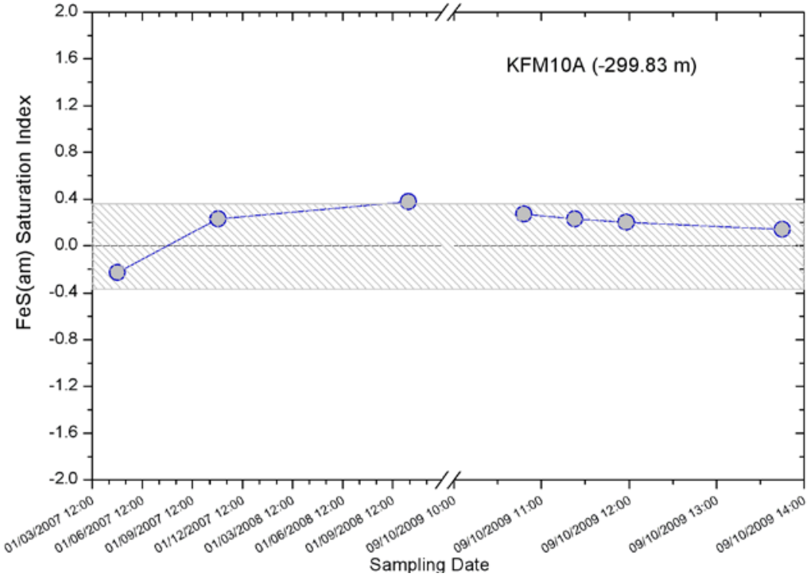

KFM10A (-214.77 m)
Mn (mg/L)
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
12/11/2006
14/11/2006
16/11/2006
18/11/2006
20/11/2006
22/11/2006
24/11/2006
26/11/2006
28/11/2006
Sampling Date

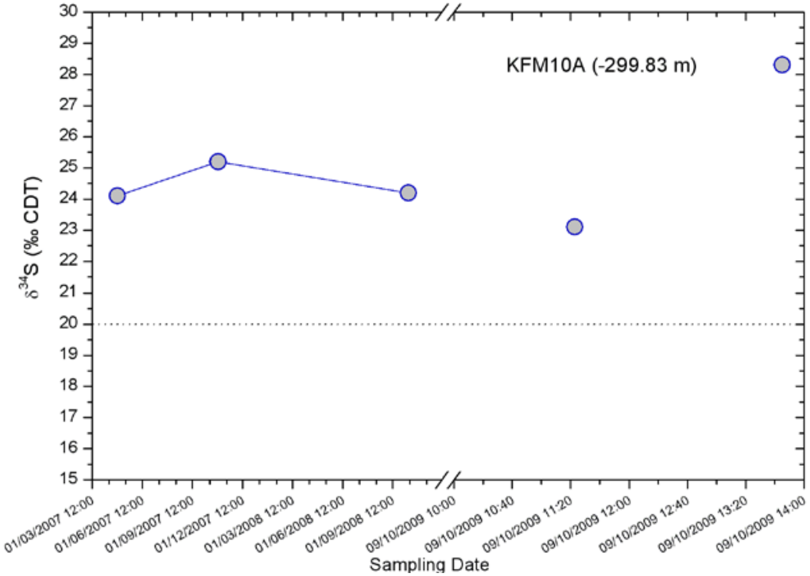
KFM10A (–299.83 m)

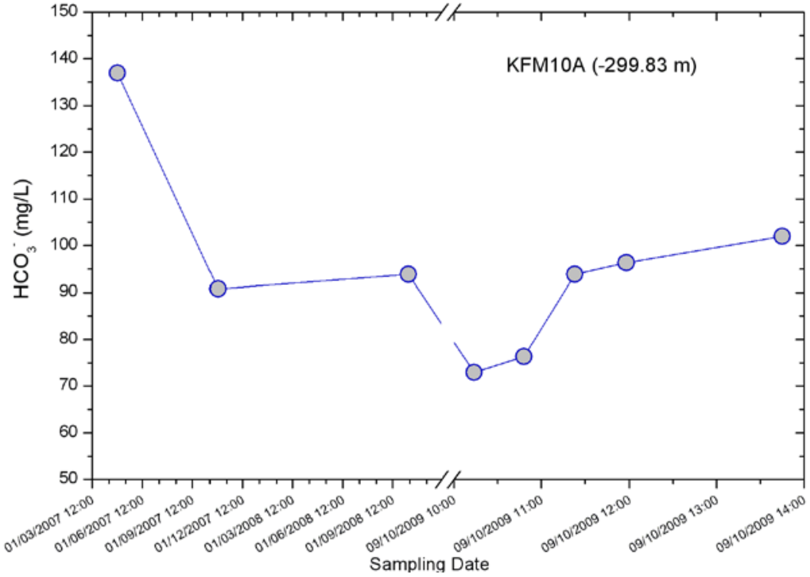


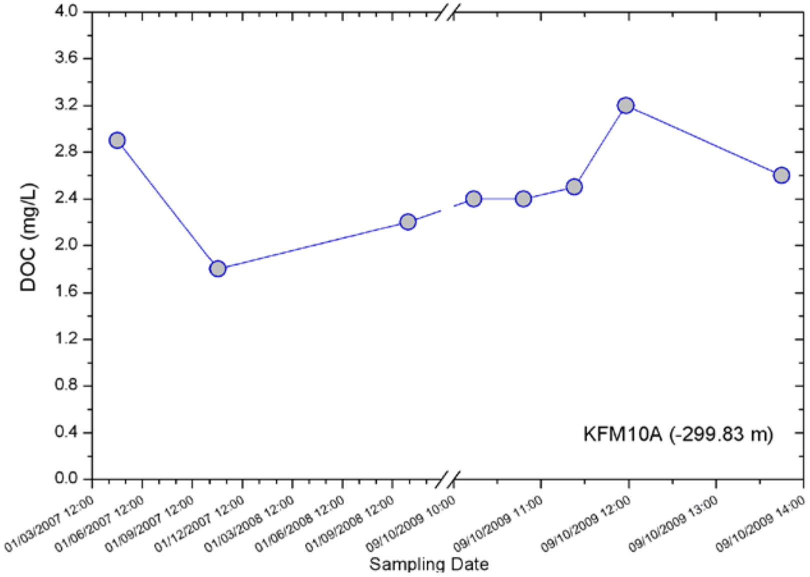

KFM10A (-299.83 m)
S(-II) (mg/L)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
01/03/2007 00:00
01/06/2007 00:00
01/09/2007 00:00
01/12/2007 00:00
01/03/2008 00:00
01/06/2008 00:00
01/09/2008 00:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date

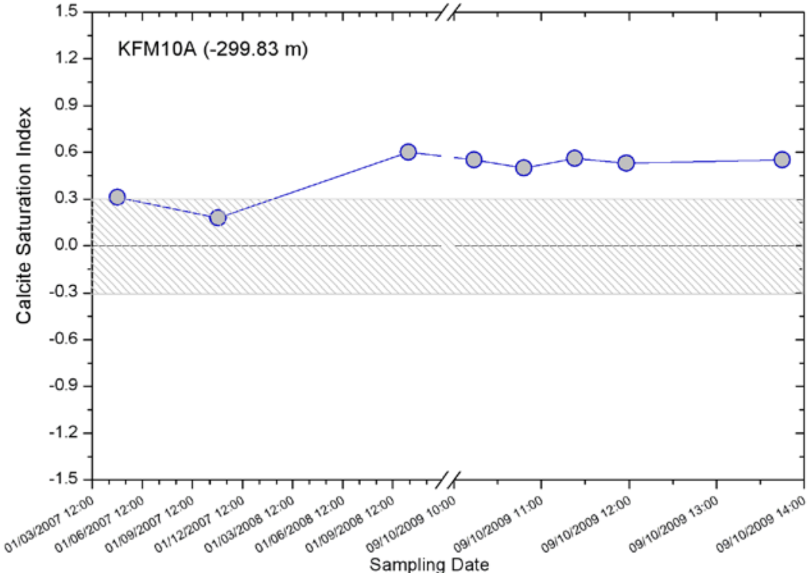

KFM10A (-299.83 m)
Fe (mg/L)
10
9
8
7
6
5
4
3
2
1
0
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date

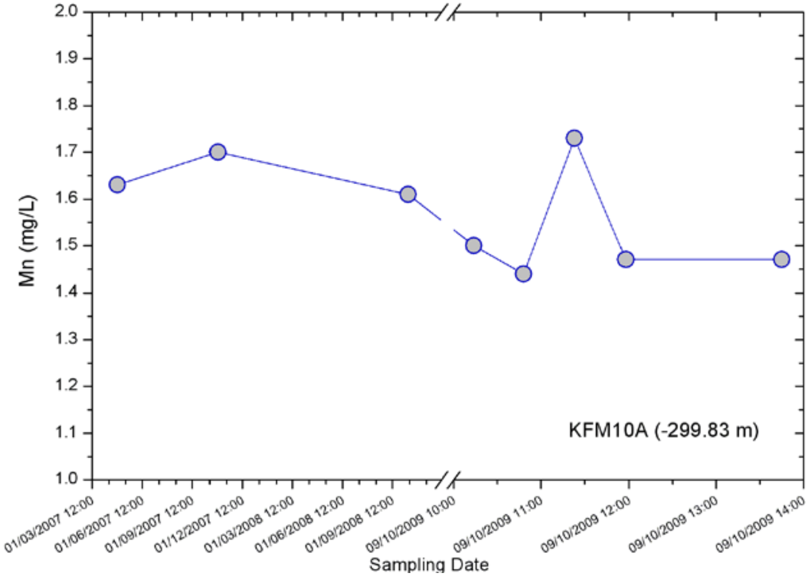

KFM10A (-299.83 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date


KFM10A (-299.83 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 10:40
09/10/2009 11:20
09/10/2009 12:00
09/10/2009 12:40
09/10/2009 13:20
09/10/2009 14:00
Sampling Date

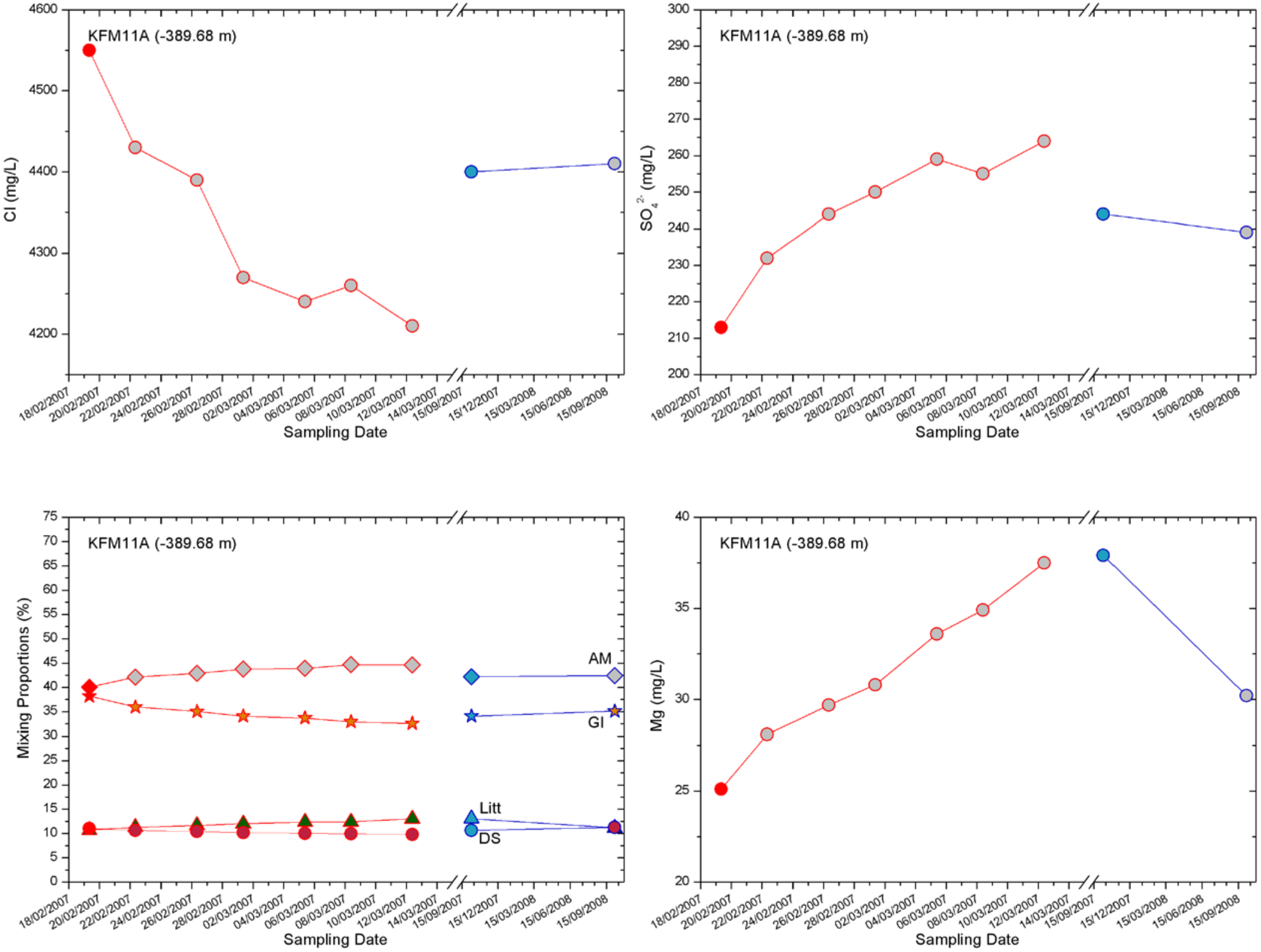

KFM10A (-299.83 m)
$HCO_3^-$ (mg/L)
150
140
130
120
110
100
90
80
70
60
50
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date

