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Redox chemistry of deep ground-waters in Sweden

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ABSTRACT

This report examines the redox chemistry from groundwater analyses collected during the Swedish study site investigations (1982-1983) for developing site guidelines for disposal of high-level radioactive waste. The redox species determinations reported from the study site investigations were evaluated by chemical equilibrium computations using both the WATEQ3 and the EQ3NR computer programs. The results of the calculations indicate that there were major problems with sample collection, sample preservation, and, perharps in some cases, sample analysis for redox species, and definitive results regarding the behaviour of redox species in these groundwaters is very difficult. Hence, it is not possible to reach conclusions about the redox state of these groundwaters in terms of heterogeneous equilibrium or kinetic processes. Some conclusions, however, can be reached regarding the types of redox species that can be encountered, and possibly their relative importance in determining redox conditions of these groundwaters, and about the usefulness of equilibrium computations. For example, elevated concentrations of dissolved sulfide and dissolved organic carbon were encountered in the groundwaters. These species play at least as important a role, if not a more important role, than the reactions involving iron. At this time it is not known the source of the dissolved sulfide nor the source of the organic carbon, but it is likely that the sulfide is an integral part of the natural conditions that exist at repository depths. The organic carbon could easily be contamination from several possible sources including surface water and drilling fluid. The results of the chemical equilibrium computations do show an excellent agreement between the redox potential measured by the platinum electrode and the dissolved sulfide developed from total sulfide determinations. This may be one of the first examples of a correlation of this type. Furthermore, redox calculations indicate that there are no significant differences between the two computer programs that were used.

1. INTRODUCTION

Redox conditions of deep groundwaters at a potential repository site are an essential part of site characterization because they affect the mobility of radionuclides and the stability of cannister and backfill materials. However, the redox potential of a natural water cannot be easily measured or calculated (Stumm and Morgan, 1981; Drever, 1982; Nordstrom and Munoz, 1985), nor is the concept of a single-valued Eh necessarily meaningful for a natural water because of internal disequilibrium among redox species (Wolery, 1983; Hostettler, 1984; Lindberg and Runnells, 1984; Thorstenson, 1985). The only rational approach is to analytically determine the concentrations of individual redox species such as Fe(II/III), As(III,V), Se(-II,IV,VI), and S(-II,0,IV,VI). Such determinations of redox species are not routine, and commonly require specialized methods of sampling, preservation, and analysis, especially at low concentrations. Examples include hydride generation/atomic absorption for arsenic (Andreae, 1983), and for selenium (Cutter, 1978, 1982, 1983), and ion chromatography and ion-selective electrode potentiometry for dissolved sulfur species (Moses, et al., 1984; Vivit, et al., 1984). When different redox species have been analyzed on the same groundwater sample, the spread of computed Eh values can be as much as 1000 mV and has little or no correlation with an electrode potential measurement (Lindberg and Runnells, 1984). Although redox potentials generally decrease downgradient in a groundwater flow path and therefore they decrease with the evolution of a groundwater, they are usually not amenable to quantitative interpretation (Thorstenson, et al., 1979).

In this report we examine and discuss the redox species determinations from groundwater analyses reported in the SKBF/KBS (Swedish Nuclear Fuel and Waste Management Company) study site investigations. These investigations were carried out to determine the suitability of the crystalline bedrock in

Sweden for high-level radioactive waste disposal (KBS-3 report, 1983). The main purpose of this report is (1) to describe the reliability of the reported analyses for redox specie determinations, (2) to describe what insights chemical equilibrium computations can provide for interpreting the redox chemistry, and (3) to compare redox computations on the same set of data using two different computer programs containing different databases.

2. ANALYTICAL DATA

The analytical data used for our interpretations are found in a series of KBS technical reports containing groundwater analyses (Laurent, 1982, 1983a, b, c) of packered borehole samples taken down to about 600 m depth in Proterozoic granites and gneisses at Fjällveden, Gideå, Finnsjön and Svartboberget, Sweden. The location of these sites is shown on the map in Figure 1.

Unfortunately, none of the samples were filtered, although super-pure hydrochloric acid was added to preserve the dissolved ferrous iron. This procedure can result in abnormally high Fe(II) and Fe(III) concentrations for the following reasons. First, any ferric hydroxide or ferric oxide particles in the sample will not be removed and will be dissolved upon acidification. Second, particles of magnetite, biotite, chlorite and epidote (common minerals in granites and fracture-fillings of granites) will dissolve upon acidification contributing ferrous iron to the sample. Finally, the acid was added to the sample after the sample was transferred to a polyethylene bottle. Waters containing ferrous iron at neutral to basic pH values will oxidize very rapidly and may have partially oxidized before the acid was mixed with the sample. The data will be examined and discussed with these problems in mind.

The classical approach to measuring redox potentials has been to use a platinum electrode with a reference electrode connected to a potentiometer
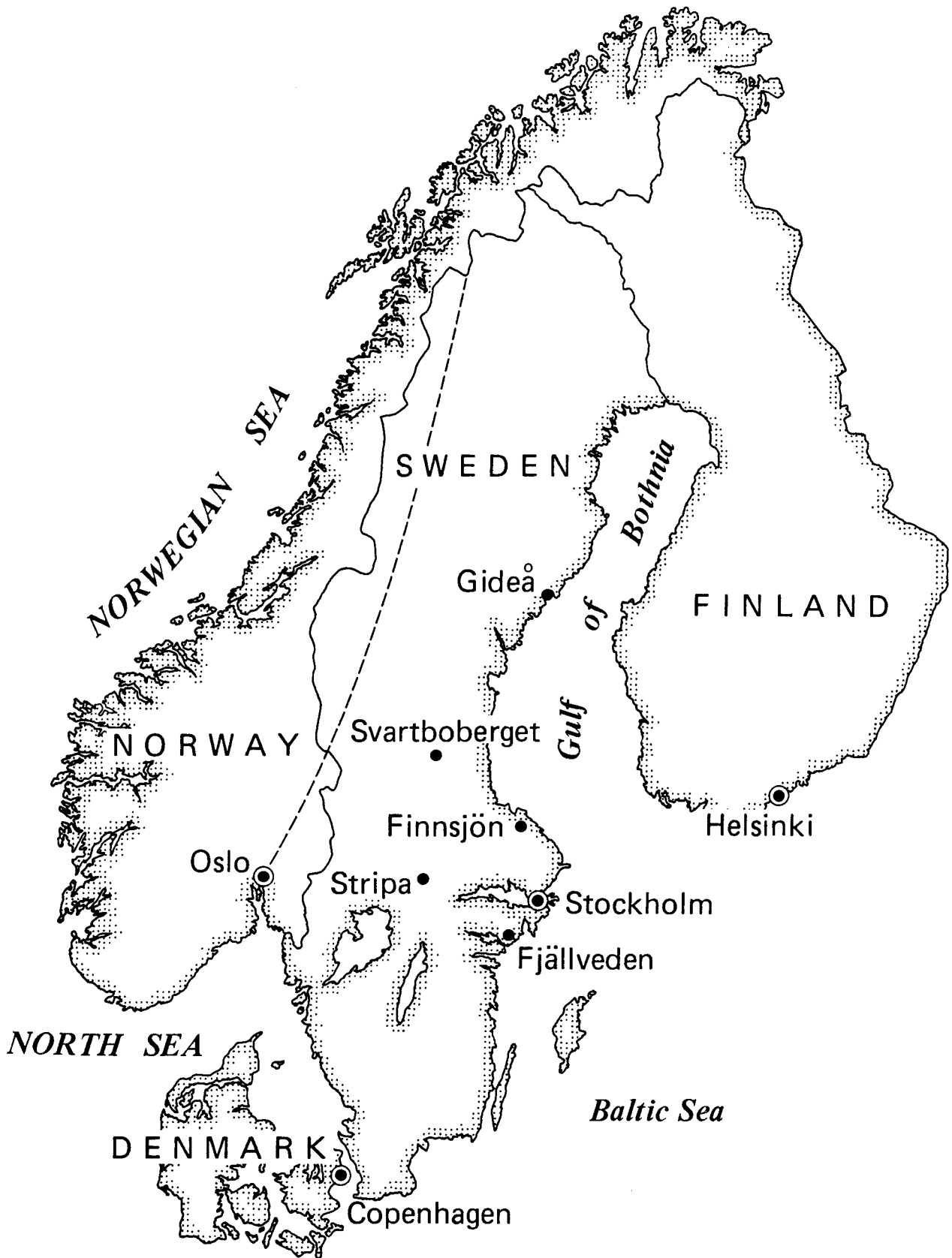
Figure 1. Map of Sweden showing major cities and the main study sites, mentioned for this report; the dashed line shows the western boundary of the preCambrian bedrock.

(Garrels and Christ, 1965; Langmuir, 1971; Bricker, 1982). In the Swedish study site investigations, redox measurements were obtained from both glassy carbon and platinum electrodes implanted in a stainless steel test chamber located in a housing above the borehole. Lab experiments had also used gold and graphite electrodes, but these proved not as reliable (Wikberg, et al., 1983). Groundwater was pumped up through teflon-coated iron piping (except at Finnsjön) from a packed off interval about 2.7 m in length directly to the test chamber preventing exposure to the atmosphere. Unfortunately, high pumping rates and drilling fluid residue (oxygenated groundwater from shallow wells or boreholes) often introduced oxygen and may have caused oxidation of iron during the measurements. Furthermore, at the points where iron pipes were connected, the iron may have made contact with the the water. An experiment carried out by Smellie (1984) at the Kamlange study site, northern Sweden, demonstrated that the pump rates used at all the sites were usually too high by a factor of 2, thereby increasing Eh measurements, O_2 content, uranium concentrations, $^{234}U/^{238}U$ activity ratios and decreasing dissolved sulfide by a considerable amount. When he employed half of the pump rate, the platinum Eh value would decrease from -50 mV to -350 mV. Since the higher pump rates were used at the study sites described in this report, it can be assumed that contamination from oxygenated water commonly occurred.

3. METHODS OF INTERPRETATION

3.1 General computational approach

Chemical equilibrium computations can be made with any one of a large number of available computer programs (Nordstrom and Ball, 1984). However, very few programs can provide redox potential calculations based on individual redox species analyses; and among those that do, there are often considerable discrepancies between the results from different programs (Nordstrom, et al., 1979). The two programs used here, EQ3NR (Wolery, 1983) and WATEQ3 (Ball,

<u>et al.</u>, 1981), are both well suited for redox calculations. Both of these programs were employed to check for consistency in the calculations and as an aid in identifying errors in the thermodynamic databases.

