Working Report 2010-53

Long-Term Stability of Bentonite

A Literature Review

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July 2010

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LONG-TERM STABILITY OF BENTONITE- A LITERATURE REVIEW

ABSTRACT

The long-term thermodynamic stability of the bentonite buffer in the evolving chemical, thermal and hydrological conditions at Olkiluoto has been evaluated by reviewing the relevant experimental data and natural occurrences of bentonite that could serve as analogues for the long-term bentonite stability in the expected repository conditions, especially focussing on mineral transformations due, among others, to thermal effects including cementation. Natural occurrences with stable smectite have been reviewed and compared with Olkiluoto groundwater compositions at present and during the expected hydrogeochemical evolution of the repository.

Alteration of the bentonite buffer is expected to be insignificant for natural groundwater conditions at present and for the evolving groundwater conditions at the expected thermal boundary conditions caused by the heat induced from the fuel canisters (<100 °C). However, it should be noted that salinity increase affects smectite stability and the current maximum allowed salinity is 70 g/l for the bedrock. The introduced foreign materials (e.g. plugs, backfill, cement based construction materials, etc.) may cause release of K^+ and SiO_2 and elevated pH due to degradation and dissolution processes. These may alter the conditions in the repository that may favour alteration and cementation processes. The amounts of foreign materials to be used in the repository will be updated along with the progress of the construction. Also the information on their impact on the barriers needs to be evaluated in more detail, including the degradation rate, mobility or dilution of the foreign materials in the repository environment.

The exchangeable cation composition of the buffer bentonite is expected to equilibrate with the surrounding groundwater during and after saturation. This process is expected to lead towards Ca-dominant exchangeable cation composition within the montmorillonite interlayer spaces in the buffer. In general it seems that the transformation towards Ca-dominated composition would favour the long-term stability of the buffer as Ca-dominated smectite (compared to Na-dominated type) has larger water retention capacity and anion incorporation to the interlayer space of montmorillonite is more extensive for divalent cations and it is not as easily eroded or dissolved in case of diluted groundwater or in case of high pH.

Although the information on cementation by thermal effects from natural bentonite occurrences may not be directly applicable to the repository conditions, they show that very high temperatures have affected the bentonites and for long periods of time and there is still unaltered montmorillonite in those deposits. Natural occurrences of bentonite and smectite provide information on the bentonite behaviour in varying conditions. How to adapt this information in the predicting the buffer behaviour is a challenging task. To be able to make a direct comparison between different natural occurrences and the buffer, more detailed information would be needed on density/compaction rate, saturation degrees, pressure conditions, chemical conditions, and duration of the thermal events for the natural bentonites as these are well known for the buffer.

Keywords: buffer, bentonite, smectite, montmorillonite, stability, natural analogue

BENTONIITIN PITKÄAIKAISSTABIILISUUS – KIRJALLISUUSSELVITYS

TIIVISTELMÄ

Tässä kirjallisuusselvityksessä on arvioitu bentoniittipuskurin pitkäaikaisstabiilisuutta nykyisissä ja tulevissa loppusijoituslaitoksen olosuhteissa. Raportissa on käsitelty lämmön-, sekä kemiallisten ja hydrologisten olosuhteiden vaikutuksia. Kokeellisten tulosten lisäksi on tarkasteltu mahdollisia luonnonanalogiakohteita, erityisesti sellaisia, joissa lämmön vaikutuksia bentoniitin muuttumiseen on voitu tarkastella. Myös sellaisia kohteita, joissa smektiitti esiintyy stabiilina faasina tunnetuissa hydrogeokemiallisissa olosuhteissa, on käyty läpi ja verrattu Olkiluodon eri pohjavesikoostumusten kanssa.

Selvityksen perusteella voidaan todeta että bentoniittipuskurin sementaatio tai muuttuminen on hyvin epätodennäköistä nykyisissä Olkiluodon pohjavesiolosuhteissa, kuten myös oletetuissa tulevissa olosuhteissa. Myöskään lämpötilagradientin loppusijoituslaitoksen kehityskulun alkuvaiheessa (<100°C) ei ole syytä olettaa aiheuttavan muuttumista tai sementaatiota. On kuitenkin mainittava, että suolapitoisuuden kasvaminen vaikuttaa puskurin toimintaan heikentävästi ja nykyinen loppusijoituskalliolle asetettu suolaisuusraja on 70 g/l. Vieraiden materiaalien (esim. tulpat, tunnelitäytöt, sementtipohjaiset rakennusmateriaalit ym.) liukeneminen ja rapautuminen loppusijoituslaitoksesssa voivat mahdollisesti aiheuttaa K^+ ja SiO_2 vapautumista ja pH:n nousua. Muuttuneissa olosuhteissa puskurin sementoituminen saattaa olla mahdollista. Vieraiden aineiden käyttömääriä ja laatua tullaan päivittämään rakennustöiden edetessä. Niiden vaikutusta päästöesteiden toimintaan on arvioitava tarkemmin, ainakin rapautumisnopeuden, liukoisuuden ja liikkuvuuden osalta loppusijoituslaitoksessa ja sen lähiympäristössä.

Montmorilloniitti bentoniittipuskurissa tulee tasapainottumaan sitä saturoivan pohjaveden kanssa ja näin ollen sen koostumus vaihtuvien kationeiden suhteen tulee muuttumaan tulevaisuudessa kohti kalsiumin dominoimaa koostumusta. Yleisesti ottaen näyttää siltä, että muutos Na-tyypin bentoniitista Ca-tyyppiseksi on puskurin toiminnalle eduksi. Ca-bentoniitilla on suurempi veden pidätyskyky ja kyky ottaa anioneita interlaminaaritilaan. Ca-bentoniitti ei myöskään erodoidu tai liukene yhtä helposti kuin Na-bentoniitti joutuessaan kontaktiin laimeiden (esim. jäätikön sulamisvedet) tai korkean pH:n vesien kanssa.

Vaikka termisiin vaikutuksiin ja sementaatioon liittyvät luonnonanalogiakohteet eivät täysin vastaa odotettuja olosuhteita loppusijoituslaitoksessa, voidaan niiden perusteella kuitenkin todeta, että montmorilloniittia on säilynyt muuttumattomana muodostumissa, joissa on vallinnut korkeampi lämpötila ja joissa vaikutusaika on ollut hyvin pitkä. Bentoniitti ja smektiitti esiintyvät luonnossa hyvin vaihtelevissa ympäristöissä. Miten tätä tietoa voidaan hyödyntää puskurin käyttäytymisen mallintamisessa, on haasteellinen tehtävä. Jotta erilaisia luonnonesiintymiä ja bentoniittipuskuria loppusijoitusympäristössä voitaisiin suoraan vertailla, tarvitaan tarkempaa tietoa luonnonesiintymien tiheyksistä, kompaktointiasteista, saturaatioasteista, paineolosuhteista, kemiallisista olosuhteista ja mahdollisten termisten tapahtumien kestosta.

Avainsanat: puskuri, bentoniitti, smektiitti, montmorilloniitti, stabiliteetti, luonnonanalogia

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FOREWORD

This report was compiled at Saanio & Riekkola Oy, Helsinki, Finland. The main writer of this report was Heini Laine. Petriikka Karttunen was responsible of the cementation topic and contributed mainly to Sections 3.3 and 4.1-4.4 as well as conclusions concerning those.

The authors would like to thank all the reviewers that provided suggestions and improvements for the report.

1 INTRODUCTION

1.1 KBS-3 concept

The KBS-3 concept is proposed in Finland and Sweden to be used for geologic disposal of the spent nuclear fuel. Currently, two variants of the KBS-3 method are under consideration, KBS-3V and KBS-3H, the former being the reference design (Figure 1-1). The KBS-3 disposal concept is based on multiple barriers, classified as either main barriers or auxiliary barriers depending on their role and position in the repository system. The main barriers designed to isolate the spent nuclear fuel from the environment are the canister, the buffer, the backfill in the deposition tunnel (KBS-3V) and the host rock. The focus of this review concerns the long-term stability of the bentonite buffer.

1.2 Buffer requirements

The buffer is expected to fill all the void spaces in the disposal hole between canisters and the rock wall (Posiva 2009a), and it should be:

- *plastic* enough to mitigate the effects of small rock movements on the canisters;
- *stiff* enough to support the weight of the canisters and keep the canister in position in the disposal hole in the long term;
- *dense* enough that microbes are metabolically barely active in the buffer and thus do not give rise to unfavourable chemical conditions at the canister surface; and
- *impermeable* enough that the movement of water is insignificant and diffusion is the dominant transport mechanism for corrosive agents present in the groundwater that may degrade the canisters and for any radionuclides released from the canister.

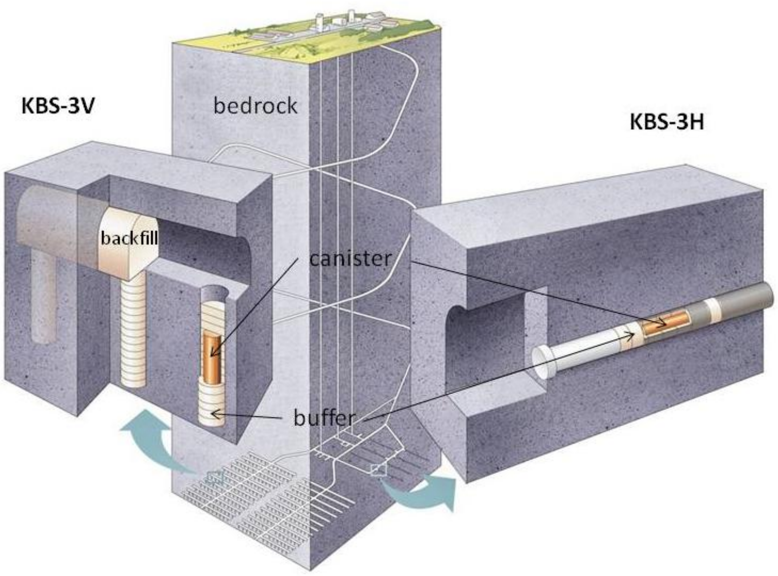


Figure 1-1. *The KBS-3V (left) and KBS-3H (right) alternative realisations of the KBS-3 spent fuel disposal method (modified from Posiva 2009a).*

The buffer should have a sufficient swelling pressure and self-sealing capability, which means that any potential advective pathways for flow and transport that may arise, for example, as a result of piping and erosion, sudden rock movements or the release of gas formed in a damaged canister are rapidly closed. Its low permeability should limit and retard the release of any dissolved radionuclides from the canisters, should any be damaged. Furthermore, it should have a fine pore structure such that microbes and colloids are immobile (filtered) and microbe- or colloid-facilitated radionuclide transport will not occur. (Posiva 2009a.)

The safety concept, safety functions, safety-related guidance to design and preliminary performance targets and target values for the buffer with applicable time windows are presented in TKS-2009 report (Posiva 2009a, Chapter 6). The target values for the buffer based on its safety functions include (Posiva 2009a, Section 6.1.4):

- a hydraulic conductivity $<10^{-12}$ m/s,
- a swelling pressure >2 MPa,
- a buffer temperature which remains below 100°C and
- a range of saturated density 1900 – 2050 kg m^{-3}.

In addition, also technical and initial state requirements are set for the buffer, which frame the design basis (Posiva 2009a, Chapter 5).

Saturation of the buffer to the required saturated density range is the key process to ensure that all the performance targets are met in the buffer. In Figure 1-2 different performance targets and their relation to the saturated density of the buffer are presented.

The initial state of the buffer refers to conditions that prevail after the installation of the buffer and backfill for an individual disposal hole. The target state will be achieved when the safety functions of the buffer are fullfilled. After reaching this quasi-steady state the key safety-relevant physical and chemical characteristics of the barriers (e.g. temperature, buffer density, composition and swelling pressure) are subject to much slower changes than in the early, transient phase (Posiva 2009a) (see also Section 1.3 of this report).

1.3 Expected thermal and chemical conditions at repository depth

The expected evolution of the spent nuclear fuel repository has been assessed in the Evolution reports for KBS-3V (Pastina & Hellä 2006) and KBS-3H (Smith et al. 2007). The evolution of the repository can be divided in three phases:

- **Transient thermal phase** (early evolution), begins with the emplacement of the first canister in the repository and ends with gradually diminishing transient processes (esp. heat dissipation from the spent fuel and saturation of the repository external to the canisters). This may take several thousands of years.
- **Long-term phase** includes subsequent evolution prior to the next major climate change and evolution affected by the next major climate change. The time frames of these depend on the climate changes expected in the long-term. The *Farthest*

future phase will last until the inevitable failure of all canisters that may take several tens of millions of years.

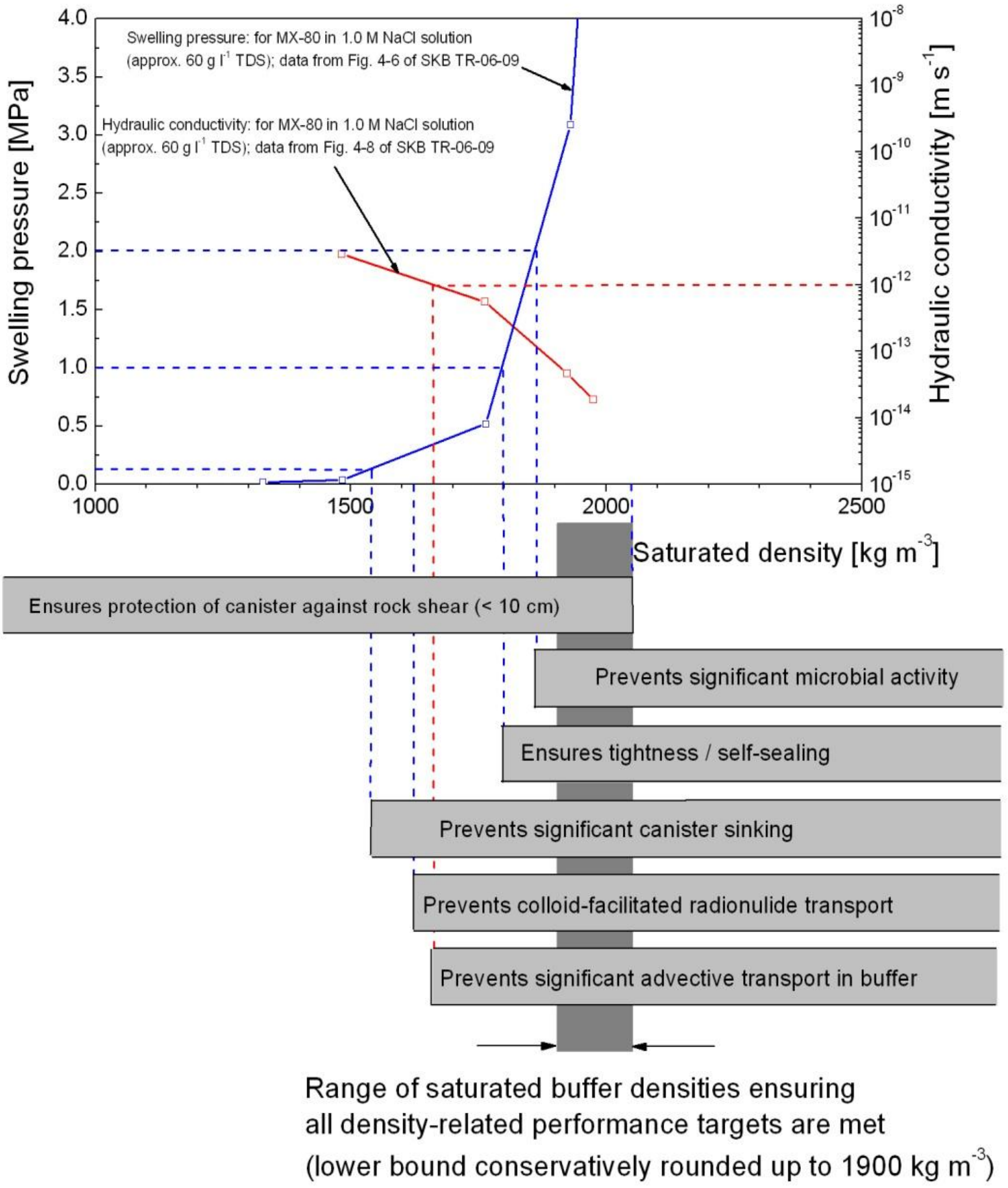


Figure 1-2. *Schematic illustration of the balance between competing requirements on buffer saturated density that results in a performance target range of about 1900 to 2050 kg m*$^{-3}$*. The density criterion is expressed for a salinity of 60 g/l (Posiva 2009a).*

1.3.1 Temperature

The temperature of the bedrock at Olkiluoto at a depth of -400 m (repository maximum depth will be -420 m) is 10.5 °C, and at -500 m is 12-13 °C (e.g. Anttila et al. 1999 and references therein). The maximum temperature at the canister surface in the most central parts of the repository may be 87.5 °C at the highest (unsaturated state) after 20 years of emplacement (Figure 1-3, red line). The maximum temperatures at the edges of the repository will be lower (Figure 1-3, blue line). Based on Figure 1-3 the temperature will decrease at the canister surface (canister/buffer interface) in the central parts of the repository, in case of unsaturated buffer, down to 76.5 °C in 100 years and after 1 000, 5 000 and 10 000 years the expected temperatures will be 54.5 °C, 33 °C and 30.5 °C, respectively. In the repository, bentonite functions as a heat conductive material and the temperature decreases as the distance from canister increases. This forms a temperature gradient within the bentonite buffer during the transient thermal phase. According to the Figure 1-3 the thermal gradient between canister and rock decreases quickly from the initial 20 °C being only ~10 °C after 100 years and only 2 °C after 1 000 years. Temperature decrease rates vary depending on the location within the repository. In 50 000 years the decay heat will be completely dissipated in the geosphere (Pastina & Hellä 2006).

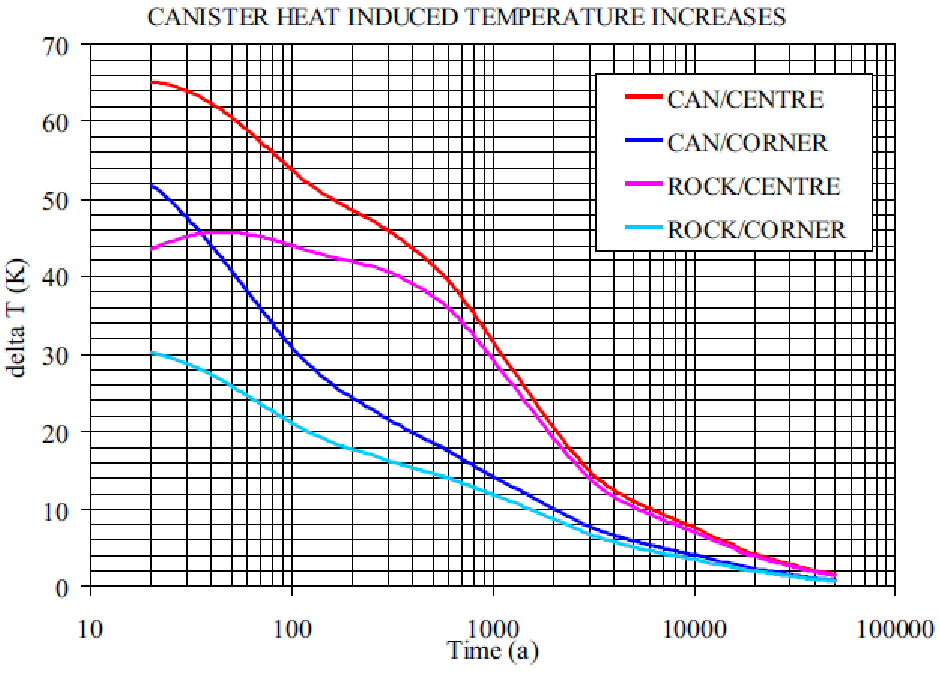


Figure 1-3. *Canister and bentonite buffer temperatures will increase in repository after closure and before the next glaciation, i.e. until 50 000 years AP. To obtain absolute temperatures, the ambient rock temperature (10.5ºC at the depth of -400 m in Olkiluoto) can be added. Temperatures are calculated with average Olkiluoto sitespecific parameters. In this figure, the bentonite is assumed to be fully saturated in all disposal holes after 20 years (if the bentonite is not fully saturated the temperature can be up to 12ºC higher). Can/centre and can/corner indicate a canister near the centre or near the corner of the repository, respectively. Rock/centre and rock/corner indicate rock temperatures near the centre or the edge of the repository, respectively (Pastina & Hellä 2006).*

1.3.2 Hydrogeochemical constraints

Depending on the hydraulic conditions in the host rock surrounding the disposal hole, and the properties of the compacted bentonite, the buffer will either stay unsaturated or it will saturate soon after emplacement. The buffer may remain partially saturated for long period of time. When the buffer is in contact with water, for instance through water conductive fractures or via backfill, the saturation will happen slowly and full saturation will be reached finally during a few years or up to few thousand years (Pastina & Hellä 2006).

The TDS (Total Dissolved Solids) close to the repository level (-420 m) at Olkiluoto is about 10-12 g/l (Posiva 2009b). Groundwater monitoring data until 2007 has been summarized in Site Description 2009 (Posiva 2009b). The groundwater chemistry over the depth range 0-1000 m at Olkiluoto is characterized by a significant range in salinity. Fresh groundwater with low total dissolved solids (TDS 1 g/l; Davis 1964) is found only at shallow depths, in the uppermost tens of metres. Brackish groundwater, with TDS up to 10 g/l dominates at depths, varying from 30 m to 450 m. Fresh and brackish groundwaters are classified into three groups on the basis of characteristic anion contents as presented in Figure 1-4; pH ranges from slightly below 7.5 up to 8.5 depending on the groundwater type (Posiva 2009b). Brackish Cl type has pH values at the higher end of the range, while the saline type shows more varying pH values (see Figure 7-32 in Posiva 2009b).

Löfman et al. (2010) have modelled the salinity evolution at the repository depth during the first 2000 years after emplacement. The results indicate that the expected average salinity will be 10-12 g/l with the minimum of 5 g/l and maximum 25 g/l. Sensitivity cases accounting for uncertainties in the location of deep conducting fractures presented by Löfman et al. (2010) show that up to 70-80 g/l salinities may occur in the repository volume (lowest point 50 m below the deposition tunnels) during the operational phase. Thus, a rather large salinity range has to be taken into account. The disturbances during the operational phase are expected to last a relatively short time and the groundwater conditions should be restored in about 100 years after closure. Another salinity pulse could be possible after the onset of the next glaciation.

An alkaline plume due to cementitious materials used may cause elevated pH in the repository system, but the position and magnitude of such plume remains to be evaluated.

1.3.3 Reference waters

The reference waters given in Grivé et al. (2007) have been used as a basis for comparison made in this review between the waters analysed from natural occurrences of bentonite and the groundwaters at Olkiluoto. Simplified chemical compositions and other relevant parameters for four main groundwater types in Olkiluoto, three types of groundwaters interacted with bentonite and glacial melt water types are presented in Table 1-1 with appropriate referencing. The four Olkiluoto ground water types have been selected to represent groundwater types observed in Posiva Oy’s monitoring programme (see Figure 1-4). These four types should well cover the expected conditions at the site at emplacement and the evolution from post-emplacement until the far future (Pastina & Hellä 2006):

I. A brackish/saline water type that may contain water outside the test section, but still representative for baseline conditions at Olkiluoto in the sampling depth of tens of meters (water sample reference: KR20/465/1).
II. A saline water type (water sample reference: KR10/498/1) describing the baseline conditions at Olkiluoto.
III. The special case of upconing of brine water (water sample reference: KR12/741/1) which is dealt with in the calculations, and
IV. A dilute/brackish water type (water sample reference: KR6/58/1) as a limiting composition of the expected possible variations in future chemical conditions.

Three of the selected groundwaters defined above have been equilibrated with bentonite (Wersin et al. 2007a) referred to as bentonite waters in Table 1-1. These are also used in some of the comparisons in this review. It should be noted that bentonite waters represent modelled composition that is an estimation of the probable porewater composition in saturated bentonite.

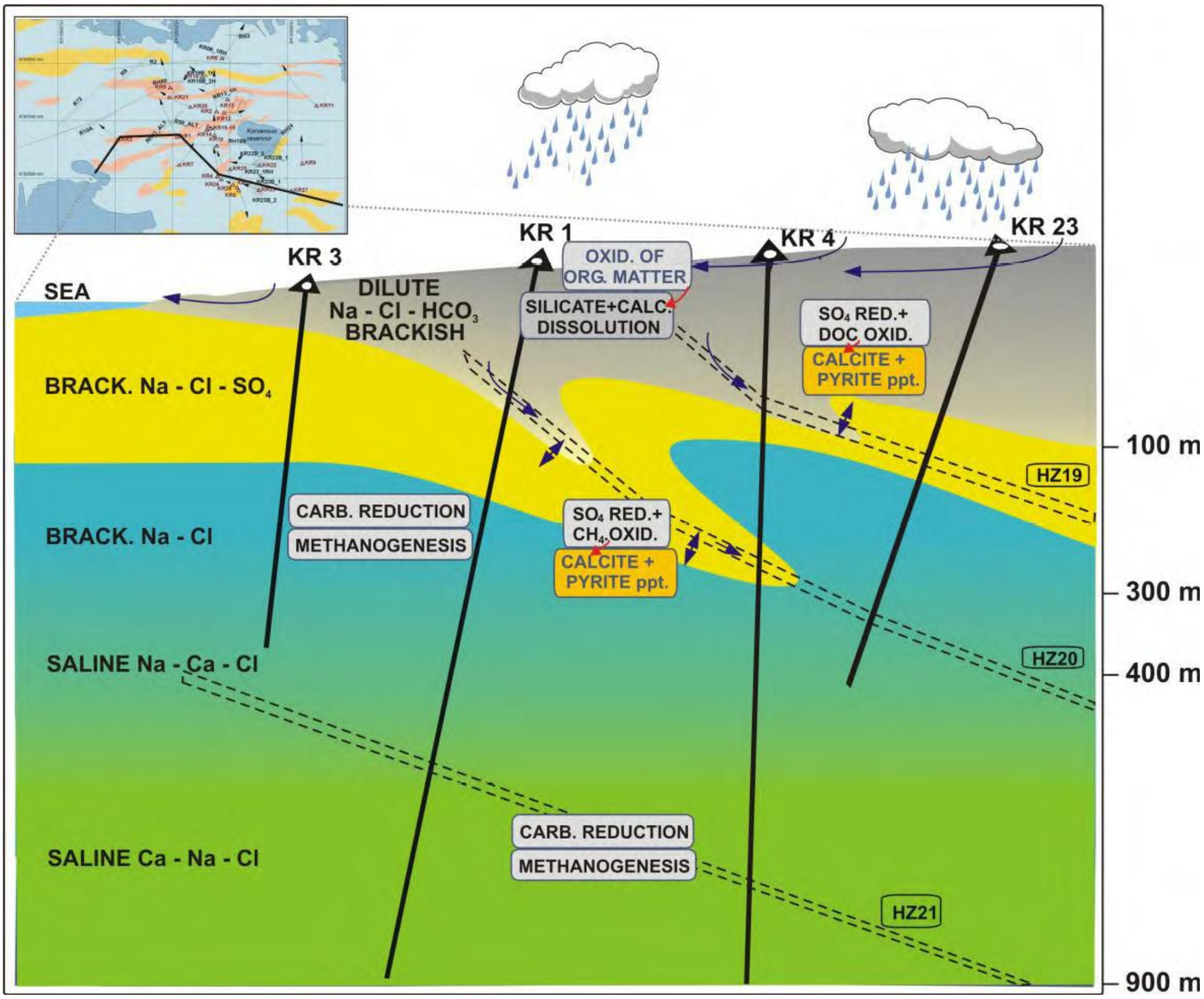


Figure 1-4. *Illustrated hydrogeochemical site model of the baseline groundwater conditions with main water-rock interactions at Olkiluoto. Changes in colour describe alteration in the water type. The hydrogeologically most dominant zones are also shown with indications of groundwater flow (→) and mixing (←→). Rounded rectangles contain the main source and sink reactions controlling pH and redox conditions. Enhanced chemical reactions dominate in the infiltration zone at shallow depths, and at the interface between the Na-Cl-*SO_4 *and Na-Cl groundwater types. Note that the illustration depicts hydrogeochemical conditions in the variably conductive fracture system, not in the diffusion-dominated pore space inside the rock blocks. (Posiva 2009b.)*

Water composition resulting from the infiltration of glacial meltwater to depth is assumed to be rather diluted. Two types of glacial meltwater have been defined by Grivé et al. (2007). These waters are: the glacial meltwater used by Pitkänen et al. (2004) and the glacial meltwater (ice melting groundwater) used in SR-Can (see Duro et al. 2006) (see Table 1-1 for composition). The former is the estimated Quaternary glacial melt water composition expected from ice melting processes. For Olkiluoto, pyrite and/or pyrrhotite are very common in fractures and thus pyrite dissolution due to oxygen present in the glacial meltwater is taken into account. This will result in a low pH value (pH 5.8). No dissolved oxygen is though expected to be transported to the repository level. The second type of meltwater corresponds to the composition of a discharging dilute granitic groundwater sampled from the Migration Shear Zone at the Grimsel Test Site (GTS) in Switzerland, as analogue for the diluted groundwater composition expected from ice melting processes. This water presents a relatively high pH (9.6) due to the interaction of very diluted water with the granitic minerals, as well as a low redox potential which is the result of redox buffering processes in the rock. This high pH glacial meltwater is also close to the expected slightly alkaline conditions buffered by bentonite.