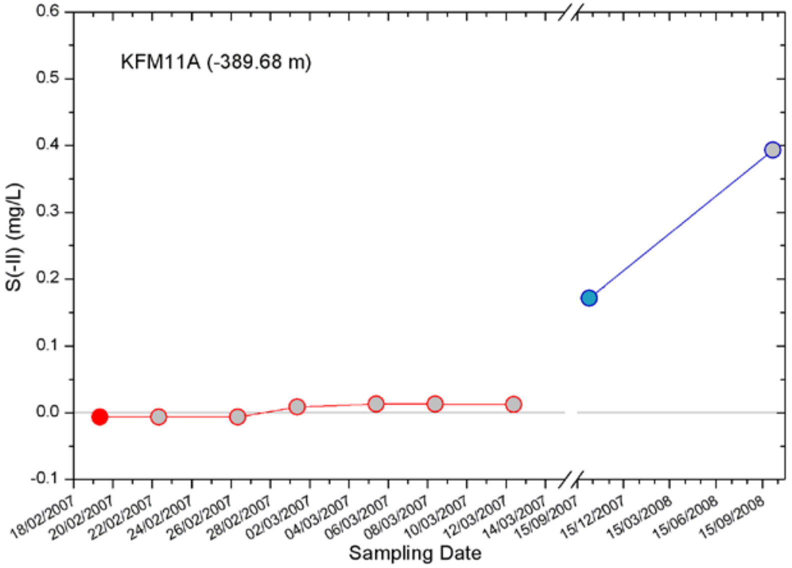

DOC (mg/L)
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
KFM10A (-299.83 m)
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date

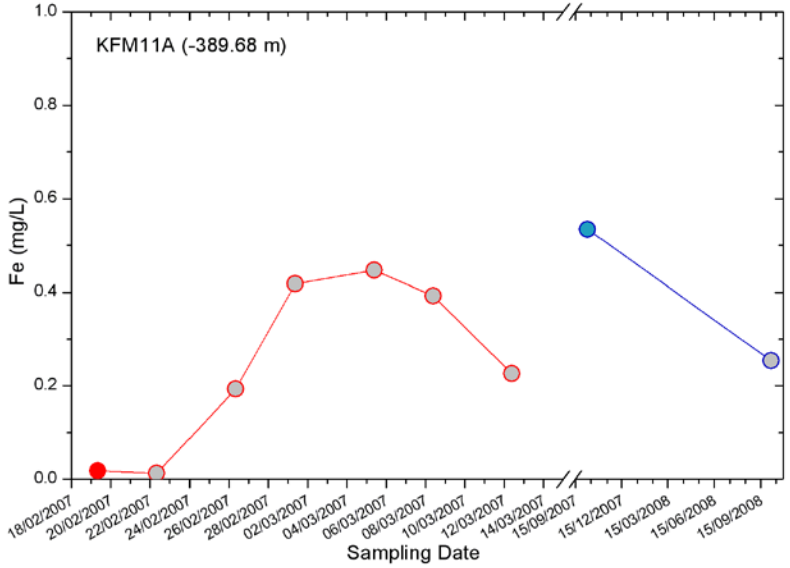

KFM10A (-299.83 m)
Calcite Saturation Index
1.5
1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date

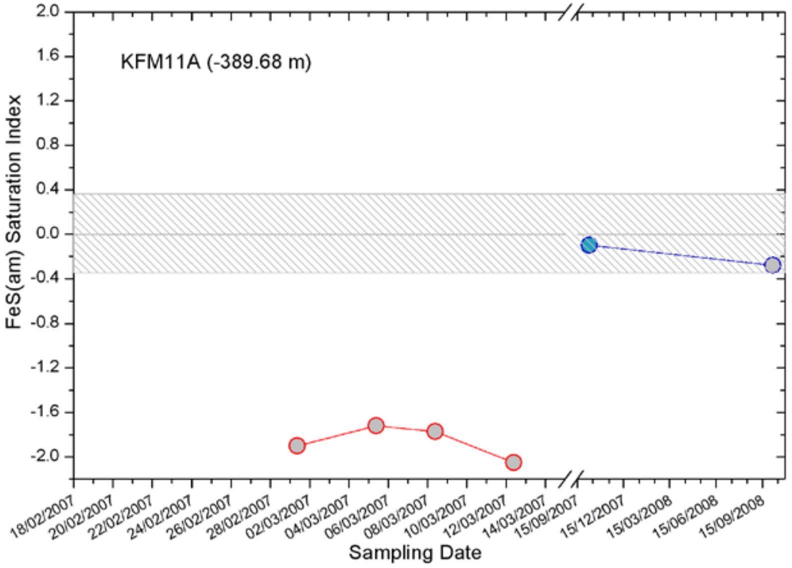

Mn (mg/L)
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
KFM10A (-299.83 m)
01/03/2007 12:00
01/06/2007 12:00
01/09/2007 12:00
01/12/2007 12:00
01/03/2008 12:00
01/06/2008 12:00
01/09/2008 12:00
09/10/2009 10:00
09/10/2009 11:00
09/10/2009 12:00
09/10/2009 13:00
09/10/2009 14:00
Sampling Date

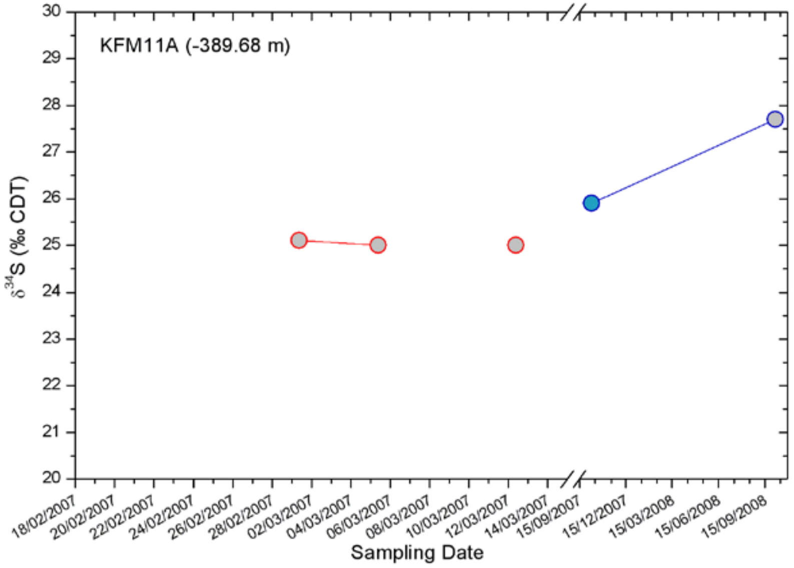
KFM11A (–389.68 m)
Eh = –203 mV

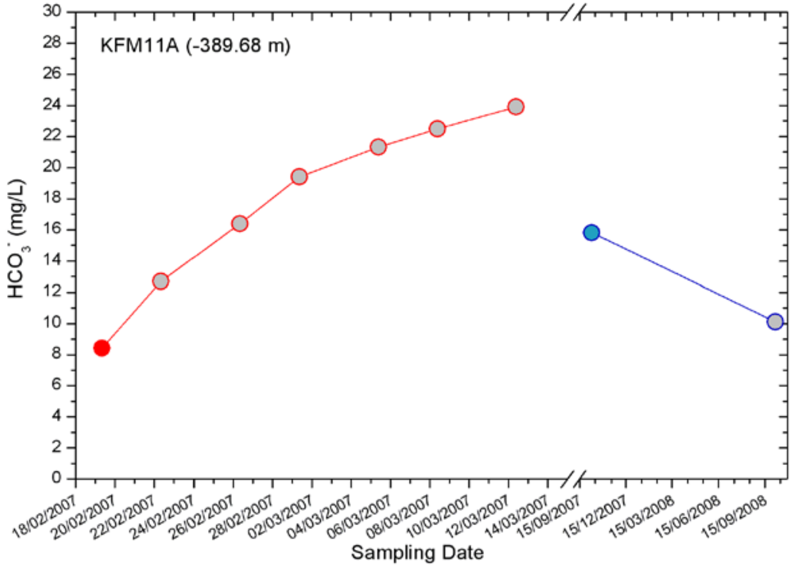


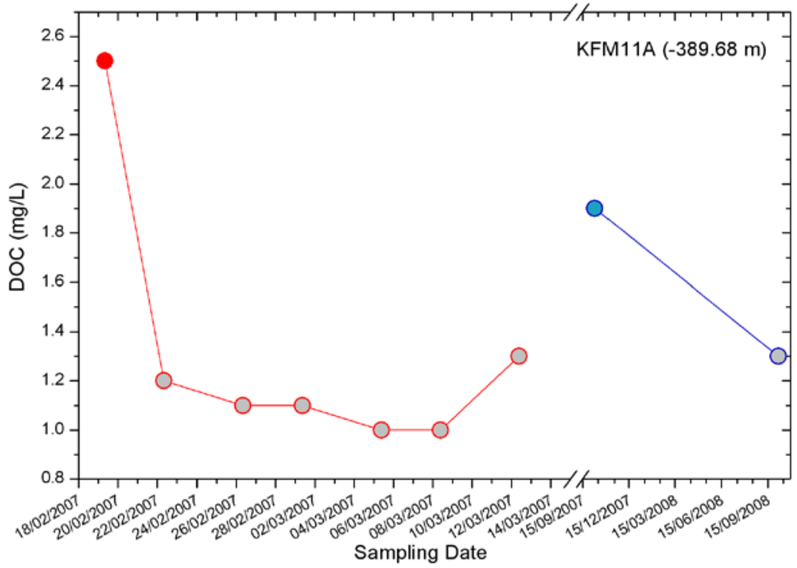

KFM11A (-389.68 m)
S(-II) (mg/L)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008
Sampling Date

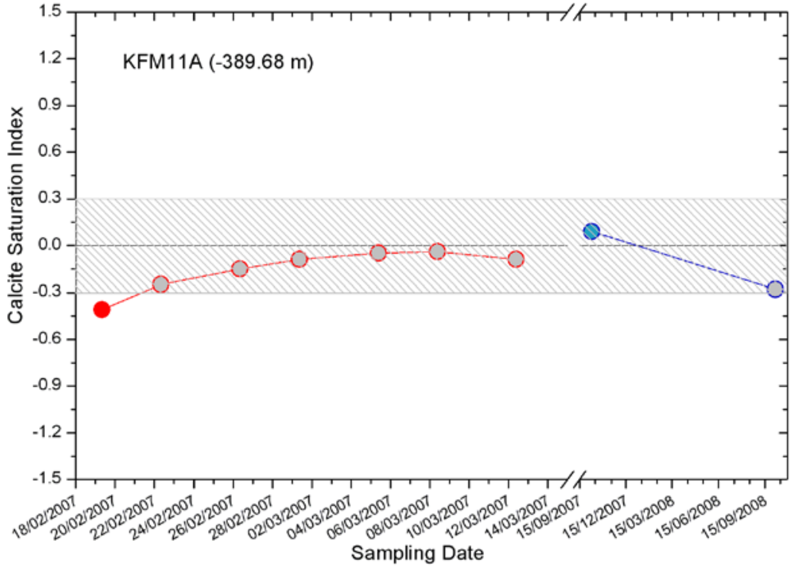

KFM11A (-389.68 m)
Fe (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008
Sampling Date

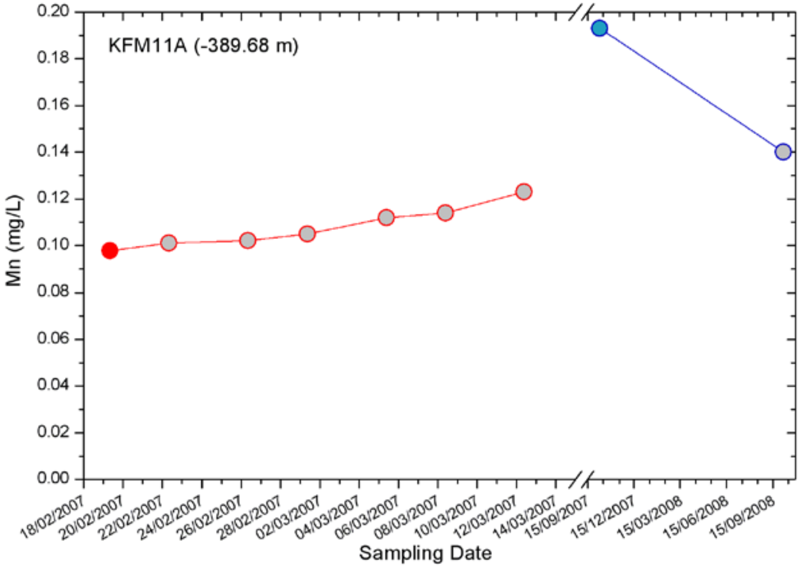

KFM11A (-389.68 m)
FeS(am) Saturation Index
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008
Sampling Date