Computations were made with Fe^{2+}/Fe^{3+}, S^{2-}/SO_4^{2-} and $NH_4^+/NO_2^-/NO_3^-$ determinations (when available) and the complete water analysis, to obtain the distribution of species, the activities of free ions and the Nernstian redox potentials from activity ratios of the free ions. Saturation indices of iron-bearing minerals, especially $Fe(OH)_3$, were also computed from the analytical redox data. This approach to the problem has the advantage that no equilibrium is assumed, but rather the degree of equilibrium (or preferably disequilibrium) can be determined.

Saturation indices are defined as the log (IAP/Ksp) where IAP is the ion activity product, and Ksp is the solubility product constant for an equilibrium mineral solubility (see Drever, 1982, or Nordstrom and Munoz, 1985). Ion-pairing reactions are accounted for, and activity coefficient corrections are made according to the Truesdell-Jones formulation (a type of extended Debye-Hückel approach, Truesdell and Jones, 1974) for WATEQ3 calculations and the "B̊" equation of Helgeson (1969) for EQ3NR calculations. Both formulations give very similar results at low ionic strengths.

3.2 Thermodynamic databases

A listing of the important standard electrode potentials, ion-pair reactions, hydrolysis reactions, and solubility product constants used in the computations is given for 25°C in Appendix I along with the reference citations. The listing provides a comparison between the WATEQ3 and the EQ3NR databases that show relatively good agreement except for the $FeHPO_4^+$ ion pair constant. The WATEQ3 value is considered to be in error since it has not been substantiated following its original publication in an abstract. There are also several reactions given in the EQ3NR database that are not in the WATEQ3

database. Some of these values are estimates for which no real values exist in the literature. Others are estimated by extrapolation from high ionic strength measurements. Although these estimates are probably reasonable, there is a larger uncertainty associated with them because they have not been documented or validated.

4. RESULTS AND DISCUSSION

4.1 Platinum electrode measurements

Measurements of Eh using a platinum electrode have been plotted as a function of depth in Figure 2. In most aquifer systems a relative decrease
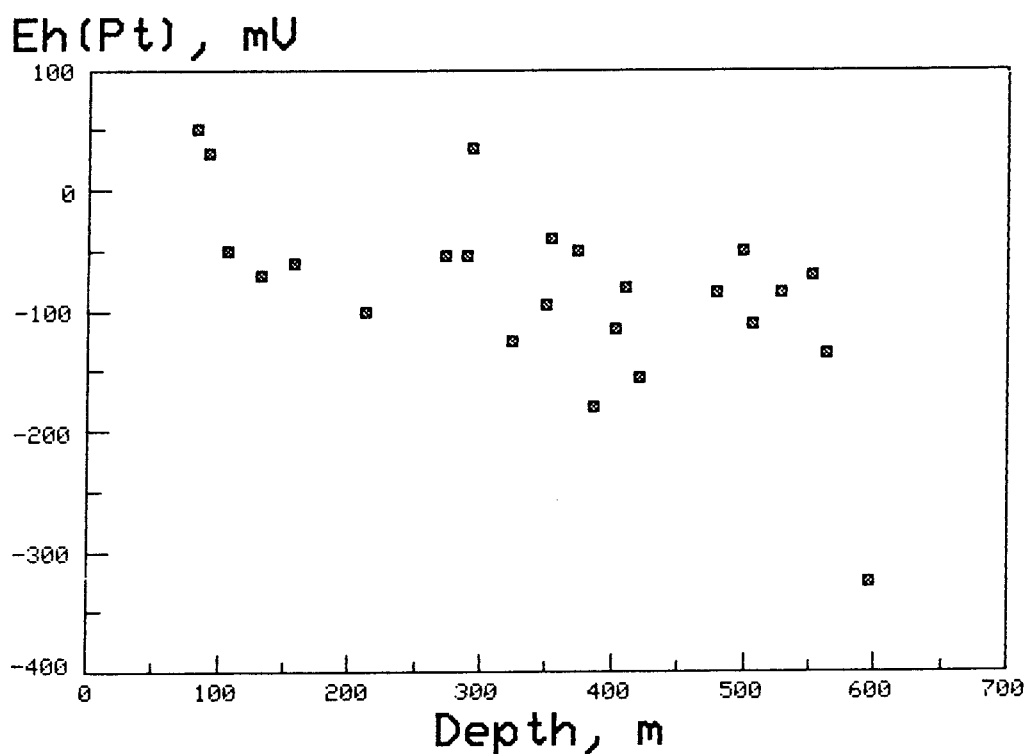

Figure 2. Platinum Eh measurements, Eh(Pt), plotted against depth.

in redox potential can usually be seen with increased evolution of the groundwater (i.e., with time and depth, Champ, et al., 1979). However, the values shown in Figure 2 show little significant change with depth between 100 and 600 m. They are fairly independent of both depth and pH (Figure 3), averaging about -100 mV. From this we conclude either that normal redox
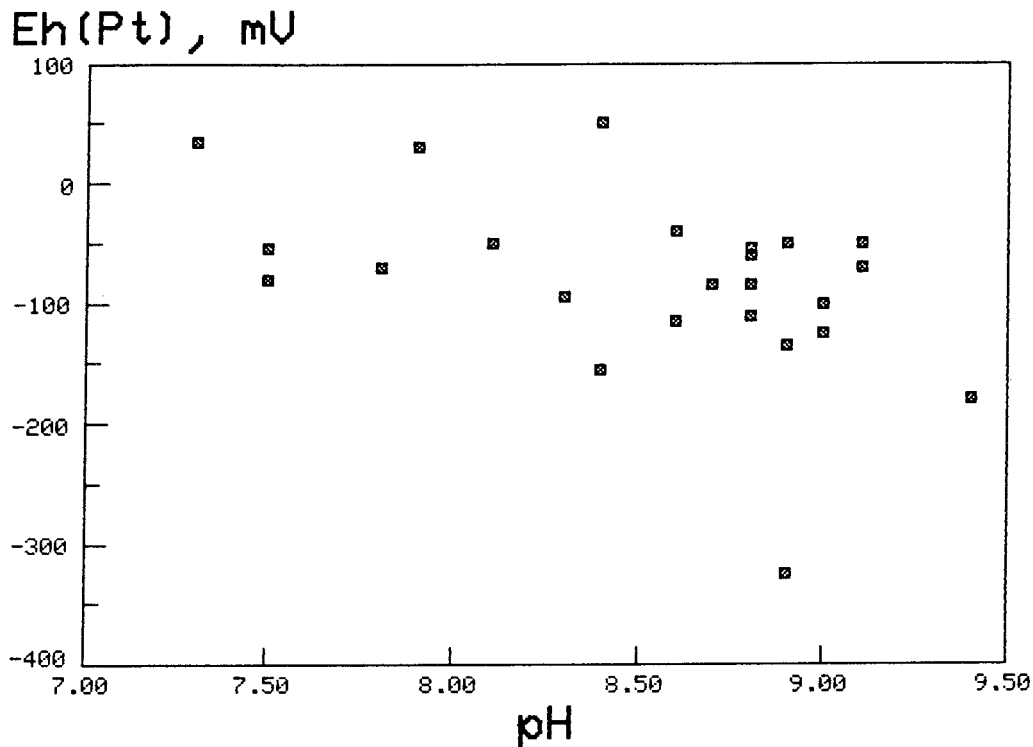
Eh(Pt), mV

Figure 3. Platinum Eh measurements plotted against pH.

processes operating in sedimentary aquifers are not applicable to crystalline rock aquifers or that the measurements are systematically in error. Systematic errors in Eh measurements due to excessive pumping rates has already been mentioned. This fact could account for the constant Eh values; however, as shown in the following discussion, there are strong implications of redox reactions related to deep groundwaters as well. The constant Eh values are **not** just a result of contamination by oxygenated groundwaters.

4.2 Review of all redox couples

The available groundwater analyses list determinations for several redox species, including NO_3^-, NO_2^-, NH_4^+, Fe^{2+}, Fe^{3+}, S^{2-}, and SO_4^{2-}. Both EQ3NR and WATEQ3 provide for independent redox potentials to be calculated for the couples: NO_3^-/NO_2^-, NO_3^-/NH_4^+, Fe^{2+}/Fe^{3+}, $S°/HS^-$ and SO_4^{2-}/HS^-. The results from either program are nearly identical, and for the purposes of plotting, the EQ3NR results were used. A plot for all the above redox couples as a function of pH is shown in Figure 4. Quite clearly there is no indication
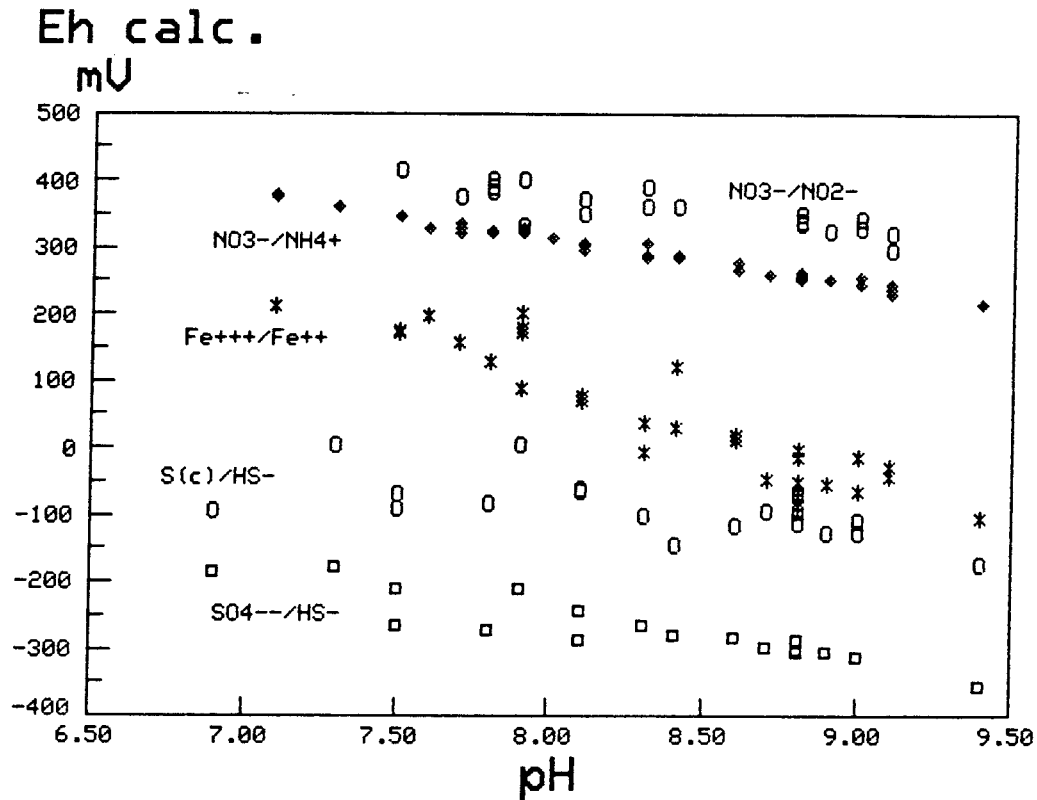
Figure 4.   Five independent redox potentials plotted against pH demonstrating internal redox disequilibria similar to the results of Lindberg and Runnells (1984).

of good agreement between these various couples. Figure 4 looks strikingly similar to the plot published by Lindberg and Runnels (1984) in which they showed that the sequence of redox couples for 30 groundwater analyses reflects differences in the standard electrode potentials and slopes from the Nernst equations, and that each water sample demonstrates a near-complete lack of internal equilibrium among redox couples. This result fully supports Stumm and Morgan's (1981) contention that equilibrium between redox couples in natural waters is not to be expected, and that the best one can hope for is a dominant redox couple to equilibrate with the platinum electrode. In addition, the aquifer contamination problem would promote further disequilibrium. The remainder of this report explores the two most electro-active elements in these groundwaters: iron and sulfur.

