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Evolution of models for conversion of smectite to non-expandable minerals

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EVOLUTION OF MODELS FOR CONVERSION OF SMECTITE TO NON-EXPANDABLE MINERALS

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ABSTRACT (English)

Hydrothermal alteration of smectite has long been regarded as conversion to illite and chlorite as concluded from investigations of Gulf sediments. As manifested by statements given earlier at various international scientific meetings and in the literature, smectite-to-illite conversion (S→I) has been assumed to be a solid-state reaction with layer-by-layer alteration via mixed layer I/S to illite. In the last 10 years this opinion has successively changed and in recent years the concept of dissolution of smectite and accessory minerals and precipitation of illite and possibly I/S has been favored by many investigators. The present report reports laboratory and field investigations on bentonite and also calculations based on geochemical codes, which all support the dissolution/precipitation process. Applying Pytte's model for calculating the rate of conversion to illite, one finds good agreement with a number of experiments and field data, and this model is therefore recommended for practical use.

ABSTRACT (Swedish)

Hydrotermal omvandling av smektit har länge betraktats som transformering till illit och klorit enligt slutsatser från undersökningar av Gulfsedimenten. Som framgår av litteraturen och av slutsatserna från internationella vetenskapliga konferenser framgår att omvandling från smektit till illit (S→I) tidigare betraktats som substitutioner i fast tillstånd ledande till skiktvis ändring via blandskiktmineral av typen I/S. De senaste 10 åren har denna uppfattning successivt ändrats och numera förordas ett koncept som innebär lösning av smektit och accessoriska mineral och utfällning av illit och eventuellt I/S i åtskilliga undersökningar. I denna rapport redovisas laboratorie- och fältförsök på bentonit samt geokemiska beräkningar som alla stöder den moderna uppfattningen. Om Pyttes modell används för beräkning av kinetiken hos processen finner man god överensstämmelse med åtskilliga experimentella resultat och fältdata, och den modellen rekommenderas för praktiskt bruk.

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SUMMARY

The issue of conversion of smectite to illite under hydrothermal conditions has been investigated for decades because of its importance in conjunction with oil prospection. Much of the work has therefore been related to investigations of deeply located sediments, primarily those of the Mexican Gulf, from which the basic conversion model of solid-state reaction of smectite to illite via I/S mixed-layer minerals stems. In the 10 year period from early 1980 to the beginning of the present decade, access to much more refined analyses using XRD and electron microscopy has led to different views, i.e. that conversion to illite and chlorite takes place through dissolution and precipitation and recently it has appeared that neoformation of illite as a separate phase and as I in I/S is very important.

The present report forms a compilation of results and ideas, describing the evolution of the models for conversion of smectite to illite. In light of this it is clear that all the R&D work peformed in SKB projects in this field fits in nicely.

The most important practically useful outcome of the work is that a mathematical model (Pytte) is now at hand for quantitative determination of the rate of conversion. Its applicability has been documented by comparing predicted and recorded conversion rates in a number of hydrothermal experiments, including the comprehensive series performed in the Stripa Project, and also by analyzing several bentonite beds serving as natural analogs.

A special process that is associated with heating of bentonite is cementation by precipitation of dissolved minerals. Both experiments, natural clay beds exposed to heat, and geochemical modelling suggest that cementation effects under *isothermal* conditions are not very significant at moderate temperatures.

SMECTITE LONGEVITY

1 INTRODUCTION

1.1 GENERAL

The basis of modern ideas concerning the stability and alteration of smectite under hydrothermal condition is the general theory of thermodynamics of hydrothermal systems at elevated temperatures (1,2). In recent time a number of small-scale experiments and field investigations dealing with smectite longevity have been completed, contributing substantially to the understanding of this matter. The present report is intended to be an updating of earlier and present smectite conversion models with the aim of pointing out to what extent they have been adjusted and what the evolution has been like. A primary goal is to find a practically useful conversion model that can be used for predicting physical long-term performance of smectitic barriers in HLW repositories. Such a model is presented in the report and it is validated by applying it to a number of practical cases.

1.2 BASICS

1.2.1 Mineralogy

We will take as a starting point the simple dioctahedral 2:1 phyllosilicate pyrophyllite $Al_2Si_4O_{10}(OH)_2$ since its structure is similar to that of the most common smectite species montmorillonite, and since the hydration and dehydration mechanisms of this mineral can be explained by considering the difference in lattice constitution of montmorillonite and pyrophyllite. The crystal structure of the latter, which is shown in Figure 1-1, has no net lattice charge and no water molecules between the layers: it is hydrophobic. If one of the silicons in each group of four tetrahedrons are replaced by aluminum - leaving the octahedral layer intact - we obtain the dioctahedral muscovite structure provided that the resulting "high charge" is balanced by interlayer potassium fitting into perforations in the surface O-sheets, which yields the formula $K_2Si_6Al_6O_{20}(OH)_4$, (Figure 1-2). If this structure is in turn altered so that part of the potassium is replaced by hydronium ions (H_3O) we obtain dioctahedral hydromica, which is commonly termed illite. It has long been known that this mineral does not have any definite chemical composition but obeys Maegdefrau's general rule:

$$M_y^I Si_{(8-y)} Al_y O_{20} (OH)_4 \left(M^{III}, \tfrac{3}{2} M^{II}\right)_4 \qquad (1)$$

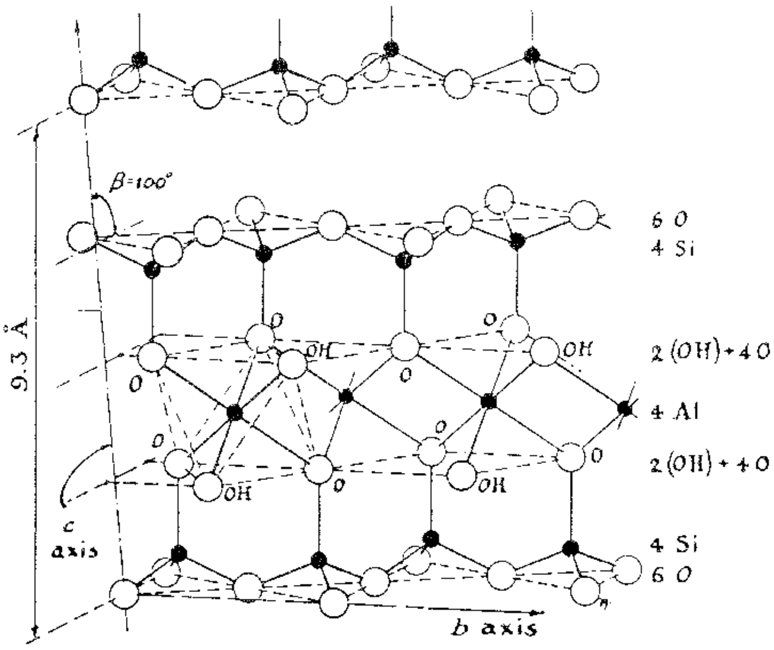


Figure 1-1 Lattice characteristics of the monoclinic mineral pyrophyllite (After Berry & Mason)

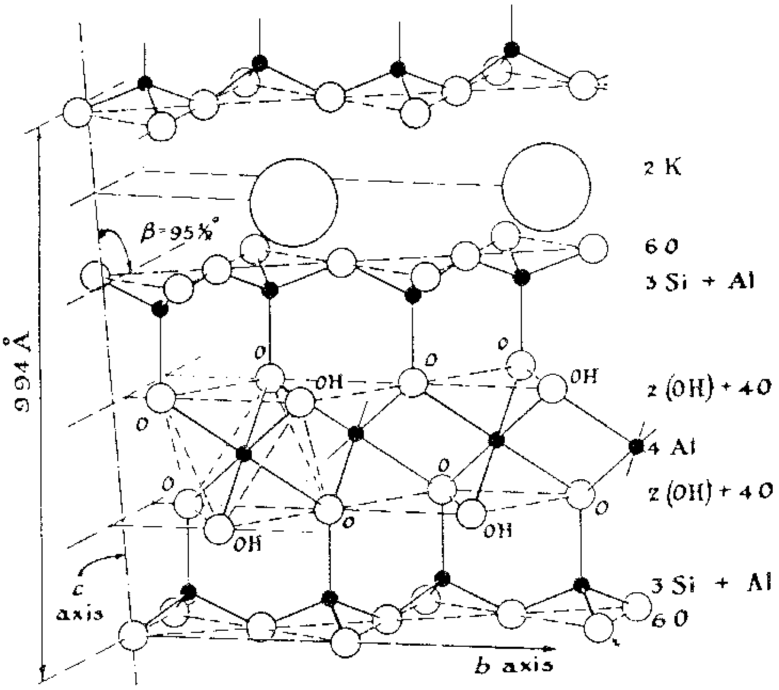


Figure 1-2 Lattice characteristics of the monoclinic mineral muscovite (After Berry & Mason)

The formula can be used for describing rock-forming micas, hydrous micas, and smectites, M^{I} representing monovalent cations, M^{II} magnesium and divalent iron, and M^{III} aluminum or trivalent iron. For y=0 the formula represents the smectite group, while y=2 is valid for the rock-forming micas. The hydrous micas have an y-value between 1 and 2, which well illustrates that this mineral group represents an intermediate, not well defined stage between micas and smectites. Since they represent a whole range of substances with the smectites and micas being end reaction products rather than a particular mineral, the term hydrous mica or hydromica is more relevant than "illite".

The hydromica layers - lamellae or flakes - are kept together by electrostatic forces between the potassium ions and the highly charged crystal lattice of neighboring lamellae. Hydrogen bonds and van der Waals forces do also combine to hold the lamellae together so strongly that very high shear stresses are required to break down stacks thinner than 30 Å, i.e. consisting of 3 lamellae (3). Hydromica stacks in natural clays commonly consist of 3 or 5 lamellae, which is in fact also the case for smectites with Na or Li as exchangeable cation.

1.2.2 The smectites

If we apply Maegdefrau's formula and let y be low and also take silicon, aluminum and magnesium to be lattice cations, we arrive at chemical compositions of common smectites excluding adsorbed balancing cations (4):

Montmorillonite $(OH)_4Si_8(Al_{3.34}Mg_{0.66})O_{20}$	(Dioct)
Beidellite $(OH)_4(Si6_6Al_2)Al_{4.44}O_{20}$	(Dioct)
Nontronite $(OH)_4(Si_{7.34}Al_{0.66})Fe_4\,O_{20}$	(Dioct)
- -	- - - - -
Hectorite $(OH)_4Si_8(Mg_{5.34}Li_{0.66})O_{20}$	(Trioct)
Saponite $(OH)_4(Si_{7.34}Al_{0.66})Mg_6O_{20}$	(Trioct)

Figure 1-3 illustrates three of the dioctahedral species.

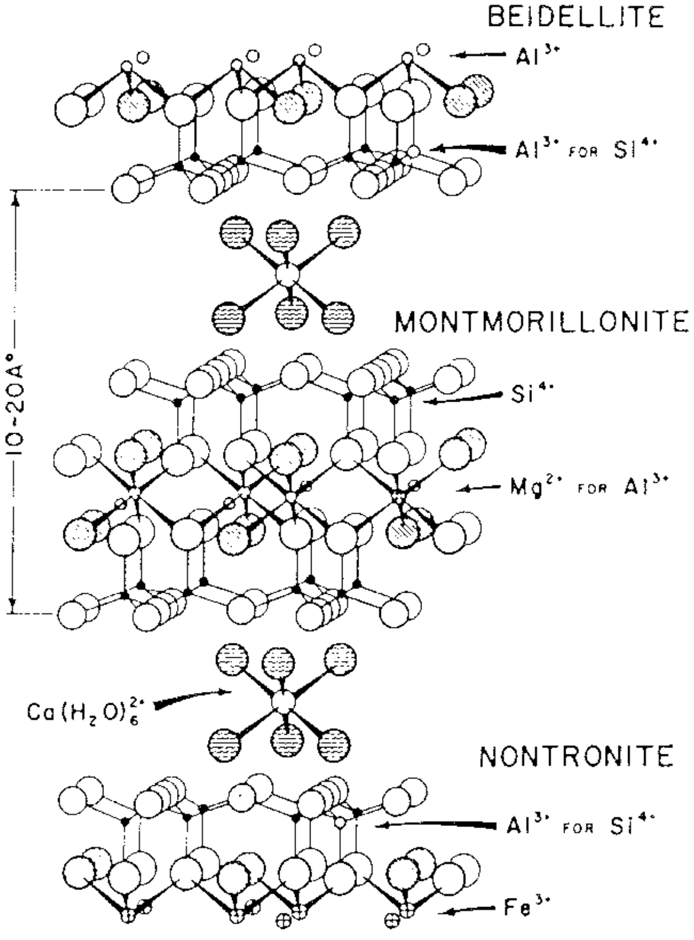


Figure 1-3 The crystal structure of the monoclinic smectite, represented by montmorillonite, beidellite and nontronite (modified from Brindley & MacEwan)

We will be dealing mostly with montmorillonite for which there are two possible lattice configurations as illustrated in Figures 1-4 and 1-5.

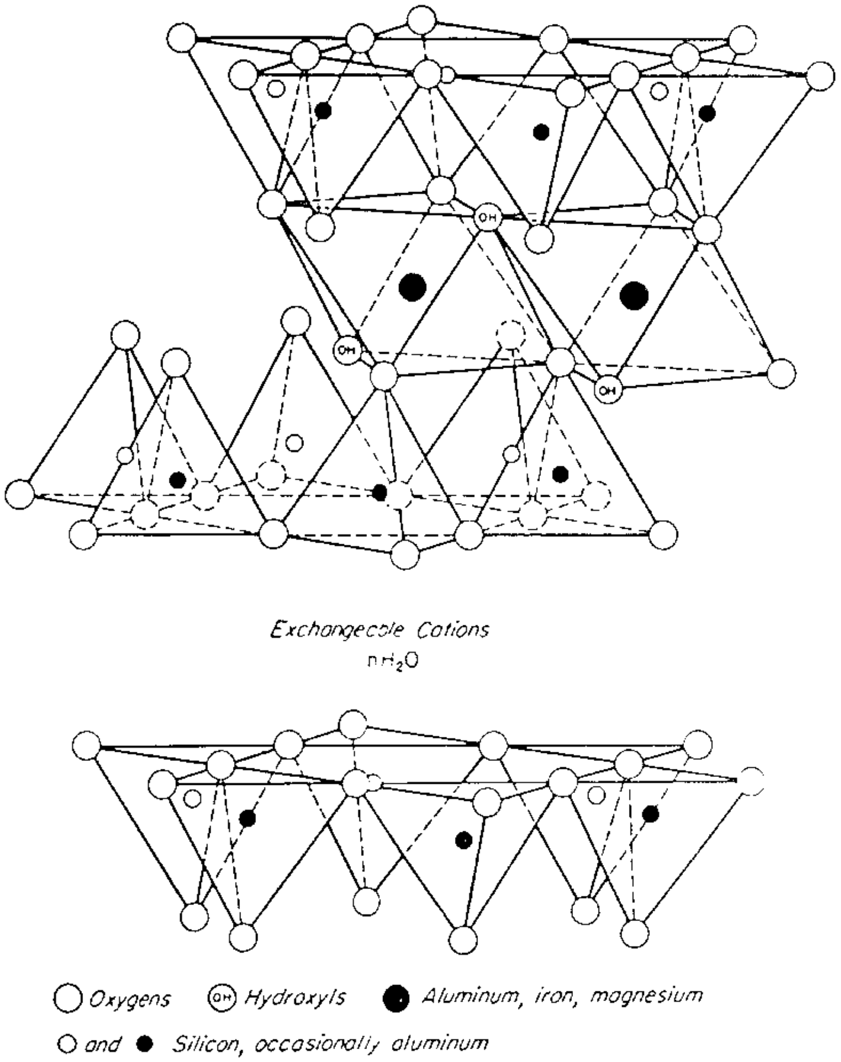


Figure 1-4 Diagrammatic sketch of the crystal structure of montmorillonite according to Hofmann, Endell & Wilm, and Marshall & Hendricks

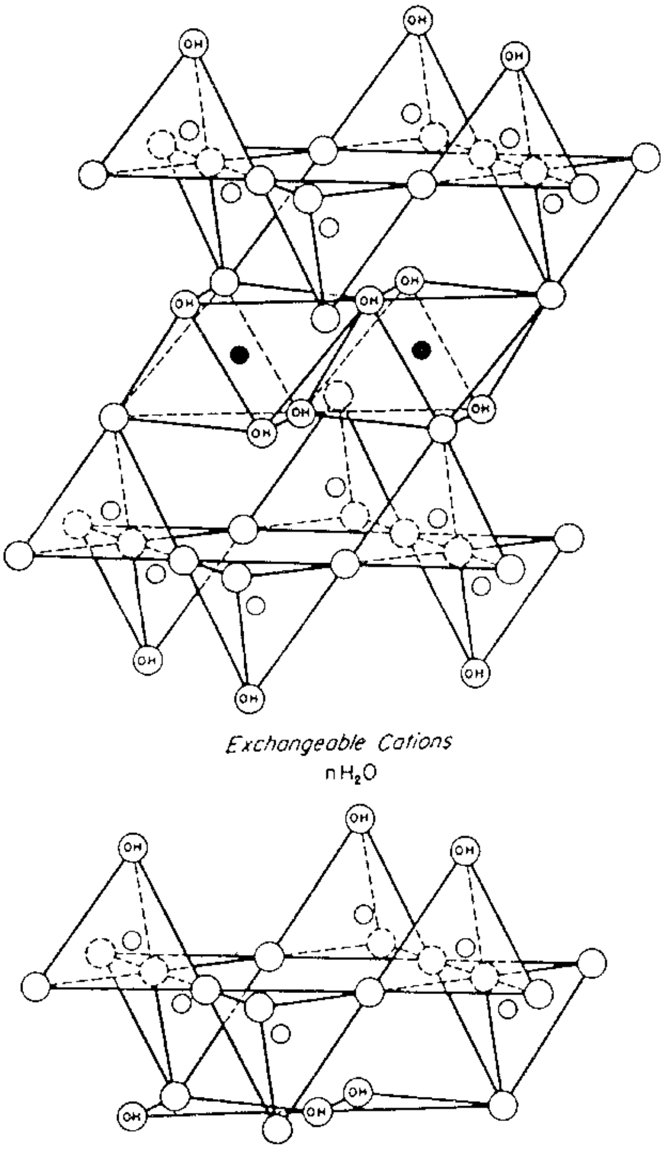


Figure 1-5 Diagrammatic sketch of the crystal structure of montmorillonite according to Edelman & Favejee

The major point in proposing the model in Figure 1-5 was that Edelman & Favejee claimed that no lattice substitution or vacancies are required to explain the cation exchange capacity of montmorillonite. However, the structure originally proposed by Edelman & Favejee has far more available OH groups than required by the exchange capacity provided by replacement of the H of the hydroxyls. This and other critical matters led to adjustment of the structural model to one with only one third of the tetrahedrons inverted (5). Such a model, proposed by Erik Forslind in the fifties, was shown by him to yield interlamellar hydrates resembling a deformed ice lattice (Figure 1-6), provided that Li or Na are in interlamellar positions, while he claimed that the model proposed by Hofmann, Endell & Wilm applies in the presence of other cations and organic molecules for size and charge reasons. Also, he stated that the latter version is valid at higher temperatures than 100-150°C.

The structures in Figure 1-6 suggest that only four hydrogen bonds can be formed between three clay unit cells and a water lattice and Forslind claimed that, for probability reasons, half of the protons would be associated with the water lattice and the other half with the clay crystal. Two units of charge would hence be transferred to the water lattice from the three clay unit cells, implying that the charge defect of the clay crystal would attain a mean value that corresponds to the average observed cation exchange of montmorillonite, i.e. about 80 meq/100 g.

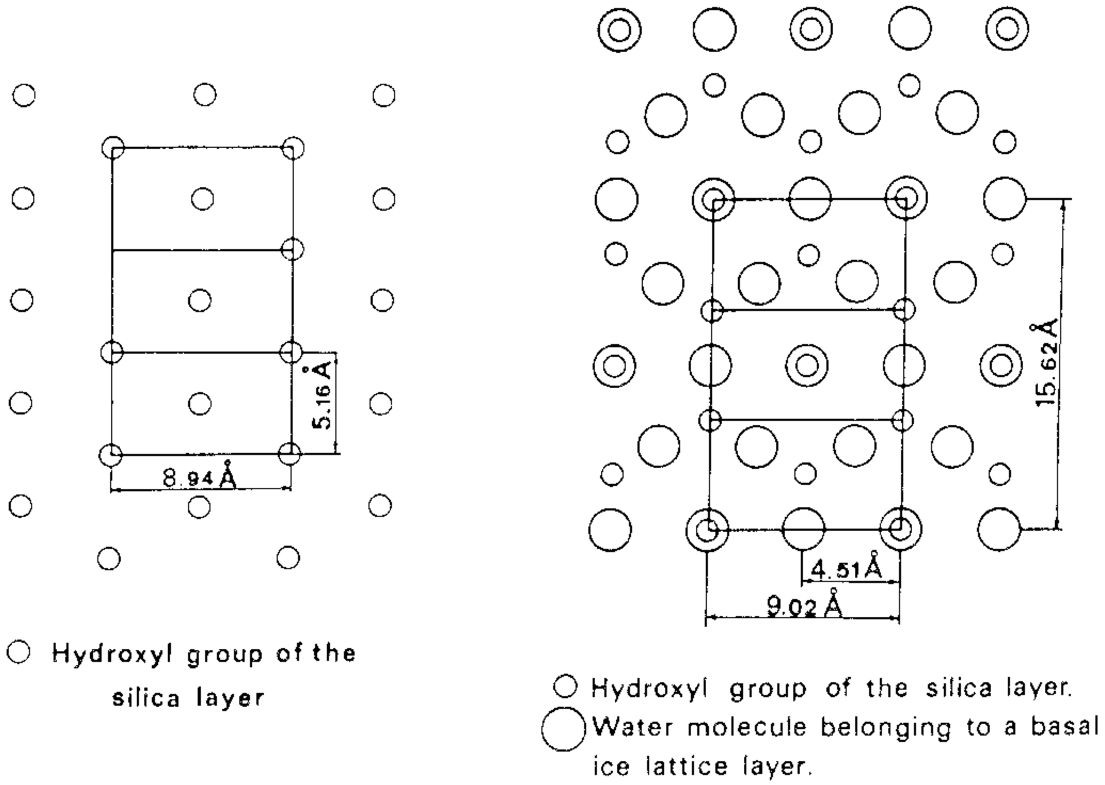


Figure 1-6 Montmorillonite/water interaction (3). Left: Protruding hydroxyl groups of trans-coordinated silica layer. Right: Basal ice lattice molecules superimposed on the hydroxyl groups

We will see later that the assumption of a "low- temperature" crystal structure with Na in interlamellar positions can help to explain two major phenomena:

- Higher chemical stability of Ca montmorillonite than of Na montmorillonite

- Unstable state of tetrahedral Si in Na montmorillonite on heating beyond a critical temperature, possibly facilitating release and interlamellar precipitation of up to one fourth of the tetrahedral silicons in conjunction with aluminum being taken up in the tetrahedrons ("beidellitization").

2 EVOLUTION OF IDEAS CONCERNING SMECTITE STABILITY

2.1 PAST (Prior to 1983)

2.1.1 Source of information

The major source of information on the chemical stability of smectites has been geological data from deep drillings, which all point to a successive conversion of smectites to hydrous mica, and analyses of clays that have undergone hydrothermal treatment in the laboratory, which also show such alteration. Still, many hydrothermal tests have been made under conditions that are not relevant to the actual conditions in a deeply located repository, i.e. they have been conducted with incomplete water saturation and a possibility of partial or complete dehydration.

2.1.2 Field evidence

The matter of conversion of smectite to hydrous mica has been an issue of growing interest since the late sixties when it was found to have occurred in all shales during burial and in overthrust zones as well as in contact metamorphism. A number of classical studies of this sort have been reported and we will give a short summary of the basic findings in this chapter.

Grim pointed out already back in the fifties that bentonites older than the Cretaceous appear to contain little smectite while no smectite-bearing shales older than the Ordovician have been found (4). This was concluded to be due to the influence of heat and pressure and Perry and Hower found that the temperature appeared to be the most important parameter controlling the reaction (6). Their plots of the relation between smectite percentage to temperature has actually been taken as a reference by many investigators involved in the study of processes in sedimentary basins, while it has become clear that other factors may have controlled the reaction kinetically as well as thermodynamically.

Burst (7) and Perry and Hower (6) were the first to reveal the continuous reaction series of montmorillonite to hydrous mica, suggesting a monotonic increase in percent hydrous mica within the assumed mixed-layered "illite"/smectite (I/S) clay phase. For the Gulf area it was found that the reaction had proceeded from about 80 % smectite to about 20 % smectite over the temperature range 50-100°C and it was also concluded that the resulting mixed-layer minerals were ordered in a regular ISIS form. The overall reaction was claimed to be:

$$\textit{Smectite} + K + Al = \textit{Illite} + Si \qquad (2)$$

using the term illite for convenience here and in the rest of the report despite its lack of relevance.

Considering only time and temperature Pytte (8) put together literature data in Table 2-1 as a support of the idea that only these two parameters are of importance for modelling smectite-to-illite conversion. The required K^+ source was assumed by him and a number of other investigators - regarding the system units to represent closed conditions except for H_2O, CaO, Na_2O and CO_2 - to be feldspars and hydrous mica, while Weaver & Beck (9) suggested K (and Mg) to have originated from great depths where they have been released by high-temperature metamorphic reactions.

Table 2-1 Summary of time-temperature constraints on the illite/smectite reaction according to Pytte (8)

Location	Time range years	Temperature range °C
Metamorph (Dikes)	$1-10^3$	250-400
"	10^6-10^7	200-500
Gulf Coast	$10^7-10^{7.5}$	90-230
Cincinnati	$10^{8.5}$	<80

Other mineralogical changes than K-feldspar dissolution have been identified and a more complete list of mineral alteration associated with the conversion of smectite to illite is:

- Decomposition of mica
- Decomposition of feldspar (not albite)
- Loss of kaolinite
- Formation of chlorite or chlorite interlayers in the smectite/illite stacks
- Formation of quartz, cristobalite and amorphous silica
- Loss of calcite

From a mineralogical standpoint the total reaction has been suggested to be the following:

$$S + F_k(+Mi) = I + Q + Chl \qquad (3)$$

where

S = Smectite
F_k = K-feldspar
Mi = Mica
I = Illite
Q = Quartz
Chl = Chlorite

Quartz has been assumed to originate from decomposed feldspars and from silica lost from the tetrahedrons of montmorillonite converted to beidellite. Chlorite was assumed to be formed from magnesium and iron lost by the smectite. Its crystal structure, which consists of true, negatively charged "mixed layer" mica layers with brucite layers corresponding to potassium ions in the micas, is shown in Figure 2-1.

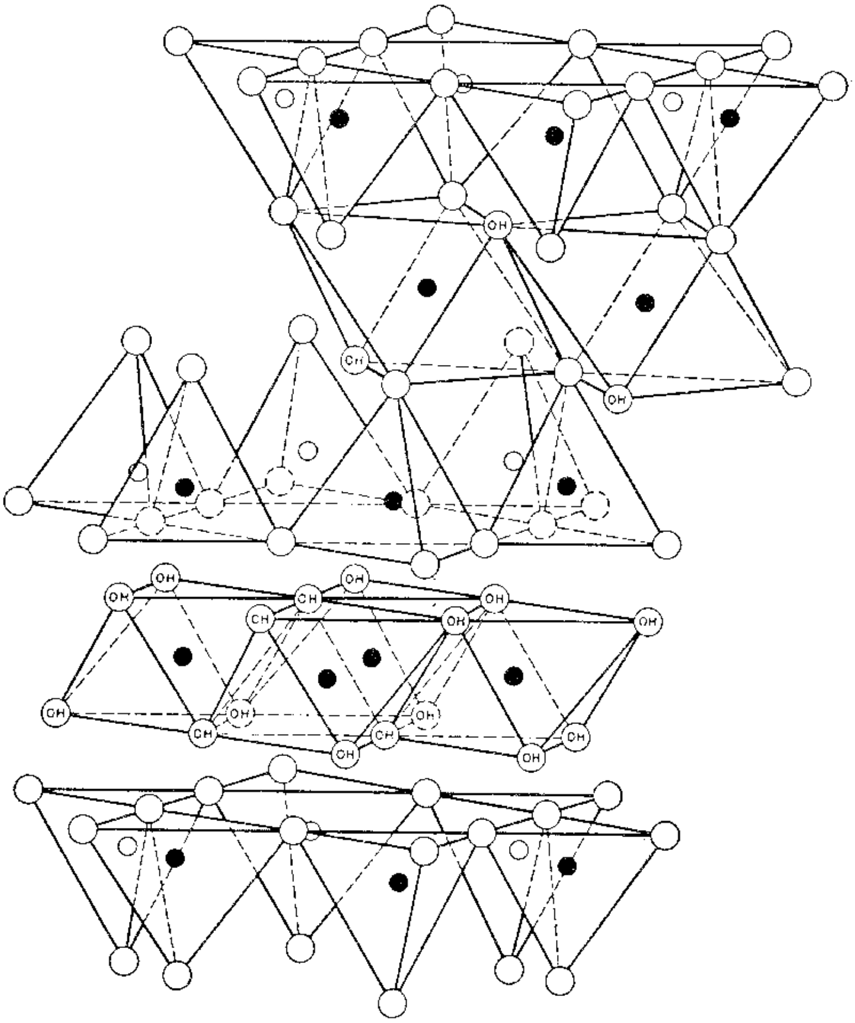


Figure 2-1 Structure of the monoclinic mineral chlorite (McMurchy). It is a three-layer pyrophyllite-like structure with 5 Mg and one Al in the octahedral positions. Brucite layers $Mg_5Al(OH)_{12}$ serve as ligands

It was early recognized and pointed out by wellknown investigators like John Hower, that the initial mineral content and thereby the smectite content may have been largely different in different parts of a deep profile (10), a matter that is naturally of great importance for scientifically sound interpretation of mineral conversion processes from field observations. We will consider, as an example, a case representing a more than 5 km thick series of Gulf sediments with special respect to possible variations in the initial mineral composition for finding out whether there may be alternative explanations of the reported smectite-to-illite conversion.

Hower et al. (10) stated that the sediment series had undergone conversion from smectite to illite down to 3.7 km depth but not below this. This is illustrated by Figure 2-2, which suggests - in general agreement with Pytte's statement - that

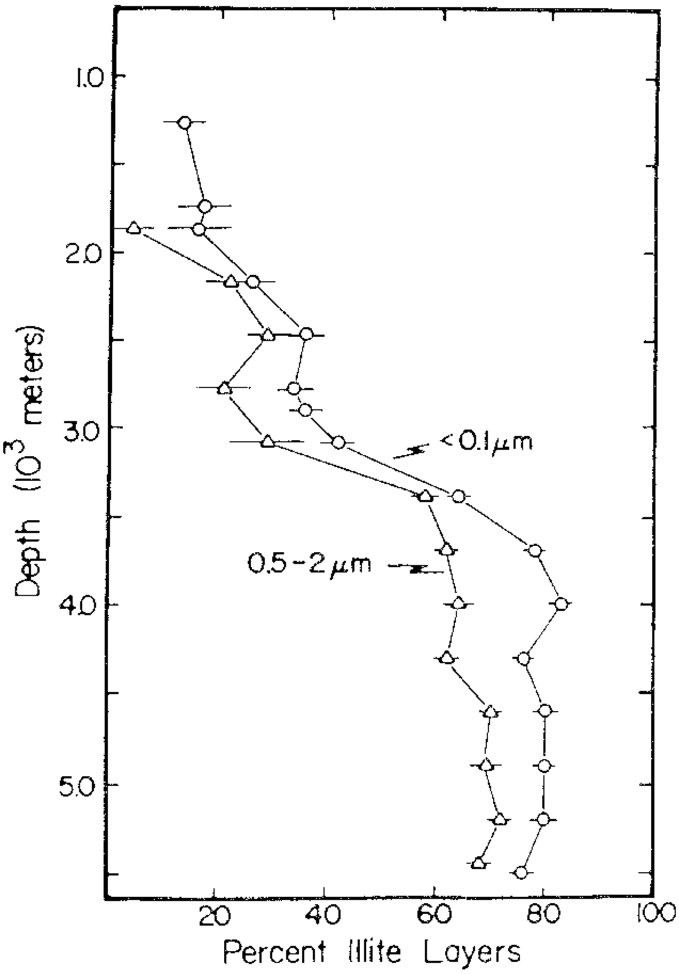


Figure 2-2 Proportion of illite layers in illite/smectite as a function of depth (10)

there is an increase in I/S ratio with the depth in the Gulf sediment series. However, it is clear that there is practically no change in the intervals 2.5-3 km and 3.5-5.5 km. Hence, the large majority of the conversion refers to the depth interval 3-3.5 km, which requires an explanation. One finds from the reported distribution in potassium (Figure 2-3) that there is a significant change below 3.5 km, where coarser fractions have lost and finer fractions gained potassium, indicating decomposition of potassium feldspars and fixation of potassium in collapsing smectite. However, there is no proof that the critical interval 3-3.5 km has experienced any significant change in potassium.

Looking closer at the diagram in Figure 2-2 one finds that the percentage of illite is actually almost constant below 3.5 km depths, which is compatible with the constant potassium content in the fine fractions according to Figure 2-3. The drop in potassium of the coarser fractions with increased depth may hence be due to differences in the initial composition of the coarser fractions rather than due to transfer to the finer fractions. Also, one can see that the average potassium content in the profile actually increases somewhat with the depth, which may either be explained by a deeply located potassium source or by initially different composition with respect to this element.

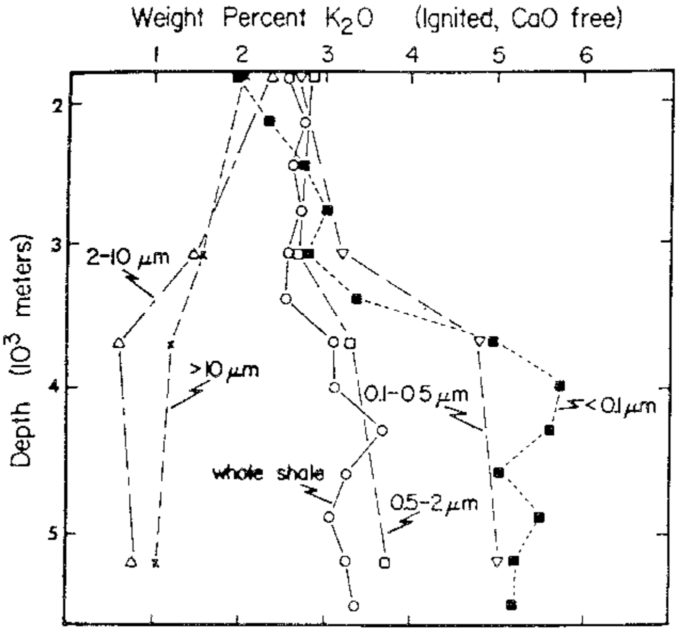


Figure 2-3 Distribution of potassium among various size fractions from different depths of ignited, CaO-free material (10). The authors concluded the curves to indicate redistribution of potassium

Apparently convincing evidence of the validity of Eq(2) is offered by the diagram in Figure 2-4, which shows the increase in aluminum and decrease in silica of the finest clay fraction with the depth. Considering the difficulty with which aluminum migrates in free form, the diagram could also be taken as a support of the hypothesis that the individual units of the sediment series behaved as chemically closed systems, implying that aluminum originates from coarser fractions. However, the fact that the I/S ratio is actually constant from 3.5 km and downwards is not compatible with the change in Al_2O_3/SiO_2 ratio and this may mirror different original compositions of the strata, or formation of some different mineral phase. By considering the diagram in Figure 2-5 one finds that chlorite appears at about this depth, which may explain the change in aluminum/silica ratio and support the validity of Eq(3), provided that chlorite was not an original component of these deeper layers.

One finds from all this that the present mineral composition of the Gulf sediment series does not validate any particular alteration model or mechanisms, except for a general irregular change in I/S ratio with depth. Hence, the initial mineral content may well be a dominant factor and it is thereby also clear that the K-source is far from established. In fact, it is possible that the electrolyte composition of the water in which sedimentation took place may have been a determinant of the access to potassium.

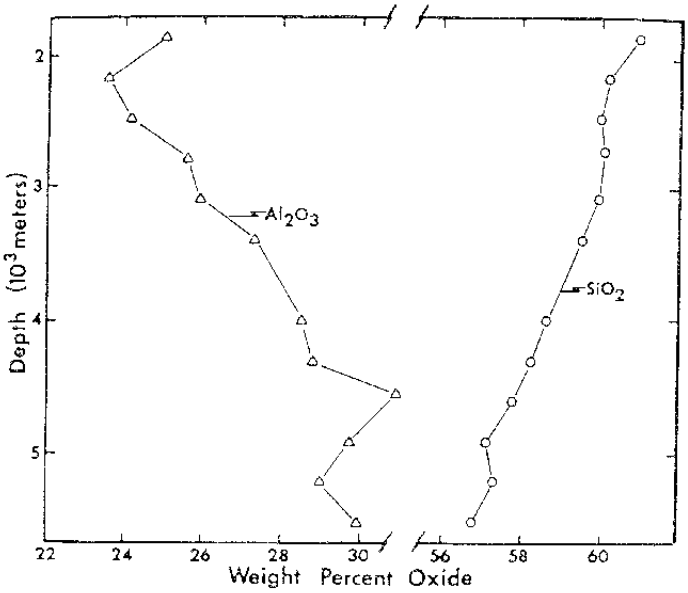


Figure 2-4 Depth-dependence of aluminum and silica in the finest clay fraction (<0.1 μm)

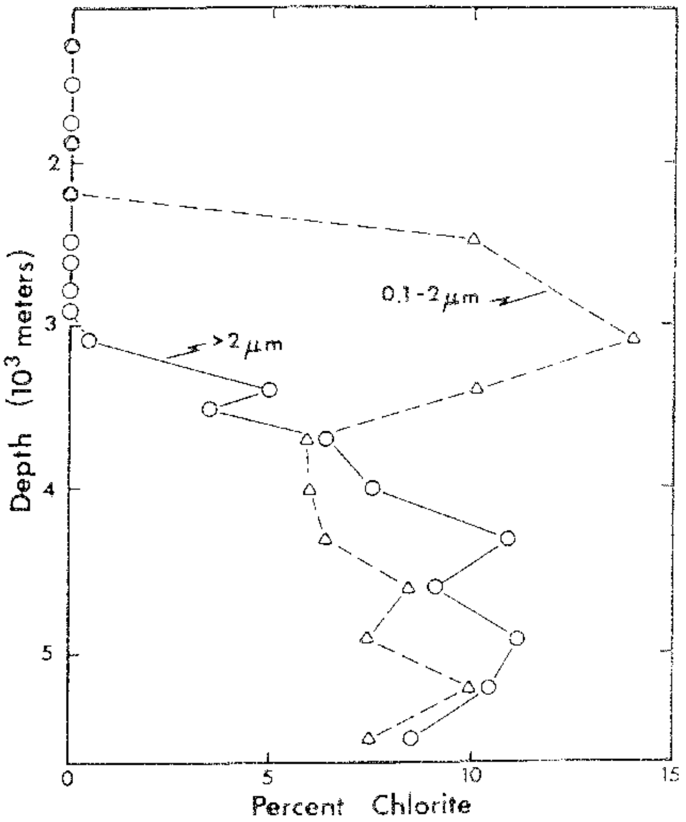


Figure 2-5 Chlorite content of the fine fractions (10)

A number of similar studies were conducted both in the US and in other parts of the world in this early period, primarily in conjunction with investigations of the formation and accumulation of hydrocarbons, and especially the ones related to contact metamorphism gave evidence of smectite-to-illite conversion at relatively low temperatures. A classical study of this sort was published by Janet Hoffman and John Hower in 1979 (11), which deserves to be referred to both because of its completeness and because it serves as a further important example of the difficulty in interpreting mineral conversion due to uncertainty in establishing the origin of mineral assemblages.

