

SKB

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REPORT**

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**Preliminary report on longevity
of montmorillonite clay under
repository-related conditions**

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December 1990

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PRELIMINARY REPORT ON LONGEVITY OF MONTMORILLONITE
CLAY UNDER REPOSITORY-RELATED CONDITIONS

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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Preliminary Report
on
Longevity of Montmorillonite Clay Under
Repository-Related Conditions

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SUMMARY

This report summarizes current work on developing complete models for predicting the chemical stability of montmorillonitic bentonite buffer materials in HLW repositories. The major degrading mechanism is the conversion of montmorillonite to hydrous mica ("illite"), the basis of the derivation of tentative models being offered by ongoing systematic hydrothermal tests, which indicate that such conversion takes place by dissolution, yielding very mobile silica, and aluminum that tends to stay in the clay voids.

The key mechanism in the transformation to hydrous mica at temperatures below about 130°C is concluded to be neoformation of the latter mineral, the controlling parameter being the access to potassium.

For temperatures ranging between 130 and 200°C, excess silica is released by beidellitization and this yields I/S mixed layer minerals on uptake of potassium, and precipitation of cementing silica in the form of amorphous silica and cristobalite. The rate of transformation of montmorillonite to hydrous mica is still controlled by the access to potassium, i.e. by the rate at which potassium enters the clay. 10 Å minerals that can be mistaken for hydrous mica can be formed by cementing collapsed stacks together.

The models appear to give montmorillonite transformation rates that are in agreement with lab results and geological examples but further calibration, primarily by using the results of ongoing hydrothermal tests in the Stripa study, are required to make them applicable to repository conditions.

Montmorillonite longevity has been the issue of scientific study for decades and various theories have been forwarded, the major ones being related to heat-induced conversion to 10 Å minerals and cementation, which for the pH interval 7 - 10 that is currently considered, are the only practically important chemical changes associated with heating up to 200°C. An attempt is made in the present report to develop a model for such alteration.

The statements in this report are preliminary since the 1 year hydrothermal experiments of the Rock Sealing Tests of the Stripa Project, which serves as a major check of the proposed models, are not finished and evaluated until mid 1991.

2.1 *The crystal structure of montmorillonite*

Fig.1 illustrates the crystal structure of montmorillonite. The Hofmann, Endell & Wilm (HEW) structure shown to the left is considered to be a "high temperature" form, while the Edelman & Favejee (EF) structure shown to the right, is assumed to represent a more hydrated state at temperatures below 100 to 120°C (1,2). This latter arrangement can be regarded as a sort of "pillared" structure with every second Si tetrahedron inverted, thus exposing apical OH:s to the interlamellar space. These hydroxyls are believed to absorb water through hydrogen bonding if sodium and lithium are present as exchangeable cations, and they form a base for the growth of strained ice-like water lattices of the type shown in Fig.2, which represents an extreme form of EF-type concepts. The charge properties of Ca induce disturbances by which the organization of water molecules is different,

implying that only two, strongly held, hydrate layers can be formed in the interlamellar space and that the crystal structure is of the HEW type at any temperature. Complete dehydration of montmorillonite requires higher temperatures for Ca than for Na saturation, which makes the Ca form more heat-resistant.

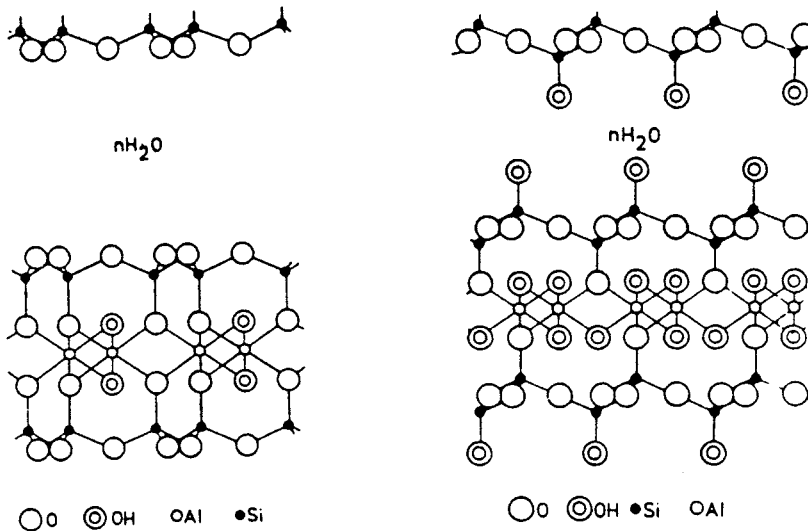


Fig.1 Montmorillonite lattice models. Left: Hofmann/Endell/Wilm. Right: Edelman/Favejee

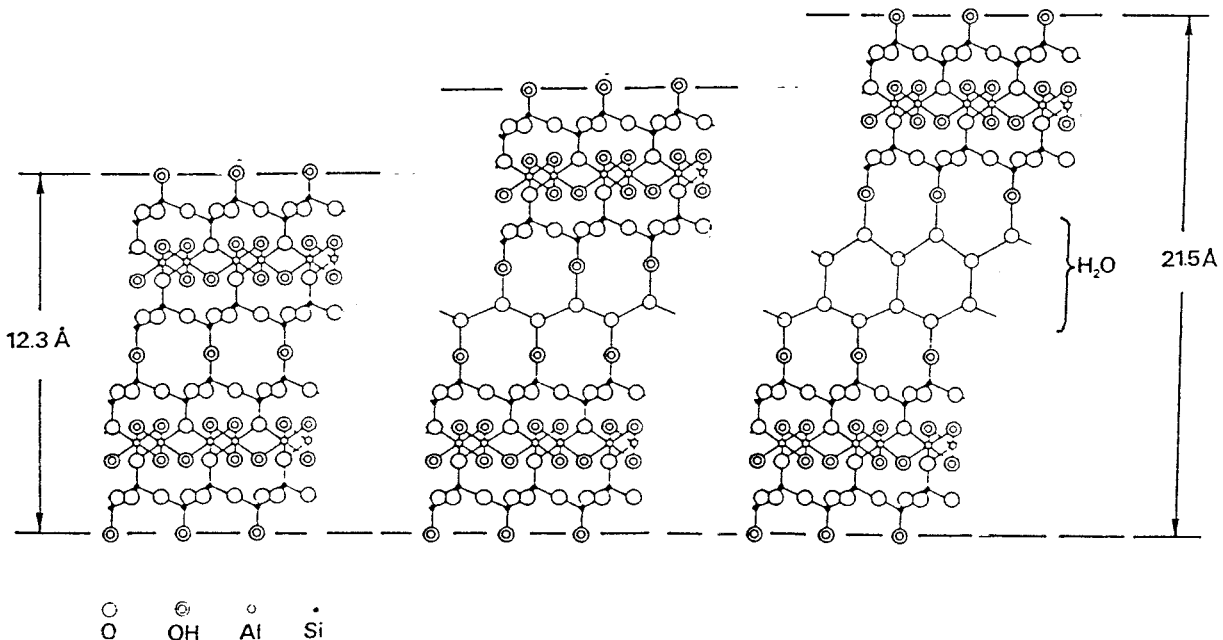


Fig.2 Schematic picture of regular H-bonded water lattices in the interlamellar space according to Forslind's concept (1)

2.2 *The microstructure of montmorillonite clay*

The geometrical arrangement of the thin flakes, which usually have an extension in the crystallographic ab-plane that is several thousand times larger than the thickness of the flakes, is strongly dependent on the bulk density of the clay. In principle, we distinguish between interlamellar ("internal") water located between crystallographically equally oriented flakes, and more or less free ("external") water between the stacks of flakes (Fig.3). The majority of the "particle contacts" are believed to have the form of hydrate layers separating the flakes, but there is still a large number of contacts of crystallographically ill-fitting basal planes or edges of adjacent stacks. These contacts may partly be solid/solid and partly established through water films in which electrical double-layers are operative.

The microstructural constitution is essential since thermally induced alteration is strongly related to the number of interlamellar hydrates and the available space for migration and precipitation of chemical elements.

3 ALTERATION MECHANISMS

3.1 *Current views*

3.1.1 Transformation of montmorillonite to hydrous mica ("illite")

The most favored explanation of transition of montmorillonite to hydrous mica can be expressed by the formula:

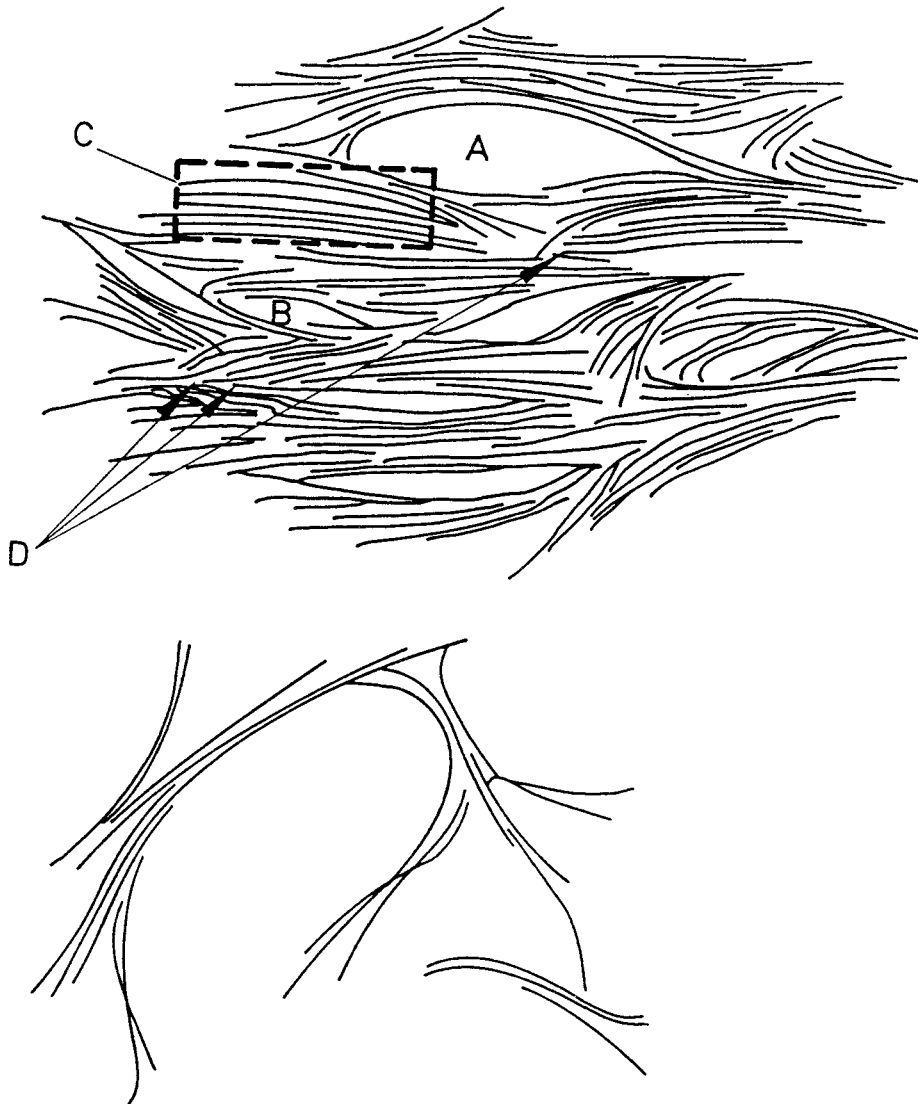


Fig.3 Microstructure of montmorillonite clay.
 Upper: Dense clay with A) & B) Pores with
 "external" water, C) Stack or "quasi-
 crystal" with interlamellar, "internal"
 water, D) Contact through either solid/solid
 interaction or through hydrates holding
 electrical double-layers