4.3 Redox computations involving iron

Although numerous determinations for dissolved Fe(II) and Fe(total) were

obtained, the lack of proper sample collection, i.e., no filtration, resulted

in extraordinarily high iron concentrations in many of the samples. Fe(III)

concentrations should be vanishingly small in deep groundwaters because of

reducing processes. Even in oxidizing groundwaters Fe(III) concentrations

should be negligible because of the insolubility of ferric hydroxide in the

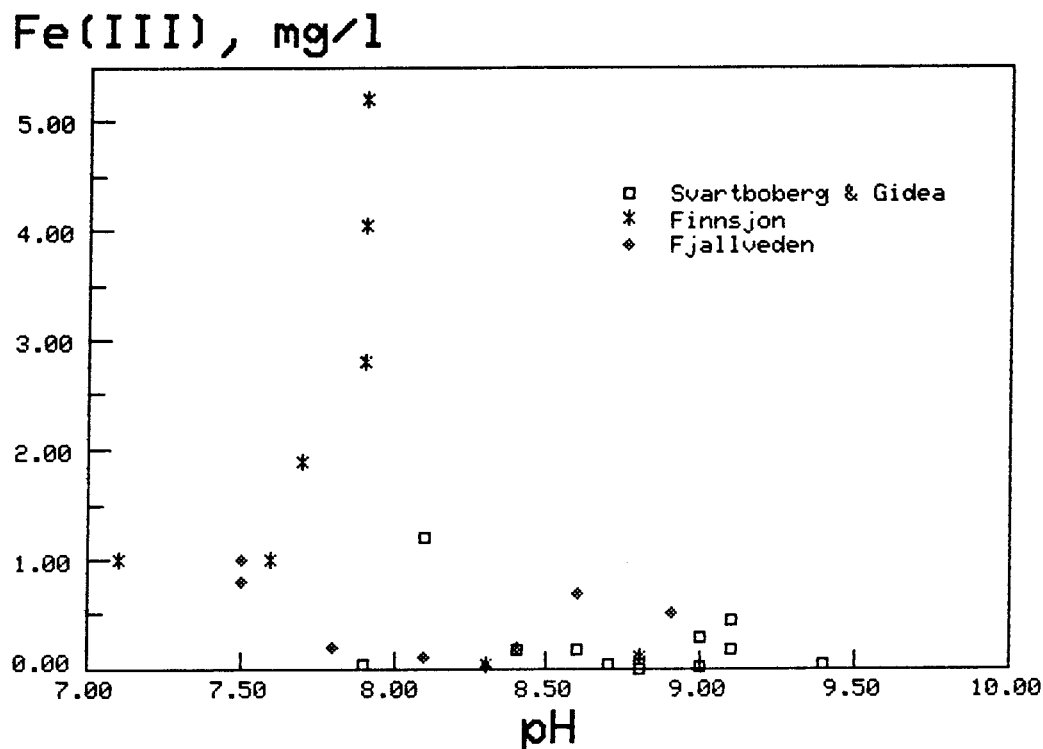neutral to slightly basic range of pH. However, Figure 5 demonstrates that

Figure 5. Iron (III) concentrations in mg/L plotted against pH showing
unrealistically high values for many of the samples.

Fe(III) concentrations were found to range up to 5 mg/L. These high values must

be due to dissolution of ferric oxyhydroxides (fresh precipitates were observed

in the sampling system) upon sample acidification or to oxidation of Fe(II)

prior to analysis. Computations for the saturation index, S.I., of ferric hy-

droxide (Figure 6) likewise show supersaturation by several orders of magnitude,

and cannot be considered to be realistic. Saturation indices for freshly pre-

cipitating ferric hydroxide have never been reported to be supersaturated

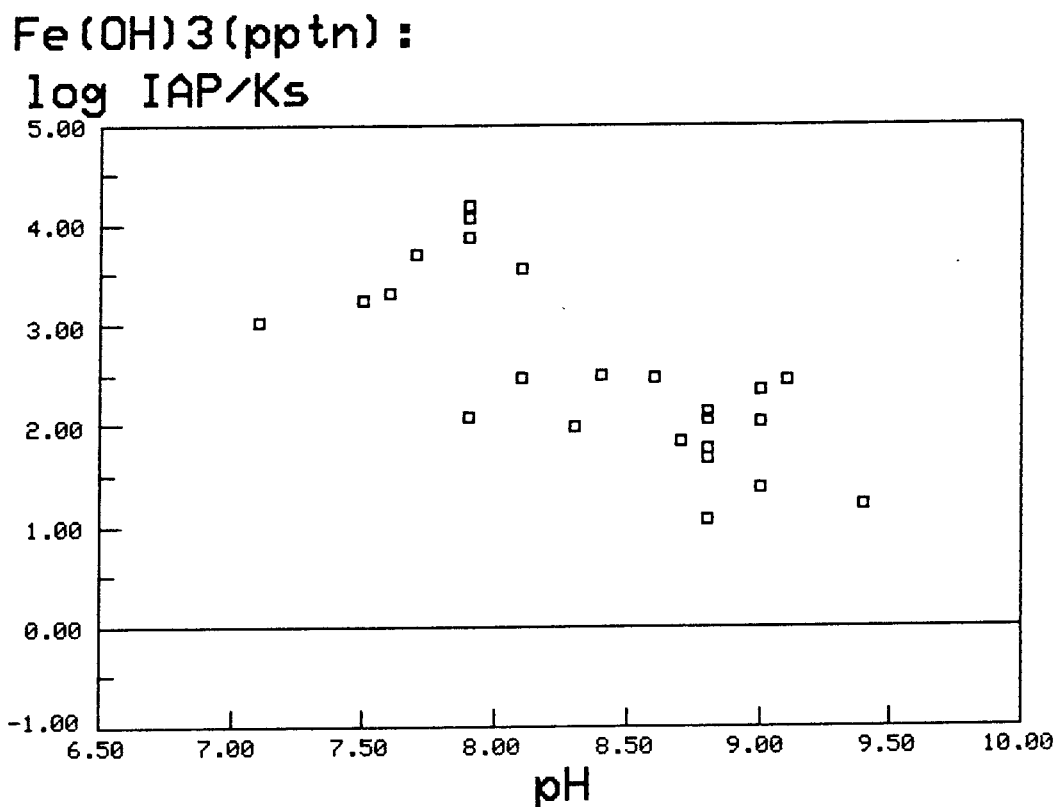relative to the saturation line in Figure 6 (Bohn, 1967; Langmuir and

Figure 6. Saturation indices for freshly precipitated ferric hydroxide plotted against pH.

Whittemore, 1971) for which the solubility product constant is $10^{-37.1}$ at 25°C.

Several of the samples from Finnsjön show the highest Fe(III) concentrations, and this fact may reflect the use of non-coated iron pipes for the sampling lines.

The plot for Eh calculated from Fe(II/III) determinations compared to the platinum Eh measurements (Figure 7) are nearly all biased. The iron redox potentials are greater than the platinum potential with only one exception. Again, this reflects the contamination of the groundwater samples with suspended iron minerals. Samples from the Stripa project results (Nordstrom, et al., 1985) are also shown in Figure 7 for comparison. The Stripa values are based on samples that were filtered through 0.1 micrometer pore size membranes. They are biased in the opposite direction compared to the other study site values. The iron concentrations are generally very low in the Stripa groundwaters (frequently below 0.05 mg/L), and the waters are
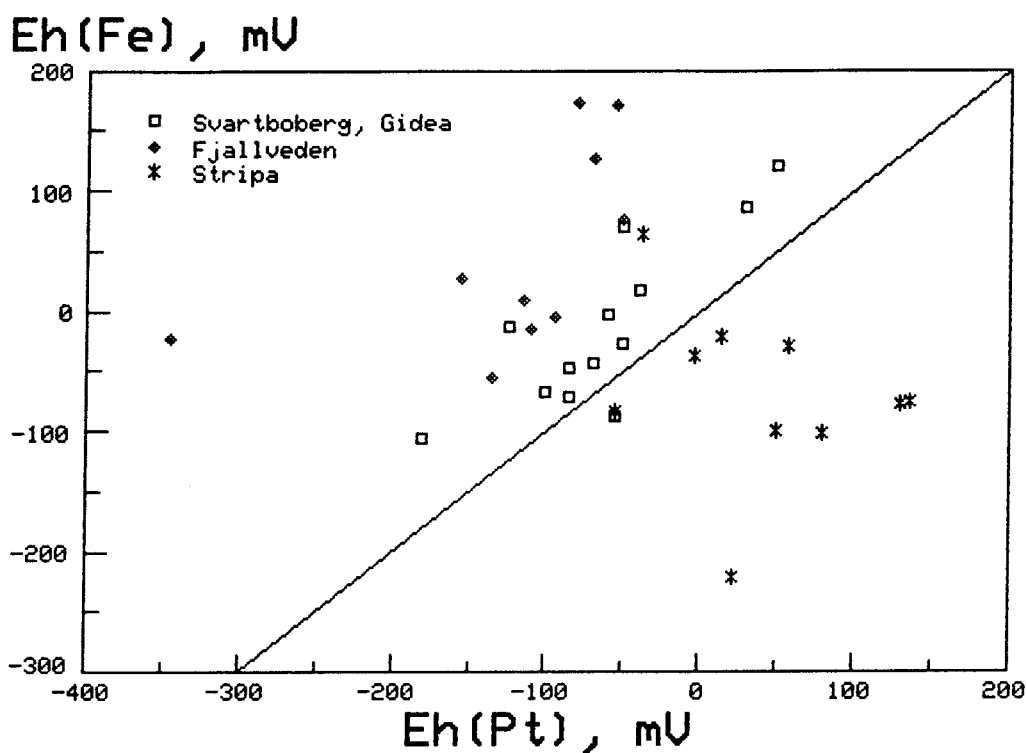
Figure 7. Eh calculated from Fe(II/III) determinations compared to platinum Eh measurements.

poorly poised. The electrode measurements frequently drift very slowly toward lower potentials. Hence, the platinum electrode measurements at Stripa are likely to be higher than the iron redox potentials due to the lack of electroactive species (dissolved sulfide is also quite low, <0.03 mg/L) and there may be oxygen contamination on the electrode surface (Whitfield, 1974). The presence of the mine also may impose some modification of redox processes in the Stripa groundwaters that would not exist in undisturbed bedrock. Nevertheless, the iron concentrations in Stripa groundwaters are more reasonable than those reported for the Swedish study sites.