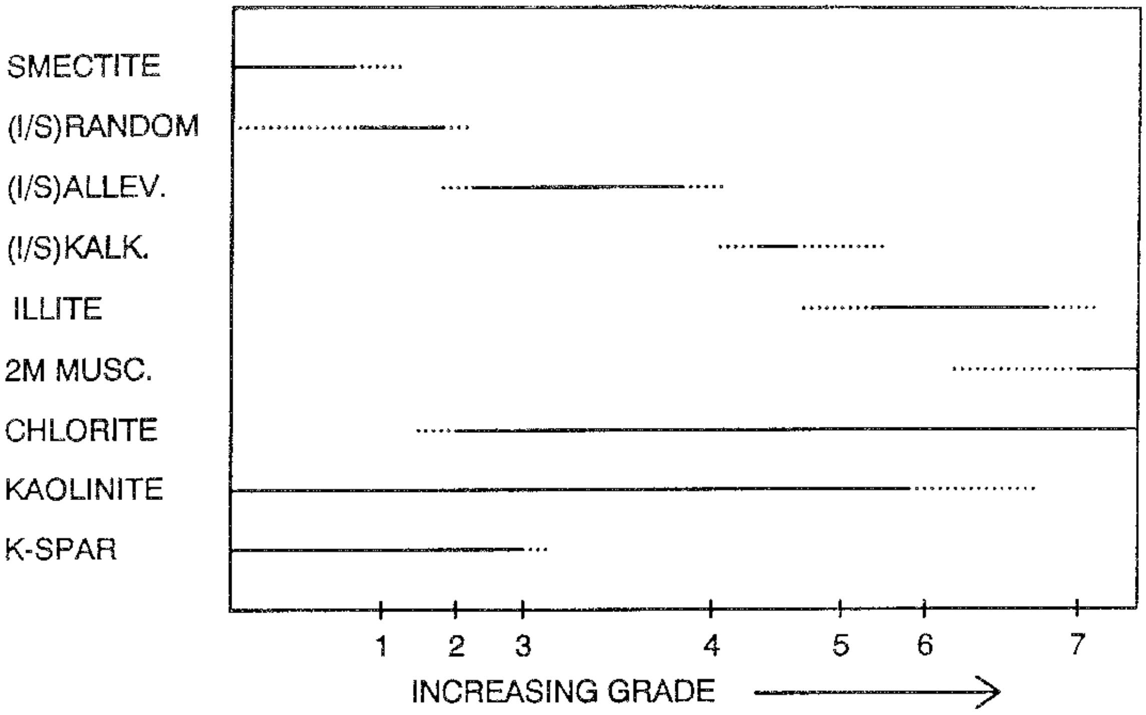


Figure 2-6 Metamorphic grade index minerals in pre-greenschist facies pelitic rocks (11)

Table 2-2 Temperatures for metamorphic grade changes with indication of the influence of reaction times as inferred from the age of the deposits (11)

Grade	Upper Mesozoic - Lower Tertiary Temp.°C	Pliocene-Pleistocene Temp.°C
1	60	60
2	100	140
3	120	-
4	175	-
5	200	-
6	-	-
7	300	-

These authors concluded that the entire shale mineralogy of the disturbed belt in Montana of Mesozoic age (> 65 million years) resulted from heating in the temperature range 100 to 200°C, which has been taken as an early warning of applying higher temperatures than 100°C in HLW repositories. The authors concluded that for undisturbed parts of the area, i.e. where the temperature has not exceeded 60°C, practically no conversion of the smectite has taken place at all.

Their conclusion was that Eq.(3) is of general validity but they also found, in agreement with earlier studies, that the role of calcium must be a dominant factor in controlling the mineralogy, i.a. because of the disappearance of calcite in very deeply located sediments. Thus, they supported Zen's model (12) according to which the following reaction takes place:

$$C + S + Q = L + CO_2 \tag{4}$$

where

C = Calcite
S = Smectite
Q = Quartz
L = Laumontite

The role of CO_2 would naturally be of great importance: the partial pressure of CO_2 will control whether clay minerals or zeolites form in calcium-holding silicate rocks. The fact that the smectite-to-illite-converted Gulf sediments and the Montana shales show depletion in calcite with depth is certainly of interest for the alteration of canister-embedding bentonite although the amount of zeolites formed at the end of the hydrothermal period cannot be dramatic. Still, these minerals are permeable and tend to increase the bulk hydraulic conductivity.

As to the reaction product chlorite in Eq.(3), Hoffman & Hower stated that ordered interstratified chlorite/smectite (corrensite) or other chlorite/expandable phases is most probably decomposition products of ferro-magnesium minerals. This is in contrast with Weaver's statement that Mg and Fe may be released from octahedral positions in smectite to form chlorite (13).

Hoffman and Hower's study also comprised a detailed study of the nature of the mixed-layers, which they interpreted as ranging from I/S random at 50-100°C, via allevardite (ISISIS..) at 100-150°C to kalkberg (ISIIISIII..) around 200°C, cf. Figure 2-7, which is a general correlation of mineral assemblages and temperatures.

The matter of mixed-layers has turned out to be of fundamental importance as discussed later in the report. It was investigated in considerable detail already in the seventies and it was demonstrated, as shown by the compilation of published data in Figure 2-8, that there is a wide range of expandable layers in I/S at any temperature, indicating that i.a. the access to K is a determinant of the conversion. It is evident that at 100°C the fraction of expandable layers in I/S mixed layers can be anything from 20 to 90%.

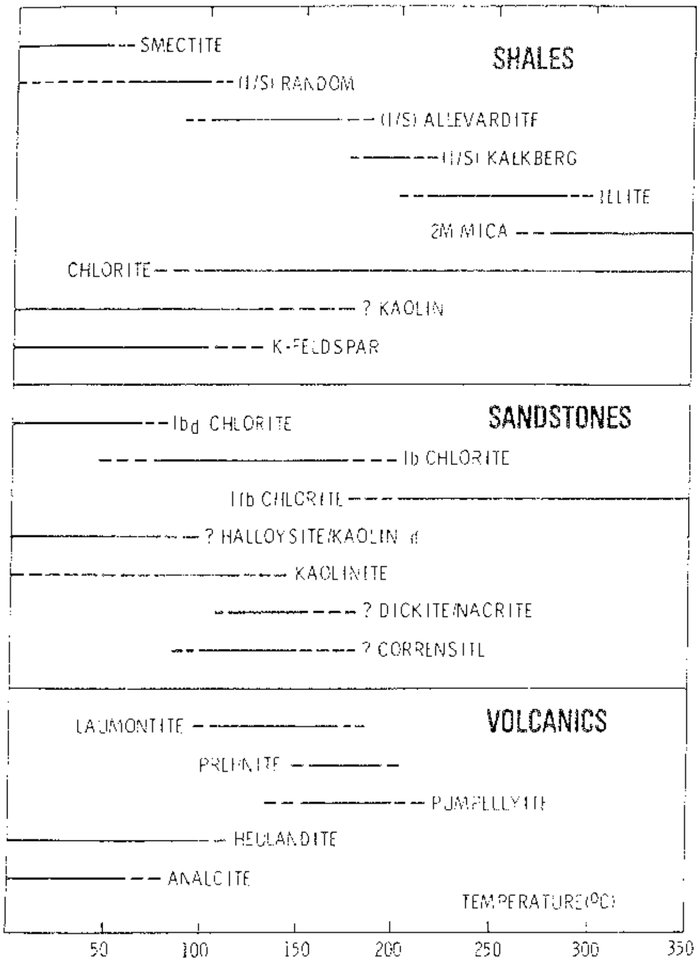


Figure 2-7 Correlation of temperature-dependent mineral assemblages in shales, sandstones and volcanogenic rocks (11)

2.1.3 Laboratory evidence

A large number of experimental hydrothermal investigations were performed in the seventies and they all seem to have been made in more or less water-saturated, closed vessels containing rather dilute clay gels. Usually, the water pressure was controlled and maintained at a level of several MPa, while no effective, i.e. grain pressure, was exerted on the clay gel and the conditions were therefore completely different from those in deeply located clay sediments. Still, it was generally concluded from this sort of experiments that smectite-to-illite conversion proceeds via the formation of continuous series of I/S mixed layers with smectite content progressively reducing from 100 to 0 % (14,15).

The kinetics in the conversion from smectite to illite was evaluated by researchers like Eberl and Hower. For a K-beidellite, they found the illitization reaction to be as shown in Figure 2-9, where the slopes of the isothermal lines represent the rate constants. An Arrhenius plot of these rate constants against the inverse of the temperature gave a straight line from which the activation energy was found to be about 19 kcal/mole. This suggests that the conversion to illite is associated with breaking of Si-Al-O bonds within the lattice, which is not compatible with the simple collapse mechanism that would follow from heating of beidellite with K in interlamellar positions. Instead it could point to another mechanism, i.e. dissolution of the beidellite and neoformation of a separate illite phase. The high temperature rates led Eberl and Hower to conclude, using the derived activation energy and applying the first order Arrhenius equation that conversion from pure smectite would yield 20 % expandable I/S mixed layers in less than 1 million years at 90 C.

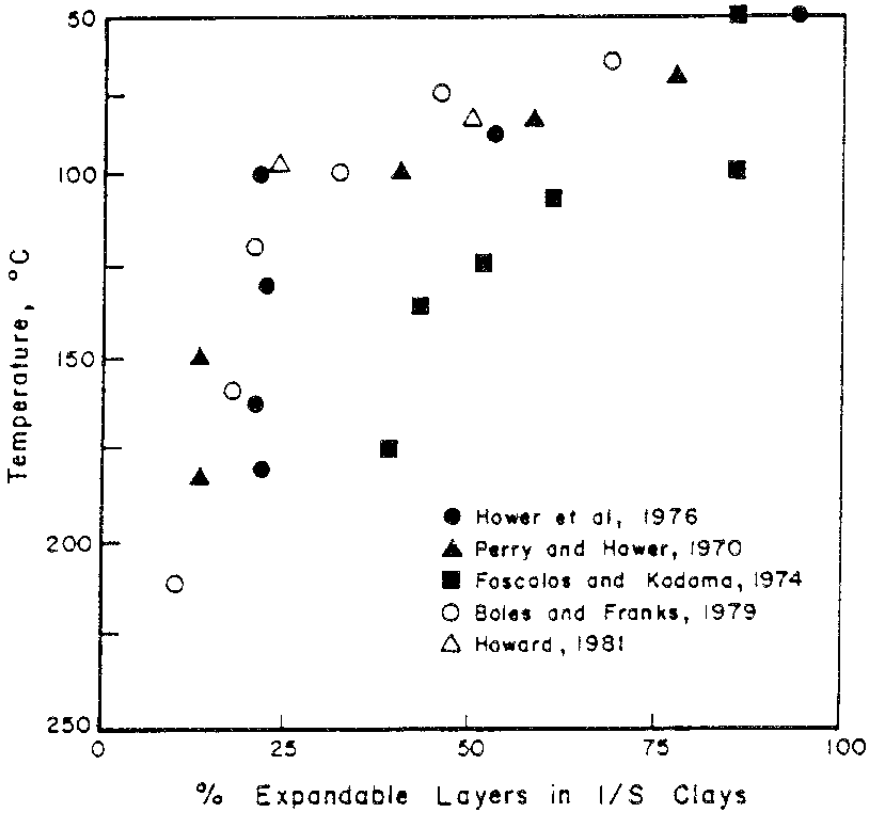


Figure 2-8 Percentage of expandable layers in natural I/S mixed-layer minerals vs temperature (Weaver)

Hydrothermal experiments reported by Eberl are of particular interest because they demonstrated the importance of the dehydration of the interlayer cation: a Na smectite was found to be stable at higher temperatures than an equivalent K-smectite (15). As we will see later, the issue of hydration/dehydration is in fact fundamental for the understanding of smectite-to-illite conversion.

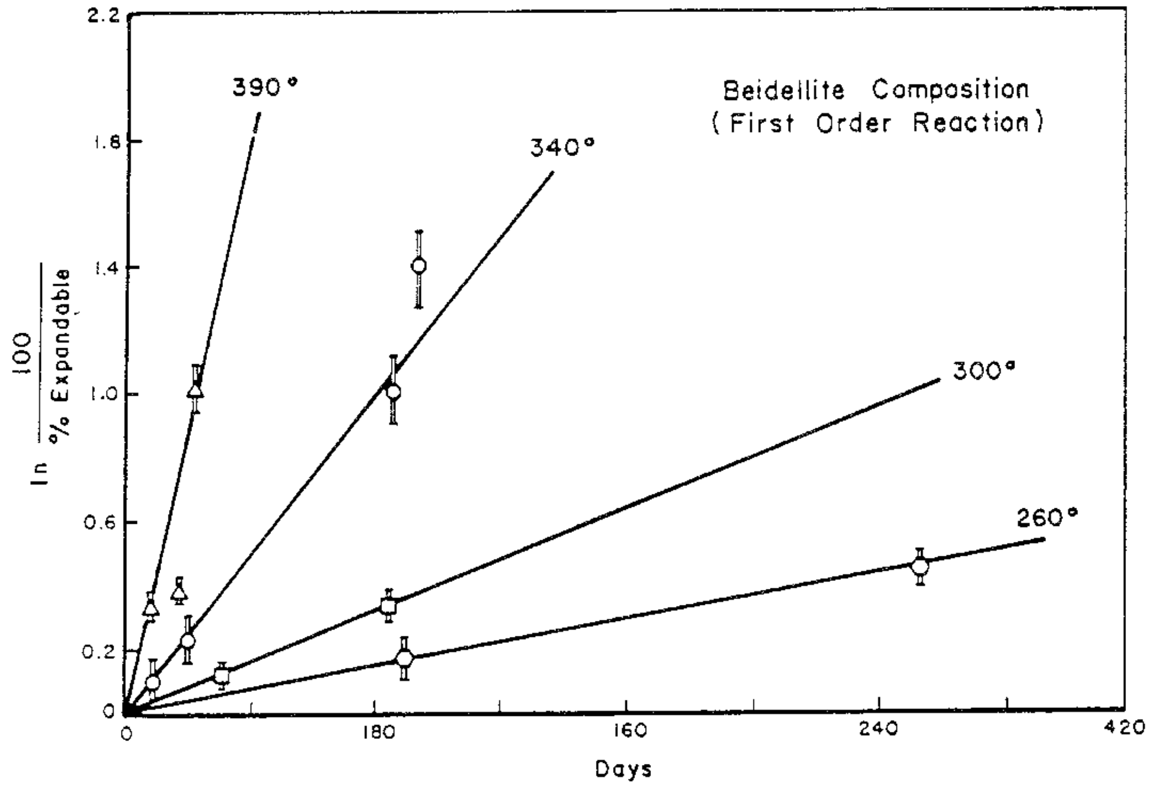


Figure 2-9 Beidellite reacting to illite as a function of time at 200 MPa water pressure (14)

2.1.4 Dehydration

Conversion from smectite to illite implies collapse and release of interlamellar water and it was early recognized that this may be a controlling factor of the rate of conversion. Here is where the question of the different types of water - interlamellar ("internal") and porewater ("external") and their densities comes in (Figures 2-10 and 2-11),(16). These matters were subject to intense research in the US and in various other countries, including Sweden, in the fifties and sixties, primarily because of its possible influence on release and accumulation of hydrocarbons. Thus, if the density of interlamellar water is lower than that of the porewater, collapse and transfer of interlamellar water to porewater is estimated to take place without difficulties, while expansion of initially dense interlamellar water would create very high porewater overpressures.

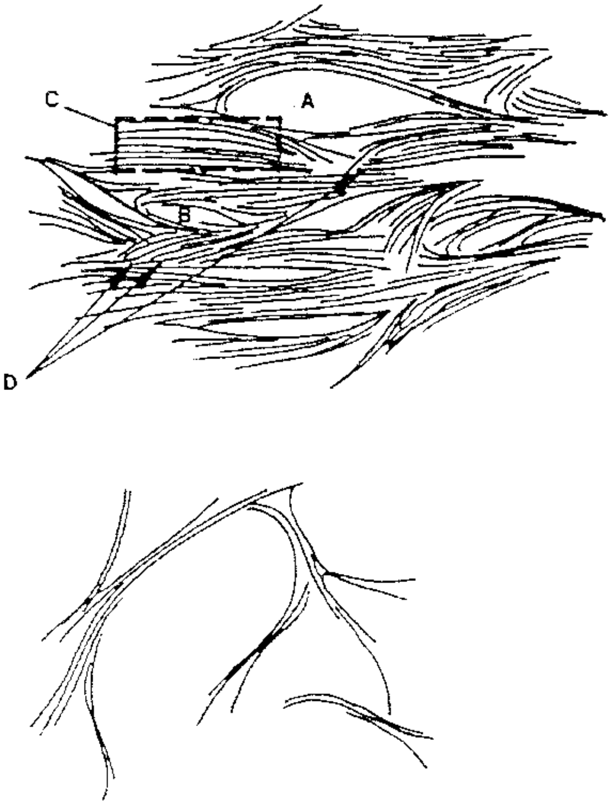


Figure 2-10 Microstructural features of smectite clays. Upper: Dense clay with A) large and B) small void "external" water, C) stack of flakes with interlamellar ("internal") water, D) interface of stacks. Lower: Expanded Na smectite clay gel with practically only "external" water

Such overpressures, which have been reported to exist at larger depths than about 2500 m in the Gulf area and to reach a maximum value at about 3000 m depth (Figure 2-12), have two implications. Firstly, they dissipate extremely slowly because of the very long flow paths, which strongly retards collapse of smectite stacks. Secondly, high porewater overpressure reduces the effective pressure and may cause unstable conditions in deep boreholes in sedimentary rock as manifested by rapid inflow of softened shale in such holes at depths of a few thousand meters (17). Powers' idea of how oil became accumulated at relatively small depth, i.e. one thousand to a few thousand meters, is that very high porewater overpressures flushed hydrocarbons from source mudrock (17).

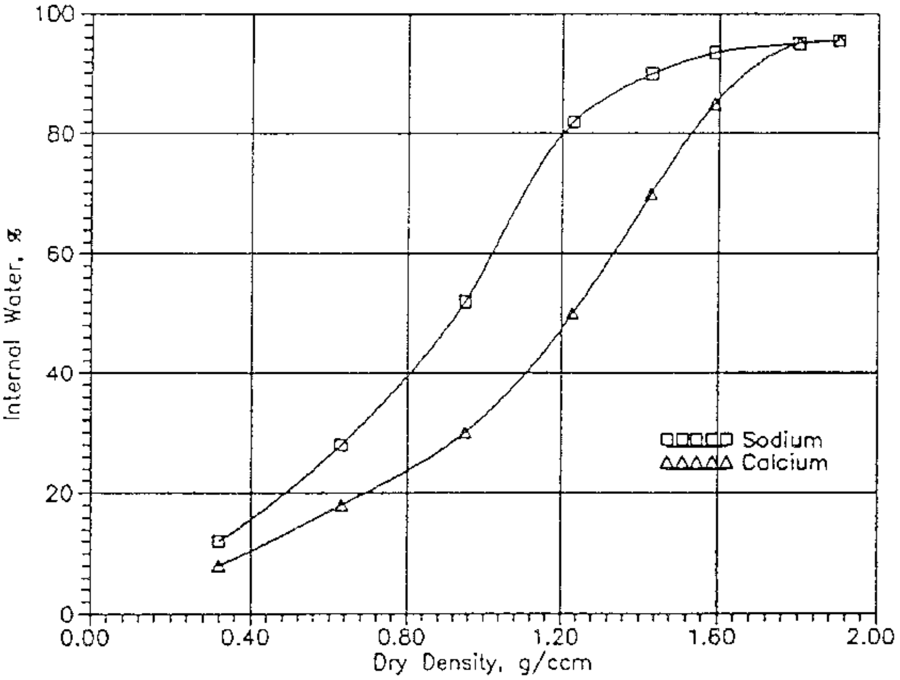


Figure 2-11 Theoretical relationship between dry bulk density and content of "internal" water expressed in percent of the total pore volume

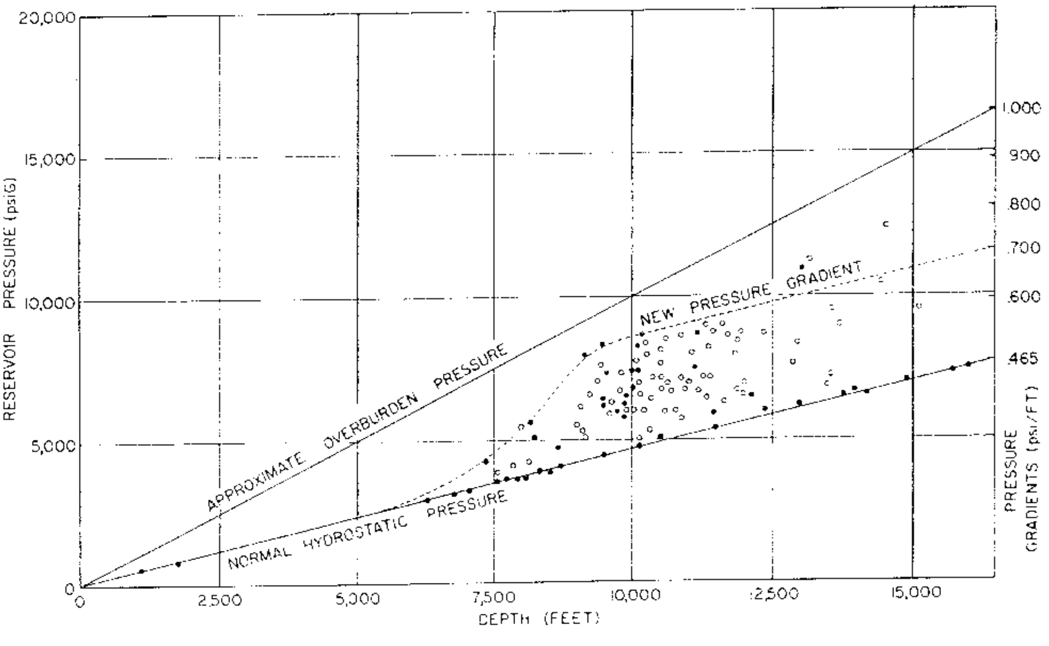


Figure 2-12 Reservoir pressures versus depth for Louisiana Gulf Coast wells. Solid circles are measured pressures and open ones estimated pressures (18)

It is striking that enrichment of hydrocarbons, generation of porewater overpressure, and conversion of smectite to illite all take place in the interval 1500-4000 meters and it speaks in favor of a density of interlamellar water higher than unity.

Experimental determination of the density of interlamellar water has yielded a whole spectrum of values, extending from less than unity up to 1.4 g/cm³ or even higher than that (19). Very careful measurements for determining the density of the water in montmorillonite clays made early in the fifties (20) pointed at average values of 0.97-0.98 g/cm³ for water contents less than 10 % (Figure 2-13), which were later reinterpreted yielding an approximate value of the interlamellar water of 0.9 g/cm³ of Na montmorillonite clay (20). This agrees with an early model of organized interlamellar water proposed by Hendricks and Jefferson (21).

The study reported in (20) indicated that the density of interlamellar water in Ca montmorillonite is higher than in Na montmorillonite and may well exceed 1 g/cm³.

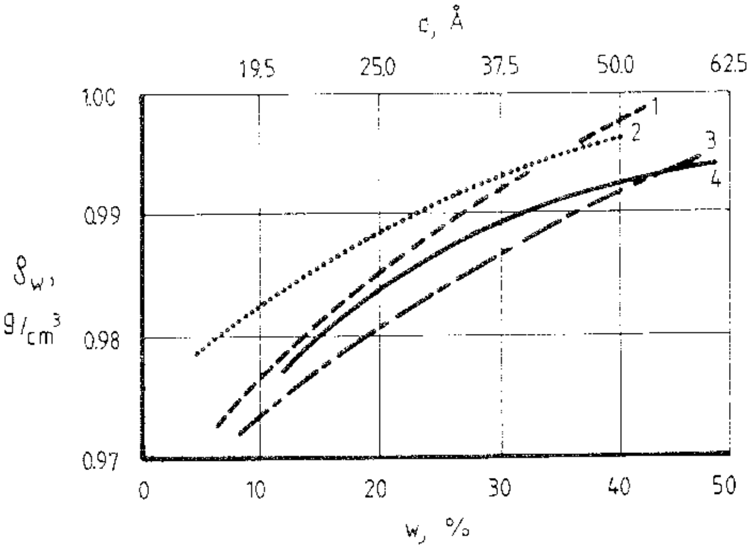
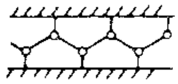
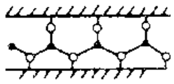
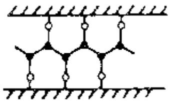
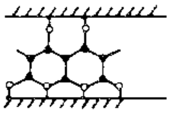
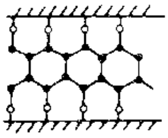
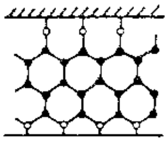
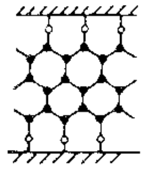


Figure 2-13 Average density (ρ_w) of porewater in montmorillonite as a function of water content (w) and electrolyte content (19). 1) K-clay at 1°C and 2) at 25°C, 3) Na clay at 25°C, 4) Li clay at 25°C

Forslind's model (Figure 1-6) for Na and Li saturated montmorillonite yields a water lattice density of less than unity considering only water molecules grouped between the apical hydroxyls. Thus, one finds the density of one stable monolayer to be 0.5 g/cm³ , while that of two and three hydrates is 0.6 and 0.7 g/cm³ (19), cf. Figure 2-14. The density of interlamellar water of his model is thus not a constant and actually a matter of definition depending on what is considered to belong to the mineral and water lattices, respectively. Still, the overall constitution of the interlamellar water is that of a strained ice-like lattice

(22). For other cations than Na and Li and for organic molecules contained in the interlamellar space, Forslind claimed that their size and charge properties would not allow development of a regular water lattice. Ca, for instance, is strongly hydrated and controls the location of interlamellar water molecules.

As implied by Forslind (5) and considered to be possible by several other investigators (23), interstitial water molecules can be hosted in organized interlamellar water lattices yielding a variation in the degree of hydration and in the density of interlamellar water. The latter may hence be either somewhat lower or higher than that of free porewater. The matter will be pursued later in the report.

	Schematic interlayer structure	H_2O molecules per unit cell	Basal spacing, Å	g H_2O/g clay	mM H_2O/g clay	Remarks
0		0	12.30	0; 0,084[a]	0; 4.667[a]	Unstable; no hydration; four OH groups per unit cell
1		2.66	15.05	0.059	3.278	Unstable
2		5.33	17.81	0.119	6.661	Stable monolayer
3		8.0	18.73	0.179	9.944	Unstable
4		10.67	21.49	0.238	13.222	Stable; two layers
5		13.32	22.41	0.297	16.5	Unstable
6		16.0	25.17	0.357	19.833	Stable; three layers

[a] At complete dehydroxylation.

Figure 2-14 Water lattice configuration in interlamellar positions of Li5 and Na montmorillonite (5)

2.1.5 Tentative conclusions

General

The basis of modern ideas concerning the stability and alteration of smectite under hydrothermal conditions is the general theory of thermodynamics of hydrothermal systems at elevated temperatures and pressures as outlined back in 1950-70. A number of field data derived in the period helped to create a general picture of the conversion of smectite to non-expandable minerals. This picture was manifested through three international meetings held in 1981, 1982 and 1983, of which the latter two were particularly devoted to the application to HLW repositories. These three events will be discussed in this chapter.

Clay Minerals Society 18 th Annual Meeting

The 1981 annual meeting of the Clay Minerals Society was held in Illinois and had as one object to discuss the issue of collapsed and hydrated Na smectite. The meeting will be shortly referred to here since it served as a basis of the colloquium on smectite alteration that was held at the State University of New York at Buffalo in 1982 and at the Shoreham hotel in Washington DC in 1983.

The major point was the processes involved in dehydration of Na montmorillonite that take place when the relative humidity of the atmosphere is reduced. The outcome of the discussions was that one hydrate layer, yielding 12.4 Å spacing, is maintained at RH=32 % and that complete dehydration, corresponding to 9.6 Å spacing, takes place at a relative humidity of 12 %.

This is in agreement with commonly observed values of d(001) at different water vapor pressures as demonstrated by the stepwise increase in spacing shown in Figure 2-15. One finds that Forslinds hydration model for Na smectite implies that the one-hydrate state in the figure equals his unstable "0-state" with only hydroxyls interacting in the interlamellar space, and that 9.6 Å spacing corresponds to conversion from trans- to cis-coordination, i.e. to a return to the HEW model with no surface hydroxyls. Forslind's unstable one-hydrate state gives d(001) approximately equal to 15 Å, hence corresponding to the two-hydrate layers in Figure 2-15.

The most probable reason for ordered interstratification of collapsed and hydrated Na smectite, i.e. regularly ordered I/S mixed layer minerals, was assumed to be reorientation of the axes of hydroxyls exposed in the interlamellar space in response to dehydration. Thus, dehydration of a discrete interlamellar space can be shown to involve a tilt by 15° of the OH axes away from the interlayer cations, reducing the repulsion between them, while OH axes on the hydrated side of the flake tilt towards the hydrated space by the same amount, thereby increasing the repulsion and preserving the hydrated state of every second interlamellar space. This hypothesis does not explain why dehydration is initiated but it implies that once it has taken place in one interlamellar space in a stack of flakes, it yields a stable condition of ordered interstratification of the stack. Further dehydration, leading to irregular ordering, requires more energy for overcoming the repulsive forces.

In light of this, Forslind's model of trans- (i.e. EF) and cis- (i.e. HEW) coordination of the SiO_2 layers can be used to represent hydrated (EF) sides of pairs of united montmorillonite flakes with the contacts of the two united flakes representing dehydrated (HEW) sides. This can be interpreted as regular stacking of ISISISIS.

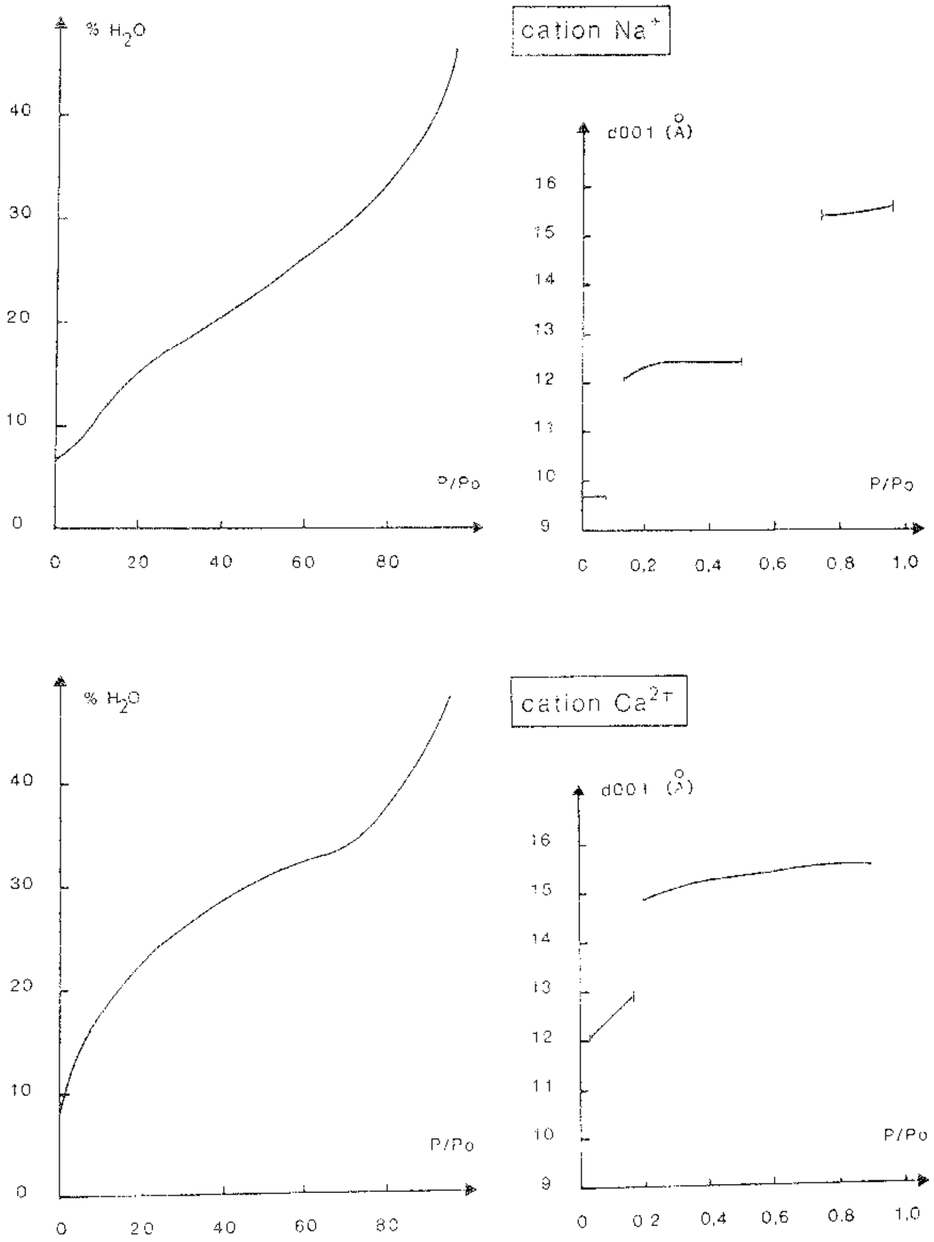


Figure 2-15 Isotherms of dehydration and d(001) versus vapor pressure ratio (RH) for montmorillonite (Glaser et al)

Colloquium at the State University of New York at Buffalo, May 26-27, 1982 (24)

The colloquium was convened to construct a summary of the most recent data and the best scientific appraisal of the process of smectite conversion to illite. The participants were the following:

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The colloquium focussed on the following issues:

1. The true nature of smectite and illite (Kittrick)
2. Necessary criteria for illitization (Roberson, Howard)
3. Mixed-layer formation (Giese)
4. Sources and migration of Al in heated smectite (Howard)
5. Sources and migration of potassium in conversion of smectite to illite (Howard, Kittrick)
6. Sealing effect of dissolved and precipitated silica, formation of chlorite (Roberson, Waddell)
7. Natural evidence compared with laboratory results and theoretical predictions (Roberson, Waddell)

1 True nature of smectite and illite

It was pointed out several times by the participants that illite is hard to define and has many forms. Kittrick made the statement that will be discussed several times in this report that illite is a (room temperature) smectite converted to K-form (high temperature), which is not the mica-like material commonly known as illite. Thus, solubility measurements demonstrate that there is more than one phase in high-temperature smectite, giving off different amounts of H_4SiO_4 when altering pH and pMg in the porewater.

2 Necessary criteria for illitization

There was complete consensus on the statement that there are two requirements for the formation of 10 Å minerals from smectite, i.e. heat and potassium.

Neglecting the retardation of the conversion by the presence of Ca and Mg, i.e. assuming that Na is readily replaced by available potassium even in very low concentrations, calculations performed at the meeting showed that a 1 m thick highly compacted Na bentonite barrier requires percolation of groundwater with 10 ppm K^+ corresponding to 10^5 pore volumes. Assuming a hydraulic conductivity of the clay of 10^{-14} m/s and 10 % pore space, 10^8 years would be required for complete conversion. This figure is not conservative, however, since the pore space is twice the applied figure and the conductivity may therefore be two orders of magnitude higher, yielding not more than 0.5 M years for complete conversion.

3 Mixed-layer formation

Mixed-layer I/S was concluded to be an intermediate stage in the transient smectite-to-illite conversion. Following up the conclusions from the 1981 Illinois congress it was stated that hydroxyl orientation is a probable reason for ordered mixed-layer sequences of illite and smectite layers. It was stated as a hypothesis that lithostatic pressure would favor order and not disorder while higher temperatures would not favor order.

4 Sources and migration of aluminum for smectite-to-illite conversion

The source of Al and how it enters the tetrahedral sheet in the beidellitization process was concluded to be an essentially unsolved problem. It was suggested as one possibility that Al is derived from the cannibalization of smectite edges; as Si is released and floats away, aluminum becomes complexed and finds itself intercalated in interlamellar positions. It was claimed that hydrothermal treatment with very pure smectite clay has been found to yield an increase in tetrahedral aluminum while octahedral aluminum remains constant. Thus, with no external Al source and with octahedral Al intact there would only be one possibility left: cannibalization.

As to the migration of Al no good explanation could be given, the only proposed mechanism being that bad fitting of adjacent lattices would allow Si to "pop-out" and Al to "jump-in".

5 Sources and migration of potassium

Dissolution of feldspar and other K-bearing minerals in the clay and surrounding rock was claimed to provide a source for potassium transported by advective flow to the rock/bentonite contact and by diffusion once within the clay. Potassium normally contained in the groundwater was also considered as available for uptake in the high-charge smectite.

Back-calculation of the rate of potassium migration in Montana bentonite beds gave the average figure 1 m per million years. At this site the concentration of potassium was high in the bentonite bed that had converted to I/S mixed layer minerals and illite and decreasing at increasing distance from the bed.

6 Sealing effect of dissolved and precipitated silica; chlorite formation

Since flow rates are very low in a canister-embedding bentonite, dissolved silica from the smectite will reach saturation and silica will be precipitated, by which the bentonite should be less permeable than originally. If pH conditions become very active, i.e. pH dropping to 3-4, Al will dissolve and one can expect Al-hydroxide-complexed smectite + Al(OH)-precipitated material + new Al-silicate phases. Chlorite or smectite-chlorite mixed-layer clays might be expected to form.

7 Natural evidence compared to laboratory results and theoretical prediction

It was brought up that Eberl's 2 months long laboratory tests conducted at 250°C, from which he found very obvious reaction of smectite towards illite, had been conducted at no water pressure, i.e. with only vapor pressure, and it was recommended to repeat the tests at 10 MPa water pressure.

Activation energies for breaking Si-O, Al-O bonds in silicates for beidellitization of smectite have been evaluated from laboratory hydrothermal tests with distilled water, yielding 20-27 kcal/mole and the figure 3200 for the pre-exponential coefficient A in Arrhenius' equation. Experiments with Mg and Ca in the water have given A-values that are 1000 to 10 000 times lower, indicating dramatically lower conversion rates and thus the obvious inhibiting effect of these cations.

Mg is strongly hydrated and is more firmly held in interlamellar positions than Ca, which is in turn less replaceable than Na. Li is most easily replaced by all other cations. If the groundwater has Ca and Mg as major cations, originally adsorbed Na would primarily be replaced by these two types of cations while K would be retained in the voids.

In summing up, Duwayne Anderson drew the following conclusions concerning the mechanisms involved in smectite-to-illite conversion:

* High lattice charge by replacement of tetrahedral silica by aluminum

* Precipitation of silica

* Influx of potassium to saturate the exchange capacity of the highly charged smectite

* Irreversible collaps of the high lattice charge smectite

Ten years later the following comments to the conclusions are relevant:

* J.J.Howard's statement: "There is no rate expression at this time in the transfer from low to high charge smectite. It appears that solution chemistry is of no help".

The meaning of this is simply that at that time it had not been demonstrated that the reaction was of Arrhenius type and that the mechanisms were not known in detail.

* J.J.Howard's statement: "Migration of Al to tetrahedral positions for replacing Si is hard to imagine".

If it is true that Al does not move from octahedral positions, it must be of external origin, i.e. emanating from dissolved silicates. Such aluminum usually forms Al(OH)-type compounds which would have to be broken down in order to make Al replace Si in tetrahedral positions. Hence, Al would rather form interlamellar complexes yielding chlorite. However, this cannot take place without any changes in the smectite lattice - Mg has to occupy 5 out of 6 octahedral positions (Figure 2-1) - and it also requires expulsion of initially present interlamellar cations. A more natural explanation for chlorite formation is neoformation, which requires access to free silica and magnesium supplied by the groundwater or from dolomite or other Mg-bearing minerals that become dissolved.

In turn, this suggests that "high-charge" smectite is not formed at all but that both illite and chlorite are neoformed

* J.J. Howard's reflexion: "The mechanism in supply of potassium to the high-charged sites is not well known".

In smectites of low charge K^+ is the least preferred interlamellar cation compared to Mg, Ca and Na such that any potassium in the system is severely inhibited in occupying interlamellar sites by the competing cations. However, the dehydratable K^+ is suddenly preferred over the other cations when layer charge is sufficiently high enough to overcome hydration energy, drive off the water, collapse the interlayer and result in a lower energy state.

Although Howard did not say this explicitely, it is not likely that conversion of this type is possible at all: collapse of stacks yielding 10 Å minerals must have another explanation and if true illite is formed it is likely to be a separate phase neoformed in the voids of the smectite clay.

Workshop convened at the Shoreham Hotel, Washington D.C., December 8-9, 1983 (25)

The purpose of the workshop was to follow up the colloquium held at Buffalo in 1982 and to focus on the detailed mechanisms in smectite-to-illite conversion, particularly the potassium source, and also to identify the change in physical properties that is associated with mineral changes.

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The following specific matters were discussed:

1. The general reaction involved in smectite-to illite conversion; preference of adsorbed cations (Eberl)
2. Potassium source and migration to yield illite (Altaner, Brusewitz)
3. Alpha and Beta radiation damage to bentonite (Beall, Ewing)
4. Physical state of interlamellar water (Carlsson, Fripiat)
5. Simulation of clay minerals/solution interaction using solid solution models (Fritz)
6. Effect of pH on smectite stability (Johnston & Miller)
7. Reaction sequence (Eberl)

1 General reaction type

Eberl pointed out that the reaction that yields illite from Na smectite not only involves release of Na and Si but also produces water, which increases the water content and leads to higher hydraulic conductivity:

$$K^+ + Al^{3+} + \text{Na-smectite} \Rightarrow \text{Illite} + Si^4 + Na^+ + H_2O \qquad (5)$$

The key question raised at the Buffalo meeting why potassium would be able to displace the strongly hydrated Ca was discussed by Eberl, who considered competition between K^+ and Na^+ in the first place:

Both sodium and potassium ions are assumed to be hydrated in interlamellar positions but the hydrated potassium ion is somewhat smaller than the sodium ion and therefore more strongly adsorbed. Assuming both ions to have an attraction for the clay and an attraction for the water hydrate, one can estimate that if the former is increased by increasing the lattice charge and the latter reduced by compressing the interlamellar space (squeezing out water), dehydrated potassium will be much more strongly fixed than dehydrated sodium.