1.4 Background and aim of this study

Identified research issues related to the processes having an impact on buffer evolution have been presented in the TKS-2009 report (Posiva 2009a) in Section 6.5.4.2. This review should contribute to the issues related to mineral transformations, both montmorillonite transformation including cementation as well as montmorillonite-groundwater interactions.

The aim of this literature study is to:

- evaluate the long-term thermodynamic stability of the bentonite buffer in the evolving chemical, thermal and hydrological conditions at Olkiluoto;
- review the relevant experimental data; and
- provide a review on natural occurrences of bentonite (and other swelling clays) that could serve as analogues for the long-term bentonite stability in the expected repository conditions, especially focussing on mineral transformations due to thermal effects including cementation.

Thermal stability is a short-term issue concerning the thermal phase (see Section 1.3), although depending on the spatial extent, this may affect the behaviour of bentonite in the long term. Mineralogical changes in bentonite may start due to thermal gradient already in nearly-saturated conditions due to THC (Thermo-Hydro-Chemical) processes; even if in the very beginning the water is present as vapour (see also Sections 3.2.2 and 3.3.1 in this report). Cementation is one of the first processes that may occur, which may modify the rheological and hydraulic properties of bentonite. Experimental and modelling studies have been planned to better understand the conditions under which the process occurs and to assess the consequences of the process (see Chapter 6 in Posiva 2009a).

Mineralogical changes due to the interaction of bentonite with cement leachates are being assessed in the BENTO programme (e.g. Lehikoinen 2009). In the long term the chemical stability of the buffer will be affected by changing groundwater composition. After the thermal phase and over the long term, the processes affecting bentonite alteration are generally very slow. The major change to occur independent from the thermal effects is the transformation of Na- to Ca-bentonite (see Section 3.4). One aim of this study is to evaluate the rate, extent and the effects of this process on the performance targets of the bentonite buffer by comparing the properties of the two bentonite types (Section 3.4.3).

Table 1-1. *Reference waters used in this review. Concentrations in mmol/l (mM).*

Water type	Abreviation	O_2	Cl(-I)	Na(I)	Ca(II)	Mg(II)	K(I)	SiO_2	pH	Alkalinity	Sample	Reference
Olkiluoto dilute brackish	ODB		10,4	9,8	2,1	1,1	0,2	0,41	7,6	2,79	KR6/58/1	Grive et al. 2007
Olkiluoto brackish saline	OBS		180,5	114,8	32,4	2,6	0,28	0,36	7,4	0,66	KR20/465/1	Grive et al. 2007
Olkiluoto saline	OS		380,8	210	89,1	1,6	0,36	0,28	8	0,11	KR10/498/1	Grive et al. 2007
Olkiluoto brine	OB		863,2	360,9	254,5	1,5	0,49	0,21	8,2	0,12	KR12/741/1	Grive et al. 2007
Bentonite brackish saline	BBS		185	271	20,8	6,32	0,85		7,28	0,52		Wersin et al. 2007a
Bentonite saline	BS		386	384	42,9	10,9	1,24		7,66	0,4		Wersin et al. 2007a
Bentonite dilute brackish	BDB		15,1	167	10,4	1,1	0,53		7,39	2,5		Wersin et al. 2007a
Glacial meltwater	GM	0,22	0,02	0,0065	0,0032	0,0041	0,0038	0,00017	5,8			Pitkänen et al. 2004
Ice melting	IM		0,16	0,69	0,14	0,00062	0,005	0,25	9,6	0,45		Duro et al. 2006

2 BASIC PROPERTIES OF BENTONITE

2.1 Bentonite types and mineralogy

Bentonites are altered volcanic tuffaceous rocks. They are widely available as commercial products. Bentonites are mainly composed of smectites, most commonly montmorillonite, which contributes to the swelling ability of bentonite.

All smectites, di- and trioctaherdal, and vermiculites are swelling clays but the swelling ability depends on the layer charge (see Section 2.2.3) and also on the exchangeable cation composition as discussed later in this review. Montmorillonite, beidellite, nontronite and volkonskoite are dioctahedral smectites. The trioctahedral group is composed of hectorite, saponite, sauconite, stevensite and swinefordite.

The composition of bentonite depends on the conditions it was formed. Usually, bentonites are formed by the alteration of rhyolitic-to-dacitic volcanic ash or tuff, either in situ or after erosion and re-sedimentation. According to e.g. Grim (1968) ash alteration is very rapid and weathering plays no role in it, thus, a decisive factor for smectite formation would not be the chemistry of the ash but the presence of water (bentonites form in lakes, lagoons, shallow sea areas). In addition to the processes mentioned above, diagenesis needs to be considered. There are several factors that support the formation of bentonite by burial: 1) transformation progressivity is measurable by the variation in the ratio of glass and clay amounts, 2) isotopic equilibration of hydrated glass and clays with resident waters, and 3) presence of CT (cristobalite/tridymite) opal in the adjacent sedimentary formations that could be related to the migration of silica by chemical diffusion from the volcanic glass dissolution zones. The quasimonomineral character of bentonites seems to be better explained by diagenesis than by sudden alteration (Meunier 2005). The volcanic origin is supported by the existence of high temperature minerals such as ß-quartz, biotite, sanidine, zircon, apatite, ilmenite and magnetite. Also volcanic glass shards may exist in incompletely smectitized bentonites (Christidis & Huff 2009).

Diagenetic bentonites are commonly used as reference stratigraphic layers and their thickness ranges from a few millimetres (esp. diagenetic origin) to about one metre (rarely more). Economically exploited deposits are often thicker, up to tens of metres e.g. Milos Island bentonite (Christidis et al. 1995) and Wyoming bentonite (Elzea & Murray 1990), the source deposits of commercial products Deponit Ca-N and MX-80, respectively. In general, the deposits younger than Jurassic (<144 Ma) are usually of economic importance (no extensive illitisation occur) with emphasis on those of the Cenozoic era (<66 Ma). However, bentonites are found in sedimentary environments as old as Ordovician in age (505-438 Ma), even when the surrounding shales are composed of mainly I/S minerals with high illite content (Velde 1985). Palaeozoic (often Ordovician) bentonites differ mineralogically from each other also depending on the contacting rocks, bed thickness, and geological history. In thick (>1 m) bentonite layers a clear zonation is observed (illite rims at the edges and high retained smectite content in between) (Huff & Türkmenoglu 1981; Altaner et al. 1984; Brusewitz 1986). In thinner layers (a few cm) mineralogical composition is homogenous and no zonation is observed (Meunier 2005).

According to Christidis & Huff (2009) bentonites (of economic importance) may form in three different ways:

- diagenetic alteration of volcanic glass,
- hydrothermal alteration of volcanic glass, or
- formation of smectite-rich sediments in salt lakes and sabkha (salt flat) environments usually from dissolution of detrital smectites (often associated with sepiolite and/or palygorskite).

To be able to form smectites instead of zeolites by alteration of volcanic glass, leaching of alkali elements and high (Mg^{2+})/(H^+) ratio are required (Senkay et al. 1984, Christidis 1998). Also large water/rock ratio in an open system is essential (Christidis 1998).

Good examples of diagenetic formation are e.g. deposits in Wyoming (see Section 4.10), Montana and Texas (USA), the fullers earth (England) and bentonites from Bavaria (Germany). Bentonite from Milos Island in Greece and from Almeria (FEBEX) in Spain represents hydrothermally altered formations (see Section 4.11).

Formation temperatures of smectites have also bee studied from several bentonite deposits e.g: Leone et al. 1983 (~ 40 ºC, see Section 4.4), Linares 1985 (50 ºC, see Section 4.4.1) Christidis et al. 1995 (< 90 ºC, see Section 4.11), Kolařiková & Hanus 2008 (30-90 ºC, see Section 4.4).

Bentonites occur in nature at similar densities as in the deep repository, although variation occurs depending on the consolidation state, drying/wetting cycles etc. Compacted bentonite will have the saturated density between 1900 – 2050 kg/m^3 while bentonites is natural conditions have densities around 1850 – 2200 kg/m^3 (e.g. Pusch et al. 1998, Pusch & Karnland 1988a, Pusch et al. 1987, Calarge et al. 2006). It should be noted that the given density range of natural bentonites is derived from very few occurrences and obviously the densities may vary more depending of the geological setting of the formation. Natural bentonites are considered as closed systems, in which the chemical potential of all elements in solution are controlled by the rock composition (Meunier 2005).

2.2 Buffer and buffer properties

Posiva’s current reference buffer material is Na-bentonite MX-80 (Wyoming, USA, see Section 4.10) and the alternative material is Ca-bentonite Deponit Ca-N (Milos, Greece, see Section 4.11). FEBEX is a Ca-bentonite (Almeria, Spain) that has been extensively studied within the NF-PRO project and provides data for comparison.

The suitability of MX-80 bentonite, containing mostly Na-montmorillonite, to be used as a buffer material in the KBS-3 type repository concept has been studied for some 30 years. This material was originally selected because of its general properties that fulfilled criteria given for the buffer at that time. Other smectite rich clays have been studied by Pusch (1999a), who has compared MX-80 to possible alternative materials that would be available in large quantities allowing their use in the repository. These materials included saponite, mixed-layer smectite, kaolinite and palygorskite. Pusch

(1999a) reported that among smectites, nontronite is too sparsely available and beidellite is too easily converted to illite to be used as a buffer material. The general conclusion was that only bentonites with montmorillonite and magnesium rich saponite would qualify.

In this chapter the known properties of MX-80 are listed, but also the properties of other bentonites are given for comparison.

2.2.1 Mineralogical and chemical composition

A general structure of a montmorillonite is given in Figure 2-1, showing the 2:1 structure of one montmorillonite sheet and the interlayer space that host the exchangeable cations (varying amounts of K^+, Na^+, Ca^{2+}, Mg^{2+}). Montmorillonite is a member of pyrophyllite – mica series as presented in Figure 2-2 that shows also the compositional positions of MX-80 and Deponit Ca-N in the smectite field.

When discussing the long-term stability of bentonite the following issues have to be taken into account to understand the full context:

- The properties of bentonite are based on its content of swelling clays i.e. smectites, and therefore the long-term stability of bentonite depends mostly on the stability of the smectites present.
- Different bentonites have distinct mineralogical compositions, concerning both the smectite mineralogy and the amount and types of accessory minerals, which may affect the long-term stability.
- Bentonites are natural products and compositional variation within a deposit may lead to variation in the end-product i.e. commercial bentonite.
- Manufacturing process that may include drying, grinding, chemical purification/ activation processes and compaction has an effect on the initial properties of the buffer material, which may differ from the natural material. Commonly manufacturing processes are designed to homogenise the material, which is an advantage in evaluation of the buffer stability.

The smectite phase in the reference bentonite MX-80 is Na-rich montmorillonite that has the structural formula of

$(Si_{7.86}\,Al_{0.14})\,(Al_{3.11}\,Fe^{3+}_{0.37}\,Mg_{0.50}\,Ti_{0.01})\,O_{20}(OH)_4,\,Na_{0.47}\,Ca_{0.05}\,Mg_{0.02}\,K_{0.01}$

And the other alternative material Deponit Ca-N has the structural formula of

$(Si_{7.74}\,Al_{0.26})\,(Al_{2.90}\,Fe^{3+}_{0.44}\,Mg_{0.58}\,Ti_{0.08})\,O_{20}(OH)_4,\,Na_{0.18}\,Ca_{0.17}\,Mg_{0.11}\,K_{0.02}$

In Table 2-1 the mineralogical composition of the materials MX-80, Deponit Ca-N, and FEBEX are presented. The data for MX-80 and Deponit Ca-N by Karnland et al. (2006) represent mean values calculated from all Siroquant determinations from XRD-diffractograms. For comparison the data presented by Knechtel & Patterson (1962) is given for Clay Spur bentonite (source of MX-80). Additional values for MX-80 and Deponit Ca-N are from SKB (2006). The data for the FEBEX bentonite is from ENRESA (2002).

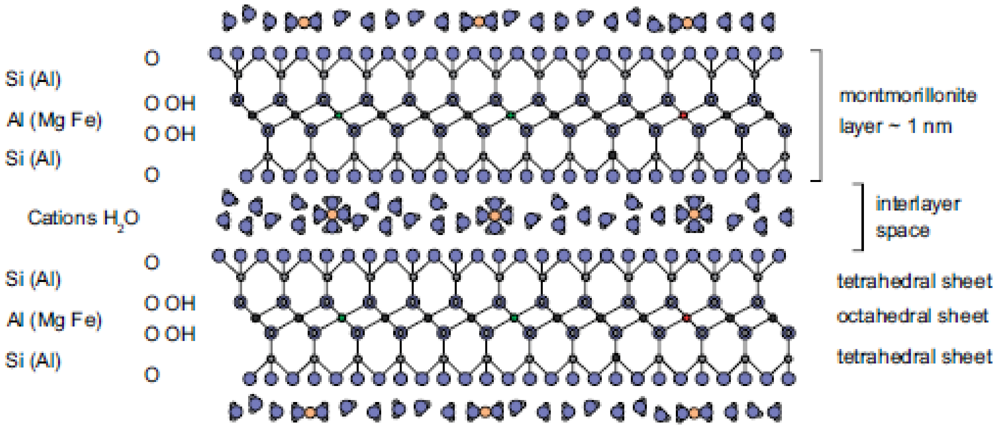


Figure 2-1. *Edge view cartoon of two montmorillonite layers with interlayer cations and water molecules (Karnland & Birgersson 2006).*

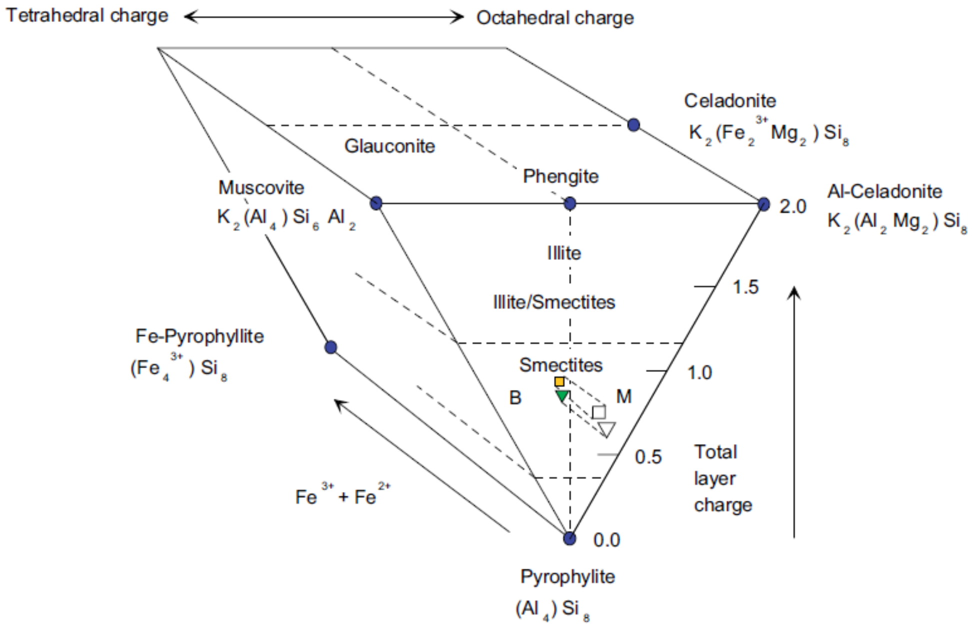


Figure 2-2. *Ideal end-member minerals in the pyrophyllite – mica series with potassium as charge compensating cation, and approximate compositional ranges for illite and smectite (modified from Newman & Brown 1987). B denotes beidellite, M denotes montmorillonite. The compositional positions of the montmorillonite minerals in the SR-CAN reference bentonite materials are indicated by a triangle (MX-80) and by a square (Deponit Ca-N). All formulas are related to the basic $O_{20}(OH)_4$ cell (Karnland & Birgersson 2006.)*

Table 2-1. *Mineralogical composition of different buffer materials (wt%). Uncertainty given in brackets. For FEBEX montmorillonite and illite % is given in brackets. See text for further details.*

Phase	MX-80	MX-80	Clay Spur bentonite	Deponit Can	Deponit Can	FEBEX
Montmorillonite	**83,5**	87 (3)	85-90	**81,4**	81 (3)	**92,0 * (79-83)**
Illite	0,7		0,0	**4,6**		**(9-13)**
Kaolin						
Anatase	0,2			0,1		
Biotite			0-5 (incl. F-spar)			
Calcite	0,2	0-1 (1)		**5,3**	10 (1)	traces
Cristobalite	0,4	2 (0,5)		0,6	1 (0,5)	**2,0**
Dolomite				**1,3**	3 (1)	
Goethite	0,2			**1,5**		
Gypsum	0,9	0,7 (0,2)		0,4	1,8 (anhydrite) (0,2)	
Hematite	0,1			0,2		
Lepidocrocite	0,7			0,3		
Maghemite						
Magnesite						
Magnetite	0,1			0,1		
Microcline	0,8			0,2		
Muscovite	**2,8**	4 (mica) (1)		**1,4**		
Orthoclase	0,7				2 (1)	traces
Plagioclase	**2,9**	3 (1)		0,5		**2,0**
Pyrite	0,6	0,07 (0,05)		**1,1**	0,5	
Quartz	**2,8**	3 (0,5)	5-10	0,4	1	**2,0**
Rutile				0,3		
Siderite				0,3		
Tridymite	**1,9**			0,3		traces
Vaterite						
Reference	Karnland et al. 2006	SKB 2006	Knechtel & Patterson 1962	Karnland et al. 2006	SKB 2006	ENRESA 2002

*)Other minor minerals present, identified by scanning electron microscopy, are micas (sericite, biotite, chloritised biotite), pyroxenes, amphiboles, pyrite, oxides (illmenite, magnetite) and phosphates (apatite, xenotime, monacite). All these come from the original volcanic rock and overall represent a proportion more of less than 1 percent. Sulphates, halite, organic carbon and amorphous phases also appear, without their together exceeding 1 percent.

The chemical composition of the buffer materials as oxides is presented in Table 2-2.

All buffer materials contain smectite (montmorillonite) ~80 % or more. Illite is found also in all materials, but in varying small amounts. MX-80 type bentonites have around 1 % of illite, whereas Deponit Ca-N has an illite content of ~5 % and FEBEX ~9-13 %. Karnland & Birgersson (2006) have studied illite content in various materials, including MX-80 and Deponit Ca-N, using several different methods i.e. Siroquant analysis, fixed potassium method and ICP/AES-analysis, all of which show consistent results.

Cation exchange capacity (CEC) of bentonites is an important buffer property and it varies between alternative materials. CEC values and percentages of individual cations for MX-80 and Deponit Ca-N are given in Table 2-3.

Table 2-2. *Chemical composition of different buffer materials. (Bentonite S-2 is another batch of the same bentonite as FEBEX)*

Buffer material	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**total carbon**	**total sulfur**	**Reference**
MX-80	57,3	18,5	3,6	2,3	1,3	2,0	0,5	0,2	0,3	0,3	Karnland et al. 2006
Deponit-Can	48,3	15,7	4,6	2,9	5,4	0,7	0,8	0,7	1,0	0,7	Karnland et al. 2006
FEBEX	58,7	18,0	3,1	4,2	1,8	1,3	1,0	0,2	0,6	0,2	Enresa 2000, CIEMAT analyses
Bentonite S-2	57,3	19,6	3,9	4,7	2,9	1,9	1,4	0,3	0,4	0,1	Enresa 2000, CIEMAT analyses

Table 2-3. *CEC and exchangeable cations determined for buffer materials (meq/g) (Karnland et al. 2006).*

Phase	MX-80	Deponit Can
CEC	0.71-0.77	0.81
Na (%)	83	24
K (%)	2	2
Ca (%)	9	45
Mg (%)	6	29

2.2.2 Porosity, particle size and orientation

The porosity of the buffer depends on the density of the bentonite material. The generalized microstructure of MX-80 is presented in Figure 2-3. Porewater can be located between individual smectite laths or in the interlayer space that are called extra layer water and interlayer water, respectively (e.g. Wersin 2002).

Smectite crystallites are lathlike particles that stack to form aggregates. The thickness of an individual mineral layer is around 1 nm and the extension in the other two directions is often several hundred nanometers (see Figure 2-1). External porosity depends on the bonding of the particles. Usually the bonds are either edge-to-edge or edge-to-face (Figure 2-3b). In suspension, smectite crystallites deform in flexible manner and show alveolar structure (Figure 2-3c; Meunier 2005). In the KBS-3V Evolution report (Pastina & Hellä 2006) it has been explained that the amount of water involved in the geochemical processes in bentonite buffer corresponds to the water in external pores and that internal water responds to changing groundwater conditions only by cation exchange. However, this subject has been under debate lately (e.g. Karnland & Birgesson 2009), which is beyond the scope of this work.

It has been suggested that hydration/dehydration cycles may affect the textural behaviour of compacted MX-80 (physical pressures from 1820 to 2080 kg/m^3) in form of aggregate cracking during hydration (Montes–H et al. 2005). However, it seems that the micro porosity (<2 nm) will remain intact. Whether this can cause decrease in the self-sealing ability is unknown. The effects of hydration/dehydration (also referred to as wetting/drying i.e. W/D cycles) may enhance alteration of smectites in some cases; this has been discussed in Section 3.2.1.

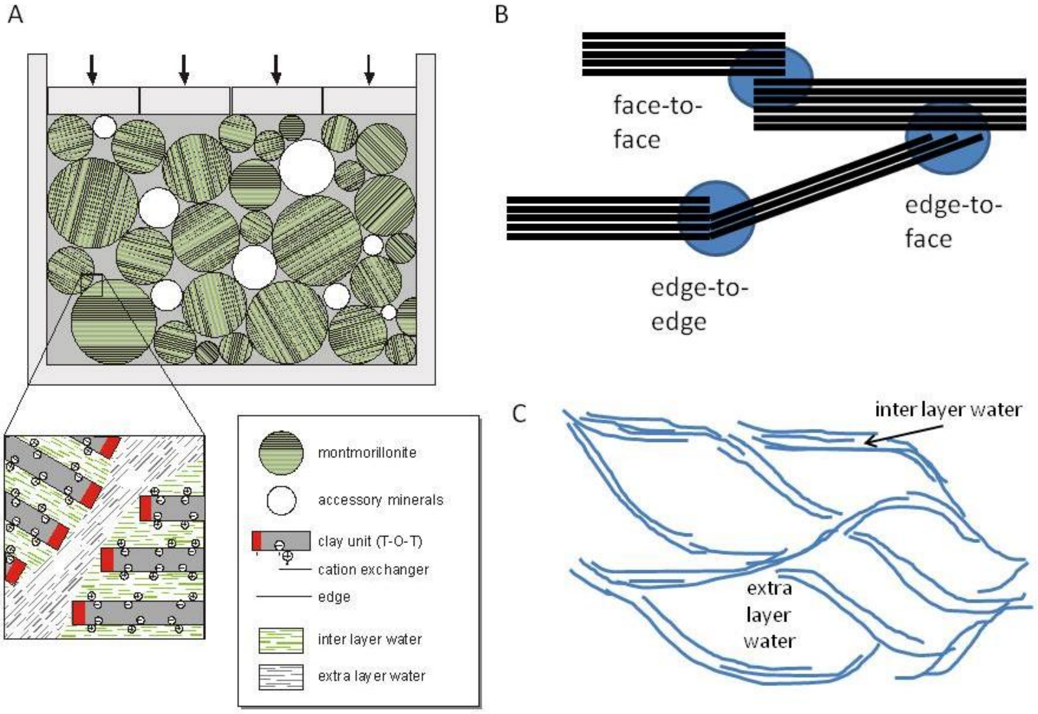


Figure 2-3. *Bentonite microstructure A) Generalized microstructure of MX-80 (Wersin 2002). Upon contact, the various chemical components of bentonite tend to equilibrate with those in groundwater in the large pores (extra layer water), in the interlamellar water (inter layer water), in the electrical double-layers and on the surfaces. The water in the large pores (extra layer water) is where the porewater chemistry is manifested. B) Particle contact types (modified from Meunier 2005). C) Alveolar structure (modified from Meunier 2005).*

2.2.3 Swelling capacity and swelling pressure

The swelling properties of the montmorillonite are based on the magnitude and the position of the layer charge (negative layer charge caused by the isomorphic substitution of Si for Al in tetrahedral sheet and Al for Mg and Fe in octahedral sheet), but also on the type of compensating cations in the interlayer space that allows the water molecules to be absorbed in the interlayer spaces. In natural bentonite the interlayer cations are rarely composed of one element alone, but rather are a mixture of both monovalent and divalent ions. Hence, natural sodium bentonite may have a major portion of Na as charge compensating cations, but other cations may be present as well in rather large quantities. A different interlayer cation composition of the MX-80 and Deponit Ca-N is the main difference affecting their swelling behaviour along with the total smectite content of the material (see Table 2-1). Swelling pressure of MX-80 as a function of dry density in 1.0 M NaCl solution is given in Figure 1-2.

The maximum hydration state of montmorillonite depends on the nature of the cation saturating the interlayer space (e.g. Meunier 2005). In the fixed volume space, such as a disposal hole, the water intake in interlayer space will reduce the initially larger external pore volume and the uptake is forced to stop when the total available pore volume is filled with water (i.e. full saturation). Water will then move within the material in order to equilibrate the interlayer ion concentration in the system.

In compacted bentonite the swelling pressure is mostly generated by crystalline swelling and double layer swelling after full saturation (Pusch 2002).

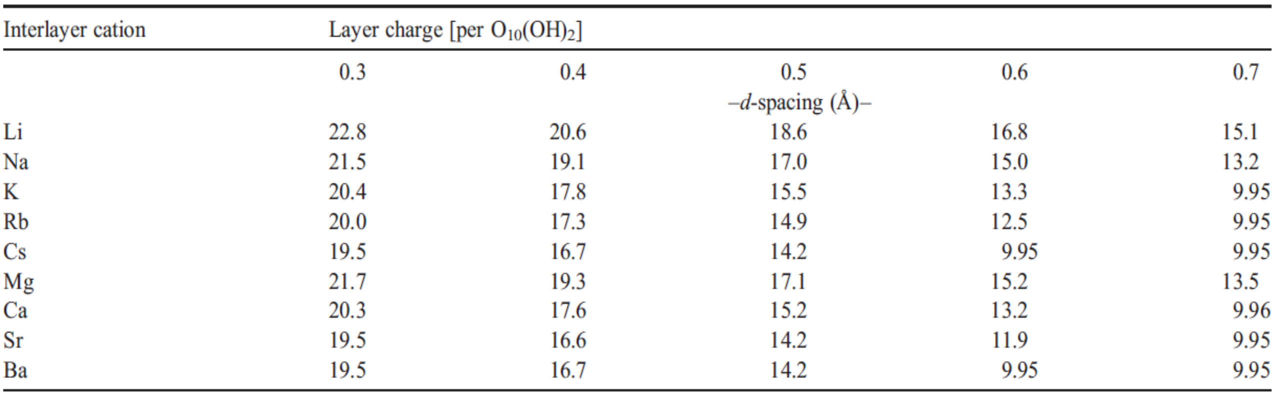
The effect of different layer charges of compensating cations on the basal spacings of expanding 2:1 phyllosilicates are given in Table 2-4. These calculated values are consistent with experimental evidence (MacEwan & Wilson 1980) and may be used as a general guideline for smectite comparison. For reference, smectites have the hydrated net layer charge per formula unit of ~0.2-0.6, while vermiculites have the corresponding range of ~0.6-0.9 (Martin et al. 1991). As a general rule, an increase in layer charge results in decreased crystalline swelling (smaller d-spacings) and increases in both the size and stability of smectite quasicrystals (Laird 2006).

2.2.4 Density and the effect of compaction on bentonite properties

Bentonite used in the buffer will be compacted to the desired dry density. Dry density will be adjusted so that the required saturated density will be achieved (~2000 kg/m^3) (see Figure 1-2) (Posiva 2009a, Chapter 5). Initial dry density for the buffer (KBS-3V block) is given in Table 2-5.

Very little information is found on the effects of the processing and compaction of bentonite material and how does the final product differ from the natural material, e.g. density, particle size, orientation. The obvious difference is the amount of bentonite in the disposal hole compared to natural occurrences. Otherwise the material properties are expected to be similar to those of natural bentonite.