KFM11A (-389.68 m)
δ34S (‰ CDT)
30
29
28
27
26
25
24
23
22
21
20
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008
Sampling Date

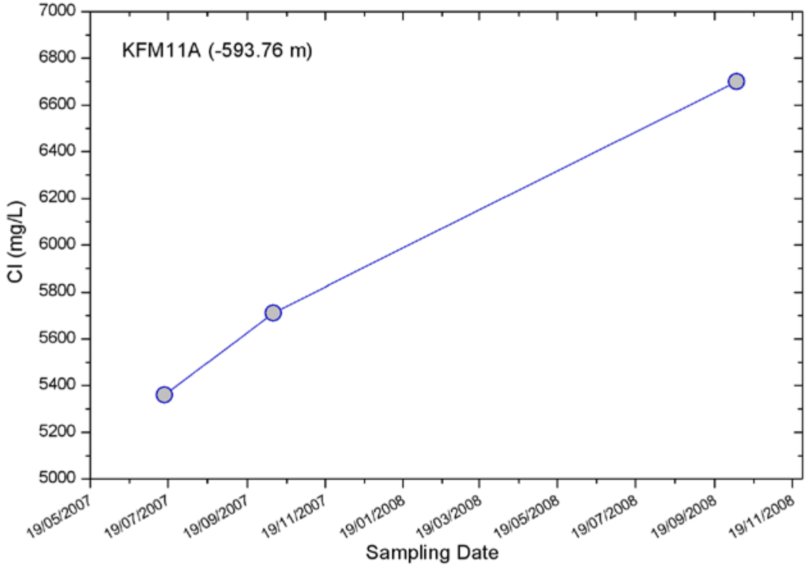

KFM11A (-389.68 m)
$HCO_3^-$ (mg/L)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Sampling Date
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008

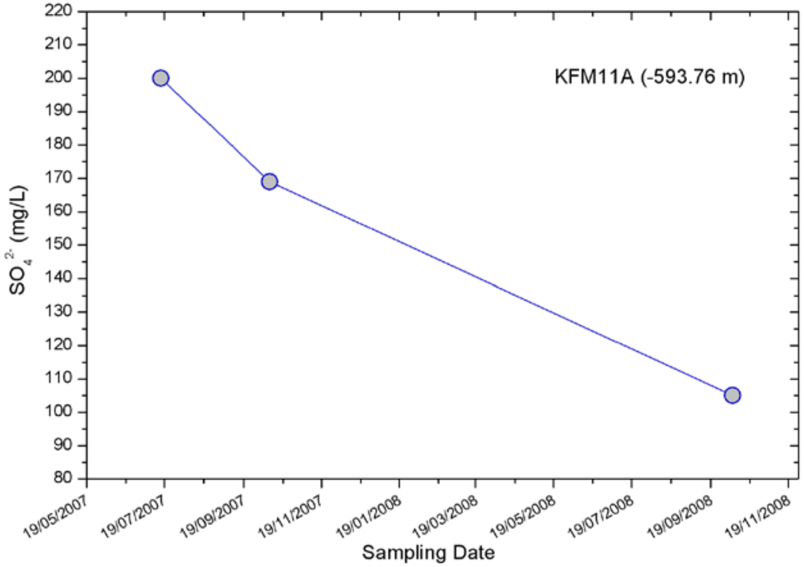

KFM11A (-389.68 m)
DOC (mg/L)
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Sampling Date
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008

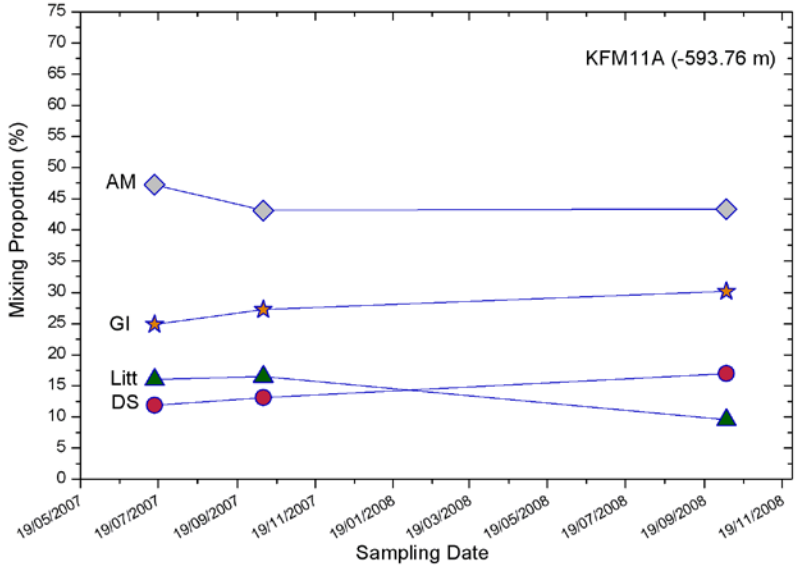

KFM11A (-389.68 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
Sampling Date
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008

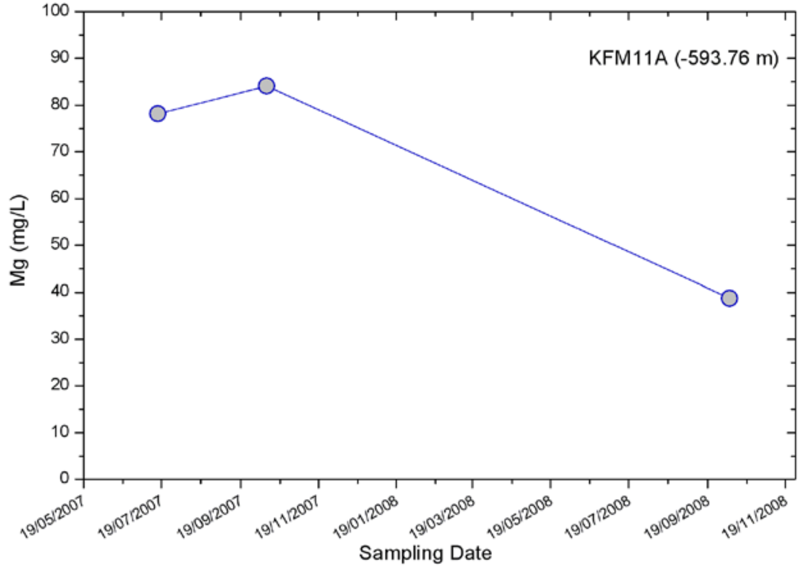

KFM11A (-389.68 m)
Mn (mg/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
Sampling Date
18/02/2007
20/02/2007
22/02/2007
24/02/2007
26/02/2007
28/02/2007
02/03/2007
04/03/2007
06/03/2007
08/03/2007
10/03/2007
12/03/2007
14/03/2007
15/09/2007
15/12/2007
15/03/2008
15/06/2008
15/09/2008

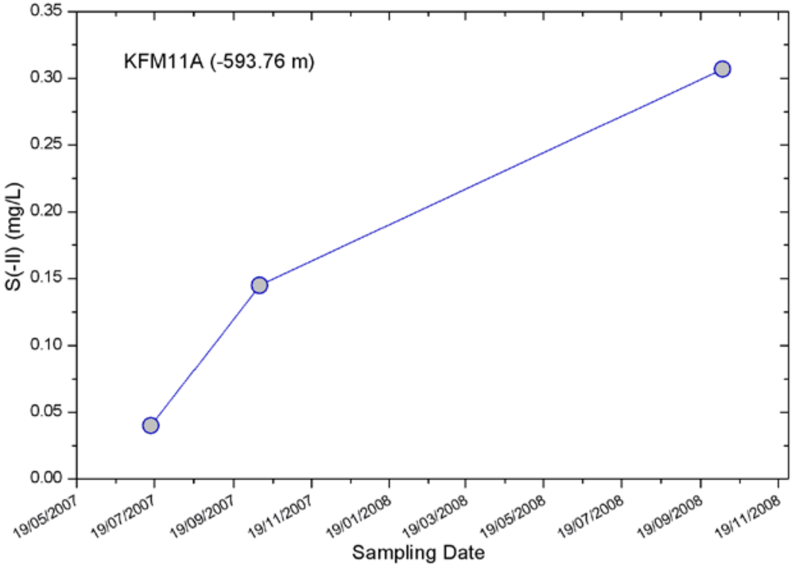
# KFM11A (–593.76 m)