Johnston claimed that pH drops strongly at heating and that Na and Ca smectites rapidly lose their capacity to buffer pH at higher temperatures than 150°C. We will see later that this can be explained by heat-induced transformation from the EF montmorillonite crystal structure to the HEW version.

2 Potassium source and migration

Altaner showed data from the Montana bentonite, which was formed from ash-fall 30-40 million years ago and which had been referred to at the Buffalo meeting as an example of heat-induced alteration of smectite to illite. These data, which resulted from analysis of 32 sites and particularly from a 2.5 m thick bentonite layer embedded in shale, demonstrated that there is a symmetric zonation from the illite-rich boundaries to the relatively smectite-rich central part. The K_2O chemistry was stated to mimic the distribution of illite and Altaner claimed that potassium probably emanated from long-range mineralogical breakdown of potassium-bearing minerals in the area.

Considering the potassium profile in the bentonite and the potassium/argon age difference as a measure of the minimum time for reaction, the diffusion coefficient for K migration could be calculated, based on the conclusion that the K-concentration in the groundwater of the shales was 200 ppm. The D-value turned out to be 10^{-11} to 10^{10} m /s.

3 Alpha and beta radiation damage to bentonite

This type of degradation requires contact of the canister-embedding clay/water system with spent fuel that gives off Pu and Am, which migrate, in a process controlled by ion-exchange, into the clay. One prerequisite is thus that the canister has a defect.

G.W.Beall (25) referred to experiments with bentonite exposed to alpha radiation and found that complete destruction, yielding an amorphous silicious mass, is obtained when the montmorillonite is saturated with plutonium and americium, which corresponds to around 5×10^{18} alpha doses per gram of clay. Using a reasonable number of alphas per ton of spent fuel and considering a single hole (manufacturing defect) in a canister from which the radionuclides migrate to form a cone of completely Pu or Am-saturated clay from the hole to the rock wall of the deposition hole, he found that 200 years would be required to destroy the bentonite of a 20/80 bentonite/quartz mixture, which, for 100 % bentonite, would give about 1000 years, which is of course very critical.

Beta radiation was concluded to have one major effect on wet smectite clay: it causes radiolysis producing carbon dioxide and hydrogen from free porewater, interlamellar water and organic substance.

4 Physical state of interlamellar water

This matter was assumed to have an impact on the mobility of interlamellar water molecules and hence of the ease of replacement of interlamellar cations and on the compressibility of the stacks ("tactoid") of smectite flakes, which could be of importance for the dehydration involved in smectite-to-illite conversion.

Fripiat stated, as based on nuclear magnetic resonance investigations (NMR), that only interlamellar water, i.e. not water adjacent to the external stack surfaces, has properties different from those of liquid water. The difference can be expressed in terms of the coefficient of self- diffusion, which is two orders of magnitude lower than of liquid water.

He claimed that individual smectite flakes do not exist, except, possibly when Li is the adsorbed cation, and that the thickness of Ca stacks of flakes is about twice that of Na the stacks.

Carlsson gave values of the relaxation time T_2 evaluated from proton NMR testing of montmorillonite saturated with different cations. They indicated that the mobility of water decreases with increasing electrolyte concentration and increases with increasing temperature.

Banin addressed thermal effects and influence of adsorbed ions on free swelling of smectites. Data were shown to indicate decrease in specific surface area, i.e. collapse of stacks, with temperature of heating for smectites with different adsorbed cations. The temperatures for initial collapse of smectites (open conditions) were indicated in relation to the adsorbed cation type as shown in Table 2-3:

Table 2-3 Temperature for initiation of collapse of smectite stacks

Element	Temperature°C
Li, Cu	100
Mn, H-Al	200-300
Fe	400

The reason for the different behavior was stated to be different hydration power of the cations. Lithium is univalent and copper bivalent, while manganese must have been bi-or trivalent in the experiments and iron was in trivalent form in the experiments. H-Al can be interpreted as trivalent aluminum.

5 Simulation of conversion by applying solid solution models

For a general clay formula like that of a simple Al-Mg smectite Fritz used the expression in Eq.6:

$$(Si_{4-x}\text{-}xAl_x)_T(Al_2 - 2yMg_y/3)_O O_{10}(OH)_2K_x \qquad (6)$$

where T stands for tetrahedral and O for octahedral positions. He stated that one can consider different ternary sets of pure end members as constituents of a quaternary unique set of possible end members like the ones indicated in Figure 2-16 (muscovite, phlogopite, pyrophyllite and talc).

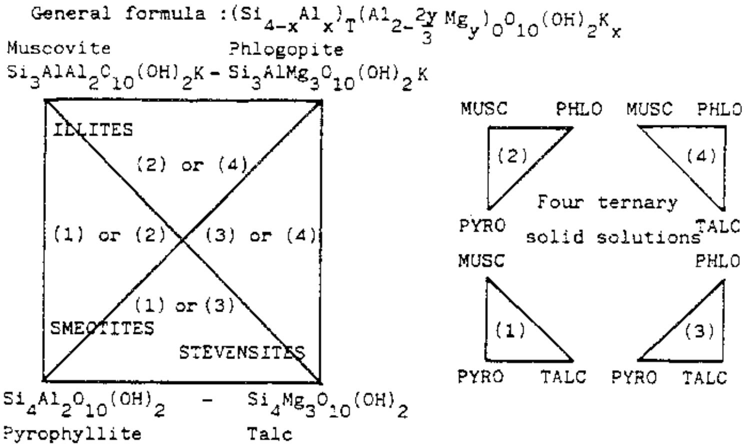


Figure 2-16 Possible ternary solid solutions in the pyrophyllite-muscovite-talc-phlogopite system (Fritz)

6 Reaction sequence; Ostwald's step rule

Eberl emphasized the idea of the Ostwald step rule in evaluating laboratory hydrothermal tests. Thus, he stated that reactions take place in steps, which requires very long duration of the experiments for identifying the ultimate reaction products.

Ten years later, approximately, the following comments to the conclusions appear to be relevant:

* D.Eberl's conclusion concerning the required processes for illitization: "A prerequisite for replacement of Na^+ by K^+ is both an increase in lattice charge and compression to squeeze out water".

The meaning of his conclusions can be interpreted such that the cation replacement requires excess potassium ions in the solution, creating K-smectite, while collapse requires a sufficiently high effective pressure. Possibly, the collapse may take place under rather moderate effective pressure if the temperature is high. This would imply that true illitization cannot be simulated in laboratory hydrothermal experiments with completely water saturated clay unless an ef- fective pressure is applied, a condition that can also be achieved by drying.

* T. Carlsson's conclusion: "The decrease in interlayer water mobility is in the order Ca=Sr<K<Na".

This implies that K^+ would replace interlamellar Na^+ without great difficulties, but not Ca^{2+}. The difference between Na^+ and K^+, expressed in terms of T_2, is only about 15 %, which is hardly sufficient for making "external" K^+ entering and displacing Na^+. Carlsson showed that there is a successive increase in T_2 when the water content is increased, which can be interpreted as long-range influence on the organization of water or as large number of interlamellar hydrates, a possibility that was denied by Fripiat. The most relevant explanation is that the recorded T_2:s reflect the proton relaxation times for both "external" and "internal" water, which Carlsson did not separate. We will see later that this explains the temperature-dependent structure of the interlamellar water.

* J.J. Fripiat's statement: "Smectite flakes practically always appear in the form of stacks, which are thicker for Ca-smectite than for Na-smectite".

This agrees very well with our present understanding of the microstructural constitution of smectite clays as examplified by the general microstructural model (GMM) (16). Also, his statement that no more than 3 hydrate layers are influenced by the clay lattice is compatible with this model.

* S. Altaner's statement: "K^+ in groundwater is a possible potassium source".

While K-bearing minerals have been proposed as the major source of potassium for converting smectite to illite, it appears that the content of K^+ dissolved in the porewater of sediments or in the rock matrix of crystalline rock may well be a major potassium source. The concentration in seawater is actually as high as 400 ppm.

2.2 INTERMEDIATE (1983-1992)

2.2.1 Starting point

The HLW repository planning concerning buffers and backfills that proceeded through the years 1983 to 1992 in Sweden rested on the statements concerning smectite longevity on which there was complete agreement in the two workshops held in the US, namely:

* The general theory of thermodynamics of hydrothermal systems yields uncertain results due to lack of reliable thermodynamic data but recently proposed geochemical codes serve as promising tools for predicting alteration of mineral assemblies of the sort we are dealing with here. We will come back to this in a later chapter.

* Although trioctahedral smectite species are not altogether different from dioctahedral ones, relatively important structural rearrangement is required to convert i.a. montmorillonite to hectorite or saponite, which also suggests that they have different origin in nature, although it is theoretically possible that salt groundwater holding much magnesium could yield conversion to these minerals by uptake of Mg in octahedral positions. On the other hand, the close relation between the three dioctahedral species montmorillonite, beidellite and illite (hydrous mica) is very obvious and suggests, at a first sight, easy conversion among them. Hence, beidellite results from replacing one fourth of the tetrahedral silicons and the octahedral magnesium in montmorillonite by aluminum. Introduction of potassium in beidellite without changing the lattice constitution at all yields the formula $(OH)_4K_2(Si_6Al_2)Al_4O_{20}$, which is a common composition of hydrous mica. While potassium in interlamellar positions of montmorillonite is rather easily exchanged, it is fixed in beidellite due to the shallow charge positions and the suitable size of the potassium ion. All this suggests that the most simple and straightforward model of alteration of montmorillonite to illite is transformation to beidellite as a first step, and then uptake of potassium yielding illite in a second step.

However, looking more closely at the prerequisites for conversion of montmorillonite to beidellite, access to aluminum and enough energy to replace tetrahedral silicon by aluminum and to drive out magnesium from the octahedral sheet are needed for the conversion. While replacement of tetrahedral silicons can be imagined to occur by assuming octahedral aluminum to move to tetrahedral positions, external aluminum is required for replacing the aluminum lost and for replacing the magnesium. Obviously, this cannot take place unless external aluminum is available for which dissolution of accessory minerals like feldspars is required, an alternative being cannibalism, i.e. dissolution of smectite to yield aluminum.

* The local conditions for access to external aluminum is of utmost importance for the conversion of montmorillonite to beidellite. Naturally, further conversion to illite requires access to potassium, which is therefore an additional major criterion. The conversion process involving charge increase through replacement of tetrahedral silicond by aluminum will be termed PROCESS I in the rest of the report. It should be pointed out that if this is the only conversion mechanism, very pure montmorillonite clay confined in a closed reaction vessel filled with electrolyte-free water would be expected to be perfectly stable for any period of time, with the exception that part of the mineral mass will be dissolved and precipitated on cooling.

* An alternative mechanism of converting smectite to non-expansive hydrous mica is neoformation of the latter by precipitation from a solution containing silica, aluminum and magnesium, emanating from dissolving smectite, and with uptake of external potassium being the triggering factor. This conversion process will be termed PROCESS II in the rest of the report.

* It is obvious that there may be great difficulties in distinguishing processes of types I and II unless one can safely identify the nature and origin of the clay minerals. As an example, attempts to use mixed-layer minerals in sedimentary rocks as indicators of the depth of their catagenetic alteration may be totally incorrect if such identification is uncertain. Similarly, if the original material in deep profiles varied with respect to the constitution of the smectite minerals, any interpretation of possible conversion mechanisms can naturally be questioned.

2.2.2 Source of information

Comprehensive field investigations and hydrothermal testing were made by a large number of investigators in the intermediate period and the literature gives a huge number of published reports that deal with the matter of smectite conversion. We will confine ourselves here to give a summary of the outcome of a series of literature-reported investigations and to focus on SKB-related research comprising three detailed field studies, which serve as reference cases, and on three series of hydrothermal experiments performed in the laboratory in order to simulate the conditions in a repository with the smectite clay confined and fully water saturated throughout the tests. Also, NMR analyses for characterization of the physical state of the porewater in smectite clay will be referred to since they supply information of the dehydration properties of such clays.

2.2.2.1 Literature

Confining ourselves to literature data that are relevant to the issue of long-term stability of canister-embedding smectite clay, major contributions in the intermediate period have been published in special issues of journals like Clay Minerals and Applied Geochemistry with summing up of current work carried out in various countries. Most of this work did not concern HLW but rather formation and accumulation of hydrocarbons but has an indirect bearing on the prospect of smectite clay survival in HLW repositories. We will cite a number of papers of fundamental importance for the understanding of the conversion from smectite to illite and chlorite, referring to the terms Process I and Process II.

PROCESS I

Field data - General remarks

In light of the outcome of the earlier studies referred to in the preceding text, i.e. that the initial composition of the clay mineral assemblage in a natural clay mass may vary to an extent that makes it hard to draw conclusions concerning mineral alteration processes, it is appropriate to mention investigations of the Ordovician "metabentonites" of Kinnekulle, southwestern Sweden, which have been studied with respect to their constitution and properties as well as to their mineralogical composition. The Kinnekulle case will be described in greater detail later in this chapter but two of the mineralogical studies deserve to be commented on already at this early stage since they show the difficulty in drawing definite conclusions concerning the nature of the parent minerals and the exact mechanisms in S→I conversion. A first difficulty in comparing the composition of different parts of the series of bentonite layers, which was formed by transformation of volcanic ash into smectite 450 M years ago, is that 35 M years passed between the formation of the upper and lower parts of the about 5 m thick sequence, which may have involved deposition of initially different material. A second difficulty is that early changes in mineral composition may have taken place before the basalt intrusion, that is thought to have caused conversion of the smectite, occurred 150 M years after the formation of the bentonites..A third and major difficulty is that laboratory routines give different results. Thus, one investigation performed by Velde & Brusewitz (26) led to the conclusion that the smectitic component of the I/S mixed-layer of the Kinnekulle bentonite, was originally low-charge montmorillonite and is now high-charge montmorillonite with 0.65-0-67 charges per formula unit, while a second investigation, performed by von Moos et al (27), showed much lower charge of the present montmorillonite; i.e. only about 0.4 charges per FU, i.e. with unaltered low-charge montmorillonite representing.the smectite phase. These two studies, which were both conducted with great care, hence demonstrate the difficulty in characterizing smectite clay and the problems in explaining how and to what they have been altered. This is explicitely stated by Brusewitz in a separate paper (28) saying: "..discrepancies (concerning the number of charges per FU) probably do not reflect different I/S compositions; more likely they result from different sample pretreatments..".

We will see that these difficulties obscure the outcome of the evaluation of comparative studies for deriving the nature of smectite alteration that has occurred in nature.

Field data - major conclusions

Meunier et al. summed up the work on S→I conversion that concerns mixed-layers and that has been conducted in the intermediate period (29,30). They pointed out the following major findings:

* Dioctahedral smectites behave as mixed-layer structures made up of three kinds of randomly stacked layers: non-expandable 10 Å layers, partly expandable 14 Å layers, and fully expandable 17 Å layers. This is explained by inhomogeneous distribution of the layer charge

* Dioctahedral minerals can be described in terms of a M^+ - 4Si - R^2 system (Figure 2.17)

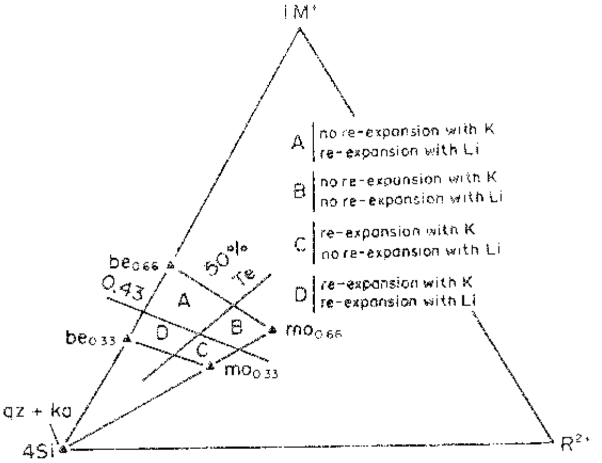


Figure 2-17 The M^+ - 4Si - R^2 system (29). A) is high-charge beidellite, B) high-charge montmorillonite, C) low-charge montmorillonite, and D) low-charge beidellite. qz is quartz and ka kaolinite. 50 % Te represents 50 % of the tetrahedral charge, 0.43 represents the border between low- and high-charge domains. Indices 0.33 and 0.66 represent low-charge and high-charge end members

* I/S mixed-layers from the same geological environment are chemically distributed along tie-lines between a unique illite pole and a unique smectite. Despite crystallographic evidence of differently charged layer components, a smectite species, like montmorillonite, can be considered as a solid solution with a certain low- and high-charge ratio, like the plagioclase series is described by the albite/anorthite ratio

* The expandable I/S mixed-layers of Cretaceous bentonites have a wide scattering in the M^+ - 4Si - R^2 graph, while older deposits are aligned between the high-charge illite pole and montmorillonite pole between the 0.33 and 0.66 end member poles (Figure 2-18). The regularity of the composition of older deposits implies or suggests two *successive* mineral reactions: first formation of 100 % montmorillonite crystals with both low- and high-charge

layers, and then progressive formation of I/S mixed-layers with increasing I. The first reaction leads to high-charge montmorillonite, quartz and kaolinite. The second reaction implies that I/S mixed-layers crystallize according to the paths: montmorillonite + Al^{3+} → illite + Si^{4+}, or montmorillonite + K^+

* The successive increase in the number of illite layers in I/S mixed-layers should no longer be considered as a layer-to-layer transformation but as a crystalline growth process. Analysis of mixed-layer particle size shows an increase indicating an Ostwald ripening effect.

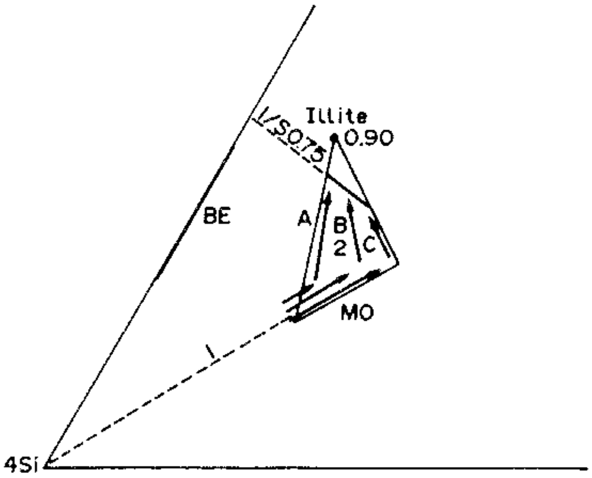


Figure 2-18 Formation of I/S mixed-layers in bentonite deposits according to Meunier & Velde (30). A) Carboniferous from Poland, B) Silurian from Great Britain, C) Silurian and Ordovician from Sweden and USA. 1) denotes formation of pure montmorillonite, 2) formation of I/S mixed-layers. MO and BE represent theoretical compositions of montmorillonite and beidellite, respectively

Laboratory data

A number of published experimental studies were performed in the intermediate period and those of observed collapse of smectite to 10 Å forms and of evaluated activation energy for such transformation are of particular interest. They will be summarized and commented on here.

* Couture performed hydrothermal experiments with exposure of rather soft Na bentonite clay to vapor with a temperature of 150-200°C and found that it caused a very significant irreversible loss of the swelling capacity and strong increase in hydraulic conductivity (31). It can be assumed that the exposure to hot vapor caused "coagulation" of the particle network and that cementation took place in the cooling phase so that part of the microstructural

rearrangement was permanented. This probably occurred by precipitation of released silica and aluminum

* Eberl et al demonstrated that smectite with potassium as exchangeable cation partly collapses to 10 Å non-expandable "illite" on cyclic drying/wetting at 60°C (32). This study comprised 12 smectites that were wetted and dried 100 times, from which it was concluded that the major part of the conversion took place in the first 20 cycles and that it led to 30-40 % "illite" (Figure 2-21). This figure suggests that one drying/wetting cycle would not convert more than 10 % of the smectite to non-expandable 10 Å minerals but higher temperatures may cause more comprehensive changes. There are indications that the conversion yields random I/S mixed-layers rather than illite (32).

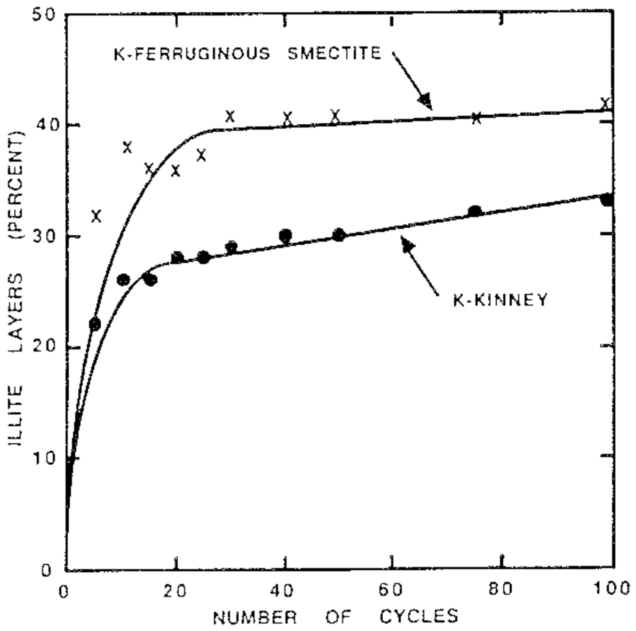


Figure 2-21 Formation of "illite" in smectite by cyclic wetting/drying at 60°C (32)

* The activation energy for creating the lattice reorganization that is required for conversion of smectite to illite has been found to be low as evaluated from laboratory hydrothermal tests. Thus, early tests performed by Eberl & Hower gave figures in the range of 16-23 kCal/mole for the formation of I/S from Wyoming bentonite starting at 150°C. Values as low as 4-8 kcal/mole have been reported for collapse of K-saturated smectite, which suggests that they represent the breakage of hydrogen bonds that is required for dehydration.

PROCESS II

Field data

Meunier et al in discussing possible evidence of PROCESS I also pointed out several examples of PROCESS II mechanisms that became obvious in the intermediate period. In fact, already in 1985 Pollastro suggested an I/S conversion model according to which illite is formed by partial dissolution of the smectite component of expandable I/S aggregates and precipitation on low-expandable aggregates (33). The same year Nadeau et al suggested a somewhat similar alteration mechanism for S→I conversion (34), which is in agreement, in a general sense, with comprehensive field investigations performed in Japan by i.a. Inoue et al (35). Güven stated that hydrothermally treated smectite has two diagnostic forms: a flakey or mossy appearance representing interstratified I/S and lath-shaped minerals representing illite (36). Major findings are:

* There are indications that two separate phases grow on the expense of the original smectite: I/S mixed layer laths and illite hexagons (37). A slightly different observation by Güven is that illite laths grow in montmorillonite drilling mud exposed to hydrothermal conditions representing those in very deep boreholes (36)

* Compositional variations in clastic reservoirs offshore Norway indicate that illite and chlorite were continuously recrystallized at depths where the temperature has been in the interval 100-160°C (38). Early-formed diagenetic chlorite appearing as void fillings are of particular interest since it is concluded to have been initiated at about 70°C, i.e. a temperature that will be reached in KBS3 deposition holes

* Jurassic North sea sediments investigated with respect to S→I conversion are reported to contain randomly and ordered I/S as well as pure illite and kaolinite and traces of chlorite and vermiculite, with all minerals except the ordered I/S being transported from the highs in the Norwegian-Danish basin and the Central Trough (39). This underlines the importance of identifying the parent material in the search for S→I conversion mechanisms. The I/S is concluded to have escaped alteration despite the rather large depth (2983 m) and relatively high temperature (at least 85°C). The ordered I/S, representing 20 Å periodicity rectorite of diagenetic origin, was found in deeper wells (3444 and 3938 m) where the temperature was estimated at 115-180°C.

An important conclusion concerning identification of the parent material in S→I conversion has been drawn from other North Sea investigations, namely that for certain sediments, like mudrock, there does not seem to be any practical way of separating detrital illite and detrital I/S from authigenic I/S clay or neoformed authigenic illite

* In contrast to earlier investigations, Gulf coast sediments exhibit different depths for S→I conversion in different areas (40). Thus, onset of the conversion varies from 1700 m to 2600 m and completion from about 2300 to 4000 m. Similarly, the temperatures vary widely: 58°C to 92°C for the onset, and 88°Cto 142°C for the completion of the conversion. The variability in temperature for conversion may be due to chemical heterogeneity of the original smectite and the composition of the surroundings. The kinetics may also be controlled by special features. Thus, the migration of necessary reactants, primarily K^+, may depend on the various initial and successively formed paths, which become wider due to the lower density of illite than of smectite. The model of Ahn & Peacor is favored; i.e. that smectite domains (aggregates of aligned flakes) dominate initially and that - in the course of conversion - illite stacks (packets or domains) grow within a shrinking matrix of smectite, i.e. on the expense of parent smectite (Figure 2-19). At completion (70-80 % illite), the clay is characterized by large illite domains with subparallel orientation

* Dissolution of smectite and neoformation of illite sets magnesium and iron free, which supply elements for formation of chlorite.

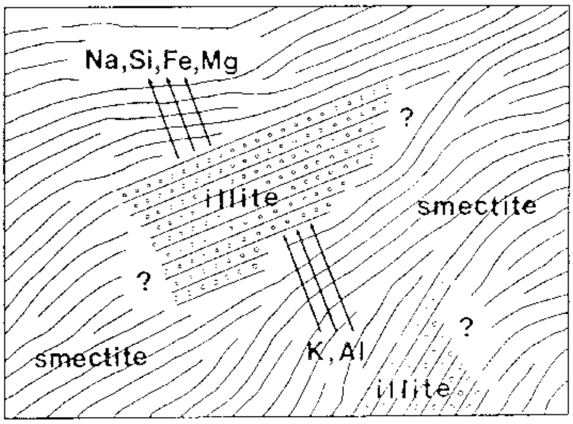


Figure 2-19 Schematic picture of conversion of smectite to illite (41)

These studies led to systematic investigations employing thermodynamics and, above all, high resolution transmission electron microscopy including element analyses. Much effort was also put in XRD investigations for distinguishing mineral phases, and a number of conclusions were drawn of which the major ones can be summarized in the way listed below. *However, the very important issue of certifying the origin and nature of the mineral constituents that are supposed to be altered, still requires further consideration. Thus, unless the temperature history and the parent material are accurately defined, no safe* *conclusions can of course be drawn concerning possible conversion mechanisms and degree of alteration.*

* Clay minerals can and should be considered as solid solutions. This can be made by applying two major models commonly referred to: The one proposed by Tardy & Fritz described earlier in this chapter, and the model proposed earlier by Mattigod & Sposito, which deals with the clay minerals as polymerization of simple hydroxides (42). The latter only refers to homoionic systems and is less generally applied than the firstmentioned one, according to which coexisting solutions in I/S mixed-layers can be regarded as separate phases

* I/S mixed-layer *particles* can be regarded as consisting of elementary smectite and illite (K-rectorite) lamellae (flakes) with a thickness of 10 and 20 Å, respectively, as illustrated in Figure 2-20, (43). Thinner illite particles than about 50 Å yield 20 Å X-ray diffraction (XRD) peaks, representing ordered systems, while thicker ones yield intraparticular 10 Å reflections (Figure 2-20),(44). This model of stacking of smectite and illite lamellae may be used for defining ordered as well as disordered systems of I/S layers. Thus the coupling of 2:1 lamellae depends on the charge distribution: tetrahedral sheets may have a very low charge as in montmorillonite or a high charge as in illite and this produces polarity. A 30 Å I/S particle may hence be formed by one central, non-polar illite "particle" and two polar lamellae with their high-charge ("illitic") tetrahedral sheets connected to the central particle by K^+ and exposing their reactive smectite tetrahedral sheets to the surroundings. The same arrangement, i.e. with stacked non-polar illite particles and reactive external smectite sheets, will yield stable particles of any thickness. Bringing such particles together yields I/S particles with maximum two interacting smectite tetrahedral sheets, yielding regular SISISISI, SIISSIIS or SIIISSIIIS or even SIIIISSIIIIS, or irregular stacks of I and S. Those with interacting S sheets will not be tightly connected, which suggests that intense mechanical agitation will tend to yield particles of types SIS, SIIS, SIIIS etc. We will return to this matter in a later chapter since it turns out to be decisive for the definition of mixed-layer minerals as well as for the understanding of how illitization takes place.

* The kinetics involved in the conversion of smectite to illite can be modeled by assuming that reorganization of the crystal lattice or dissolution/neoformation is an Arrhenius-type process, i.e. controlled by the temperature. Two such models have been proposed, one by Bethke and Altaner (45), which is purely theoretical and assumes that different groupings of smectite and illite lamellae (SSS, SSI, and ISI) have different relative reactivities, yielding the diagram in Figure 2-21 for the geothermal gradient 25°C/km, and the earlier mentioned semi-empirical model proposed by Pytte, with the K/Na ratio as major parameter in addition to the activation energy and the temperature (8).

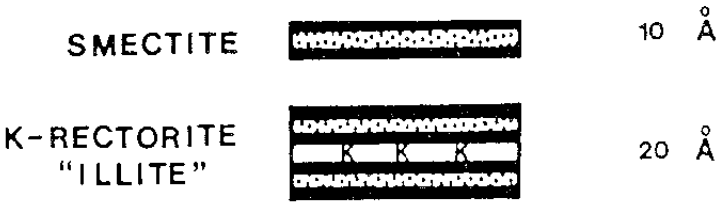


Figure 2-19 Elementary particles of smectite and K-rectorite (illite). Black lines represent tetrahedral sheets and hatched areas octahedral sheets (43)

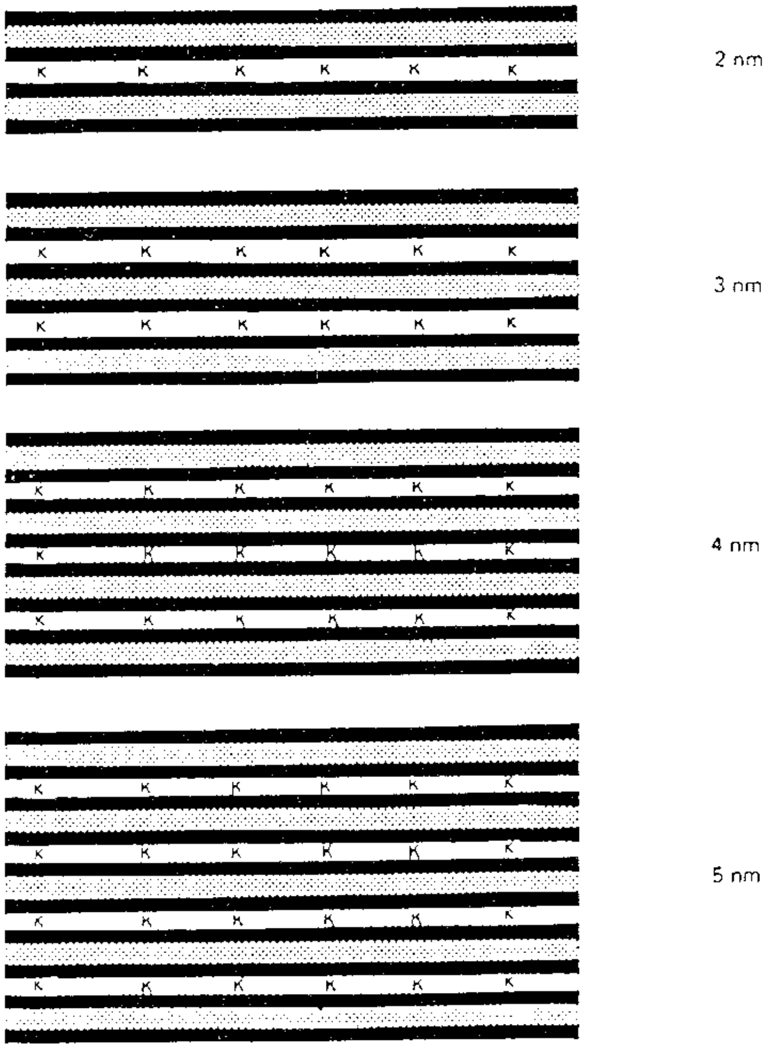


Figure 2-20 Schematic picture of illite stacks (44)

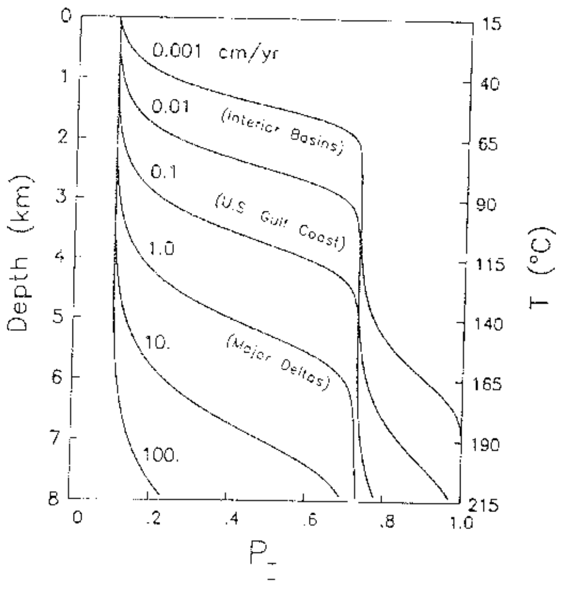


Figure 2-21 Calculated rate of conversion of smectite to I/S-mixed layers at different rates of overburden growth. P_I represents the illite fraction (45). For a depth of 3-4 km in sediments formed slowly like in the US Gulf Coast the smectite content would be in the range 40-80 %, i.e. which is in line with Figure 2-2

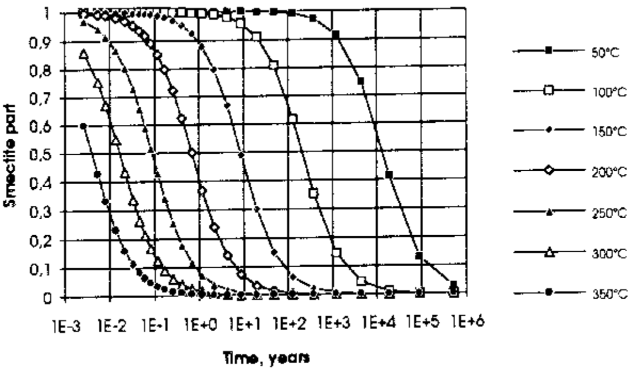
Pytte's model specifies the rate of reaction to be as follows:

$$-dS/dt=Ae^{-U/RT} f(K^+/Na^+)g(S) \qquad (6)$$

where A=Constant
U=Activation energy
K^+ and Na^+=Concentration of potassium and sodium, respectively
S=Mole fraction of smectite in I/S assemblages
f=Function of K/Na ratio
g=Function of smectite concentration in I/S
R=Universal gas constant
T=Temperature

The model has been used in various contexts applying different activation energies. Inserting the constants proposed by Huang et al. (46) one arrives at a conversion rate that is strongly dependent on the activation energy and on the temperature as demonstrated by the diagrams in Figures 2-22 to 2-25.

smectite fraction at start	S0		0	1
time	t	s		0
frequence factor	A	1/s		80800
activation energy	Ea	cal/mol		20000
gas constant	R	cal/(deg*mol)		1,987
temperature	T	K		323
K+ concentration	(K+)	mole/l		0,001



smectite fraction at start	S0		0	1
time	t	s		0
frequence factor	A	1/s		80800
activation energy	Ea	cal/mol		20000
gas constant	R	cal/(deg*mol)		1,987
temperature	T	K		323
K+ concentration	(K+)	mole/l		0,1

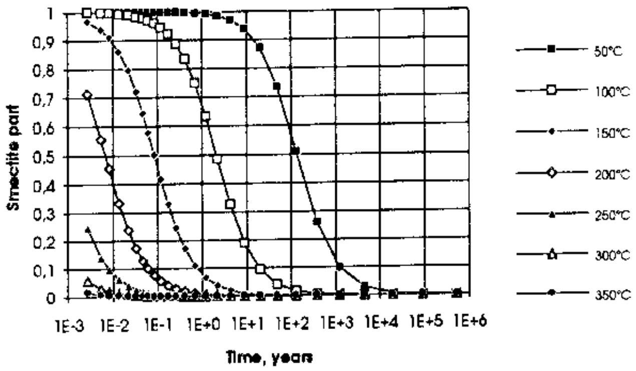
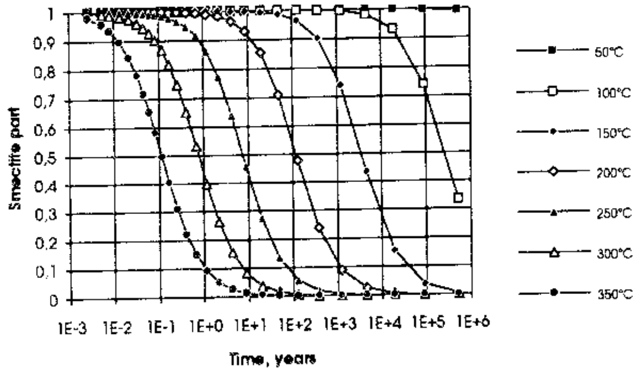


Figure 2-22 Rate of conversion of smectite to illite according to Pytte's model. Activation energy 20 kcal/mole. Upper: K^+ concentration 0.001 moles per liter (about 40 ppm). Lower: K^- concentration 0.1 moles per liter (4000 ppm)

smectite fraction at start	S0	0	1
time	t	s	0
frequence factor	A	1/s	80800
activation energy	Ea	cal/mol	27000
gas constant	R	cal/(deg*mol)	1,987
temperature	T	K	323
K+ concentration	(K+)	mole/l	0,01



smectite fraction at start	S0	0	1
time	t	s	0
frequence factor	A	1/s	80800
activation energy	Ea	cal/mol	27000
gas constant	R	cal/(deg*mol)	1,987
temperature	T	K	323
K+ concentration	(K+)	mole/l	0,1

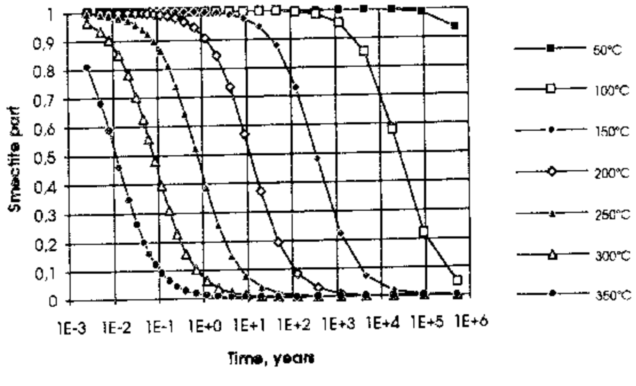
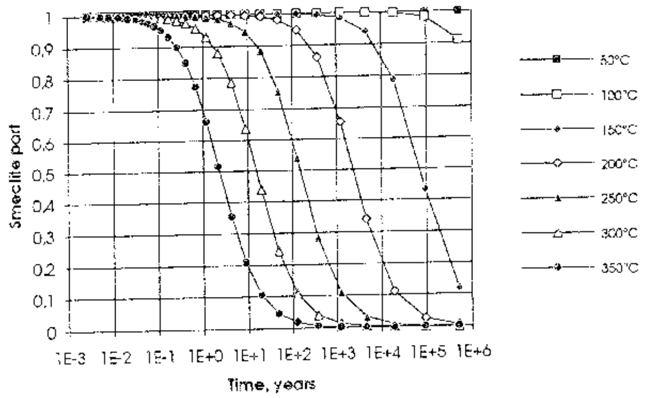


Figure 2-23 Rate of conversion of smectite to illite according to Pytte's model. Activation energy 27 kcal/mole. Upper: K^+ concentration 0.01 moles per liter (about 400 ppm). Lower: K^+ concentration 0.1 moles per liter

smectite fraction at start	S0	0	1	
time	t	s	0	
frequence factor	A	1/s	80800	
activation energy	Ea	cal/mol	27000	
gas constant	R	cal/(deg*mol)	1.987	
temperature	T	K	323	623
K+ concentration	(K+)	mole/l	0.0005	



smectite fraction at start	S0	0	1	
time	t	s	0	
frequence factor	A	1/s	80800	
activation energy	Ea	cal/mol	26000	
gas constant	R	cal/(deg*mol)	1.987	
temperature	T	K	323	623
K+ concentration	(K+)	mole/l	0.0005	

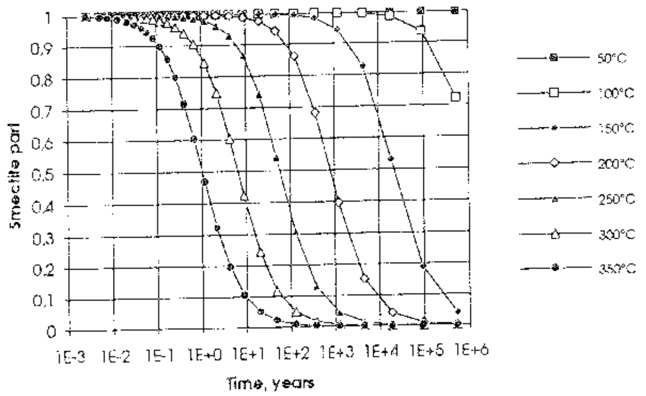
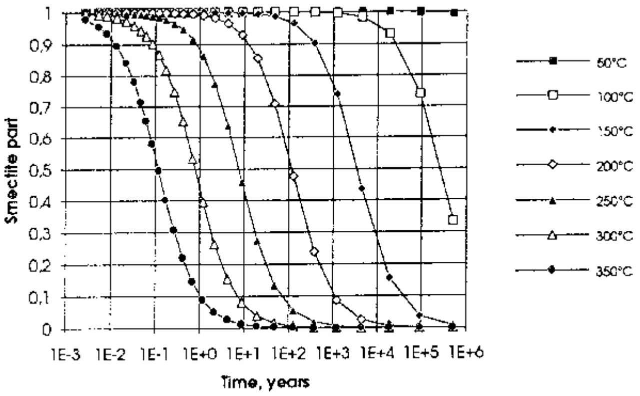


Figure 2-24 Rate of conversion of smectite to illite according to Pytte's model. K^+ concentration 0.0005 moles per liter (about 20 ppm). Upper: Activation energy 27 kcal/mole. Lower: Activation energy 26 kcal/mole

smectite fraction at start	S0		0	1	
time	t	s		0	
frequence factor	A	1/s		80600	
activation energy	Ea	cal/mol		27000	
gas constant	R	cal/(deg*mol)		1,987	
temperature	T	K		323	623
K+ concentration	(K+)	mole/l		0,01	



smectite fraction at start	S0		0	1	
time	t	s		0	
frequence factor	A	1/s		80600	
activation energy	Ea	cal/mol		26000	
gas constant	R	cal/(deg*mol)		1,987	
temperature	T	K		323	623
K+ concentration	(K+)	mole/l		0,01	

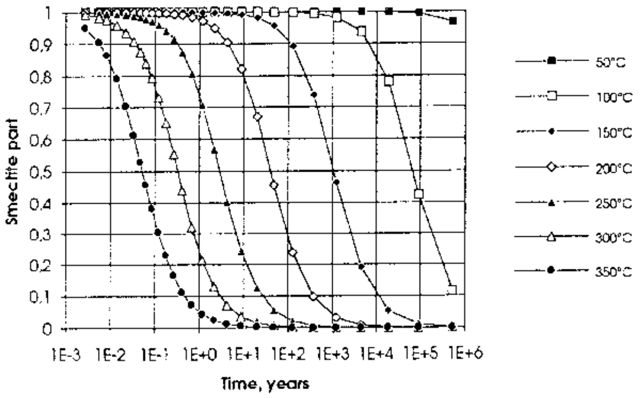


Figure 2-25 Rate of conversion of smectite to illite according to Pytte's model. K^+ concentration 0.01 moles per liter (about 400 ppm). Upper: Activation energy 27 kcal/mole. Lower: Activation energy 26 kcal/mole

One finds from Figure 2-22 that if the activation energy for conversion to illite would be 20 kcal/mole, almost complete conversion in somewhat more than 1000 years would be caused at 100°C if the potassium concentration is about 40 ppm, and in a couple of decades if the concentration is two orders of magnitude higher. At 200°C the latter potassium concentration would give almost complete loss in smectite in less than a month. This is not in agreement with experimental results as we will see below and the activation energy - as it appears in Pytte's formula - is therefore higher. Figure 2-23 shows that 50 % conversion to illite at an activation energy of 27 kcal/mole and a potassium concentration of 40 ppm would require several hundred thousand years and some thirty to forty thousand years when the potassium concentration is 400 ppm. Also, one finds that about 70 % smectite would remain after a couple of months at 250°C at the higher potassium concentration, which is supported by certain hydrothermal tests as referred to in the subsequent paragraph. Figure 2-24 shows the interesting fact that, according to Pytte's model, insignificant conversion to illite would be caused at 100°C even in several hundreds of thousands of years irrespective of whether the activation energy is 26, 27 or 28 kcal/mole if the potassium concentration is as low as is commonly the case at large depths in crystalline rock, i.e. 20 ppm. On the other hand, marine conditions yielding K^+ values of 400 ppm, would give 50 % conversion at 100°C in somewhat more than 50 000 years as indicated by Figure 2-25. We will return several times to these diagrams in order to draw conclusions regarding the validity of Pytte's model in the present context.