Although the iron data are not environmentally relevant, they do offer an opportunity to compare redox calculations between EQ3NR and WATEQ3 at high iron concentrations. A systematic difference between EQ3NR and WATEQ3 was observed for S.I. values of ferric hydroxide and iron redox potentials. This difference is partly ascribed to differences in the Ksp for ferric

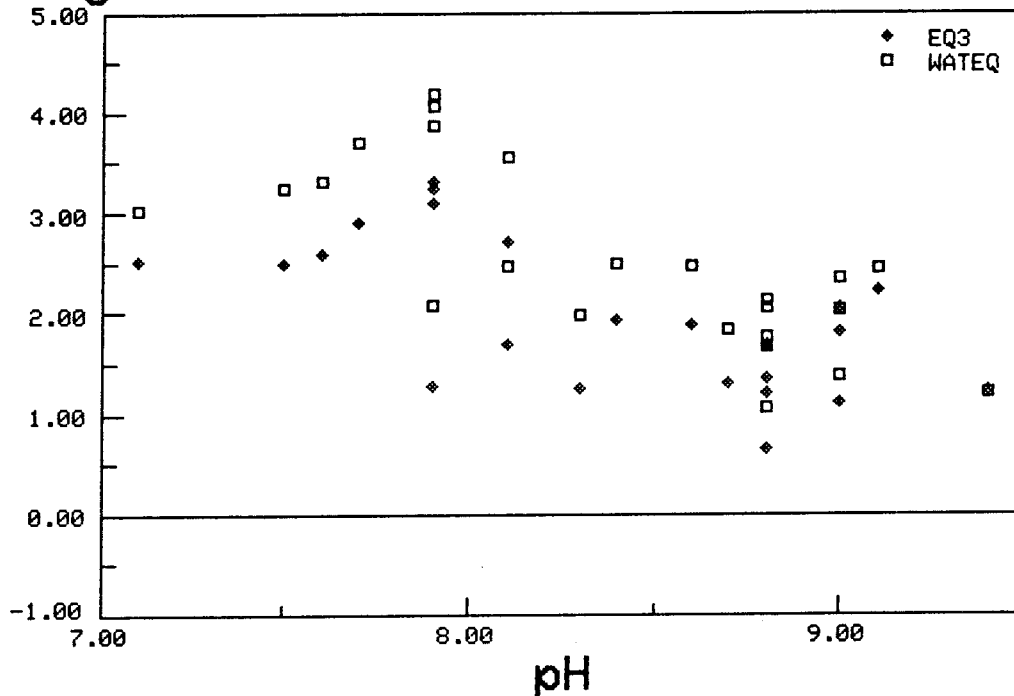hydroxide and partly to differences in stability constants. Figure 8 shows

Figure 8. Saturation indices for freshly precipitated ferric hydroxide computed by both EQ3NR and WATEQ3 as a function of pH.

the S.I. values of ferric hydroxide calculated from both programs as a function of pH. Note that there tends to be slightly better agreement at the highest pH values. This pattern would suggest that there might be additional ion pairs of Fe(III) in the EQ3NR program. A check of the database listing in Appendix I confirms this suggestion. The $FeCO_3^+$ ion pair is present in EQ3NR but not in WATEQ3. Furthermore, slight differences in the hydrolysis and stability constants for $Fe(OH)_3$, $Fe(OH)^+$, $FeCO_3$ aqueous species, the Fe^{2+}/Fe^{3+} redox couple and their temperature dependence account for the observed discrepancies in the ion computations.

The comparison of iron Eh computations by WATEQ3 compared to EQ3NR is shown in Figure 9. A bias is seen that changes from EQ3NR Eh values being higher at the lower potentials to WATEQ3 being higher at the higher potentials. More revealing is a plot of the difference in computed Eh vs. pH (Figure 10).

Eh(Fe(II)/Fe(III)), mV

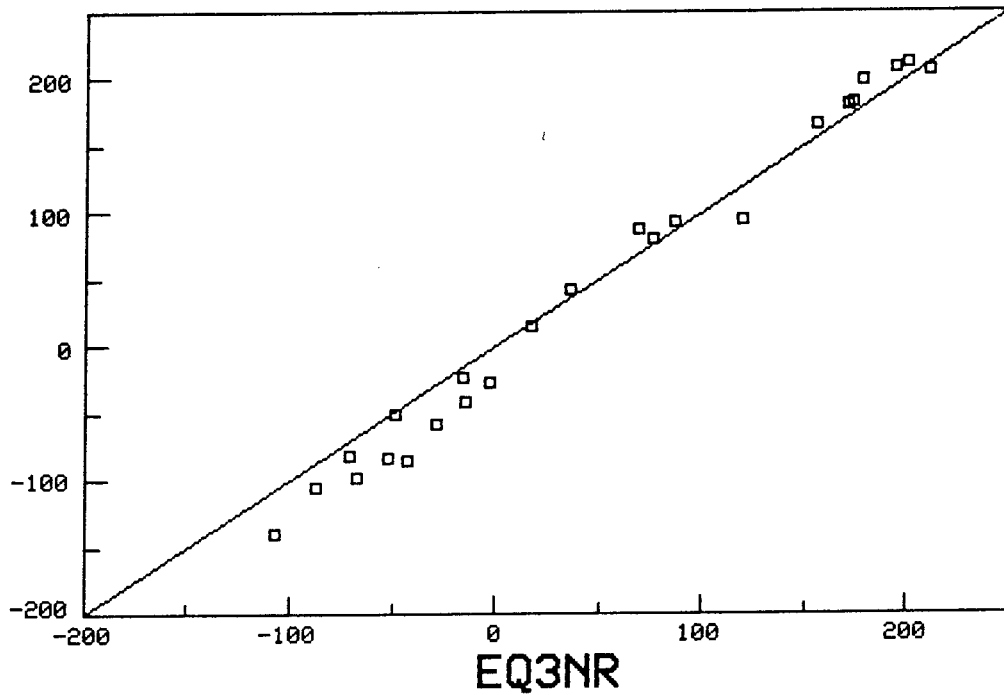## WATEQ3

Figure 9. Eh computed from WATEQ3 compared to Eh computed by EQ3NR, based on Fe(II/III) determinations.
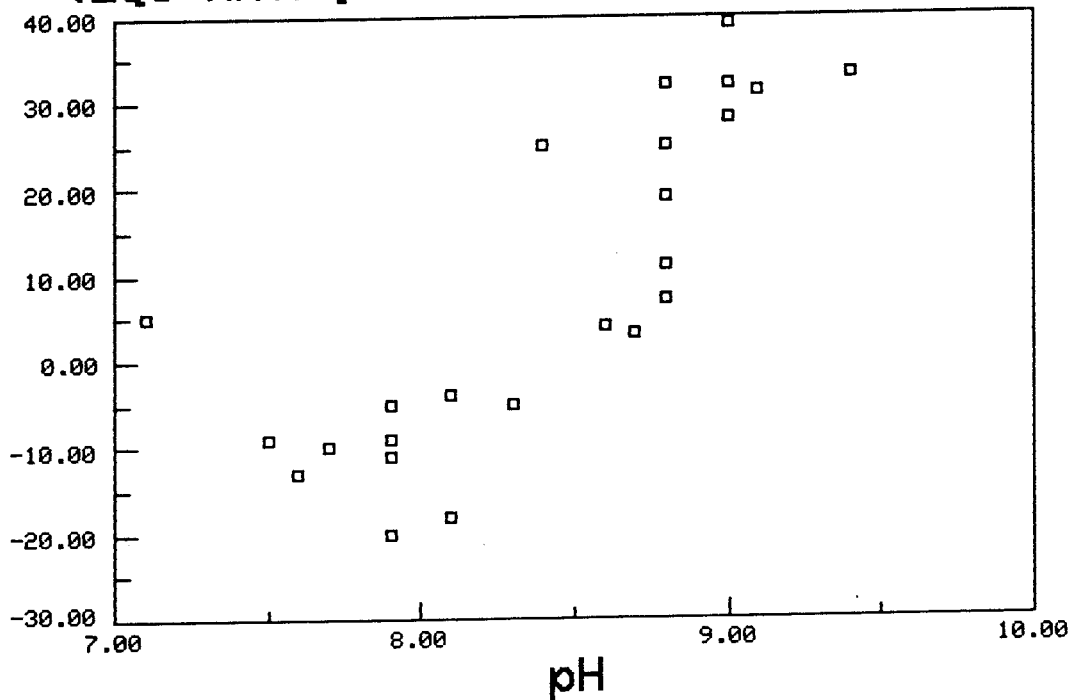
Eh(Fe) diff. (mV)
(EQ3-WATEQ)

Figure 10. Difference in Eh computed by EQ3NR and WATEQ3 as a function of pH.