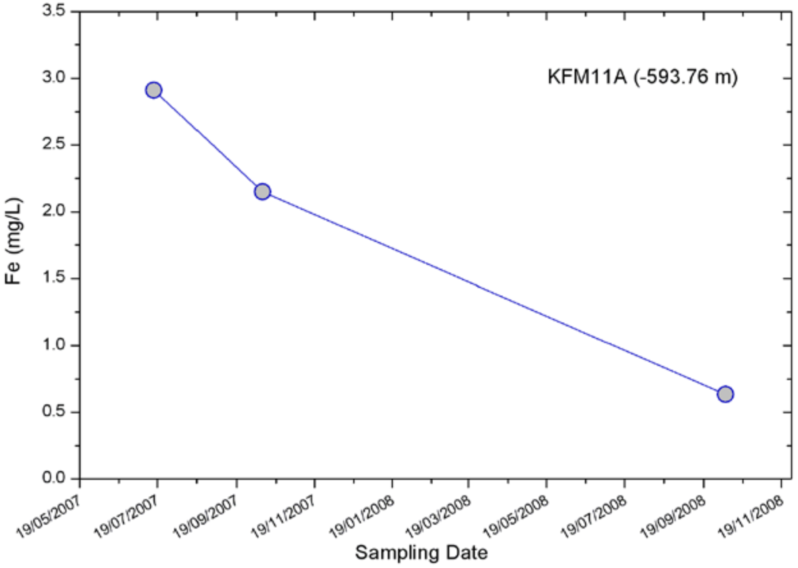


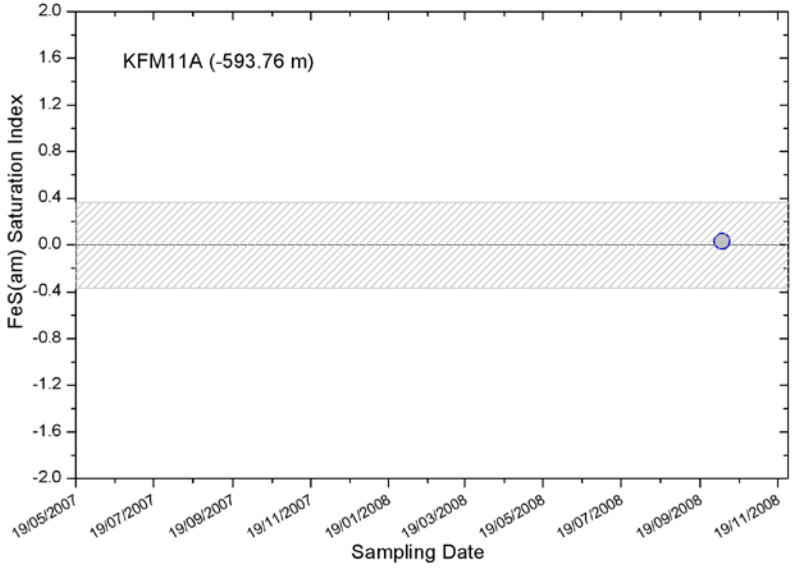


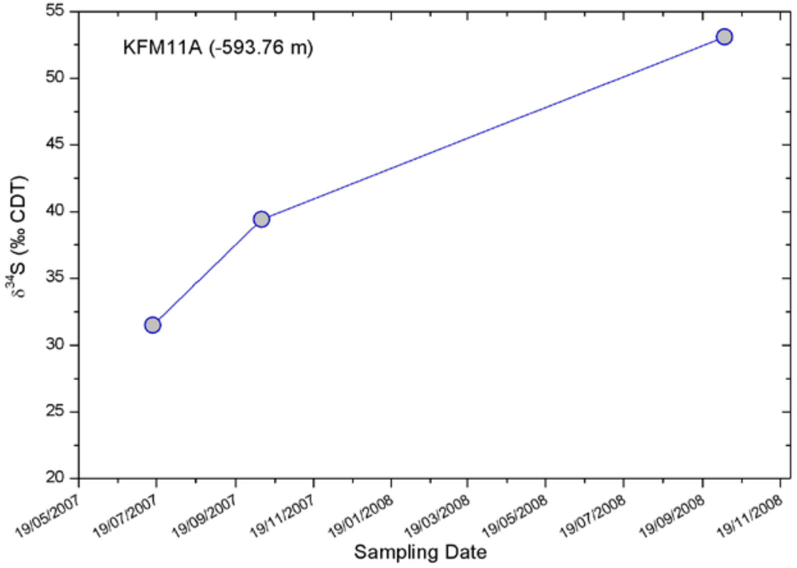


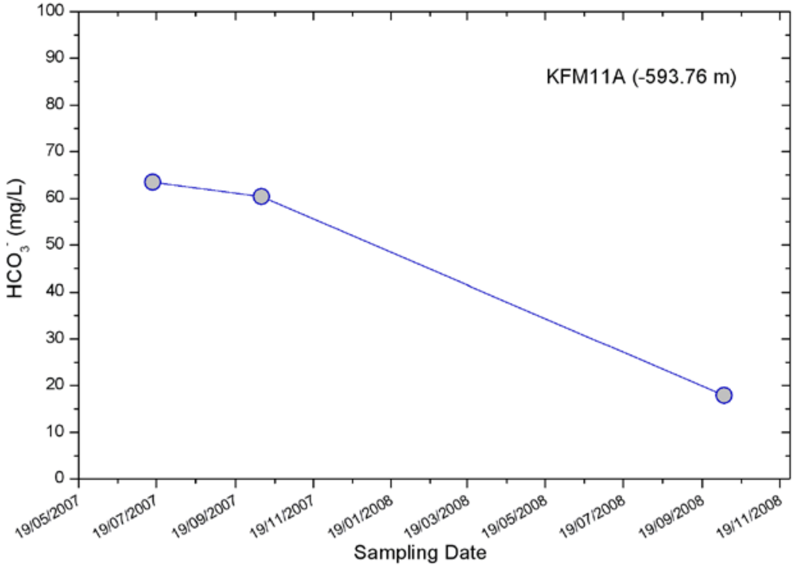


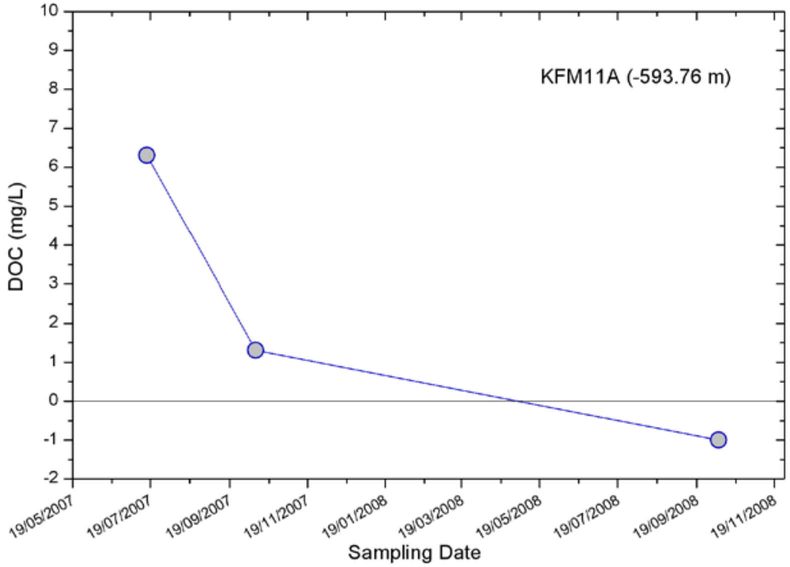

KFM11A (-593.76 m)
S(-II) (mg/L)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date

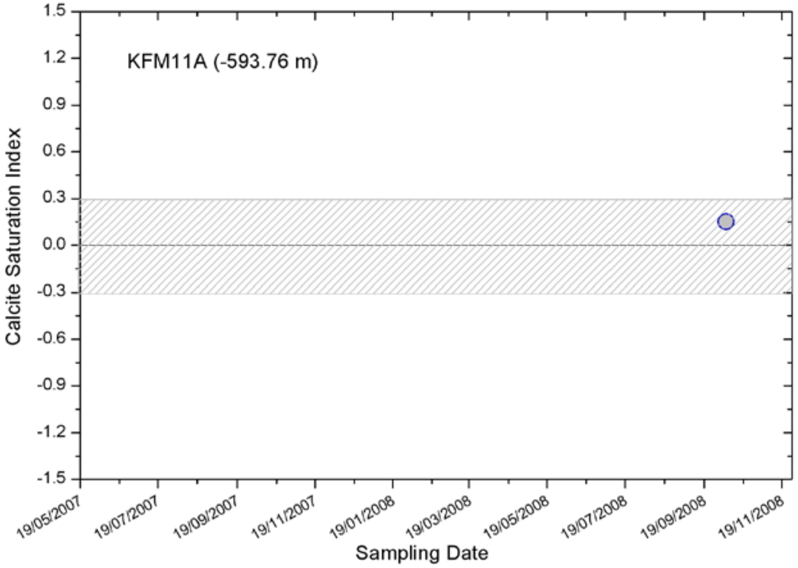

KFM11A (-593.76 m)
Fe (mg/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date

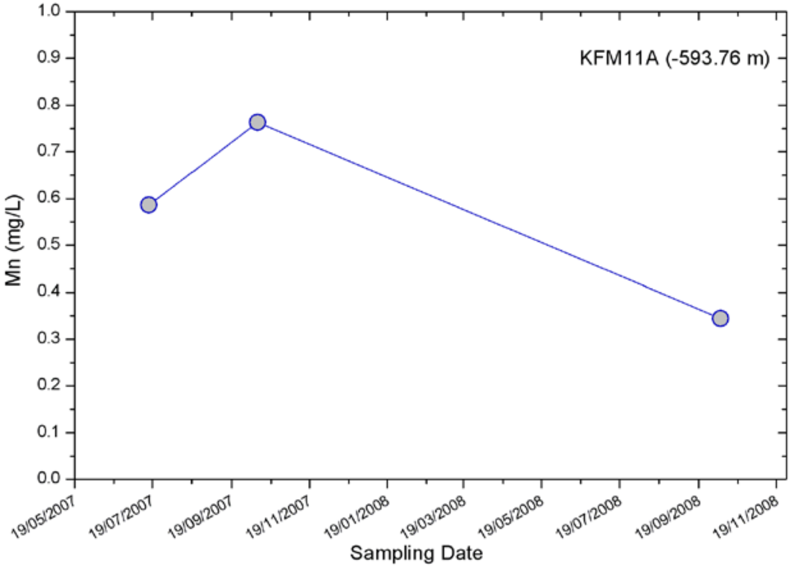

KFM11A (-593.76 m)
FeS(am) Saturation Index
-2.0
-1.6
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
1.6
2.0
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date


KFM11A (-593.76 m)
δ34S (‰ CDT)
20
25
30
35
40
45
50
55
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date


KFM11A (-593.76 m)
$HCO_3^-$ (mg/L)
0
10
20
30
40
50
60
70
80
90
100
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date


KFM11A (-593.76 m)
DOC (mg/L)
-2
-1
0
1
2
3
4
5
6
7
8
9
10
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date


KFM11A (-593.76 m)
Calcite Saturation Index
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
0.3
0.6
0.9
1.2
1.5
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date


KFM11A (-593.76 m)
Mn (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
19/05/2007
19/07/2007
19/09/2007
19/11/2007
19/01/2008
19/03/2008
19/05/2008
19/07/2008
19/09/2008
19/11/2008
Sampling Date

# Appendix 3

## Sulphate reduction rates in groundwater systems

Traditionally dissolved sulphide in the groundwaters represents an important parameter in the safety assessment of the Swedish and Finnish concepts (e.g. /SKB, 2006; Smith et al. 2007/: sulphide concentrations in the fracture groundwaters can react with the copper canisters causing corrosion and, therefore, reducing their expected lifetime).

This is why sulphide concentrations in present-day groundwaters need to be defined as an initial condition or as a basic reference level. But, also, an assessment of the expected changes during a complete glacial cycle is required in order to evaluate the extent of the corrosion of the canisters over long periods of time.

Determination of reliable sulphide contents during groundwater sampling at depth in the Site Characterization Programs has been much more complicated than previously thought /Smellie et al. 2008; Laaksoharju et al. 2009; Gimeno et al. 2009/. As it has been demonstrated in the present and previous works, pristine dissolved sulphide and sulphate reducing bacteria (SRB) contents can be affected by different types of disturbances (cf Sections 3 and 5.5 in the main report).

The evaluation of the changes in sulphide concentrations during the future evolution of a groundwater system would require knowledge of the rates of sulphide production. This knowledge would also help to put into context the results obtained during the monitoring program and the concentrations of dissolved sulphide in present-day groundwaters. Unfortunately, studies on sulphide production rates in the Swedish and Finnish sites are practically inexistent, as conditions and limiting factors for microbial sulphate reduction are still poorly known.

Thus, in this Appendix, the available information on sulphate reduction rates (SRR) in sedimentary and crystalline aquifers has been reviewed to obtain a basic reference framework for the studied systems. Moreover, SRR have been calculated from data obtained during the monitoring program, from previous modelling results in Olkiluto and Laxemar and from some selected old saline groundwaters in Laxemar and Forsmark. Obtained results support an anthropogenic origin for the highest measured values of dissolved sulphide in the monitoring program. Furthermore, they provide for the first time a set of "*in situ*" sulphate reduction rates at different depths and conditions for the Swedish sites. These rates could be used as a preliminary reference to frame the future evolution of dissolved sulphide.

### A3.1 Introduction

There is a substantial amount of information on sulphate reduction rates (SRR) and, in general, on the respiration rates associated with different metabolisms (or on the overall or composite respiration rates) in surface systems like soils, lakes, and, specially, marine sediments. However, data on *in situ* rates of microbial metabolisms in aquifers are still scarce, especially in crystalline systems. Here the available information on SRR in groundwater systems has been reviewed and results are summarized in Figure A3-1, where a detailed caption lists the sources of information that have been used in its compilation.

Data are presented separately for sedimentary and crystalline groundwater systems. In the former case, shallow (e.g. less than 50 m in detritic, sandy materials) and deep aquifers (hundred of meters in siliciclastic and carbonatic rocks and long residence time groundwaters, e.g. 6,000–40,000 years; /Plummer et al. 1990; Chapelle and Lovley, 1990; Murphy and Schramke, 1998/ are differentiated. In deep sedimentary aquifers, in order to complete the scarce information available, some overall respiration rates have also been included. These values represent the cumulative effects of the respiration rate of individual electron acceptors (e.g. iron reduction rate + sulphate reduction rate + ...) on the total carbon turnover along the examined flow path. Thus, the corresponding sulphate reduction rate would be equal or, more probably, lower than the stated overall values. The age of the materials hosting the aquifers is also indicated.

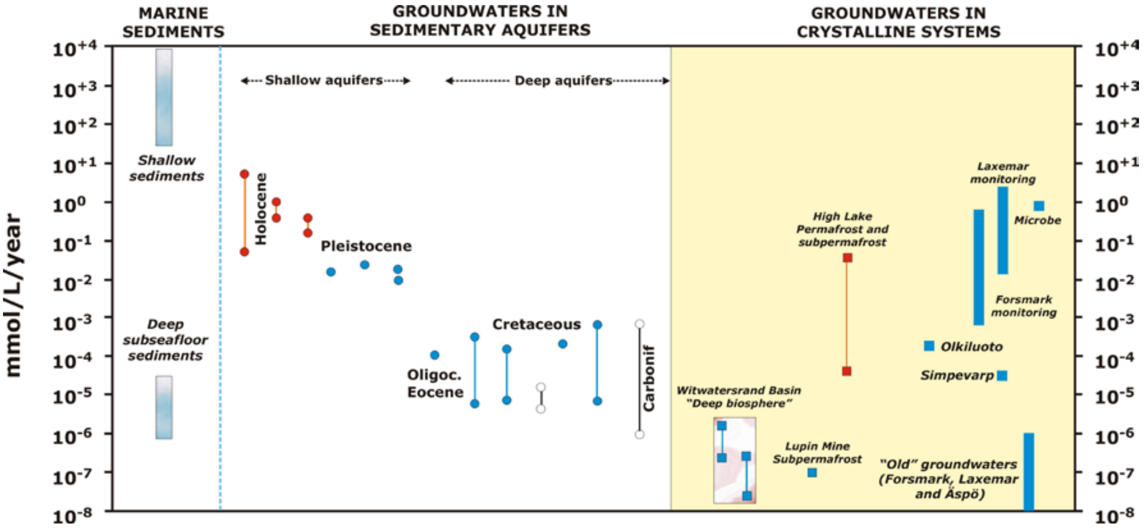


***Figure A3-1.*** *(IN LANDSCAPE) Compilation of published sulphate reduction rates (SRR) in marine sediments and in groundwaters from sedimentary and crystalline aquifer systems. Red filled symbols represent experimentally determined SRR, while blue filled symbols represent rates obtained from geochemical modelling (inverse approach). Open symbols represent overall or "composite" respiration rates (see text), also from geochemical modelling. Rates for marine sediments include those obtained in shallow sediments from the Ballastplaat mud flat (Belgium; data from /Panutrakul et al. 2001/), the Gulf of Mexico (data from /Lin and Morse, 1991/), the North Sea /Bottcher et al. 2004/ and from sediments at 241 m depth in the Gotland Basin (from /Piker et al. 1998/). Rates obtained in deep, subseafloor sediments (from 400 to 5,000 m below the sea level and down to 400 m under the seafloor) are also included /D'Hondt et al. 2004; Wang et al. 2008/. Rates for shallow, sandy aquifers correspond to the Romo (data from /Jakobsen and Postma, 1994, 1999; Hansen et al. 2001/), Tuse Naes /Jakobsen and Postma, 1994/ and Asserbo aquifers /Jakobsen and Cold, 2007/ in Denmark; to the Führberg and Bocholt aquifers in Germany /Jakobsen and Postma, 1994/ and to the Sturgeon Falls aquifer in Canada /Jakobsen and Postma, 1994/. Rates for deep aquifers correspond to the Florida aquifer (Oligocene-Eocene limestones; /Plummer, 1977; Jakobsen and Postma, 1994/); to the siliciclastic Northern Atlantic Coastal Plain Aquifers (Middendorf, Black Creek and Cape Fear aquifers; data from /Chapelle and Lovley, 1990; Murphy and Schramke, 1998; Park et al. 2006/); to the Fox Hills aquifer (silciclastic, cretaceous materials; /Thorstenson et al. 1979; Jakobsen and Postma, 1994/); and, finally, to the Madison aquifer (carboniferous limestones and dolostones; /Plummer et al. 1990/). Data for the crystalline systems are from the $H_2$-rich and old (15–25 Ma) brackish fracture waters at 2.8 km depth in the Mponeng gold mine (Witwatersrand Basin, South Africa), representative of a deep biosphere dominated by sulphate reducing bacteria /Lin et al. 2006; Chivian et al. 2008/; from the brackish to saline, subpermafrost groundwaters in the Lupin Mine (Canada) at depths between 890 and 1,130 m (data from /Onstott et al. 2009/); from permafrost and subpermafrost groundwaters in High Lake (Canada) at depths between 340 to 530 m depth /Stotler et al. 2010/; from the MICROBE experiment at the Underground Research laboratory in Äspö /Hallbeck and Pedersen, 2008a/; and, finally, from calculations performed in this study with data collected during the monitoring program in Forsmark and Laxemar, with previous modelling data from Olkiluoto and Simpevarp, and with data of old and deep saline (> 600 m depth) groundwaters from Laxemar, Forsmark and Äspö.*