Table 2-4. *Effect of layer charge and exchangeable cation on basal spacings of expanding 2:1 phyllosilicates (Laird 2006).*



Interlayer cation	Layer charge [per $O_{10}(OH)_2$]				
	0.3	0.4	0.5	0.6	0.7
			–*d*-spacing (Å)–		
Li	22.8	20.6	18.6	16.8	15.1
Na	21.5	19.1	17.0	15.0	13.2
K	20.4	17.8	15.5	13.3	9.95
Rb	20.0	17.3	14.9	12.5	9.95
Cs	19.5	16.7	14.2	9.95	9.95
Mg	21.7	19.3	17.1	15.2	13.5
Ca	20.3	17.6	15.2	13.2	9.96
Sr	19.5	16.6	14.2	11.9	9.95
Ba	19.5	16.7	14.2	9.95	9.95

2.2.5 Hydraulic conductivity

Hydraulic conductivity is dependent on the swelling pressure/dry density, but also on void ratio, groundwater salinity and temperature. In the expected densities in the disposal hole the buffer is expected to maintain the hydraulic conductivity required (Figure 1-2). High density and low electrolyte content of the clay mineral give rise to a very low hydraulic conductivity for Na-smectite. The conductivity of Ca-type is slightly higher because of the dense particle arrangement. Hydraulic conductivity changes related to cation exchange are discussed in Section 3.4.3.

2.2.6 Thermal conductivity

The thermal conductivity of bentonite increases almost linearly with increasing dry density and water content. At nearly full saturation and at a dry density of 1 600 kg/m^3 the thermal conductivity is 1.35 W/mK (Börgesson et al. 1994).

2.2.7 Rheological properties

Stress- and time-dependent strain for clay materials is described by several parameters:

- **Stress-strain behaviour** at shearing (shear strain properties)
- S**hear strength** (maximum shear stress that material can resist under defined boundary conditions)
- **Creep properties** (change in strain with time at constant stress)

Shear strength depends on the microstructure of montmorillonite. Shear strength q can be expressed in a generalized manner as a function of the mean effective stress p (Equation 1-1):

$$q=ap^b \tag{1-1}$$

Where $a=q$ for p=1kPa; and b is the slope of log p/log q curve (see Figure 2-4). The parameter a is much higher for coarser grained clays than fine grained clays. Börgesson & Hernelind (1999) have performed triaxial tests for bentonite buffer materials (Figure 2-4). The illustration shows twice as high a values for Ca^{2+}-smectite than for Na^+-smectite. Also salt water strengthens the smectite by coagulation (Pusch 2006).

Creep occurs when critical strain has been reached and when comprehensive breakdown of the microstructure takes place. Creep occurring in the buffer clay (MX-80) has been modeled by Pusch (1999b) and the results show that the creep settlement occurring in the disposal hole will be very small and it is insignificant for the integrity of the buffer.

Plasticity and hydration capacity are closely related rheological properties. As Na-montmorillonite has the largest hydration properties of smectites (capability of taking 3 molecules within the interlamellar space) it also has the highest plasticity. Also ductility is increased with plasticity (Pusch et al. 1995).

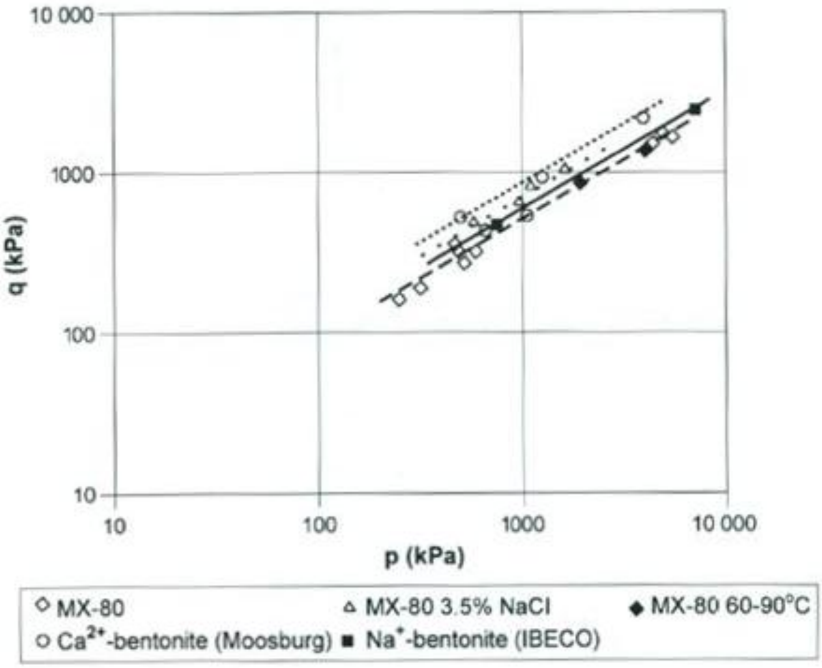


Figure 2-4. *Triaxial tests on bentonite as buffer materials (Börgesson & Hernelind 1999). q = shear stress, p = average effective normal stress.*

2.2.8 Homogeneity

Even though bentonite deposits are often described as homogenous and monomineralic, the bentonite material itself is neither homogenous nor monomineralic *sensu stricto*. Deposits are often composed of bentonite layers that may represent different volcanic events and thus may have differences. These variations may be diminished by the manufacturer by using mixing or other homogenization processes. Variations occur especially at micro scale. Density of the unprocessed bentonite material may vary extensively and the smectite itself may be present in different forms, such as gel or aggregates, which have an effect on the rheological properties of bentonite (Pusch et al. 1999). This inhomogeneity in bentonite is illustrated in Figure 2-5.

Quality demands of many commercial bentonite products do not usually meet those needed in quality control for the bentonite used in the deep repository especially concerning accessory minerals. However some attempts have been made to evaluate the homogeneity of commercial materials e.g. by Karnland et al. (2006) and Ahonen et al. (2008).

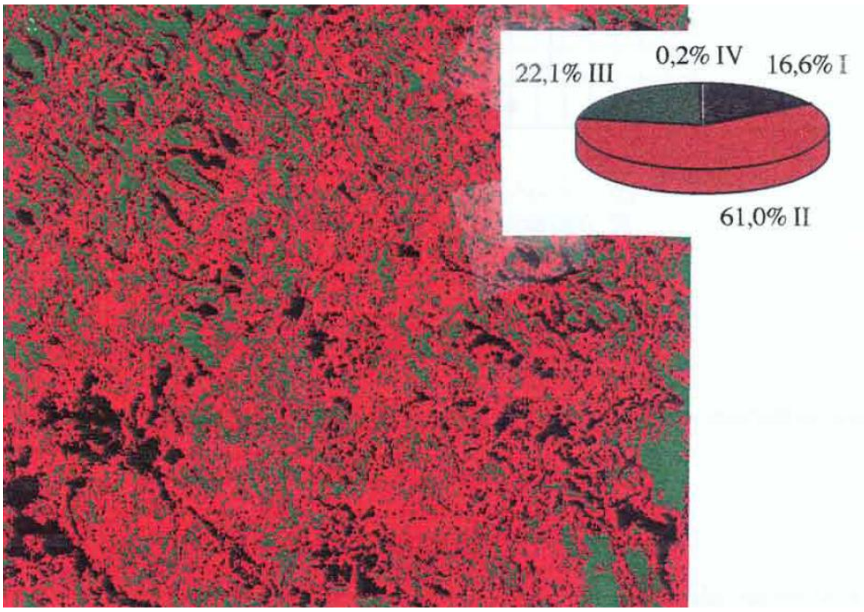


Figure 2-5. *Transmission electron micrograph of MX-80 clay with a bulk density of 2 000 kg/m3. The micrograph has been digitalized to make density variations obvious: Black: Most dense parts (exceeding 2 000 kg/m^3), Red: Second densest parts (about 2000 kg/m^3), Green: Medium dense parts (1 500-2 000 kg/m^3), and White: Soft gels or open voids (<1 500 kg/m^3) (Pusch et al. 1999).*

2.2.9 Initial state

The buffer bentonite will be compacted to a certain density and the water content will be adjusted. The initial physical properties of the bentonite blocks to be used in the buffer are listed in Table 2-5 (Posiva 2009a).

Table 2-5. *Initial state of the buffer in the reference solution (Chapter 5 in Posiva 2009a).*

Buffer property	**Value**
Gap between buffer blocks and rock	25 mm
Gap between buffer blocks and canister	10 mm
Water content of the blocks calculated from dry material	16,0 %
Dry density of the blocks	1810 kg/m^3
Density of saturated blocks	2130 kg/m^3
Average dry density of the buffer	1610 kg/m^3
Average density of saturated buffer	2000 kg/m^3

2.3 Buffer chemistry and evolution

The chemical evolution of the buffer is affected by several factors: groundwater chemistry, porewater chemistry, canister heat induced temperature, possible interaction with degradation products of structural and stray materials, possible colloid release/chemical erosion, and microbial processes (Pastina & Hellä 2006).

The evolution of porewater chemistry will depend on the initial porewater composition at the time of emplacement and the changing temperature and groundwater conditions. In the long-term, the concentration differences between ground- and porewater tend to equilibrate by diffusion. The pH value of porewater depends partly on the salinity of the diffusing groundwater.

At saturated state, the buffer will undergo fast chemical processes in the water trapped inside its pores and slow processes affecting its mineral structure (chemical alteration/ erosion) (Pastina & Hellä 2006). Fast (within minutes to days) chemical reactions in bentonite are reversible and may take place already in operational phase e.g. complexation in solution, surface reactions at clay surfaces, dissolution/precipitation of accessory minerals (carbonates, oxides, sulphates) and dissolution of soluble salts. Slower reactions with longer equilibration times that are especially relevant to repository conditions affecting the porewater chemistry are ion exchange reactions of calcium (Ca^{2+}) for sodium (Na^{+}), which will be discussed in Section 3.4. Kinetically controlled alteration reactions are even slower, if occurring at all. Mineral alteration is discussed in Chapter 3.

The chemical changes occurring in the external pores of bentonite are illustrated in Figure 2-6 (Luukkonen 2004).

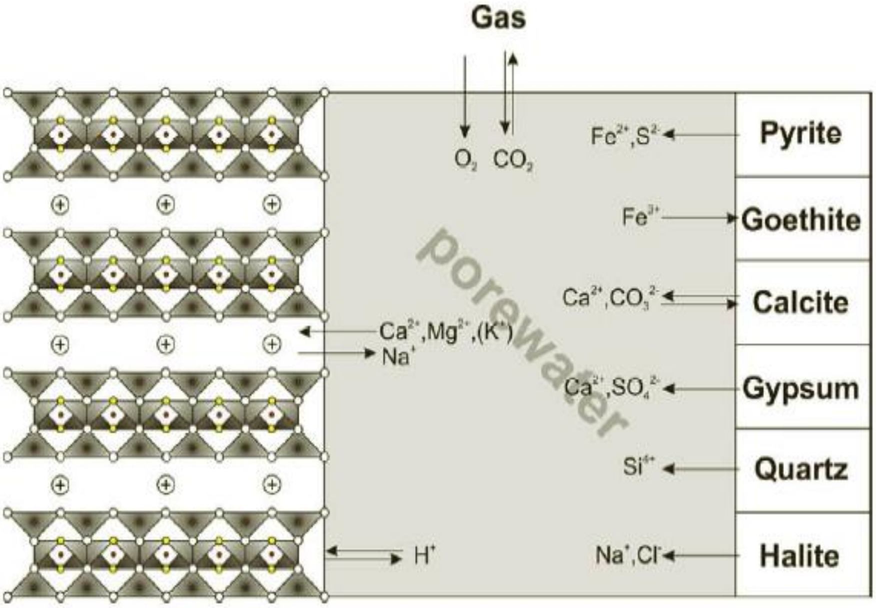


Figure 2-6. *Schematic illustration of geochemical equilibrium processes used in modelling by Luukkonen (2004). The montmorillonite layering and interlayer sites are seen on the left, the mineral equilibria on the right and the entrapped gases on the top.*

Attempts to reveal the chemical composition of the bentonite porewater have been made by Fernández et al. (2001) for FEBEX and Bradbury & Baeyens (2003), Muurinen (2003, 2006), Muurinen & Lehikoinen (1999) for MX-80, among others. Porewater compositions for compacted MX-80 have been calculated by Bradbury & Baeyens (2003) for a range of dry densities. These porewater compositions have been suggested to be independent of the saturating fluid. Porewater compositions of MX-80 have been calculated also for bentonites in interaction with Olkiluoto ground waters and the porewater composition reflects the saturating fluids (Wersin et al. 2007a). These results have been given as a reference bentonite water types in Grive et al. (2007) for Olkiluoto conditions (see Section 1.3.3). Birgesson & Karnland (2009) have proposed recently that the previous porewater models are inaccurate and suggest that anions can be incorporated in the interlayer space.

However, as the aim of this review is to discuss the stability of smectite (montmorillonite) in varying groundwater conditions the actual porewater chemistry is insignificant for the purposes of this work. The main focus is in the evaluation of the consequences of the changing hydrogeochemical and thermal conditions.

The initial conditions in bentonite buffer are considered to be oxidizing due to the storing in normal atmospheric conditions. However, oxygen will be consumed in the early stage mainly by oxidation of Fe(II)-bearing mineral impurities in bentonite such as pyrite (FeS_2) and by dissolved methane gas in the rock at the buffer/rock interface and also to some extent by copper oxidation. Wersin et al. (1994) have calculated that the change from oxidizing conditions to reducing would take place in a few to 300 years after closure. Pastina & Hellä (2006) consider based on the available information (Stroes-Gascoyne et al. 2002, Muurinen 2006) that for practical reasons it can be assumed that the oxygen consumption takes place roughly in the same time frame as the full saturation of the buffer (few years to few thousand years). Hence, conditions in the long term are assumed to be anoxic.

Time estimations of the evolution of the porewater chemistry have been made using a mixing-tank model by Wanner et al. (1992), which is based on the assumption that groundwater flowing past the repository will mix completely with the near field. They have estimated that one water exchange cycle will last 13 800 years, during which the porewater of bentonite will be completely exchanged. It is expected that fresh groundwater will equilibrate with bentonite in each cycle. In case of non-saline groundwater, it is concluded that 27 to 81 cycles are needed for complete dissolving and removal of calcite. Exhaustion of calcite in bentonite will eventually allow the pH in the bentonite porewater to decrease, but this is not expected before the next glacial phase if ever.

After emplacement and soon afterwards bentonite can be eroded by flowing groundwater, through a process called piping erosion. In case the groundwater pressure gradient differences gives rise to the formation of a flow channel or channels and the flow surpasses the ability of the bentonite to absorb water. Mechanical erosion could take place during the operational phase due to this gradient, if groundwater flows from the deposition hole into open excavations; the risk is highest before saturation. Erosion depends on the inflow rate and ionic strength of the groundwater. Intrusion of bentonite particles into a rock fracture or into the backfill may also contribute to erosion.

Chemical erosion is a process where rock fractures may provide pathways for the continued, localised, free swelling of the buffer material. These free swelling environments could lead to the continued hydration and expansion of the buffer until, ultimately, colloid-sized (or larger) particles separate by diffusion or shear (caused by flowing groundwater) from extruded gel fronts. However, the colloid formation is reduced or totally prevented by sufficiently high salinity levels (e.g. Laaksoharju & Wold 2005).

3 POSSIBLE MINERALOGICAL CHANGES IN BENTONITE DURING EVOLUTION OF THE BUFFER

Alteration of smectite is affected by thermodynamic conditions (temperature, pressure) and groundwater composition, especially the acid-base character of the environment (pH, ionic strength) as well as the saturation state and solid/liquid ratio. This chapter discusses the stability of smectite, especially montmorillonite and the mineralogical changes that may take place during the evolution of the buffer, both during the relatively short thermal period as well as in the long-term. Natural occurrences supporting the evaluation of the long-term stability of bentonite are discussed in Chapter 4. In natural hydrothermal systems smectite formation is limited to the temperature range between 3ºC, precipitation at the sea floor (Cole 1985) up to 200ºC in hydrothermal systems for example in Iceland (Kristmannsdottir 1979). Smectite is not stable at higher temperatures and begins to alter to more stable and less swelling silicate phases such as illite/smectite mixed-layer minerals, illite, chlorite, micas and zeolites as the temperature rises. Depending on the hydrogeochemical circumstances alteration may take place in variable temperature ranges. Processes that may be relevant for the buffer stability in the expected repository conditions are discussed below.

Smectites as a group, all show swelling ability and resemble quite closely one another, but, they are generally formed in different conditions and subsequently may be stable in different conditions. Hence, the smectite stability in general cannot be directly applied to montmorillonite in particular, but has to be carefully evaluated. Especially, when the aim is to model or to evaluate the stability of montmorillonite in the disposal hole conditions, it has to be ensured that the laboratory studies and the studies of natural occurrences referred are truly analogous (i.e. comparable). As true analogues are difficult to find, it is essential that the comparability is evaluated case by case. In addition to smectite minerals, also differences between montmorillonites with varying exchangeable cation compositions have to be taken into account. This topic is discussed in Section 3.4.

3.1 Stability constraints for smectites

3.1.1 Temperature and pressure

Eberl et al. (1978) have studied the smectite reactivity in water with changing temperatures (smectite:water is 1:1). Test with different smectites in identical hydrothermal conditions (pure water) show different alteration results. For montmorillonite, highly elevated temperatures cause changes especially when K is available in the starting material (Table 3-1). Ca and Na-type montmorillonite remain as montmorillonite after 30 days at 300ºC, but quartz is produced (Table 3-1). Saponites are less reactive as no changes are observed after 34 days in temperatures from 300 up to 485ºC (Table 3-2). Different smectites, as well as different montmorillonites, behave differently in changing thermal conditions. Also, the smectite stability in high temperatures is evident, even at 300ºC Na-, Ca- and Mg-montmorillonite remains as the main product after 30 days. Saponite shows even more persistency. At significantly lower temperatures, such as the expected temperature in the disposal hole, one would expect very little alteration if any at all, even though exposure to high temperature conditions is longer than in the experiments outlined above. However, the main weakness in the laboratory experiments is the effect of time which cannot be directly studied.

Also pressure affects the transformation. In Table 3-3 the pressure effect is demonstrated by montmorillonite samples (Wyoming) with different cations. For example at 405ºC (17 days) Na-montmorilonite alters to smectite/rectorite/kaolinite/albite/quartz at 0.5 kbar while at 2 kbar the reaction pruducts are smectite and quartz.

The data given in Table 3-1 to 3-3 show mineral transformations reported for elevated temperatures >250ºC (most experiments >400ºC) and, thus, are not representative of the temperatures at the canister-bentonite contact. Pressures used are in range of 0.3 – 2 kbar of which the lower values are close to the maximum pressure estimate during a glaciation for the canister is 45 MPa = 0.45 kbar (Posiva 2009a). However, the effect of pressure is very small compared to that of temperature.

As discussed below in Sections 3.2, 3.3 and 3.4 in relation to alteration, the chemical composition of the environment plays a major role in alteration. Stability field diagrams are used to illustrate the equilibrium between end-menbers in various systems (see for example Aagaard & Helgeson 1983). In Figure 3-1 a silica mineral equilibria with the partial component of potassium is presented at 25 °C.

Table 3-1. *Autoclave runs for montmorillonite (Eberl et al. 1978).*

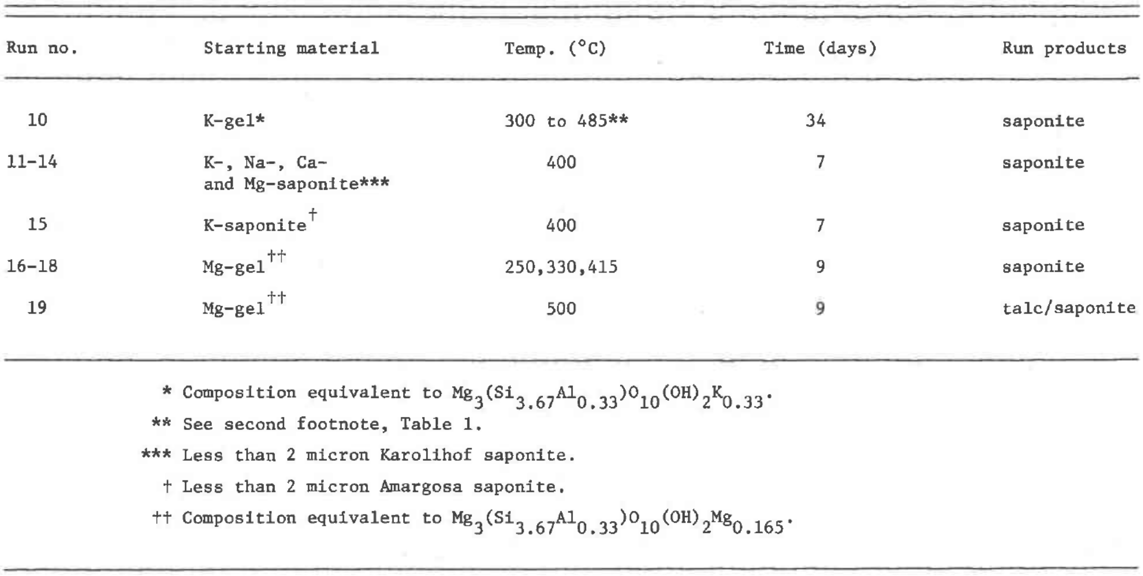
Run no.	Starting material	Temp. (°C)	Time (days)	Run products
1	K-gel*	300 to 485 **	34	illite, cristobalite pyrophyllite
2-5	K, -Na-, Ca- and Mg-montmorillonite***	400	7	mica/smectite, quartz, kaolinite, ± feldspar
6	K-montmorillonite***	300	30	illite/smectite, quartz, kaolinite
7-9	Na-, Ca-, and Mg-montmorillonite***	300	30	montmorillonite, quartz,

* Composition equivalent to $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2K_{0.33}$.

** Large temperature range due to failure of temperature regulator.

*** Less than 2 micron size fraction of Wyoming bentonite, plus a small amount of quartz.

Table 3-2. *Autoclave runs for saponite (Eberl et al. 1978). (In foot note the ref to Table 1 is Table 4-2 in this report)*



Run no.	Starting material	Temp. (°C)	Time (days)	Run products
10	K-gel*	300 to 485**	34	saponite
11-14	K-, Na-, Ca- and Mg-saponite***	400	7	saponite
15	K-saponite†	400	7	saponite
16-18	Mg-gel††	250,330,415	9	saponite
19	Mg-gel††	500	9	talc/saponite

* Composition equivalent to $Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2K_{0.33}$.

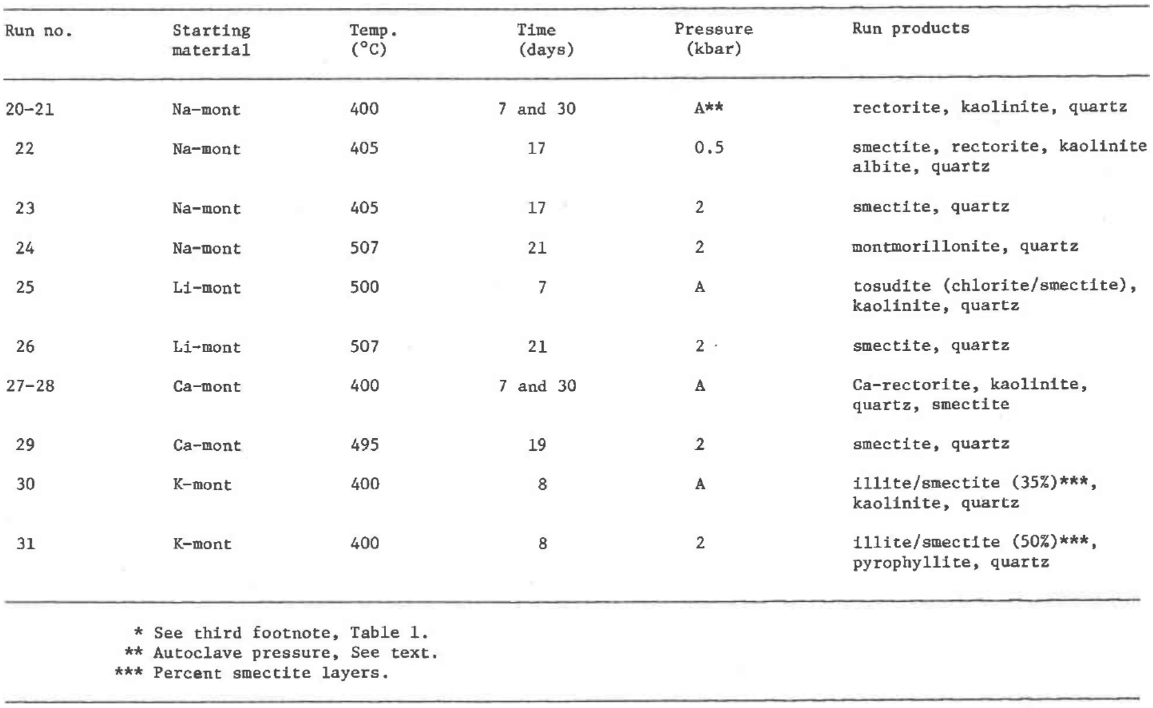
** See second footnote, Table 1.

*** Less than 2 micron Karolihof saponite.

† Less than 2 micron Amargosa saponite.

†† Composition equivalent to $Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2Mg_{0.165}$.

Table 3-3. *Pressure effect on the reaction of Wyoming montmorillonite (Eberl et al. 1978). Autoclave pressure (A) is 0.3 kbar. (In the foot note the ref to Table 1 that is Table 4-2 in this report)*



Run no.	Starting material	Temp. (°C)	Time (days)	Pressure (kbar)	Run products
20-21	Na-mont	400	7 and 30	A**	rectorite, kaolinite, quartz
22	Na-mont	405	17	0.5	smectite, rectorite, kaolinite albite, quartz
23	Na-mont	405	17	2	smectite, quartz
24	Na-mont	507	21	2	montmorillonite, quartz
25	Li-mont	500	7	A	tosudite (chlorite/smectite), kaolinite, quartz
26	Li-mont	507	21	2	smectite, quartz
27-28	Ca-mont	400	7 and 30	A	Ca-rectorite, kaolinite, quartz, smectite
29	Ca-mont	495	19	2	smectite, quartz
30	K-mont	400	8	A	illite/smectite (35%)***, kaolinite, quartz
31	K-mont	400	8	2	illite/smectite (50%)***, pyrophyllite, quartz

* See third footnote, Table 1.

** Autoclave pressure, See text.

*** Percent smectite layers.

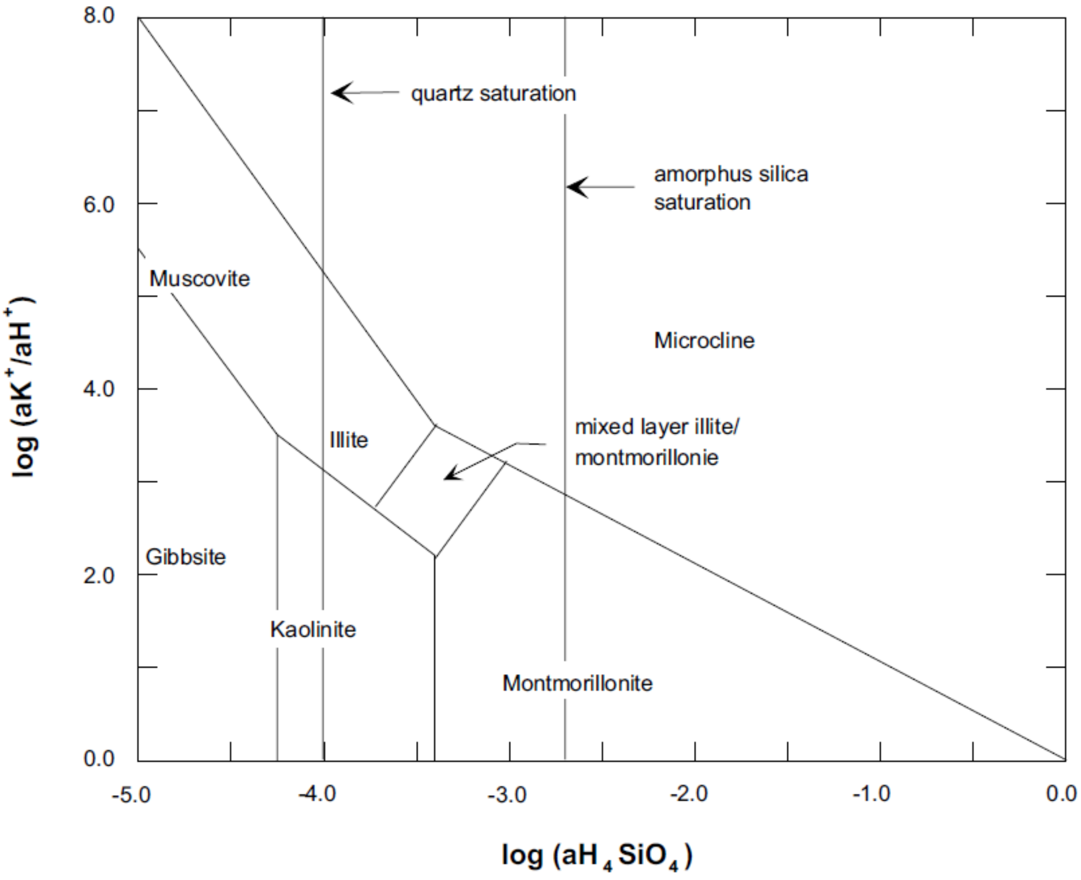


Figure 3-1. *Silica mineral equilibria with the partial component potassium at 25°C. Simplified from Aagard & Helgeson (1983).*

3.1.2 pH

The dissolution of smectite is also dependent on H^+ ion concentration (Furrer et al. 1993, Zysset & Schindler 1996). With increasing pH the dissolution of smectite increases (e.g. Amram & Ganor 2005). High pH values ($11.5 \leq pH \leq 13.9$) lead to smectite dissolution independently of the aqueous silica or aluminium concentrations (Zysset & Schindler 1996; Bauer & Berger 1998). As smectite dissolves the Si is released, which may lead to cementation (see below). Equilibrium diagrams for Ca-montmorillonite and Na-montmorillonite (Figure 3-2) show that montmorillonite is stable at higher pH and in more concentrated solutions than for example gibbsite. In Figure 3-2 also water compositions from different locations are shown. Concentrated waters from arid countries fall in the montmorillonite domain, while dilute waters collected from humid areas fall in the kaolinite domain close to the gibbsite boundary (Tardy 1971).