The discrepancy is greatest at the highest pH values. Since the hydrolysis constants are nearly identical, it had to be caused by some other ion pair stability constant. A plot of Eh difference against the CO_3^{2-} concentrations shown in Figure 11 indicate that the discrepancy is due to differences in
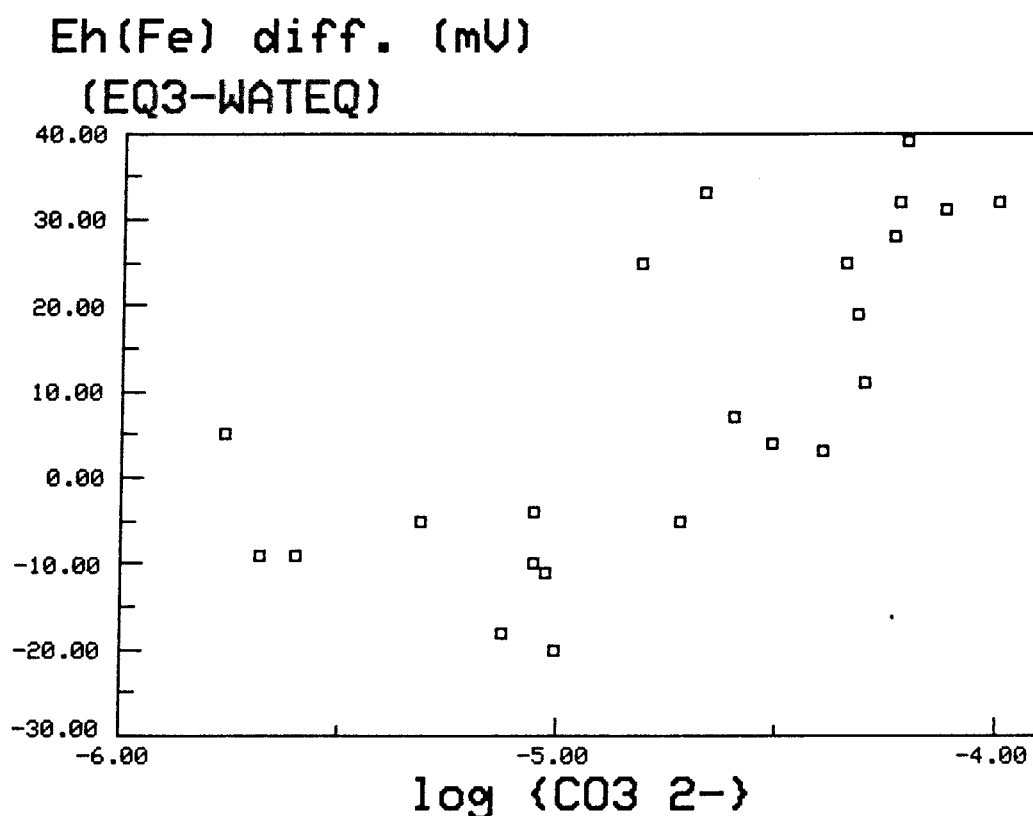

Figure 11. Difference in Eh computed by EQ3NR and WATEQ3 as a function of carbonate activity.

carbonate ion stability constants between the two programs. In fact, the inclusion of the $FeCO_3^\circ$ ion pair in EQ3 and not WATEQ3 caused the Fe^{2+} activity in EQ3 to be noticeably lower and consequently decreased the Fe_{2+}/Fe^{3+} activity ratio so that the Eh was higher for the EQ3 computations.

4.4 Redox computations involving sulfur

Many determinations of dissolved sulfide have been made and two independent methods were used: sulfide ion-selective electrode (ISE) and colorimetry on samples preserved with zinc acetate. ISE measurements were made on site with an electrode placed in the stainless steel test chamber along with the other

electrodes (for pH, conductivity, etc.) and were identified as "pS" values

because the potentials should be responding to changes in activity of $S^{2-}_{(aq)}$.

Sulfur redox couples may include SO_4^{2-}/HS^-, $SO_4^{2-}/S_{(c)}$ and $S_{(c)}/HS^-$.

However, those involving SO_4^{2-} seem least likely to be operative because the

number of electrons transferred in the redox reactions are too large to be

done in a single step. For example, eight electrons are transferred during

the reduction of sulfate to bisulfide and that would be kinetically unfeasible

for a simple one-step mechanism. Furthermore, no one has shown that the

SO_4^{2-}/HS^- or $SO_4^{2-}/S_{(c)}$ couple is operative from field studies of natural

waters. The $S_{(c)}/HS^-$ couple, however, has been shown to be reversible and at

equilibrium with platinum electrode surfaces in sulfidic waters (Berner,

1963; Kryukov, et al., 1962; Skopintsev et al., 1969; Whitfield, 1969; Boulegue

and Michard, 1979). Excellent correlations have been demonstrated between

platinum Eh measurements and the pS values of sulfide electrodes (Berner,

1963; Boulegue, 1978) in sulfide-containing waters and laboratory solutions.

The Swedish study-site groundwater pS values have been plotted in Figure 12

in terms of the $S_{(c)}/HS^-$ redox potential vs. the platinum redox potential.

The correlation is very poor compared to previous studies. This plot indicates

that there is a serious error either in the technique or in the data reduction.

Sulfide concentrations range up to several tenths of mg/L (10^{-4} M) and should

correlate excellently with platinum electrode measurements for these groundwaters.

An examination of the total dissolved sulfide data ($[HS]$ tot) led to much

more encouraging results. Figure 13 shows a plot, similar to Figure 12, in which

total sulfide has been speciated by the EQ3NR program and the Eh calculated for

the $S_{(c)}/HS^-$ redox couple from the activity of HS^- and the Nernst equation:

$$E(S(c)/HS^-) = -65 - 28.3(\log\{HS^-\}+pH)$$

for 12°C. The results show excellent agreement between the platinum Eh and

the bisulfide-sulfur Eh over a 200 mV range. This correlation means that an

Eh(S(c)/HS-)
  mV

Eh(Pt), mV
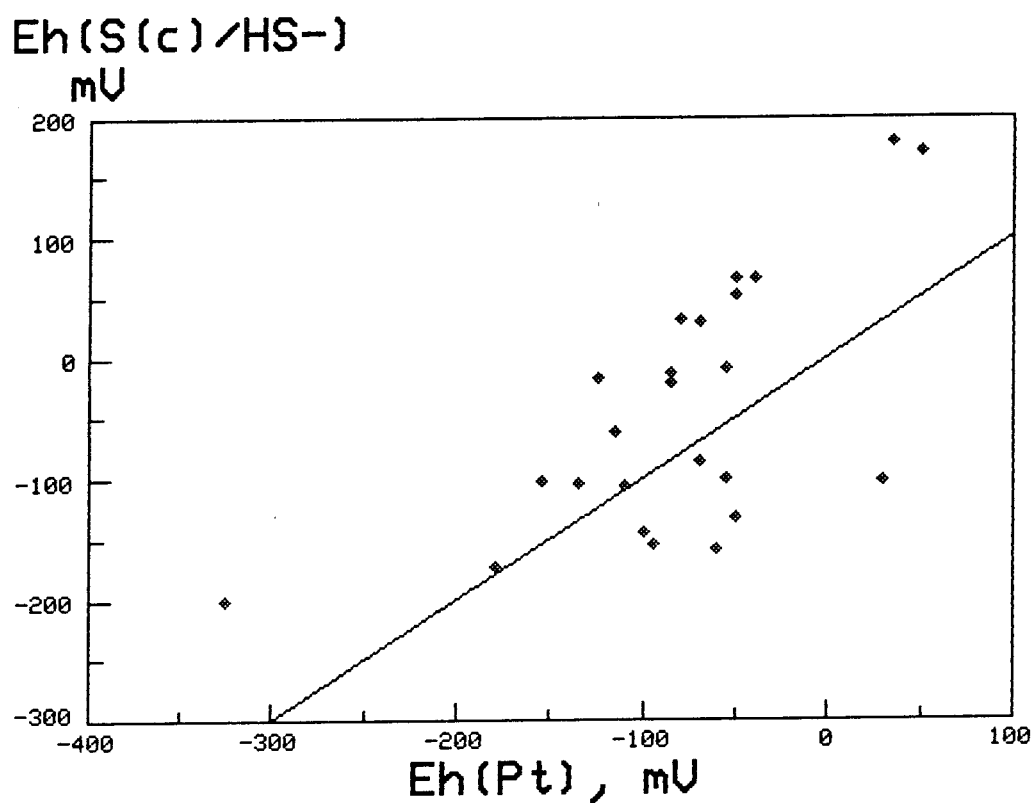
Figure 12.   Eh for the $S_{(c)}$/HS⁻ redox couple computed from pS data compared
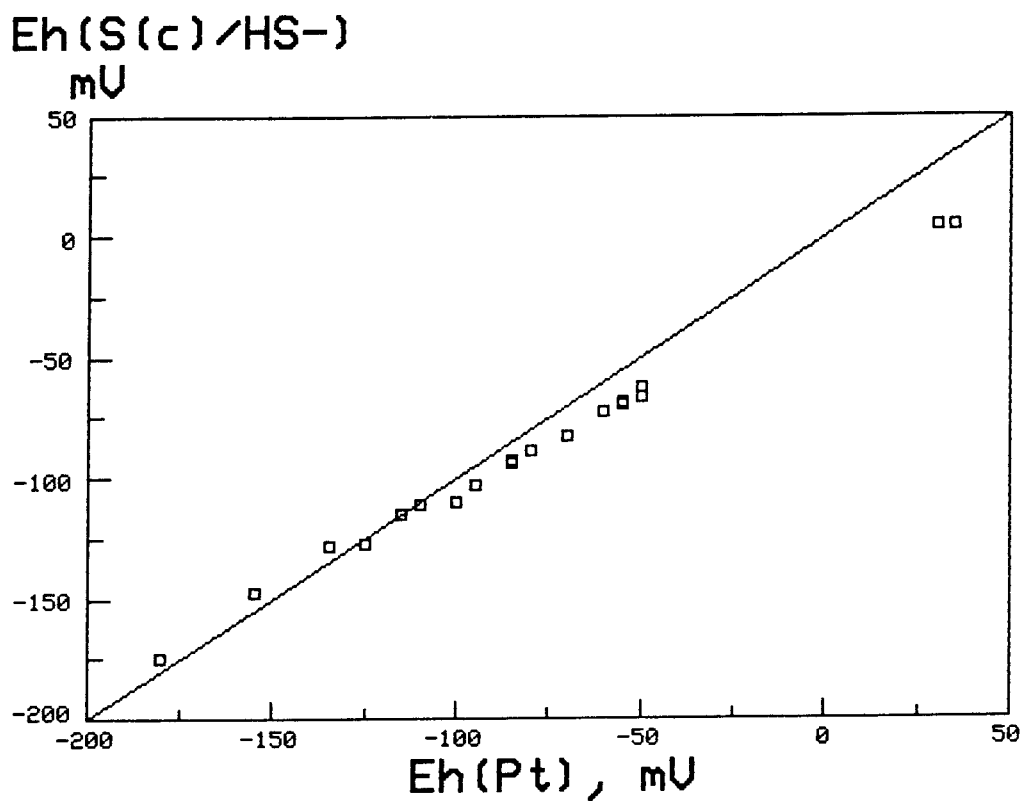to the platinum Eh measurements.