Published data for crystalline aquifers come from research on the "Deep Biosphere" in the gold mines of the Witwatersrand Basin (South Africa), on the permafrost and deep subpermafrost environments in Lupin and High Lake (Canada) and from the MICROBE experiment at the Äspö Underground Laboratory (Sweden). The aquifers in the Witwatersrand Basin and Lupin-High Lake sites are hosted in metamorphic rocks (Archaean metabasalts and Archaean metaturbidites, respectively). Thus, they are different from the "granitic" materials usually examined in the investigations performed in the Canadian and Fennoscandian Shields but they are also "crystalline rocks" by definition.

Finally, some SRR for shallow and deep sub-seafloor marine sediments have been included for comparative purposes, as SRR in shallow marine sediments are amongst the highest measured rates whereas the subseafloor biosphere is usually considered the bacterial habitat with the lowest (or some of the lowest) metabolic rates /D´Hondt et al. 2002; Parkes et al. 2005/ (see Figure A3-1).

The sulphate (and composite) reduction rates for groundwater systems presented here have been estimated by two methods: a) inverse approaches on geochemical data of natural systems, usually involving inverse geochemical modelling calculations (mass balance) with isotopic restrictions (e.g. /Plummer et al. 1990; Murphy and Schramke, 1998; Lin et al. 2006/); and b) laboratory radiotracer methods on core samples extracted from the aquifers (e.g. /Jakobsen and Postma, 1994, 1999; Stotler et al. 2010/).

Some cautions must be exercised when comparing the results of these two different methodologies as a sharp contrast usually exists between the respiration rates determined by them /Chapelle and Lovley, 1990; Phelps et al. 1994; Murphy and Schramke, 1998/. This discrepancy may reflect the effects of the procedures followed for the direct measurements on core sediments (microbial activity stimulation by the addition of substrate or electron acceptors, and the physical disruption during drilling and sampling processes). But it may simply be a reflection of the spatial and temporal measurement scales (spatial distribution of samples and time-frames represented by the respiration measurements; see the discussion in /Murphy and Schramke, 1998/).

Rates determined by geochemical modelling are based on chemical mass-balance along a flow path and, therefore, represent a spatially and temporally averaged respiration rate (e.g. SRR), commonly over tens to hundreds of kilometres and thousands of years in deep aquifers /Jakobsen and Postma, 1994; Murphy and Schramke, 1998/. Thus, they provide valuable information on the net effects of biogeochemical processes on groundwater composition despite the spatial and temporal heterogeneity likely to characterise deep-aquifer systems.

## A3.2 Rates in sedimentary aquifers

Maximum sulphate reduction rates found in sedimentary aquifers (in the shallow Romo aquifer) are still three orders of magnitude lower than the maximum rates reported for shallow marine sediments (Figure A3-1) and almost an order of magnitude lower than those for lake sediments /Jakobsen and Postma, 1994, 1999/. SRR in deep aquifers are much lower, eight to ten orders of magnitude, than the maximum rates in shallow marine sediments, overlapping the range found in the highly oligotrophic, deep, subseafloor marine settings. Obviously, they are also lower than the rates observed in shallow aquifers (three orders of magnitude).

These differences are the result of the different reactivity (bioavailability) of organic matter in these systems, much lower in aquifers and in subseafloor environments than in shallow marine and lacustrine settings /Jakobsen and Postma, 1994, 1999; D'Hondt et al. 2002; Parkes et al. 2005/ and lower in deep aquifers set in old materials than in shallow aquifers located in modern rocks (Holocene-Pleistocene). The difference found between shallow and deep sedimentary aquifers can be justified by the fact that the metabolic activity in these systems is thought to rely on the photosynthetically-derived organic matter accumulated in the sediments. Although the particular nature and diagenetic history of the organic matter in the aquifers may also play a role, the reactivity of the organic matter shows an overall decrease with burial and age /Chapelle and Lovley, 1990; Jakobsen and Postma, 1994, 1999/.[1]

There is no obvious relationship between dissolved sulphate concentrations and SRR in the reviewed studies. For example, high sulphate contents (around 2,000 mg/L $SO_4^{2-}$, 20.8 mmol/L) are present in aquifers with low metabolic rates (Madison Aquifer), and low sulphate concentrations (lower than 15 mg/L ≈ 0.16 mmol/L) are present in aquifers with some of the lowest SRR (e.g. the Middendorf aquifer) but also in some with the highest (e.g. the Romo aquifer, with contents < 10 mg/L $SO_4^{2-}$ or 0.1 mmol/L).

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[1] The highest SRR in groundwaters from sedimentary aquifers were determined in shallow Holocene-Pleistocene aquifers, reaching values as high as 4.5 mM/year in the Romo aquifer /Jakobsen and Postma, 1994/. These rates seem consistent with the higher reactivity of organic matter in "modern" aquifers. However, as stated above, they may also be "magnified" by the methodology used (radiotracer methods on core samples; /Jakobsen and Postma, 1994; 1999; Hansen et al. 2001; Jakobsen and Cold, 2007/). Spatially-averaged recalculations performed by /Murphy and Schramke, 1998/ with the highest SRR in the Romo aquifer gave a rate of 0.05 mM/year, which is similar to the lower value reported in the work by /Jakobsen and Postma, 1994/. In any case, this uncertainty does not change the overall SRR trend in sedimentary aquifers observed in Figure A3-1.

There is also no relationship between SRR and dissolved sulphide contents in the groundwater. In most cases, sulphide content is extremely low (or even undetectable) irrespective of the SRR. For example, in the Holocene-Pleistocene shallow aquifers with the highest SRR, dissolved sulphide contents are low (0.01 mg/L $\approx 3.12 \cdot 10^{-4}$ mmol/L or below detection limit). In deep aquifers with lower SRR, dissolved sulphide is also low (e.g. 0.003 to 0.03 mg/L. $9.4 \cdot 10^{-5}$ to $9.4 \cdot 10^{-4}$ mmol/L) though values up to 4 mg/L (0.125 mmol/L) have been found in some of the examined flow paths in the largest deep aquifers (e.g. the Madison aquifer; Plummer et al. 1990).

This lack of correlation is due to the fact that even with high sulphate reduction rates, sulphide contents are kept in low or undetectable amounts if Fe(II) or iron oxyhydroxides are present in the system (as, for example, in the Romo aquifer; /Jakobsen and Postma, 1999; Hansen et al. 2001/). The inorganic reductive dissolution of iron oxyhydroxides by dissolved sulphide is kinetically very fast: it proceeds via the oxidation of dissolved sulphide at the mineral surface, followed by the release of the produced Fe(II) to solution. The subsequent reaction of this dissolved Fe(II) with additional dissolved sulphide promotes FeS precipitation, also a very fast process (see /Gimeno et al. 2009/ and references therein). These processes seem to be effective in most of the examined aquifers. Only locally, in some flow paths, the exhaustion or absence of iron oxyhydroxides allows the accumulation of dissolved sulphide in significant amounts.

In summary, organic matter reactivity appears to have a much larger influence than sulphate contents on SRR. The presence of dissolved sulphate is indispensable for microbial sulphate reduction[2] but the amount of dissolved sulphate, *per se,* is neither indicative of the presence or absence of sulphate reduction activity nor necessarily related to SRR in groundwaters.

## A3.3 Rates in crystalline aquifers from South Africa and Canada

As stated above, available SRR data in crystalline systems are much more scarce than in sedimentary aquifers and most of them deal with "particular" situations like the research on the "Deep Biosphere" in the gold mines of the Witwatersrand Basin (South Africa) or on microbiological investigations in permafrost and subpermafrost groundwaters.

*South African mines* are unusual in that they routinely attain depths of around 3 kilometres below land surface, thereby accessing ancient, anaerobic groundwaters distinct from the more frequently studied, shallower subsurface aquifers. The studies performed in fracture groundwaters at 2–3 km depth frequently evidence the existence of a very simple microbial community dominated by a single phylotype (most probably a sulphate reducer) and several closely related methanogens /Kieft et al. 2005; Moser et al. 2005; Lin et al. 2006; Sherwood-Lollar et al. 2007) or, even, by only one species of $H_2$-utilzing SRB as it was found by /Chivian et al. 2008/ in one of the $H_2$-rich dominated old (15–25 Ma) brackish (1,900–3,000 mg/L Cl, 53.6–84.6 mmol/L) fracture waters at 2.8 km depth at level 104 in the Mponeng gold mine (one of the mines in the Witwatersrand Basin).

*In situ* rates of microbial sulphate reduction were estimated by /Lin et al. 2006/ for fracture groundwaters at level 104 in the Mponeng mine. Obtained SRR are between 0.22 and 1.45 nM/year (by mass balance calculations) or between 0.025 and 0.25 nM/year (from rates of radiolytic $H_2$ generation[3]). These values represent extremely slow metabolic rates (equal or even lower than those in deep aquifers or deep subseafloor sediments; Figure A3-1); and more so if we take into account the high $H_2$ contents of these groundwaters (from 1.9 to 3.7 mM) and the meaningful concentration of dissolved sulphate (51 to 179 mg/L, 0.53 to 1.86 mmol/L). Reconciling the presence of $H_2$ users with m*M*-level concentrations of dissolved $H_2$ suggests that factors other than substrate availability are limiting microbial activity (e.g. the availability of inorganic nutrients like N, P, or Fe, the presence of inhibitors, etc; /Kieft et al. 2005; Lin et al. 2006; Sherwood-Lollar et al. 2007/).

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[2] In fact, rates in marine sediments decrease with the decrease of sulphate concentration for sulphate contents lower than 1mM; /Boudreau and Westrich, 1984; Jakobsen and Postma, 1999/.

[3] Lin et al. (2006) showed that, over the My timescale (15–25 My) estimated rates of $H_2$ generation of 0.1–1 nM/year for groundwaters in the Mponeng mine are sufficient to produce the observed mM concentrations of dissolved $H_2$ in the groundwater. If a steady state is assumed in which production rate is equal to consumption rate, then the $H_2$-utilising sulphate-reducing rate would be 0.025 to 0.25 nM/yr.

Despite the extremely low SRR in fracture groundwaters, dissolved sulphide concentrations are very high, between 1.06 and 1.39 mM[4]. The long residence time of groundwaters in the Witwatersrand Basin (on the order of millions to tens of millions of years; /Lippmann et al. 2003; Lin et al. 2006/) provides a setting in which the products of SRB metabolism can accumulate /Sherwood-Lollar et al. 2007/ without apparent sinks for this component (e.g. groundwaters are subsaturated with respect to FeS).

Extremely low microbial SRR of 0.1 nM/year (Figure A3-1) were also obtained by /Onstott et al. 2009/ in a very different context: the brackish-saline (Cl from 1,631 to 23,397 mg/L, 46 to 660 mmol/L), subpermafrost groundwaters from the *Lupin Mine* (at depths between 890 and 1,130 m). Genomic DNA and geochemical data indicate that SRB dominate the subpermafrost microbial ecosystem (in this case, both autrotrophic and heterotrophic SRB can be active) and $SO_4^{2-}$ appears to be the dominant electron acceptor despite its low concentration (less than 0.1 mM; /Onstott et al. 2009; Stotler et al. 2010/). The concentration of dissolved sulphide in these groundwaters is low ($1.5·10^{-3}$ to $5.6·10^{-3}$ mM; 0.048 to 0.18 mg/L) and this may be related to the removal of dissolved sulphide by FeS precipitation (the analysed groundwaters are in equilibrium with respect to “amorphous” FeS); but also to the existence of pathways identified by /Onstott et al. 2009/ between the subpermafrost fracture network and the overlying oxygenic biosphere (e.g. through taliks) that intermittently breaks the “isolation” condition at depth.