Laboratory investigations

Laboratory investigations of relevance to PROCESS II have been reported in the intermediate period, primarily concerning the role of water in the S→I conversion process and mineral transformations in hydrothermal experiments. Four such studies deserve mentioning not because they give any definite proof or even safe indication of neoformation of illite but because they offer valuable information on the importance of the conditions under which smectite undergoes alteration and on the difficulty of identifying the true nature of illite in I/S.

The first study was performed by Whitney et al. who made a comprehensive and very informatory investigation of hydrothermal alteration of montmorillonite (SWy-1 sample of the <0.1 μm) saturated with potassium and mixed with distilled water to water contents ranging from 5 to 100 % (47). The samples were contained in tight gold capsules that were heated to 250-400°C and 100 MPa pressure for up to 60 days. It was demonstrated that the water content is of fundamental importance for a number of involved processes, namely:

1. At the lowest water contents the percentage of expandable layers (S) in I/S was about 82 % after 60 days, while the percentage was 57 % at 100 % water content. 10 % water content gave about 62 % (Figure 2-26)

2. The reaction rate was significantly slower at low water contents. Thus, at 5 % water content the reaction apparently stopped after about 30 days, while at 100 % water content it continued at a rate that would imply around 40 % expandability (proportion of smectite layers) after 1 year at 250°C. The reported kinetic data are in approximate agreement with Pytte's model, applying the activation energy 27 kcal/mole, but the fact that the water/solid ratio has a significant effect on the rate of reaction demonstrates that the model lacks an important parameter, namely the rate of diffusion of dissolved species in the clay/water system

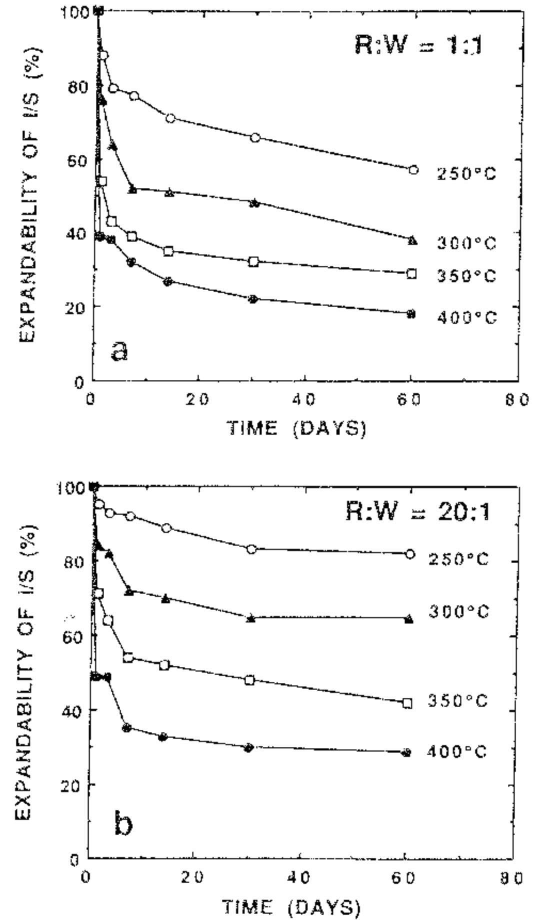


Figure 2-26 Reaction trends for illitization at different water contents and temperatures (47). Upper: R:W=1:1, i.e. 100 % water content(ratio). Lower: R:W=20:1, i.e. 5 % water content. The term "expandability of I/S" is equivalent to "fraction of smectite layers of the I/S".

3. At high water contents significant amounts of "illitization" byproducts were precipitated: chlorite, cristobalite and quartz, while at low water contents only amorphous silica was produced in opal form in addition to the illite. It was found that the I/S was more difficult to disperse and orient in specimens extracted from samples with lower water contents, suggesting enhanced cementation at grain contacts. Although Whitney did not specify it, neoformed illite might well have served as a cementing agent

4. Non-saturated conditions with respect to water significantly retards illitization

The second study was performed by Eberl et al. (48). It had the form of hydrothermal studies on montmorillonite clay (including some beidellite) at very high water contents using low temperatures (30 and 60°C) with and without drying/wetting cycles. Solutions of KOH with very high pH were used and it was found that illite formed up to about 30 % after 270 days. Some reduction in expandability was observed also when distilled water was used. It was concluded that I/S of R1-type and discrete illite had been formed and that drying/wetting accelerated the conversion in the experiments, which were conducted at pH conditions that are geologically unrealistic but resemble those in cement porewater (9-13).

The third study was performed by Veblen et al. for identifying the nature of I/S material by applying High Resolution Transmission Electron Microscopy (HRTEM) with electron diffraction, ordinary transmission electron microscopy (TEM), and XRD (49). The major conclusion was that I/S in hydrothermally altered volcanic rock from the Japanese volcano Showa Shintzan and another similar material, contained very thin, coherently stacked crystallites that extended across the fundamental particles postulated by Nadeau. I/S particles appeared to have separated only along smectite interlayers in the preparation for XRD.

The fourth study was performed by Altaner et al (50) and it is of great value because it sheds considerable light on the nature of I/S and on cementation processes with smectites involved. The study was performed by use of magic angle spin (MAS) NMR technique which has been applied by various investigators for estimating the coordination of Si in phyllosilicate minerals as indicated in presenting SKB:s mineral alteration studies. The basis of the study is the two concepts of I/S particles shown in Figure 2-27, with the Markovian model representing stackings - called MacEwan crystallites - of illite (two half octahedral layers and two complete Al-rich tetrahedral sheets collapsed on K^+ ions) and smectite layers (two half octahedral layers and two complete Si-rich tetrahedral sheets separated by hydrates and cations) with unit cell divisions centered on the smectite, and the other understood as fundamental particles consisting of integral multiples of 10 Å illite particles separated by hydrate layers and cations. According to the fundamental particle model a 10 Å thick particle is interpreted as an isolated 2:1 layer and termed *fundamental smectite* *particle*, while particles with a thickness equal to or larger than 20 Å are interpreted as layers linked by potassium ions and termed fundamental illite particles. Nadeau and coworkers suggest that accumulations of fundamental particles behave as MacEwan crystallites with interlayers *within* fundamental particles being perceived as illite (cf. Figure 2-27) and hydrated interfaces *between* particles forming smectite layers.

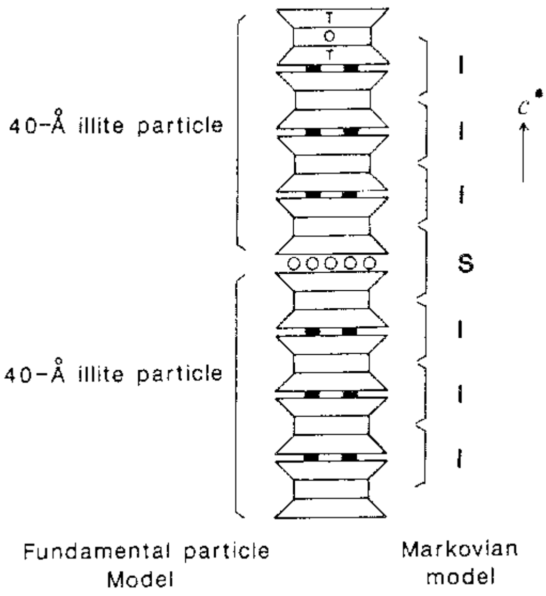


Figure 2-27 I/S shown as a MacEwan crystallite (right) and as an accumulation of two 40 Å thick fundamental particles (left). T is tetrahedral sheets and O octahedral. Black spheres are interlayer K^+ and white ones water and cations (50)

The major difference between the two models is that the fundamental particle theory proposes that illite-rich I/S consists of only one thermodynamic phase, i.e. illite, while Markov theory implies that illitic I/S contains both expandable layers of smectite although of a special kind. XRD and HRTEM cannot distinguish between the two concepts but the authors claimed that MAS NMR with respect to ^{29}Si is able to distinguish between Si in illite and smectite sites.

The reason is said to be that Si nuclei undergo more rapid relaxation in smectite due to the nearness to exchangeable sites if they are occupied by polyvalent cations like Mn. The iron content must be low in order to avoid paramagnetic effects.

The results of the study can be summarized as follows:

1. Analysis of the NMR spectra showed that both illite and smectite are present in the material and that the composition of the illite could be expressed as $Si_{3.19}Al_{0.81}$ while that of the smectite was $Si_{3.66}Al_{0.34}$. Simulation of NMR spectra indicated that illite forms 78 % and smectite 22 %

2. The XRD pattern is best modelled by a calculated pattern with 94 % illite layers and R3 order

3. TEM examination reveals no fundamental particles thinner than 37 Å, meaning that are no smectite particles

4. The differences in smectite content according to NMR and XRD can be explained by assuming that the top and bottom tetrahedral layers of the MacEwan crystallites are smectitic

5. I/S in bentonites seem to contain much thicker crystallites than inferred from XRD modelling (10-50 layers)

6. Thin fundamental particles are interpreted as resulting from cleavage of MacEwan crystallites along smectite interlayers

The study by Altaner et al does not indicate the process of conversion of smectite to illite; it may have occurred in the form of lattice rearrangements or as neoformation of I/S crystallites, which would then have had such a high illite content that they, from a practical point of view, can be regarded as pure illite. At any rate, it should be noted that both views, i.e. the Markovian and fundamental particle theories, allow for the interpretation that smectite particles in illite-rich I/S may not exist as true smectite but rather as hydrated interfaces between illite particles that originate from collaps of smectite lamellae around K^+ by dehydration, or from growth in the pore solution.

2.2.2.2 SKB-related research

Field investigations

Four major studies have been performed in the study of natural analogs with the primary purpose of comparing TEM and XRD with special respect to the physical properties. The investigations concerned Sardinian smectite clay of presumed bentonite origin (51), two Gotland bentonites, one of Ordovician and one of Silurian age (51,52), and Ordovician Kinnekulle bentonites (53). One of the investigations comprised a pilot study of the accuracy of numerical techniques for simulating XRD spectra.

BUSACHI, SARDINIA

Applying the mode of formation of Miocene Sardinian bentonites proposed by Mezzetti Gorelli and assuming the present overburden of rhyolite rock to originate from magma outflow, it was concluded that samples extracted at Busachi from 0.2 to 5.0 m depth below the rock/clay boundary represented smectite clay exposed to temperatures ranging between 20 and 750°C. Two levels were investigated, one where the temperature - evaluated from finite element method (FEM) analyses - had been at about 500°C for 5 days, 200°C for 2 months, and 60°C for about 1 year, and the other where the temperature cannot have been higher than about 20°C.

XRD investigations showed that the content of smectite (montmorillonite) was 70-75 % of the heated clay and 85-90 % of the unheated material, which is currently exploited for commercial bentonite production. This is in agreement with the finding that the liquid limit was 72 % for the heated material and 92 % of the unheated, which are both in Ca-state.

TEM investigations showed a stronger tendency for the heated clay to contain "collapsed" stacks of flakes and it also showed frequent opaque nodules in and adjacent to clay aggregates. These nodules may represent silicious material emanating from the smectite in the heating period (Figure 2-28).

Since the core samples had undergone drying, no undisturbed material could be investigated with respect to the physical properties but artificially prepared clay materials using distilled water and dry coarse clay powder were investigated. The dry density was 1.25 g/cm^3 (1.8 g/cm^3 at saturation), which approximately corresponds to the conditions in situ. The hydraulic conductivity at percolation by distilled water was found to be $3x10^{-11}$ m/s for the heated material and 10^{-11} m/s for the unheated one, while the swelling pressure were 0.48 and 0.51 MPa, respectively. The differences are very small but especially the higher conductivity of the heated material suggests that it has less ability to self-heal, probably due to some cementation. This hypothesis is supported by the different creep behavior of the two materials; for the heated clay no strain appeared until the shear stress had reached a threshold value, representing the critical shear stress required for breaking the brittle bonds of cementing agents (Figure 2-29). At this stress creep started in a jerky fashion indicating successive breakage of brittle bonds, in contrast to the behavior of the unheated clay that exhibited creep at low stresses in a much smoother mode.

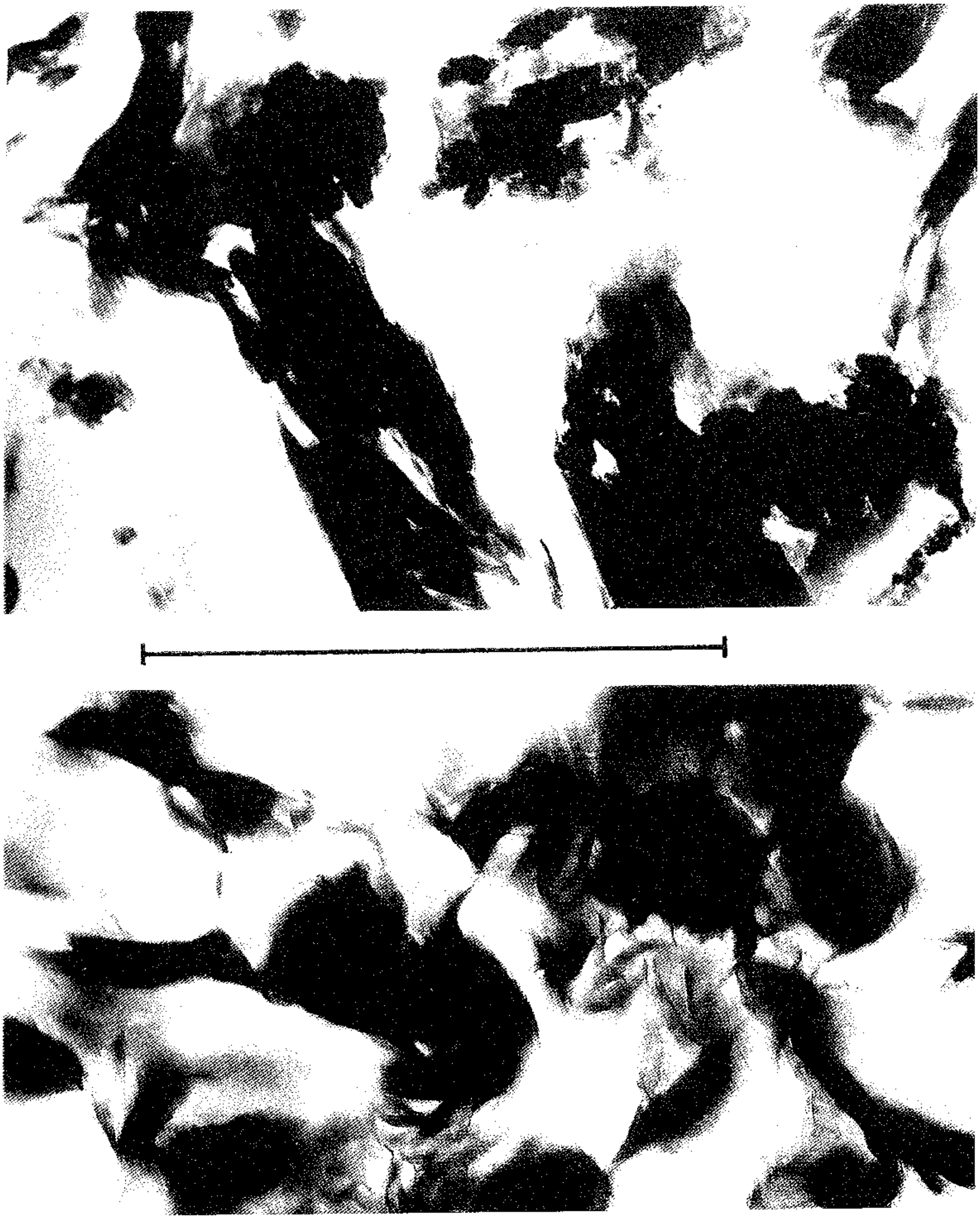
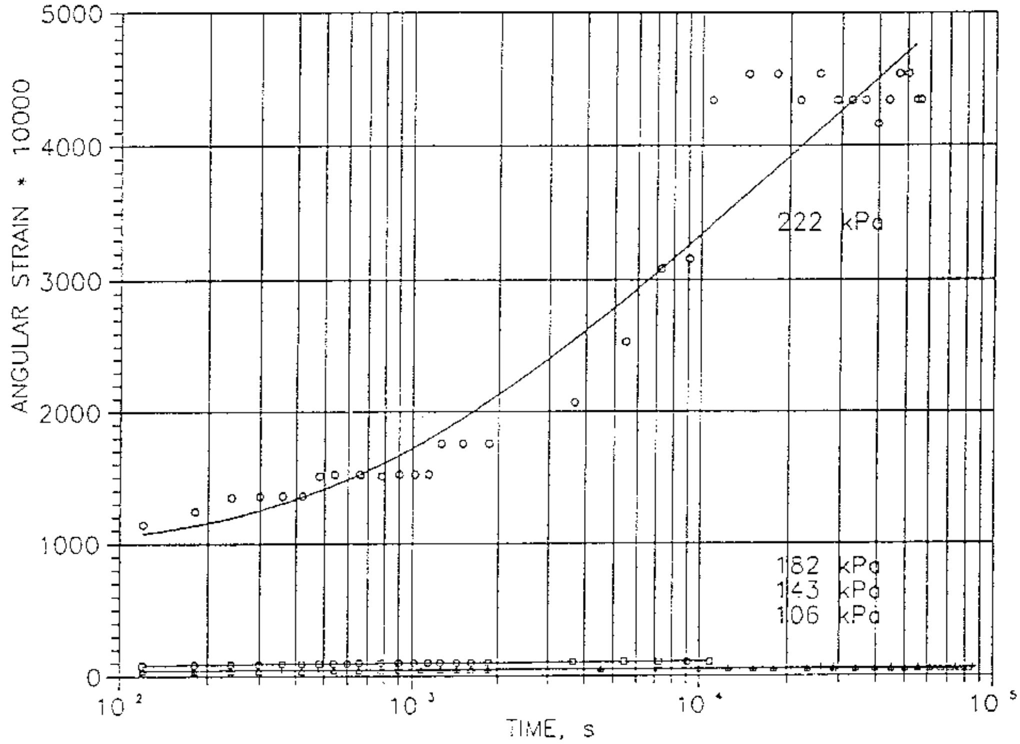


Figure 2-28 TEM pictures of Busachi bentonite. Upper: Heated clay from 0.7 m depth. Lower: Unheated clay from 4.7 m depth. Scale is 1 μm



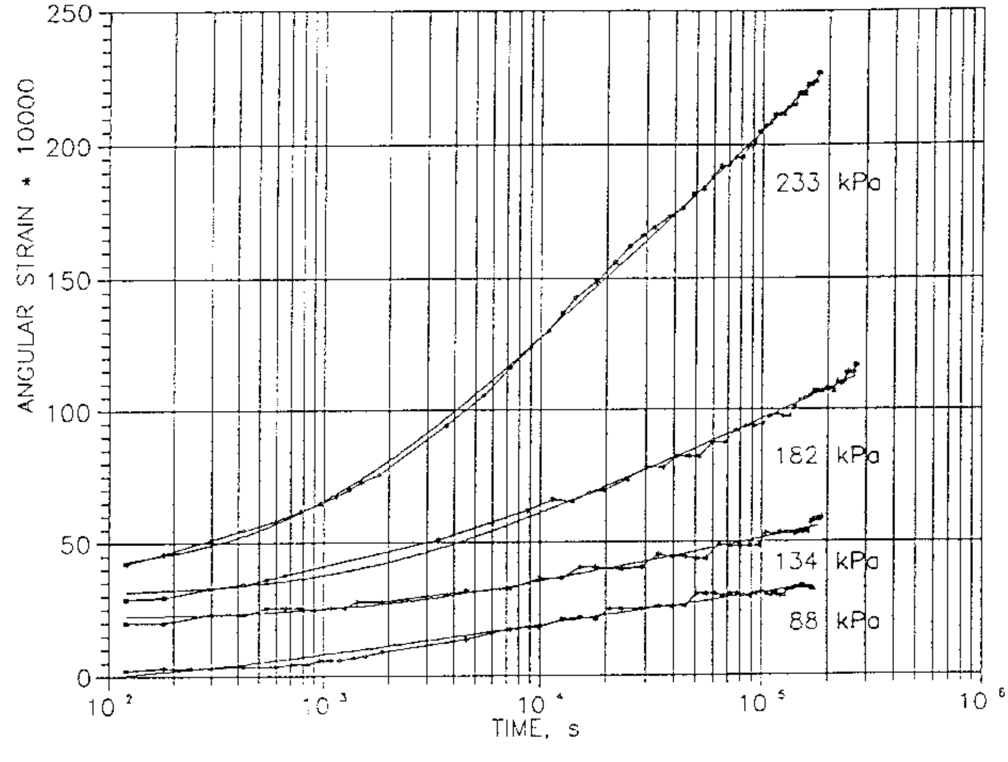


Figure 2-29 Creep strain versus time of Busachi bentonite clay with a density of 1.8 g/cm^3 prepared in the laboratory. Upper: Heated clay from 0.7 m depth; notice that no strain is caused until the shear stress is raised to 222 kPa. Lower: Unheated clay from 4.7 m depth

GOTLAND, HAMRA

The marine Ordovician sediment sequence on southern Gotland contains a number of thin bentonite layers of which the deepest one is a 0.3 m thick bed. Core samples from this bed, which is located at 525 m depth, were put to our disposal through courtesy of Oljepropspektering AB (OPAB) and investigated in approximately the same fashion as the Sardinian clay samples (51). Several facts combine to give a safe temperature and pressure history; the clay bed is concluded to have been exposed to 110-120°C for at least 10^6 years and to a vertical effective pressure of about 30 MPa due to the deposition of at least 2 km of Devonian sediments.

XRD analyses of equivalent bentonites on Gotland were interpreted by the Swedish Geological Survey as "allevardite" i.e. I/S with 50-70 % illite and this was assumed to be the case also for the Hamra bentonite, which was very fine-grained with a minus 2 micrometer content of 87 % and cation exchange capacity (CEC)=36 mE/100 g. It was investigated using XRD for checking the applicability of Reynold's method of evaluating the illite/smectite relation by comparing the actual X-ray spectra to synthetic ones with known I/S ratios. The actual spectrum of ethylene glycol-treated clay (EG), with P denoting pyrophyllite additive for quantification purposes, is shown in Figure 2-30.

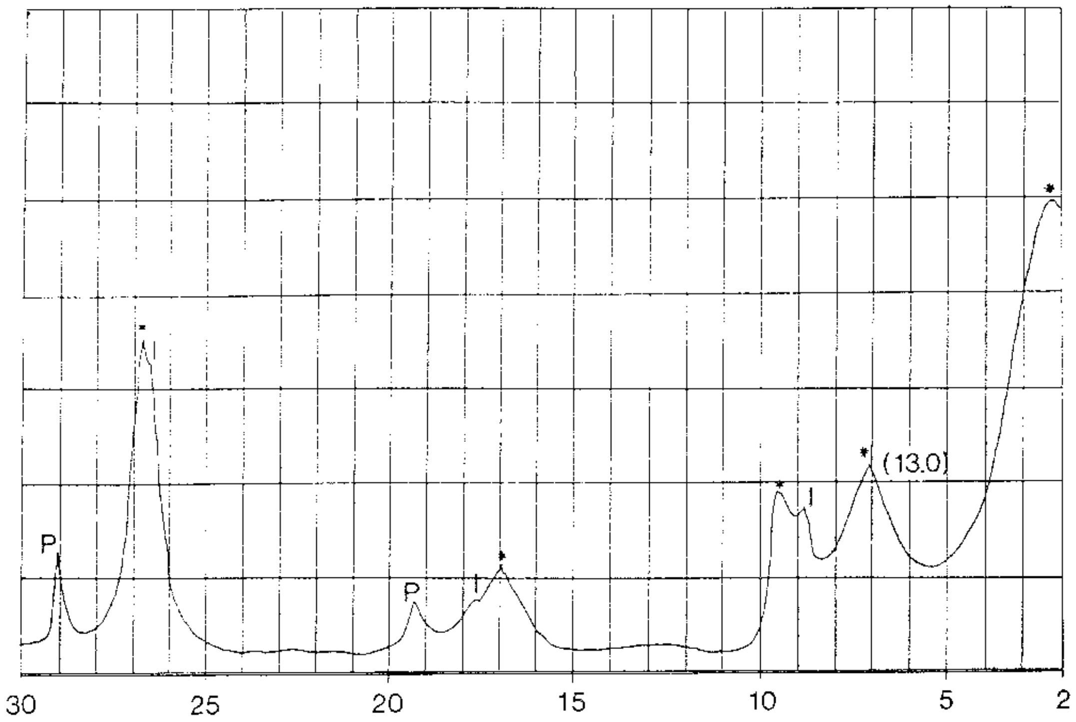


Figure 2-30 XRD spectrum of EG-treated Hamra material (<2 μm) with P-peaks indicating 10 % artificially added pyrophyllite (51)

The recorded spectrum did not fit synthetic spectra with R=0, i.e.with random stacking. However, spectra with R=1, i.e. of ISISIS type for I/S saturated with potassium were in reasonable agreement as shown by Figure 2-31, but Figure 2-32 demonstrates that the fit is not too bad even for R=0.5 and K, Na or Ca in interlamellar positions (paragonite-type minerals) and with a separate illite phase corresponding to 20 % of the mixture. In fact, it turned out that at least three combinations yield spectra of approximately the recorded type, namely:

A. 100 % mixed-layer I/S with 50 % S in the I/S (R=1.0) and K fixed in the illite

B. 70 % mixed-layer I/S with 40 % S in the I/S (R=0.5) and K fixed in the illite + 20 % pure illite + 10 % pyrophyllite

C. 70 % mixed-layer I/S with with 40 % S (R=0.5) in the I/S and Na or Ca in the "illite" + 20 % pure illite + 10 % pyrophyllite

Since pyrophyllite is not present in the natural clay it is estimated that the actual composition can be anything between the following two extremes: 100 % I/S with 50 % S and 75 % I/S mixed layers with 40-50 % montmorillonite and 25 % pure illite with Na, Ca or K in interlamellar positions. This is compatible with the cation exchange capacity 36 mE/100 g assuming the major adsorbed cation to be Ca.

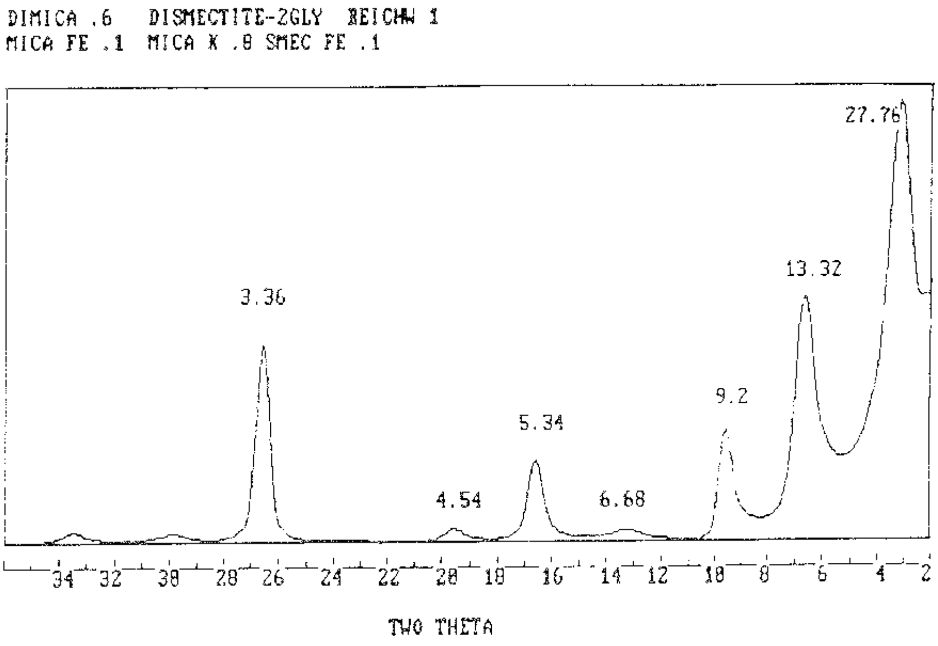


Figure 2-31 Synthetic XRD/EG spectrum of pure I/S with 50 % montmorillonite in the I/S and K in the hydrous mica (R=1)

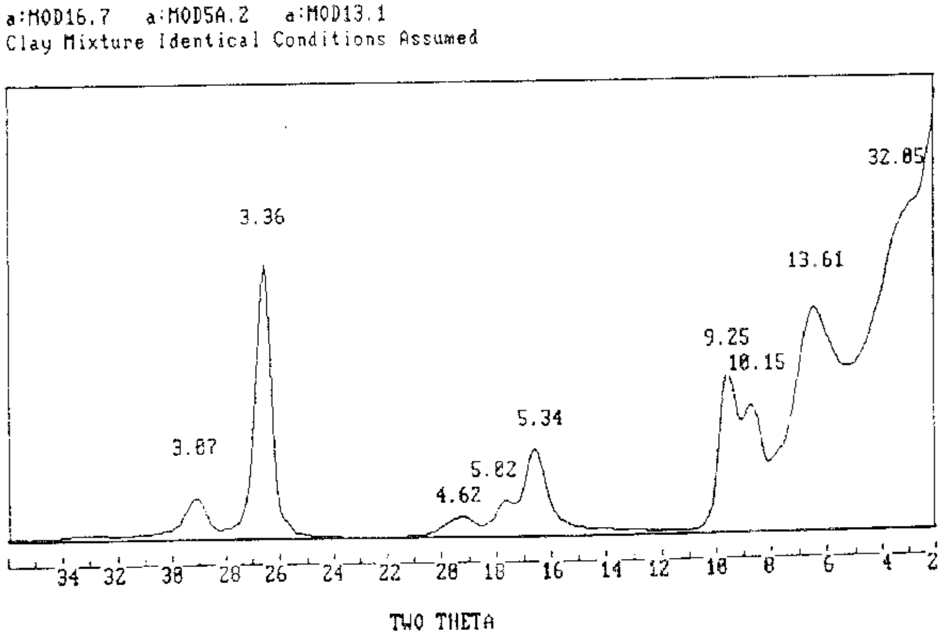


Figure 2-32 Synthetic XRD/EG spectrum of 70 % I/S with 40 % montmorillonite in the I/S and Na or Ca in the hydrous mica (R=0.5) + 20 % pure illite and 10 % pyrophyllite (51)

TEM investigations of the undisturbed clay showed the typical wavy pattern of dense smectite clay (Figure 2-33) and also a clear orientation of the microstructure due to the heavy preconsolidation. Close-ups demonstrated microstructural inheterogeneities in the form of a network of dense, more or less interconnected 100 to 500 Å thick aggregates of aligned particles with a homogeneous porous matrix of well crystallized thin minerals occupying the void of the network (Figures 2-34 and 2-35). Spot EDX analyses indicated that the dense aggregates had approximately the same chemical composition with a Si/Al ratio of about 66/19 and some more potassium than sodium and calcium, while the matrix was richer in potassium. This was taken as a strong support of the idea that illite is present as a separate phase, represented by the matrix, and that the aggregates mainly consist of I/S stacks. The mass ratio of the matrix and the aggregates is estimated to be in the range of 1:3, i.e. not very different from the figure 1:4 evaluated from the XRD.

It was concluded from this study that XRD and CEC as well as chemical analyses are not sufficient to yield a true picture of the mineral composition;

microstructural analyses with EDX are in fact also required to give a complete picture.

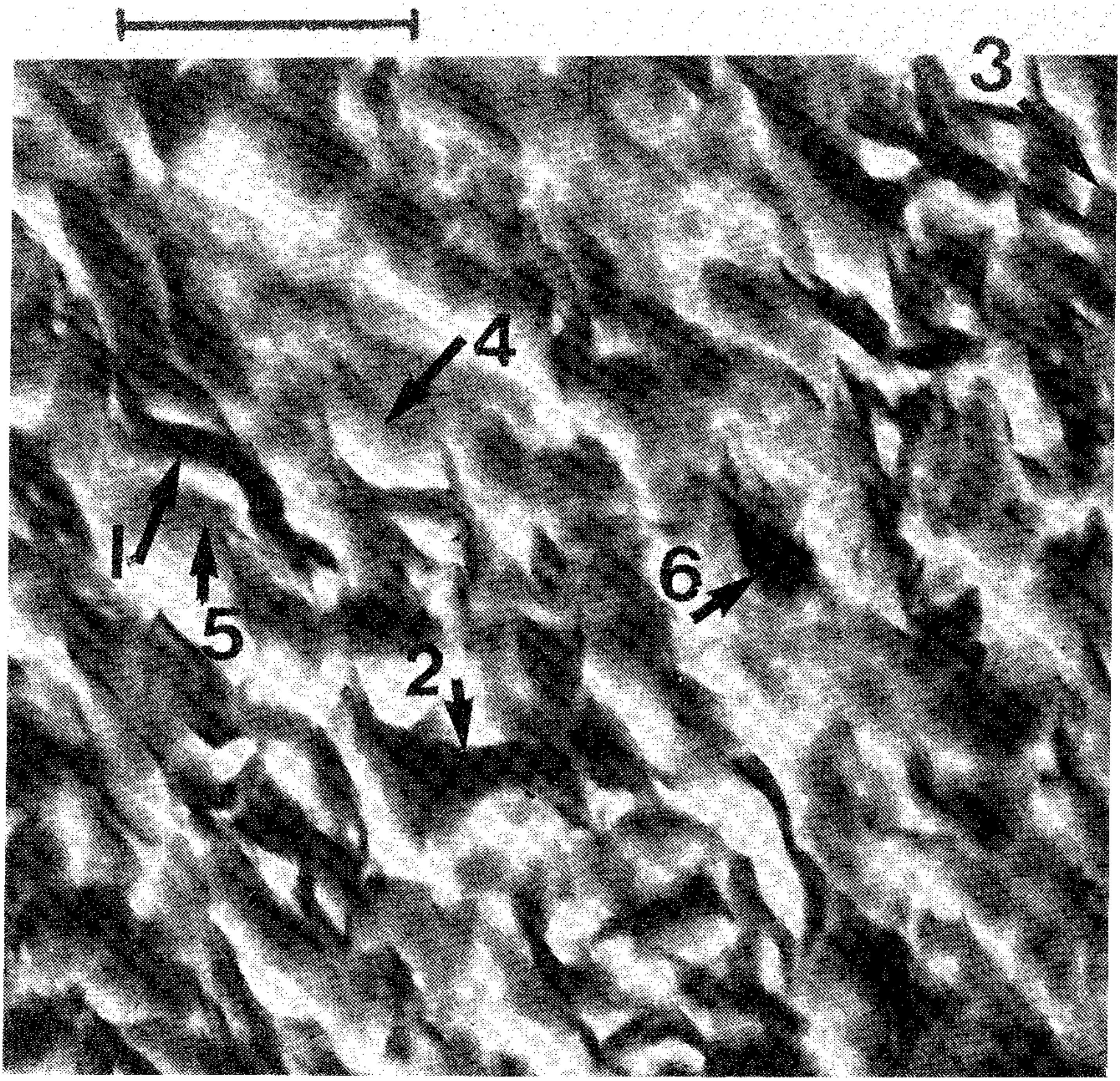


Figure 2-33 TEM photo showing the general microstructural pattern of the Hamra clay. The figures denote where spot analyses were made (51). Scale is 1 μm

Figure 2-34 TEM photo showing dense I/S aggregates and presumed neoformed illite in large pores (uppermost part). Scale is 0.1 μm (51)

Figure 2-35 TEM photo showing homogeneous matrix of well crystallized illite in Hamra clay. Scale is 0.1 μm (51)

The physical properties of the Hamra clay could be determined after restoring the samples to the state they had in nature. This required complete water saturation since some slight drying had taken place despite the effective sealing of the drill cores in the 10 years storage. The saturation was made in the shear box by letting the confined samples take up Forsmark groundwater (total salt content 11820 ppm, with the ionic strengths: Na^- 2530 ppm, Ca^{2+} 950 ppm, Mg^{2+} 21.7 ppm, and K^+ 5.4 ppm). This gave a dry density of 1.72 g/cm^3 (2.09 g/cm^3 at complete water saturation), and a swelling pressure of about 3 MPa and a hydraulic conductivity of $5x10^{-13}$ m/s using distilled water. These data are in good agreement with experimental data of mixtures of 40 % montmorillonite and well graded ballast. The fact that the swelling pressure is only about 40 % of the present overburden pressure and only about 10 % of the maximum preconsolidation pressure in Devonian time and in the Pleistocene glaciation period indicates that the clay has undergone both expansion and compression without loosing its plastic nature. Creep testing was made by using a sample that had been consolidated in the shear box under an effective normal pressure corresponding to the present in situ conditions. The creep behavior, which turned out to be very similar to those of artificially prepared Na bentonite clay of Wyoming type, is illustrated in Figure 2-36. The diagrams in this figure demonstrate the smooth creep behavior of non-cemented clay and also that the shear stress 990 kPa yielded critical strain, which initiated failure that was fully developed when the shear stress was increased to 1.32 MPa.