Eh(S(c)/HS-)
  mV

Eh(Pt), mV

Figure 13.   Eh for the $S_{(c)}$/HS⁻ redox couple computed from total dissolved
sulfide compared to the platinum Eh measurements.

equilibrium has been established between the dissolved sulfide and the platinum electrode. In other words, the platinum electrode is sensing changes in sulfide activity.

Furthermore, the presence of polysulfides is clearly indicated by the equilibrium calculations. In Figure 14 the $S_{(c)}/HS^-$ redox potential has been
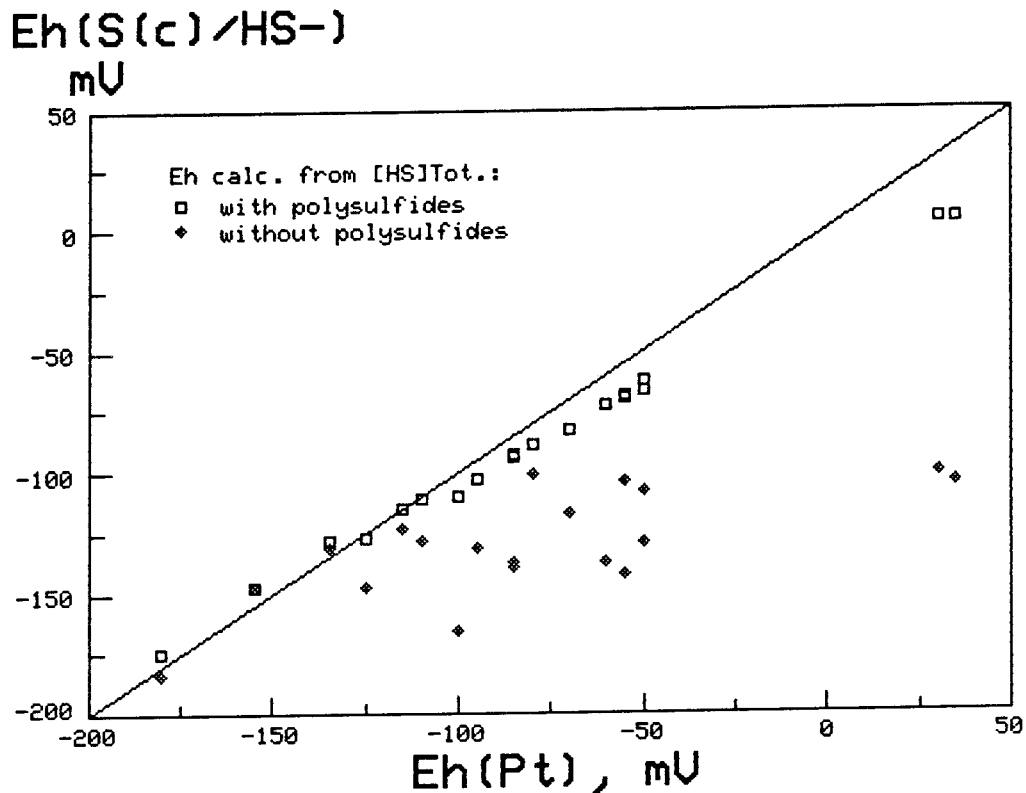

Figure 14. Eh for the $S_{(c)}/HS^-$ redox couple computed from total dissolved sulfide compared to the platinum Eh measurements showing the effect of polysulfide speciation on the computed Eh.

calculated with and without polysulfide speciation. There is no difference at the low Eh values of -130 to -200 mV but as the potential increases there is an increasing deviation from the ideal correlation line that is accounted for by increasing polysulfide formation. This deviation is explained by the fact that polysulfides are of higher oxidation states than monomeric sulfide. This relationship is shown clearly in Figure 15 where the equilibrium distribution of the various forms of sulfide ions is shown as a function of pH while varying total sulfide and Eh. At higher Eh values (-177) and modest
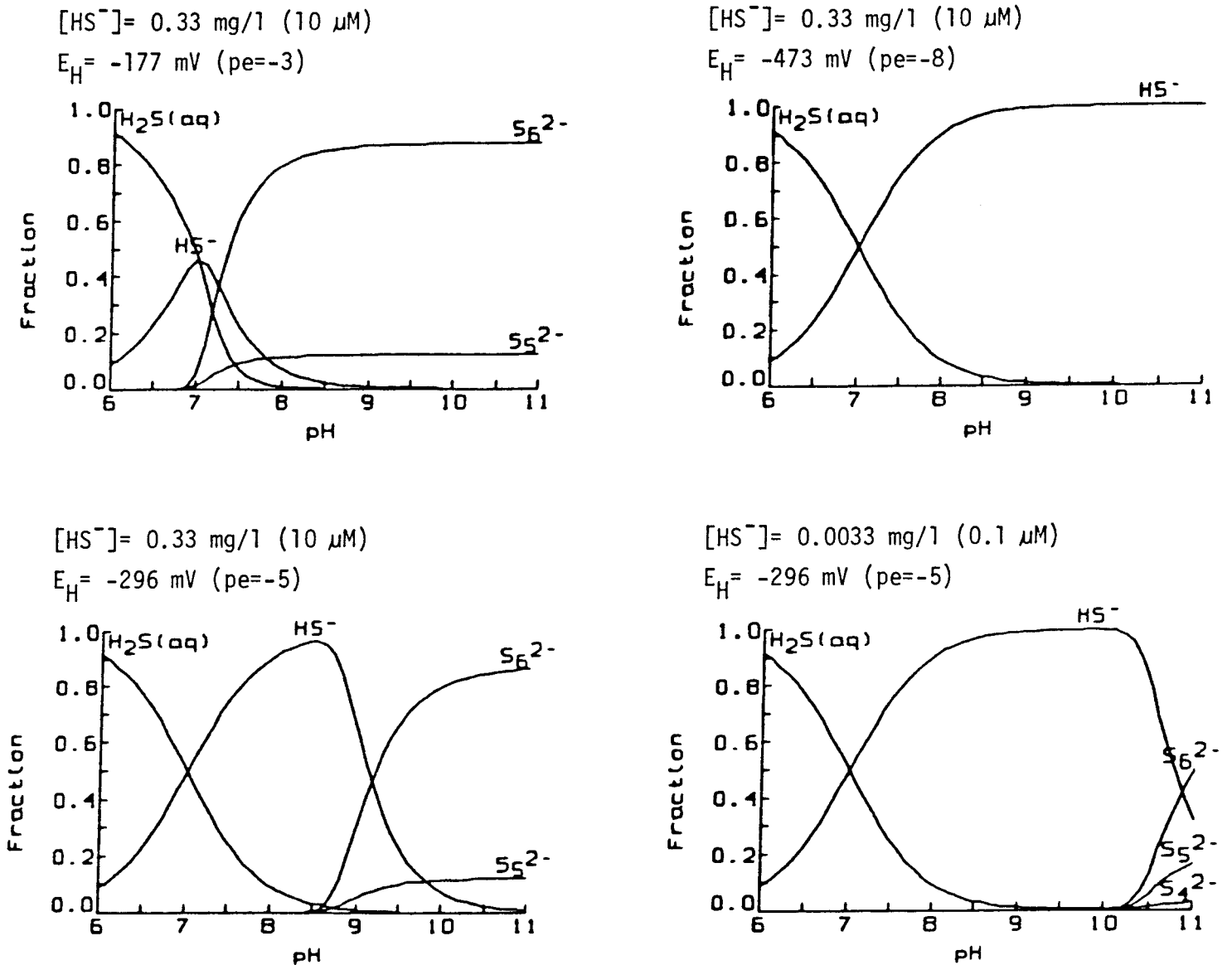
Figure 15. Four examples of the equilibrium distribution of monosulfides and polysulfides in a homogeneous solution as a function of pH. Three different Eh values (-177, -296 and -473 mV) and two different concentrations (10 and 0.1 µM) were used. Figures B and C show the decrease in polysulfide formation with decreased redox potential at constant sulfide concentration (relative to Figure A). Figure D shows the decrease in polysulfide concentration (relative to Figure C) with decrease in sulfide concentration at constant Eh.

sulfide concentrations (10^{-5} M) the S_6^{2-} polysulfide dominates over a large

range of pH. If either the total sulfide or the Eh is significantly decreased,

the polysulfides become negligible.

No adequate correlation can be found between the ion-selective electrode

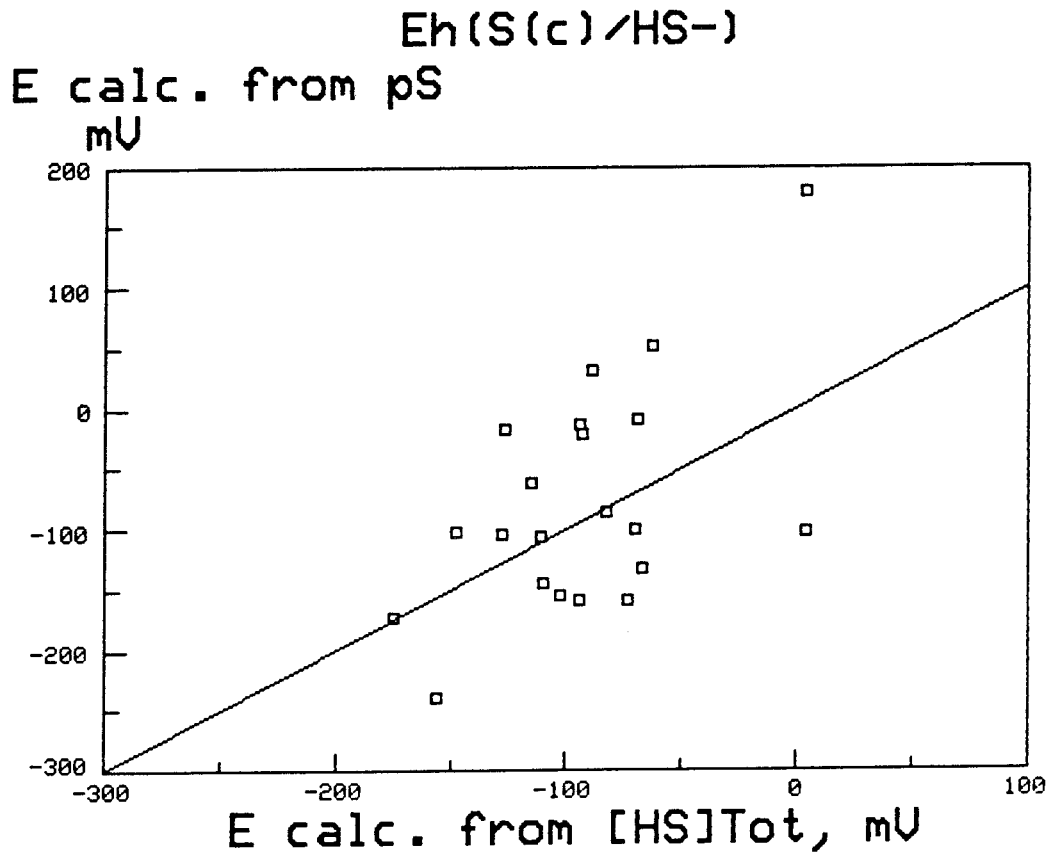measurements and the speciated sulfide data as shown in Figure 16. The

Figure 16. Eh computed from pS data compared to Eh computed from total dis-
solved sulfide data.

conclusion must be that there were inherent difficulties in making the pS

measurements.