Lower: Low density with thin stacks, and
 very little "internal" water

Montmorillonite + aluminum ions + potassium ions
yield
hydrous mica and free silica

This process implies replacement of tetrahedral silica by lattice- or external aluminum (beidellitization). Uptake of potassium to yield charge equilibrium is conventionally assumed to lead to formation of mixed-layer IS* and ultimately to 100 % hydrous mica. The temperature dependence is usually assumed to be Arrheniusian and Pytte (3) concluded, by analysing a number of alteration profiles adjacent to basalt dikes, that it can be described in following form:

$$dS/dt = A \times e^{-U/RT} \times K^+ \times Na^+ \quad (1)$$

where A is a constant and U the activation energy, K^+ and Na^+ the concentration of dissolved potassium and sodium, respectively, and S the mole fraction of smectite in I/S assemblages.

The idea of smectite conversion via mixed-layer minerals, developed or supported by investigators like Boles & Franks, Eberl, and Hower, implies solid solution processes, and various attempts have been made in recent years to find out the exact ordering of montmorillonite and hydrous mica flakes in the presumed successive alteration of pure montmorillonite to pure hydrous mica through various "mixed-layer" I/S stages, in order to account for this mechanism.

* I in IS is conventionally used as a synonym of hydrous mica

While investigators like Aagaard and Helgeson have claimed that mixed-layer minerals of I/S type represent *one solid solution* of variable composition, Tardy et al (4) recently indicated that it may be a matter of *two separate phases*, pointing out the poor coupling of smectite and hydrous mica flakes as concluded both from geometrical aspects and energy points of view.

The coexistence of montmorillonite and neoformed hydrous mica as separate phases in hydrothermally affected montmorillonite in nature has been demonstrated by several investigators (5,6). The prerequisite of such neoformation is that there are sufficient amounts of silica and aluminum, dissolved from the montmorillonite, and of potassium available in the porewater or moving in from the surroundings. The idea of potassium resulting from "cannibalization" of mixed-layers is not feasible if Tardy's concept of separate smectite and hydrous mica phases is correct. Recently, the existence of true IS mixed layer minerals has been seriously questioned on the basis of a detailed study of the application of Reynold's method and it appears possible that the "I" component is mistaken for 10 Å minerals formed by collapsed montmorillonite stacks with Na or Ca in interlamellar positions ("brammalite"-type minerals), (6,7).

3.1.2 Cementation effects

The generally accepted view that silica is released in conjunction with the formation of hydrous mica is backed by the observation that silification is frequent in the surroundings of hydrothermally affected bentonite beds and in montmorillonitic drilling muds. It is manifested by the presence of quartz and cristobalite (often platy crystals in bentonite) and of

amorphous silica and opal. The latter occasionally appears in the form of micro-spherules with a diameter of around $0.03 \mu\text{m}$ and may be the kind of precipitate that has been found in the Kinnekulle bentonites (Fig.4). It should be added that cristobalite in bentonites is commonly attributed to neoformation from solution that stems from the smectite minerals but may be derived from quartz.

Silica precipitations are concluded to form cohesive particle bonds in smectites like in silt- and sandstones and they can be broken by relatively weak forces at least in moderately cemented clays (8,9).

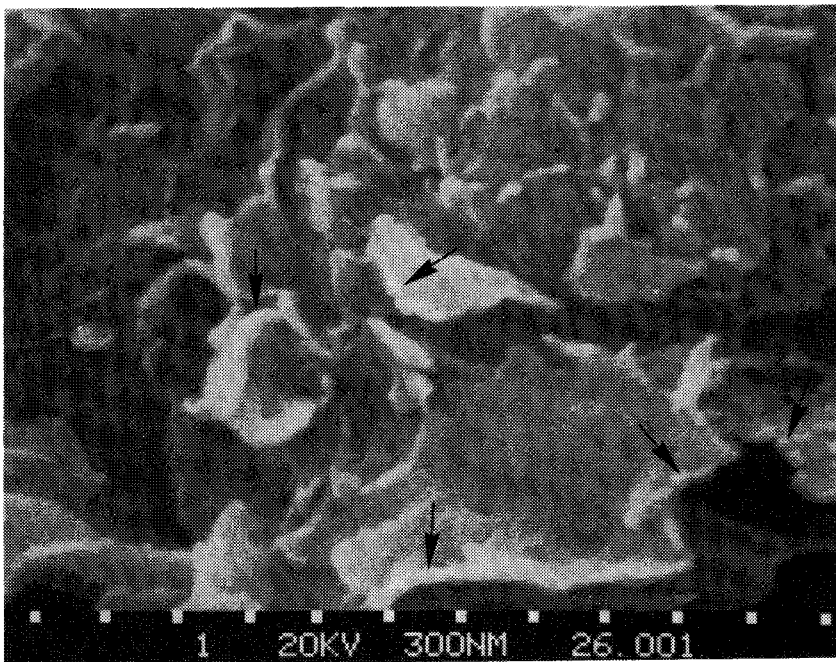


Fig.4 SEM picture showing spherical nodules at the edges of smectite stacks in Kinnekulle bentonite heated to $110 - 160^{\circ}\text{C}$ for about 1000 years (magnification 30 000 x)

3.2 *Hydrothermal experiments*

3.2.1 General

Numerous hydrothermal experiments have been performed by various investigators for making the picture of smectite alteration more clear and to get data for checking the validity of various quantitative geochemical models. Usually, the experiments have been evaluated by chemical analyses and XRD, and in a few instances also by electron microscopy. Almost no study has comprised rheological investigations although such tests offer a very good measure of microstructural changes, like homogenization and cementation.

The SKB study is primarily oriented towards determination of the influence of hydrothermal treatment on the physical properties of montmorillonite and has therefore included comprehensive testing of the swelling properties, the hydraulic conductivity and the rheological behavior. The study, which is partly integrated in the ongoing Stripa project, also comprises chemical, mineralogical and microstructural analyses and they form the basis of the present report. It contains a tentative chemical alteration model, which is applied to three geological case histories in a preliminary attempt to test its validity.

3.2.2 Laboratory tests

Hydrothermal tests of various kinds have been performed and the clay residues tested in order to identify major changes in crystal structure, mineralogical composition, microstructural order, and physical properties in bulk (Table 1).

Table 1 Hydrothermal test series (Rh stands for rheological test, D=distilled water, C=CaCl₂-type, and N=NaCl-type water)

No	Temp. °C	Pr. MPa	Water	Open/ closed	Density g/cm ³	Analyses
I	200	15-30	D	Closed	1.3	XRD, TEM, Rh
II	105-225	0-70	D	Closed	1.3-2.1	XRD, STEM, Rh
III	90-200	0-70	CN	Closed	1.6	MAS/NMR
IV	90-200	2	CND	"Open"	1.1	XRD, STEM, Rh

SERIES I

This series comprised hydrothermal treatment for 10 days of very pure Na montmorillonite (SWY1). The major purpose was to check whether mineralogical changes could be identified, especially with respect to precipitation of silicious compounds, and whether permanent microstructural reorganization takes place on heating and also if rheological changes occur.

The hydrothermal treatment gave only very slight changes in the XRD spectra. Thus, neither the shape or height of the low angle peaks nor the basal spacing of hydrated and glycolated specimens were substantially changed even in samples that had been heated to 200°C.

Transmission electron microscopy (TEM) indicated that heat treatment to 200°C had actually yielded a more homogeneous microstructural network than in unheated, artificially prepared clay although a "second order" structure of dense branches also seems to be formed (Fig.5). In addition, specimens heated to 200°C had a much higher frequency of agglomerates of dense par-

ticles than unheated clay and they were also much larger. Electron diffraction analysis gave evidence of amorphous silica formed on primary quartz particles in these large agglomerates and of cristobalite crystals in the agglomerates as well as on montmorillonite stacks (10,11,12).