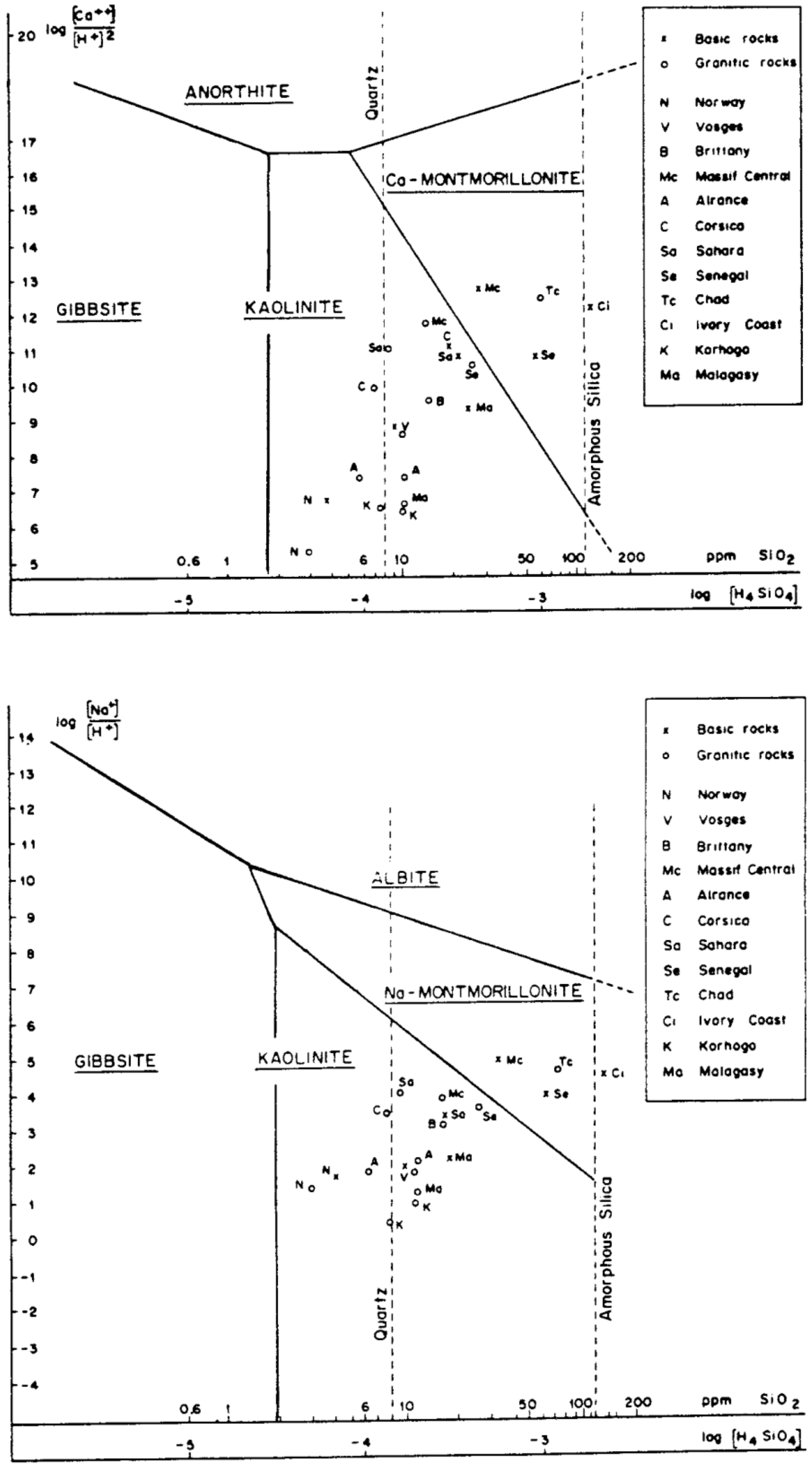


Figure 3-2. *Stability field diagram of gibbsite, kaolinite and montmorillonite and location of drainage waters collected in different climatic environments (Tardy 1971). Solubility data at 25 °C (Tardy et al. 1987).*

Effects of high pH on the stability of smectite (and bentonite) have been studied by several authors, and the main conclusions based on these studies are:

- Swelling pressure of montmorillonite (MX-80) decreased significantly at high pH (>13), but at pH 12.9 or lower no such effect was seen (Karnland et al. 2007);
- According to Fernández et al. (2009) K-silicates are not formed in highly alkaline solutions from Mg-saturated compacted FEBEX bentonite, but a cemented rim form at the bentonite – solution interface (few mm) consisting mainly of brucite, a chlorite-like phase and Mg-smectite. Reaction solutions were highly alkaline K-Na-OH (pH 13.5) and Ca-$(OH)_2$ (pH 12.5) and the temperature 60 ºC. In these experiments montmorillonite was partly dissolved and partially remained shielded by the newly-formed cement crust. The process was attributed to cation diffusion through the interlayers of montmorillonite. Mineral reactions observed also hindered the diffusion rate of the high pH front in the bentonite.
- Bentonite alteration by hyperalkaline fluids (10 < pH < 13) was recently reviewed by Savage et al. (2007). They consider that the most likely minerals to form from the cement-bentonite systems are at lower pH (pH <11) zeolites (clinoptilolite, phillipsite), and at higher pH (pH>11) C(A)SH, illite, feldspars and more aluminous zeolites (analcime, heulandite). Also predominantly Na-. K-bearing solids will be transformed to those dominated by Ca as the composition of cement porefluid evolves with time. See Figure 3-3 for an overview.

The leachates from the low alkali cement planned to be used in the repository have an initial pH 10.5-11.5 (Posiva 2009a). Preliminary modelling calculations by Lehikoinen (2009) suggested that pore clogging on the surface of the bentonite buffer would occur at pH 12.17, 11.60 and 9.70 after 10, 18 and 5900 years after the onset of the interaction showing minor mineral alteration at the outer edge of the buffer, which does not endanger the performance of the buffer. Cement-bentonite interaction studies are ongoing by Posiva (Posiva 2009a).

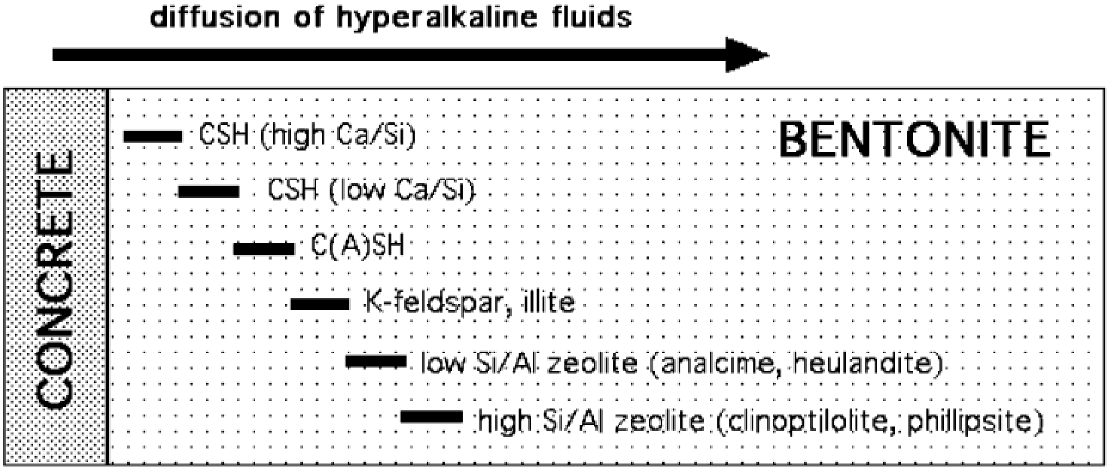


Figure 3-3. *Schematic diagram of the potential sequence of secondary minerals due to the migration of hyperalkaline pore fluids through bentonite. As the composition of cement pore fluids evolves with time, sodium-potassic phases will be replaced by more calcic varieties (Savage et al. 2007).*

Solubility of one of the major minerals in bentonite, quartz, increases as a result of increasing pH in the groundwater. Dissolved silica may precipitate at the ends of smectite stacks at lower pH conditions and then cause further cementation of bentonite (Pusch et al. 1998) (see Section 3.3 below).

3.1.3 Salinity

As seen in Figure 3-2 montmorillonite stability fields are constrained by the pH range as well as the ionic strenght of the water. Smectite stability is affected by very dilute environments as well as by highly saline ones as discussed below. Smectite stability in nature is discussed in Chapter 4 using the data available from the porewaters/ groundwaters where smectite has been observed to occur as a stable phase. In this section the focus is on experimental and theoretical information.

Smectite behaviour in highly saline conditions has been studied also by Herbert et al. (2004) who have evaluated smectite stability in repositories planned to be located in salt formations. Conditions differ greatly from other studies as the boundary conditions include highly saline brines (Figure 3-3), a wide range of possible pH, high solid/liquid ratio in compacted bentonite (MX-80) and elevated temperature. Herbert et al. (2004) have concluded that MX-80 bentonite is not stable in brines in the short or in the long term. Experimental results of Herbert et al. (2004) also suggest that in highly saline conditions a certain percentage of montmorillonite in MX-80 type bentonite will be transformed into kaolinites and pyrophyllites rather than illite. In these experiments typical brines of the German Zechstein salt formations, a NaCl-$CaSO_4$ saturated and a Mg-rich, carnallite saturated solution (Figure 3-3), were used. Initial pH of the brines was 6.5, and also lower and higher pH experiments were conducted. The observed mineralogical alterations follow thermodynamic pathways of kaolinisation/ pyrophyllitisation in "closed" systems with high Si content. The brines used in this study were very different compositionally (high Mg-content for example) from those expected in Olkiluoto (see comparison to Olkiluoto Brine in Figure 3-4). Thus, these results do not provide usable information on the bentonite stability for the Olkiluoto conditions.

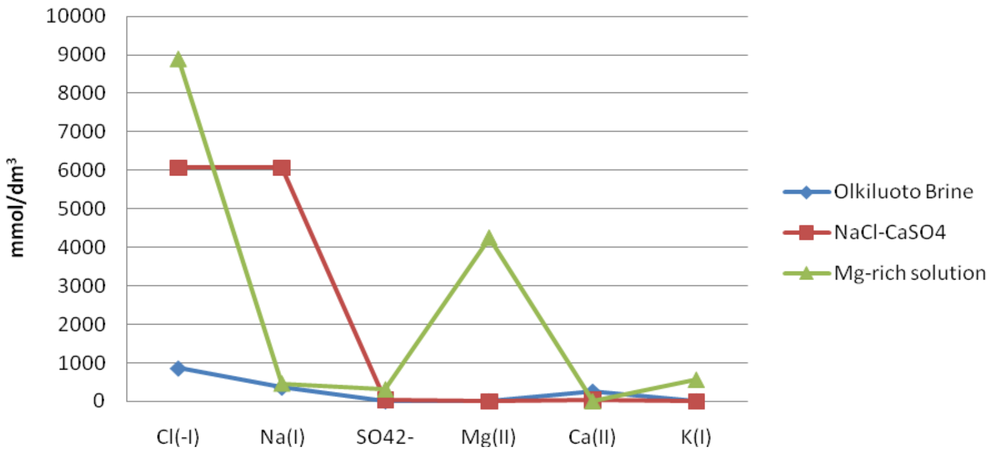


Figure 3-4. *The difference between the experimental waters NaCl-$CaSO_4$ saturated and the Mg-rich solution used by Herbert et al. (2004) and Olkiluoto Brine.*

The more recent study by Herbert et al. (2008) was conducted with a wide variety of solutions from distilled water I(M)=0 to highly saline brines I(M)= 15.482. For comparison, the ionic strength of Olkiluoto reference waters vary from I(M) 0.02 (dilute brackish) to 1.2 (brine). Both batch experiments and experiments with compacted bentonite were done, with low and high solid/liquid ratios, respectively. Only minor mineralogical changes were observed during the 3 year experiment. However, the swelling pressure was observed to be affected by the increasing salinity, as expected (Figure 3-5 a and b). Compacted samples in highly saline systems and cementitious system showed collapse of swelling pressure at 2 years time. This phenomenon has been explained by the mineral alteration affecting the layer charge of the smectite, which is observed in all samples, but causes the swelling pressure collapse when a certain critical point is exceeded. This phenomenon is observed only in the compacted experiments suggesting an accelerating effect of high solid/liquid ratio due to higher acidity in the porewater; see Figure 3-5 for compacted samples (black symbols and YCP). This process has been explained by kaolinisation/ pyrophyllitisation and excess of Si. Herbert et al. (2008) have concluded that the long-term mineral transformation could potentially lead to significant loss of swelling pressure in repository in salt or if cement is involved. However, the effects on the lower salinity systems are yet to be explained as the drop in the layer charge is seen in all batch experiments (Figure 3-5c).

Castellanos et al. (2008) have studied the hydro-mechanical behaviour of compacted Ca-type FEBEX bentonite under varying salinity conditions. They have concluded that FEBEX bentonite compacted to 1.65 g/cm^3 looses almost half of its initial swelling pressure when saturated with >2 M $CaCl_2$ and NaCl solutions, that represent concentrations of about 220 g/l and 115 g/l respectively. Salinities expected in the repository should remain below < 70 g/L. At low salinities (granitic water 0.004 M) the swelling pressure of bentonite was not affected in the dry density range from 1.4 to 1.7 g/cm^3.

The effect of high salinity, 70 g/l solution composed of calcium and sodium chloride at a Ca^{2+}/Na^+ mass ratio of 3:2 (representing the upper salinity limit set for the repository conditions), on the swelling pressure of compacted MX-80 have been studied by Schatz & Martikainen (2010). The Ca/Na ratio has been set to resemble conditions possible in the repository level in case of upconing of saline water. The preliminary results from the experiments show that the presence of $CaCl_2$ could lead to a somewhat higher swelling pressure decrease than what is seen in experimental results in presence of NaCl (Karnland et al. 2006; see Figure 3-16).

Whereas high salinities may lead to mineral transformation and decrease in swelling pressure, a dilute environment may cause delamination and dispersion. This depends on the composition of exchangeable cations. This topic is discussed in more detail in Section 3.4.

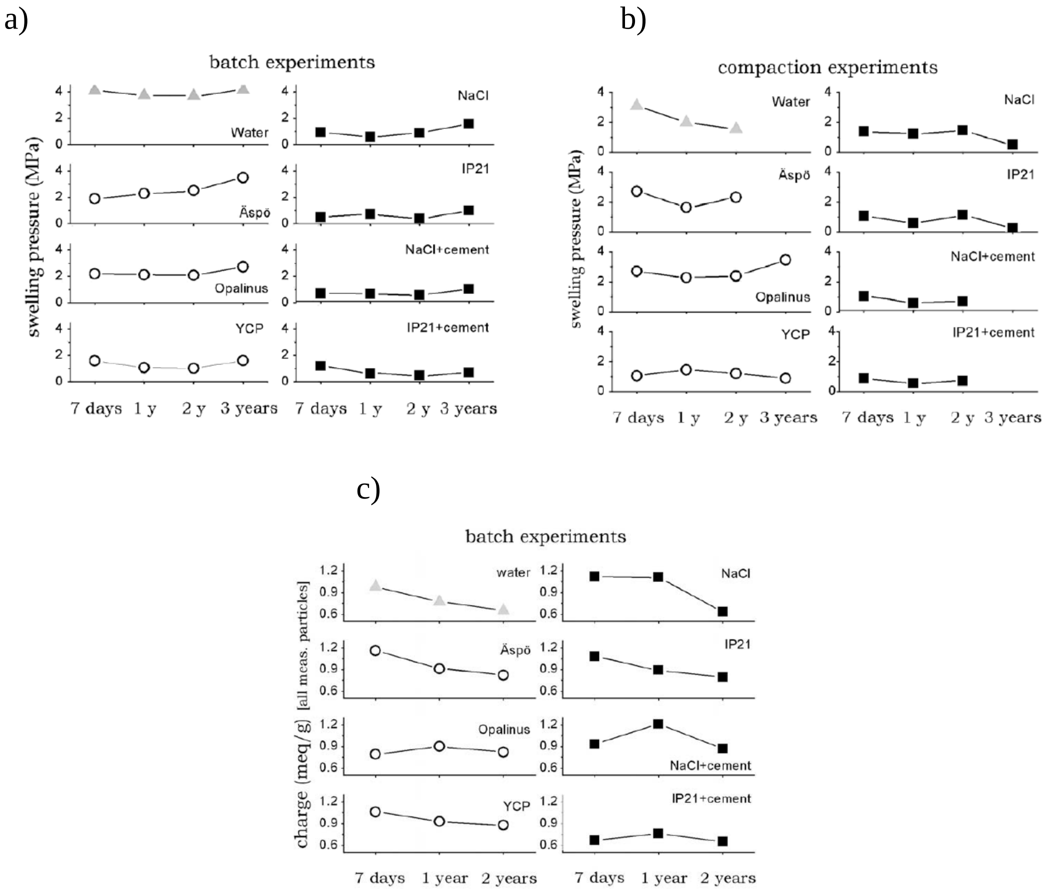


Figure 3-5. Development of swelling pressure in 3 year experiments in variety of solutions: a) Batch experiments, b) experiments with compacted bentonite and c) development of interlayer charge in batch experiments. I(M) of different waters: water (distilled water)=0, Äspö (groundwater granitic) =0.124, YCP (young cement porewater) =0.203, Opalinus (groundwater clay formation)= 0.377, NaCl+ cement=6.508, NaCl=6.686. IP21 ($MgCl_2$ rich brine)+ cement=13.013, IP21=15.482. (Herbert et al. 2008.)

3.2 Mineral alteration types and rate

Changes in the surrounding chemical environment cause mineral alteration, but the rate and extent is controlled by themodymamic and kinetic laws. Kinetics of the reactions defines the rate that alteration may take place. Also, availability of ions, such as K^+ ans Si^{4+}, controls the possible transformation paths as seen in the examples given below. In nature, alteration may occur in a wide range of comditions and in this section the focus has been set on those that according to the literature could be important during the evolution of the deep repository.

3.2.1 Illitisation

In nature, illitisation of smectite occurs in the vicinity of intrusions, geothermal fields as well as in diagenetic environments. Illitisation rate varies not only due to thermal history, but also due to the different hydrogeochemical conditions. According to Wersin et al. (2007b) the illitisation reaction is strongly dependent on temperature, time, K^+ ion concentration in pore water, pressure, the chemical composition of smectite, layer charge of smectite and the nature of the initial interlayer cation.

The illitisation process is accompanied by changes in the tetrahedral layer charge and changes in the mineral lattice due to decreasing contents of Si^{4+}, Mg^{2+}, and Fe^{3+} and increasing Al^{3+}, Fe^{2+} and K^+ contents (Cuardos & Linares 1996, Amouric & Olive 1991). Hence, the composition of the reacting fluid plays a major role in smectite transformation along with the thermal conditions and prevailing solid/liquid ratios.

Illitisation reaction of smectite can be written in two ways depending on whether Al is considered in the reaction or not. An isovolumetric rection has been suggested by Hower et al. (1976),

$K + Al + \text{Smectite} \rightarrow \text{Illite} + Na + Ca + Fe + Mg + Si + H_2O$

Boles & Franks (1979) have proposed a reaction based on the cannibalization of smectite,

$K + \text{Smectite} \rightarrow \text{Illite} + Na + Ca + Fe + Mg + Si + O + OH + H_2O$

In illitisation of smectite K^+ is necessary. If there is no K^+ available the release of SiO_2 through the illitisation reaction cannot occur (Karnland & Birgersson 2006).

According to several experimental studies illitisation of smectite is temperature dependent and occurs above 120ºC or even above 250 ºC (e.g. Inoue 1983, Inoue 1995, Eberl et al. 1993, Tsutomu et al. 1995, Batchelder et al. 1996, Cuadros & Linares 1996, Roaldset et al. 1998), which is well above the expected temperatures in the repository conditions (see Section 1.2). Illitisation in natural bentonite occurrences is discussed in Chapter 4. The illitisation effect is pronounced in higher temperatures (Figure 3-6). Also wetting and drying cycles have been observed to increase the illitisation rate significantly (Eberl et al. 1993).

Modelling (Karnland & Birgersson 2006) supports the long term stability of smectites at low temperatures and low K concentrations in groundwater as presented in Figure 3-7 (compare to Olkiluoto referencewaters in Section 1.3.3, Table 1-1). Changes seen in the expected repository temperatures (see Section 1.2) are very small and considered neglible.

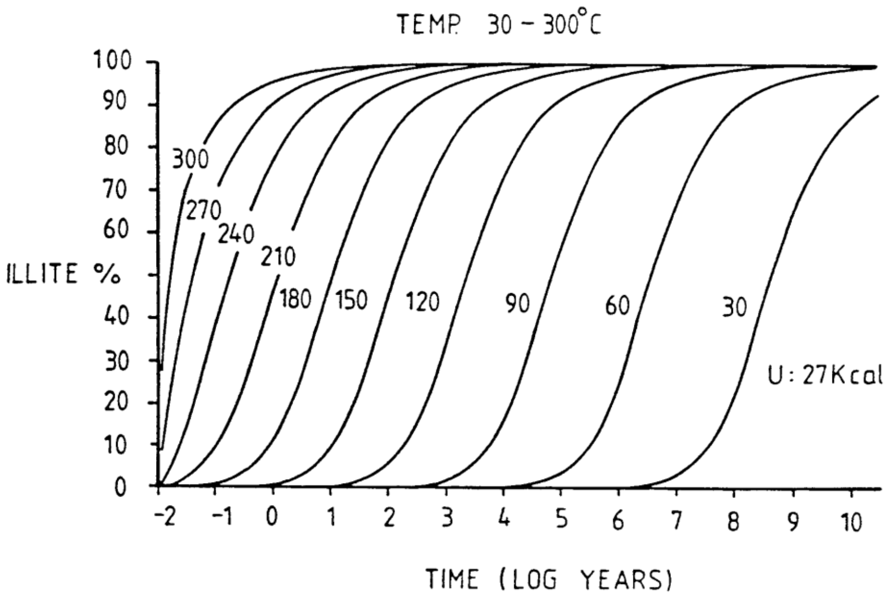


Figure 3-6. *Illitisation rates at different temperatures (Pusch & Karnland 1988b).*

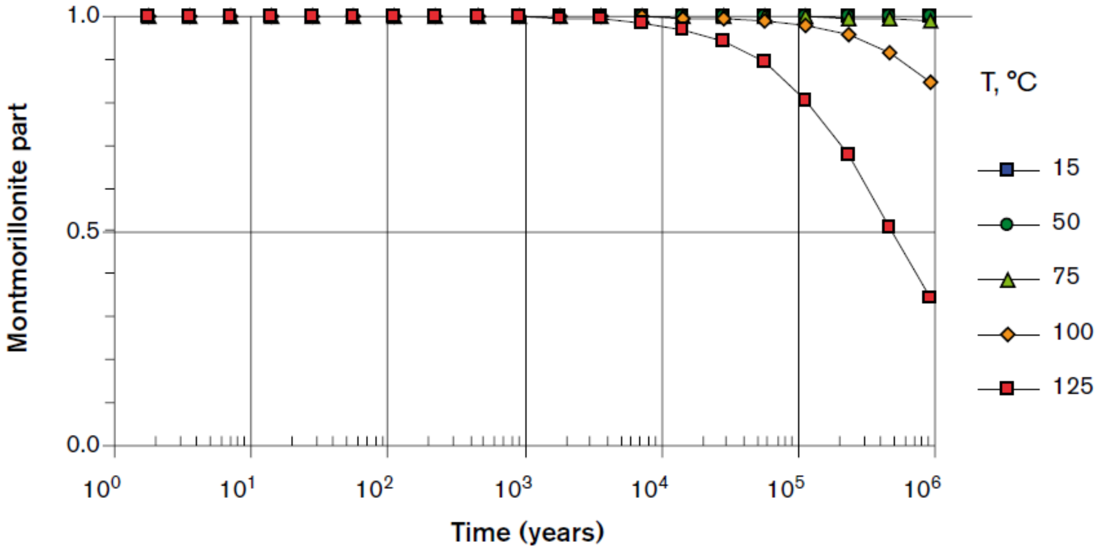


Figure 3-7. *Remaining smectite for different temperatures [°C] in a hydrothermal system with [K$^+$] = 0.002 mole/litre (80 ppm) according to the (Huang et al. 1993) kinetic model and laboratory determined constants (Karnland & Birgersson 2006).*

According to Meunier et al. (1998) diagenetic reactions i.e. illitisation/cementation are too slow for a million year timescales and thus more rapid reactions should be considered for manmade systems, such as repositories discussed here. Karnland & Birgesson (2006) have concluded that high-charge montmorillonite may be formed instead of illitisation in case of absence of potassium and presence on sodium. According to them, a high-charge montmorillonite should behave well as buffer material, but the subsequent ion-exchange should be taken into account (i.e. fixation of K). Consequently, the potassium supply must be considered during the whole repository lifetime.

The effect of pH on illitisation

As discussed in Section 3.1.3 pH is one of the controlling parameters in smectite stability and thus affects the transformation and alteration reactions as well. pH affects illitisation process (Eberl et al. 1993, Huang et al. 1993, Bauer & Velde 1999). High solution pH allows illite to form from smectite at low temperatures such as 35 ºC and 60 ºC at pH > 13 (Eberl et al. 1993) and 35 ºC and 80 ºC (Bauer & Velde 1999) in experimental systems. The pH in the repository is expected to be significantly lower (near neutral, Posiva 2009b). Illitisation process is inhibited by low amounts of liquid and high amounts of reacting smectite (Kascandes et al. 1991, Whitney 1990), which is also the case in the repository.

Accelerating effect of high pH on the illitisation process has been studied for Na- and Ca-type smectites experimentally. This is of interest as the cation conversion may occur in the repository envitonment during the evolution (see Section 3.4). In case of Wyoming type Na-smectite (Ceca) (corresponds to MX-80, nearly pure smectite) and Ibeco Ca-smectite with 35 % beidellitic charge the latter shows smaller dissolution rates at pH range studied (13-14.5) at 35 and 80 °C (Figure 3-8) (Bauer & Velde 1999). As seen in the Figure 3-8, pH has the more pronounced effect on the dissolution of smectite the higher the temperature. The reactivity rate of the Ca-smectite is observed to be higher compared to the Na-type the more the solid/liquid ratio increases; this is not affected at all by the pH increase practically and especially at 80 °C. This would suggest even larger differences at the repository conditions where the expected solid/liquid ratio is even larger. The effects of elevated salinity and pH are discussed also in Sections 4.4.2, 4.5, and 4.9.

3.2.2 Other types of alteration

Experimental studies proposing accompanied beidellitisation and/or saponitisation

Pusch & Kasbohm (2002) have studied compacted MX-80 bentonite (dry density 1200–1300 kg/m^3) and stability in 10 % and 20 % NaCl solutions (30 days) at 110 ºC. Experimental set ups were made to study both saturated and partly saturated conditions. In both cases no significant changes were observed in hydraulic conductivity or in swelling pressure. XRD analysis showed a clear difference in mineral constitution between the two test series. Some very minor changes were observed in the saturated experimental set up, while dry clay exposed to 20 % NaCl showed changes, though very limited. In the latter case Na-illite of fully contracted layers was formed and Mg migrated from the octahedral lattice implying partial dissolution (or beidellitization). Also slight cementation was observed in the dry case. In the air-dry clay exposed to NaCl solutions the process may be related to vapour attack. Pusch & Kasbohm (2002) conclude that while the changes observed were minor and the temperature and the salinity of the water higher than what is expected in a Swedish or Finnish repository, the test only took 30 days which is a very short time compared to that expected during the thermal transient phase.