The presence of polysulfides and the good correlation for the $S_{(c)}/HS^-$

redox couple might suggest that there was elemental sulfur in the system, at

least at the higher redox potentials. For all of the samples that required

polysulfide speciation to correct the Eh calculation, sulfur supersaturation

is indicated (Figure 17), being greatest at the highest redox potentials.

This trend also shows up as a function of depth. That is, the degree of

sulfur supersaturation decreases with increasing depth as shown in Figure 18.
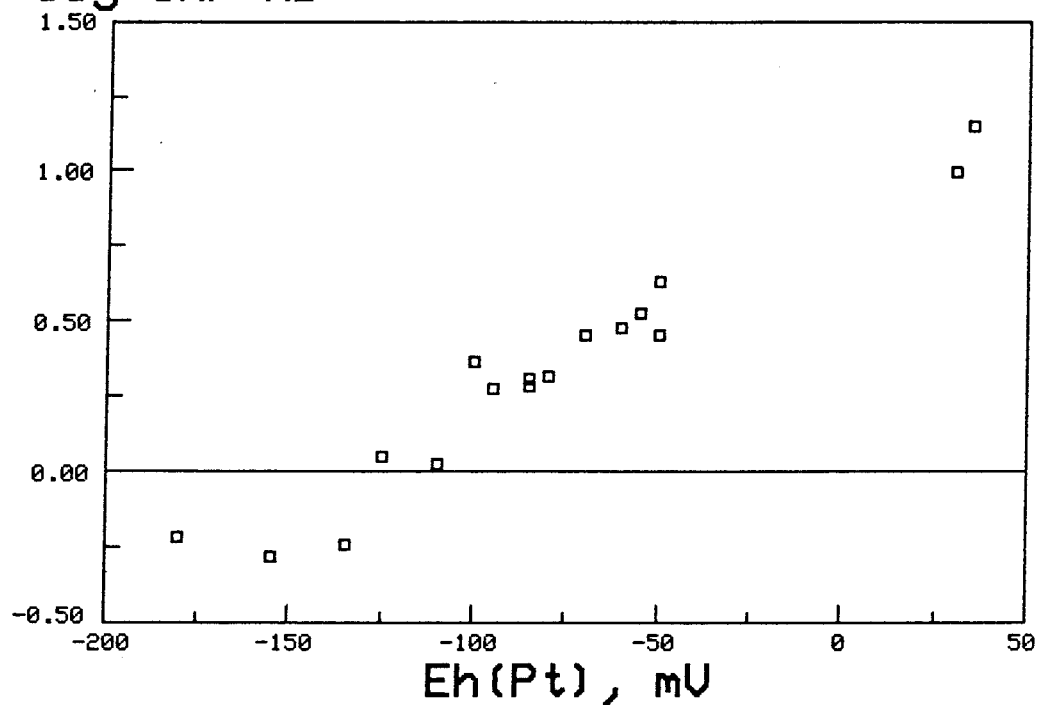
Sulfur(c,rhomb.):
log IAP/Ks

Figure 17. Saturation indices for rhombic sulfur as a function of Eh.
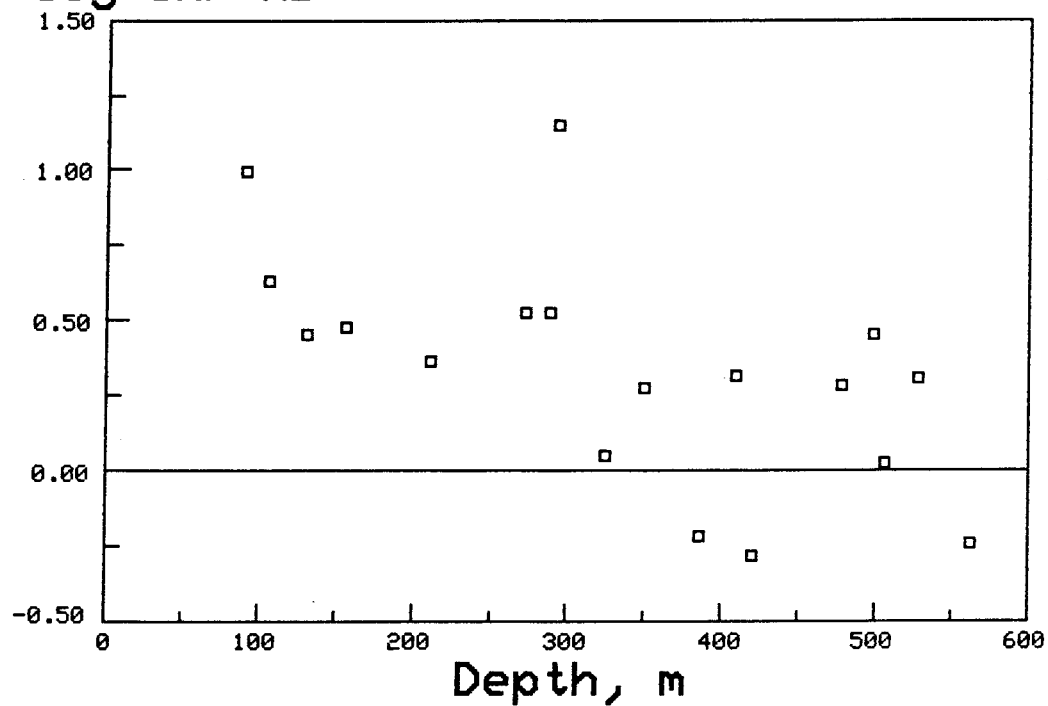
Sulfur(c,rhomb.):
log IAP/Ks

Figure 18. Saturation indices for rhombic sulfur as a function of depth.

This result is encouraging because it reinforces the concept that deeper groundwaters should be older and more reduced than shallow groundwaters. The three values lowest in sulfur saturation (actually undersaturated by nearly a factor of two) are among the deepest groundwater samples collected. However, most of the water samples are known to be contaminated by shallow groundwaters with measurable tritium and to contain freshly precipitating ferric hydroxides which can react with dissolved sulfide to form saturated polysulfide solutions (Berner, 1962, 1963). That is, Fe(II) is oxidized to Fe(III) by oxygen in the contaminating freshwaters and the Fe(III) then oxidizes dissolved sulfide to polysulfides. This process might explain the presence of polysulfides in the groundwater samples and it is consistent with the other contaminated aspects of the redox chemistry. Hence, the true background composition of the ground-waters need not contain elemental sulfur or polysulfides but simply monomeric sulfide, which could be important in governing redox reactions in these grani-tic groundwaters. Furthermore, the sulfide data can be compared to the investigations by Boulegue (1978) and Boulegue and Michard (1979) to indicate that uncontaminated sulfide redox potentials should fall in the range of -100 to -250 mV as measured by platinum electrode, depending on total sulfide concentration and pH. (It should be noted that the sulfide redox potential may not necessarily relate to other redox potentials and that it must be assumed that platinum sulfide is not forming on the electrode surface, which is not a safe assumption when the electrodes are measuring continuously in the waters over a period of several days).

4.5 Redox processes involving carbon

Reliable interpretations of redox reactions involving carbon usually require isotopic compositions and gas analyses in addition to dissolved organic and inorganic carbon determinations. Very few data of this type are

available, but many dissolved organic carbon determinations were made and these deserve some comment.

Occasional increases in chloride concentrations have been observed in groundwaters at Gideå and Fjällveden. For example, GI4 borehole water has contained up to 310 mg/L of chloride and FJ4 up to 220 mg/L of chloride along with a dissolved organic carbon of 50 mg/L. The higher chloride concentrations are often indicative of less contaminated background water composition. If this is true then the organic carbon (DOC) might also be natural rather than introduced contamination. More commonly the DOC is 1-10 mg/L which is still significant for a groundwater and suggests that carbon may play an important role in redox processes. Investigations at Stripa (unpub. data) have found DOC up to 70 mg/L, further supporting this contention. Further research on carbon geochemistry is highly recommended.

5. CONCLUSIONS

In spite of the inherent problems with interpreting groundwater analyses that show contamination from oxygenated waters derived from shallow sources, surface sources or residual drilling fluid, it is possible to draw some conclusions about redox processes:

I. Oxidation of ferrous iron has occurred during sample collection due to the introduction of oxygenated waters at high pump rates. This oxidation has caused the precipitation of ferric hydroxide particles in the pumped water samples. Acidification of samples without filtration has caused high concentrations of Fe(III) to be determined in the analyses. In turn, the ferric hydroxide has probably oxidized some of the dissolved sulfide to form polysulfides and possibly colloidal sulfur. By extrapolation of the data, i.e., by assuming the original waters were unoxidized, the original deep groundwaters probably contained only monomeric sulfide.

II. The method of measuring dissolved sulfide by ion-selective electrode has not proven to be reliable for pumped water samples; however, samples collected by zinc acetate preservation and later lab analysis appear to be very reliable. Some of the difficulties in making electrode measurements have been described by Wikberg, et al. (1983).

III. The excellent agreement between the sulfur-sulfide redox couple and the platinum electrode measurements indicates that dissolved sulfide is the dominant electroactive species in the deep groundwaters of the crystalline bedrock of Sweden. Hence, it is very important to know the source of the dissolved sulfide so that it is possible to estimate the reducing capacity of the water and the possible retardation effect on radionuclide migration. In addition, any reactions involving sulfide may be affected by microbial activity, and this possibility must be investigated (West, et al., 1985).

IV. The redox chemistry of the uncontaminated groundwaters is probably dominated by sulfide and organic carbon and much less so by iron, which is probably all in the Fe^{2+} form. The deep groundwaters are probably reduced enough to exclude polysulfide formation and may not be much different in character than some low salinity sedimentary basin aquifiers dominated by silicate mineralogy.