In order to complete the knowledge of the permafrost at shallower levels, /Stotler et al. 2010/ studied the permafrost system at *High Lake (Nunavut, Canada)*, an undisturbed location (no mining operations) 169 km north of Lupin Mine. To determine the vertical distribution of microbial sulphate reduction activity, $^{35}S$ microautoradiography was performed on 18 cores from 340 to 530 m depth. SRR (associated, probably, with acetate-consuming SRB) ranged from 36.5 nMol/year to 36.5 µM/year and appear to increase with depth. The lowest SRR correspond to permafrost conditions and they are in the range of organic matter-depleted deep sedimentary aquifers. However, the highest rates in basal subpermafrost conditions are in the range of shallow sedimentary aquifers enriched in organic matter (Figure A3-1).

These surprisingly high SRR for pristine permafrost groundwaters may be associated with the stimulation of microbial activity when radiotracer methods are used (see above) or with problems with the experimental setup (see below). Thus, more information is needed to resolve this open question.

## A3.4 Rates in crystalline aquifers from the Fennoscandian Shield

The available SRR data come from the sulphide monitoring program set up at Forsmark and Laxemar and from the MICROBE experiment at Äspö /Hallbeck and Pedersen, 2008a/. These rates are based on the amount of dissolved sulphide produced in a time interval and, considering that some dissolved sulphide might have been lost during the accumulation period (e.g. by FeS precipitation), the measured dissolved sulphide could be lower than that actually produced. This uncertainty is not important as explained below.

Apart from these rates additional calculations have been performed based on the geochemical modelling results of /Pitkänen et al. 2004/ in Olkiluto and of /Gimeno et al. 2009/ in Laxemar. Some preliminary scoping calculations based on dissolved sulphide for long residence time groundwaters have also been performed.

### A3.4.1 Results from the monitoring program and the MICROBE experiments

Calculation of the rates of sulphide production during the different periods of monitoring sampling and analysis is based on the difference between sulphide values measured at the end of one period and the values measured at the beginning of the next monitoring campaign. These values are then divided by the time elapsed between campaigns. Using this methodology, SRR for Forsmark groundwaters in

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[4] Dissolved sulphide contents in groundwaters from the Witwatersrand Basin (South Africa) are usually high. In the work by /Onstott et al. 2006/ on 170 water samples from different zones of the Witwatersrand Basin (at depths between 700 and 3,400 m) an average of 0.73 mM of dissolved sulphide was found and values as high as 5.63 mM were measured.

borehole sections with meaningful sulphide accumulations range from 7.8·10$^{-4}$ to 0.48 mM/year. In Laxemar, calculated rates are higher, between 1.4·10$^{-2}$ and 3.3 mM/year. Figure A3-2 shows that there is no clear correlation between SRR and depth and that values higher than 1 mM/year can be observed at Laxemar both at shallow depths (50 m) and deeper in the basement (700 m) whereas in Forsmark the highest values occur at depths between 340 and 530 m.

In the MICROBE experiment, a circulation system connected to a conductive fracture was installed at a depth of 447 m in the Äspö Hard Rock Laboratory. In this experiment groundwater is pumped from the fracture through flow cells and then back to the fracture again while being maintained under *in situ* conditions /Hallbeck and Pedersen 2008a/. Dissolved sulphide was measured in a closed mode, where the connection to the aquifer was blocked but pressure was maintained and groundwater was re-circulated through the flow cells in the system. The observed increment of dissolved sulphide for approximately 60 days corresponds to a SRR of 0.9 mM/year /Hallbeck and Pedersen 2008a/, a rate similar to the highest values observed in Forsmark and Laxemar (Figure A3-2).

These SRR are large relative to the sulphide concentrations usually found during the Site Investigation Program /Gimeno et al. 2008, 2009/. Assuming that these estimated high SRR are valid for pristine conditions, /Hallbeck and Pedersen 2008a/ suggest that the fact of finding low sulphide contents during the Site Investigation Program is due to its removal from groundwaters in the form of pyrite. However, despite the recognition of the important role played by the inorganic reductive dissolution of iron oxyhydroxides and the precipitation of FeS in the control and consumption of dissolved sulphide in groundwaters /Gimeno et al. 2006, 2008, 2009/ the obtained rates still seem too high.

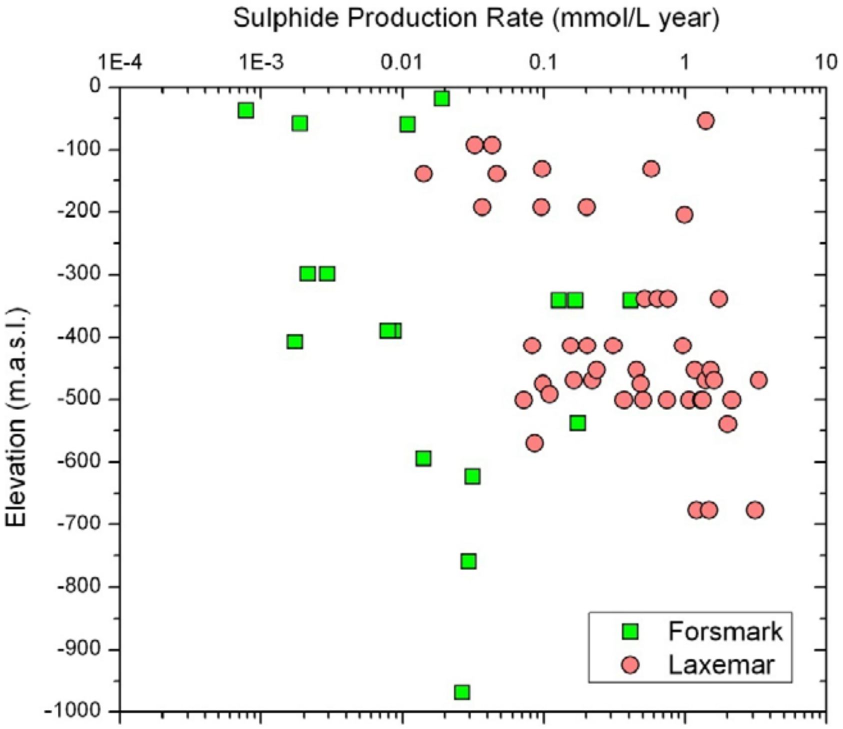

***Figure A3-2.** Sulphate reduction rates vs. depth estimated from data in monitored sections from Forsmark and Laxemar.*

For example, considering the apparent radiometric ages ($^{14}C$) of the groundwater in the examined sections in Forsmark, Laxemar and Äspö (4,000 to 10,000 years[5]) and assuming a sulphate reduction rate of 1 mM/year (close to the SRR obtained in the MICROBE experiment by /Hallbeck and Pedersen, 2008a/), one mol of dissolved sulphide (32,000 mg/L) should be produced in 1,000 years in some points of the system. It is not clear that the iron system in the fractures could buffer such amounts of dissolved sulphide. Moreover, such high SRR would imply a massive precipitation of biogenic iron sulphide minerals (e.g. pyrite). However, extensive mineralogical studies performed in the Forsmark and Laxemar areas clearly indicate that this type of "recent" sulphide minerals are uncommon in Laxemar and practically inexistent in Forsmark /Sandström et al. 2008; Drake and Tullborg, 2009/. Even more important, at such high rates of sulphate reduction all dissolved sulphate in groundwaters (maximum values of around 600 mg/L ≈ 6.25 mmol/L between 200 and 600 m depth in both sites; e.g. Figure 5-1 in the main report) would be consumed in less than 7 years if sulphate is not replaced at the same rate by an unknown mechanism in these long residence time groundwaters.

Finally, most of the obtained rates, especially at Laxemar and Äspö, are in the range of shallow sedimentary aquifers with high availability of organic matter (Figure A3-1), a situation difficult to justify in the pristine conditions of these granitic groundwaters.

The only possibility left is that this high availability of organic matter might have been antropically induced in the borehole sections or in the more controlled experimental conditions. During sampling in the monitored sections high dissolved sulphide concentrations were observed in the first sample after a more or less prolonged time without pumping. This enhanced sulphide concentration is considered to be the contribution from the initial stagnant water still remaining in the downhole tubings and in the borehole section (see Section 3.1.5 in the main report). Thus, SRB activity could have been enhanced in these residual waters, allowing the accumulation of dissolved sulphide with time. The origin of this increase in sulphate reduction activity is most probably related to the degradation of organic man-made materials (plastics, resins, etc[6]) in the borehole section, providing an additional source of nutrients and, thus, increasing microbial activity. High levels of DOC in the first sample from many monitored sections (cf. Section 5.3.1 in the main report) strongly support this possibility.

The effects of the degradation of man-made materials have been observed in laboratory experiments as it was exemplified by the results obtained in the REX project. In the supporting laboratory experiment of that project (the replica experiment; /Trotignon et al. 2002/), waters with dissolved oxygen were injected periodically (pulses) during 1 year in a core section extracted from the REX borehole. The return from oxic to reducing conditions was monitored between each series of pulses, including chemical (e.g. DOC, TOC, dissolved sulphide and acetate) and microbiological analysis of waters. Also, biofilm investigations were performed on solid surface samples collected at the end of the experiment, both from the core and from the experimental setup (resins, PETP – polyethylenterephthalate- cap, O-ring, etc).

An artefact, associated to an unexpected carbon source supplied by the experimental setup, was discovered. DOC and TOC concentrations in solution reached 40 mM during the anoxic periods. Some of the main organic contributors to the bulk DOC and TOC were identified to proceed from the PETP cap and the epoxy resin used to seal the cylindrical part of the core. Biofilm investigations confirmed this finding: fermentative anaerobes were present mostly on the sealing epoxy resin; aerobes and IRB were present at significant levels both on plastic surfaces and on the core. Organic carbon concentration increased in solution from the first to the last pulses (from 0.1 to 46 mM) and because of this extra carbon source, an "explosive" development of heterotrophic iron reduction bacteria and fermentative bacteria was favoured in this experiment.

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[5] Some of the deepest monitored sections in Forsmark (at 759 and 969 m depth, with estimated rates of 2.6 and $2.9 \cdot 10^{-2}$ mM/year) have average residence times of the order of 1.5 Ma based on $^{4}He$ concentrations and $^{36}Cl$ data /Smellie et al. 2008/.

[6] Decomposition of organic materials (including microbial biofilms, tobacco, plastics, cellulose, hydraulic oil, surfactants and cement additives) in the repository is considered an important aspect in the safety assessment. Inventories of organic materials and assessments of their impact on microbial processes (mainly SRB activities) were prepared by /Hallbeck et al. 2006/ for Sr-Can and more recently by /Hallbeck 2010/ for Sr-Site.

In summary, SRR estimations in these works appear to be enhanced by additional human-induced sources of organic matter, initially not present in the pristine environment. This fact would explain the high SRR, similar to those observed in shallow sedimentary aquifers with high availability of organic matter. Moreover, it would support an antropically-induced origin for the "peaks" of high dissolved sulphide concentrations recorded in the monitoring program.

### A3.4.2 Additional calculations based on geochemical modelling

Some additional SRR estimations can be made from results in previous geochemical modelling calculations performed in Olkiluoto /Pitkänen et al. 2004/ and Laxemar /Gimeno et al. 2009/.

The ***first case*** corresponds to the effects of sulphate reduction associated with the infiltration of marine Littorina waters in Olkiluoto. Littorina waters are the only important source of dissolved sulphate in the Holocene palaeohydrological record from Forsmark and Olkiluoto, as saline groundwaters (e.g. Deep Saline end-member) in these sites are depleted in this component (below 10 mg/L or 0.1 mmol/L; /Pitkänen et al. 2004; Gimeno et al. 2008/).

Mass balance calculations with isotopic constraints performed by /Pitkänen et al. 2004/ during infiltration of Littorina waters at Olkiluoto indicate a loss of dissolved sulphate of between 0.64 and 0.74 mmol per kg of water. Assuming that the infiltration of marine water occurred at the maximum salinity stage of the Littorina Sea (4500 to 3000 BC), values of SRR between $1.0 \cdot 10^{-4}$ and $1.5 \cdot 10^{-4}$ mM/year can be estimated. These values agree with the upper limit of SRR determined in deep sedimentary aquifers (Figure A3-1).

However, the reduction of dissolved sulphate may have mainly occurred in sea-bottom sediments during the infiltration of marine waters and prior to the circulation in the bedrock /Pitkänen et al. 2004/. Thus, sulphate reduction rate in the fractures should be even lower than the one estimated above (or even zero). Lower SRR during the infiltration of Littorina waters into the bedrock would be in agreement with the quasi-conservative behaviour of dissolved sulphate in Olkiluoto and Forsmark /Pitkänen et al. 2004; Gimeno et al. 2008/. Thus, it appears that sulphate reduction rates were not high during an apparently favourable "marine period" with intrusion of dissolved sulphate (and probably also of organic matter) in the bedrock.