Assuming the Hamra bentonite to have been nearly 100 % smectite from start, and applying Pytte's S$\rightarrow$I conversion model, one finds that the expected conversion to about 40 % S would require some 500 000 years if the K^+-concentration had been 400 ppm and the activation energy 27 kcal/mole (Figure 2-23, upper diagram), and several million years if the activation energy is 28 kcal/mole. This brings up the question what the potassium source really was, a matter that has been treated at some length in various SKB papers.A simple and straightforward model is that the primary K^+ source was the potassium dissolved in the seawater in which the primary smectite substance was formed, yielding a concentration of about 400 ppm. Applying the principle that the reaction zone of S$\rightarrow$I conversion created a potassium sink that maintained the concentration of free potassium at zero in the clay, a concentration gradient would be formed in the adjacent sediments that successively brought in more potassium by diffusion under stagnant groundwater conditions and by flow under the influence of hydraulic gradients (54). Since stagnant conditions must have prevailed because of the absence of piezometric and thermal gradients, pure diffusion is concluded to have been the major transport mechanism at Hamra. Taking the diffusion coefficient to have been 10^{-11} to 10^{-9} m^2/s and the average potassium concentration related to the actual porosity of the sediment series to be 80 ppm, the conversion rates will be those indicated in Figure 2-37. Stoichiometrically, complete conversion of smectite to illite requires uptake of potassium corresponding to about 5 % of the solid smectite mass. Assuming the net effective diffusion coefficient of potassium to be 10^{-11} m^2/ s one finds the exhaustion of potassium from the porewater to be represented by the concentration profiles in Figure 2-38. It is clear from this diagram that the access to potassium in the porewater of the adjacent 50 m of sediments was sufficient to provide the clay with the required amount of this element for the actual degree of S→I conversion.

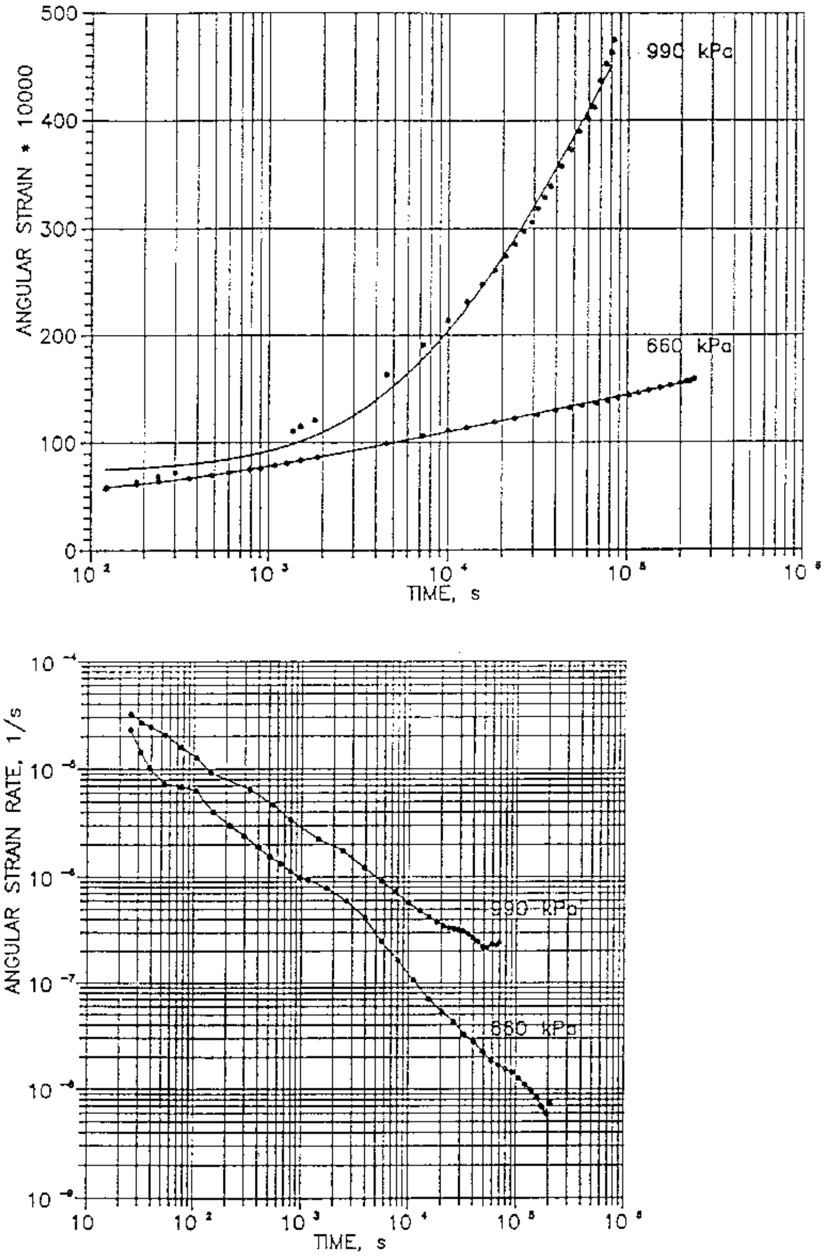


Figure 2-36 Creep behavior of the Hamra clay. Upper: Creep strain versus time. Lower: Strain rate versus time exhibiting pure log-time creep for 660 kPa shear stress

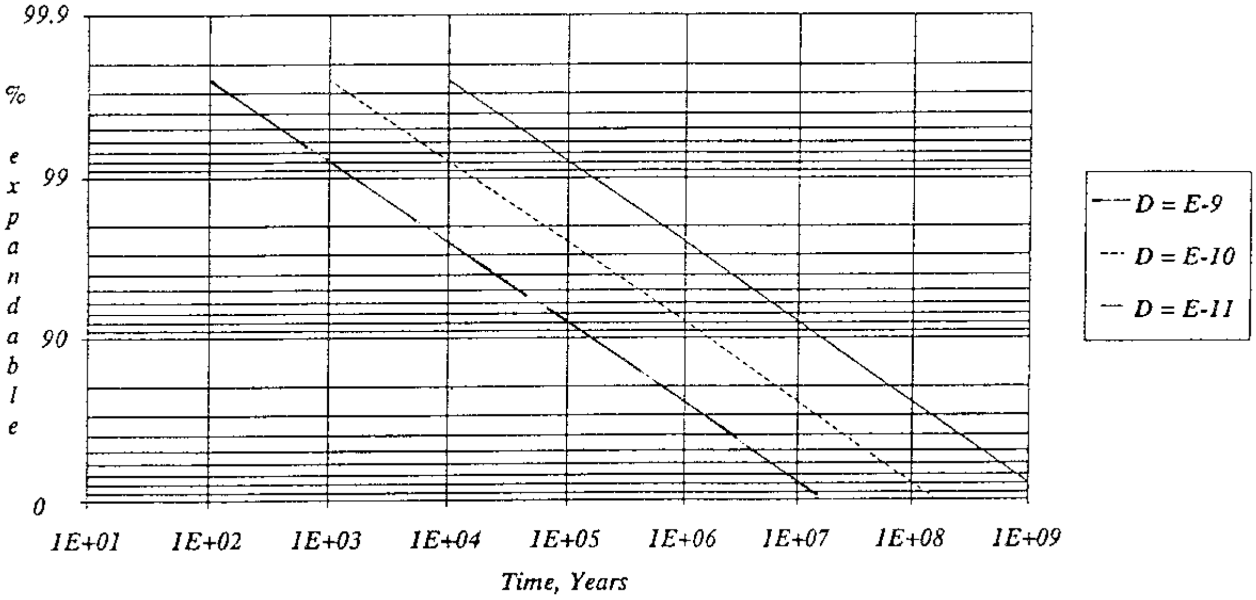


Figure 2-37 Rate of conversion of the Hamra bentonite assuming the uptake of potassium to be the controlling variable. Initial K^+ concentration is 400 ppm and the thickness of the bed 0.3 m, which is assumed to attract potassium only from above (54)

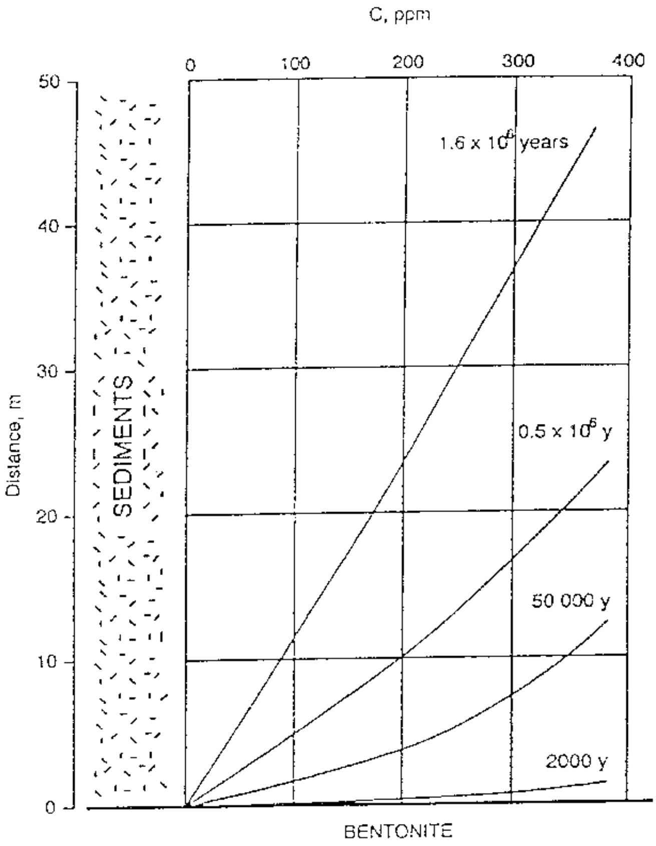


Figure 2-38 Calculated K^+ profile in the porewater of sediments overlying the Hamra bed (54)

GOTLAND, BURGSVIK

Some 10 km north of Hamra, Silurian strata are exposed at the present sea level and they are concluded to originate from ash-fall, i.e. to be true bentonites, i.a. because of their microstructural constitution. Earlier investigations (55) and a recently performed study of drill cores from down to 75 m depth (52) have shown that this sediment series contains a large number of clay layers with almost identical mineralogical composition characterized by illite, quartz, chlorite and calcite (Figure 2-39). Like in the Hamra area, the Burgsvik sediments are concluded to have been covered by about 2 km of Devonian sediments, which is estimated to have caused a high pressure and temperature - around 25 MPa and 90-100°C at Burgsvik - during a few to ten million years. The Burgsvik case is considered to be of particular interest since it is assumed to represent a case where 100 % conversion of smectite to illite has taken place.

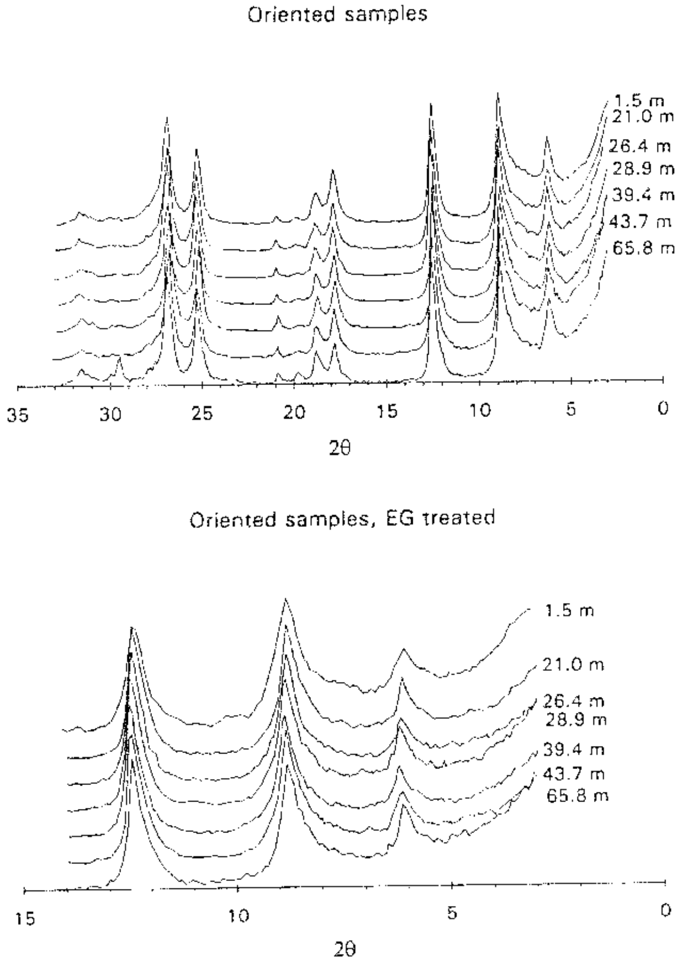


Figure 2-39 XRD spectra showing that practically only illite, quartz, chlorite and calcite are present in the sediment sequence from the sea level to about 70 m depth at Burgsvik (52). The absence of lattice expansion at EG treatment demonstrates that smectite is not present. Major peaks expressed in 2Θ are: Chlorite (14.26, 7.03 and 3.53), Illite and mica (10.0, 4.78), Quartz (4.25, 3.33), Chlorite (14.26, 7.03, 4.72), Calcite (3.03)

TEM investigations showed a wavy network of flaky particles which appears to be the same as for other heavily compressed smectitic clays (Figure 2-40), and a matrix of well crystallized particles similar to what was found in the Hamra clay (Figure 2-41). The matrix undoubtedly represents illite and chlorite since no smectite is present according to the XRD analyses.

Figure 2-40 TEM photo showing the general microstructural pattern of the Burgsvik clay with local soft clay gels of randomly grouped crystallites - presumably illite and chlorite - in the voids of a wavy network of denser aggregates of illite/chlorite. Scale is 1 μm

Figure 2-41 TEM photo of Burgsvik clay showing well crystallized minute particles - presumably illite and chlorite - in the voids between dense aggregates. Scale is 1 μm

The physical properties of the Burgsvik clay have been investigated by using an undisturbed sample that had a dry density of 1.76 g/cm^3 , i.e. 2.11 g/cm^3 at complete water saturation (56). It was found to have a hydraulic conductivity of 1.5x10^{-11} m/s at percolation perpendicular to the stratification, using distilled water and hydraulic gradients ranging between 10^2 to 10^3. Creep testing with the sample contained in a shear box was made at a normal pressure of 120 kPa - corresponding to the present overburden - yielding the creep behavior shown in Figure 2-42. The plotting of the creep strain showed insignificant strain at stresses lower than 92 kPa, indicating cementation in the way exhibited by the heated Busachi bentonites. Failure occurred at a shear stress of 127 kPa. Typical log time creep behavior was recorded at all stress levels after about 1000 seconds, showing that the cementation was still not very significant, which was also indicated by the smooth character of the creep curves. However, the upward concave shape of the initial part of the creep curves ("negative t_o") for the three intermediate stress levels in the lower diagram illustrates the commonly observed fast retardation of the creep strain of cemented soils, indicating that precipitation of silicious agents took place in conjunction with the assumed conversion from smectite to illite.

Assuming the Burgsvik clay fraction to have been nearly 100 % smectite from start, and applying Pytte's conversion model for 100°C temperature and 400 ppm potassium concentration in the porewater, one finds that complete conversion should have taken place in about one million years, i.e. well in the period of time when this temperature prevailed, provided that the activation energy for S→I conversion was 27 kcal/mole (cf. Figure 2-23). As in the case of the Hamra clay the question is naturally whether potassium was actually available to the extent required for complete conversion, which was investigated using the same method as for the Hamra clay, i.e. assuming that the conversion caused fixation of potassium taken up in the clay and creation of a concentration gradient in the surroundings.

The Burgsvik sediments consist of marl containing about 30 clay layers with an average spacing of about 2.5 m down to about 70 m, the total clay layer thickness being about 0.33 m with an estimated initial content of smectite of about 20 % of the total mineral mass. This shows that the potassium content in the porewater of the marl was far from sufficient to yield complete conversion to illite (56), but assuming that potassium was also taken up from the lower 200 m part of the Devonian sediments, the necessary amount would have been supplied. However, the rate of transport of potassium from this remote supply also had to be sufficient to cause conversion in the heating period and one finds that if only pure diffusion of K^+ dissolved in the porewater of the sediments took place, the coefficient of diffusion must have been appreciably higher than down in the Hamra sediments, namely the unlikely high figure 10^{-9} m^2/s. Alternatively, dissolved K-bearing minerals like microcline in the Devonian sediments may have provided potassium by which the diffusion coefficient may still have been as low as in the Hamra case. Furthermore, groundwater flow in the Devonian and Silurian sediments may have brought in marine water into the sediment series, contributing to the supply of dissolved potassium.

These considerations indicate that identification of the potassium source and finding a plausible explanation of the rate of supply of dissolved potassium to converting smectite layers are major issues in evaluating natural analogs.

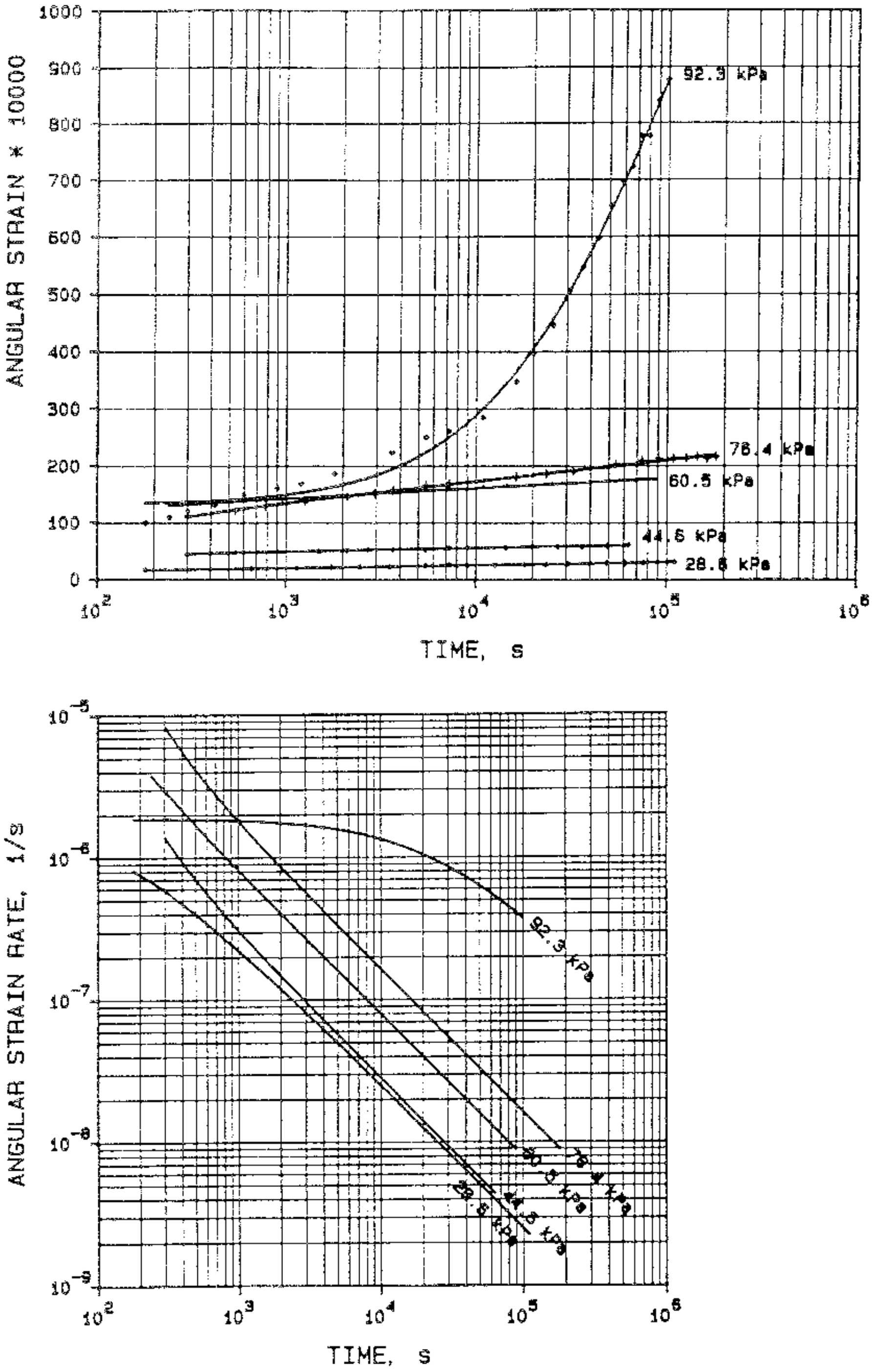


Figure 2-42 Creep behavior of the Burgsvik clay. Upper: Shear strain versus time. Lower: Strain rate versus time (56)

KINNEKULLE

The Chasmops series of Kinnekulle, southwestern Sweden, contains bentonite layers that have been the subject of several mineralogical investigations and a few studies of the physical properties of the clay (53,56). Figure 2-43 shows the stratigraphy of the Kinnekulle area with a diabase layer, presently at the top, resulting from lateral penetration of magma in Permian time. Various ways of estimating the temperature history, including FEM and conodont analyses, have led to the conclusion that the clay layers were exposed to 150°C for about 300 years, and to 130°C for another 300 years and subsequently to 100-130°C for 400 years. The temperature then dropped back to the original in an approximately 2000 year long period.

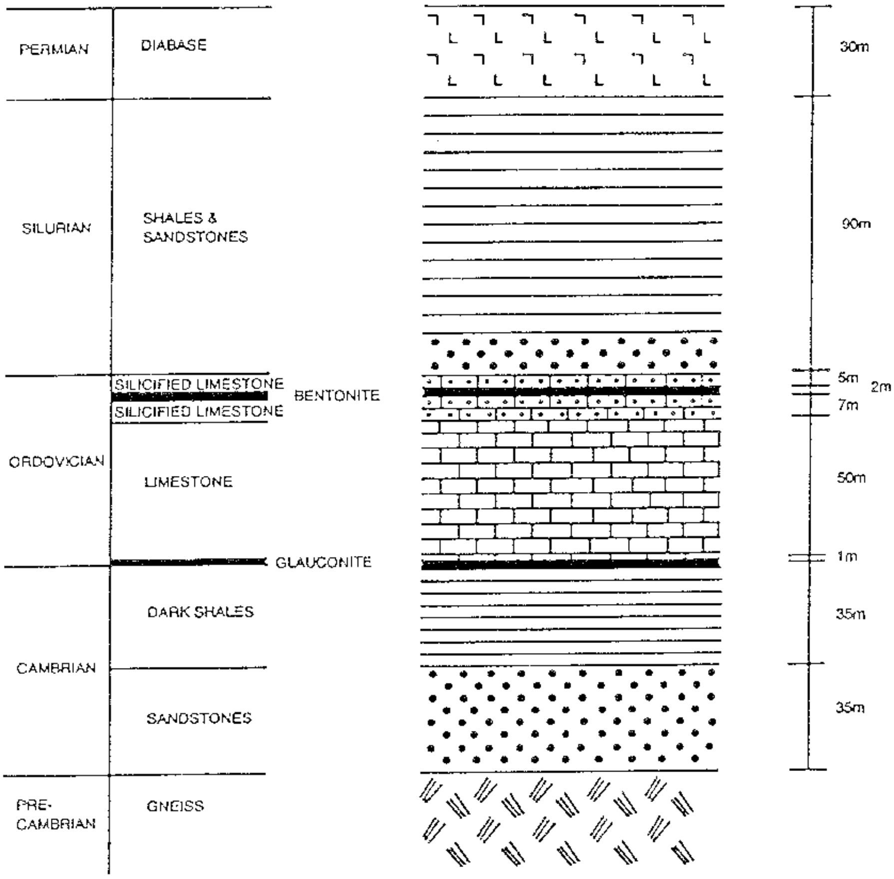


Figure 2-43 The Kinnekulle strata (53)

The uppermost part of the about 2 m thick main bentonite bed and adjacent thinner layers are concluded to be more silicified and to have a different mineral content of the <1 µm fraction than the equally heated central part, namely I/S with 30-60 % smectite in the I/S, biotite, chlorite, quartz, feldpars (including the K-bearing feldspar sanidine) and also amorphous silica. The central part of the bed has 50-70 % smectite in the I/S and the aforementioned accessory minerals, the higher smectite content being due to less uptake of potassium in the heating period. A pure illite phase is also concluded to be present (cf. Figure 2-44) in the relatively porous matrix of I/S material (Figure 2-45). The illite, and possibly also the I/S probably represent neoformed components.

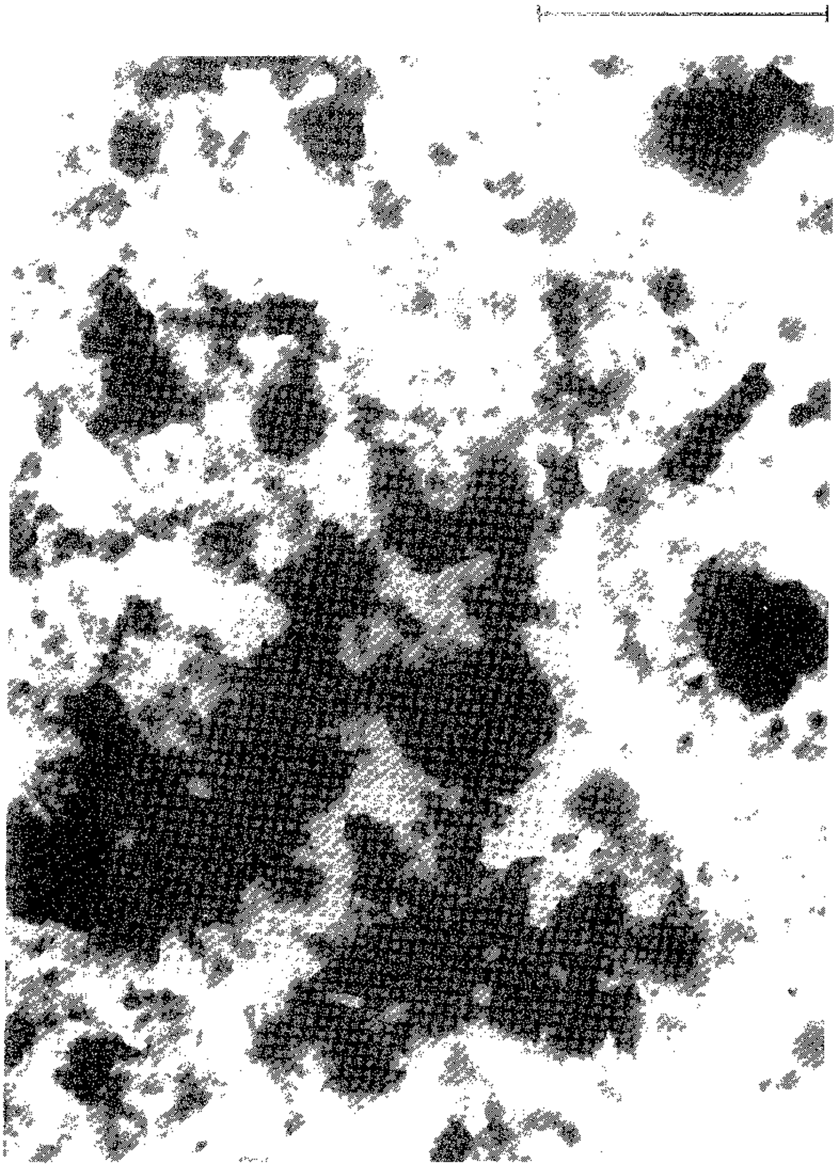


Figure 2-44 Presumed neoformed illite particles in the Kinnekulle bentonite (53). Scale is 5 µm

Figure 2-45 Microstructure of Kinnekulle bentonite showing random grouping (fluffy aggregates) and orientation of I/S stacks and neoformed illite and chlorite. Scale is 1 μm

The micrograph in Figure 2-45 demonstrates that the bentonite clay where sampling took place, i.e. where the present effective overburden pressure is now only 0.1 MPa but where the maximum preconsolidation pressure has been 5-10 MPa in Permian time and up 30 MPa in the period of Pleistocene glaciation, is rather porous. The porosity in the heating period in Permian time is estimated to have been 30-40 %, implying no restraint to mineral neoformation in the voids. The present porosity of the central part of the main bed at the shallow sampling site is on the order of 50 % and the dry density about 1.66 g/cm^3 (2.05 g/cm^{3}at water saturation), while the more illiticized part at the upper boundary of the main bed was found to have a porosity of about 38 % and a dry density of 2.02 g/cm^3 (2.29 g/cm^3 at water saturation). This difference may have two reasons; 1) silica precipitations in the latter material may have increased the density and reduced the pore volume, and 2) the more extensive conversion to illite must - in combination with the stronger silification - have led to less swelling ability and therefore to preservation of the compressed state under earlier heavy overburden pressure.

The Atterberg liquid limit is 75 % of the central, most smectitic parts of the main bed, which is surprisingly high since Ca is the major adsorbed cation, and the cation exchange capacity is up to about 90 mE/100 g, which is also remarkably high (53). The physical properties of the clay from the peripheral and central parts of the main bed have been determined using small undisturbed samples (56). The hydraulic conductivity of the peripheral more illitic parts of the main bed has been found to be about $4x10^{-12}$ m/s while that of the central more smectitic part is around $2x10^{-13}$ m/s at percolation with distilled water. This difference is clearly related to the higher smectite content of the central part of the bed since the density of this part is actually lower than the density of the peripheral, more illitic part. Creep tests of a sample from the central part of the main bed gave the relationships between strain and time and strain rate shown in Figure 2.46, from which one finds that the log time creep law applies except near failure, and that the creep strain took place in a jerky fashion, indicating some cementation also of this part of the bed. This conclusion is also supported by the fact that the first load step caused insignificant strain while the second one (64.5 kPa) gave large strain and the upward concave curve of strain rate versus time that is typical of cemented soil (56).

Application of Pytte's model for S→I conversion, taking the activation energy to be 27 kcal/mole, shows that as much as 85 % of the smectite would remain after about 1000 years assuming potassium-rich water (400 ppm) to be available (cf. Figure 2-25) while only 20 to 40 % would remain if the activation energy is taken at 26 kcal/mole. The latter agrees well for the peripheral part of the main bed and adjacent thinner layers but the higher figure may still be valid since the temperature may in fact have been as high as 185°C. At any rate, the kinetics are in fact controlled by the access to potassium as demonstrated by the fact that the peripheral parts of the uniformly heated parts of the main bed (maximum gradient 0.05°C/cm) have undergone significantly more illitization than the central part. The conversion profile is concluded to be a good proof of the validity of the hypothesis that potassium is transported into the clay by creation of a K-sink in the clay that generates a concentration gradient. The picture of a "frozen" illite profile strongly supports the assumption that the conversion took place in the heating period and not subsequently.

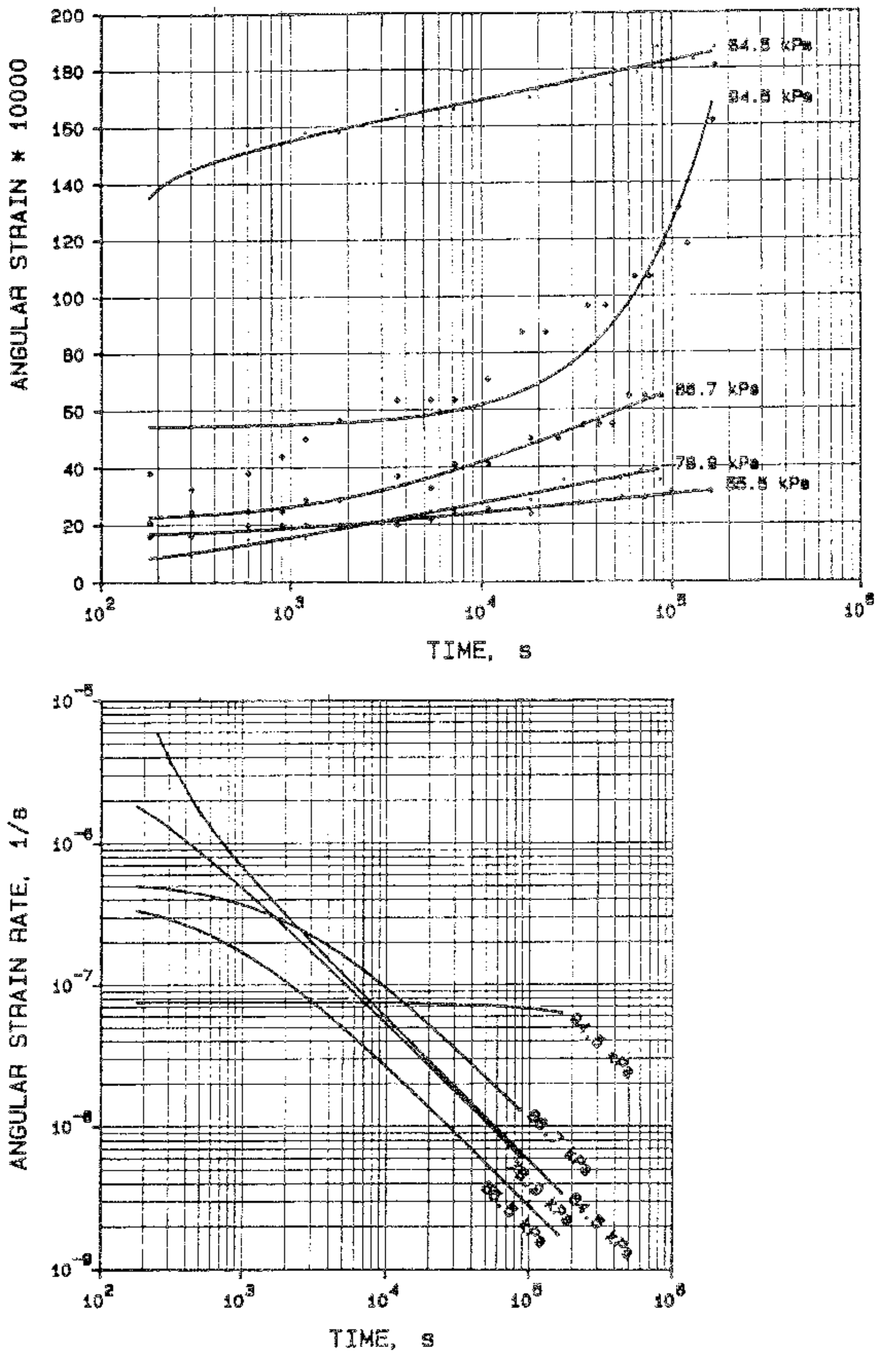


Figure 2-46 Creep properties of the smectite-rich Kinnekulle bentonite. Upper: Creep strain versus time. Lower: Strain rate versus time

The amount of precipitated silica compounds, which may be quartz, cristobalite or amorphous silica, is estimated to be up to 3 % (57), which seems to be too small to have led to the actual cementation, which is in fact clearly demonstrated by the difficulty in dispersing the material despite intense ultrasonic treatment and boiling in 5 % soda solution (Figure 2-47). In this context it is of great interest to see that while conversion of montmorillonite to illite by uptake of external aluminum according to Eq.2 - which specifies the reaction of low-charge smectite to high-charge (beidellite-type) smectite - causes release of slightly more than 4 weight percent of silica, neoformation of illite by dissolution of smectite ("cannibalization") sets about 30 % of the mass free in the form of SiO_2. Such an amount of silicious compounds naturally has a significant impact on the porosity and a very strong cementing effect.

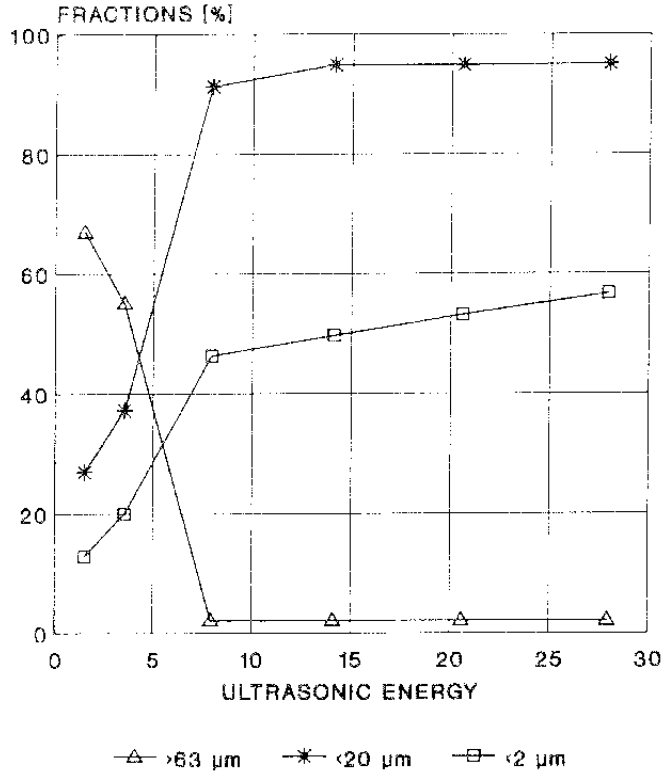


Figure 2-47 Grain-size distribution of sample from the central part of the main bed determined by applying different ultrasonic energies expressed in 10^{-8} m^2s. Frequency at 20 kHz (57)

As for the other field investigations the question arises what source and mechanisms that provided the amount of potassium that was taken up in the illitization process. Applying the same criterion as for the Hamra and Burgsvik bentonites, i.e. that complete conversion requires an amount of potassium of 5% of the total smectite mass to produce illite, one finds that potassium can only have been exctracted from the next few meters or possibly a few tens of meters of adjacent sediments in the short heating period, applying a reasonable diffusion coefficient. Even more important is that the potassium contained in the voids of the entire series of sediments would not have been sufficient to convert more than about 10-15 % of the smectite to illite, which means that potassium must have been brought to the bentonite beds by other mechanisms. The fact that K-bearing minerals are still found in the bentonite and in the vicinity indicates that dissolution of such minerals cannot have been a major potassium source and the most plausible explanation is that the strong local heating caused by the intruding magma caused intense groundwater convection and advection by which potassium-rich groundwater was brought to the vicinity of the bentonite layers (53).

MAJOR CONCLUSIONS FROM THE FIELD STUDIES

The four field studies all indicate that conversion from smectite, particularly montmorillonite, to non-expanding 10 Å hydrous mica minerals - interpreted as illite - and to chlorite takes place in the following fashion:

1. The conversion is associated with release of silica which forms cementing agents. This is particularly obvious where there is a temperature gradient as at Busachi and Kinnekulle. Where practically no temperature gradients prevail and the surrounding sediments are poor in silica-rich minerals, like at Hamra, Si seems to diffuse out from the clay yielding practically no cementation. At Burgsvik, where the temperature gradient is also assumed to have been very low, the profile from which samples were taken for creep testing are very rich in quartz silt and sand, which indicates that such conditions prevent diffusion of silica released from the clay from migrating into the surroundings. It is instead precipitated and causes the observed cementation effects

2. The conversion rate can be rather accurately described by Pytte's model assuming an activation energy of 26 to 27 kcal/mole, provided that the temperature history is known and that the potassium concentration in the porewater of the converting clay is about 400 ppm (marine conditions)

3. Access to potassium controls the conversion rate at temperatures exceeding 50-100°C. In practice, it can be limited by low conductivity of the surroundings and absence of hydraulic gradients. Where no groundwater flow takes place that can bring new potassium-holding water to the converting smectite clay, the alteration process stagnates and results in a "frozen" illitization profile even in a very long perspective.

Although more comprehensive investigations of the North Sea marine sediments are still to be performed, it seems as if the conclusions from the just described field studies apply. Thus, Cretaceous smectite-rich clays that have been exposed to temperatures on the order of 100°C for tens of millions of years, which - using Pytte's model - should have been completely converted to illite in about 1 million years at an activation energy is 27 kcal/mole and continuous access to potassium to maintain the concentration at 400 ppm, have an actual smectite content of 60-70 %. Such high values can be explained by delay in diffusive migration of potassium through exhaustion of this element in the surroundings as in the Hamra case. Thus, application of a diffusion coefficient of 10^{-11} to 10^{-10} m^2/s means that the actual smectite contents are actually arrived at. The fact that the temperature gradient has been very small explains why cementation effects are insignificant where clay layers are located in silica-poor sediments like limestone.

Laboratory investigations

Hydrothermal testing using closed cells

In the period 1986-1989 a number of hydrothermal experiments were conducted with soft water saturated smectite clay of a well defined type, i.e. SWY-1 (natural Wyoming-type smectite clay from the Source Clays collection of the Clay Minerals Society) contained in closed cells and exposed to temperatures of up to 225°C and pressures in the interval 0-70 MPa. The porewater solutions consisted of distilled water and NaCl and $CaCl_2$ solutions with a ionic strength corresponding to that of seawater except for one test series, which was performed with 3.7 M KCl solution. The latter test was run for 2 months while the others lasted 0.5 to 1 year (58, 59, 60). Testing was made by use of XRD and electron microscopy as well as by simple rheological measurements in the form of unconfined compression of undisturbed samples extracted from cells.