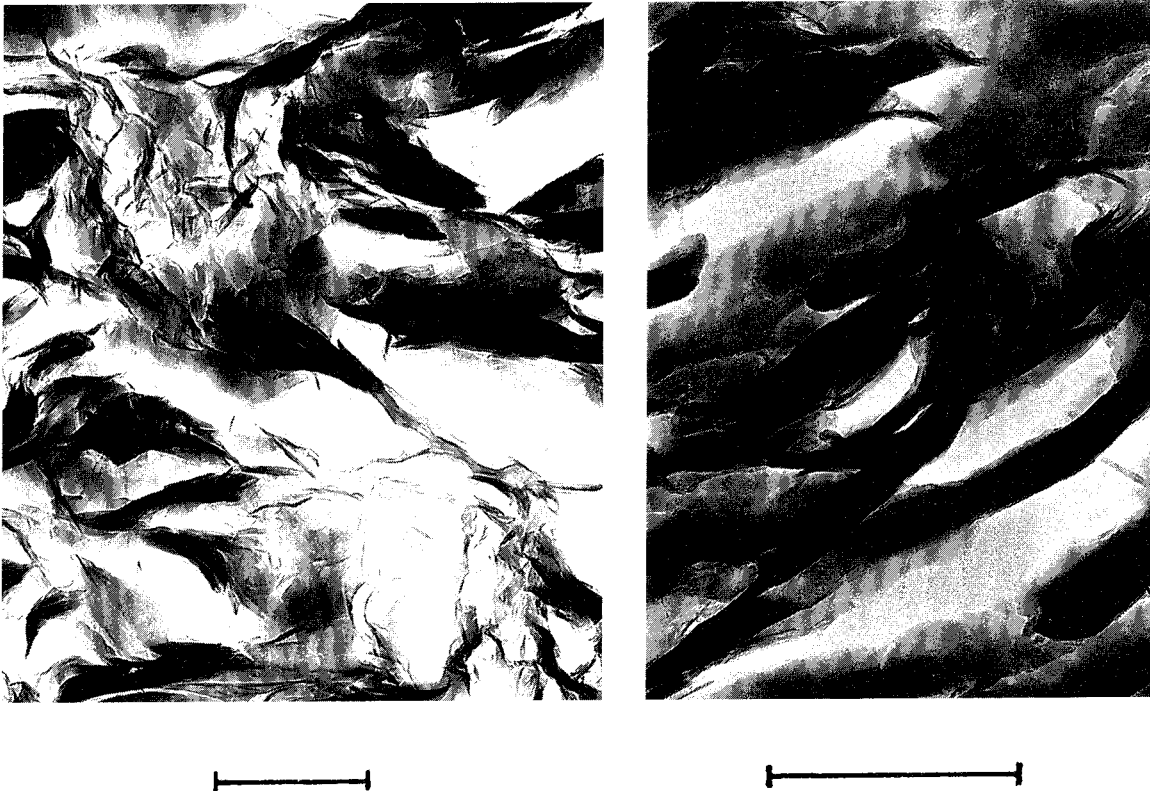


Fig.5 Characteristic TEM micrographs of Na montmorillonite clay. Left: Unheated, Right: Heated to 200°C. Scale represents 1 μm

Part of the identified amorphous silica, which was estimated to form about 1 % of the total solid mass, may have been precipitated from the porewater solution in the course of the preparation for the microscopy, while all the cristobalite is concluded to have been formed under the hydrothermal test conditions.

The rheological testing had the form of simple uni-axial compression tests, typical results being shown in Fig.6. They clearly show the significant stiffening that takes place on heating to 200°C even after short treatment, but one also finds that heating to 105°C causes some increase in the deformation modulus.

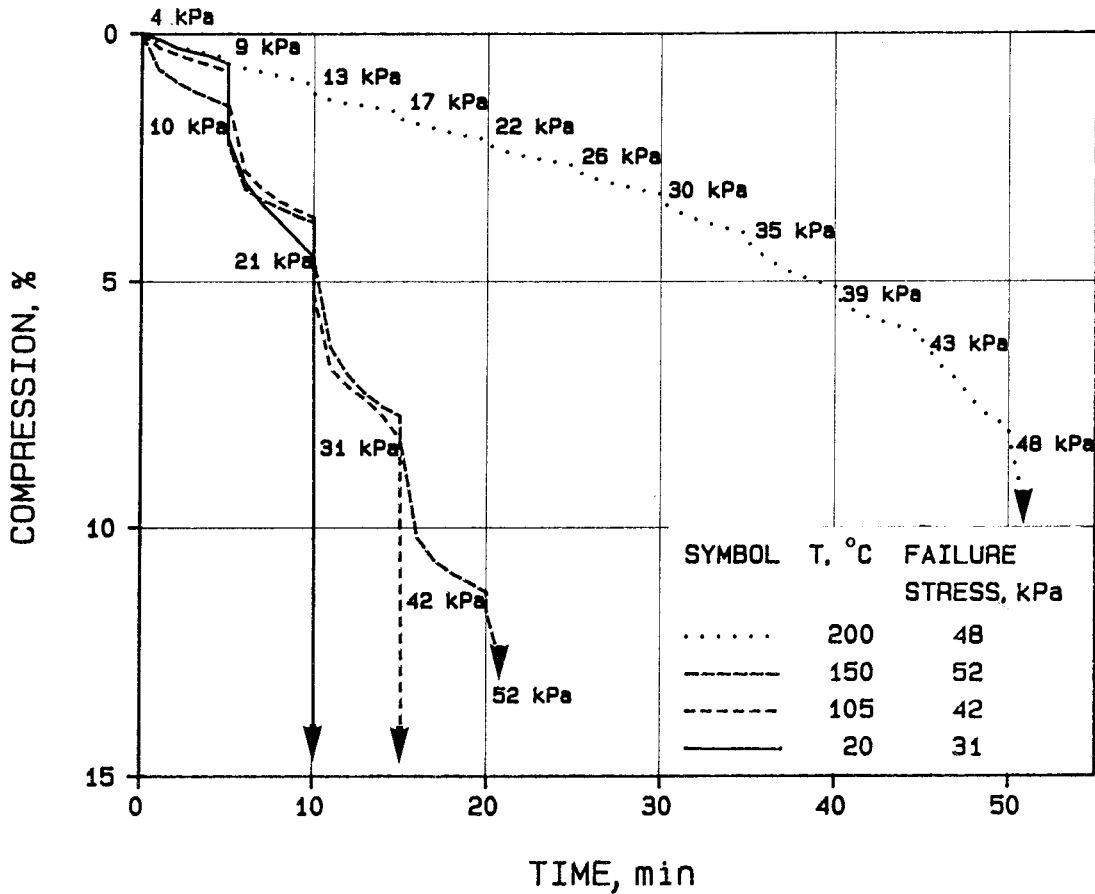


Fig.6 Axial compression versus time at unconfined compression tests. Arrows indicate failure

SERIES II

This study was conducted in the same way as SERIES I, i.e. the clay was saturated with distilled water and hydrothermally treated under closed conditions, but the study covered a wider temperature spectrum

and included also some tests in which percolation with KCl solution was made after the hydrothermal treatment in order to check whether hydrous mica (illite) was formed. Special effort was made to find out what information XRD offers with respect to identification of mineral alteration, and to check the conclusions from SERIES I concerning silica release and precipitation, microstructural "blueshift", and strengthening, on heating. The latter three issues will not be discussed here because the study unambiguously validated the conclusions drawn in SERIES I.

The most characteristic measure of possible mineral alterations was assumed to be illustrated by XRD analysis of specimens treated with ethylene glycol. Two important conclusions could be drawn from the study (cf. Fig.7): 1) The $d=17 \text{ \AA}$ peak becomes more intense on heating to 150 and further to 200°C , and 2) a small amount of 10 \AA minerals is formed at 200°C . The first-mentioned effect was interpreted as resulting from enhanced alignment of stacks when the heat-induced dehydration and formation of thicker and stronger network branches. The 10 \AA mineral formation was assumed to be due to permanent collapse of completely dehydrated stacks of flakes.

Hydrothermally treated SWY1 clay saturated with distilled water and then transferred to porous cells submerged in 3.7 M KCl solution for 2 months was expected to be transformed to hydrous mica assuming beidellite to have been formed. The fact that only the same insignificant amount of 10 \AA minerals as in correspondingly treated Na montmorillonite actually appeared (cf. Fig.8) led to the conclusion that beidellitization, i.e. release of tetrahedral silica and replacement by octahedral aluminum, had not taken place. This finding, which is of tremendous practical importance, is compatible with the results of the studies in SERIES III and IV.

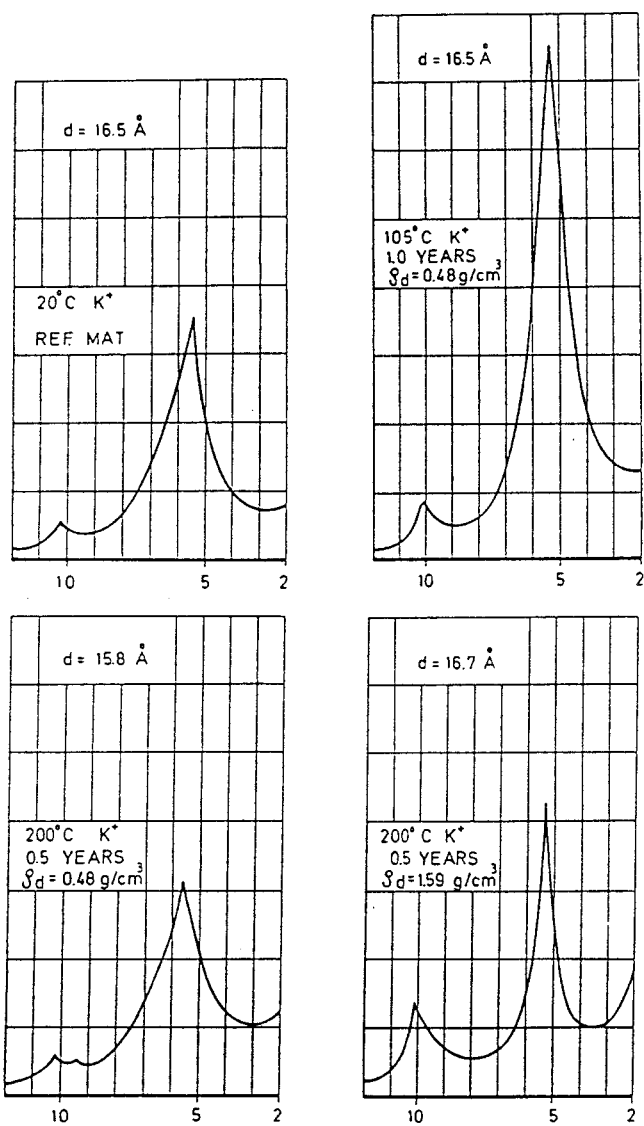


Fig.7 Smoothened XRD patterns of EG-treated SWY1 samples. The figures on the horizontal scale refer to $2\theta^\circ$