The ***second case*** is related to some groundwaters in the Simpevarp subarea, mainly in borehole KSH01A between 240 and 530 m depth. The main compositional characters of these groundwaters (with Cl contents between 5,500 and 8,000 mg/L, 155.1 to 225.6 mmol/L) can be explained by the mixing and/or mixing and reaction (calcite equilibrium, cation-exchange) between a deep saline end-member and a dilute glacial end-member, as simulated by /Gimeno et al. 2009/. However, dissolved sulphate contents are lower than expected (Figure A3-3) and, thus, the most feasible explanation is the actuation of sulphate reduction processes in these groundwaters.

The calculation consists of assuming that the predicted concentration of dissolved sulphate from mixing (for the KSH01A groundwaters) is the initial value (1mM) whereas the present value (from 0.21 to 0.51 mM) is the result of the sulphate reduction process. The last glacial meltwater intruding into the bedrock (one of the mixing end members) was hydraulically injected > 13,000 years ago. Using this age, SRR for these groundwaters would be between $3.8 \cdot 10^{-5}$ and $6.1 \cdot 10^{-5}$ mM/year, in perfect agreement with the range obtained for deep sedimentary aquifers (Figure A3-1).

### A3.4.3 Scoping calculations based on dissolved sulphide in deep groundwaters

A precise quantitative estimation of groundwater residence times by the usual dating methods (short-lived and long-lived radioisotopes) in the studied crystalline systems is complicated by different factors (like the existence of mixing processes; see /Smellie et al. 2008/ for further discussion). However, chlorine-36 data from the Laxemar, Äspö and Forsmark areas indicate that secular equilibrium seems to have been achieved in some deep saline non-marine groundwaters (Cl > 10,000 mg/L or 282 mmol/L).

This is the case of the saline groundwaters at 750–970 m depth in Forsmark (KFM07A and KFM03A boreholes) where the combined use of $^{36}$C and $^{4}$He systematics has provided identical residence times of the order of 1.5 My /Smellie et al. 2008/. A similar age was obtained by Louvat et al. (1999) for KAS03 groundwaters at around 900 m depth with Cl =12,300 mg/L (347 mmol/L) and more recently by /Mahara et al. 2008/ on samples from the Äspö tunnel with Cl > 10,000 mg/L (282 mmol/L).

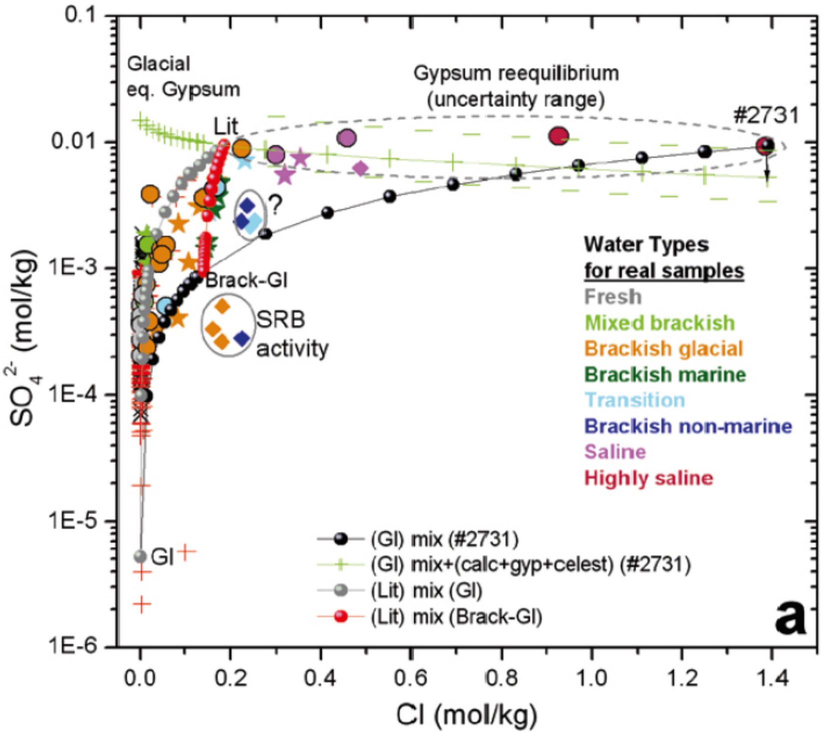

***Figure A3-3.** Sulphate and chloride content results for conservative mixing and mixing + equilibrium simulations between the different end members. Measured values are also shown (stars: Äspö GW; circles: Laxemar GW, red crosses: Laxemar NSGW; diamonds: Simpevarp GW; black x: Simpevarp NSGW). The results of gypsum re-equilibration are calculated with an uncertainty range of ± 0.25 for gypsum solubility. The samples inside the grey circle marked with SRB activity are those used in the SRR calculation in this section. From /Gimeno et al. 2009/.*

Finally, /Laaksoharju et al. 2009/ indicate residence times that appear to be at least several hundreds of thousands of years for the brackish to saline non-marine groundwaters found at depths around 600 to 1,000 m in Laxemar.

Hydraulic conditions and estimated ages at these depths would indicate very low groundwater flow or stagnant conditions and, if SRB activity is present, dissolved sulphide could be accumulated through time. Thus, SRR may be theoretically obtained from dissolved sulphide provided that S(-II) behaves “conservatively” (without reactions after its production by SRB).

However, as stated above, the inorganic reductive dissolution of iron oxyhydroxides and precipitation of FeS can modify this behaviour and both processes seem to be active in the studied systems (see /Gimeno et al. 2009/ for details). Thus, to calculate an SSR with this approach, groundwaters with meaningful dissolved sulphide contents, undersaturated with respect to amorphous FeS and mackinawite, and with low dissolved Fe(II) concentrations have been selected from the aforementioned set (Table A3-1). All selected groundwaters have shown very constant contents of dissolved iron and sulphide during the successive sampling in the CCC (Complete Chemical Characterisation), with drilling water < 1%. Only one selected section (from the KFM07 borehole; Table A3-1) has been studied during the monitoring program. For this section two representative groundwater samples have been used, the representative sample selected from the CCC and the representative sample selected from the monitoring period.

A residence time of 200,000 years has been assigned to samples from KLX01, KLX03 and KSH02 boreholes and of 1.5 Ma for samples from KAS02 and KFM07 boreholes. Results are also shown in Table A3-1. Most SRR are of the order of $10^{-8}$ mM/year, including groundwaters without dissolved iron (KLX03, Table A3-1) and with low contents of dissolved iron (KAS02, KAS03 and KSH02, Table A3-1). Thus, reductive dissolution of iron oxyhydroxides by dissolved sulphide may affect the SRR obtained for some of the groundwaters but it appears that this effect does not drastically change the obtained values.

**Table A3-1. Selected samples from deep saline non marine groundwaters in Äspö, Forsmark, Laxemar and Simpevarp, and their estimated SRR. Dissolved chloride, sulphide and ferrous iron contents as well as saturation index with respect to "amorphous" FeS are indicated. The only selected section with data from both the CCC and the monitoring program is that from the KFM07 borehole. In this case, the values for the selected sample from the monitoring period are also indicated between brackets. Sample 1516 in the KLX01 borehole has 2.6% of drilling water (see text).**

| | Depth (m) | Sample | Cl (mg/L) | $S^{2-}$ (mg/L) | $Fe^{2+}$ (mg/L) | SI FeS(am) | SRR (mM/year) |
|---|---|---|---|---|---|---|---|
| KAS03 | 914.01 | 1582 | 12,300 | 1.280 | 0.077 | –0.86 | $2.7\cdot10^{-8}$ |
| KAS02 | 881.20 | 1560 | 11,000 | 0.720 | 0.051 | –2.73 | $1.5\cdot19^{-8}$ |
| KFM07 | 763.22 | 8843 | 14,400 | 0.062 | 0.262 | –1.43 | $1.3\cdot10^{-9}$ |
| | (795.22) | (16613) | (14,400) | (0.029) | (0.076) | (–1.14) | $(6.0\cdot10^{-10})$ |
| KLX03 | 922.45 | 10076 | 10,500 | 0.090 | Bdl | ——— | $1.4\cdot10^{-8}$ |
| KSH02 | 951.70 | 11185 | 11,185 | 0.299 | 0.055 | –2.49 | $4.7\cdot10^{-8}$ |
| KLX01 | 672.95 | 1516 | 4,870 | 2.500 | 0.029 | –0.60 | $4.0\cdot10^{-7}$ |

Something different happens to groundwaters from KFM07 borehole where the obtained SRR is, at least, one order of magnitude lower ($1.3\cdot10^{-9}$ to $6\cdot10^{-10}$ mM/year; Table A3-1). This would agree with the very low amount of SRB found in this section (MPN = 0.2 cell/mL; /Hallbeck and Pedersen, 2008c/). But, in this case, dissolved iron is noticeably higher than dissolved sulphide (Table A3-1) suggesting that the reductive dissolution of iron oxyhydroxides has distorted the SRR. This is also supported by the fact that such extremely low SRR have not been detected in any other natural system (Figure A3-1).

Groundwaters with the highest measured dissolved sulphide content in the Forsmark and Laxemar areas (KLX01 borehole, at 672 m depth), although with a drilling water content of 2–3%, could be also included in this type of long residence time groundwaters (200,000 years). The SRR for this groundwaters is $4.0\cdot10^{-7}$ mM/year, one order of magnitude higher than for groundwaters with "similar age" (KLX03 and KSH02 boreholes; Table A3-1). Dissolved iron contents are very low, close to the usual reporting limit (0.02 mg/L or $6.25\cdot10^{-4}$ mmol/L) in SKB's analytical methodology, suggesting the absence of meaningful amounts of iron oxyhydroxides in this zone (as it also occurs in the KLX03 borehole).

Thus, as expected from their dissolved sulphide contents, SRR are higher in borehole KLX01 than in borehole KLX03 (with the same residence time for calculations). Furthermore, this difference would agree with the detected SRB populations in both sections, below the detection limit in KLX03 /Hallbeck and Pedersen, 2008b/ and high in the KLX01 section /Hallbeck, 2006/.

Despite the cautions taken in the selection of data, the results presented in this section are subjected to uncertainties related to:

a) the age of the groundwaters and

b) the assumption that the selected dissolved sulphide concentrations correspond to the pristine conditions of the groundwaters.

A critical point in these estimations is the residence time of the groundwaters. This is why groundwaters with the most "precise" quantitative age estimations have been used. However, even the selected deep groundwaters may contain a glacial signature /Smellie et al. 2008; Gimeno et al. 2009/ and, thus, it can be argued that they could have a more modern character than the one assumed in the calculations.

This scenario could be important if sulphate reduction begun after the intrusion of the "last" glacial melt waters (13,000 years ago). However, it must be taken into account that:

a) the assumption that sulphate reduction started with the input of glacial meltwaters is hard to justify as this entrance would produce the dilution of the electron donors and acceptors involved in the process (organic matter and sulphate),

b) with the available data, the input of waters from the last glaciation down to these depths (600–900 m) is difficult to justify (e.g. /Smellie et al. 2008/), and therefore, they would be even older, and

c) even assuming and age of 13,000 years for the beginning of the sulphate reduction process, SRR would be around ≈ $10^{-6}$ mM/year, in the lower range observed in deep sedimentary aquifers, in agreement with those determined in grondwaters from the South African mines (Figure A3-1).

On the other hand, some of the dissolved sulphide concentrations measured during the CCC program are relatively high (e.g. KAS03 and KLX01 boreholes; Table A3-1). These high dissolved sulphide concentrations could be related to the long delay between drilling and sampling (up to eight months) (cf. Section 3.1.6 in the main report). In this manner, the concentration of sulphide may increase during this period and could not correspond to pristine conditions. If this was the case, SRR would be even lower (not higher) than the calculated ones (Table A3-1).

Thus, this latter type of uncertainties do not change the overall interpretation of the results and thus estimated SRR for these old deep groundwaters should be very low. Moreover, the obtained rates agree with those obtained by /Onstott et al. 2009/ in similar old deep groundwaters from the Lupin Mine (at depths between 890 and 1,130 m; Figure A3-1) using more sophisticated geochemical modelling calculations; and also with some other independent estimations (see below). Finally, results presented here also emphasise the importance of iron oxyhydroxides in the modulation of dissolved sulphide contents: at such low SRR, dissolved sulphide can be accumulated only in locations lacking iron oxyhydroxides or where they have been already exhausted.

## A3.5 Discussion

Despite the important differences between aquifers in sedimentary and crystalline settings, the available information from the first ones can be used as a useful comparative term to qualitatively support some of the results presented in this work.

Sulphate reduction rates in shallow sedimentary aquifers range from $10^{-2}$ to 10 mM/year, always lower than those observed in shallow marine sediments (30 to $10^{4}$ mM/year; see Figure A3-1); and from $10^{-4}$ to $10^{-6}$ mM/year (i.e., extremely low) in deep sedimentary aquifers, in the same range as SRR in deep highly oligotrophic subseafloor marine settings ($10^{-4.5}$ to $10^{-6}$ mM/year; see Figure A3-1). The reactivity of organic matter accumulated in the original sediments (conditioned by the age of the aquifer hosting materials) appears to have a much larger influence on SRR than sulphate contents.