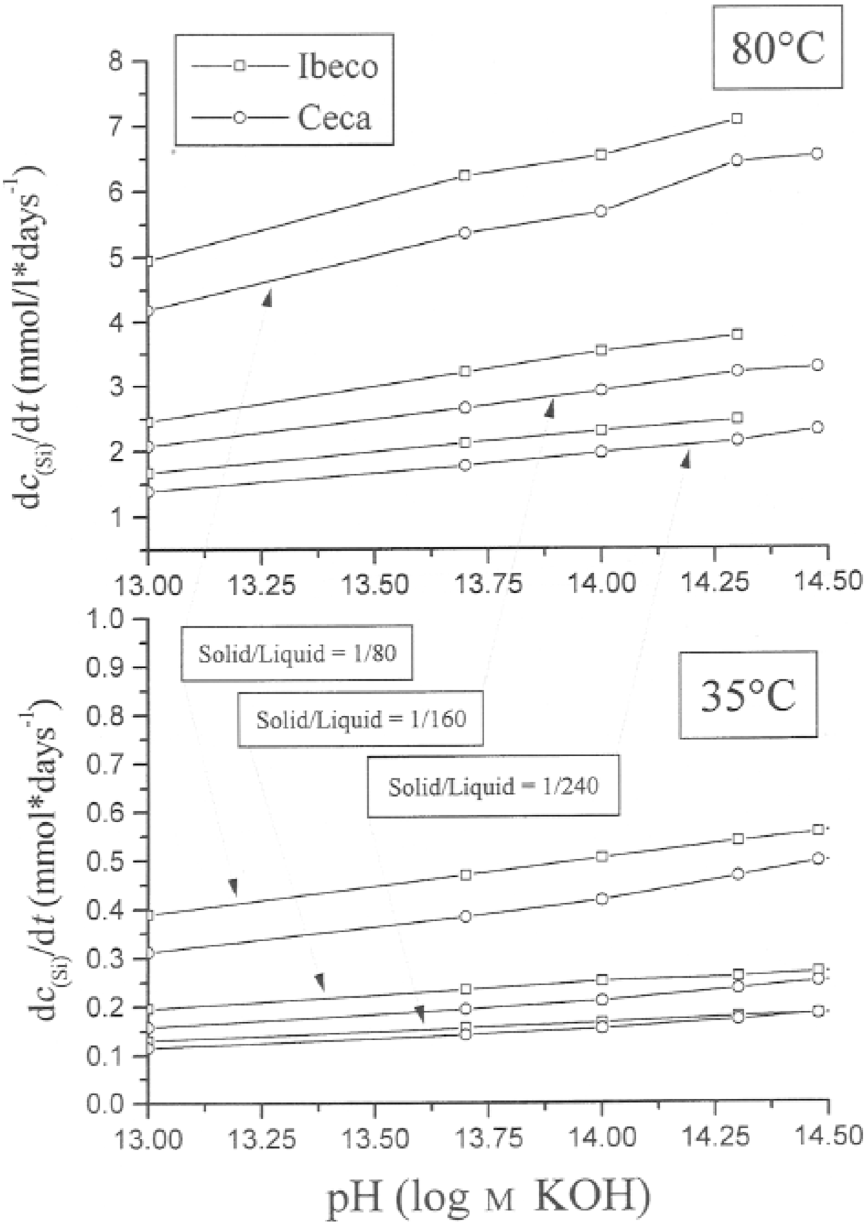


Figure 3-8. *Smectite dissolution rates (in mmol/l days -1) are plotted against log (M KOH) or pH (Bauer & Velde 1999).*

Meunier et al. (1998) have proposed that illite is not necessarily produced in the laboratory experiments conducted with purified montmorillonite. Reaction products seen in diagenetic sequences are not repeated always in the laboratory experiments. While it is uncertain whether the experimental results are valid in natural occurrences, the information on the kinetics from the experiments may be used with reasonable confidence to predict the life span of the clay barriers (Meunier et al. 1998). Meunier et al. (1998) have proposed a reaction that should be envisaged instead of the illitisation process:

low-charge montmorillonite → high-charge beidellite + saponite + quartz

It should be noted that also in this case the difference of the purified montmorillonite and natural material is highlighted, which has to be taken into account when evaluating the buffer performance (see also Chapter 5).

Yamada et al. (1991) and Yamada & Nakasawa (1993) have shown that saponite-beidellite assemblage crystallises from smectites from the montmorillonite-beidellite series under hydrothermal experimental conditions (> 375 °C). Experimental results are presented in Figure 3-9 that illustrates the effect of temperature and starting material on the reaction products. This type of alteration would lead Fe and Mg to concentrate in a separate phase as shown by Grauby et al. (1993) by experimental synthesis of clays, which would result in a beidellitic smectite in the resulting mixed-layer I-S (Meunier & Velde 1989). The illite component resulting then from the beidellite destabilisation would be richer in Al than what is seen in the diagenetic series (Meunier & Velde 1989).

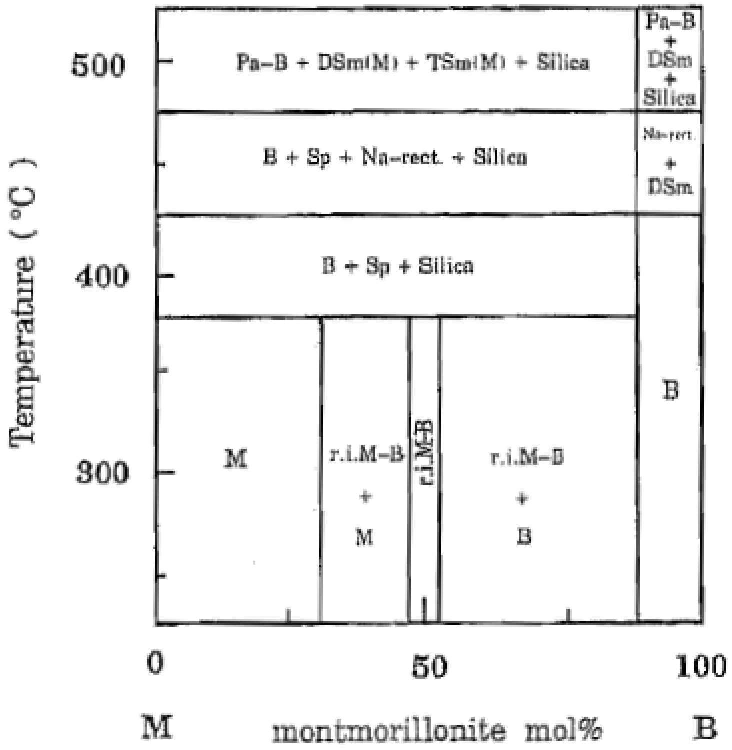


Figure 3-9. Schematic phase relations in the montmorillonite-beidellite pseudo-binary system. M=montmorillonite, B= beidellite, Sp=saponite, r.i.M-B= regularly interstratified montmorillonite-beidellite, Na-rect= Na-rectorite (regularly interstratifies paragonite-beidellite), Pa-B= randomly interstratified paragonite-beidellite, DSm(M)= dioctahedral smectite with octahedral charges, TSm(M)= trioctahedral smectite with octahedral charges, Silica= silica mineral (cristobalite and/or quartz). (Yamada et al. 1991.)

Thermally induced beidellite and saponite formation has been observed in I/S (mixed layer illite/smectite, S% max. 40) bearing calcareous mudstones due to thermally induced alteration around a basaltic dyke (Henry et al. 2007). In the reaction aureole similar evolution is seen both sides of the dyke. Quartz, kaolinite, illite and calcite disappear while Ca-silicates, albite and saponite-beidellite form. The formation of new swelling phases with high retention capacity linked to a short duration of the large temperature increase was observed. This process would favour the buffer properties instead of impairing them. Beidellitisation/saponitisation reactions described by Henry et al. (2007) are faster than illitisation. The starting material in the clay formation is however very different from bentonite by having already been subjected to diagenesis prior to thermal effect of the dyke. Thus the significance of these reactions in crystalline bedrock with bentonite with high smectite content is unclear. Henry et al. (2007) also conclude that below 100 °C no major mineral and chemical modifications were observed in the formation studied, indicating that the clay mineralogy is quite stable under such temperatures over very long time periods, such as under diagenetic conditions.

Montmorillonite → illite reaction performed in closed system in laboratory leads to precipitation of saponite-stevensite type smectite (Si^{4+} and Mg^{2+} consumed from the illitisation reaction) in the absence of CO_2 (Beaufort et al. 2001). In the presence of CO_2 Fe-Mg carbonates are formed (Meunier 2005).

Chloritisation

According to Karnland & Birgesson (2006) chloritisation can not be excluded from the buffer alteration processes considered as the chloritisation can be a parallel reaction to illitisation. It may also occur in lack of potassium and in access to Mg, Fe or Al, also in case without illitisation. However, there is no reason to believe that chloritisation process should be any faster than illitisation in the repository conditions. In case of chloritisation the effects would be similar to those of illitisation i.e. reduction of expandability.

Eberl et al. (1993) observed chloride formation from pure smectite in one experiment that was conducted in 0.5 M KOH at 35 °C for 270 days.

Changes in the octahedral layer charges

Iron is at maximum oxidation state in commercial materials (bentonite) due to exposure to the air. According to Stucki et al. (1984) the transformation reaction could be relatively fast under repository conditions where Fe(III) in the octahedral layer would be reduced to Fe(II). This reaction leads to an increase of total layer charge and adds a risk of fixation of interlayer cations if the charge is high enough (Karnland & Birgesson 2006). This alteration type is however restricted by the iron content in the montmorillonite. However, in theory, in case of canister failure the access to the iron insert could make the iron available for the complete transformation. In cases of MX-80 and Deponit Ca-N the maximum possible layer charge due to this process would be significant but not high enough for the fixation of potassium (Karnland & Birgesson 2006). Fe-bentonite interactions are studied in more detail in the KBS-3H (horizontal deposition), see for example Wersin et al. (2007a).

Also thermally induced changes in the octahedral layer may take place. Small interlayer ions appear to be able to move into the leyer structure and change the octahedral layer charge at temperatures between 200 and 400 °C (Hoffmann & Klemen 1950, Greene-Kelly 1953). This type of reaction is irreversible and lead to permanent loss of swelling properties. Karnland & Birgesson (2006) have raised a question whether or not this type of reactions could take place at low temperatures and at what rate. They have considered that due to dehydration involved in these types of reactions the reaction rate would be significantly reduced under repository conditions.

3.2.3 Experimental evidence on the stability of the buffer clay

Pusch et al. (2009) have evaluated the experimental data on the stability of the buffer clay in repository like conditions (in granitic rock). The synthesis presented is based on several studies: SKB/ANDRA at Saclay (laboratory experiments, Pusch et al. 1993), Stripa Project (hydrothermal laboratory tests, Pusch et al. 1991), Czech half-scale mock-up tests (Fe-rich montmorillonite buffer, Pacovsky et al. 2005) and full-scale field experiments in SKB’s underground laboratory in Äspö (Pusch et al. 2009). Main conclusions of the synthesis are that:

- Montmorillonite remains the major clay mineral in the buffer at temperatures up to 150ºC.
- Rate of conversion is not yet known and should be further studied.
- Similar mineralogical changes were observed in all studies reviewed, i.e. dissolution. of accessory minerals (calcite, feldspars), but also quartz and montmorillonite and cementation that lead to significantly reduced expandability.
- The use of bentonite with high content of very pure montmorillonite is suggested.
- The short-term nature of the tests is emphasised as well as the possible differences between the conditions in the repository and laboratory experiments.

3.3 Cementation

The two main processes that may lead to reduced swelling pressure and loss of plasticity as well as increased hydraulic conductivity and diffusivity of the buffer are precipitation of SiO_2 (Section 3.3.1) and/or montmorillonite transformation to non-expandable minerals (Section 3.3.2) (e.g. illite that has similar crystalline structure as montmorillonite but the lattice charge is higher, Brindley 1980, Wersin et al. 2007b). Cementation by silica precipitation may be related to smectite alteration (e.g. illitisation) or it can occur due to excess silica source. Also cementation that is caused by precipitation of agents other than Si occurs in nature, these are briefly mentioned in Section 3.3.3. Arthur & Zhou (2005) attribute cementation in natural bentonite formations to be mainly a result of the smectite/illite conversion reaction.

The temperature gradient in the buffer, which is expected during the thermal period (see Chapter 1), may cause migration of dissolved compounds towards the area where the component is in equilibrium with prevailing conditions and where the precipitation is possible (e.g. T, pH) (Pusch et al. 1998, Pusch 2001, Pastina & Hellä 2006, Wersin et al. 2007b). The temperatures for dissolving and precipitation are characteristic for each cementating compound.

Wersin et al. (2007b) have reviewed the temperature related cementation of bentonite as follows:

- No significant cementation seems to occur below the temperature 110 ºC.
- Slight cementation at 130 ºC.
- Significant cementation at 150 ºC.

Silica polymorphs (quartz, cristobalite and amorphous silica) can precipitate at a quite wide temperature range as shown in Table 3-4, where the precipitation temperatures range from 18 to 500 ºC depending on the prevailing salinity/pH conditions.

Regardless of the origin of the SiO_2, it may precipitate and cause cementation of bentonite. SiO_2 content in groundwater in the repository may be controlled for example by the following reactions:

- Dissolving of smectite and other minerals of bentonite
- Dissolving of minerals of host rock
- Dissolving of cement based construction materials
- Dissolving of silica based grouting material
- Dissolving of the crushed rock components of backfill material

Smectite dissolution is assumed to be a temperature related reaction (Wood 1983, Pusch et al. 1996) that is also affected by the solid/liquid ratio of the system (see above Figure 3-4 and related text). The dissolution of smectite may release silica and Al. The Gabo de Gata (Almeria, Spain) smectite dissolution reaction (at 80 °C) is seen in Equation 3-1 (Cama et al. 2000):

$$\begin{aligned}\text{Smectite} + 20H_2O &\rightarrow 0.51Na^{+} + 0.19K^{+} + 0.195Ca^{2+} + 1.1Mg^{2+} + \\ &0.42\,Fe(OH)^{-}_4 + 2.79Al(OH)^{-}_4 + 7.77H_4SiO_4 + 0.08OH^{-}\end{aligned} \tag{3-1}$$

The released Si may later function as a cementing agent in bentonite. In addition to possible cementation, the density and other desired properties of bentonite may be affected.

3.3.1 Other types of cementation

Precipitation of agents dissolved from sulphates and carbonates

According to Pusch (2001) and Pastina & Hellä (2006) sulphate and carbonate minerals (e.g. gypsum and calcite) in bentonite can dissolve and form ionic sulphate, carbonate, calcium, magnesium and iron that may migrate towards the area where the temperature is elevated and subsequently precipitate in this hot area (Pusch 2001, Pastina & Hellä 2006, Wersin et al. 2007b).

Precipitation of iron hydroxides and oxyhydroxides

Iron hydroxides and oxyhydroxides, which may be releaseased from iron bearing minerals and Cu-iron canisters or the supercontainer steel shell in the KBS-3H design variant, may also act as cementing agents (Pusch 2001, Wersin et al. 2007b).

Precipitation of agents dissolved by hot water vapor

Water may occur in the repository in gaseous (vapour) or liquid form depending on the temperature and the degree of saturation. In dry parts the buffer material may be affected by hot vapour (Pusch 2001).

Pusch (2000) has studied the effect of hot water vapour on the bentonite and concluded that the water vapour (temperature 90-100 ºC) may cause silica dissolution and further precipitation. At temperatures below 100ºC the effect is small and confined to a 2 cm distance from the surface of the canister.

Table 3-4. *Precipitation temperatures, activation energies, Q (stoichiometric coefficient)/Keq (equilibrium constant) and solution compositions of different silica polymorphs gathered by Carroll et al. (1998).*

Phase	**T [ºC]**	**E_a [kJ/mol]**	**Q/Keq**	**Solution composition**	**Reference**
Am. silica	18 – 300	49.8	1.7	distilled water	Rimstidt & Barnes (1980)
Am. silica	60 – 120	0	4	pH 5 – 8, 1 N NaCl	Bohlmann et al. (1980)
Am. silica	25 – 50	54.8	10	pH 4 – 8, 0.1 – 1 m NaCl	Fleming (1986)
Am. silica	80 – 120	61	<1.3	pH 3 – 7, I 0.13 M, geothermal waters	Carroll et al. (1998)
Am. silica	60 – 117	50	1 - 2	pH 7 – 8, geothermal waters	Carroll et al. (1998)
α-cristobalite	18 - 300	49.8	1.7	distilled water	Rimstidt & Barnes (1980)
β-cristobalite	150 - 300	52.9	2		Renders et al. (1995)
β-cristobalite	18 - 300	49.8	1.7	distilled water	Rimstidt & Barnes (1980)
Quartz	300 - 420	57 - 164	-	0.5 m NaCl	Laudise (1959)
Quartz	18 - 300	49.8	1.7	distilled water	Rimstidt & Barnes (1980)
Quartz	300 - 500	88 - 159	-	0.1 – 1 m NaCl	Hosaka & Taki (1981a)
Quartz	300 - 500	29.3 - 33.5	-	0.1 – 1 m KCl	Hosaka & Taki (1981b)
Quartz	120 - 255	34	2		Bird et al. (1986)

Cementation caused by the interaction with foreign materials in the repository

Cement-bentonite interaction

As discussed in Section 3.1.2 elevated pH may cause alteration of smectite. Cement-bentonite interaction may lead to formation of non-expandable mineral parageneses that cause cementation of the buffer. This process is dependent on the amount of cementitious materials used in the repository and the rate of degradation. In Figure 3-7 a schematic diagram of the potential sequence of secondary minerals due to the migration of hyperalkaline pore fluids through bentonite is presented. Cement-bentonite interaction is, however discussed and studied elsewhere according to the plans presented in Posiva 2009a.

Iron-bentonite interaction

Due to the possible use of steel compounds in the repository the availability of iron may be increased in the repository conditions. This is also possible in case of canister failure which would open access to the cast iron insert and possibly launch interaction between bentonite buffer and iron. This process may also cause cementation in case of precipitation of iron-oxide (Wersin & Snellman 2008). However this applies for oxic conditions that are not expected in the repository. Alteration due to repleacement of Al in montmorillonite octahedral layer for Fe could lead to transformation of montmorillonite to iron rich clays that may have differing swelling behaviour (Miller & Marcos 2007). Actions planned to address iron-bentonite interaction related issues has been described in Posiva 2009a.

3.4 Interlayer cation exchange: Na-bentonite – Ca-bentonite

The exchangeable cation composition has an effect on the properties of bentonite. The following section discusses the cation exchange expected to occur in the disposal hole, i.e. Na- type bentonite transformation to Ca-bentonite.

Main cation exchange reactions taking place in montmorillonite are:

$NaX + K^+ \leftrightarrow KX + Na^+$
$2NaX + Ca^{2+} \leftrightarrow CaX_2 + 2Na^+$
$2NaX + Mg^{2+} \leftrightarrow MgX_2 + 2Na^+$

Cation exchange studies have shown that, under a given set of conditions, various cations are not equally replaceable and do not have the same replacing power. In principle, the following law of replacement power applies (e.g. Pusch 2001):

$Li < Na < K < Ca < Mg < NH_4$,

This implies preferential replacement of e.g. Na^+ by Ca^{2+} than vice versa.

The replacement series given above is not a single universal one. In experimental studies it has been observed that replaceability varies depending on the experimental conditions, the cations involved, and the kind of smectite mineral and it is controlled by a considerable number of factors as discussed below:

1) Ion concentration

The replacement of Ca^{2+} and Mg^{2+} by Na^+ in montmorillonite increases as the concentration of Na^+ in the solution increases (as expected since cation exchange is a stoichiometric reaction and the laws of mass action holds, implying that an increased concentration of the replacing cation causes greater exchange by that action) (Pusch 2001).

The cation exchange equilibrium is described by the selectivity coefficient K_s. Selectivity varies with electrolyte concentration, the more diluted the solutions, the greater the selectivity. Selectivity order of different cations is defined by size of hydration diameter.

2) Cation type and valence

The effects of concentration depend on the kind of cation that is being replaced and also on the valence of the cation. The complexity of cation exchange processes is indicated by the fact that with cations of about similar replacing power and the same valence, dilution has a relatively small effect on the exchange, while with cations of different replacing power and different valence, for example Na^+ vs. Ca^{2+}, dilution produces significant differences in exchange. Na^+ vs. Ca^{2+} represents a particularly important case of competition (Grim 1967). Thus, it is a well known fact that as the amount of exchangeable calcium on the clay mineral becomes less, it becomes more and more difficult to release. Sodium, on the other hand, tends to become easier to release as the degree of saturation with sodium ions becomes less. Magnesium and potassium are not affected by the degree of saturation to the same extent as calcium and sodium, which is believed to be caused by the charge and size conditions.

3) The nature of the anions in replacing solutions

The exchangeability of Na^+ in montmorillonite by Ca^{2+} depends on whether there is dissolved calcium hydroxide or calcium chloride in the solution. The most important factor that determines the replaceability power of cations is the valence. The higher the valence of the cation the higher the replacing power except for hydrogen, which behaves like a divalent or trivalent ion.

For ions of the same valence, the replacing power increases with the size of the ion, meaning that smaller ions are less tightly held than the larger ions. Potassium is an exception, which is explained by the fact that its ionic diameter 2.66 Å is about the same as the diameter of the cavity in the oxygen layer, so that the potassium ion can just fit into one of these cavities. As a consequence, the potassium ion is rather difficult to replace.

However, it is commonly stated that it is the size of the hydrated ion, rather than the size of the non-hydrated ion, that controls the replaceability. Thus, it appears that for ions of equal valence, those which are least hydrated have the greatest energy of replacement and are the most difficult to displace when present upon the clay (Grim 1967).

The selectivity for calcium in montmorillonite is dependent on the strength of the electrolyte. The selectivity for calcium increases when the strength of the electrolyte decreases (diluted electrolyte) as presented in Figure 3-10.

3.4.1 Cation exchange in the repository conditions

Olkiluoto groundwater at repository depth -420 m may be either saline Na-Ca-Cl type (observed at depth range -350 m to -470 m) or highly saline Ca-Na-Cl type (observed at depth range -410 m to -600 m) (Posiva 2009b). The interface between these two types mentioned above is very close to the repository level at -420 m. It should be noted that spatial variation may also occur withing the disposal area due to the variation in conductive fracture network in the Olkiluoto bedrock. Of the reference water types used in this study 'Brackish saline' is sampled at 465 m depth and represents the water at the repository depth in undisturbed conditions. Salinity increases with depth as well as the Ca/Na ratio of groundwater. Concentrations develop from 465 m (Brackish saline) to 498 m (Saline) to 741 m (Brine) as presented in and in Figure 3-11.

These concentrations will favour the cation exchange towards Ca-dominant composition. Another source of Ca in bentonite is from dissolution of the accessory minerals e.g. calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2\ H_2O$). In the current groundwater conditions and during the predicted groundwater changes in the long term, it is not expected that the cation exchange direction should be reversed.

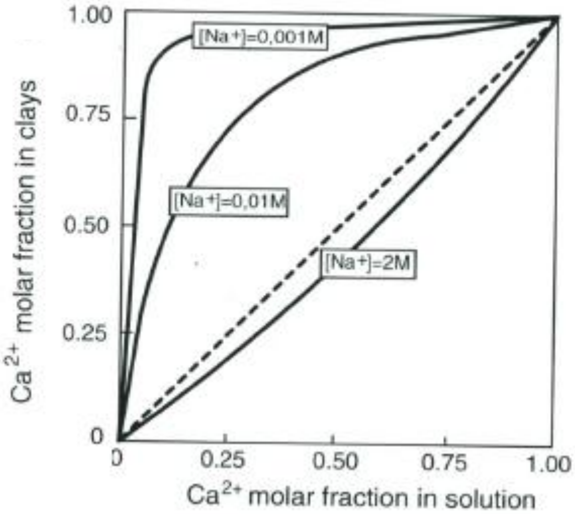


Figure 3-10. *Relationship between the Ca^{2+} contents in the exchanger (montmorillonite) and the solution. The more diluted the electrolyte, the greater the selectivity (K_s) for Ca^{2+} (Meunier 2005).*

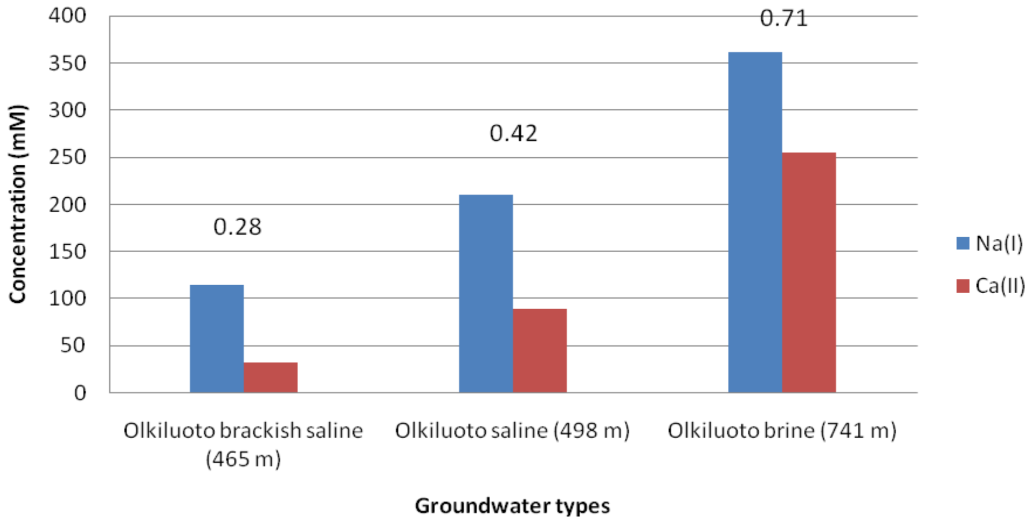


Figure 3-11. *Na and Ca concentrations in different groundwaters at Olkiluoto (sampling depths given in brackets). Ca/Na ratios are given above the colums. Data from Table 1-1.*

Muurinen & Lehikoinen (1999) have studied experimentally bentonite groundwater interaction. The results indicate that the cation exchange towards Ca- dominat composition takes place when bentonite interacts with Olkiluoto saline groundwater (Figure 3-12). The smallest value in the Figure 3-12 (B/W = 0.015) describes the situation where the bentonite buffer has been equilibrated with a large amount of groundwater after a long perioid of time. Information of the actual rate and extent of this process was not found in the literature based on the expected groundwater evolution information and hydrological conditions in the disposal hole.

3.4.2 Modelling work

Modelling of the natural bentonite weathering (Kuroishi mine in North Japan)

The long term alteration rate of Na-smectite to Ca-type in bentonite deposits in Kuroishi mine (Japan) have been evaluated by Ohe et al. (1998). Even though weathering is a different phenomenon than what is expected in the deep repository, Na depletion occurs also in this environment and replacing cations are Ca and Mg, while the level of K seems to be stable. Measured exchangeable cation compositions from the drill core profiles are presented in Figure 3-13.

Ohe et al. (1998) have calculated the migration of the reaction front in the water-saturated zone using simple analytical calculations. The results of these calculations indicate the average alteration rate of 0.17-25 cm/1000 years. Ohe et al. (1999) have reported similar results using cation diffusion convection modelling that indicate alteration rate of 4 cm/1000 years. These values are equivalent to the alteration rate value of 4 cm/1000 years independently obtained by geomorphological studies (Ohe et al. 1998). Concentration measurements of the groundwater samples indicate that the ion exchange equilibrium with Na and Ca has been attained at each level of the alteration zone.

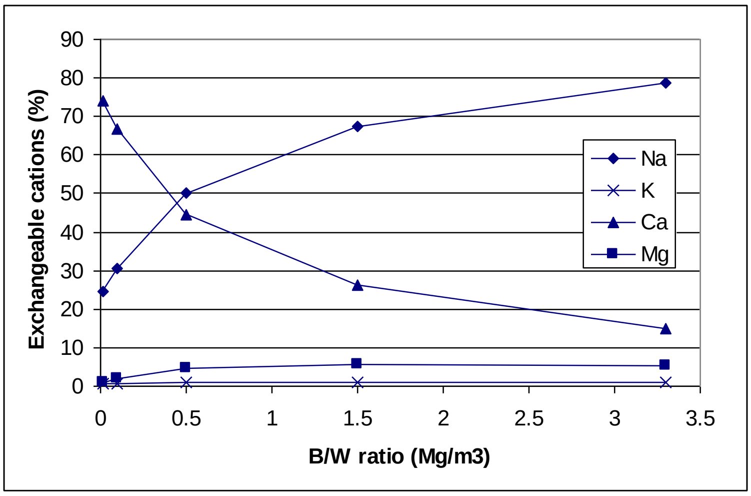


Figure 3-12. *Fraction of exchangeable cations in bentonite when MX-80 was equilibrated with saline Olkiluoto groundwater rich in calcium ions at B/W 0.015 to 1.5. The values at bentonite/water (B/W) ratio 3.3 represent the situation in MX-80 when it was saturated in 100 % relative humidity i.e. the initial state in bentonite (without addition of any salts) (Muurinen & Lehikoinen 1999)*

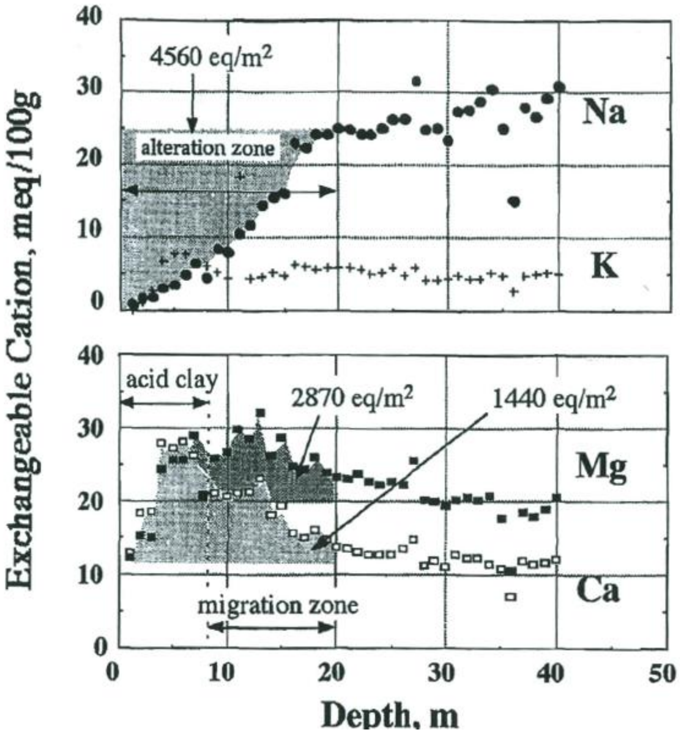


Figure 3-13. *Vertical profiles of exchangeable Na, K, Ca and Mg in the drilled core samples (Ohe et al. 1998).*

Bentonite seems to equilibrate relatively fast with the surrounding groundwater, at least concerning Na and Ca, but the penetration into the thick bentonite deposit is rather slow as indicated by the alteration rates (Ohe et al. 1998).