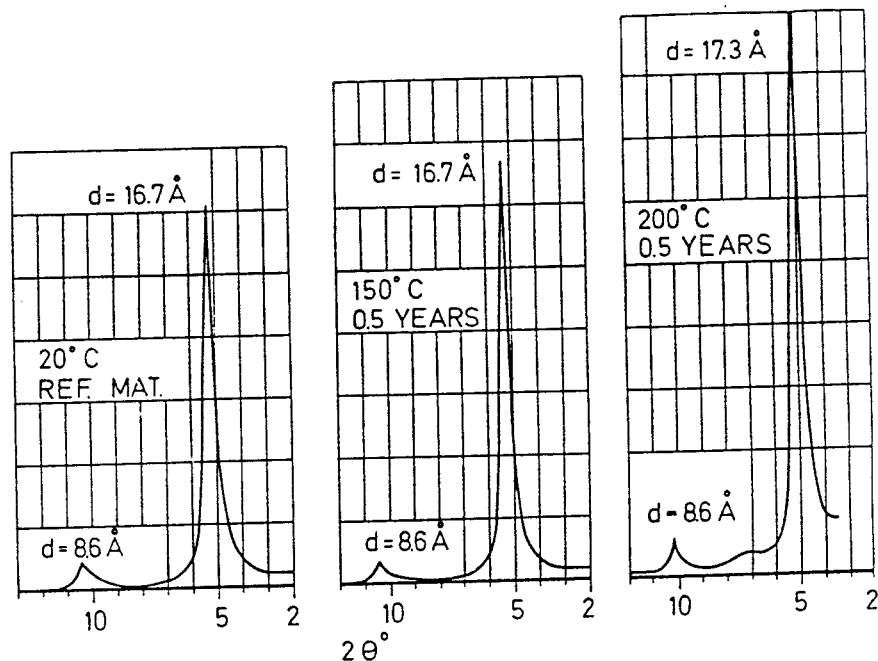


Fig.8 Smoothened XRD patterns for EG-treated SWY1 soaked with KCl after hydrothermal treatment

SERIES III

Thermally induced crystal lattice alterations in the form of breakdown or isomorphous atom replacements implying chemical shift, are likely to be identified by use of nuclear physical tests, of which NMR should be particularly useful. In recent years the introduction of "magic angle spin" NMR has greatly increased the resolution power of NMR and a few exploratory tests have been made that yield some interesting, relevant information.

Samples of a commercial Texan Ca-dominated bentonite, Bentolite L, that is very poor in iron, were saturated with distilled water after conversion to sodium and calcium states, respectively, and then hydrothermally treated for 10 days at 90, 130, 160 and 200°C. Analyses were made with respect to ²⁹Si and ²⁷Al, the major results being the following:

- * Si is associated with varying numbers of oxygens yielding a major peak at -85 to -100 ppm. A peak in the interval -107 to -118 ppm is indicative of less ordered silica like amorphous silica and silica coordinated with hydroxyls (Fig.9)
- * For Na montmorillonite the major peak gets smaller on exceeding a threshold temperature in the range of 100 - 130°C as seen from the integrated peak area:

20°C	90°C	130°C	160°C	200°C
100	102	93	88	93

- * At the same time the second peak undergoes both a change in size and shape suggesting an altered coordination of Si and OH when the threshold temperature is exceeded (Fig.10)
- * Only insignificant Al is in tetrahedral positions in unheated montmorillonite as demonstrated by the negligible "beidellite" peak at 75 ppm and remains to be so up to about 160°C. At higher temperatures there is a slight trend towards beidellite of both Na and Ca montmorillonite

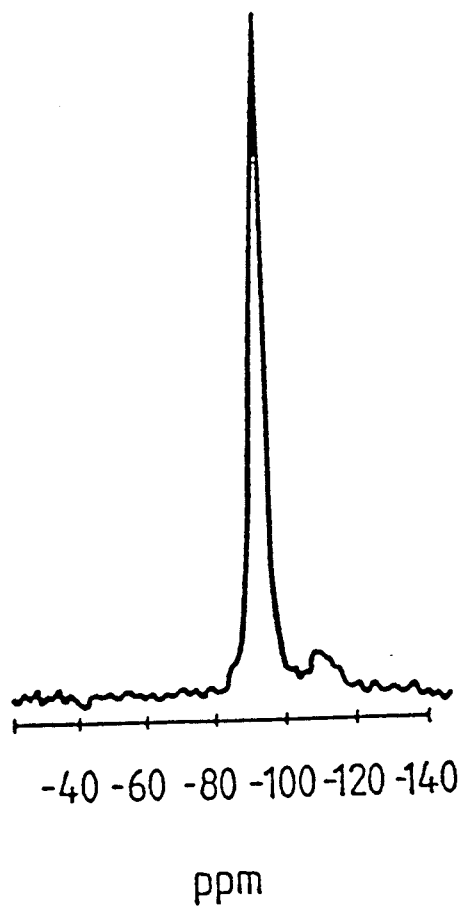


Fig.9 Major Si/O peak in montmorillonite (-85 to -100 ppm), and minor peak at -107 to -118 ppm

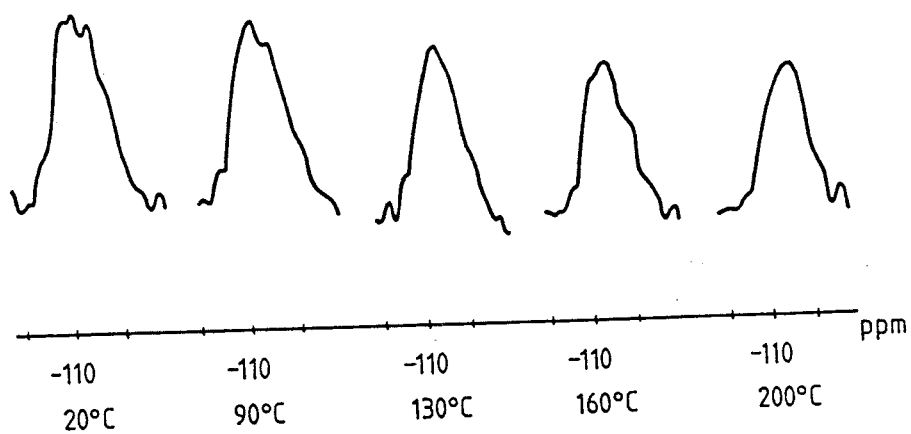


Fig.10 Change in size and shape of the minor Si peak on heating from room temperature to 200°C

It can be assumed that the altered Si/O and Si/OH coupling in Na (but not in Ca) montmorillonite on exceeding a critical temperature of 100 - 130°C, is associated with transformation from *trans* to *cis* coordination, which may be understood as a transfer from Edelman/Favejee's lattice structure to that of Hofmann/Endell/Wilm (Fig.1).

SERIES IV

This series was conducted within the framework of the Rock Sealing Test of the international Stripa Project. It comprises tests of 0.3, 3 and 9 months duration, of which only the first two have been completed so far.

The clay material is a natural rather iron-rich Ca bentonite with a very high content of montmorillonite that has been converted to Na-state by sodium carbonate treatment on an industrial scale. Clay samples were prepared with distilled water to a bulk density of about 1.15 g/cm³ and filled in 6 ml teflon cells with filters at both ends. These cells were put in 600 ml "autoclave", teflon-coated cylinders which were filled with either distilled water, Ca-rich water or Na-rich water with a salinity corresponding approximately to 50 % of that of sea water (cf. Table 2). The liquids in the cylinders were kept at 2 MPa pressure throughout the hydrothermal treatment by pressurizing tightly fitting pistons, and water samples were taken at the end of the experiments for analysis with respect to pH and all major elements.

The clay samples were extruded and their undrained shear strength determined by use of a laboratory vane bore, and undisturbed parts were investigated by TEM and SEM EDX. XRD and chemical analyses of the clay samples were also conducted.

Table 2 Water compositions

Ion	Ca-rich water		Na-rich water	
	g/l	moles/l	g/l	moles/l
Ca ²⁺	2.10	0.0524	0.41	0.0102
Na ⁺	1.66	0.0722	10.77	0.4685
Mg ²⁺	0.21	0.0086	1.29	0.0531
K ⁺	0.04	0.0009	0.40	0.0102
Cl ⁻	6.30	0.1777	19.35	0.5458
SO ₄ ²⁻	0.37	0.0039	2.71	0.0282
F ⁻	0.01	0.0003	0.00	0.0001
HCO ₃ ⁻	0.40	0.0066	0.14	0.0023

The major outcome of the study can be summarized as follows for the highest temperature 200°C:

- * The XRD spectrograms show that the major changes were similar for all three waters, i.e. that 1) calcite was dissolved, 2) both K- and Na-feldspars were largely dissolved, 3) quartz was strongly attacked, and 4) montmorillonite was not significantly altered. However, symmetric widening of the 001 basal peak was found, especially for the distilled water case, indicating primarily some formation of 10 Å minerals (Fig.11). The widening towards lower angles corresponds to 14 Å reflections.
- * The chemical analyses of the water surrounding the sample cells show that practically no aluminum had left the clay, while around 5 % of the initial silica content of the clay had been dissolved and diffused into the surroundings in 10 days and 8 % in 90 days. In distilled water the

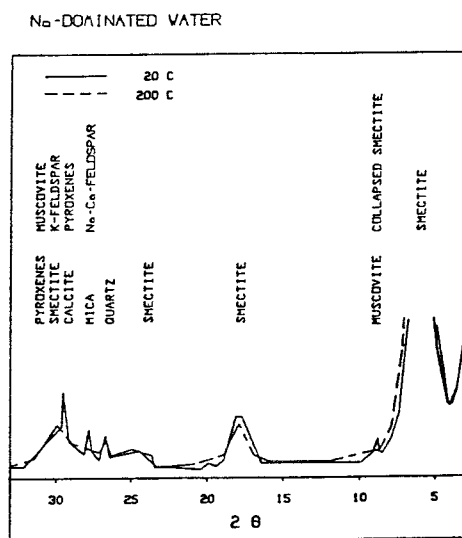
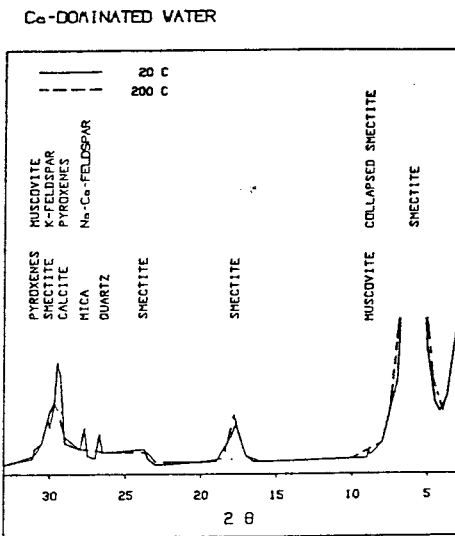
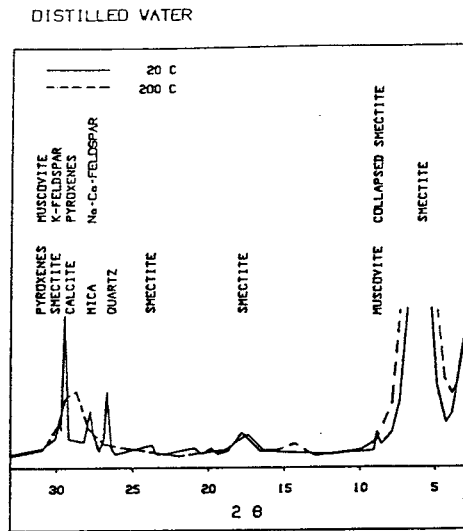