Crystalline systems, like those considered in the Swedish and Finnish concepts, have a much more limited source of photosinthetically-derived organic matter (organic carbon is only present as trace amounts of asphaltite). Only dissolved organic matter (DOC) in the recharge waters from different mixing events can be considered a suitable source. However, even this source is limited, as DOC contents are expected to decrease during infiltration due to microbial activity leaving remaining DOC at deeper levels as a less suitable substrate for microbial use (it has been exposed to microbial degradation at shallower depths, reducing its metabolic suitable part, e.g. short-chain organic molecules like acetate; /Kotelnikova, 2002/).

Thus, if the amount of surface-derived organic substrates is the limiting factor for SRB activity in the long residence time groundwaters usually found at repository levels (e.g. 3,000–10,000 years), SRR are expected to be equal to (or even lower than) those in deep sedimentary aquifers of similar residence times. This assumption agrees with the still scarce SRR (≈$10^{-5}$ mM/year) deduced in Section 3.2 for groundwaters at around 500 m in the Fennoscandian crystalline systems. The renewal rate of organic carbon will be extremely slow under the very low groundwater flow velocities or near-stagnant conditions present at depths greater than 500 m, thus imposing very stringent conditions for SRB activity (or any other heterotrophic microorganism). In fact, estimated SRR in crystalline systems at 500–900 m depth ($10^{-7}$–$10^{-8}$ mM/year; Sections 2 and 3.3) are even lower than in deep sedimentary aquifers (Figure A3-1).

In the absence (or very low amounts) of superficial organic carbon, deep-sourced $H_2$ and $CH_4$ may be the key factors in the control of putative sulphate reduction. Sulphate reduction activity in groundwaters may be supported by autotrophic microorganisms, directly by $H_2$-utilising SRB (with or without coupling with anaerobic methane oxidation) or, indirectly, by suitable organic matter liberated by other $H_2$-utilising microorganisms (e.g. autotrophic acetogens). Data on reaction rates associated with this activity in crystalline aquifers are practically inexistent. However, some "indirect" evidences do indicate extremely low SRR associated with these processes.

This type of microbial activities would be limited by the flux of $H_2$ and $CH_4$. The detected amounts of these gases in Forsmak and Laxemar are very low /Gimeno et al. 2009/ and fluxes and maximum productions of methane and hydrogen have been estimated based on these groundwater gas contents /Delos et al. 2010/. The calculated fluxes range from 0.2 to 1.2 $10^{-10}$ mol/($m^2$ yr) for $CH_4$ and from 0.5 to $9.0 \cdot 10^{-10}$ mol/($m^2$ yr) for $H_2$ and, thus, SRR would be in the range of $10^{-6}$ to $10^{-8}$ mM/year (assuming all $CH_4$ and $H_2$ is used by sulphate-reducing activity). This range is in agreement with the estimated values for the deeper and older groundwaters (Section 3.3) where no assumption on the type of SRB activity has been made. Finally, the only available work on SRR associated to autotrophic SRB /Lin et al. 2006/ in deep environments also points to extremely low sulphate reduction rates for $H_2$-utilizing SRB's (by the way, in a $H_2$-rich environment).

Much more data are needed on sulphate reduction rates in pristine crystalline systems. However, all these preliminary results suggest that reduction rates would be low and similar to (or lower than) those typical of deep sedimentary aquifers depleted in organic matter.

Moreover, for Forsmark and Laxemar sites, these low SRR would agree with the very low amounts of non-magmatic/hydrothermal and "late" pyrites[7] found in fracture fillings (Section 5.2.2 in the main report). As the word "late" refers to biogenic pyrite formed from the Late Palaeozoic to the Present /Sandström et al. 2008; Drake and Tullborg, 2009/, overall low SRR would have been maintained at least over a 100 million years period.

The presence of dissolved Fe(II) sources, mainly iron oxhydroxides, exerts a major control on the dissolved sulphide produced by the SRB activity in sedimentary and crystalline groundwaters. This control is not only associated with the precipitation of FeS, as it is usually assumed, but also with surface processes related to the reductive dissolution of iron oxyhydroxides (/Gimeno et al. 2009/ and references therein). However, the absence or exhaustion of these Fe(II) sources may promote the local accumulation of dissolved sulphide in some points of the groundwater system. At the slow sulphate reduction rates characteristic of deep sedimentary and crystalline systems, these "accumulations" would need, at least, tens of thousands of years to reach tens of mg/L of dissolved sulphide (e.g. 1 mmol/L). The construction of the repository may induce changes in the SRR and thus, as suggested by /Bath and Hermansson 2009/, more detailed mineralogical and geochemical data on the spatial variability of Fe(II) mineral sources would be necessary to estimate the "buffering" capacity of the system for dissolved sulphide.

Considering all the above evidences, a straightforward conclusion could be advanced: the "peaks" observed in dissolved sulphide during the monitoring program (and the corresponding high SRR; Figures A3-1 and A3-2) have been antropically induced. Such high SRR, only observed in shallow aquifers enriched in organic matter, are exceedingly high to justify the observed dissolved sulphate concentrations at the repository level in Forsmark and Laxemar.

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[7] At low temperature conditions, pyrite formation relies on the existence of microbial sulphate reduction activity and, thus, pyrite is considered a diagnostic redox mineral for the identification of past biologically-mediated sulphate reduction (see the review by /Gimeno et al. 2006/).

The very high dissolved sulphide concentrations are considered to be the contribution of the stagnant water remaining in the downhole tubings and in the borehole section since the latest pumping (months ago). The "isolation" of these residual waters from the iron sources in the fractures and the availability of important amounts of organic matter (from the own equipment), have promoted an increase in microbial activity and thus, the observed sulphide accumulation. Whether these results may help to understand sulphate reduction processes in the repository after closure remains to be explored.

Finally, it must be stated the "obvious": SRR depend on the active presence of SRB in the studied system. Sulphate reducing bacteria have been identified in the Forsmark and Laxemar groundwater systems, but they are not ubiquitous and their amounts (as most probable numbers, MPN) are not homogeneously distributed with depth. In fact, SRB data are scattered over the sampled elevation range without any clear trend /Hallbeck and Pedersen, 2008 b,c/ and little is known on the factors conditioning the presence of SRB's, the size of their populations and, therefore on the distribution of SRR in a more detailed level.

The microbiological studies performed in these systems have been focused on the "traditional" limiting factors on sulphate reduction activity (amounts of electron donors and acceptors). The results indicate that SRB data do not show any clear trend with respect to the amounts of dissolved sulphate and no significant correlation exists with respect to DOC, TOC and hydrogen /Hallbeck and Pedersen, 2008 b, c/.

However, sulphate reducers (both $H_2$- and acetate-oxidisers) require a minimum amount of chemical energy (ΔG) to proceed /Hoehler et al. 1998; Jakobsen and Cold, 2007; Jin and Bethke, 2009/. This means, for example, that the sulphate reduction reaction might cease before the electron donor or sulphate have been consumed, if the ΔG is below the required minimum energy. To perform this type of bioenergetic calculations additional data are necessary (e.g. acetate, formate, etc) as well as more and better-quality data on $CH_4$ and $H_2$ in the Forsmark and Laxemar groundwaters /Gimeno et al. 2009/. As the energy availability (ΔG) constitutes a primary control on the distribution and rate of microbial sulphate reduction in nature /Jin and Bethke, 2009/, it would be highly advisable to explore this line of research.

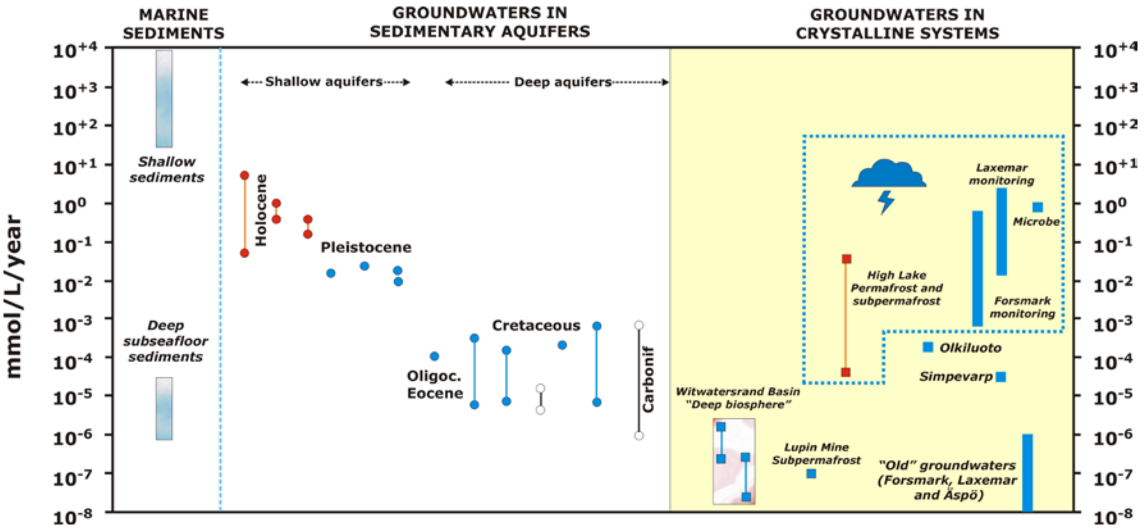

*Figure A3-4.* *Compilation of published sulphate reduction rates (the sources of information are listed in Figure A3-1) including those values calculated in this study (Littorina-enriched groundwaters from Olkiluoto; brackish non marine groundwaters from Simpevarp at 250–500 m depth; and old, deep (> 600 m depth) saline groundwaters from Forsmark, Laxemar and Äspö). Conflictive or unrealistic rates are included in the dotted area.*

## A3.6 Conclusions

Sulphate reduction rates (SRR) in sedimentary and crystalline aquifers have been reviewed and some SRR calculations have been performed for the Laxemar and Forsmark groundwater systems (Figure A3-4).

In deep and long residence time groundwaters from sedimentary aquifers, SRR are extremely low, as low as those observed in deep highly oligotrophic subseafloor marine settings. The main control of such SRR is the low availability of suitable, surface-derived organic matter. In crystalline aquifer systems, where the availability of this type of organic matter is much more limited, SRR must be equal to (or even lower than) those in deep sedimentary aquifers. Thus:

The estimated SRR for groundwaters at repository level with residence times of 3,000–15,000 years are between $10^{-4}$ and $10^{-5}$ mM/year (being the lower value most probable, as the higher one corresponds to Littorina-enriched groundwaters from Olkiluoto; see Section 4.2; Figure A3-4 in this Appendix), inside the range of values for deep sedimentary aquifers.

In deeper (600–1,000 m depth) and longer residence time groundwaters from Laxemar and Forsmark, SRR would be of the order of $10^{-6}$–$10^{-8}$ mM/year, in agreement with the scarce available values in crystalline systems at these depths, and lower than the values for deep sedimentary aquifers (Figure A3-4).

Autotrophic metabolisms, based on deep-sourced $H_2$ and $CH_4$, may also participate in the control of sulphate reduction rates in crystalline systems. These type of microbial activities is limited by the flux of $H_2$ and $CH_4$ and, with the presently available data on these fluxes, SRR would be in the range from $10^{-6}$ to $10^{-8}$ mM/year. These values are compatible with independent calculations based on dissolved sulphide contents in old deep groundwaters from Laxemar and Forsmark and in agreement with the scarce data mined in literature.

The presence of dissolved Fe (II) sources, mainly iron oxhydroxides, exerts a major control on the dissolved sulphide produced by the SRB activity. In absence of these Fe(II) sources, local accumulation of dissolved sulphide occurs in some points of the groundwater systems. At the low SRR typical of pristine conditions in deep sedimentary and crystalline systems, buildup of meaningful concentrations of dissolved sulphide would need long periods of time. In any case, more detailed data on the spatial variability of Fe(II) mineral sources would be necessary to estimate the "buffering" capacity for dissolved sulphide at repository levels.

In this context, the SRR obtained from the dissolved sulphide "peaks" during the monitoring program or in other "experimental" setups in crystalline systems (like the MICROBE experiment; Figure A3-4) are too high to be considered representative of the pristine conditions. SRR as high as those obtained in the monitoring program are only observed in shallow aquifers enriched in organic matter. This fact, as well as other lines of evidence, supports an enhancement of SRB activity by additional, human-induced sources of organic matter.

Sulphate reducing bacteria have been identified in the Forsmark and Laxemar groundwater systems but they are not ubiquitous and their amounts (as most probable numbers, MPN) are not homogeneously distributed with depth. SRB data do not show any clear trend with respect to the amounts of dissolved sulphate and no significant correlations exist with respect to DOC, TOC and hydrogen. Thus, factors conditioning the presence and distribution of SRB, the size of their populations and, therefore, the distribution of SRR in a more detailed level in the sites are still poorly known.

The ultimate limiting factor on the rate of sulphate reduction is not necessarily the amounts of electron donor and sulphate. Energy availability ($\Delta G$) constitutes a primary control on the distribution and rate of microbial sulphate reduction in nature that needs to be evaluated in the studied systems.

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