The results are relevant in the evaluation of model reliability as the model repeats what is observed in nature.

3.4.3 Ca- and Na-bentonites – A comparison

Exchangeable cations and their effect on water retention

One key rheological property of the montmorillonite in bentonite is its water retention capacity. Villar (2007) has studied water retention of compacted (natural state) FEBEX and MX-80 bentonites at different dry densities. Experiments were done at constant temperature of 20 ºC and at constant volume. Two methods were developed, the cell method and the sensor/block method, which gave consistent results. The results indicate that for most of the relative pressure range, the retention capacity of predominantly divalent (Ca and Mg) smectites is greater than that of sodic ones. This observation is consistent also with other published results e.g. Hall & Astill (1989), Dontsova et al. (2004), Caballero et al. (2004) and Saiyouri et al. (2004). Bentonite behaviour with respect to water adsorption is mainly controlled by exchangeable cations, which is not affected by varying accessory mineral compositions and textures of these natural materials (Villar 2007).

Villar (2007) has also concluded that the interlayer swelling is not hindered by external confinement (at least in the tested ranges of relative humidity RH and dry density) and that in the saturated conditions in the same environment there is a predominace of interlayer water.

The effect of temperature on the water retention properties have been studied by Tang & Cui (2005). They have observed that in case of MX-80 for given water content the suction decreases slightly with increasing temperature. These results are in accordance with studies on Boom clay (Romero et al. 2001, Bernier et al. 1997), French Fo-Ca7 bentonite (Olchitzky 2002), Kunigel V-1 bentonite (Kanno & Wakamatsu 1993) and Cabo de Gata bentonite (Villar 2000, Pintado 2002). Hence, one would expect that the temperature effect on the water retention behaviour of Na- and Ca- montmorillonites is similar as the behaviour of such a vast selection of bentonites and clays show similar results.

Rheological properties

Swelling pressure of bentonites has been studied by many authors by measuring pressure changes using oedometers in varying conditions. Karnland et al. (2006) have studied the effect of the initial dry density on the swelling pressure (Figure 3-14). Reference material MX-80 and purified and converted pure Na- and Ca- types are presented in the figure when subjected to changing salinities (NaCl or $CaCl_2$). In all cases at lower densities the swelling pressure is affected by the type of exchangeable cation, Ca exchanged type shows significantly lower values, but at higher initial densities the effect is rather small and reversed.

The exponential fit does obscure the real differences especially at the high end in Figure 3-14, in which practically no differences are seen above ~1500 kg/m^3. Therefore, the

MX-80 data and additional data from Milos bentonite (Deponit Ca-N) (Karnland et al. 2006) have been reproduced and presented on normal scale allowing direct comparison of sodium and calcium type bentonites, respectively. The lower densities have been shown in Figure 3-15 and higher densities in Figure 3-16. Also preliminary data from the studies made for MX-80 in Ca/Na (3:2) solution by Schatz & Martikainen (2010) are shown for comparison (Figure 3-16).

Observations made from the Figures 3-15 and 3-16:

- The Ca:Na (3:2) solution 70g/l (about 2 M) used in the swelling pressure tests on MX-80 by Schatz & Martikainen (in preparation) produce swelling pressure values close to those of salinity 3.0 M $CaCl_2$ or NaCl solutions used in Karnland et al. (2006) for both MX-80 and Deponit Ca-N.
- Quite few samples that have cation converted variants show the same initial density, slightly complicating the interpretation.
- Both Na and Ca cation exchanged bentonites show higher swelling pressure than the natural bentonite material at higher densities.

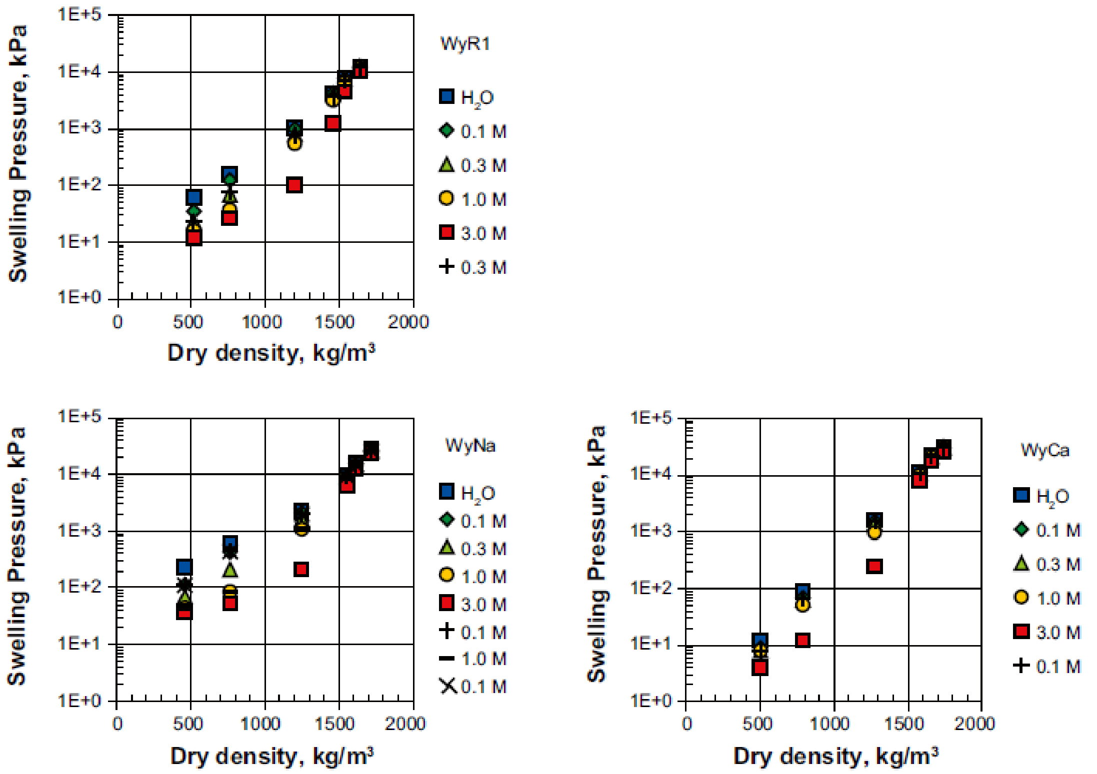


Figure 3-14. *Swelling pressure in the Wyoming MX-80 reference material WyR1 (upper) and the corresponding sodium WyNa (lower left) and calcium WyCa (lower right) converted and purified materials (i.e. montmorillonite). The legends show the NaCl concentrations in the test solutions in successive contact with the MxR1 and MxNa materials and* $CaCl_2$ *concentrations in the solutions in successive contact with the MxCa material. (Karnland et al. 2006.)*

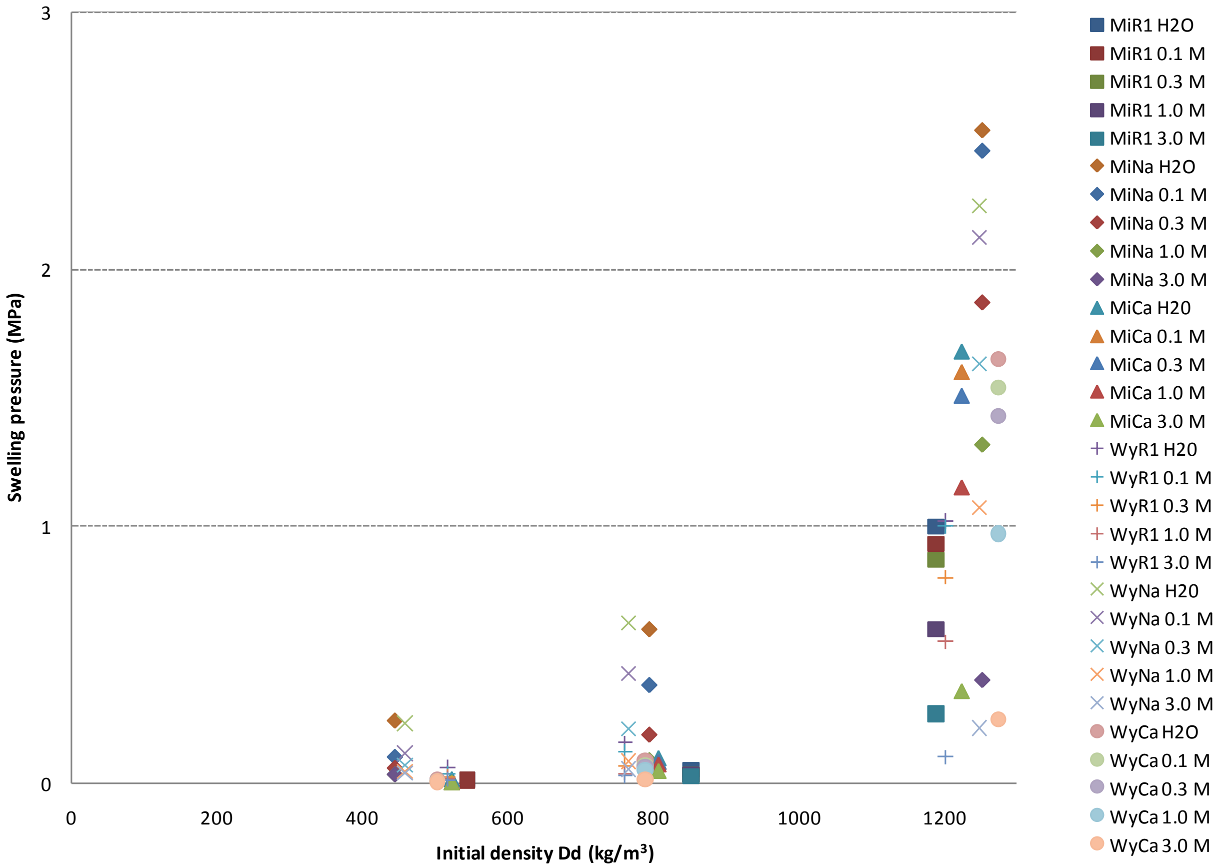


Figure 3-15. *The effect of dry density and salinity on the swelling pressure. Dry density range 0-1300 kg/m^3. Key: Milos, Deponit Ca-N (Mi), Wyoming MX-80 (Wy), material as received (R1), Na exchanged (Na), Ca exchanged (Ca). Solutions for Milos R1 and Ca exchanged varieties $CaCl_2$ and for Wyoming and Na exchanged varieties NaCl.*

The effect of highly alkaline solutions on the swelling pressures of MX-80 bentonite has been studied by Karnland et al. 2007. These studies were performed on the MX-80 and also Na- and Ca- exchanged variants. Sufficiently high pH >13.3 will reduce the swelling pressure of compacted bentonite as well as increase the CEC accompanied with silica release. No effect on swelling pressure and only minimal mineralogical/ chemical changes were observed at pH 12.4. No significant differences are observed between Na- and Ca-montmorillonite types.

Differences due to hydration capacity of monovalent and divalent exchangeable cations in smectites may lead to plasticity differences.

Plastic viscosity is observed to decrease with increasing Ca concentration (Elzea & Murray 1990) related to face-to-face contact increase and microstuctural changes (Brandenburg & Lagaly 1988).

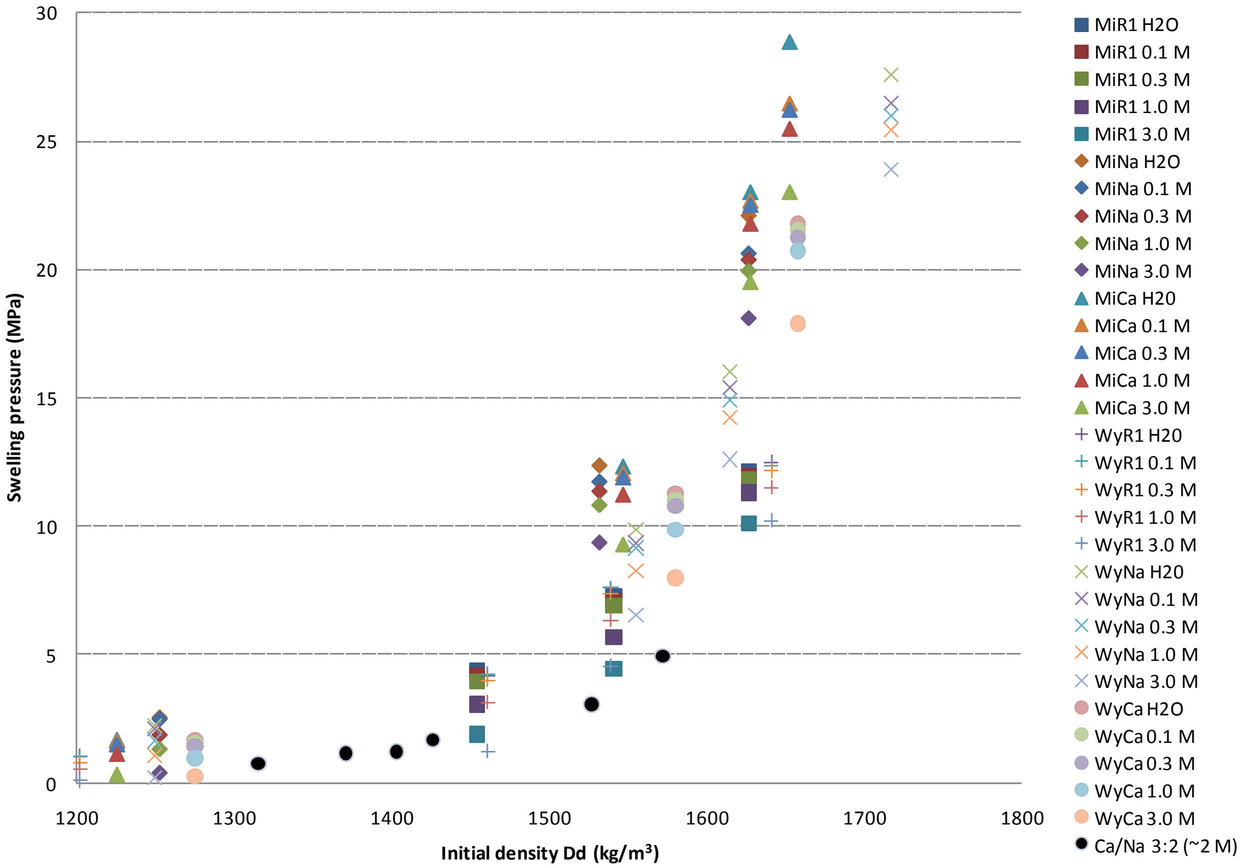


Figure 3-16. *The effect of dry density and salinity on the swelling pressure. Dry density range 1200-1800 kg/m*^{3}*. Key: Milos, Deponit Ca-N (Mi), Wyoming MX-80 (Wy), material as received (R1), Na exchanged (Na), Ca exchanged (Ca). Solutions for Milos R1 and Ca exchanged varieties CaCl2 and for Wyoming and Na exchanged varieties NaCl, except for MX-80 Ca/Na (mix solution Ca/Na is 3:2, 70g/l TDS) (Schatz & Martikainen 2010).*

Hydraulic conductivity

The effect of cation exchange on hydraulic conductivity is closely related with changes seen in swelling pressure (see above Figures 3-14, 3-15 and 3-16). In Figure 3-17 the hydraulic conductivities of MX-80 and Deponit Ca-N are presented for different dry densities (Karnland et al. 2006). Experiments were done for raw material (denoted R1) and cation exchanged varieties, both Na and Ca. The largest differences are seen at the lower densities (~<1500 kg/m^3). Hydraulic conductivity of Deponit Ca-N (MiR1) is slightly higher at ~1500-1600 kg/m^3 dry densities than that of MX-80 (WyR1). However, this difference becomes obvious only at low densities. For lower densities Ca-smectite becomes more conductive because of the lack of micro-structural continuity and coherence (Pusch 2006).

Cation exchange for sodium leads to higher conductivities at low densities for both materials, but at densities >1500 kg/m^3 the effect is reverse. The effect is similar also in case of Ca exchanged samples.

Based on the results discussed above (Karnland et al. 2006) the hydraulic conductivity is not affected by the cation exchange significantly at the expected buffer densities (1610 kg/m^3 for the buffer in KBS-3V, see Section 2.2.9).

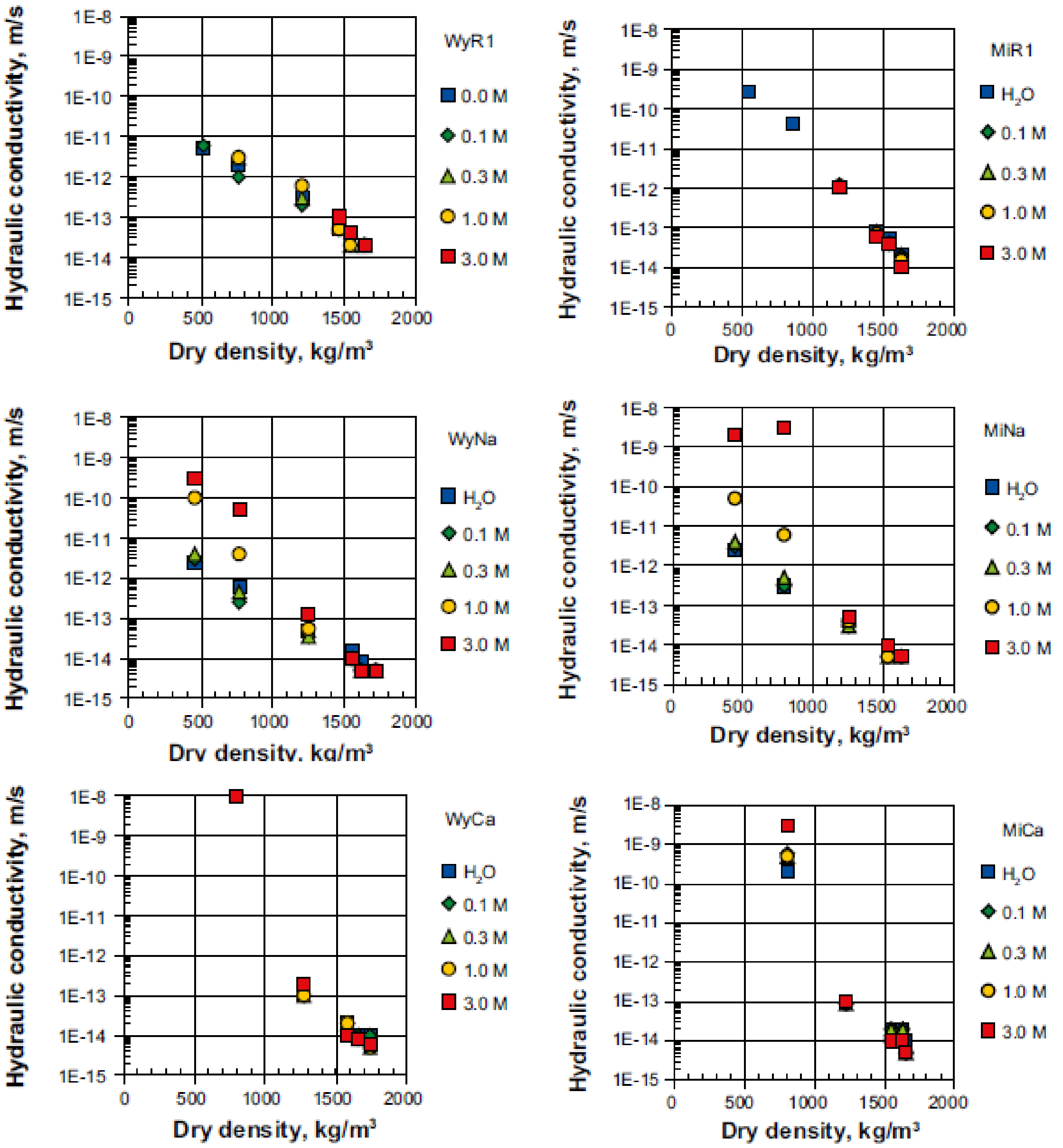


Figure 3-17. *Hydraulic conductivity in the Wyoming MX-80 reference material (left upper) and the corresponding sodium (left middle) and calcium (left bottom) exchanged and purified material (legends show the NaCl concentrations in the solutions successively in contact with the WyR1 and WyNa samples, and the $CaCl_2$ concentration in the test solutions successively in contact with WyCa samples) and in the Milos Deponit CA-N reference material (upper right) and the corresponding sodium (right middle) and calcium (right bottom) exchanged and purified material (right) (legends show the $CaCl_2$ concentrations in the test solutions successively in contact with the MiR1 and MiCa samples, and the NaCl concentrations in the test solutions successively in contact with the MiNa sample).*

Microstructural differences

The microstructure of bentonites is not very well known. Some studies however are available on the subject. The dominating cation type in the exchanger affects for example the incorporation of chloride in the interlayer space. As observed by Muurinen (2009) Ca type bentonite can incorporate more Cl than Na-types.

Demixing of cations affects the microstructure of smectite in Na/Ca-smectite systems (Laird 2006). Na ions will tend to be segregated in certain interlayers and Ca ions in others. If the clay is then shaken, the quasicrystals will break apart along the interlayers dominated by Na. This could have an effect on the mechanical strength of the buffer in case of sudden movements in the geosphere.

It is a well known fact that Na-smectites are prone to delamination in distilled water, while Ca-smectites do not spontaneously delaminate (see also colloid formation below).

Swelling capability of smectites is reduced when the mineral is subjected to intensive drying (Tessier 1990). Intensive drying decreases the swelling ability by reorganising the particles. The stacking order (c-direction) increases with the drying intensity or with the drying-wetting (D/W) cycle repeat (Mamy & Gautier 1976, Eberl et al. 1986) i.e. increasing preferation for face-to-face contacts (see also Section 3.2.1 on the D/W effects on illitisation). Ionic saturation affects the particle arrangement as well. Hysteresis effect is lower for Na^+ or K^+ saturated clays and much higher for Ca^{2+} or Mg^{2+} saturated clays (Meunier 2005). This leads to different stacking arrangements and wall thicknesses in polygonal network (Figure 3-18).

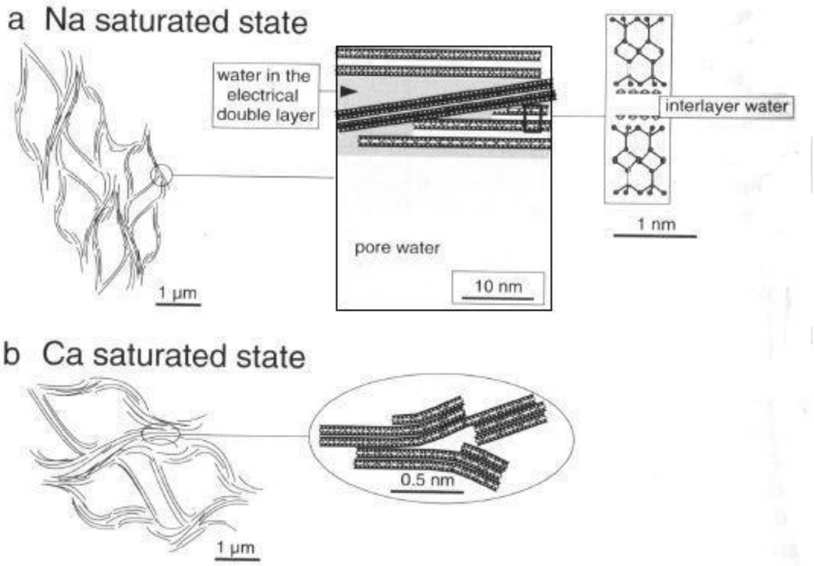


Figure 3-18. *Effect of ionic saturation on the arrangement of smectite particles. a) Water saturated Na-smectite is composed of layers with two water layers. Crystallites are more or less disorderly stacked (tactoids), forming relatively thin walls of a polygonal network that traps the pore water. b) Ca-smectite forms a polygonal network of greater size, quasicrystals are thicker and are more coherently stacked. According to Meunier (2005).*

Colloid formation and erosion

Exchangeable cations affect colloid formation and their stability. Na-montmorillonite is more prone to colloid release than Ca-montmorillonite (SKB 2006, table 2-18). Dispersion of the buffer material may occur in the fractures at the walls of the disposal hole due to free swelling. Free swelling ability is dependent on the exchangeable cation composition. Figure 3-19 illustrates the free swelling tests done using Wyoming bentonite at varying Ca/Na compositions (also monocationic) in deionised water (Neretnieks et al. 2009). Pure Na-benonite swells the most but a noteworthy observation is that Wyoming bentonite with 60/40 Ca/Na ratio swells almost as well and even when the Ca/Na ratio is 80/20 swelling is still notable. Only 100/0 Ca/Na ratio in this experiment shows no swelling at all. This is an important observation as in natural waters, such as in Olkiluoto, the possibility of formation of monocationic Ca-bentonite is unrealistic.

Separation of the montmorillonite layers will lead eventually to the dispersion of individual mineral layers or small aggregates. Maximum free swelling is dependent on the salinity of groundwater; at low salt concentrations colloid release may be expected to occur due to large enough distances between the individual layers in montmorillonite buffer. This process is also dependent on the exchangeable cation composition. In Figure 3-20 basal spacings for different smectites are presented as a function of salinity. Ca smectite has a maximum basal spacing of <2 nm, which is quite constant at salinities <3 (eq/l). At higher salinities basal spacing of Ca-smectite drops down to ~1.5 nm. These spacings represent four and two pseudo-layers of water in the interlayer space. On the contrary to the maximum basal spacing of Ca-type smectite, Na- and K- type smectites may reach infinite values at low salt concentration (Figure 3-20, Lagaly & Fahn 1983).

Dispersion is controlled by the critical coagulation concentration (CCC) that depends on the properties of the clay and chemical environment. CCC can be used as a conservative limit for colloid release. In general values below the given CCC allow colloidal transport, assuming that colloids are stable. According to SKB (2004) the groundwater salinity has to be at least 0.1 M with respect to sodium (monovalent) or at least 0.001 M to calcium (divalent) in order to neglect the colloid formation. In the recent studies it is concluded (Neretnieks et al. 2009) that when the pore waters contain more than about 50 mM monovalent cations the smectite gel is cohesive and does not release individual particles by Brownian motion. For calcium only about 1 mM is needed to generate a cohesive gel.

Smectite gels with practically only divalent charge compensating ions (calcium) behave differently from gels with monovalent ions. Calcium gels will not separate the smectite into individual sheets as sodium gels do. The sheets are held together in larger particles, such as stacks or more complex structures. These larger particles are not seen to separate from the gel by Brownian motion in an upward gravity field. It is not known if the gel formed of these larger particles is cohesive in the sense that particles would not be released in a downward facing gravity field. However, more than about 90 % of the charge compensating ions must be calcium in calcium/sodium clays for these conditions to prevail. With less than this amount of calcium the smectite behaves more like a pure sodium mineral (Neretnieks et al. 2009).