Fig.11 Generalized XRD diagrams for the 200°C and unheated samples (dotted). Upper: distilled water, Center: Ca-rich water, Lower: Na-rich water

only additional process was that about 75 % of the adsorbed sodium was released from the clay to the surroundings in 90 days, while in the other waters there was a considerable uptake of sodium and calcium and also an uptake of almost the same amount of magnesium as the loss of silica. pH dropped from 10 to 6 in the distilled water and to around 3 in the other waters.

- * As to the anions, about 5 to 10 % of the chlorine content was given off from the salt solutions and taken up in the clay porewater but the most significant observation is that 25 to 50 % of the SO_4 content did not remain in dissolved form. Since both calcium and sodium tended to diffuse out of the the clay samples, one concludes that sodium and calcium sulphates were formed in the salt surrounding water at this high temperature

The 160°C samples gave off approximately half as much as silica as the 200°C samples, while the release of sodium and calcium was about the same at both temperatures. Also, the uptake of magnesium of the clay from the surrounding salt solutions was not very different for the two highest temperatures, nor was there any significant difference in anion transfer.

130°C represents a breakpoint with respect to the influence of heat. Thus, the XRD spectra show significantly less dissolution of feldspars and quartz and the chemical changes are also less obvious. Actually, from 130°C and downwards, the silica release from the samples was roughly proportional to the temperature

expressed in centigrades and at 130°C it was about 1/3 of that at 200°C in distilled water, 1/4 in Ca-rich water and 1/6 in Na-rich water. The behavior of magnesium is very obviously connected to the significant drop in silica content and it was quite different for the Na- and Ca-rich solutions. Thus, while the Mg-uptake was about 1/3 of that at higher temperatures in the calcium-rich water, it was not significantly less than the uptake at the highest temperature in the sodium-rich water. This suggests that the Mg-uptake, which is obviously very strong in both waters, starts in the interval 90 to 130°C in sodium-saturated montmorillonite while it begins in the interval 130 to 160°C in calcium-saturated montmorillonite.

The following conclusions can be drawn from SERIES IV:

1. Aluminum stays in the clay-water system
2. In electrolyte-poor water, silica is given off from the clay at a rate that is determined by temperature according to some power law
3. Beidellitization takes place only in salt water holding Mg (or Fe), since octahedral Al cannot leave to replace Si in the tetrahedrons unless Mg (or Fe) moves in to replace it. This process takes place at 90 - 130°C in Na montmorillonite and at 130 - 160°C in Ca montmorillonite
4. Sodium is given off quickly from Na montmorillonite to the surroundings and it is replaced by protons, which yields the wellknown high pH. In Ca montmorillonite, the adsorbed cations are more firmly held to the basal planes in the interlamellar

space and are not easily exchanged by protons. pH is therefore considerably lower than in Na montmorillonite

5. In Ca-rich water, free Ca and SO_4^{2-} react to form gypsum at temperatures higher than about 130°C
6. Potassium was rather given off from the clay than taken up. Thus, there was no definite sign of formation of hydrous mica except for the slight tendency of 10 Å mineral formation at 160 and 200°C

3.2.3 Conclusions

The experimental work gives a rather complete picture of the involved processes under the respective test conditions. The major ones can be described as follows:

A first, major mechanism is congruent dissolution of the montmorillonite lattice at a rate that is determined by the concentration of dissolved silica in the water and by the temperature, silica being precipitated in the form of cristobalite or amorphous silica on exceeding the solubility (SERIES I-IV). These precipitations act as cementing substances and reduce or prevent spontaneous swelling. Charge equilibrium considerations suggest that the dissolved silica is present in the form of univalent anions. A very important fact is that aluminum stays in the clay/water system, meaning that possible neoformation of aluminum-bearing minerals like hydrous mica will take place in the voids of the montmorillonite clay, which tends to maintain a low hydraulic conductivity.

A second, incongruent dissolution process is the release of silica from tetrahedral positions without breakdown of the crystal lattice and only intralattice migration of aluminum to replace the silica (SERIES III and IV). There is strong evidence that this so-called beidellitization, i.e. the commonly assumed first stage of "illitization", requires both magnesium (or iron) in the porewater of the clay and heating to a critical temperature that may be in the range of 90 - 130°C in Na-saturated montmorillonite and 130 - 160°C in Ca montmorillonite (SERIES I, II, and III). This suggests that no solid/solid transformation of montmorillonite to hydrous mica takes place below these "critical" temperatures. Thus, at lower temperatures neoformation of hydrous mica is the only mica-producing process. Formation of 10 Å minerals, possibly creating false I/S mixed layer minerals, is simply caused by permanent contraction at complete dehydration at more than 100°C. Neoformation of hydrous mica is controlled primarily by the concentration of dissolved silica and potassium in the reacting clay/water system and by the access to these elements from the surroundings.

Putting all this together one arrives at the phenomenological model shown in Fig.12. It will be taken as a basis of the formulation of a quantitative chemical alteration model but before coming to that we will consider the background of some of the processes in greater detail.

3.2.4 Discussion

The reason for the stronger heat-sensitivity of Na montmorillonite is not obvious but it may be related to the possible existence of inverted SiO_4 tetrahedrons when Na (or Li) is in interlamellar positions. Thus, rather recently it has been suggested that replacement of silica by aluminum may have the form of

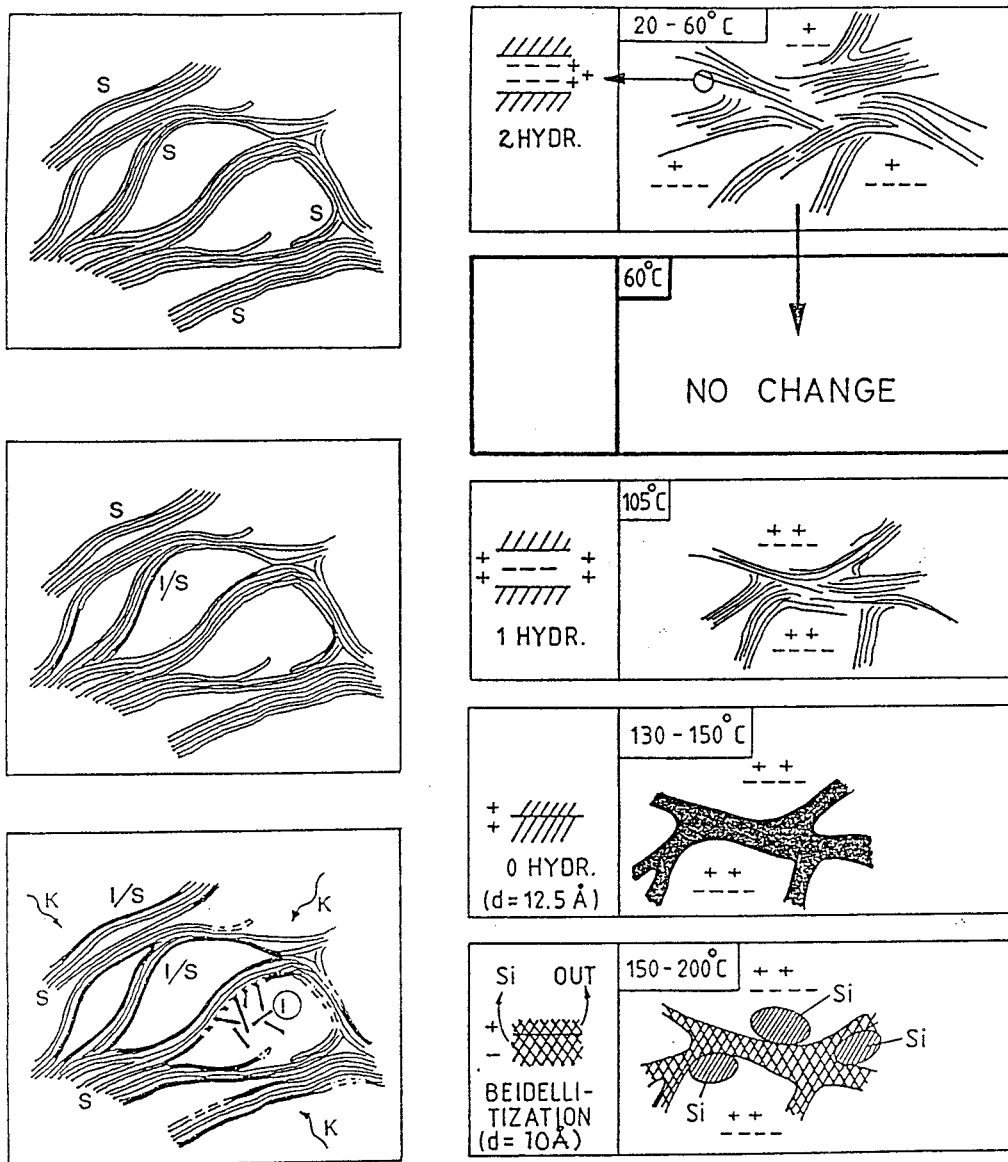


Fig.12 Major features of the authors' smectite alteration model.

Left row shows congruent dissolution, I/S (I representing 10 Å minerals) transformation and neof ormation of hydrous mica.