The experiments with distilled water and chloride solutions gave only insignificant changes in XRD fingerprints, and the ones conducted with potassium chloride were also largely unchanged as illustrated by Figure 2-48. The softest clay of the latter type showed some insignificant formation of illite at 200°C in 0.5 years while the denser ones and those exposed to lower temperature did not undergo any illitization. However, all the tests tended to show a more intense 001 peak after heating to 150 and 200°C, which is interpreted as resulting from heat-induced disintegration of aggregates. Thus, in the preparation of specimens for XRD by sedimentation more effective orientation was obtained as manifested by the changed peak shape.

Applying Pytte's model and taking the activation energy to be 27 kcal/mole and the potassium content almost as high as in the experiment (Figure 2-49), one finds that the smectite content should be reduced by about 50 % in 0.5 years, which was not the case in the experiment at 200°C. This may be explained by assuming that the actual activation energy was in fact higher, or by unsufficient accuracy of the model for short reaction times. However, for 105°C and 1 year treatment the model yields practically zero conversion, which was also what the experiment showed.

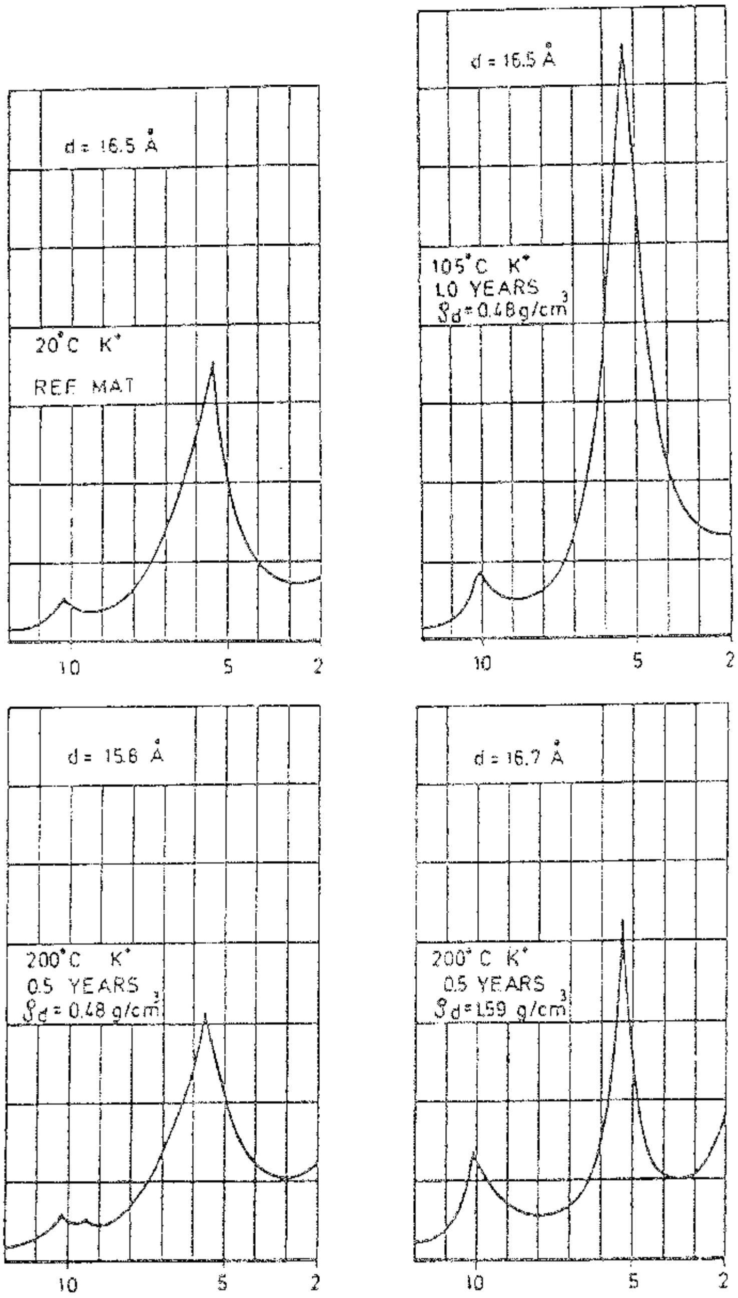


Figure 2-48 Smoothened XRD patterns of EG-treated SWY-1 samples. The figures at the base of the diagrams denote 2Θ

smectite fraction at start	S0		0	1
time	t	s		0
frequence factor	A	1/s		80800
activation energy	Ea	cal/mol		27000
gas constant	R	cal/(deg*mol)		1,987
temperature	T	K		323
K+ concentration	(K+)	mole/l		3

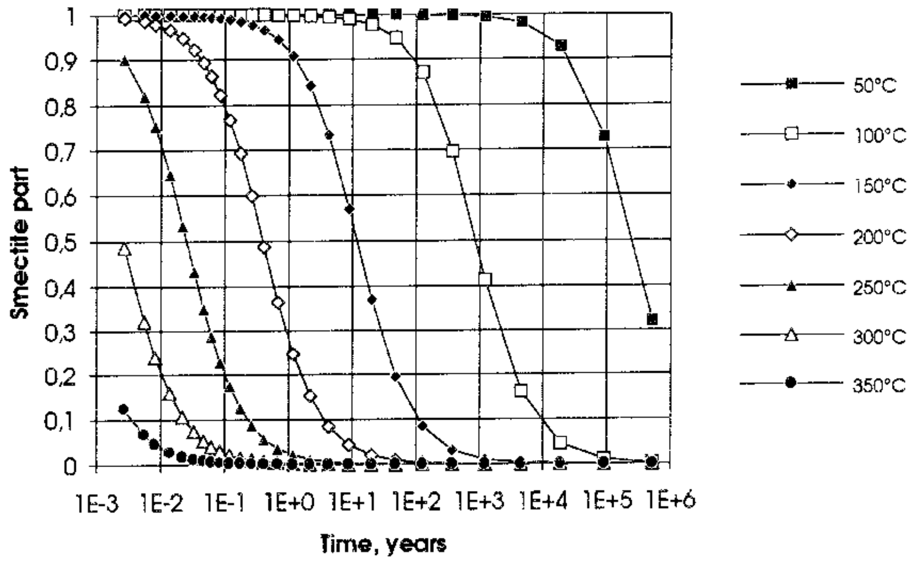


Figure 2-49 Conversion rate of S→I according to Pytte for 27 kcal activation energy and 3 mole/liter K^- concentration

TEM pictures were taken of unheated and heat-treated specimens prepared by various techniques and although no statistical treatment was made of morphological and textural features it was estimated that at least denser clay samples underwent microstructural changes, primarily by formation of an interwoven, continuous network of relatively dense branches as indicated by Figure 2-50. This led to the conclusion that heating of fully water saturated clay causes contraction of stacks of flakes and widening of the external voids at constant volume, which should result in enhanced hydraulic conductivity and reduced swelling pressure. Numerous laboratory determinations of the swelling pressure of heated, water saturated Ca bentonite verify this, while the opposite effect is found for Na bentonite (Figures 2-51 and 2-52). The explanation for this discrepancy has been assumed to be that two competing processes yield different net effects *under the condition of no external compressive stress*: 1) interlamellar dehydration yields lower contact pressures between stacks and 2) heating introduces thermal stresses which break up aggregates of stacks and creates more stack contacts where expansive electrical double-layers are formed. The firstmentioned effect probably requires high temperatures, while the lastmentioned, which is much more pronounced in Na than in Ca bentonite, becomes effective already at 50-60°C. In recent time it is estimated that interlamellar dehydration requires very high temperatures except *under the condition of external compressive stress* as will be discussed in Chapter 4.

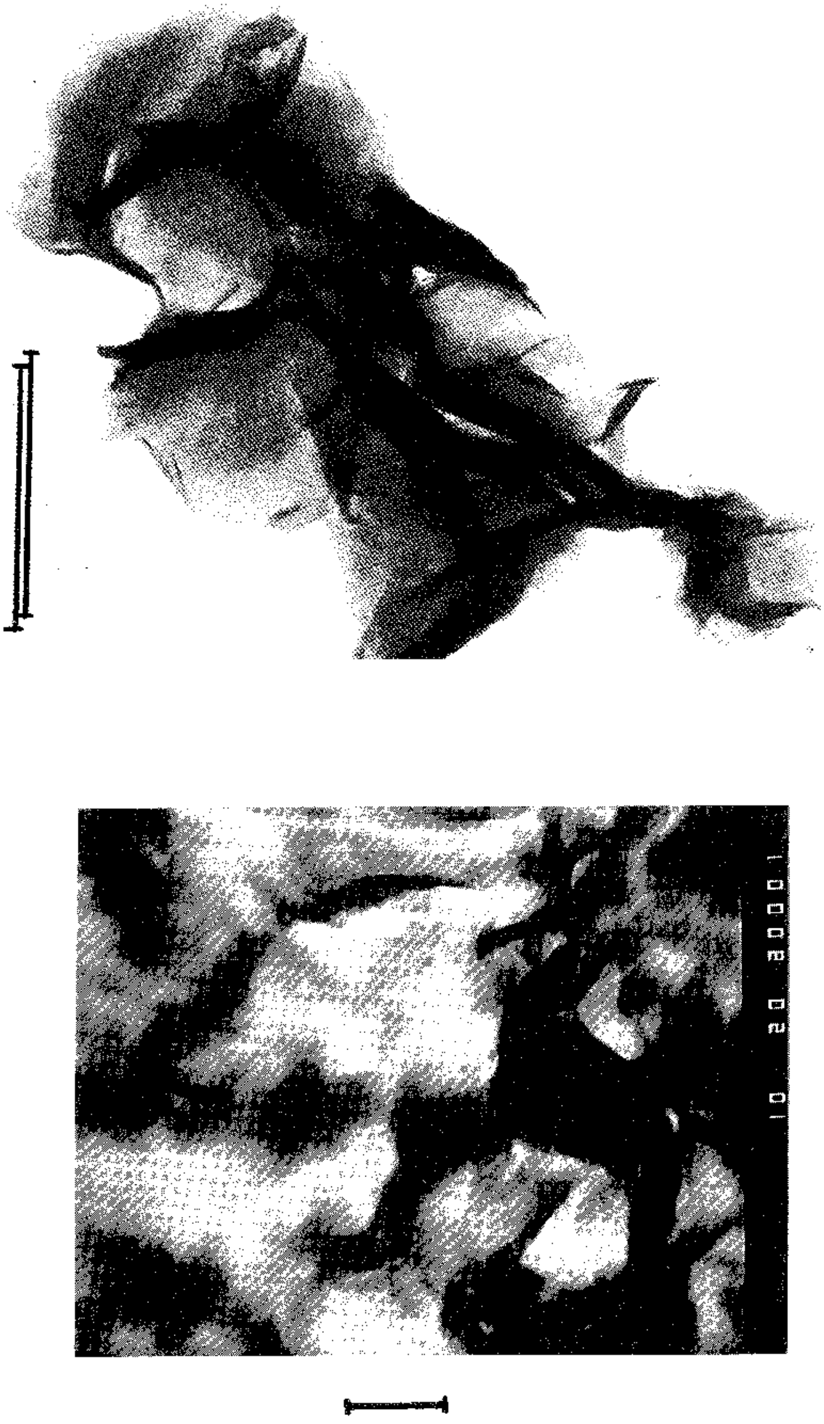


Figure 2-50 Network with dense branches of smectite stacks as appearing after hydrothermal treatment with distilled water; bulk density 2.0 g/cm^3. Upper: Na bentonite after heating to 200°C for 30 days. Lower: Na bentonite after heating to 200°C for 0.5 year. Dark parts represent aggregates of smectite stacks. Bright parts represent voids filled with resin that replaced porewater in the preparation phase. The scale is 1μm

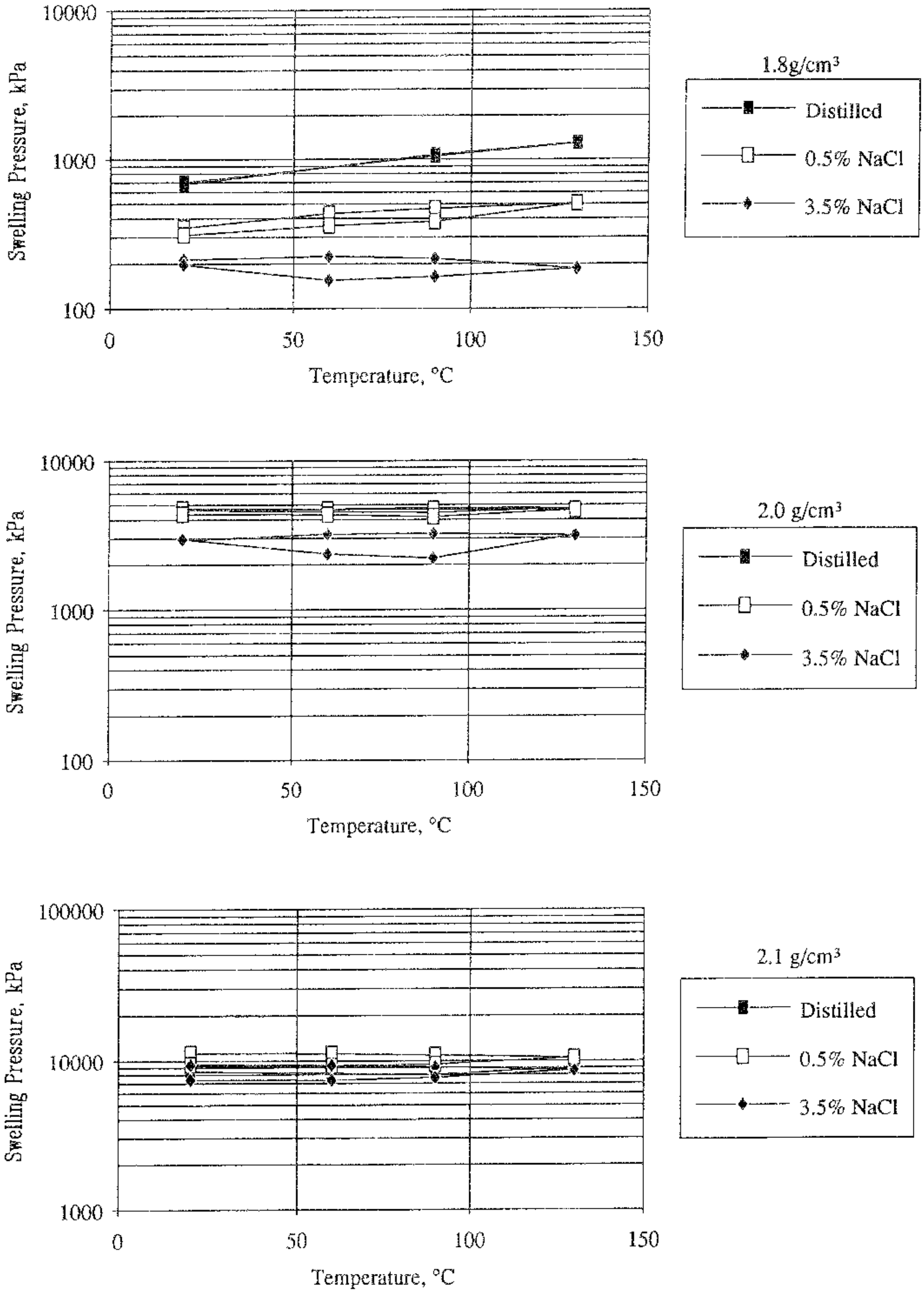


Figure 2-51 Swelling pressure of Na bentonite at different ionic strength of the porewater and different temperatures

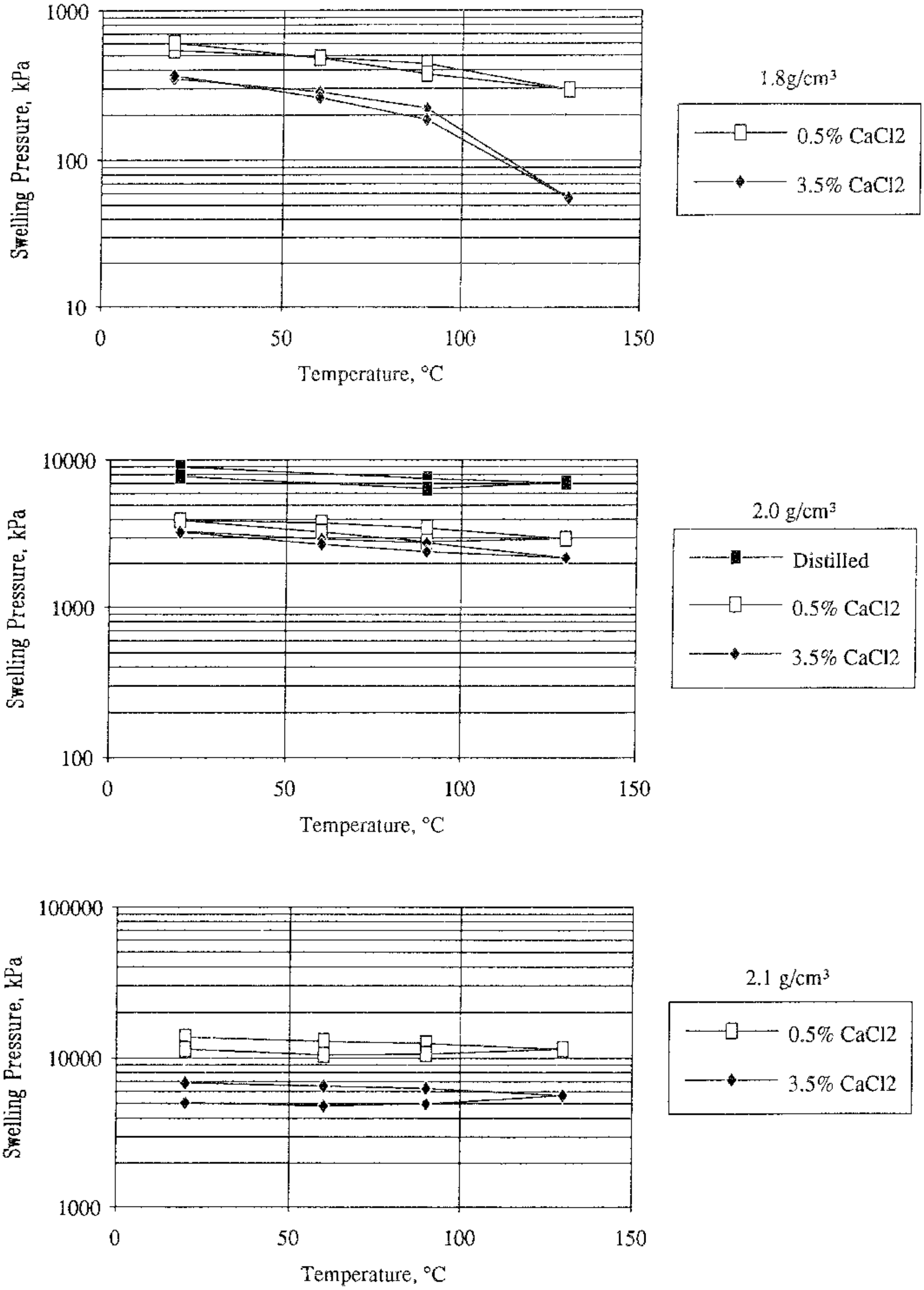


Figure 2-52 Swelling pressure of bentonite in calcium form at different ionic strength of the porewater and different temperatures

An important finding from hydrothermal experiments of the very pure SWY-1 clay as revealed by TEM is that cristobalite, quartz and amorphous silica precipitate within a period of only a few months (59,60). Figure 2-53 illustrates this phenomenon, which yielded objects with a size of 0.1-1 μm in tests performed at 150°C for 4 months, and precipitations even larger than 1 μm in tests at 200°C with a duration of 0.5 years. They were generally formed as dense, subrounded inclusions or contourless accumulations in clay aggregates. Basing the evaluation of the amount of precipitated crystalline silica on TEM pictures from the experiments with distilled porewater at 150 and 200°C it was estimated that about 1 % by weight of the total mass had been neoformed. Both crystalline and amorphous silica compounds in the initially very pure montmorillonite clay were identified by applying EDX and electron diffraction techniques, the first-mentioned giving diagnostic, very high Si/Al ratios of both subrounded crystalline and contourless amorphous features as seen in TEM (Figure 2.54). The latter certified the lack of organized mineral lattices in the contourless material. The amount of neoformed amorphous silica, which also appeared to be integrated in larger clay aggregates, was estimated at about 1 % of the total mass. The accuracy of the estimates of precipitated silica is low, however, and coatings and very small nodules must have escaped identification.

Figure 2-53 TEM photo of Na smectite clay hydrothermally treated at 200°C for 0.5 years. Subrounded silica-rich inclusion (arrow) is integrated in the smectite clay

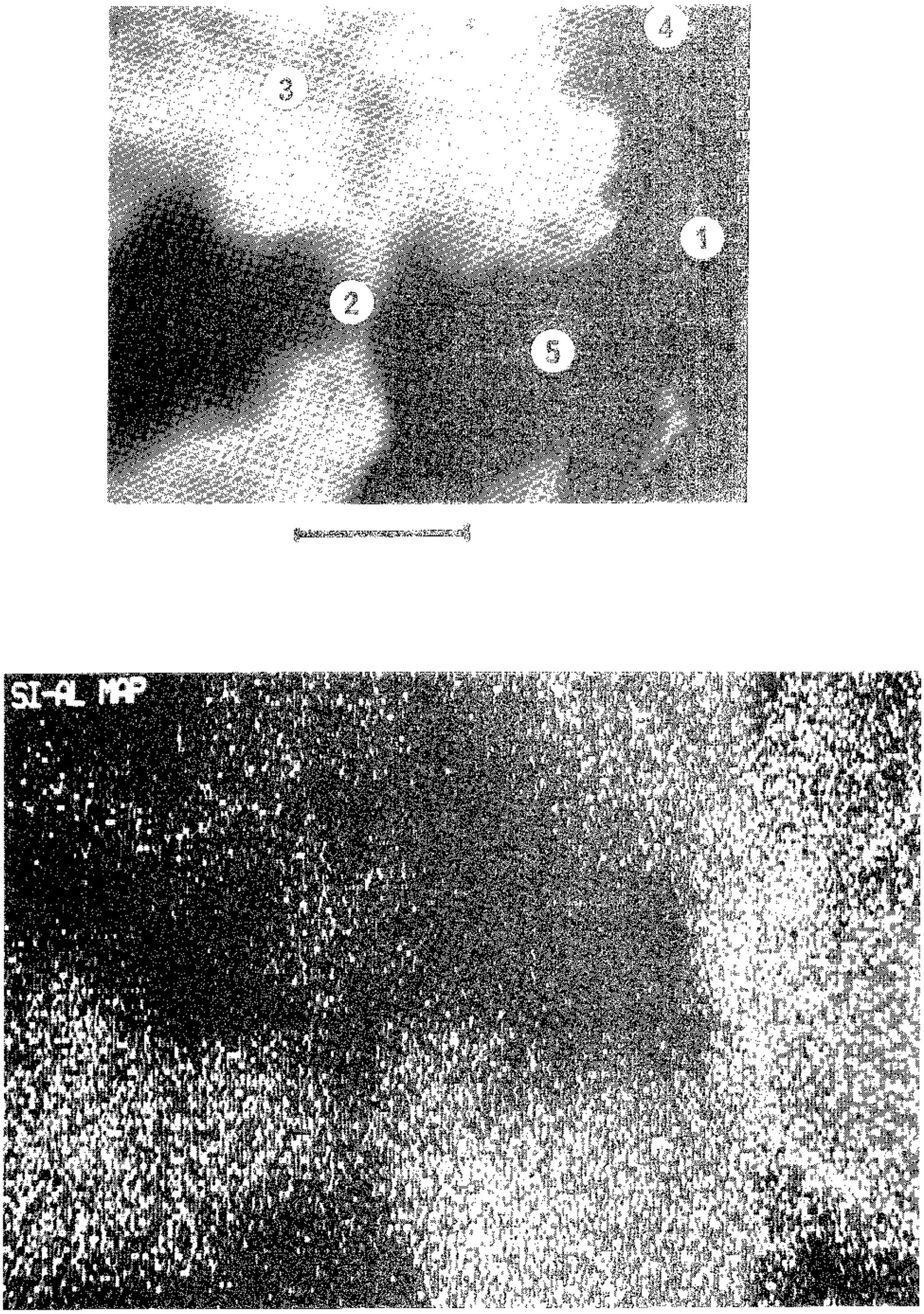


Figure 2-54 Example of element analysis for identification of silica-rich compounds. Upper: TEM photo being a detail of the micrograph in Figure 2-50 (lower) with spots (1-5) marked for element analysis using EDX (Scale is 1 μ m). Lower: Mapping of Si and Al superimposed on the (somewhat enlarged) upper picture. White areas represent typical Si/Al ratio of montmorillonite, while grey areas show excess Si. The grain at the right border is silica-rich and silica-enriched zones are also seen at the edges of several aggregates of stacks

The rheological behavior, determined by use of simple uniaxial compression, gave the important information that hydrothermally treated clay, saturated with distilled water, gains strength even at very moderate temperatures. This is demonstrated by Figure 2-55, which shows that an unheated montmorillonite sample with a dry density of 0.48 g/cm^3 (1.3 g/cm^3 at saturation) failed at an axial pressure of 21 kPa, while heating at 105°C for 1 year gave a strength that was about 50 % higher. Hydrothermal treatment at 150°C for 1 year and at 200°C for 0.5 year gave an increase by 100 %. The highest temperature caused an increase in the compression modulus very significantly as demonstrated by the diagram. The strengthening and stiffening were ascribed both to micro-structural rearrangements and - primarily - to precipitation of silica compounds.

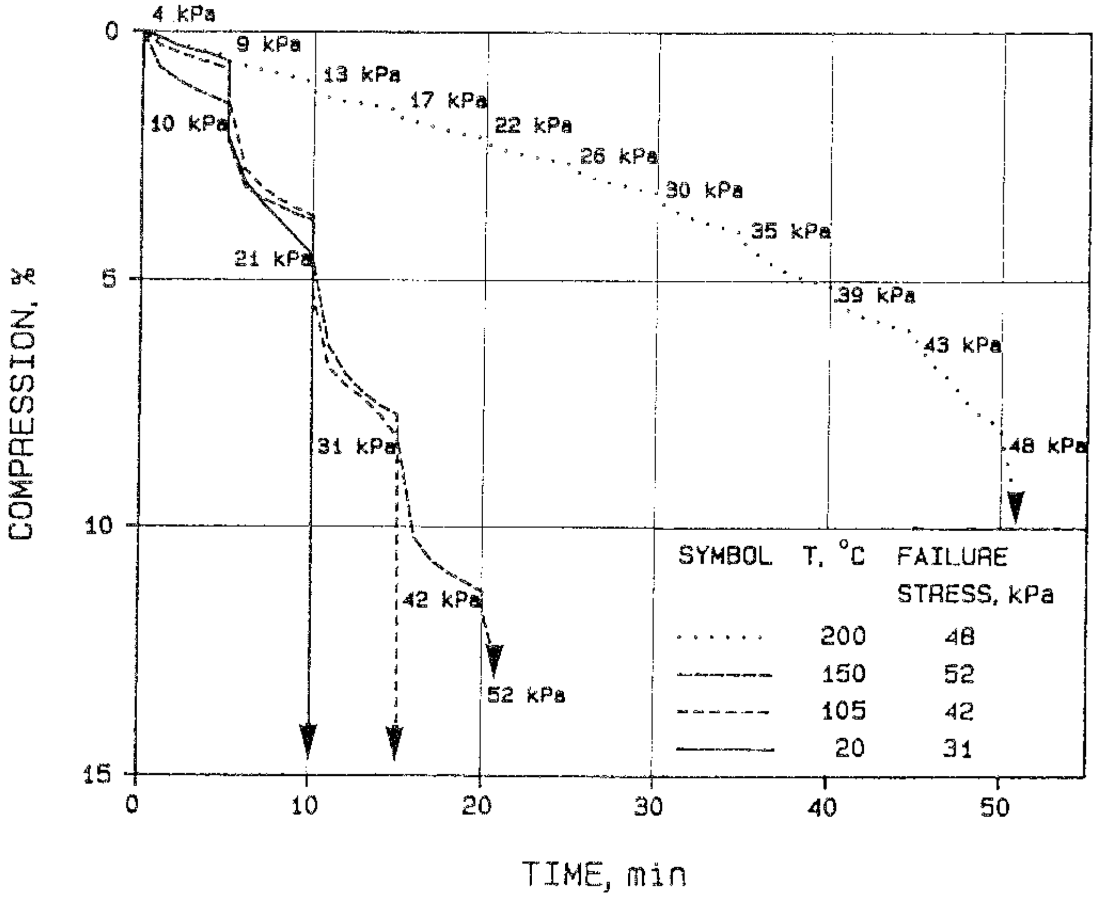


Figure 2-55 Axial compression versus time at unconfined compression testing of smectite clay exposed to hydrothermal treatment

Hydrothermal testing using "open" cells

Such investigations were made in two separate studies: The Stripa Project and a SKB/CEA joint venture.

For the Stripa test series (61) a special equipment was developed for conducting hydrothermal tests under water saturated conditions and constant water pressure, while letting soft smectite clay samples interact with defined amounts of solutions of different kinds (Figure 2-56). The smectite clay was of commercial type (Sardinian bentonite converted to Na form) with quartz, feldspars, calcite and iron sulphide as major accessory minerals but with at least 80 % montmorillonite (90 % of the clay fraction). The density of the clay samples, which were prepared by use of three types of water, i.e. distilled water (D), strongly brackish Ca-rich water (FF), and artificial seawater with 1.8 % electrolyte content (SEA/2), was in the range of 1.1 to 1.4 g/cm^3 for pure bentonite and up to about 1.5 g/cm^3 for mixtures of bentonite and quartz powder. The hydrothermal treatment was conducted at 90, 130, 160 and 200°C for 10, 90 and 270 days, and testing comprised recording of XRD spectra, CEC, chemical analysis of clay and porewater, and determination of the shear strength by laboratory vane testing. A few special tests with 5000 ppm potassium solution, 10 000 ppm K/Mg solution and 15 000 K/Mg/Na solution with chlorine as major anion were also made. In certain experiments the piping resistance and erosion character were investigated as well.

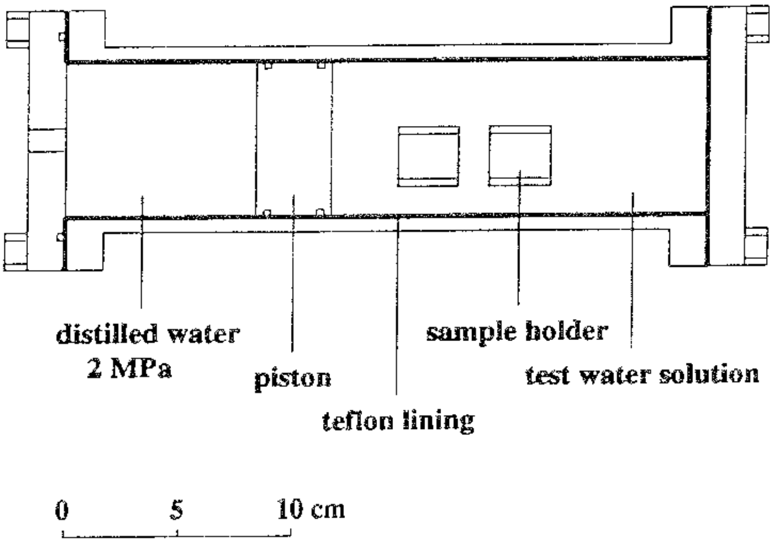


Figure 2-56 Hydrothermal cell arrangement

The mineralogical investigations gave the result that the smectite content had undergone practically no change in any of the experiments with D-water, FF-water or ocean-type water (Sea/2), except - possibly - for a very small amount of illite in the 270 days experiment at 200°C with SEA/2-water, which had a potassium content of 200 ppm. The special tests with potassium-rich solutions ran only for 1 month and they did not yield significant conversion of the montmorillonite either. However, the XRD spectra indicate a very small 10 Å peak for all three solutions and the chemical analyses of the clay indicated a small but clear drop in the Si/Al ratio, suggesting that some very small S→I conversion had taken place (Figure 2-57). Some of the silica that was lost, leading to a reduction of the Si/Al ratio from initially 2.65-2.75 to around 2.4 and to an increase in Si from almost zero to about 120 ppm in the solution, emanated from accessory minerals, especially from feldspars, which were completely dissolved in the 200°C tests. Aluminum, on the other hand, did hardly appear in the solutions and must have been retained in the clay, forming complexes and - possibly - some small amount of illite.

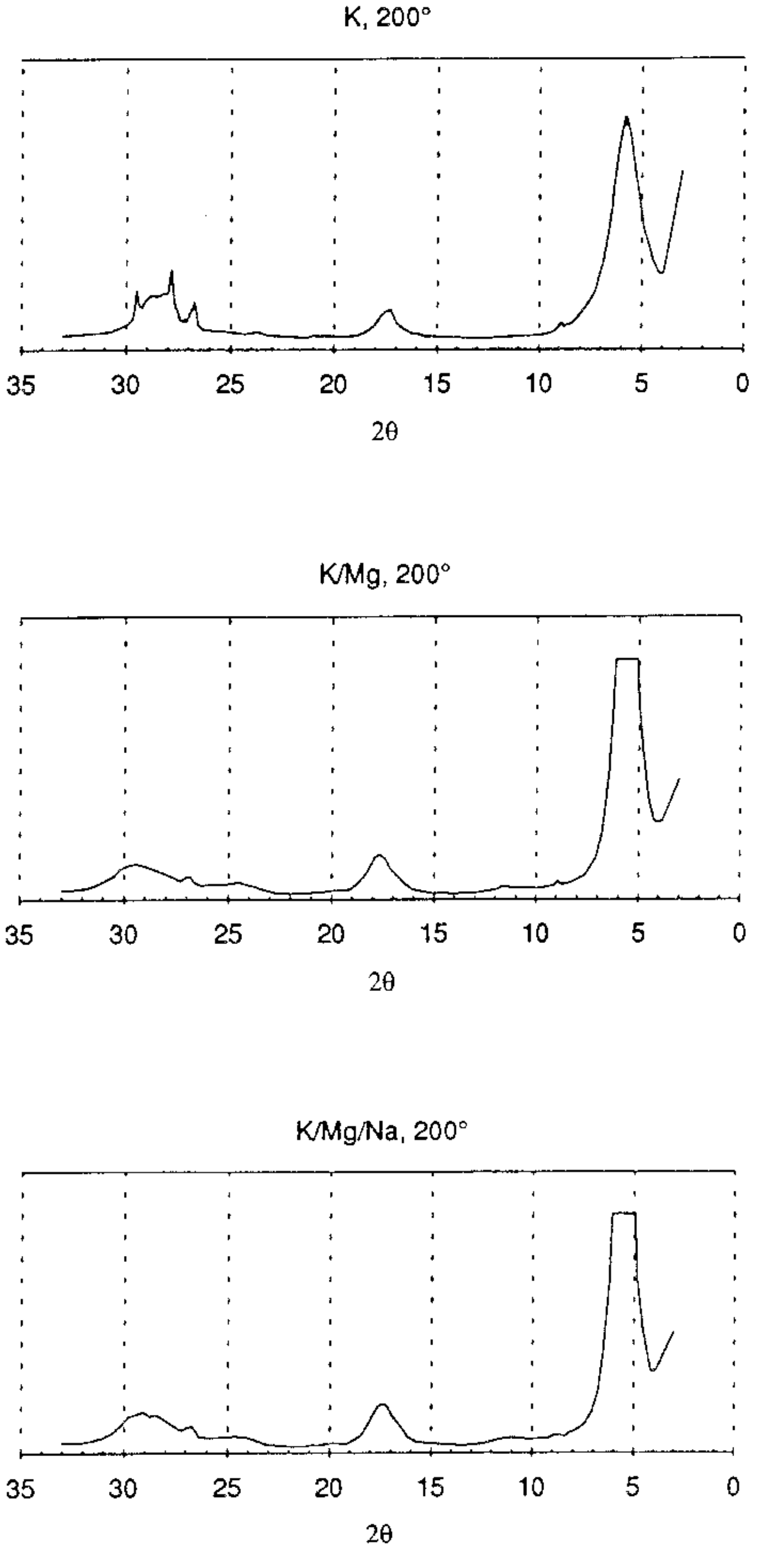


Figure 2-57 XRD spectra of oriented specimens emanating from hydrothermally treated samples exposed to 200°C for 1 month

The analyses of the liquid phase, i.e. the solutions in the hydrothermal cells with which the filter-equipped sample holders were contacted, showed that pH dropped significantly, i.e. from initially 7 (FF-water yielding Ca-conditions) and to 9.5 (Distilled water) down to 3.5-4.5 after 270 days at 200°C (Figure 2-58). The pH conditions in the clay samples are not known but the very moderate attack on the clay indicates that the buffering capacity was significant. The content of H_4SiO_4 ions emanating from dissolved clay and accessory minerals is assumed to be the major cause of the pH drop.

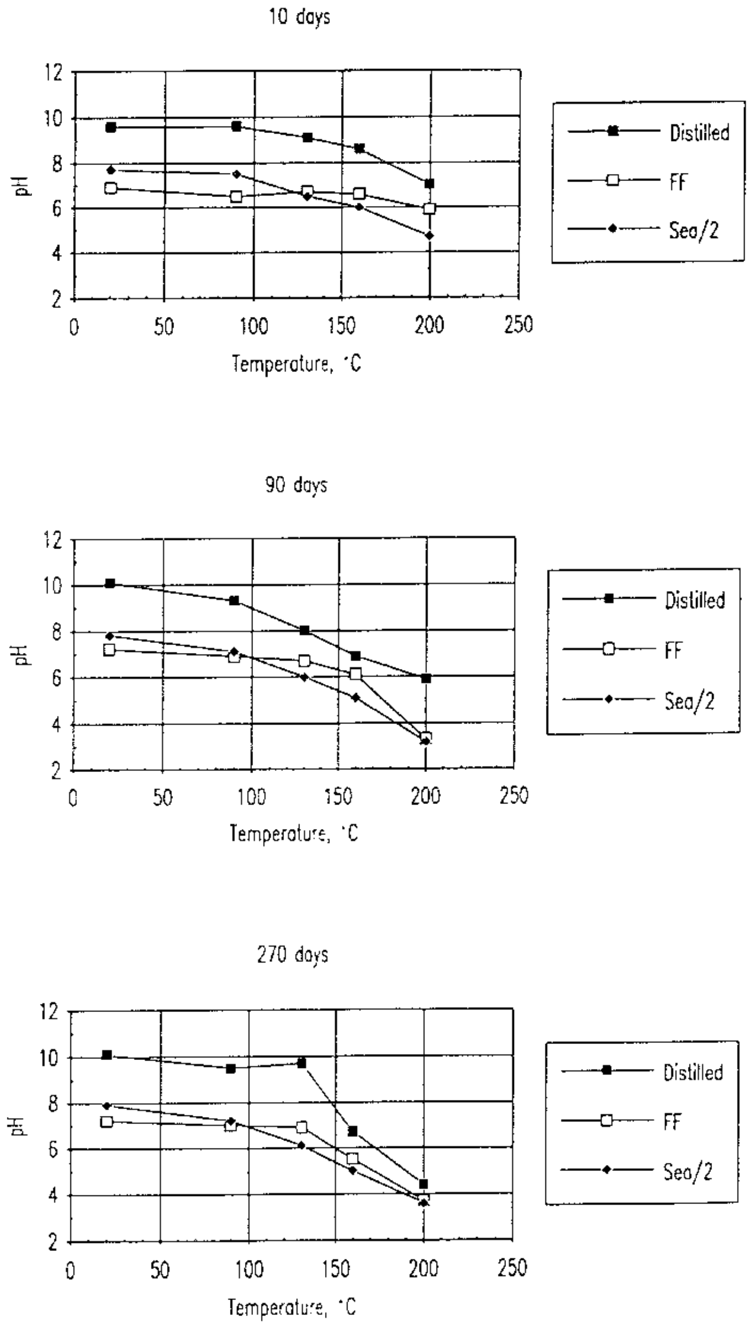


Figure 2-58 Change in pH in the hydrothermal cell solutions

The main conclusions from the very comprehensive mineralogical and chemical Stripa test series were the following:

1. Aluminum stayed in the clay/water system up to 200°C irrespective of the chemical composition of the ambient solution. This confirms the general idea that the mobility of Al is very small in natural soils and rock and it suggests that neoformation of minerals requiring aluminum - like illite - utilizes available Al that emanates from dissolution of accessory Al-bearing minerals as well as from smectite ("cannibalization")

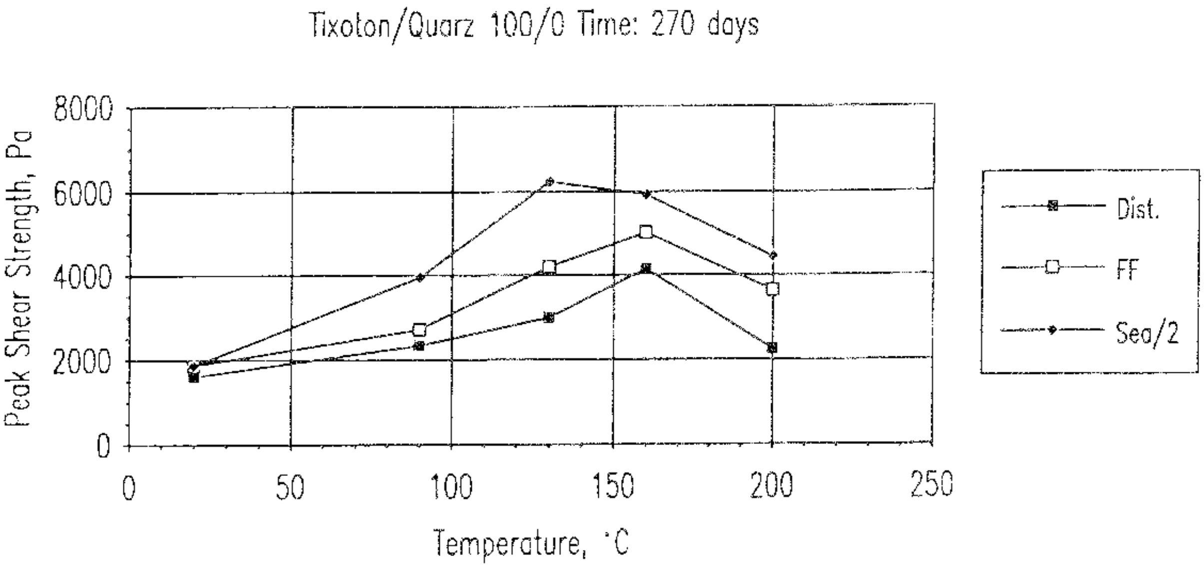
2. Release of silica from the clay increased exponentially with temperature. The obvious increase in released silica at temperatures exceeding about 100°C in short-term experiments like the Stripa laboratory tests is probably related to dissolution of accessory minerals, primarily quartz and feldspars

3. The only sign of illitization was when the potassium content was significant, i.e. at least 200 ppm, but the illite content was very small. The only additional alteration process that had to do with the clay minerals was a very weak tendency of formation of a 14 Å peak that may be related to interlamellar establishment of aluminum or magnesium hydroxy complexes at the highest temperatures

4. Experiments with 50 % quartz powder mixed with the bentonite caused some increase in dissolved silica. Cementation is thus expected to have been stronger than in pure bentonite (see below).