V. Actual redox potentials for the sulfide system in uncontaminated groundwaters probably range around an Eh of -100 to -250 mV depending on depth, pH and total sulfide content. At Eh values less than -200 mV and modest sulfide concentration, detectable dissolved iron should be in the ferrous state.

VI. The assumption that the iron (II/III) redox couple is the prime redox-determining reaction in these groundwaters (Allard, et al., 1983) does not appear to be validated. Heterogeneous reactions involving iron minerals, although they may be occurring, do not correlate with platinum electrode potentials (especially if the concentration of either $Fe^{2+}_{(aq)}$ or $Fe^{3+}_{(aq)}$ is

below 10^{-6} molar, which is commonly true for uncontaminated groundwaters).
Therefore, chemical modeling of redox conditions in these groundwaters based
on such equilibria as goethite-siderite or goethite-pyrite are likely to be
very misleading. All redox considerations must be prepared to include dis-
solved sulfide and dissolved organic carbon and should be based upon samples
properly collected and preserved for redox specie determinations.

VII. Several investigations have indicated that the ferrous iron-bearing
minerals in crystalline bedrock will have the largest capacity to reduce and
retard leaking radionuclides (Torstenfelt, et al., 1983; Neretnieks and Åslund,
1983a, b; Neretnieks, 1984). Unfortunately, the lab experiments that demon-
strated oxygen reduction by crushed granite have questionable application to
field conditions, and the possibility of microbial reduction during the
experiments cannot be ruled out. Furthermore, the total divalent iron con-
tent of the bedrock is assumed to represent the total reducing capacity of
the disposal environment. Not only does the oxidation rate of iron in min-
erals such as magnetite, slow down considerably due to a coating of precipi-
tated ferric hydroxide or goethite, but we have shown that such reactions do
not dominate the redox chemistry of these groundwaters. Better information
is needed on the actual reduction of oxygen by uncrushed fracture-fill miner-
als in the absence of microbial activity. Then this should be compared with
the same experiments with microbes present. Finally, the source of dissolved
sulfide and carbon needs to be determined so that estimates can be made con-
cerning its capacity to affect the mobility of radionuclides.

Bricker (1982, p. 59) pointed out that: "It should be stressed that the
redox potential, no matter in what units it is expressed, is strictly an
intensity factor. It provides no information about the capacity of a system
for oxidation or reduction. The capacity of a system to donate or accept
electrons is determined by the sum of the equivalent concentrations of all

of the oxidant species above the reference redox potential minus the sum of the equivalent concentrations of all of the reductant species below the reference redox potential (electron condition)." The capacity factor can be calculated for aqueous species, but when considering solid phases a reliable kinetic database is needed before any conclusions can be drawn.

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APPENDIX I.

Reaction	EQ3NR		WATEQ3	
	log K	Ref.	log K	Ref.
$Fe^{2+} + H_2O = FeOH^+ + H^+$	-10.17	1	-9.5	7
$Fe^{2+} + 2\ H_2O = Fe(OH)_2 + 2\ H^+$	-21.42	1	-20.57	21
$Fe^{2+} + 3\ H_2O = Fe(OH)_3^- + 3\ H^+$	-34.23	1	-31.00	7
$Fe^{2+} + F^- = FeF^+$	1.52	2	--	
$Fe^{2+} + Cl^- = FeCl^+$	0.38	3	--	
$Fe^{2+} + 2\ Cl^- = FeCl_2$	0.1	3	--	
$Fe^{2+} + SO_4^{2-} = FeSO_4$	2.2	4	2.25	22
$Fe^{2+} + CO_3^{2-} = FeCO_3$	3.66	3	--	
$Fe^{2+} + HCO_3^- = FeHCO_3^+$	1.3	3	--	
$Fe^{2+} + H_2PO_4^- = FeH_2PO_4^+$	2.7	5	2.7	5
$Fe^{2+} + HPO_4^{2-} = FeHPO_4$	3.6	5	3.6	5
$Fe^{2+} + PO_4^{3-} = FePO_4^-$	7.4	3	--	
$Fe^{2+} + 2\ HS^- = Fe(HS)_2$	--		8.95	23
$Fe^{2+} + 3\ HS^- = Fe(HS)_3^-$	--		10.99	23
$Fe^{2+} = Fe^{3+} + e^-$	-13.01	6	-13.02	24
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	-2.19	7	-2.19	7
$Fe^{3+} + 2\ H_2O = Fe(OH)_2^+ + 2\ H^+$	-5.67	7	-5.67	7
$Fe^{3+} + 3\ H_2O = Fe(OH)_3 + 3\ H^+$	-12.02	1	-13.6	25
$Fe^{3+} + 4\ H_2O = Fe(OH)_4^- + 4\ H^+$	-21.60	1	-21.6	7
$2\ Fe^{3+} + 2\ H_2O = Fe_2(OH)_2^{4+} + 2\ H^+$	-2.95	7	-2.95	7
$3\ Fe^{3+} + 4\ H_2O = Fe_3(OH)_4^{5+} + 4\ H^+$	-6.3	7	-6.3	7
$Fe^{3+} + F^- = FeF^{2+}$	6.03	8	6.2	26
$Fe^{3+} + 2\ F^- = FeF_2^+$	11.58	9	10.8	26
$Fe^{3+} + 3\ F^- = FeF_3$	13.89	10	14.0	26
$Fe^{3+} + Cl^- = FeCl^{2+}$	1.48	11	1.48	22
$Fe^{3+} + 2\ Cl^- = FeCl_2^+$	2.13	11	2.13	22
$Fe^{3+} + 3\ Cl^- = FeCl_3$	1.13	11	1.13	22
$Fe^{3+} + 4\ Cl^- = FeCl_4^-$	-0.79	11	--	
$Fe^{3+} + NO_2^- = FeNO_2^{2+}$	3.15	12	--	

APPENDIX I. (Cont.)

Reaction	EQ3NR		WATEQ3	
	log K	Ref.	log K	Ref.
$Fe^{3+} + NO_3^- = FeNO_3^{2+}$	1.0	13	--	
$Fe^{3+} + HSO_4^- = Fe(HSO_4)^{2+}$	1.71	14	--	
$Fe^{3+} + SO_4^{2-} = FeSO_4^+$	4.11	9	3.92	22
$Fe^{3+} + 2\ SO_4^{2-} = Fe(SO_4)_2^-$	5.39	9	5.42	27
$Fe^{3+} + CO_3^{2-} = FeCO_3^+$	9.70	15	--	
$Fe^{3+} + H_2PO_4^- = FeH_2PO_4^{2+}$	4.17	16	5.43	28
$Fe^{3+} + HPO_4^{2-} = FeHPO_4^+$	9.92	16	5.43	29
$Fe^{3+} + H_4SiO_4 = FeH_3SiO_4^{2+} + H^+$	-0.59	17	--	
$Fe^{3+} + B(OH)_3 + H_2O = Fe(B(OH)_4)^{2+} + H^+$	-1.50	18	--	
$Fe^{3+} + 2\ B(OH)_3 + 2\ H_2O = Fe(B(OH)_4)_2^+ + 2\ H^+$	-3.92	18	--	
$Fe(OH)_3(pptd) + 3\ H^+ = Fe^{3+} + 3\ H_2O$	4.89	19	4.89	19
$FeS(Troilite) + H^+ = Fe^{2+} + HS^-$	-3.76	6	--	
$FeCO_3(Siderite) = Fe^{2+} + CO_3^{2-}$	-10.55	6	-10.55	19
$Fe_3(PO_4)_2 \cdot 8H_2O(Vivianite) =$ $3\ Fe^{2+} + 2\ PO_4^{3-} + 8\ H_2O$	-36.00	5	-36.00	5
$HS^- + H^+ = H_2S(aq)$	7.02	12	6.99	9
$2\ HS^- = S_2^{2-} + 2\ H^+ + 2\ e^-$	-10.81	9	-12.42	30
$3\ HS^- = S_3^{2-} + 3\ H^+ + 3\ e^-$	-8.29	20	-9.06	30
$4\ HS^- = S_4^{2-} + 4\ H^+ + 4\ e^-$	-3.19	20	-3.50	30
$5\ HS^- = S_5^{2-} + 5\ H^+ + 5\ e^-$	-0.97	20	-1.16	30
$6\ HS^- = S_6^{2-} + 6\ H^+ + 6\ e^-$	0.93	20	0.67	30
$HS^- + 4\ H_2O = SO_4^{2-} + 9\ H^+ + 8\ e^-$	-33.66	6	-33.64	9
$S(c,rhombic) + H^+ + 2\ e^- = HS^-$	-2.11	9	-2.11	9
$NH4^+ = NH_3(aq) + H^+$	-9.28	6,9	-9.25	9
$NO_3^- + 10\ H^+ + 8\ e^- = NH_4^+ + 3\ H_2O$	119.07	6	119.08	9
$NO_3^- + 2\ H^+ + 2\ e^- = NO_2^- + H_2O$	27.69	6,9	28.57	9

APPENDIX I. (Cont.)

References:

1 -- Tremaine and Leblanc (1980)

2 -- Bond and Hefter (1972)

3 -- estimated

4 -- Izatt et al. (1969)

5 -- Nriagu (1972a)

6 -- SUPCRT[1]

7 -- Baes and Mesmer (1976)

8 -- Ahrland (1967)

9 -- NBS[2]

10 -- Aziz and Lyle (1969)

11 -- Helgeson (1969)

12 -- Martell and Smith (1982)

13 -- Sykes (1952)

14 -- Dousma et al. (1979)

15 -- Turner et al. (1981)

16 -- Galal-Gorchev and Stumm (1963)

17 -- Olson and O'Melia (1973)

18 -- Elrod and Kester (1980)

19 -- Langmuir (1969)

20 -- Boulegue and Michard (1978)

21 -- Sweeton and Baes (1970)

22 -- Smith and Martell (1976)

23 -- Naumov et al. (1974)

24 -- Nordstrom et al. (1984)

25 -- Ball et al. (1979)

26 -- Nordstrom and Jenne (1977)

27 -- Nordstrom (1977)

28 -- Nriagu (1972b)

29 -- Nriagu (1971)

30 -- Cloke (1963a, 1963b)

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1. SUPCRT refers to the SUPCRT computer code and data base, and the following
   references: Helgeson and Kirkham (1974a, 1974b, 1976),
   Helgeson et al. (1978, 1981), and subsequent update notices from Helgeson.
2. NBS refers to Wagman et al. (1968, 1969, 1971, and 1982).

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University of Linköping, Sweden
March 26, 1986