Right row shows heat-induced contraction of smectite stacks, permanent collapse at a critical temperature, and precipitation of silica under closed conditions

establishing inverted tetrahedrons of the type proposed by Edelman & Favejee (13). The transfer of aluminum from octahedral positions to replace Si in inverted tetrahedrons would actually be easier than transfer to tetrahedrons of the Hofmann/Endell/Wilm structure and since the latter process takes place in Ca montmorillonite it appears more resistant than Na montmorillonite. Indeed, this may be the true nature of the interlamellar establishment of aluminum hydroxy complexes that has been proposed by Johnston & Miller (14) and that is claimed to be the reason for the appearance of a 14 Å reflection, i.e. widening towards low angles of the 001 peak that was also observed in the hydrothermal experiments with distilled water in SERIES IV. This process is concluded to release H^+ to the solution giving it a low pH.

3.3 *Formulation of chemical alteration model*

3.3.1 General

The finding that different degrading processes take place in different temperature regimes leads us to outline two models. Simplifying the matter a bit we consider the congruent dissolution/neoformation process to be the only major transformation that takes place below 130°C, thus forming the basis for the formulation of a "low-temperature" model. A corresponding "high-temperature" model, covering the range of 130 - 200°C, also includes beidellitization through superimposed non-congruent dissolution of silica and true I/S mixed layer formation.

3.3.2 Low temperature alteration model

There is no doubt that the dissolution rate of smectite is controlled by temperature and there are good reasons to believe that the process is of Arrhenius' type with an activation energy of 25-30 kcal/mole and a dissolution rate constant that depends on pH, and on the type and concentration of the electrolyte. This would make Eq(1) applicable and offer a way of predicting the change in I/S since Pytte's model does not rule out the possibility that transformation of smectite to hydrous mica takes place in the form of growth of a separate hydrous mica phase. Taking the activation energy to be 27 kcal/mol the transformation rate under isothermal conditions would then be as indicated in Pytte's diagram shown in Fig.13.

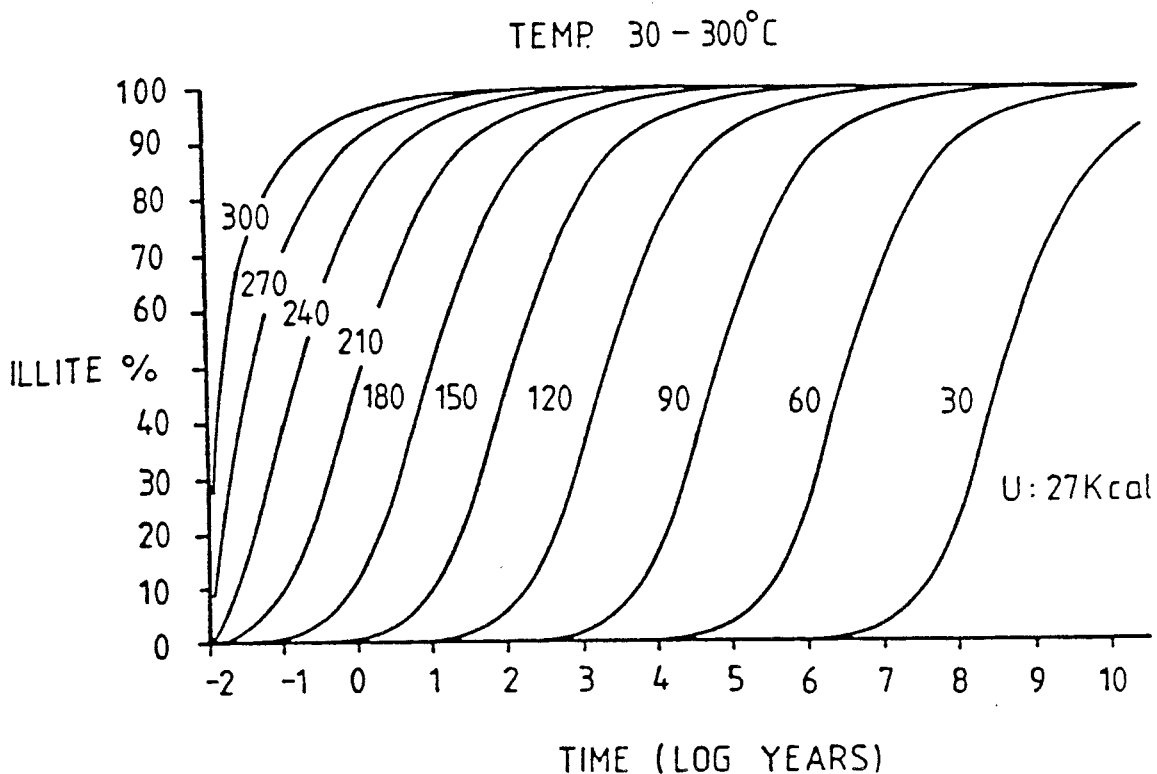


Fig.13 Rate of alteration of montmorillonite at an activation energy of 27 kcal/mol according to Pytte (3)

This would mean that if the maximum bentonite temperature in a KBS3 repository is taken as 130°C, prevailing for about 2000 years, practically all the montmorillonite would be preserved after 10 years, while 10 % would be transformed in 100 years, and 65 % at the end of the heating period. Taking the activation energy to be 29 kcal/mol, which was recently suggested by Japanese researchers in conjunction with the analyses of the heat-affected Murakami bentonites (15), one finds that about 60 % of the montmorillonite would be transformed after 2000 years at 130°C.

Applying Pytte's theorem to the Swedish Hamra bentonite, which is located at 500 m depth and has been exposed to 110 - 120 °C for 10⁷ years and still holds 25 % montmorillonite, it is concluded that the process is actually much slower than indicated by his model. A probable reason for this is that the controlling factor is the fashion in which potassium is made accessible for the transformation. *Thus, it is possible that the porewater of the smectite generally can be taken to be saturated with silica and aluminum at depth and that it is precipitated in the form of hydrous mica at the same rate at which potassium diffuses into the reaction zone. The idea is based on the presumption that the reaction takes place momentarily and that the resulting removal of dissolved potassium from the porewater solution creates a sink that provides the driving force to bring in more potassium.*

One realizes that such a model is a true kinetic one and that the properties of the system, as exemplified by the Hamra Strata in Fig.14, must be specified, i.e.:

1. The geometry of the system
2. The initial potassium concentration in the clay and in the surrounding medium

3. The rate of transport of potassium in the surrounding medium to the reaction front, and in the clay. Under stagnant groundwater conditions the transport mechanism is diffusion, the controlling parameter being the diffusion coefficient of potassium
4. A criterion concerning saturation of potassium in the clay, i.e. when the transformation to hydrous mica is complete. A practical measure of the corresponding potassium content is 10 % by weight

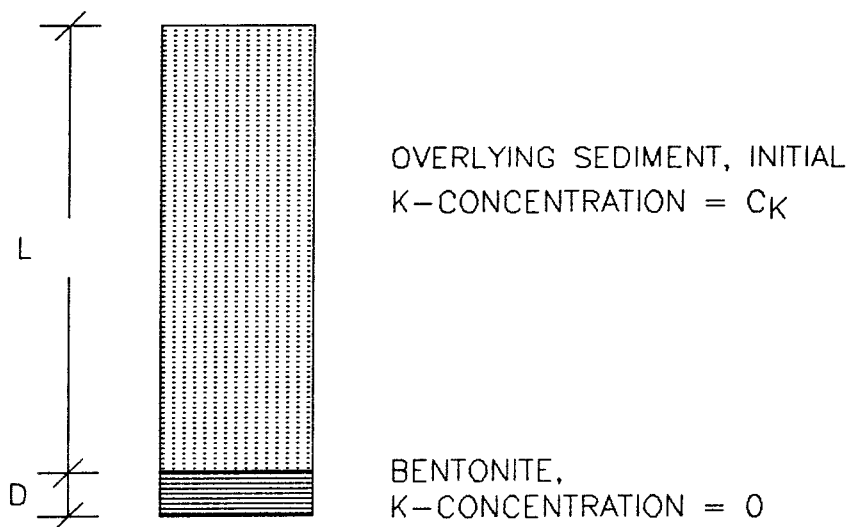


Fig.14 Clay with surrounding K-holding medium. The clay is initially free of potassium which is successively taken up and fixed, by which the K-concentration is kept at 0 in the clay voids. Complete transformation is when the K-content has reached a maximum value that corresponds to hydrous mica (illite)

Laboratory tests

The model can be checked by considering the laboratory tests referred to earlier in the report and a test conducted as part of the CEA/SKB joint research program. Considering first SERIES I - IV, most tests in SERIES I and II were conducted without any potassium at all in the porewater and logically exhibited no hydrous mica at the end of the hydrothermal treatment. The fact that the samples exposed to potassium solutions after the treatment only showed insignificant formation of 10 Å minerals is fully explained by the fact that no neoformation of such minerals could take place in the hydrothermal period in the absence of potassium, and that no beidellitization occurred in this period in the absence of Mg (or Fe), which would have yielded hydrous mica on subsequent exposure to potassium.

The SERIES III tests were conducted with salt solutions holding no potassium and consequently showed no sign of hydrous mica. SERIES IV did not show any clear indication of the formation of hydrous mica except that, at the highest temperatures, potassium tended to be taken up by the clay from the surroundings.

The CEA/SKB study comprised a 1 year laboratory test of MX-80 Na montmorillonite clay saturated with very weakly brackish Allard water with a potassium concentration of 4 ppm. The clay was located in a cell with one end closed by a steel plate that was exposed to rather heavy γ radiation, while the other end consisted of a sintered steel filter, through which the porewater contacted external, pressurized Allard water, thus forming open conditions. This test will be fully reported elsewhere and we will only give a condensed presentation of the major results here.

XRD and chemical analyses, as well as electron micrograph interpretations and rheological measurements were of major concern in the study. Specimens were cut from different parts of the 7 cm long sample that had been heated to 130°C at the radiated end and to 90°C at the "open" end.