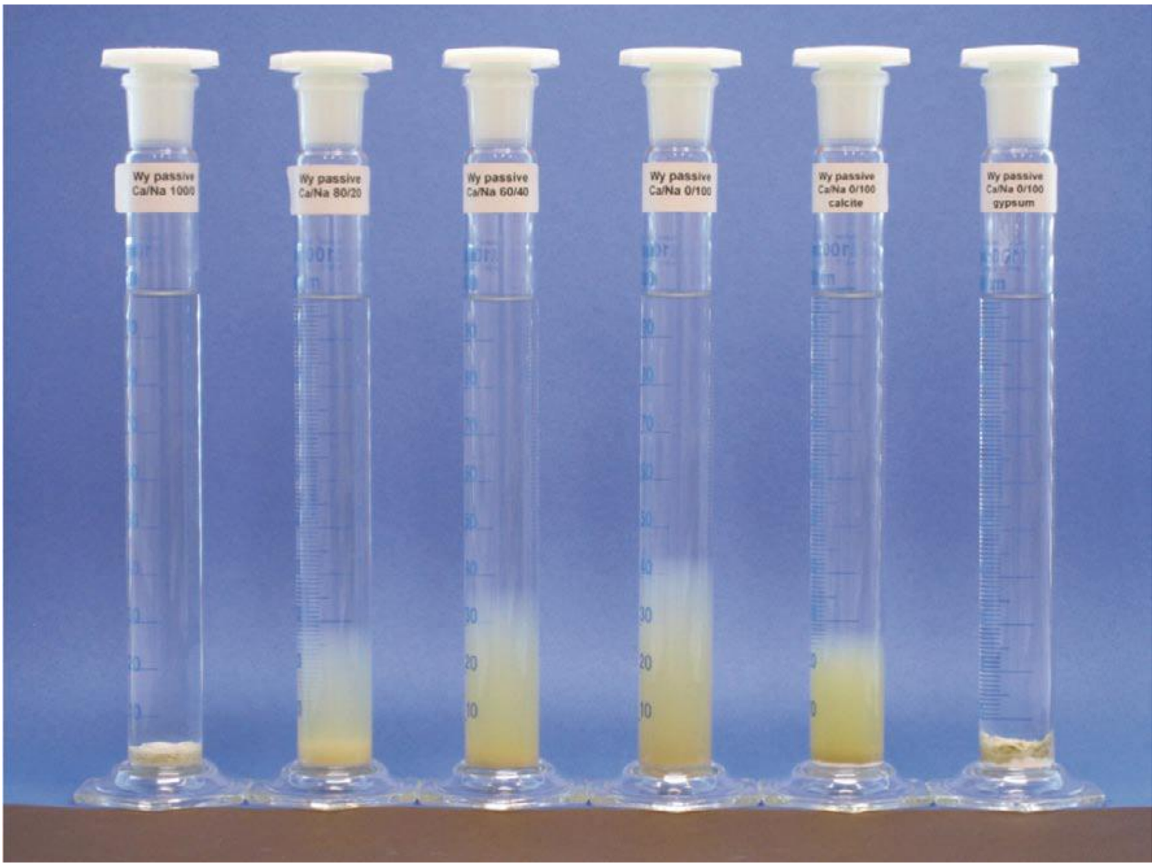


Figure 3-19. *Free swelling tests after 165 days with 0.5 grams of homoionic smectite prepared to contain the following* Ca^{2+}/Na^{+} *ratios: 100/0 (left), 80/20 (second from left), 60/40 (third from left), 0/100 (third from right), 0/100 mixed with calcite (second from right), 0/100 mixed with gypsum (right) (Neretnieks et al. 2009).*

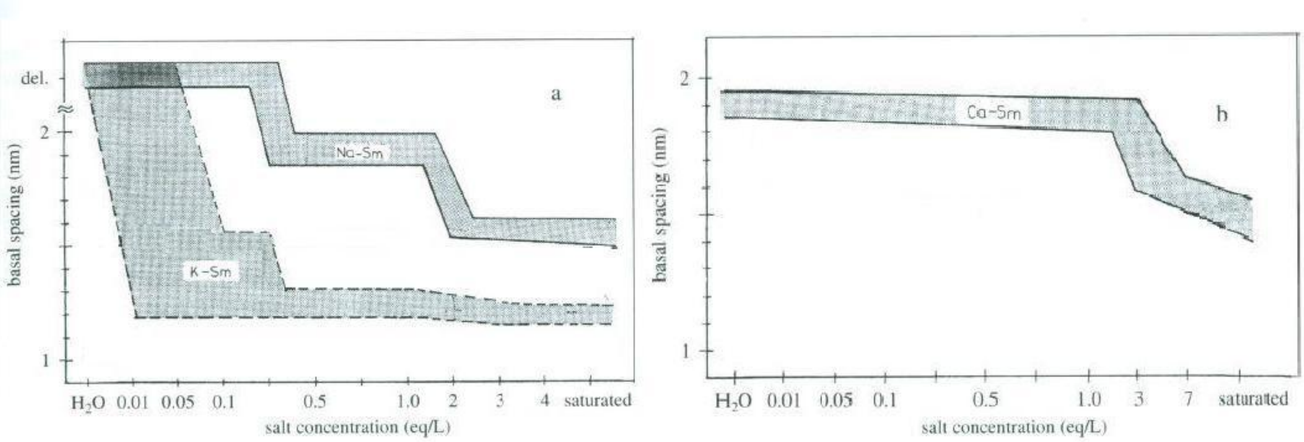


Figure 3-20. *Basal spacings of smectites as a function of salt concentration; note the different scales. Sodium smectite and NaCl (Na-Sm), potassium smectite and KCl (K-Sm) and calcium smectite and* $CaCl_2$ *(Ca-Sm), del = delamination (Modified from Lagaly & Fahn 1983).*

In Olkiluoto the groundwaters well exceed the salinity level given above. However, during glaciation diluted groundwaters may have access down to repository level. In this case the stability of the colloidal systems may become important. A recent study by García-García (2007) shows that the stability of colloidal systems depends on the ionic strength, pH, the $CaCl_2$ and NaCl concentrations, and the temperature. MX-80 bentonite was used in the experiments. CCC values obtained in this study give a value of 0.70 ±0.05 for Na-montmorillonite (cation exchanged) and a value of 0.0062 ±0.0005 for Ca-montmorillonite (cation exchanged; García-García et al. 2007). These values are higher than SKB's values given above and other values given in the literature (Frey & Lagaly 1978, Tombácz et al. 1989, Chheda et al. 1992, Lagaly & Ziesmer 2003). SKB (2004) has given CCC value for MX-80 material, but no further information is given on the methodology. One disadvantage of the García-García et al. (2007) study is that no MX-80 was analysed "as received", all samples were cation exchanged for the analysis. Stable conditions for colloids and subsequent colloidal transport is favoured by low ionic strength, increasing pH, increasing temperature at pH >4 but < 10 (at pH >10 increasing temperature stabilizes suspension, García-García 2007) Also, montmorillonite suspensions were observed to be more sensitive to $CaCl_2$ concentration than NaCl concentration, CCC value obtained for $CaCl_2$ was two orders of magnitude lower than that for NaCl.

Based on the results presented in above sections, cation exchange of Ca for Na expected to occur should favour the long-term stability of bentonite. This concerns especially glacial conditions and diluted groundwaters.

3.5 Summary of mineralogical changes and significance in Olkiluoto case

Mineral alteration and cation exchange processes have to be evaluated on the basis of the possible effects on the long-term performance of the buffer as set by the performance targets (see Section 1.2). The conditions in the disposal hole may change from saline (maximum limit <100 g/l TDS) to dilute glacial waters (<1 g/l TDS) leading inevitably to situations where the buffer will be in disequilibrium with the surrounding water. Minerals occur in nature also in disequilibrium and thus the main task is to evaluate what is the actual potential for the mineralogical alteration controlled by the thermodynamic and kinetic contraints. In other words, the alteration rate is the most important parameter in the long term stability assessment. Modification of the interlayer cation composition is inevitable, as the groundwater composition will favour the exchange. The rate and extent of cation exchange during the evolution of the repository are still to be evaluated.

Illitisation process and cementation are related to the silica mobility and the availability of K^+ as well as temperature. In the Olkiluoto repository conditions silica may be released into groundwater from illite/smectite conversion reaction (requires the source of K^+), from dissolution of smectite or other minerals (from host rock, buffer bentonite, backfill material) and from cement based construction materials (cementitious and silica based grouting materials, concrete) and it may function as cementing agent in bentonite if the conditions are favourable for precipitation. Silica may be the most potential cementing agent in repository conditions. The amount and probability of silica release will be estimated in the future evaluations. Similar evaluation is to be made concerning the availability of K^+ from the backfill, both deposition tunnel backfill and main tunnel backfill (both clay minerals and the crushed rock) and from cementitious materials. The expected evolution of the natural hydrogeochemical conditions in Olkiluoto may not favour illitisation and further cementation of bentonite based on the limited concentration of potassium in the groundwater and low temperatures. Modelling results by Karnland & Birgersson (2006) show that the illitisation of smectite in repository conditions (same K^+ availability in groundwater) at low temperature (<75 °C for 10^6) years is unlikely.

As mentioned above, the availability of K^+ is limited in Olkiluoto groundwater. Groundwater concentrations of potassium falls in the range of 0.20 – 0.49 mM (mmol/dm^3) depending on the groundwater type, though it increases with depth (Table 1-1). Additional sources of K^+ in the repository are for instance:

- K-bearing minerals of bentonite or other clay minerals used in the backfill (Pellegrini et al. 1999, Cama et al. 2000)
- K-bearing crushed rock component of the backfill material (Korkiala-Tanttu 2009)
- Cementitious construction materials (e.g. Vuorinen et al. 2004)

The potential amount of K-leaching from foreign materials is to be evaluated when the needed information on the design is available.

Alkaline pH conditions accelerate illitisation process at least at pH>13. The effect of slightly lower values is somewhat unclear. Elevated pH affects also mineral transformation other than illitisation. Zeolite formation is suggested to occur already at pH<11 which is similar to the cement leachates (pH 10.5-11.5) possibly expected in the repository. However, again there is no clear understanding how these leachates will dilute in the repository environment and how long time periods this event would possibly have an effect. Information on the total amount and distribution of cementitious materials that will be used and left permanently in the final closed repository will be gathered as the design processes and construction proceed. Current closure principles are to be reported in 2010. Further studies are necessary to evaluate alkalinity in relation to the Si and K releases. Alkalinity effects are being studied within the cement-bentonite interaction studies that are not discussed here in detail.

Illitisation is generally considered to be a too slow process to occur in the expected repository conditions during the relevant time scales; however, experimental results show that other mineral transformation reactions could take place more likely. Some studies indicate that the main process affecting bentonite transformation may not be illitisation or related cementation, but beidellitization may occur (see Section 3.1) that may be accompanied with saponite formation. It has also been emphasised that the diagenetic series are not necessarily reproduced in the laboratory experiments done with purified montmorillonite. Saponitization is not neccessarily harmful for the buffer behaviour as it is also a swelling clay and has been considered suitable for buffer material in preliminary studies (Pusch 1999a). In the same study beidellite is not considered suitable as buffer material. The current available data suggests saponitization and beidellitization at high temperatures (> 375 °C). Also the experimental set up does not reflect the composition of the buffer (MX-80), but purified montmorillonite-beidellite system. Thus, this may not be directly adopted in the buffer evaluation. However, the differences in experimental set ups vs. natural processes in bentonties should be acknowledged.

Illtisation has been considered to be dependent on the availability of water, and thus retarded in dry conditions. However, it has been considered that also water vapour could act in the illitisation/cementation process (Pusch & Kasbohm 2002) (see also Section 3.2.2). The disposal hole may be dry for long periods of time and saturation times of the disposal holes may vary considerably depending on their location in the repository. Differient saturation conditions have not been studied in relation to mineral transformation in the literature in detail.

Salinity affects also smectite stability by causing loss of swelling ability. This has been observed in brines (decade higher salinities that those of Olkiluoto brines) and has been suggested to be related to kaolinitisation and pyrophyllitisation rather than illitisation. In highly saline conditions also a swelling pressure collapse is observed, but the implications for lower salinities (relevant in Olkiluoto) are unclear. Also at lower salinities swelling pressure decreases have been observed, especially in case of FEBEX Ca-montmorillonite already 115 g/L concentration of NaCl causes swelling pressure decrease to half of the initial at dry density 1.65 kg/m^3. On the other hand the preliminary results conducted with 3:2 (Ca/Na) solutions for MX-80 suggest that the presence of $CaCl_2$ would lead to more pronounced swelling pressure decrease than what is observed in experiments using NaCl and MX-80.

It seems that cation exchange towards the more Ca- dominated composition in montmorillonite interlayer composition will occur in the expected groundwater conditions in the deep repository. The rate of cation exchange (Na type to Ca type) according to natural (weathering) bentonite deposit in Japan (Section 3.2.3) has been estimated to be 4 cm/1000 years. The density of the formation was not given, which causes difficulties in the interpretation of the results. However, the exchangeable cation composition of bentonite has been observed to be in equilibration with the groundwater at each sampled alteration level in relation to Na and Ca, indicating fast equilibration, but slow penetration of the surficial water. An open question is how much the saturation process alone will change the exchangeable cation composition? Very little data was found on the rate of the cation exchange processes in varying hydrological conditions (i.e. w/r ratios, temperature, water composition etc.). The exchange process may lead to demixing of cations that may cause segregation of Na cations to individual layers that may decrease the mechanical strength of the buffer. The following can be summarised from the literature reviewed aiming at comparing Ca- and Na- bentonites (see also Section 3.3):

- The water retention capacity of Ca-bentonites is greater that that of sodic ones and the water adsorption is mainly controlled by the exchangeable cation composition (rather than varying accessory mineral composition or temperature for example).
- Anion incorporation to the interlayer space of montmorillonite is more extensive for divalent cations than for monovalent ones, i.e. higher for Ca-type.
- Na-montmorillonite is proner to groundwater dilution and consequently to erosion during glacial melting than Ca-montmorillonite. In glacial conditions where diluted water may occur Ca-type would be preferred due to sodium montmorillonite’s

infinite swelling and as colloids are released more easily from Na-bentonite than Ca-bentonite.

- Monocationic composition causes increase in swelling pressure for both Na and Ca types, but it seems that the 3:2 Ca/Na solution (Olkiluoto 70 g/l salinity) leads to a slight loss of swelling pressure compared to 1M-3M NaCl /$CaCl_2$ solutions at high densities. Is should be noted that experiments were preliminary and more data is needed before final conclusions can be drawn.
- Alkalinity affects bentonite behaviour, but no significant differences were found between sodium and calcium types.
- Experimental results show that Na-montmorillonite is more easily dissolved at high pH >13 especially at elevated temperatures (>80 °C) and at high solid/liquid ratios.
- Cation composition affects the hydraulic conductivity of the buffer but this effect is not significant considering the buffer performace.
- It is apparent that monocationic montmorillonites behave differently from natural benonites with mixed exchangeable cation composition in relation to e.g. swelling pressure development and free swelling. This important to notice when using the experimental data in the long-term safety assessment of the buffer.

4 NATURAL OCCURRENCES SUPPORTING THE LONG-TERM STABILITY OF BENTONITE BUFFER

In the following chapter selected studies of natural occurrences of bentonite and smectites that could serve as analogues for the long-term buffer stability in the deep repository are described. The occurrences are presented in the order that would best follow the expected conditions i.e. occurrences displaying thermal short term effects are presented first and occurrences related to the slower and increasingly chemically induced changes have been introduced later on. The last two natural occurrences concern the deposits where the reference and alternative buffer materials come from.

The studies of natural ocurrences of bentonite that could serve as analogues for bentonite cementation (Sections 4.1-4.4) have been selected using some prerequisities:

- The occurrence should be a bentonite deposit.
- The smectite content should be high.
- Thermal source (intrusion, vein, dome) should exist in the vicinity of bentonite.
- Observations about possible cementation and hydrothermal effects in bentonite should be reported.

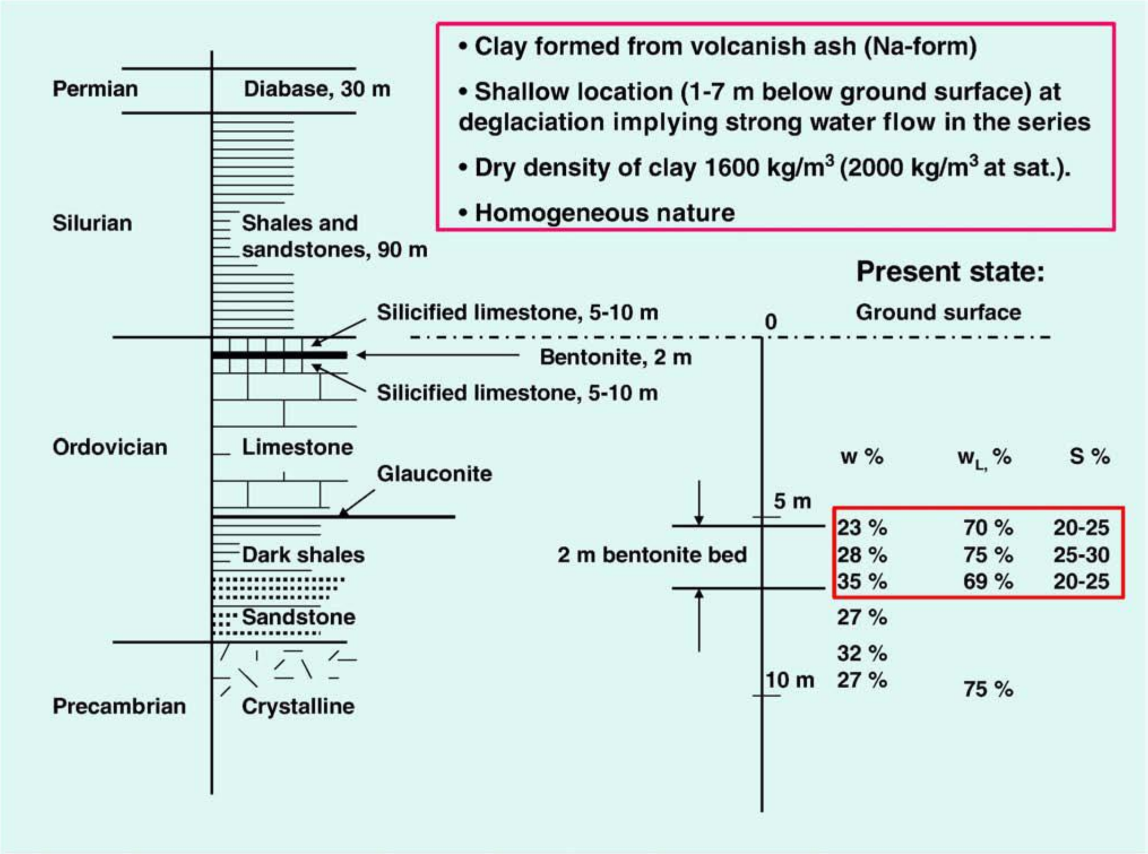
These bentonite formations are considered as analogous of the conditions in the repository, because they offer applicable information on the thermal and hydrothermal effects on bentonite during relatively long time periods (i.e. millions of years), which cannot be simulated in laboratory conditions.

Other chemical stability related smectite and/or bentonite occurrences have been selected on the basis of the existing porewater/groundwater data.

4.1 Kinnekulle (Sweden)

According to Pusch et al. (1998) Ordovician Kinnekulle bentonite formation is located about 150 km from Gothenburg to the northeast in southern Sweden (Figure 4-1). The Permian age diabase forms the top of the formation, which is about 200 m thick (Figure 4-2). Below the diabase, there is a series of shales, limestones and sandstones, which are deposited on the crystalline basement. The bentonite layers are below the diabase at the depth of 95 m (the distance between diabase and bentonite). The thickness of the bentonite layer varies between 2.5 m and 0.1 m (Pusch et al. 1998, 2009). The volcanic ash (rhyolitic or dacitic), from which the bentonite has been formed, was deposited into the seawater about 450 Ma ago (Pusch et al. 1998) on top of calcareous sediments and muds. After this, several hundred meters thick series of marine sediments was deposited on top of the ash causing consolidation at a pressure of 5–10 MPa. About 300 Ma ago a basaltic magma moved through the sediment series and penetrated laterally into it forming a several meters thick layer (Pusch et al. 1998, 2009) that heated the sediment series causing illitisation and silicification of bentonite. Part of the diabase layer has been later removed by Prequaternary erosion and Quaternary glaciations. The maximum pressure has been about 20 - 30 MPa during the Quaternary (Pusch et al. 1987, 1998). According to Pusch et al. (1987, 1998) the pressure, caused by the Quaternary glaciations, decreased the water content of about 15 - 20 %. Present water content is 22-35 %. Nowadays the overburden causes a pressure of about 100 kPa (Pusch et al. 1987). There is no information about the temperature conditions before intrusion.

Figure 4-1. *Location of Kinnekulle bentonite formation in southern Sweden.*



- Clay formed from volcanish ash (Na-form)
- Shallow location (1-7 m below ground surface) at deglaciation implying strong water flow in the series
- Dry density of clay 1600 kg/m^3 (2000 kg/m^3 at sat.).
- Homogeneous nature

Figure 4-2. *The sediment strata of Kinnekulle formation (modified from Pusch 1983).*

The temperature evolution following the intrusion has been studied and presented in various reports at different level of detail, as listed below:

- The initial temperature of the magma has been estimated to have been about 1100 ºC (Pusch 1983, Pusch et al. 1998).
- Duration of elevated temperatures (110-160 ºC) on the Kinnekulle bentonite has been assumed to been about 1 000 years (Pusch 1983, Pusch et al. 1987, 1998).
- The temperature of the bentonite has been about 140 ºC for about 200 years after the intrusion and it has stayed above 100 ºC for about 600 years. After 1000 years from the intrusion the temperature has been 60-90 ºC and 30-60 ºC during the subsequent 1000 years. The temperature evolution of bentonite is shown in Figure 4-3 (Pusch et al. 1998).
- Temperature gradient has been 5 ºC/m 70 years after the intrusion and 1 ºC/m during the next 400 years (Pusch et al. 1998).

In the Kinnekulle bentonite silica is abundant (30-40 %) in several forms: as quartz, cristobalite and amorphous silica precipitated on the flaky minerals and on smectite stacks (Pusch et al. 1987, 1998). According to Pusch et al. (1998) about 0.5 % of the total mineral content is amorphous silica. The clay fraction forms about 35-40 % of solid phase and consists of montmorillonite, illite and mixed layer minerals (Pusch et al. 1987, 1998). The dominant clay minerals are illite and smectite. Illite content varies in the bentonite layers; in the uppermost and lowermost parts the illite content is the highest, which indicates that illitisation has begun from these parts (potassium source from the most abundant surrounding rock). According to Pusch et al. (2009) the bentonite contains about 25 % of intact montmorillonite. Very small microstructural silica nodules have been observed in the edges of dense montmorillonite stacks (Pusch et al 1987). Also calcite precipitation, in a form of filling in macroscopic fissures, is present. According to Pusch et al. (1987, 1998) in mineral fraction smaller than 1 μm the quartz content was the highest near the interface of bentonite (5-8 %) and surrounding rock and the smallest near the centre of the bentonite layer (3 %).

According to swelling pressure tests, the bentonite, which occur near the bentonite/adjacent rock-interface, the swelling pressures were lower than the pressures of samples taken from the central part of the bentonite layer. This has been assumed to indicate the highest cementation degree in parts close at the bentonite and surrounding rock interface reflecting commonly observed pattern seen in bentonites. I/S rations change from 0.65 (close to the interface) to 0.45 (at central parts) corresponding to 8 wt. % and 25 wt. % smectite, respectively (Pusch et al. 1998).

The shear strength values of Kinnekulle bentonite were high; the measured shear strengths were about twice the strength of MX-80 clay with the same densities (Table 4-1, Pusch et al. 1998). According to Pusch et al. (1987, 1998) the stress/time curves possibly indicated microstructural breakdowns in the form of successively fractured cementation bonds. The bentonite sustained a rather large strain before failure. This indicates that only a part of the strength producing components caused by cementing bonds was mobilized initially. According to Pusch et al. (2009) the bentonite has lost its original ductile nature and it has become brittle because of silica precipitation.

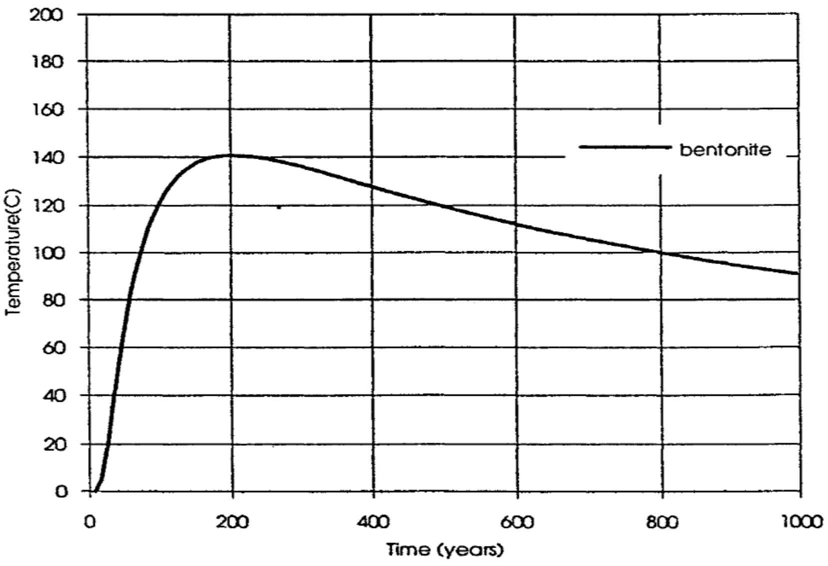


Figure 4-3. *The temperature evolution of Kinnekulle bentonite formation after the magma penetrated into the sediment (Pusch et al. 1998).*

Table 4-1. *The swelling pressures (Muller-Vonmoos et al. 1994), shear strength (Pusch et al. 1987) and quartz contents of samples taken from Kinnekulle bentonite (Pusch et al. 1998).*

Sample taken from	**Swelling pressure [MPa] / density at water saturation [kg/m^3]**	**Shear strength [KPa] / density at water saturation [kg/m^3]**	**Quartz content [%]**
Uppermost part	3.8 / 2100		6
Central part	15 / 2100		3
Unknown		300 KPa / 1850	

Several features, which indicate thermal effects and cementation, have been observed in Kinnekulle bentonite:

- Precipitated silica was observed by SEM (Scanning Electron Microscopy) on the rock forming minerals and on the smectite stacks (Pusch et al. 1998).
- Calcite precipitations in fissures (Pusch et al. 1987).
- Quartz, illite and smectite contents vary within bentonite layers (Pusch et al. 1987, 1998).
- The swelling pressure tests indicated that some samples had significantly lower swelling pressure than others (Pusch et al. 1998). The samples in which the swelling pressure was low the quartz content was higher. This high quartz content in some samples may indicate quartz precipitation.
- The stress/time values of the some samples measured by shear box were quite irregular and discontinuous (Pusch et al. 1998). This can be explained by microstructural breakdown of successively fractured cementation bonds.
- Bentonite has lost its original ductile nature and it has become brittle because of silica precipitation (Pusch et al. 2009).

Even though the thermal source is above the formation, the most extensive cementation in bentonite is observed at the bentonite/host rock interface, also below. This means that the K^+ source in the surrounding rocks has played a major role in the cementation process supporting the conditions in Olkiluoto where K^+ source could be limited. It should be noted that 25 % intact montmorillonite is not enough to maintain the ductile nature of bentonite. Calcite precipitation is partly responsible of the cementation but the source is available from the adjacent limestones. In Olkiluoto such conditions are not available.

4.2 Busachi (Sardinia)

The Busachi bentonite is located in central Sardinia (Figure 4-4). It formed during the Miocene in the following stages: In the Miocene a submarine fine mesosilic pyroclastic eruption took place. The hot glassy particles argillificated rapidly due to contact with sea water. The altered material was transported and sorted. Finally the smectite rich fraction precipitated into water. The rather soft Sardinia bentonite was covered by magma, which outflowed from several sites on the clay bed during the eruptive cycle (Figure 4-5). There are two possible assumptions about the deposition environment. The first is that the outflow has happened into the sea bottom at the depth of 10 m and the formed rhyolitic top bed has been 2 m thick. The temperature of the seawater has been assumed to be in the range of 30 ºC to 75 ºC. The other assumption is that the overflow occurred on the dry land formed of consolidated clay series with a water content of about 30 % (Pusch & Karnland 1988a).

The uppermost part of the bentonite has been affected by a short hydrothermal event based on the optical microscopy studies (the marks of recrystallization) (Pusch & Karnland 1988a).

There is no information about the temperature and pressure conditions in Busachi bentonite formation before the intrusion.

Pusch & Karnland (1988a) calculated the temperature conditions of the magma in three depositional situations (flow into water with temperature of 30 ºC; flow into water with temperature of 75 ºC and flow on to dry land) by using different heat conductivity values, heat capacities and applying FEM (Finite Element Method). The calculated temperatures as a function of depth in three different environments are given in Table 4-2. The calculated temperature evolution of the bentonite in dry crustal environment as a function of time is presented in Figure 4-6. The temperature drop was quite fast: the temperature was about 800 ºC for the first day after the intrusion, 500 ºC after the first week and about 200 ºC after two months. The pressure on the bentonite has not been significantly higher than the present pressure, which is about 50 – 200 kPa (Pusch & Karnland 1988a).