The rheological experiments, which had the form of laboratory vane testing, showed that strengthening by cementation due to precipitation of silica compounds was very obvious. For the FF-water and Sea/2 water it was concluded from the XRD spectra that sulphates were precipitated, which can have contributed to the increase in strength, but precipitation of amorphous silica is believed to have been more important. Figure 2-59 demonstrates that the investigated pure bentonite (Tixoton) with D-water got its shear strength increased by about 40 % when exposed to 90°C for 270 days, and by more 100 % at 160°C, while it dropped back to practically the initial value at 200°C. The strength reduction at the highest temperature was probably due to micro-structural changes, possibly fissuring, but it may also be that the contact between the sample and the sample holder was less good due to loss in mass and shrinkage of the samples.

Figure 2-59 also indicates that the relative increase in strength is somewhat higher when quartz powder is added. For 50% quartz the relative increase is about 100% higher than without quartz, which suggests that this additive should not be used for buffer materials, although the increase in thermal conductivity that it offers is an attractive property.



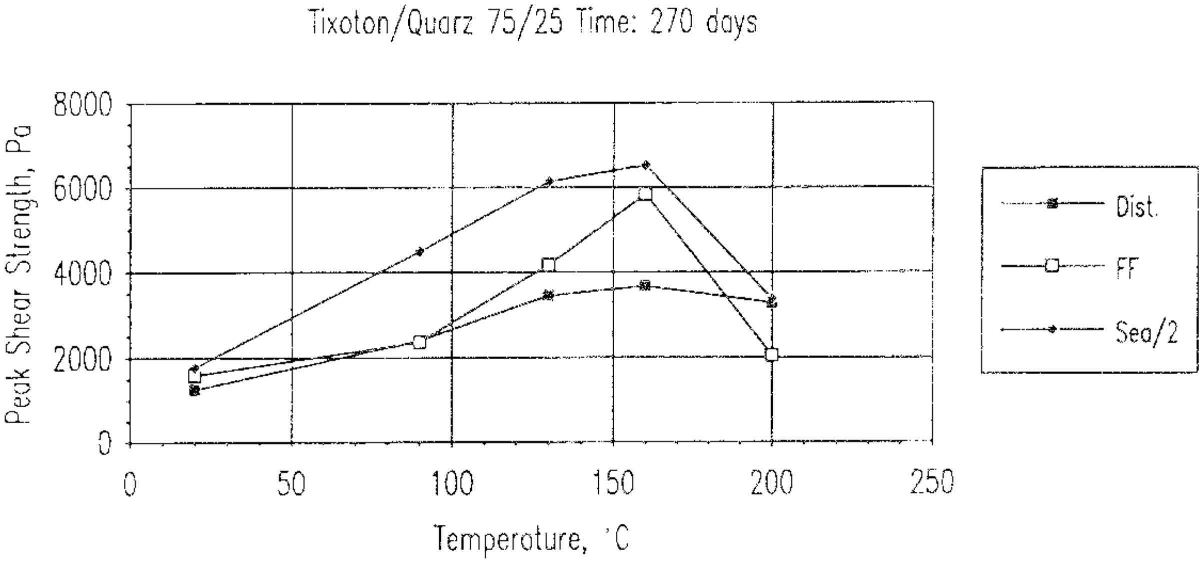


Figure 2-59 Shear strength of smectitic clay exposed to hydrothermal treatment. Upper: Tixoton bentonite. Lower: Mixture of Tixoton/quartz to a ratio of 75/25

A last point is to use the information from the Stripa tests to check the applicability of Pytte's model. We immediately realize that only the experiments at 200°C and very high potassium contents would give any sign of conversion according to this model and this fits well with the recordings. Thus, with the very high potassium concentration of the KCl solution (12 times that of ocean water) the diagram in Figure 2-23 (lower) indicates that a few percent would be converted in one month, which corresponds to the small but clear sign of 10 Å mineral formation seen in the upper diagram of Figure 2-57. This is also in agreement with the finding that this this experiment was the only one in which uptake and fixation of potassium by the clay from the solution actually took place.

The SKB/CEA joint venture was conducted at Saclay with an equipment that made it possible to expose the sample - which was prepared from MX-80 powder compacted to a bulk density of 2.05 g/cm^3 (dry density 1.65 g/cm^3) by saturation with very weakly brackish, Na-dominated "Allard" water - to a temperature gradient and to gamma radiation (62). The high-temperature end was a tight steel plate that was maintained at 130°C and exposed to radiation from a ^{60}Co radiation source that gave an adsorbed dose rate of about 4000 Gy/h at this end and about 500 Gy/h at the opposite end of the 70 mm long sample (termed IR). It contacted a steel filter through which the porewater in the sample could interact with an external solution of Allard water that was pressurized at 1.5 MPa (Figure 2-60). The filter end was kept at 90°C and the temperature gradient was thus about 6°C/cm, which is significantly higher than in a KBS3-type repository. Parallel tests were made with heating but no irradiation (samples termed NONIR), and also with neither heating nor irradiation (REF).

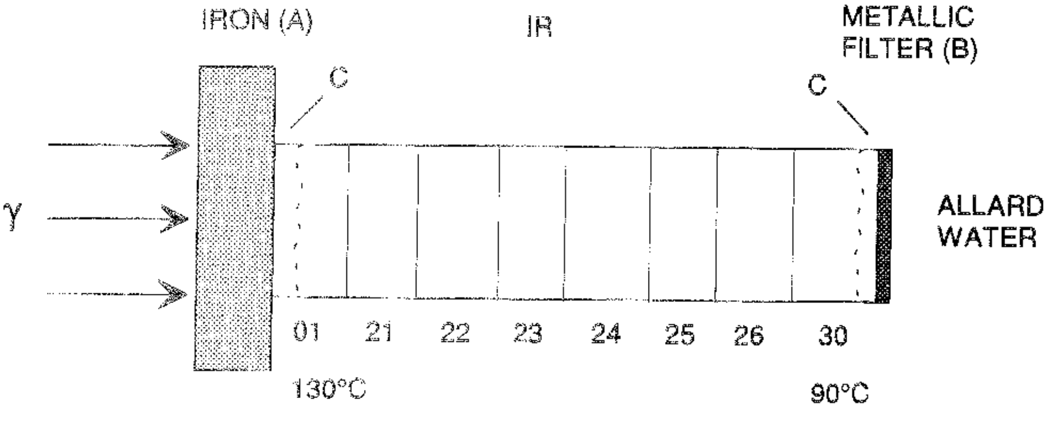


Figure 2-60 Schematic picture of the irradiated MX-80 sample

The major outcome of the study, which was conducted for 1 year, was that the smectite underwent only very small changes.The main results can be summarized in the following way:

XRD spectra showed that the low-charge montmorillonite making up the large majority of MX-80 remained largely intact in both the IR and NONIR samples (Figure 2-61). However, they also indicated some slight broadening and displacement to low angles of the (001) montmorillonite peak, suggesting a tendency of formation of chlorite-type minerals, possibly in the form of iron hydroxide in interlamellar positions. Furthermore, the spectra demonstrated that the major mineralogical changes were complete disappearance of feldspars at 130°C and partial loss of these minerals also at about 90°C. At the end of the samples heated to 130°C, sulphate formation (gypsum, anhydrate, and probably hexahydrate) was very obvious, and such minerals were also formed - although to a lesser extent - in the colder parts of the sample. Small amounts of quartz were formed in all parts of the sample except at the hottest end.

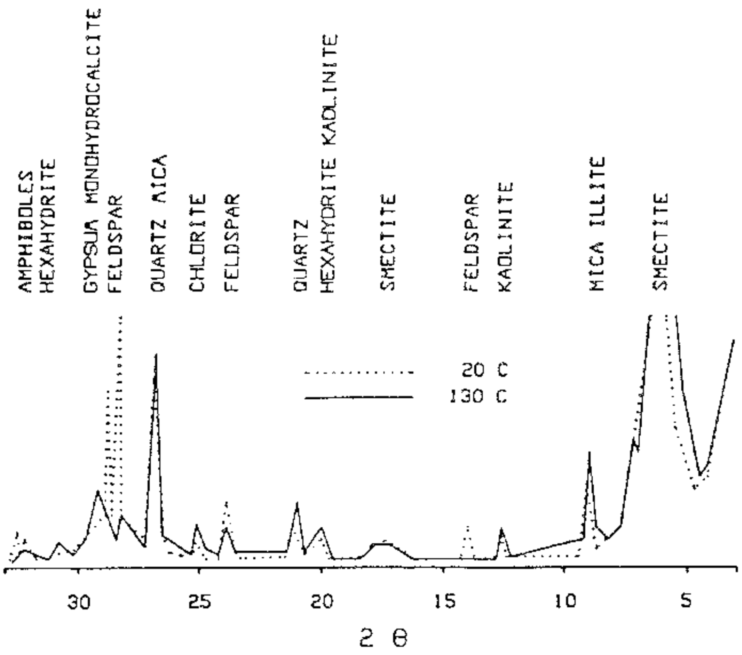


Figure 2-61 Rectified XRD spectra of samples 00 (20°) and 01 (130°C)

The REF sample had a higher content of sodium, calcium and silica, expressed in Na_2O, CaO, and SiO_2, than the other samples, while iron, expressed in Fe_2O_3 and emanating from the hot, irradiated steel, had increased throughout the IR and NONIR samples, especially at their hot ends. The XRD spectra indicate that iron was present as poorly crystallized hematite.

TEM studies showed that the most obvious change was that the IR and NONIR samples were microstructurally more homogeneous than the REF sample. Another observation was that the 130°C samples contained much precipitations as illustrated in Figure 2-62, and EDX analyses indicated that many of them were sulphates and calcite (monohydrocalcite).

A general conclusion of the mineralogical and chemical investigations was that heating without irradiation caused nearly the same changes as when irradiation was also applied, but that they were slower and less well developed.

The physical properties of the IR sample were investigated with respect to the hydraulic conductivity and the rheological behavior. The conductivity turned out to be practically the same irrespective of the temperature and irradiation to which they had been exposed and it was also almost the same as that of the REF sample. The creep behavior indicated strenghtening of the materials that had been exposed to 115 and 130°C but the smooth character of the creep curves demonstrated that the ductile behavior of the virgin clay was preserved and that cementation could not have been very significant (Figure 2-63).

Experiments were also made with free expansion of samples by reducing the confining pressure in the creep tests from 6 to 5 MPa. The expansion took place in a smooth, continuous fashion as indicated in Figure 2-64, which shows that the REF sample (00) and the most heated and irradiated end (01) behaved almost identically, also suggesting that cementation was insignificant.

Finally, checking of what degree of conversion that Pytte's model would predict for an activation energy of 27 kcal/mole and a very low potassium content, one finds by applying the diagram in Figure 2-24 (upper) that no conversion to illite would be expected at all. This is in perfect agreement with the outcome of the experiments.

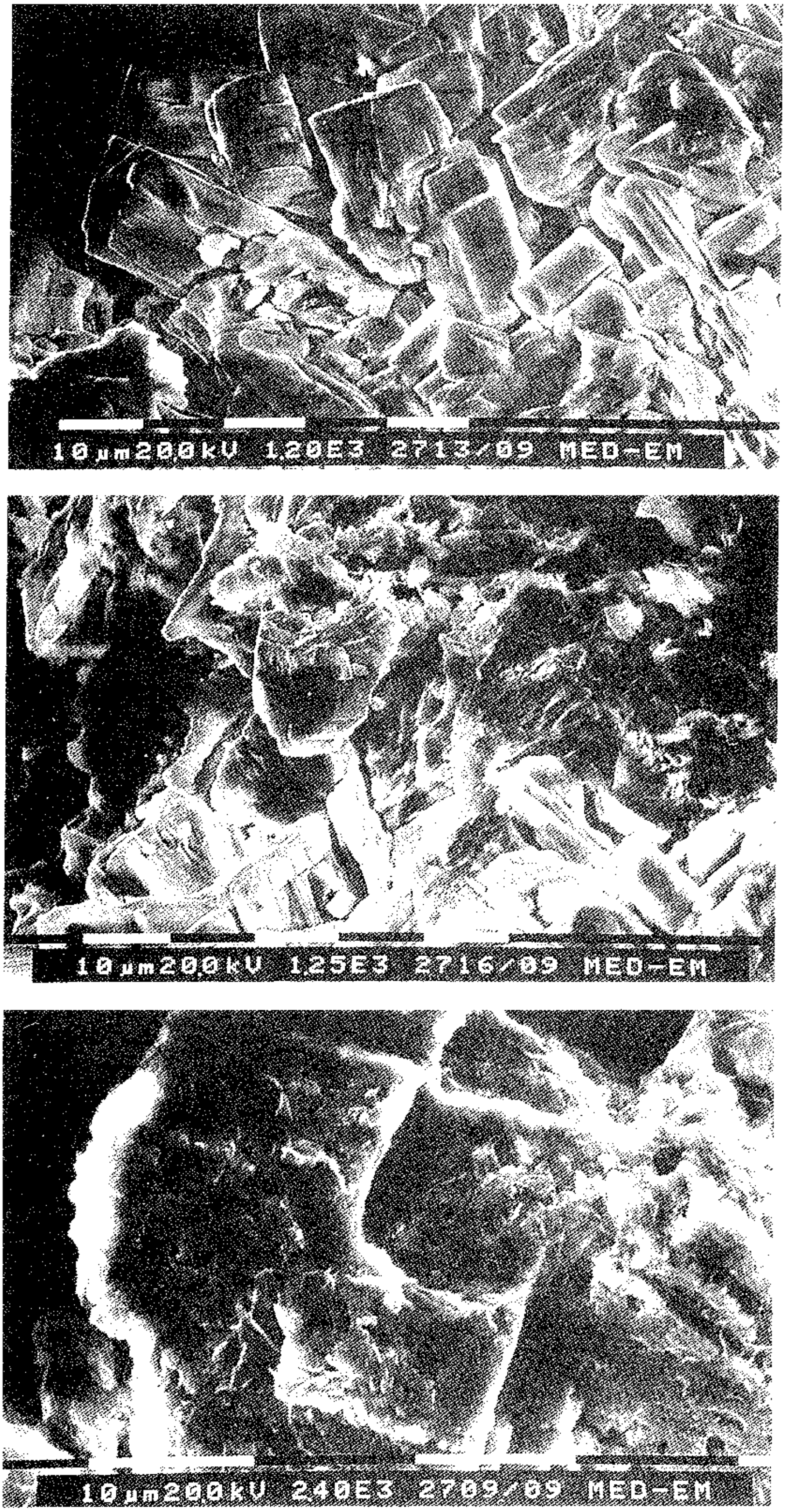
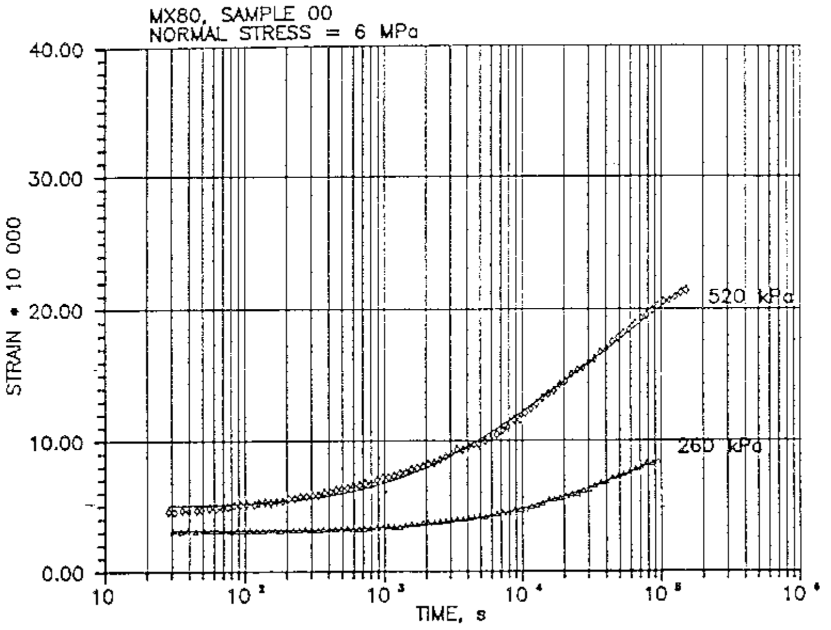


Figure 2-62 Precipitations in the most strongly heated (130°C) and irradiated part of the IR sample. Upper and center: Calcium sulphate. Lower Precipitates rich in iron and calcium. Scale bars are indicated in the micrographs



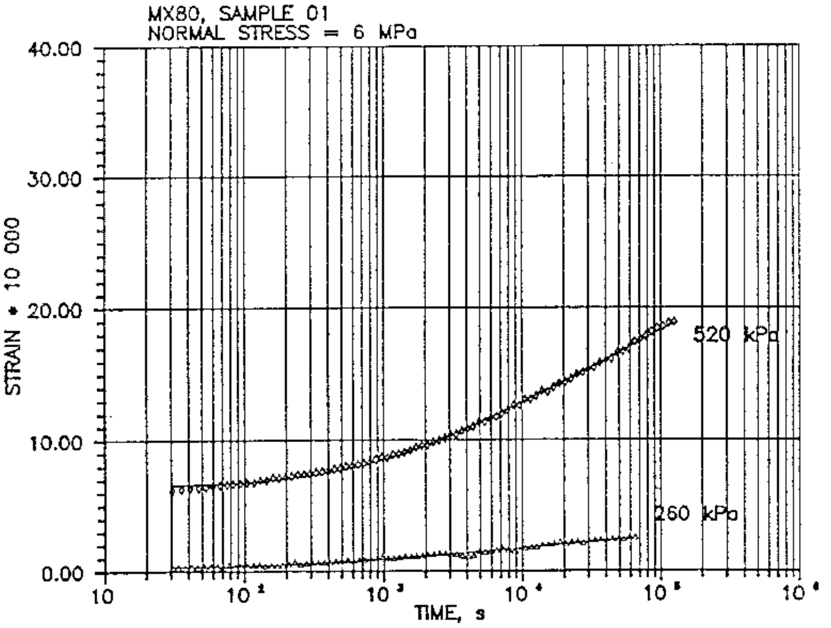


Figure 2-63 Creep curves of MX-80. Upper: REF sample. Lower: Most strongly heated (130°C) and irradiated part of the IR sample

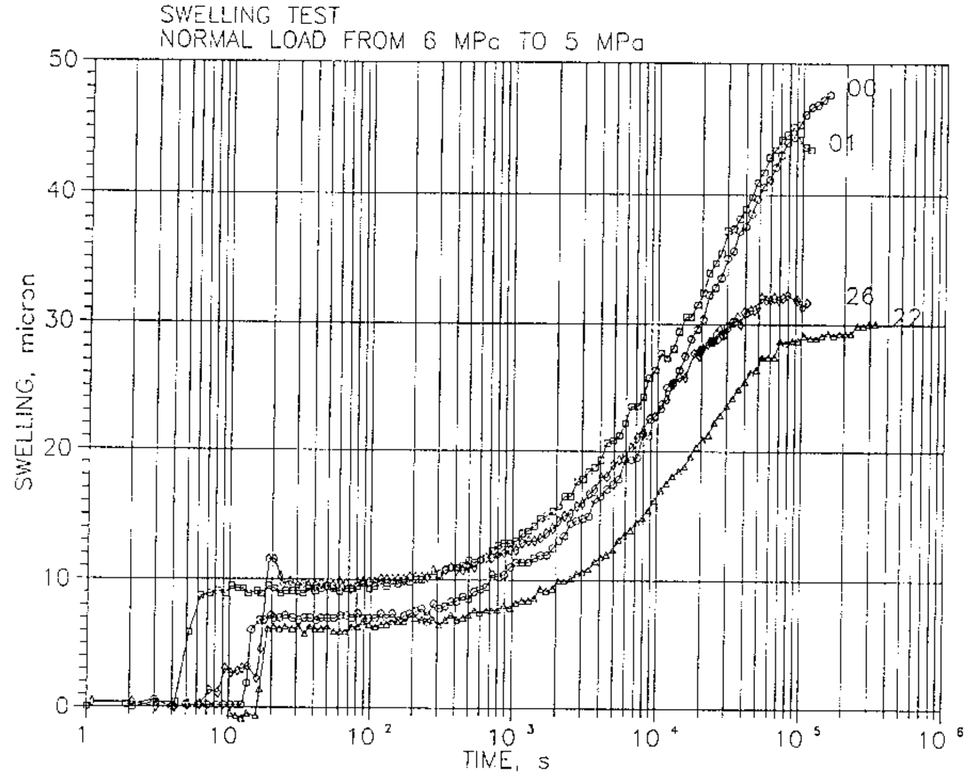


Figure 2-64 Expansion of specimens from samples 00 (REF), 01 (most heated and irradiated part of the IR sample), 22 (115°C) and 26 (95°C)

MAJOR CONCLUSIONS FROM THE LABORATORY TESTS

The comprehensive laboratory tests have shed considerable light on the processes that take place in hydrothermal testing of bentonite both under closed and open conditions, but not very much information has been gained concerning the processes involved in S→I conversion since very little true alteration to or neoformation of illite has been obtained. The reason for this is concluded to be that, at the temperatures applied, there has not been access to sufficiently much potassium or to sufficiently much time, to cause significant conversion. The only experiments in which illite formation was significant are recently performed cyclic drying/wetting tests (63) using very potassium-rich solutions, much in the same way as those reported by Eberl (32). However, also the 1 month long Stripa experiment with such a solution gave a clear although insignificant indication of formation of illite, which fits Pytte's semi-empirical illitization model for an activation energy of 27 kcal/mole and parameter values given earlier in this report.

Other informations from the laboratory studies can be summarized as follows:

1. Hydrothermal treatment at 90°C and higher temperatures causes an increase in strength and less creep. For temperatures up to about 130°C this can have two reasons: the microstructure becomes more homogeneous, and there is some slight cementation. At higher temperatures, cementation may be more significant and microstructural changes may also involve formation of denser branches of the network and possibly some shrinkage

2. A considerable part of the silicious cementing agents appear to originate from feldspars, which may be completely dissolved at 130°C. If they are made up of K-bearing species, a significant potassium source for illitization is created, and a present estimate is that the content of such minerals should therefore be less than a few percent in canister-embedding buffer materials

3. Sulphide minerals tend to become dissolved even at about 90°C and supply the clay porewater with sulphate ions, which, together with those being present in the ambient groundwater, cause precipitation of calcium and magnesium sulphates at the hot end of clay exposed to a temperature gradient. Strong enrichment of such minerals and also of calcite, which exhibits similar dissolution properties, is expected at the canister surface if the content of sulphur-bearing accessory minerals exceeds a few percent and if groundwater percolates the nearfield at a sufficiently high rate. Strong cementation effects are expected but also clogging of voids in the clay, which may yield a considerable drop in hydraulic conductivity

Special investigations

Two special studies using nuclear magnetic methods of the NMR type have been performed with the attempt to get more detailed information on two issues, the first one being possible charge changes in montmorillonite (replacement of tetrahedral silica by aluminum) in hydrothermal experiments with no potassium available, and the other one concerning the bonding of interlamellar water to the clay lattice.

The HEW and EF versions of the montmorillonite crystal lattice

The idea of the first study was that Forslind's hypothesis (5) that there are two, temperature-dependent crystal lattice forms (Figures 1-4 and 1-5) could give an explanation of how silica leaves tetrahedral positions in the beidellitization process and how interlamellar precipitation of silica may take place (64). By comparing the crystal constitutions in Figures 1-4 and 1.5 and considering the interlamellar water to be very little influenced by the interlamellar cation Na, which is supported by various investigators (65), and to have the form of organized lattices dominated by hydrogen bonding (Figure 2-14), one finds that breakdown of the lattices at a critical temperature would imply inversion of the apical Si/O tetrahedrons (cf. Figure 2-65), yielding an unstable condition of the silicons. If such inversion takes place in conjunction with transfer of octahedral or "external" aluminum to the tetrahedral sheet, about one fourth of the tetrahedral silicons would easily be moved into the interlamellar space where precipitation of silica in amorphous form may take place in the fashion indicated in Figure 2-66. Since Ca in inter-lamellar exchange positions does not allow for the build-up of water lattices of this type, Ca montmorillonite would be more stable than Na montmorillonite, which is claimed by several investigators as pointed out earlier in the text. MAS NMR gives information on the different coordination of silicons and aluminum in the HEW and EF states and also on free silica and this technique was therefore applied.

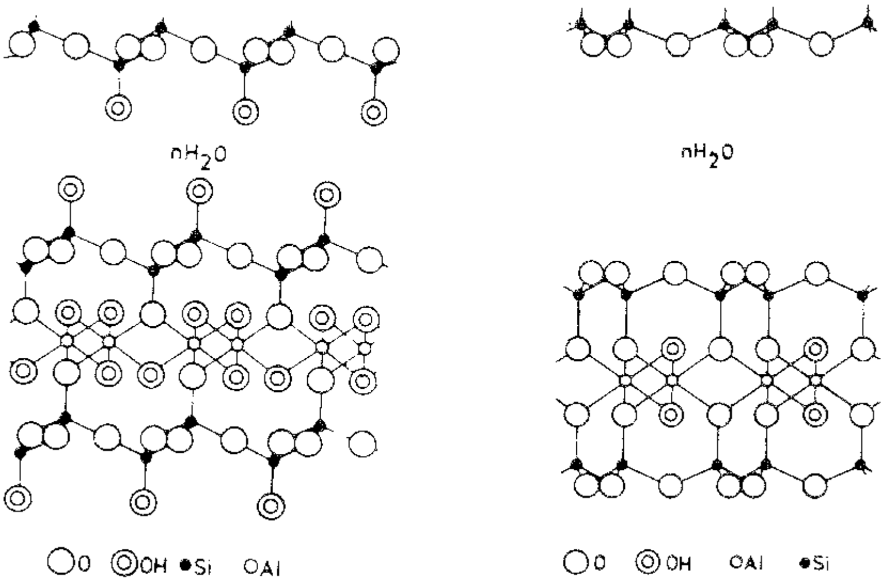


Figure 2-65 Inversion of the EF structure with apical tetrahedrons to the left to the HEW "conventional" structure to the right (cf. Figures 1-4 and 1-5)

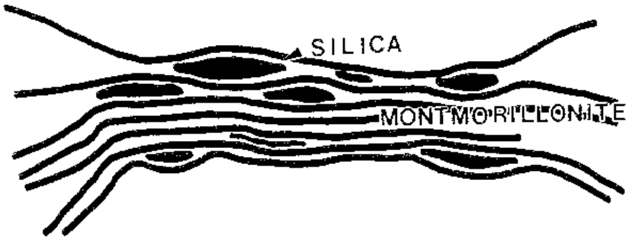


Figure 2-66 Distribution of precipitated amorphous silica in montmorillonite (After Meike)

Very iron-poor montmorillonite samples (Clay Spur and Texan), saturated with distilled water, were hydrothermally treated at 200°C for 3 weeks and investigated with respect to ^{29}Si with similar tests being conducted also on untreated reference material. The major outcome of the study was that Na montmorillonite showed a spectrum that corresponds, in principle, to the EF structure while Ca montmorillonite would better agree with the HEW type (54). Thus, the ratio of the integrated areas of primary (-93 ppm) and secondary (-107 to -118 ppm) peaks was consistently different by about 50 % for Na and Ca montmorillonite, which is a definite sign of different coordination of the silicons in the two types of clays (54). Thus, much more silica is in *cis*-coordination of tetrahedrons of conventional HEW type in Ca montmorillonite, while in Na montmorillonite, a significant part appears to be in *trans*-coordination in apical tetrahedrons (pers. comm. Tore Skjetne, SINTEF, Norway). This is a strong support of Forslind's crystal lattice model and also of the idea that montmorillonite should be more stable in Ca form than when Na is in interlamellar positions.

Corresponding investigations were made with respect to the coordination of lattice aluminum (^{27}Al). They showed that tetrahedral aluminum was almost absent in the virgin material and that the hydrothermally treated clay samples showed a negligible increase in tetrahedral aluminum. Hence, the crystal constitution, initially different in Na and Ca montmorillonite, remained unaffected in both types of clay even in the high-temperature tests.

Both the ^{29}Si and ^{27}Al MAS NMR studies hence demonstrated that the hydrothermal treatment with temperatures up to 200°C did not cause permanent transfer from the assumed initial EF state to the HEW state of the Na montmorillonite. However, a separate study of ^{29}Si using cross polarization in fact indicated a slight but significant change in shape of the main -93 ppm peak on heating to more than about 100°C, which has been interpreted as at least partial transfer from the EF state to HEW (54). It is expected that if such transfer took place at all, it would in fact have been reversed at cooling and therefore hardly recorded in the NMR experiments, all of which were performed at room temperature.

The other NMR study was made in the years 1978-1985 and it was focused on the hydration properties of montmorillonite, for which purpose proton NMR was applied. The key parameter that was determined and that is a measure of the proton mobility is the relaxation time T_2. Very short T_2 values, i.e. on the order of a fraction of a millisecond, indicate a high degree of ordering of protons, like in lattice hydroxyls, while for protons in liquid, free water ,T_2 is on the order of 2 seconds. This means that if the relative amounts of differently associated protons is known, one can determine their average physical state, which was used for the porewater in montmorillonite. The basis of the investigation was experimental T_2 data for different clay densities, temperatures, and porewater solutions published by Carlsson and shown in Figure 2-67, (66). These data show that the average mobility of water molecules increases with temperature and bulk density and that it is higher when Na is the dominant cation than when Ca is the major one. However, from these values one cannot distinguish between the physical state of water in interlamellar positions and in external voids.

Recent reinterpretation of Carlsson's data using the GMM microstructural model, gives a more clear picture. Thus, using Woessner's (67) expression for converting two relaxation contributions (T_{2i} for the interlamellar water and T_{2e} for the porewater) into one "averaged" as recorded by NMR (T_e), the following expression is obtained:

$$1/T_2=fs/T_{2i} + fb/T_{2e} \qquad (7)$$

where
fs=fraction of interlamellar water
fb=fraction of porewater (external)

Now, using the diagram in Figure 2-11 for the partition of the two types of water and using Carlsson's recorded T_2-values in Figure 2-67, one gets the T_{2i}-values in Table 2-4. The data for the state with Na in interlamellar positions are more comprehensive in order to make it possible to see the influence of a larger range of water contents.

Table 2-4 T_{2i} in µs for different water contents (w) and cations in the two temperature regions 17-23°C, and 75-82°C

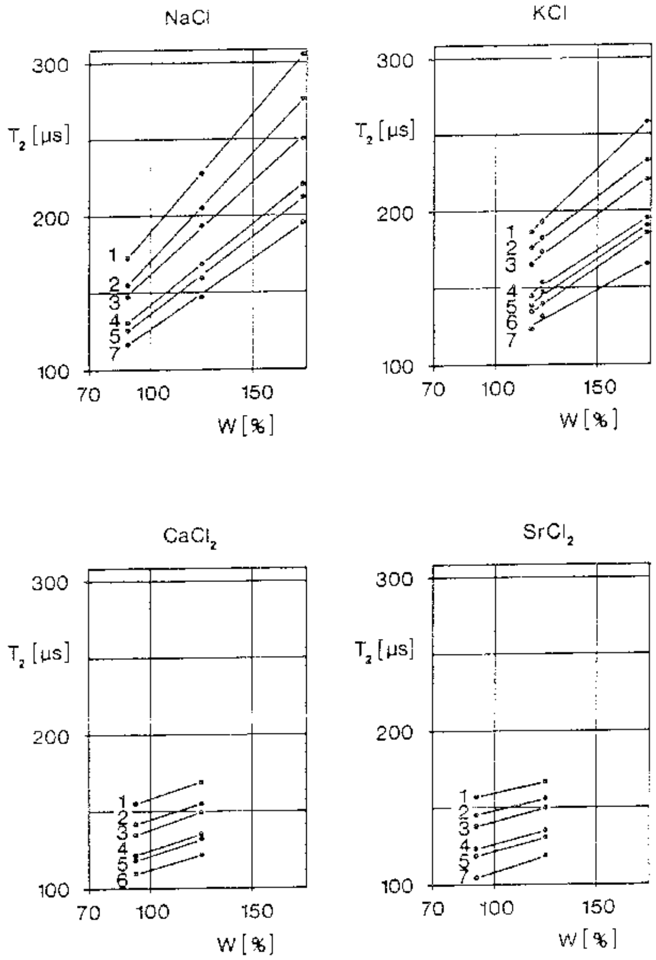
w, %	Na	K	Ca
	17-23°C		
23	43		
68	49		
90-115	44	29	22
125-150	39	-	20
	75-82°C		
23	59		
68	70		
90-115	66	44	31
125-175	57	-	27

A first observation is that although there is scattering, the T_{2i}-values are not significantly dependent on the water content, which is in agreement with the applied principle of partitioning. This suggests that all the hydrates in the interlamellar space are approximately in the same physical state, i.e. that the water molecules in the assumed 3 hydrates in Na montmorillonite with lower bulk densities than about 1.5 g/cm^3 (w>90 %) and the molecules in the 1-2 hydrate layer in such clay with higher bulk densities than about 2.1 g/cm^3 (w<23 %), are nearly equally bonded (cf Table 2.5). This suggests that the interlamellar water molecules in Na montmorillonite form a pseudo-crystalline lattice.

Table 2-5 Relationship between density and basal spacing of Na montmorillonite (68)

Bulk density, g/cm^3	Basal spacing, Å	Average number of hydrates Forslind/EF	HEW
2.1-2.2	13.7-14.6	1	1-2
2.0-2.1	14.6-16.5	1	2
1.9-2.0	16.5-18.3	1-2	2-3
1.7-1.9	18.3-19.3	2	3
1.5-1.7	19.3-23	2-3	3[1)]
1.4-1.5	23.0-27	3	3[1)]

[1)] Assumed maximum expansion



(°C): 1) +81.5, 2) +67.1, 3) +56.5, 4) +41.0,
5) +33.4, 6) +23.9, 7) +17.4

Figure 2-16 Proton relaxation times of montmorillonite/electrolyte systems according to Carlsson's NMR tests (66)

Another interesting result is that an increase in temperature from about 20 to about 80°C increases the relaxation time by around 50 % for Na and K montmorillonite and about 40 % for Ca montmorillonite. This is significantly less than the change in viscosity of free water, which is around threefold (1.0 cP at 20°C to 0.35 cP at 80°C), from which one concludes that interlamellar water is in a significantly different physical state than free water, which is in agreement with the idea of pseudocrystalline, highly viscous, interlamellar water lattices (5, 22, 69).

We also see from the table that there is a clear and consistent difference in proton mobility for the different clays, indicating that water molecules are most strongly organized when calcium ions are in interlamellar positions and most loosely held in sodium montmorillonite. When potassium is in these positions the mobility of the water molecules is intermediate to that of the other two states. This yields the important conclusion that exchange of calcium ions initially located in the interlamellar space by sodium or potassium ions is strongly hindered as suggested already by Howard (p.31). The figures are in qualitative agreement with the Forslind's idea (5) that, for sodium montmorillonite, the water molecules form interlamellar lattices in which the sodium ions are only weakly hydrated and easily moved under the influence of concentration gradients, while replacement by potassium ions breaks down and reorganizes the water molecule lattice, a process that requires an energy input corresponding to the activation energy of the hydrogen bond. The same goes for replacement of sodium by calcium ions, which - with their effectively attached water hulls - become most strongly held in interlamellar positions

The major conclusions from the NMR studies can be summarized as follows:

1. The coordination of lattice silicons is different in Na and Ca montmorillonite. In principle, this is in accordance with the Forslind/EF model for Na montmorillonite, and with the conventional HEW model for Ca montmorillonite

2. Heating of water saturated montmorillonite up to 200°C under hydrothermal conditions does not cause permanent change in the coordination of lattice silicons

3. Interlamellar water molecules seem to form a hydrogen-bonded lattice with uniform properties in Na montmorillonite; the Na ions appear to be very weakly hydrated. In Ca montmorillonite the Ca ions are strongly hydrated and determine the physical properties and stability of the hydrate layers

4. Heating up to 200°C under water saturated conditions and water pressures sufficiently high to prevent vaporization, does not seem to cause interlamellar dehydration.

2.3 RECENT (After 1992)

2.3.1 General

Considering first the evolution of concepts of how conversion of smectite to illite takes place, it is interesting to see that while the workshops convened in 1981 to 1983 still maintained that the major mechanism is the one termed PROCESS I in this report - i.e. solid-state reaction implying replacement of tetrahedral silica by aluminum and fixation of K^+ in interlamellar positions in combination with dehydration of the interlamellar space - the same doubts were raised as today, namely how silicons can actually move from their lattice positions and be replaced by aluminum, how potassium can replace Na and particularly Ca in interlamellar positions, and how the dehydration can take place. At this early time mineralogical and chemical analysis of samples from the Gulf Sediments served as reference examples of $S \rightarrow I$ conversion, implying that it has taken place successively through layer-by -layer transition via I/S mixed layer minerals. However, the difficulties in explaining the detailed mechanism in the formation of illite layers in I/S early led to the concept of neoformation of illite as a separate phase or in neoformed I/S.

In the intermediate period, the access to high resolution TEM and more refined evaluation of XRD spectra gave evidence of illite formed as a separate phase in many deep sediments, the mechanism being dissolution (cannibalization) of smectite and precipitation of illite triggered and controlled by uptake and fixation of potassium, i.e. PROCESS II. Also, quite different interpretation of the nature of I/S was introduced, meaning that I/S can be understood as only apparent and caused by interference phenomena of systems of illite particles.

Recent research, involving laboratory tests and comprehensive analyses of bentonite beds with fairly well known pressure and temperature histories, supports the idea that transformation from low-charge to high-charge smectite and further alteration to illite is not realistic, but that neoformation of illite - and possibly I/S - is the major conversion mechanism , and that the access to potassium is a major rate-controlling parameter at higher temperatures. Also, it has become clear that the composition of the *virgin* material is of great importance for the actual chemical processes including dissolution and - particularly - precipitation of not only illite but also of i.a. chlorite, quartz, cristobalite and amorphous silica.

With today's perspective it appears that although a number of important problems related to the conversion of smectite to non-expanding minerals have been completely or largely resolved, it remains, however, to explain how the reaction actually takes place, which is basically a matter of if and how I/S minerals can be formed. This issue will be focussed on first in this chapter.

2.3.2 The I/S issue

2.3.2.1 Meaning and nature of I/S

A basic question is naturally whether I/S minerals are really true, well defined clay minerals or if they are in fact only apparent. We have seen in this report that investigators like Peacor concluded that what is commonly considered as mixed layer I/S is in fact two distinctly different kinds of domains (stacks) interpreted as smectite with irregular flake spacing and illite, formed by dissolution/crystallization. According to this school of clay science, smectite and illite represent two coexisting separate phases, the growth of illite stacks proceeding in an Ostwald-step-rule-like approach toward a state of chemical equilibrium. Nadeau's views that I/S can be understood as accumulations of fundamental particles with interlayers within such particles representing illite and hydrated interfaces between them representing smectite is an alternative interpretation of I/S crystallites.