The XRD analyses showed a similar pattern for all temperatures as SERIES IV, i.e. no definite sign of formation of hydrous mica but partial dissolution of calcite and feldspars (Na, Ca, and K) at 90° and almost complete disappearance of the latter minerals at 130°C when also quartz was dissolved. The smectite peaks showed hardly any change except for a slight broadening of the base of the (001) reflection at 130°C. The widening towards lower angles can be ascribed to some insignificant formation of 10 Å minerals, which may have been neoformed hydrous mica or permanently collapsed smectite stacks. The very low potassium content explains that only very insignificant amounts of hydrous mica could have been formed. The widening towards higher angles may be explained by the earlier described establishment of aluminum hydroxide complexes in the interlamellar space.

Geological analogues

The obvious difficulty in deriving a correct stress- and temperature history of ancient geological strata, and finding changes in their chemical environment, naturally mean that they cannot serve as a proof of the validity of any geochemical model. However, smectite strata with a generally accepted history should at least give a rough indication of the applicability of the models, and we will consider a few cases of this sort in a first checking attempt.

As to the "low-temperature" cases we will use data from North Sea sediments, the Busachi and Fish clays, while the Kinnekulle clay will be used as a "high-temperature" example. The Hamra clay, which is concluded to have been exposed to 120°C for at least 10^7 years (6), is expected to represent an intermediate case, with which we will start our examination.

The Hamra case

The Hamra bentonite profile from southern Gotland is relevant since it comprises a 30 cm bentonite layer that is presently located at about 500 m depth in a complex series of limestones, mudstones and shales. It is concluded to have been exposed to 120°C for about 10^7 years and to temperatures ranging between 20 and 120°C for 4×10^8 years (6). Its clay fraction still has a montmorillonite content of 35 %, which we take as the residue of an initial montmorillonite content of 100 % in the clay fraction. For application of the model one needs to take the actual stratigraphy into consideration, i.e. the existence of additional bentonite horizons, a major one of about the same thickness as the presently discussed bed being located about 120 m higher up in the profile.

Using the figure 400 ppm for the initial concentration of potassium in the voids of the sediments we find the average potassium concentration of the whole overlying marine sediment volume to be about 80 ppm. Complete conversion to hydrous mica is taken as 10 % of the solid smectite mass, which corresponds to 200 000 ppm per unit bentonite volume, and using these parameter values one finds the transformation rate to be as indicated by the diagram in Fig.15. Assuming the potassium diffusion coefficient of the overlying sediment series to be $10^{-9} \text{ m}^2/\text{s}$, we find that the actual amount of 35 % montmorillonite of the clay fraction of this deep-lying bentonite bed would

be left at the end of the 10^7 year long period of enhanced temperature. $D=10^{-10}$ m^2/s would have yielded 75 % montmorillonite and $D=10^{-11}$ m^2/s over 90 % montmorillonite. Assuming that the conversion process went on for the entire 400 million year period, 35 % remaining montmorillonite would yield a diffusion coefficient of around 5×10^{-11} m^2/s .

Smectite to Illite transformation controlled by K diffusion

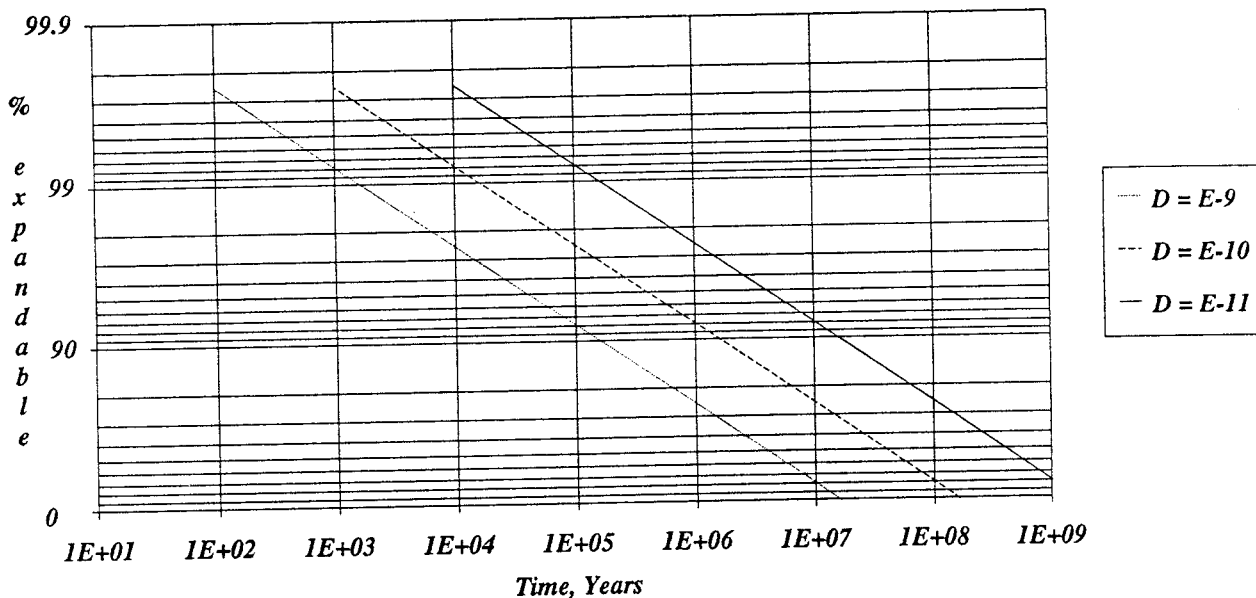


Fig.15 Predicted rate of alteration of montmorillonite according to the model (cf. Fig.14). c_K is 400 ppm and the thickness of the bed 0.30 m

Now, considering the fact that there are additional potassium-absorbing bentonite horizons in the profile, migration by diffusion could only have proceeded according to this model until the K concentration profile was affected by neighboring bentonite layers. This is illustrated by Fig.16, which shows the successive concentration profiles for $D=10^{-11}$ m^2/s , from which we see that it would take about 2 million years until the concentration dropped below 400 ppm

at half the distance to the next major bentonite layer in the overlying sediment mass. One concludes from this that the diffusion coefficient may have been considerably higher than $10^{-11} \text{ m}^2/\text{s}$ and that the uptake of potassium and conversion to hydrous mica must have been strongly retarded after a few million years. Since field diffusion experiments with KCl in soft Quaternary soil profiles (15) have yielded D-values of around $10^{-10} - 10^{-9} \text{ m}^2/\text{s}$, it is probable that the diffusion coefficient in the Hamra series was still not higher than 10^{-11} to $10^{-10} \text{ m}^2/\text{s}$.

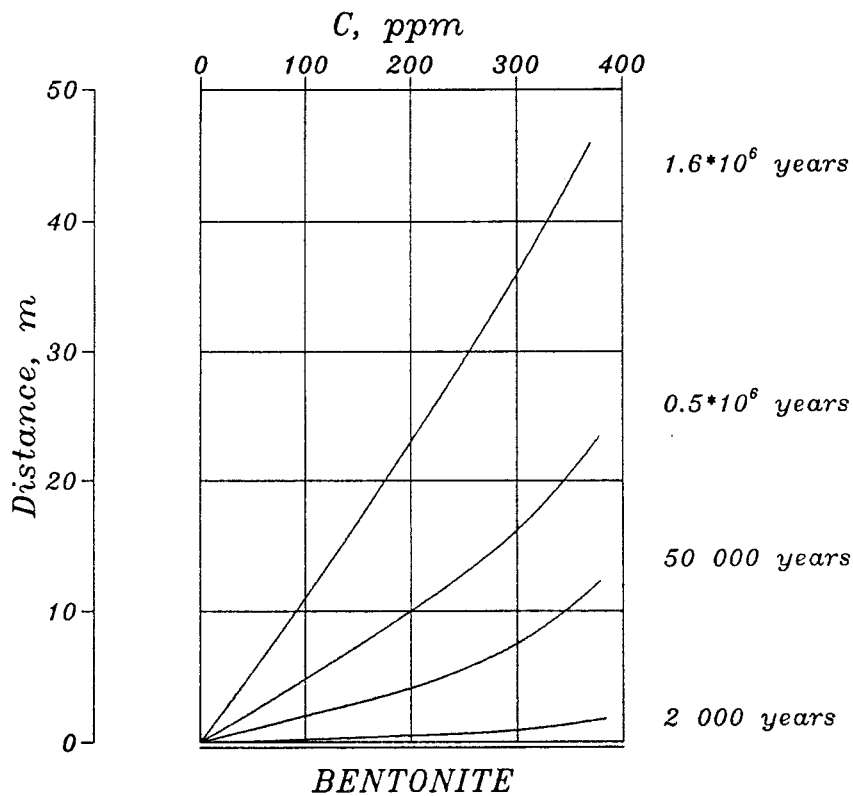


Fig.16 Calculated change in potassium concentration in the sediment overlying the lowest Hamra bentonite bed

It must be realized also that K-bearing minerals like microcline provided some potassium to the solution and this would suggest that the actual average K diffusion coefficient is around 10^{-10} m²/s rather than 10^{-11} m²/s. At any rate it appears probable that most of the conversion of montmorillonite to hydrous mica took place in the 10^7 year period of maximum heat.

Low-temperature cases

Relevant examples are marine Upper Cretaceous, smectite-rich clays in the North Sea area that were recently described by Elen Roaldset*. They have been exposed to temperatures on the order of 50 - 100°C and have smectite contents of not less than 60 - 70 %. Applying the model to these clays and taking them to be 7×10^7 years old, one finds the expected percentage of expandable clay to be around 50 - 80 % for the diffusion coefficient span 10^{-11} to 10^{-10} m²/s, i.e. of the right order of magnitude.

The same limiting effect on access to potassium in the Hamra case was probably valid also for the North Sea sediments, i.e. there are several major clay horizons that interact and affect the K-concentration profile. Also, some contribution to the amount of dissolved potassium is probably offered by K-bearing minerals and the actual conversion rate may therefore well be explained by a K diffusion coefficient of around 10^{-10} m²/s.

* Data given at the fall meeting in Stockholm (1990) of the Nordic Society for Clay Research

A further example is given by the part of the Busachi clay profile in Sardinia that was exposed to a heat pulse of maximum 100°C for much less than one year (6). The clay is assumed to have been deposited under marine conditions in Tertiary time, yielding an approximate age of about 3×10^7 years. The assumed history implies that it was covered by rhyolite magma and that it is expected to have been supplied with potassium mainly from very dense, underlying sediments. A diffusion coefficient of 10^{-11} to $10^{-10} \text{ m}^2/\text{s}$ yields a montmorillonite content of 70 - 90 %, which is on the same order of magnitude as the actual present content of around 80 - 90 %.

Finally, the marine Cretaceous Fish clay forming a 5-10 cm bentonite bed in partly silicified limestone on Sjælland, Denmark, offers an example of "low-temperature" montmorillonite clay of considerable age (about 7×10^7 years), cf. (8). The present profile has been covered by younger sediments of unknown thickness which were eroded in Tertiary time. Weak folding has occurred due to peripheral effects of the Laramic phase of orogeny but the maximum temperature to which the clay has been exposed is not expected to have reached 100°C .

The montmorillonite is thought to originate from volcanic ash although it may possibly have resulted from asteroid impact. At any rate the clay sediment was strongly contaminated by terrigenous material, mainly calcite and quartz, so that the clay minerals make up only about 50 % of the clay fraction. Montmorillonite is concluded to constitute about 50 % of the clay minerals, the rest being 10 Å minerals. Applying the diagram in Fig.15 and assuming that potassium went in from overlying sediments forming approximately the same profile as at Hamra, we find that a K diffusion coefficient of 10^{-11} to $10^{-10} \text{ m}^2/\text{s}$ would yield the actual amount of 50% montmorillonite.

3.3.3 High-temperature alteration model

While the low-temperature model is aimed at describing transformation of montmorillonite to hydrous mica at temperatures up to around 130°C, implying congruent dissolution and complete silica saturation throughout the process, the high-temperature model is proposed for the temperature interval 130 - 200°C assuming incongruent dissolution and expulsion of excess silica to the solution. This process is associated with beidellitization of the montmorillonite and this means that hydrous mica will be formed both by neoformation and possibly also by "mixed-layer" transformation. Still, the controlling factor of both processes is the access to potassium, which makes the alteration from smectite to hydrous mica in principle the same as in the low-temperature case. The only significant difference between the two models is therefore that *the high-temperature version implies that silica is forced out of the smectite and yields precipitations in the form of amorphous silica or cristobalite that partly prevent dehydrated smectite stacks from expanding on exposure to water.*

As to the rate of conversion to hydrous mica, the same basic calculation model is assumed to be valid as for the low-temperature model, but the major parameter, i.e. the diffusion coefficient is expected to be higher. Thus, for temperatures in the interval 150°C - 200°C it is assumed to be one order of magnitude higher than at 50 - 120°C, i.e. 10^{-10} - 10^{-9} m²/s.

Concerning the precipitation of silica from the supersaturated solution, it is assumed to be very rapid. Thus, the entire release of silica in the course of beidellitization is assumed to be completed in days, weeks, or months rather than years. The model

implies that beidellitization yields release of about one quarter of the total Si amount almost momentarily. Expressed in terms of SiO_2 , about 8 % of the total solid mass is hence precipitated, creating amorphous silica compounds or cristobalite. The precipitations serve as a silica source that keeps up the degree of saturation at 100 %. Assuming the precipitations to have the form of 100 Å diameter nodules located uniformly over the periphery and basal planes of 5 flakes thick stacks, their spacing would be around 500 Å, suggesting considerable "welding" and impediment to expansion. If they are taken to be 1000 Å in diameter, they would have a spacing of microns with little effect on the expandability of the stacks, while they may instead form strong bridges between stacks that may affect the rheological properties to a significant extent (8).

3.3.3.1 Preliminary checking

The Kinnekulle bentonite serves as an example of smectite clay that has undergone heating to a critical temperature, i.e. at least 130°C by magma intrusion (17). The 2 m thick clay bed is a member of a series of Ordovician marine sediments, i.e. around 4.5×10^8 years old, probably covered by several hundred meters of Silurian and Devonian sediments that were later eroded.

Assuming that the ambient potassium concentration was initially the same as in the Hamra case, i.e. 400 ppm, and implying that the conversion process went on for the entire 450 million year period, a K diffusion coefficient of $5 \times 10^{-11} \text{ m}^2/\text{s}$ would yield around 20 % expandable minerals in the uppermost 0.3 m thick part. The actual value is in fact around 20 %, while it is about 30 % in the center of the 2 m thick bed, the K content being 50 000 ppm at the upper end and about 30 000 ppm in the center (17,18).

However, considering that there are several bentonite horizons as in the Hamra case, it is logical to believe that the situation was more or less like the one in Fig.16, which leads us to believe that the actual diffusion coefficient was in fact higher, presumably in the interval 10^{-10} to 10^{-9} m^2/s in the 1000 year long heating period and around 10^{-11} to 10^{-10} m^2/s thereafter. It is clear, though, that the conversion cannot have been completed in the 1000 year long period of maximum temperature since this would have required very much faster K diffusion. The fact that there is still a gradient in potassium concentration and hydrous mica content, suggests that it was formed in a relatively short time, i.e. some tens or hundreds of thousand years and that it became "frozen in" when temperature finally dropped.

A detailed analysis of the concentration profiles of K, Si, Al and Mg within the thick bed is expected to reveal further details in the diffusion characteristics.

The model predicts release and precipitation of tetrahedral silica at temperatures exceeding about $130^{\circ}C$ and this actually took place in the Kinnekulle clay as documented by the appearance of many 100 - 1000 Å large precipitations (cf. Fig.4), and by the brittle behavior due to even larger precipitations as demonstrated by creep tests (8). The fact that the heating to about $130^{\circ}C$ lasted for a relatively short period of time demonstrates that the release of excess silica in conjunction with beidellitization is a rather quick process.

This latter function of the model is also documented by the most heat-affected part of the Busachi bentonite profile (6). Thus, the whole microstructural pattern of this part, which is concluded to have been heated to 200° for about 2 months, is very similar to

that of montmorillonite clay that has been exposed to 150 to 200°C under hydrothermal conditions in the laboratory with respect to the presence of nodular precipitations.

4

COMMENTS AND TENTATIVE CONCLUSIONS

The preliminary models appear to give reasonable results with respect to the rate of transformation of montmorillonite to hydrous mica and of silica precipitation. The parameters that control the transformation is firstly temperature, especially whether it exceeds a critical level of around 130°C or not, and secondly the uptake of potassium from external sources. While it is certainly a simplification to assume that the concentration of reactive silica and aluminum are sufficient to take potassium as the sole controlling agent in the transformation of montmorillonite to hydrous mica, this assumption is still reasonable at temperatures exceeding 70°C in an environment that is rich in silicate minerals, as indicated by geological data (19).

A valuable feature of the proposed models is that while they yield data on conversion of montmorillonite to hydrous mica that are in line with those given in geological literature, the key function of potassium migration enables us to explain why the literature provides many examples of no temperature influence, and examples of huge variation in conversion at one and the same temperature.

Although it is a bit premature at this stage, a number of consequences can be drawn respecting the survival of montmorillonite buffers in HLW repositories:

1. Low-electrolyte groundwater in the host rock minimizes transformation of montmorillonite to hydrous mica. Thus, water that is very poor in Mg or Fe does not allow for beidellitization and thus not for conversion to I/S minerals, nor does it allow for release of tetrahedral silica and precipitation of silica compounds if the temperature is raised beyond 130^oC
2. Temperatures below about 130^o and low-electrolyte groundwater that is very poor in potassium yield very significant longevity, i.e. many millions of years will pass until the montmorillonite content drops
3. Stagnant salt water with a potassium content corresponding to that of ocean water transforms montmorillonite to hydrous mica by dissolution of the virgin mineral and neof ormation of the latter. This process takes place by potassium diffusion at a rate that depends on temperature. Very slow transformation rates and an appreciable content of preserved montmorillonite are expected even after millions of years
4. Rapid flow of salt water with 400 ppm K concentration in the nearfield of VLH, VDH or KBS3 holes, or through KBS3 tunnel backfills, will keep up the K concentration in the vicinity of the canister-embedding clay and create very rapid transformation to hydrous mica. Hence, for 30 cm montmorillonite clay contacting ocean water, 90 % transformation to hydrous mica will take place in less than 1000 years

5. *Heating beyond about 130°C in the presence of salt water causes quick beidellitization, yielding I/S minerals on uptake of potassium and precipitation of silica compounds that yield cementation and brittle behavior*

6. *Ca montmorillonite seems to undergo lattice alteration to beidellite at a higher temperature than Na montmorillonite, making it less vulnerable to lattice alteration, but this needs further confirmation*

It is believed that these conclusions can be applied in a preliminary functional analyses of HLW concepts, while the ongoing, remaining hydrothermal tests must be completed before such analyses can be relied on. Application of the models to concepts implying clay confined by crystalline rock requires that adequate K-diffusion coefficients be used since the ones derived from the sedimentary rock environment given in this report would be too conservative.

In order to strengthen the models, more detailed studies of geological analogues representing smectite-holding clays with known geological and temperature histories should be made and for this purpose North Sea sediments seem to be especially well suited. Also, some hydrothermally generated weathered clays in granite should be investigated.

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December 1990

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Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil I: Osamu Utsumi uranium mine

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December 1990

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Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil II: Morro do Ferro

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Isotopic geochemical characterisation of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil

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Geomorphological and hydrogeological features of the Poços de Caldas caldera, and the Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil

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Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Natural series nuclide and rare earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Testing of geochemical models in the Poços de Caldas analogue study

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Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil

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Near-field high temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine analogue site, Poços de Caldas, Brazil

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Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil

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The Poços de Caldas Project: Summary and implications for radioactive waste management

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Kinetics of UO₂(s) dissolution reducing conditions: numerical modelling

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The effect from the number of cells, pH and lanthanide concentration on the sorption of promethium on gramnegative bacterium (Shewanella Putrefaciens)

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Isolation and characterization of humics from natural waters

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Complex forming properties of natural organic acids.

Part 2. Complexes with iron and calcium

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Characterization of humic substances from deep groundwaters in granitic bedrock in Sweden

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Licentiate thesis**

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Th, REE and other trace elements**

Ove Landström¹, Eva-Lena Tullborg²

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Applications to radionuclide waste
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front in the uranium mine in Poços de
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Lars Rosengren¹, Ove Stephansson²

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Ground water in crystalline bedrock

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**Development of clay characterization
methods for use in repository design with
application to a natural Ca bentonite clay
containing a redox front**

Ola Karnland, Roland Pusch

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