The question is naturally how a material composed of two different phases, each with defined spacings, can give a diffraction pattern with peaks indicating mixed-layers, but this is actually the case as demonstrated by the earlier mentioned application of High-Resolution Transmission Electron Microscopy (HRTEM) and XRD (34). They revealed that smectite layers detected by XRD actually represent the interfaces between particles consisting of only 1-3 phyllosilicate lamellae, and that randomly interstratified I/S can be synthesized from mixed suspensions of elementary 10 Å smectite and 20 Å "illite" particles. The "mixed-layer" state in such experiments is thus concluded to be an interparticle diffraction effect, while mixed-layer minerals had currently been taken to represent an intermediate conversion state with smectite layers, in response to increasing Al^{3+} for Si^{4+} tetrahedral substitution, collapsing about interlamellar K^{+}.

Applying these views, i.e. that illite is formed as a separate phase by dissolution/recrystallization, the entire issue of S→I conversion is seemingly very simple: smectite is cannibalized or other silicates dissolved yielding necessary components for neoformation of illite in the natural voids of the smectite clay or in the voids created by the dissolution processes. The indications from some of the field studies referred to earlier in the report that I/S can be neoformed is not in line with this philosophy, but with Nadeau's definition of fundamental particles, illite formation may still be the single cause of crystallization of (apparent) I/S

Still, one cannot exclude the possibility that I/S results from collapsed units of smectite in more or less regular ordering, with sodium or calcium ions- or of course potassium ions - in interlamellar positions since EDX-type analysis cannot give accurate information on the alkali content of thin stacks of flakes. The 10 Å constituents may thus be paragonite or brammalite, and the collapse simply caused by very high overburden pressure in combination with high temperature. In this context the importance of temperature is very obvious as inferred from the proton NMR study described in the last part of Chapter 2.

Thus, already an increase from 20 to 80°C gives a significant drop in ordering and strength of the hydrate lattice in Na montmorillonite and higher temperatures may well lead to dehydration of the interlamellar space *provided that a sufficiently high compressive external effective pressure is exerted on the clay.* Such collapse is most probable where stress concentrations prevail, which is determined by the microstructural pattern of the clay (Figure 2-17). Considering the actual (stepwise) variation in the number of hydrate layers it appears possible that 0 hydrates may be frequent even at moderate temperatures (100-150°C) and effective pressures (30 MPa). It can therefore not be excluded that the very high *average* effective pressures that prevail at more than 3 km depth, i.e. at least 40 MPa, have led to collapse of certain interlamellar openings.

However, the fact that enhancement of the potassium concentration is always associated with conversion of smectite to illite in natural sediments exposed to heat under fully water saturated conditions, demonstrates that collapse of smectite to 10 Å minerals with other cations than potassium in interlamellar positions can hardly be a dominant process, except if much chlorite - absorbing potassium - has also been formed.

From a practical point of view it is important to realize that the possibility that very high effective stresses, induced by the overburden, and high temperatures, may lead to local collapse of smectite stacks - or even welding together of adjacent, equally oriented stacks - does not have a bearing on the behavior of Na montmorillonite as canister-embedding buffer. This is because there is no external effective pressure exerted on the clay as long as the surrounding rock has not undergone so much creep that the deposition holes start to compress. In fact, even extreme creep-induced compression of the holes will not have any dramatic effect since the maximum lateral pressure than can be exerted on the clay cannot exceed the primary rock stresses, which will hardly exceed a few MPa.

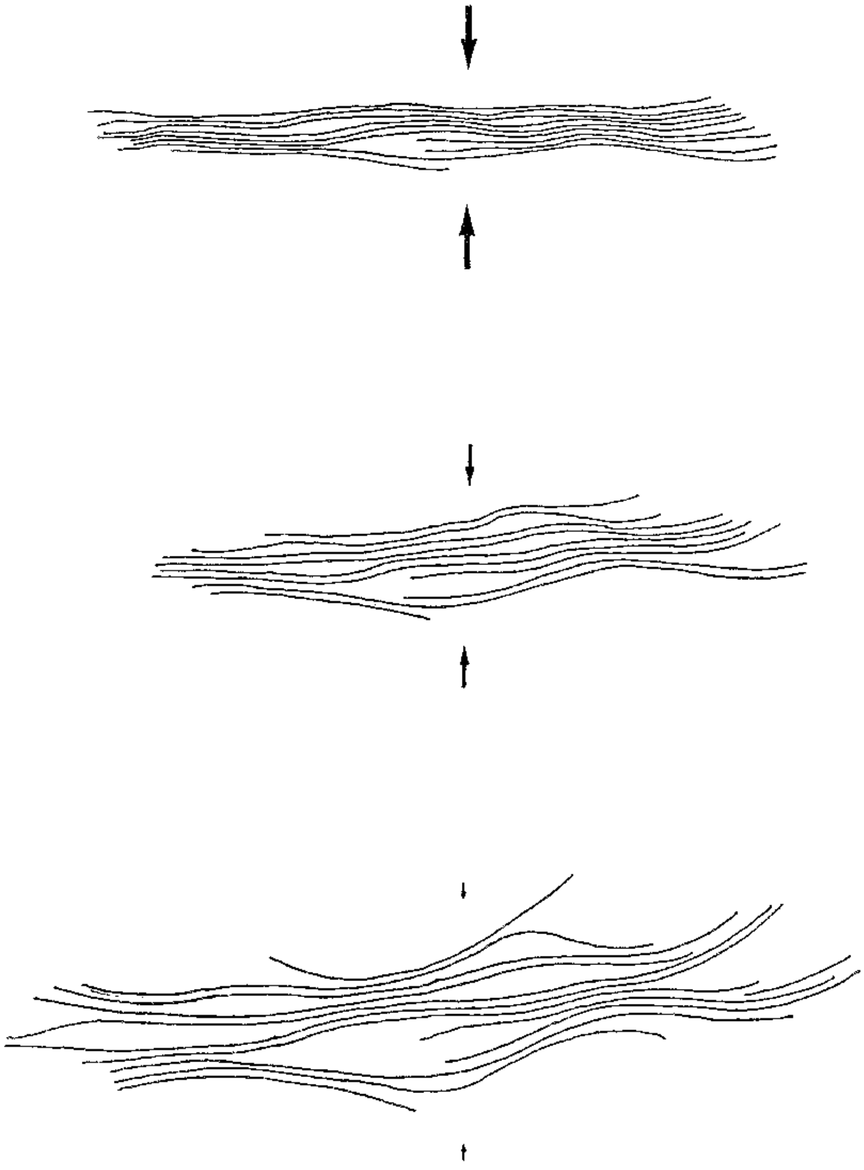


Figure 2-17 Schematic picture of local and regional variations in microstructure of Na montmorillonite at different effective pressures, yielding a change from a fully hydrated state with 3 hydrate layers (upper picture), to 1-3 hydrates (lowest picture)

2.3.2.2 Tentative ideas concerning S→I conversion

Starting with the issue of S→I conversion through I/S as an intermediate stage it must be concluded that although the detailed processes are not yet fully understood, there are good reasons to believe that dissolution of smectite and neoformation of illite and possibly I/S are actually the dominant conversion mechanisms. Very recently, additional support of this hypothesis has been offered through scientific papers by Eberl (70) and Awwiller (71). Thus, Eberl demonstrated by reinterpreting published data of shale cuttings from the Gulf of Mexico - like the ones quoted in the first chapters of the present report - that there appears to be three reaction zones for illite formation: 1) Coalescence of smectite 2:1 layers around K^+ (1.85-3 km), 2) neoformation of illite where K-bearing accessory minerals were dissolved by organic acids (3-4 km), and 3) recrystallization of less stable to more stable illite crystals at larger depth (>4 km). While earlier interpretations implied only *one* mechanism of illite formation from smectite, namely gradual solid-state transformation according to Eqs (2, 3 and 5) with aluminum and potassium supplied by dissolved K-feldspar and smectite, and released silica, magnesium and iron forming quartz and chlorite, Eberl concluded that rather than a gradual increase in the propertion of illite layers in I/S, most illite neoformed abruptly. He also made the point that previous ideas that the clay fraction catalyzed decarboxylation and maturation of detrital organic material, yielding petroleum, it is rather the reverse: illite formation is probably promoted by organic maturation.

Eberl distinguished between three zones in the Gulf of Mexico, of which Zone 1, extending from 1-3 km depth, is characterized by about 50 % I/S, 20 % quartz, 10-15 % kaolinite, 0-5 % chlorite, 3-8 % calcite, 3-5 % K-feldspar, 2-5 % plagioclase, and 3 % mica (Figure 2-18). TEM and SEM of material from this zone have shown large, straight illite particles randomly mixed with smectite crystals containing small domains of illite formed in the smectite matrix. In Zone 2, which extends from 3 to 4 km depth, I/S makes up a somewhat smaller fraction of the clay, while quartz increases and K-feldspar and mica disappear, and in Zone 3 (4-6 km), I/S drops to about 40 % while quartz and chlorite increase to almost 40 and 8 %, respectively. TEM of material from the deepest zone showed large, well-defined packets of illite.

Finally, Eberl concluded that the change with depth from disordered, anhedral, flaky crystals in Zone 1 to more ordered, euhedral illite crystals in Zone 2 to larger anhedral crystals in Zone 3 resulted from different mechanisms for illite formation. His assumption that coascelence of high-charge smectite layers around interlamellar K^+ dominated in Zone 1, yielding the recorded increase in non-expandable minerals from 20 % of the source material to about 35 %, may still be due to variations in source material since the required potassium does not seem to originate from K-feldspars, and if it actually took place it may still have been caused by illite growth within smectite packets as is in fact indicated by the electron microscopy. At any rate, all the conversion from smectite to illite in the 3 km thick underlying sediments seems to be due to neoformation of illite, which hence, gives a totally different picture of S→I conversion than assumed earlier for the Gulf sediments.

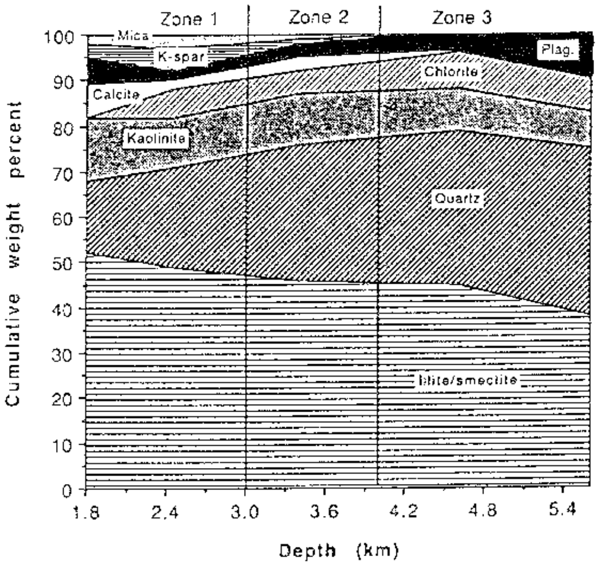


Figure 2-18 Change in mineralogy with depth in Gulf sediments (69)
XRD spectra indicate a sharp change in ordering over 600 m depth at the bottom of Zone 2, i.e. over this short interval, I/S changes from R0, 65 % expandable, to R1, 15 % expandable, a fact that may indicate that the source material varied significantly in the sediment series and that modelling of the conversion is uncertain

In a recent paper Awwiller outlined a scenario for S→I conversion in Wilcox sandstones (Texas Gulf Coast) that is similar to Eberl's (71). Like Eberl he introduced new views and interpretations of mineral changes induced by heat and pressure in this type of rock and his major conclusion was that the conversion of smectitic to illitic I/S was a dissolution-precipitation reaction rather than the previously believed solid state reaction with $K^{+}+Al^{3+}$for Si^{4+} substitution. Awwiller pointed out that burial diagenesis modified the detrital character of the sandstones in conjunction with the reaction of smectite to illite, and that albitization and dissolution of K-feldspars took place, as well as neoformation of some chlorite. A most important statement was that the presence of K_2O was almost the same as in Eberl's study, i.e. a sharp increase between 2.8 and 3.5 km, and constancy deeper down, the explanation of the sudden increase being that marine groundwater was percolated through the pervious sandstone at a rate corresponding to at least 1000 times the pore volume. This is in agreement with the author's explanation of how potassium was probaly supplied in the Gotland Burgsvik case and in the Kinnekulle case. (52,53).

The depth-depending trends claimed by Awwiller were a general increase in quartz, plagioclase (including albite) and siderite, and a decrease in total clay, calcite and K-feldspar. Particularly obvious changes are that the percent of illite in I/S increases (Figure 2-19), that kaolinite decreases, and that discrete illite (mica) increases with depth. As in the cores referred to by Eberl, the percent of illite in I/S ranged from 25 to about 85 %, and I/S ordering from random (R0) to perfect (R3).

Awwiller stated that at least for the Texas Wilcox case, compositional evolution of the octahedral layer implies that the S→I reaction proceeded by a complete dissolution-precipitation reaction, referring to investigations by Nadeau and others in this respect (72). He also brought up the crucial issue of variations in the composition of the source material and stated that some of the downhole mineralogical trends could definitely be of detrital origin. A major difficulty appeared in the interpretation of "whole rock" and "minus 0.5 μm" XRD data; the total clay content was found to decrease as shown by the first type of data, while the content of I/S in the "minus 0.5 μm" fraction increased on the expense of kaolinite (Figure 2-20). This means that the I/S content is almost the same for the shallow and very deeply located sediments, from which the author concluded that smectitic I/S was not cannibalized for aluminum but that illite and particularly kaolinite were consumed. *This finding is of utmost importance, since it means that illitization emanating from dissolution of other minerals than smectite does not produce much free silicons that can cause cementation.*

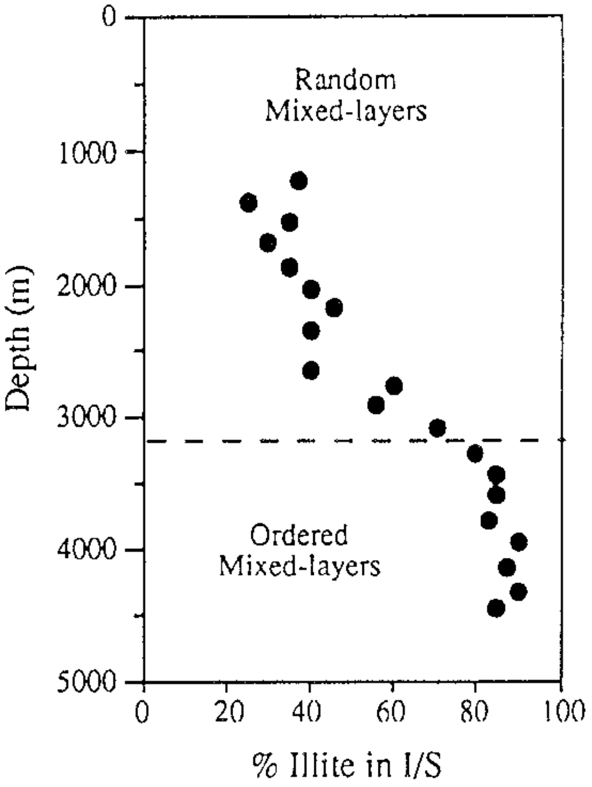


Figure 2-19 Percent illite in I/S from the minus 0.5 µm fraction. Notice that practically all the depth-related change in ordering takes place in the interval 2600- to 3200 m (71)

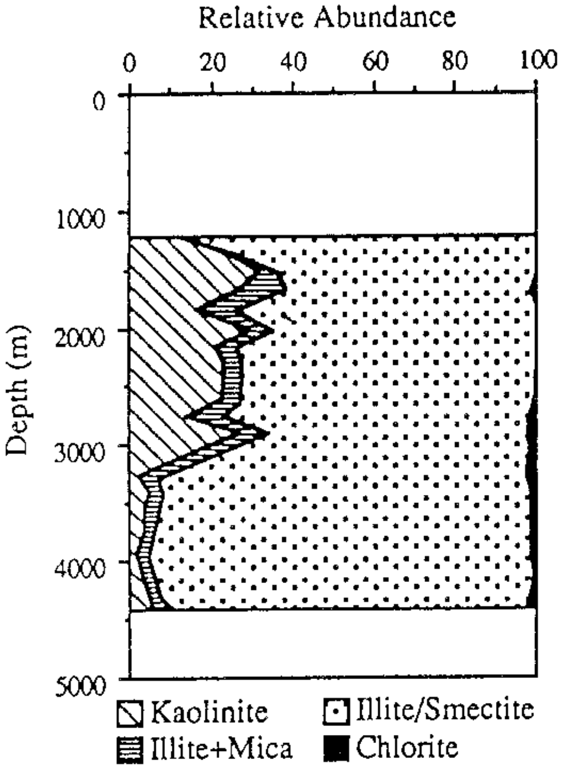


Figure 2-20 Relative abundances of kaolinite, illite (illite+mica), I/S, and chlorite in the minus 0.5 µm fraction (71)

A further note with particular bearing on formation of free silica was that different reaction mechanisms have different impact on the mass balance. Thus, Eqs (2) and (3) yield authigenic quartz (sink for silicons), gain of aluminum by consumption of kaolinite, and gain of potassium from various sources, through which the clay mineral mass is preserved and maintains a constant number of I/S moles, while smectite cannibalization is aluminum-conservative and yields less I/S moles. The latter mechanism hence releases considerably more Si, Fe and Mg than the firstmentioned and it consumes less K-feldspar and no kaolinite. The successive increase in quartz with depth in the Gulf sediments demonstrated by Eberl's diagram in Figure 2-18, would be in agreement with this latter model but the parallel drop in kaolinite content points to consumption of this mineral for a reaction that yields illite (in I/S). Hence both Eberl's and Awwiller's results indicate that consumption of accessory minerals yield the silica and aluminum that is required for neoformation of illite, while potassium is supplied by dissolved K-feldspar and mica as well as by potassium in the groundwater.

We will see later that although these tentative ideas about S→I conversion are basically correct they do not fully agree with geochemical modellings and certain hydrothermal experiments.

2.3.3 The issue of cementation

2.3.3.1 Processes

Cementation associated with conversion from smectite to illite can take place in several ways of which the following are considered to be important:

1. Silica released from dissolving accessory silicate minerals as well as from smectite is known to precipitate as quartz, cristobalite and amorphous silica in the course of S→I conversion

2. Silica and aluminum released from dissolving accessory silicate minerals may precipitate as amorphous alumino-silicates, gluing smectite aggregates together

3. Neoformed illite (and possibly I/S) as well as chlorite may create bridges between smectite aggregates and serve as cementing agents

4. Iron emanating from dissolved biotite, sulphate and sulphide minerals, as well as from iron oxide, is concluded to be largely used up in the formation of chlorite or to form intercalations in the interlamellar space of the montmorillonite stacks, but - depending on pH - it may also precipitate as cementing oxyhydroxides

5. Where temperature gradients prevail, sulphate and carbonate precipitates may be formed in the hot region, yielding cementitious compounds.

Confining ourselves to consider only cementation by silica precipitation , which is the dominant process under isothermal conditions, there are three sources of information as to the extent of cementation of this sort, namely theoretical estimates based on geochemical reactions, laboratory, and field data. The data are given in the present report and summarized below.

2.3.3.2 Theoretical estimates

Taking expressions of type Eqs(3,5) as a basis for calculation of the resulting amount of silica in SiO_2 form, one finds that alteration from low-charge to high-charge smectite would yield 3-4 percent by weight (57). Cannibalization of smectite to give the required silica and aluminum for precipitation of illite would give much higher values, i.e. around 30 percent by weight. In both cases most of the silica is assumed to be used up in the formation of quartz as implied by geochemical models, which would not necessarily imply comprehensive uniform cementation.

Dissolution of accessory silicates like K-feldspar, mica and kaolinite provides free silica (and aluminum) that, according to the S→I conversion model, is used up in the formation of illite. Hence, when potassium is available for consumption of the released silica and aluminum only small amounts of excess silica is expected to precipitate as quartz or cementing amorphous silica. However, with no or little potassium available, these compounds are expected to be formed, which means that if the content of accessory minerals is high, cementing processes may be very significant.

2.3.3.3 Field data

Except for the upper part of the Busachi profile, which is assumed to have underwent heating to 500°C for a few days and 200°C for a couple of months by close-by magma flow, none of the other investigated bentonite layers show strong cementation although they were exposed to more than 100°C for several thousand years. Thus, both the Burgsvik and Kinnekulle clays have an expansion potential, and shearing appears to activate them by breaking the relatively weak cementing bonds by which the surface area is increased. The Hamra bentonite, which was exposed to at least 100°C for millions of years, does not show significant cementation at all, which - as pointed out earlier in the report - may be due to migration of released silica out from the bed into the surrounding silica-poor environment. It is estimated that the amount of cementing silicious compounds in the three Swedish bentonites does not exceed about 5 percent by weight.

A general conclusion of practical importance is that heating-induced cementation by precipitation of silicious compunds has not led to very substantial stiffening and brittleness even where complete conversion of smectite to illite has taken place (Burgsvik). This demonstrates that if cannibalization of smectite supplied the clay with the majority of the silica and aluminum for illitization, precipitation of excess silica must either have migrated away by diffusion or occurred in the form of quartz formation with little cementing effect.

2.3.3.4 Laboratory data

The hydrothermal experiments with distilled water referred to in Chapter 2.2.2.2 show that precipitated quartz and cristobalite hardly represented more than about 1 percent by weight even when the temperature was held at 200°C for about 1 year. This would naturally be expected since illitization by providing silica and aluminum through cannibalization of the smectite could not take place because of the absence of potassium, and also since the amount of accessory minerals was very small. Thus, release of only very little silica took place and quickly led to saturation and to precipitation of crystalline silica like quartz and cristobalite with little cementing effect. In agreement with this, the rheological testing demonstrated that although a stiffer behavior was actually recorded, the strength was not very much increased (Figure 2-55).

Open hydrothermal conditions and the use of a bentonite clay with feldspars, mica and kaolinite forming about 5 % of the total mineral mass showed more significant cementation effects as manifested by a strength increase by 40-100 % at temperatures ranging between 90 and 160°C. These experiments showed that the large majority of the strength increase occurred in the first 10 days when the temperature was 90°C while it proceeded successively at 160°C, which seems to be related to the more comprehensive and time-consuming dissolution at higher temperatures than 90°C. As in the tests under closed conditions the precipitated silica did not result from S→I conversion but simply from dissolution of silicate minerals. The stronger cementation in the tests under open conditions is assumed to result primarily from the comprehensive dissolution of accessory silicate minerals.

2.3.3.5 Tentative ideas concerning cementation

Considering only precipitation of silica, which is tentatively concluded to be the dominant process *under isothermal conditions*, it is assumed that it primarily emanates from dissolved accessory minerals like K-feldspar, mica and kaolinite and that the precipitates are mainly quartz, cristobalite and amorphous silica with only little cementing effect as long as the content of such minerals is small, i.e. less than 5-10 percent by weight. In very pure smectite clay saturated with low-electrolyte water and very little potassium, silica precipitation is insignificant and mainly in quartz form with insignificant cementing effect.

Under the influence of thermal gradients the conditions may be very different, with release of silica in hotter parts and migration to and precipitation in zones where the temperature is lower. This matter needs further consideration as does also the migration of sulphate and carbonate ions released from accessory minerals or supplied by the natural groundwater, forming precipitates where the temperature is higher.

3 GEOCHEMICAL MODELLING

3.1 GENERAL

3.1.1 Codes

Very recently, geochemical modelling has been applied by Fritz and colleagues for checking whether such models -, DISSOL, THERMAL, KINDIS and CISSFIT yield data that agree with the experiments referred to earlier in this report, i.e. the hydrothermal tests under open conditions described on pages 90-95. The models have the following features (73):

* DISSOL

This code is based on a purely thermodynamic approach of irreversible mass transfers between minerals that are unstable in a given solution, and reversible mass transfers between secondary minerals that are initially at equilibrium with the solution

* THERMAL

This code is used for calculation of mass transfers between a solution and minerals in equilibrium along a thermal gradient

* KINDIS

This code considers irreversible dissolution of minerals as a function of time by ascribing to each reactant a specific dissolution rate. For complex minerals like clay minerals the applicability is still uncertain

* CISSFIT

The code is termed "Clay Ideal Solid Solution Fitting" and refers to an ideal solution model for 2:1 clays. For a given clay composition, the model considers the unique distribution of end-members, with activities equal to mole fractions in the solid solution that fit the equilibrium conditions in an aqueous solution at a given temperature.

3.1.2 Basic assumptions

The calculations were based on the same water contents as in the experiments and using the same solutions (D= Distilled water, FF= Strongly brackish calcium-dominated Forsmark-type water, and SEA/2= Ocean-type, Na-dominated water with a ionic strength equal to 50 % of that of seawater).

The codes were used to determine the successive evolution of the mineral assembly, taken as described in Table 3-1 as evaluated from data from the Tixoton manufacturer (73).

Table 3-1 Mineralogical composition of the bentonite

Mineral	Weight %	Mole %	Mg per cell
Microcline $KAlSi_3O_8$	5.00	4.93	38.10
Calcite $CaCO_3$	5.00	13.70	38.10
Quartz SiO_2	3.00	13.69	22.86
Pyrite FeS_2	1.00	2.29	7.62
Amorphous silica SiO_2	1.00	4.56	7.62
Montmorillonite $Si_{3,69}Al_{0.31}Al_{1.27}Fe^{III}{}_{0.30}Mg_{0.42}Ca_{0.15}Na_{0.50}O_{0.10}(OH)_2$	85.00	60.83	647.70
Sum	100.00	100.00	762.00

In the first comprehensive sets of calculations all feldspars were taken to be microcline, a case of particular interest, but additional runs were also made with Na/Ca feldspars making the large majority and these calculations did not deviate significantly from those with K-feldspars, which are referred to here.

3.1.3 Summary of data from the experiments

The evaluation of mineralogical changes as based on XRD and chemical analyses of the solid substance and the solutions certified that changes in the mineral mass could be determined with acceptable accuracy. The major conclusions, valid for all three solutions except were deviations are marked, are summarized in Table 3-2.

Table 3-2 Major changes in mineral composition in the experiments recorded at 20 and 200°C. 3+ means abundant, 2+ present, + traces, - absent

Mineral	Duration					
	10 days		90 days		270 days	
	20°C	200°C	20°C	200°C	20°C	200°C
Montmorillonite	3+	3+	3+	3+	3+	3+
Quartz	2+	-*	2+	+**	2+	2+
Feldspars	2+	-	2+	-	2+	-
Calcite	2+	+	2+	+?	2+	-

* 2+ for SEA/2
** - for D-water

Ion exchange from Na to Ca took place already in 10 days at all temperatures probably due to early release of calcium from the calcite. A drop in 001 reflections from about 15-16 to about 14.5 at heating to 200°C for the longest period of time may indicate chloritization. XRD tests on packed samples from such treatments also suggest that halite and sulphates, like anhydrite tended to precipitate.

3.2 RESULTS

Fritz and DelNero arrived at the mineral compositions given in Tables 3-3, 3-4 and 3-5 for the three solutions. It was recognized at an early state that chlorite would precipitate and form a significant part of the reaction products and to get reasonable fitting with the experiments this process had to be suppressed and chlorite was therefore not allowed to precipitate in the 270 days reaction period.

3.2.1 Distilled water

The data are collected in Table 3-3

Table 3-3 Mineral composition in weight perecnt after 270 days of hydrothermal treatment with distilled water for best fitting of calculated and true composition of the solution (73)

Minerals	20°C	90°C	130°C	160°C
Dissolved:				
K-feldspar	5.0	4.6	4.2	3.3
Calcite	5.0	4.6	4.2	3.3
Quartz	3.0	3.2	2.5	2.0
Pyrite	1.0	0.9	1.0	1.1
Amorph. silica	1.0	0.9	0.8	0.7
Montmorillonite	85.0	78.3	71.5	56.8
Precipitated:				
Laumontite	-	2.8	6.7	14.9
Kaolinite	-	2.8	4.4	6.8
Hematite	-	4.2	0.0	0.0
Secondary 2:1 clay mineral	-	1.3	4.7	11.1
	100.0	100.0	100.0	100.0

The reduction in feldspar and calcite is in principle in agreement with the experiments although the loss in feldspars at 200°C was practically complete already in 10 days. The calculated reduction in montmorillonite is much stronger than in the experiments, where it was hardly noted. However, the secondary 2:1 minerals appearing in the simulations may partly compensate for this. Laumontite and kaolinite may have escaped attention in the experiments if the crystal size was small enogh to make them X-ray amorphous.

The predicted pH-values were found to vary significantly in the course of the reaction. For D-water the simulations gave the range 6-10 for 20°C, 6-9 for 90°C and 6-9 for higher temperatures, while the recorded pH was about 7-10 for all temperatures below 200°C.

3.2.2 SEA/2-solution

The results are compiled in Table 3-4.

Table 3-4 Mineral composition in weight percent after 270 days of hydrothermal treatment with SEA/2 solution for best fitting of calculated and true composition of the solution (73)

Minerals	20°C	90°C	130°C	160°C
Dissolved:				
K-feldspar	5.0	2.2	1.7	1.8
Calcite	5.0	2.2	1.7	1.8
Quartz	3.0	2.0	1.0	1.1
Pyrite	1.0	0.4	0.9	0.9
Amorph. silica	1.0	0.4	0.3	0.4
Montmorillonite	85.0	36.9	28.3	31.3
Precipitated:				
Kaolinite	-	24.8	13.3	12.2
Hematite	-	3.6	0.0	0.0
Secondary 2:1 clay mineral	-	17.7	48.4	46.3
Secondary quartz	-	9.8	0.0	0.0
Secondary pyrite	-	0.0	4.4	4.2
	100.0	100.0	100.0	100.0

The calculated stronger reduction in feldspar content and calcite than in the tests with distilled water is in better agreement with the experimental results, while the dramatic change in montmorillonite content does not agree with the recordings. However, as for the distilled water, the secondary 2:1 clay mineral may partly compensate for this although one finds that the total sum of this mineral and the remaining montmorillonite does not make up more than 43 % at 160°C, which would definitely have been observed experimentally. The same goes for kaolinite particularly at 90°C. A most interesting phenomenon is the precipitation of secondary quartz, which is in agrement with the appearance of quartz in the Sea/2 case after 10 days.

The calculated pH was 7.5-8 for 20°C, 6-7.5 for 90°C and 6-9 for 130 and 160°C, while it was somewhat lower, i.e. 5-8 in all the experiments.

3.2.3 FF-solution

Table 3-5 Mineral composition in weight percent after 270 days of hydrothermal treatment with FF solution for best fitting of calculated and true composition of the solution (73)

Minerals	20°C	90°C	130°C	160°C
Dissolved:				
K-feldspar	5.0	2.8	3.2	2.2
Calcite	5.0	5.0	5.0	5.2
Quartz	3.0	2.9	1.9	1.3
Pyrite	1.0	0.6	0.6	0.4
Amorph. silica	1.0	0.6	0.6	0.4
Montmorillonite	85.0	48.3	54.8	35.8
Precipitated:				
Kaolinite	-	19.4	14.7	24.8
Hematite	-	2.7	0.0	0.0
Calcedony	-	5.6	0.0	0.0
Secondary 2:1 clay mineral	-	12.1	4.7	11.1
	100.0	100.0	100.0	100.0

The same aspects apply as in the other two runs, i.e. the actual reduction in feldspars was much stronger than suggested by the calculations. The stable conditions of calcite would indicate the effect of the composition of the FF-water but the experiments showed that calcite definitively disappeared in the 200°C test of longest duration. As in the other simulations the loss in montmorillonite is not in agreement with the experiments although it is compensated to some extent by the formation of a secondary clay mineral. Kaolinite cannot have been formed to the extent indicated by the codes. In conclusion, the calculations of the reactions with FF-water were in less good agreement with the experiments than those with D-water and Sea/2 solution, of which the latter fitted best.

The simulations gave pH-values in the range of 6-8.5 for 20°C and about the same for 90C and higher temperatures, while the experiments gave somewhat lower values, i.e. 5.5-7.

3.3 GENERAL CONCLUSIONS FROM THE GEOCHEMICAL CALCULATIONS

3.3.1 Mineral reactions

The major reactions in all the different chemical environments were the dissolution of montmorillonite and precipitation of a secondary 2:1 clay mineral and kaolinite, and -in the absence of electrolytes - also of the zeolite laumontite. Also chlorite would be formed but this process was deliberately suppressed. All other reactions, except the dissolution of feldspars and calcite at the highest temperature, were not complete and less important. Thus, excepting the formation of kaolinite, one thus finds the reactions to be those expected in marine environment as concluded from the numerous cases discussed in the report.

The calculations were based on the presumption that all reactive components were available for interaction from the very start, which was not the case in the experiments. Thus, the solutions were contained in the hydrothermal chambers while the clay, saturated with distilled water, was located in the small cell in the chamber, a fact that must have caused a delay in reaction by the migration of ions from the solutions to the cell and vice verse. This means that the reactions appeared to be much slower in the experiments but this cannot explain some of the most obvious differences between the actually observed and the calculated changes for the longest reaction time. Thus, the dissolution of montmorillonite and the formation of chlorite and the hypothetic 2:1 clay mineral, which may be illite, are concluded to be kinetically controlled and very much slower than the codes indicate.

3.3.2 pH

As to pH one finds that the calculations gave data that were not too different from the ones recorded in the experiments, although the latter were usually somewhat lower. The calculations showed significant variations in the course of the reactions as examplified by Figure 3-1, which also shows the evolution of CO_2 concentration and Eh. All three parameters, and particularly pH, undergo significant changes in conjunction with saturation of the porewater with respect to minerals like quartz and calcite.

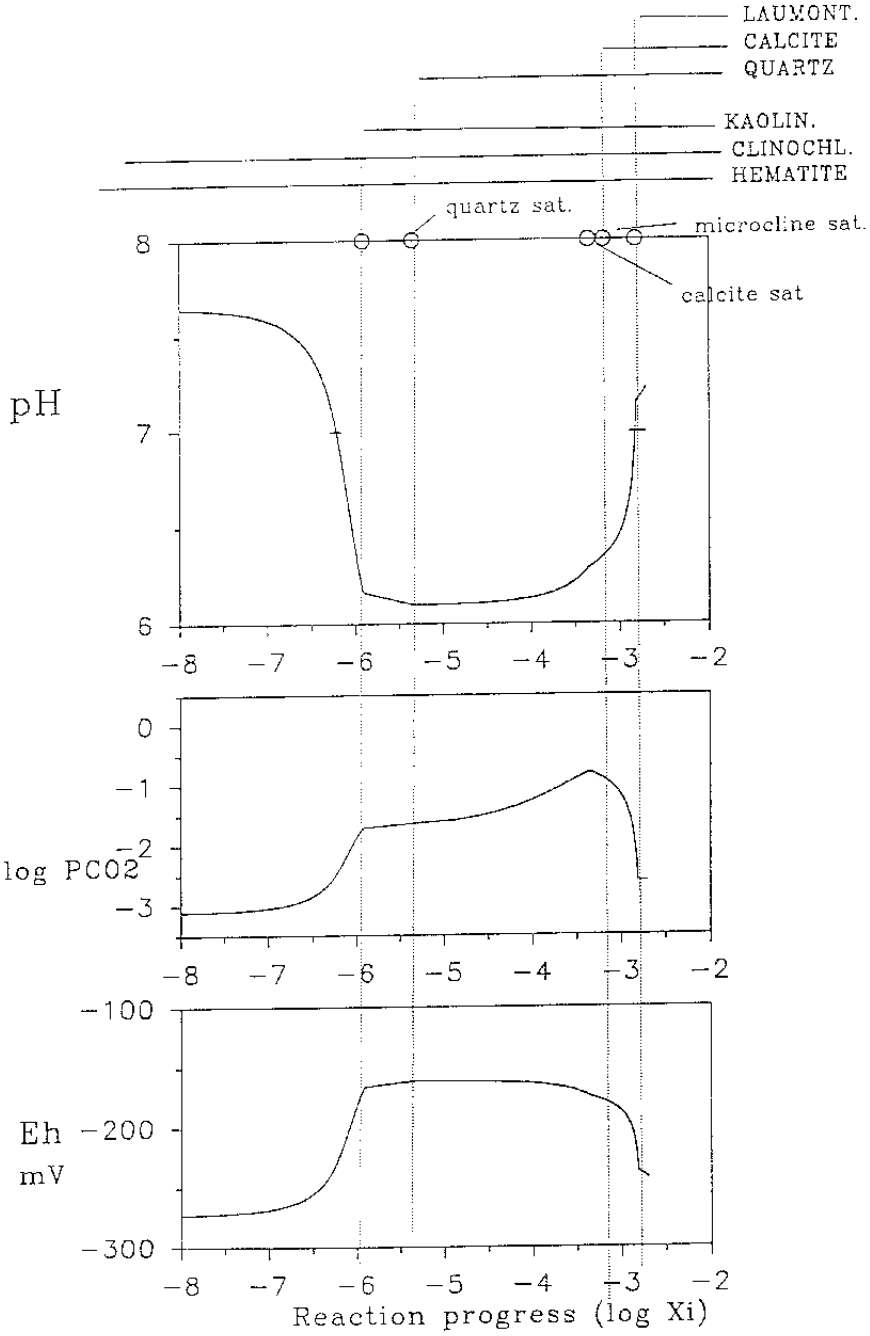


Figure 3-1 Evolution of pH, CO_2 concentration and Eh in the course of the bentonite reaction in SEA/2 water (73). log Xi represents the reaction progress expressed in terms of the fraction of bentonite dissolved in 1kg H_2O. For instance, Xi=-4 means 0.01 % units, each containing 100 moles of minerals (60.69 of montmorillonite, 5 moles of calcite etc)

4 FORMULATION OF WORKING MODELS FOR S→I CONVERSION

4.1 MODEL FOR ILLITIZATION

With today's perspective it is still not definitely proven if conversion of montmorillonite to illite actually takes place by formation of true I/S minerals or by illite growth with I/S being only apparent, and by growth of chlorite as a separate phase or as intercalations. Solid-state transformation of smectite from low-charge to high-charge state with replacement of Na^+ or Ca^{2+} by K^+ in the interlamellar space with subsequent dehydration is hardly probable, as indicated by Howard already at the colloquium back in 1982 (page 31). Formation of non-expandable 10 Å minerals with Na^+, Ca^{2+} in the interlamellar space, i.e. paragonite-type minerals, may be mistaken for illitization but it requires very high effective pressures (probably higher than 50-100 MPa) and much chlorite to explain the enhanced K-content. However, in combination with heating, such stresses may yield transformation of Na montmorillonite from the EF state to HEW and further to paragonite-type minerals with any of the interlamellar cations Na^+, Ca^{2+} or K^+.

Precipitation of illite (and possibly I/S) is concluded to be the major conversion mechanism. Dissolution of accessory silicate minerals is expected to yield the silica and aluminum as well as some of the potassium that are required for the formation of illite, but potassium available in the groundwater is also an important K^+ supply. Cannibalization of smectite minerals is not assumed to be a major process but merely dissolution of accessory minerals, primarily K-feldspars and micas.

The proposed working model for S→I conversion is therefore that heat-induced dissolution of accessory minerals is the rate-controlling factor if potassium is available in unlimited quantities, and that the availability of potassium is the rate-controlling factor if the release of silica and aluminum from dissolving silicates is a not limiting process.

The dissolution of silicate minerals and recrystallization of illite (and possibly I/S) represent an Arrhenius-type process that can be quantified by applying Pytte's model, using an activation energy of 26-27 kcal/mole and appropriate, empirical material constants (cf. for instance Figure 2-24 and 2-25).

The supply of potassium to converting smectite is very quick if K^+ is furnished by accessory minerals contained in the clay. External potassium is brought to the clay from the surroundings by diffusion if stagnant groundwater conditions prevail and this causes exhaustion of the potassium content in the surroundings. The successively dropping concentration gradient in the vicinity of a converting clay layer then leads to a strongly retarded uptake as in the Hamra clay. Pressure-induced groundwater flow, generated by thermal effects, can keep up the potassium concentration in the vicinity of the clay layer, and this may cause rapid conversion if the percolation rate of the surroundings is high as presumed in the Kinnekulle case.

4.2 MODEL FOR CEMENTATION

It is clear that at least under isothermal conditions, stagnant groundwater environment with normal K^+ content (<400 ppm), and temperatures below 100°C, very pure smectite clay does neither convert to illite to a significant extent nor undergo substantial cementation in less than a few hundreds of thousands of years. However, smectite clay with much accessory minerals like feldspars, micas, kaolinite, carbonates and sulphides, may be converted to illite in conjunction with significant precipitation of silicious compounds in a few thousand years. It is possible that such compounds can have the nature of neoformed illite and chlorite and this sort of cementation may therefore be developed parallel to the formation of these two minerals. While this would give the kinetics and the amount of this particular kind of cementation, the associated influence on the rheological properties of the clay in bulk is still not known.

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[1] Clay Technology AB, Sweden
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