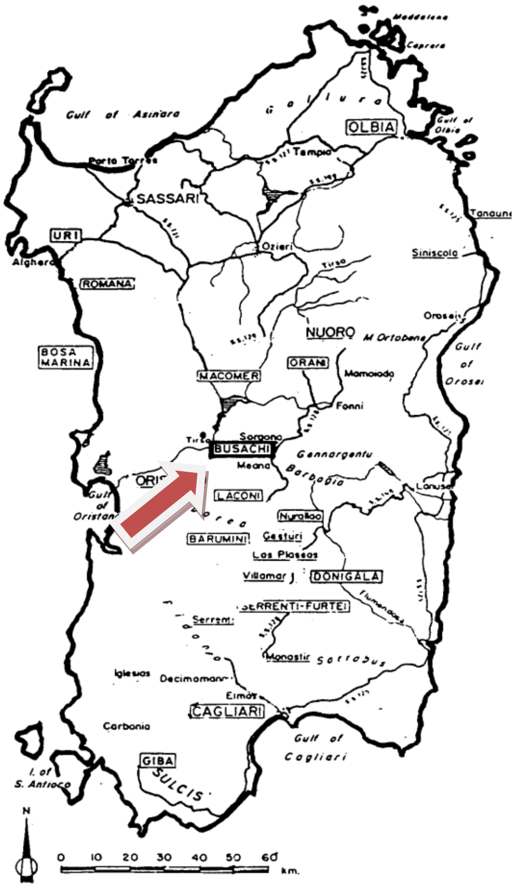


Figure 4-4. *Location of Busachi site (Pusch & Karnland 1988a).*

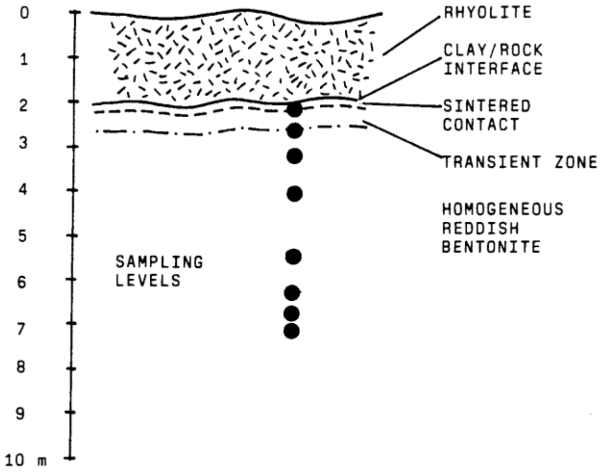


Figure 4-5. *Stratigraphy of the Busachi formation (Pusch & Karnland 1988a).*

Table 4-2. *Calculated maximum temperature (ºC) of the Busachi bentonite * (Pusch & Karnland 1988a).*

Depth below rock boundary [m]	Dry crust case	Wet case, 30 ºC	Wet case, 75 ºC
0.2	800	750	700
0.7	300	280	250
1.2	170	155	150
2.1	80	65	60
3.5	50	35	25
4.3	35	25	20
4.7	25	20	20
5.1	20	20	20

*)20ºC is taken as the minimum temperature in calculations.

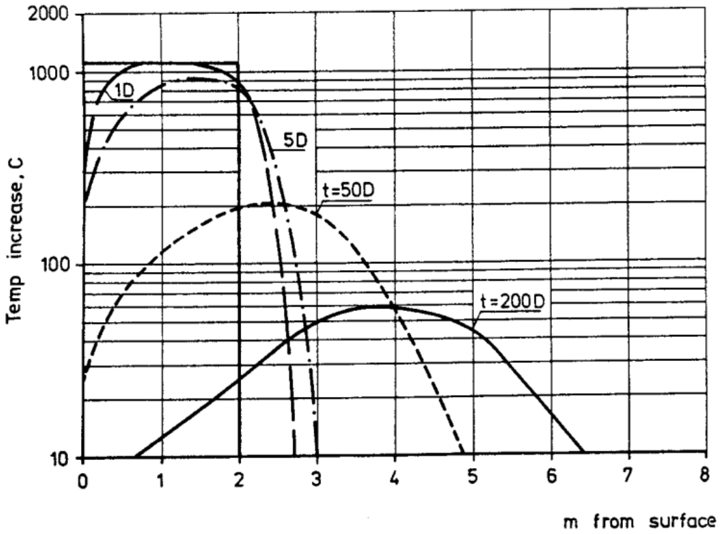


Figure 4-6. *Temperature evolution of the bentonite in dry crustal environment after eruption as a function of depth. Cases after 1, 5, 50 and 200 days (Pusch & Karnland 1988a).*

The Busachi bentonite is a typical iron bearing bentonite. The whole rock composition is given in the Table 4-3. The cation echange capacity has been measured from the two depths and the results were following: 90 meq/100g (depth 0.2 – 1.0 m from the interface) and 96–103 meq/100 g (below the earlier sampling depth, Table 4-4). (Pusch & Karnland 1988a.)

Table 4-3. *Whole rock composition of the Busachi bentonite.*

Oxide	Concentration [%]
SiO_2	55 - 60
Al_2O_3	16 - 20
Fe_2O_3	3 - 6
MgO	1 - 3
CaO	3 - 5
Na_2O	0.2

Busachi bentonite is rich in montmorillonite, in which the Ca is the major absorbed cation. The main accessory minerals are cristobalite, opal and zeolites. Clasts of plagioclase with glass inclusions are present. The montmorillonite content at several depths was determined by XRD-method (X-Ray Diffraction) yielding the result of 60-90 % (Table 4-4). (Pusch & Karnland 1988a.)

According to Pusch & Karnland (1988a) the light microscopy studies of the sample taken from the depth of 0.2-0.5 m indicate that the montmorillonite stacks of the bentonite have been retained quite well despite of the high temperature effect of magma (several hundred centigrades). The montmorillonite stacks were aligned because of sedimentation and consolidation. Some millimeter sized grains with sharp boundaries have formed as a result of recrystallization. There are also marks of weathering.

Two samples from the depths of 0.7 m and 4.7 m were studied by transmission electron microscopy (Pusch & Karnland 1988a). From the sample taken from 0.7 m below the clay/rock interface denser particle groups and nodules with size of 0.01-0.05 μm were observed. These are assumed to be silica precipitates formed during the cooling period.
The water content of the samples taken from the 0.2 m distance from the rock interface was 6 % and from the distance of 0.5 m 30 % (Table 4-4). The swelling pressure of the sample taken from 0.7 m (from the interface) was 0.48 MPa and from the distance of 4.7 m was 0.51 MPa. The hydraulic conductivities were 3 x 10^{-11} and 10^{-11} respectively (Table 4-4). The creep test indicated that the sample taken from the depths of 0.7 m and 4.7 m behaved differently. The sample taken from the depth of 4.7 m indicated the behaviour of non-cemented smectite rich clay and the sample from the depth of 0.7 m indicated behavior of heat-affected clay (Pusch & Karnland 1988a).

The following results are assumed to indicate cementation of the samples taken from the bentonite at depth of 0.7 m from the rock/clay interface. (Pusch & Karnland 1988a):

- Particle groups and nodules. These recrystallized millimeter sized grains indicates considerable dissolution and precipitation in the uppermost part of the clay caused by the short hydrothermal treatment.
- Rheological properties. The creep test results of the bentonite near the clay/rock interface (0.7 m depth) were similar to the results generally expected for thermally affected bentonites.

Table 4-4. *The water content (some drying of the samples during the transport was evident), temperature, montmorillonite content, swelling pressure and cation exchange capacity of the Busachi clay series (Pusch & Karnland 1988a).*

Depth below clay/rock interface [m]	**Water content [%]**	**Max. temperature [ºC]**	**Montmorillonite content of the clay fraction [%]**	**Swelling pressure [MPa]**	**Hydraulic conductivity [m/s]**	**Cation exchange capacity [meq/100 g]**
0.2	6	700	60 - 70			90
0.5	30					90
0.7	27	250	70 - 75	0.48	3 x 10^{-11}	90
1.2	29	150	70 - 80			
2.1	30	60	75 - 85			
3.5	27	25	70 - 80			
4.3	36	20	75 - 90			
4.7	32	20	85 - 90	0.51	10^{-11}	96-103
5.1	28	20	70 - 80			

The heat effect is assumed to have caused quite small effects on the bentonites from the depth of 0.7 m on. Cementation took place at very high temperatures dropping from 800 °C below 100 °C in 50 days. The samples taken from the depth 4.7 m were not cemented (Pusch & Karnland 1988a).

4.3 Ishirini (Libya)

The effect of intrusive heating has been observed in the Ishirini bentonite formation as changes in geochemical and mineralogical composition and it has been considered as potential natural analogue of bentonite clay barrier (Kolaříková & Hanus 2008, Kolaříková et al. 2005).

The Ishiri area is located in northeastern part of Jabal al Hasawnah in Libya (Figure 4-7). The Ishiri area can be divided into five geological units, which are the Cambrian Hasawnah formation, the Miocene Ahurfin formation (a thin sediment sequence), and the Miocene volcanic series concerning several phonolite or andesite bodies, the Pliocene Hishar bentonite formation and the Pliocene-Pleistocene basalt (Kolaříková & Hanus 2008). The bentonite deposit occurs in the southeastern part of the Ishirini area. The clays have been formed as a result of alteration of pyroclastic rocks and a few lava flows (Kolaříková & Hanus 2008). Some bentonite sequences in Hishar have been crosscut by subvolcanic basaltic domes and dikes, which have caused metamorphic aureoles around the intrusions (Kolaříková et al. 2005, Kolaříková & Hanus 2008). The subvolcanic andesitic magma intruded into bentonites about 20.2 Ma ago (Abdelkader 1997). The age of some basaltic dikes is 1.8 Ma (Abdelkader 1997). The assumed temperature of the basalt has been about 850-900 ºC and the width of the contact aureole around the dome is about 15 cm (Kolaříková & Hanus 2008).

Figure 4-7. *The location of the Ishirini bentonite deposit in Jabal al Hasawnah in Libya.*

Based on the isotopic composition of the unmodified smectites, it has been concluded that the alteration of the pyroclastic rocks have been caused by heated meteoric water with low amounts of geothermal water (T = 30-90 ºC; Alhodiari 1995). The contact aureole around the basalt dome has been formed as a result of thermal action caused by the basalt (Kolaříková & Hanus 2008). The brittle structure of the rock has enabled the circulation of the hot magmatic fluids through the clay. Five major groups of fluids from five hydrothermal events have been observed using microthermal measurements from fluid inclusions from the 20 cm wide silicified zone. These major groups of fluids were following:

- Early high temperature aqueous-carbonic fluid (elevated heat flux),
- Late aqueous-carbonic fluid,
- Hypersaline fluid and
- Two low temperature aqueous fluid (cooling of the hydrothermal system).

Alteration of the pyroclastic rocks into bentonites has happened mainly by heated meteoric waters with temperature of about 30-90 ºC (Kolaříková & Hanus 2008) as concluded also in previous studies. Information about the pressure evolution before intrusion was not found.

The temperatures, as a function of the distance from the basalt dome, have been estimated based on the variation of the oxygen isotopic composition (Table 4-5). Thermal effect based on the isotopic study and the corresponding mineralogical results are presented in Figure 4-8.

Fluid inclusion studies have been done for the quartz grains of bentonite. The inclusions contained liquid H_2O, liquid CO_2 and gaseous CO_2 in room temperature. The content of CH_4 was in zone I (the earliest aqueous inclusion phase) about 30 – 35 mol% and in zone II < 10 mol%. Both the primary and the secondary inclusions occur in the silicified zone. The minimum trapping temperature in the 5 cm wide zone (zone I) from the contact of dome was calculated to had been 430-470ºC and in the zone (zone II) which exists between 5 and 10 cm from the contact the temperature had been 295-300 ºC. The hypersaline secondary fluid inclusions in zone I homogenized at the temperature of 270-300 ºC (Kolaříková & Hanus 2008).

The bentonite deposit is composed mainly of montmorillonite with Ca as the dominant interlayer cation (Kolaříková & Hanus 2008). Quartz and kaolinite occur as accessory minerals. Most of the bentonite samples studied by Kolaříková & Hanus (2008) consisted of 90 % montmorillonite. Small amount of montmorillonite has been altered to kaolinite by saline hydrothermal solutions. The major components of bentonite vary as a function of distance from the interface of bentonite and volcanic rock as seen in Figure 4-8 **(**Kolaříková et al. 2005, Kolaříková & Hanus 2008). The illite content is higher close at the bentonite rock interface.

The cation exchange capacity was about 90 mmol/100 g at the distance of 160 cm from the interface of the rock and bentonite and about 35 mmol/100 g at the distance of 15 cm from the interface (Kolaříková & Hanus 2008). Information about the bulk composition of bentonite was not found.

Table 4-5. *The thermal effect of volcanic intrusion concluded from the oxygen isotope variation in smectites (Kolaříková & Hanus 2008).*

Distance from the contact [cm]	**δ18O SMOW (standard) [‰]**	**T [°C]**
20	+ 12.4	200
40	+ 12.8	
100	+ 13.3	
150	+ 13.6	
200	+ 13.8	
300	+ 14.0	170

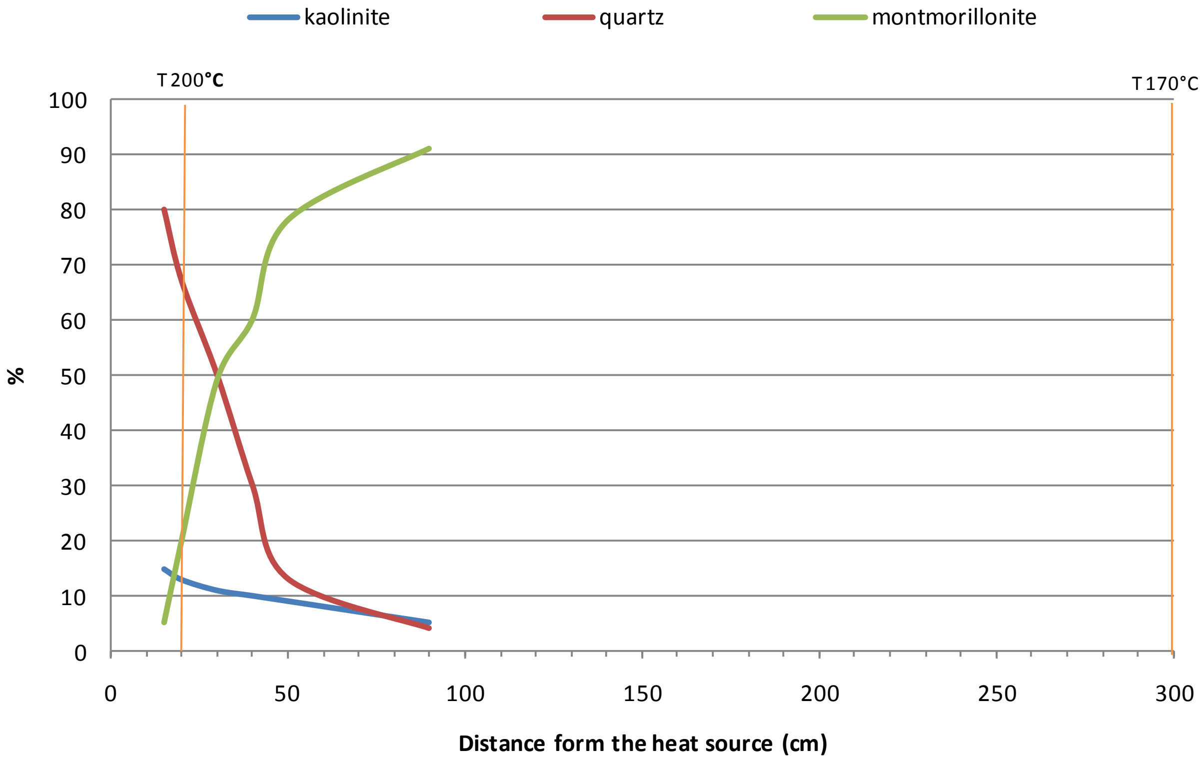


Figure 4-8. *Major components of the Ishirini bentonite as a function of the distance of the interface of the bentonite and volcanic rock and the thermal effect (given as orange lines) based on the oxygen istope study from smectites; Modified from Kolaříková et al. (2005) and Kolaříková & Hanus (2008).*

This natural occurrence restricts the cementation well above 170°C closer to 200 °C. However, the duration of the elevated temperatures is unknown. Oxygen isotope results show linear trend, which would suggest T >190 °C for cementation. The cemented aureole width is small, after 90 cm montmorillonite content is >90 %. More detailed study from this area would be of interest, at least concerning the estimate of the cooling rate and duration.

4.4 Cabo de Gata region (Spain)

Several bentonite occurrences have been described from this region in in southeastern Spain that may be of interest as natural analogues for processes expected in the deep repository. The following locations Morrón de Mateo, San Jose and Cortijo de Archidona have been described in separate sections as the processes of interest are different between the occurrences.

Bentonite occurrences at Cabo de Gata region (Figure 4-9) in Spain are about 10 Ma old (Bellon et al. 1983, Di Battistini et al. 1987, Zeck et al. 1999) and differ quite much from the MX-80 deposits in Wyoming (Karnland et al. 2004). Bentonites occur at two regions namely Serrata de Nijar (in land) and Sierra de Cabo de Gata (close to the sea) (Figure 4-9). FEBEX bentonite comes from the deposit Cortijo de Archidona located in Serrata de Nijar.

Isotopic studies performed at Cabo de Gata region suggest that bentonisation took place due to the effect of meteoric fluids at low temperatures, of around 40ºC in the case of the Serrata de Níjar (SN) deposits (Leone et al. 1983). However, Caballero et al. (1985) consider that the hydrothermal solutions that caused the alteration of the volcanic rocks of the Serrata de Níjar into bentonites were of chloride-sodium type, with a neutral or slightly acid pH. Chloride-sodium type suggests marine origin for the altering fluid. In addition, isotopic studies (Delgado 1993) show that the bentonite deposits of the Cortijo de Archidona (in SN) were produced as a result of the alteration of intensely brecciated volcanic glasses. The first hydration and devitrification states of the rock included the intervention of hydrothermal solutions, the temperature of which subsequently decreased to environment values, with which the smectites present in the deposit are in equilibrium (ENRESA 2002).

Recently Caballero & Jiménez de Cisneros (2010) have published new isotopic results from Serrata de Nijar (SN) and Sierra de Cabo de Gata (SG) bentonites (Figure 4-9). These results have been consistent with the previous studies showing differences between the formational fluids. They have also estimated formation temperatures of 25 and 49 ºC for SG and from 6 to 25 ºC for SN. Sierra de Cabo de Gata is thought to have been formed in the presence of solutions dominated by bicarbonate (Ca, Mg) indicating meteoric origin of the fluids (Caballero et al. 2005).

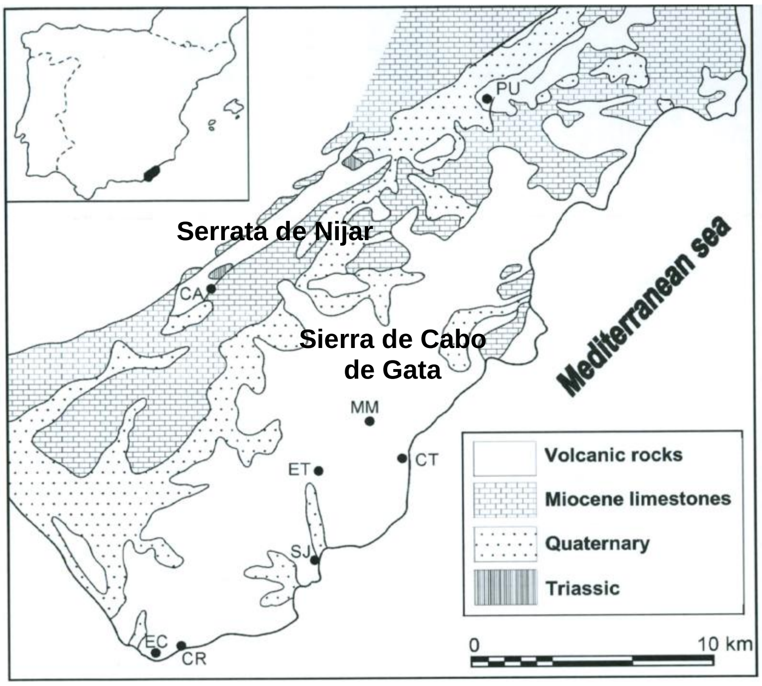


Figure 4-9. *The location of Cabo de Gata region. Morrón de Mateo (MM), Cortijo de Archidona (CA), San José (SJ) (Caballero et al. 1985).*

4.4.1 Morrón de Mateo

This bentonite formation has been generated from acidic tuff by hydrothermal solutions derived from volcanic activity (Cabellero et al. 1985, Delgado & Reyes 1993) and/or reheated meteoric waters (Caballero et al. 1985). The sediment series from the bottom to the top in the Morrón de Mateo are is the following: hornblende-rich andesite rock, layer of marine calcarenites-calcirudites, white layered tuffs, marine sedimentary rocks and grey tuffs (Pérez del Villar et al. 2005). The calcarenite beds are formed about 11.6 Ma ago (Betzler et al. 1997). After deposition of the volcanoclastic and sediment material, a volcanic dome, called Morrón de Mateo, intruded into this complex (Fernández-Soler 2002, Pérez del Villar et al. 2005). Magmatism of the Cabo de Gata took place between 10.5 ± 0.5–12 Ma ago (Zeck et al. 1999). It is estimated that the temperature of the magma has been about 820 ºC (Fernández-Soler 1992). Detailed geology and cross sections of the deposit is given in Figure 4-10.

The bentonites in the area of Morrón de Mateo have been formed as a result of the hydrolysis of porous volcanic materials (Linares 1985). Temperature of these solutions has been about 50 ºC. The origin of water is assumed to be either meteoric or volcanic (Linares 1985, Pérez del Villar 2005) (see also above Section 4.4).

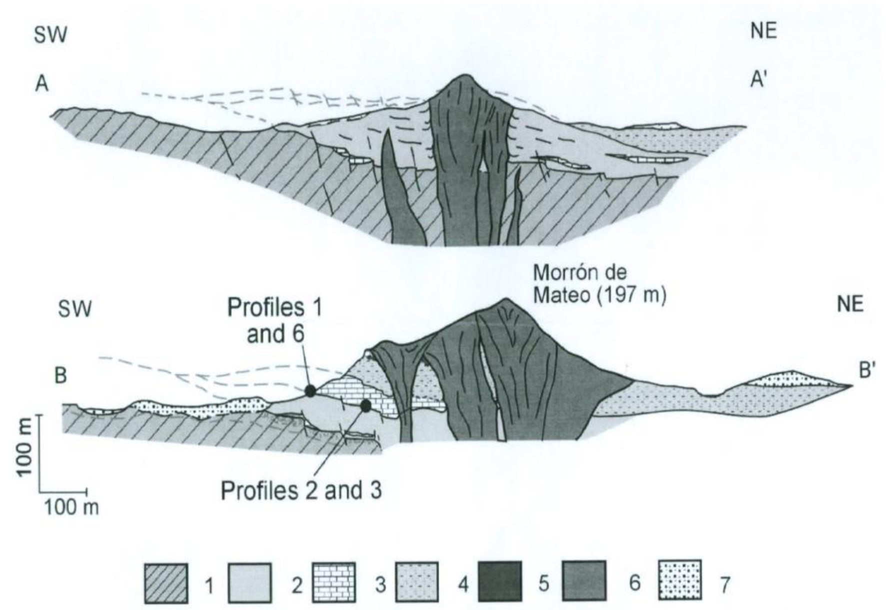


Figure 4-10. *Two cross-sections of the Morrón de Mateo dome. Illustrative cross-sections A-A´ and B-B´ (see location in Figure 4-9) through the Morrón de Mateo sequence, showing the intrusive relation between the Morrón de Mateo dome and the volcano-sedimentary sequence. 1: hornblende andesite breccias and lavas; 2: layered tuffs; 3: Tortonian marine sedimentary rocks (limestones, calcarenites, conglomerates and sandstones); 4: grey tuffs; 5: white dacitic pyroclastic tuffs; 6: the Morrón de Mateo dome; 7: recent alluvial sediments (Fernández-Soler 2002).*

According to Delgado & Reyes (1993) the Morrón de Mateo intrusion heated the seawater. The heated water (temperature about 70-90 ºC) caused further interaction with the rock. According to Peréz del Villar et al. (2005) the temperature has been about 55-66 ºC during the formation or transformation of smectite depending on the distance from the dome. Transformation and neoformation of minerals indicate that the temperature change has been about the same level in the entire area around the dome. Because of this, there is no clear thermal gradient observed between samples taken from the near field of the dome and the samples taken farther (Pérez del Villar et al. 2005).

There are no significant differences in the chemical compositions of the volcanogenic sediments around the Morrón de Mateo dome. The compositions of the samples taken from the sediments located near the dome are about the same as the compositions of the samples taken farther. The only differences are in MnO, As, and Ba contents. The MnO and As contents are higher in the proximal than in the distal part and the Ba contents are the highest in the distal part. The abundance of exchangeable cations has assumed to been following: $Mg^{2+} \geq Na^{+} > Ca^{2+} > K^{+} >> Sr^{2+}$. It has been noticed that the K^{+} amount is lower in the clay fraction than in the bulk samples. In almost all samples the content of exchangeable cation Mg^{2+} is high (Peréz del Villar et al. 2005). The whole rock composition of the clay is not reported.

The mineralogical composition of the clay samples taken from the places 1-6 (Figure 4-11) are given in Table 4-6**.** The smectite contents of the smectitised tuffaceous samples were: 1. = 94%, 2. = 95 %, 3. = 97 %, 4. = 86 – 98 %, 5. = 89 % and 6. = 76 %

(Peréz del Villar et al. 2005, see Figure 4-11). The christobalite contents were following: 1. = 4 %, 2. = 0 %, 3. = 0 %, 4. = 0 or 6 % (three analyses), 5. = 11 % and 6. = 5 %. As a conclusion of these results, the samples consist mainly of high-crystalline dioctahedral smectite. The minor minerals are cristobalite, plagioclase, calcite and zeolites. These results were semi-quantitative and they have been analyzed from the clay fraction.

Information about the cementation of Morrón de Mateo bentonite formation was not found. Nevertheless, some marks, such as variation of quartz and smectite contents (see Table 4-6), which has in some cases connected to cementation, are seen in the Morrón de Mateo bentonite formation.

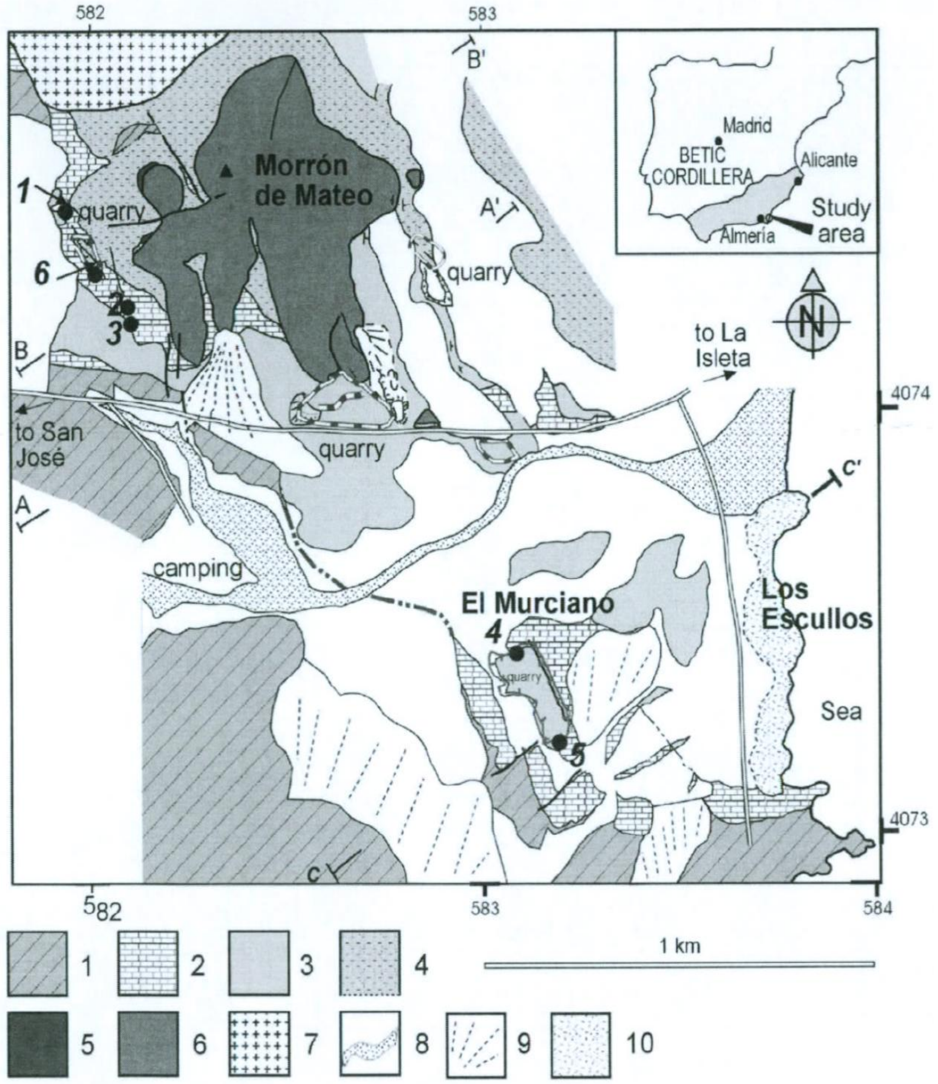


Figure 4-11. *The places from which the samples 1-6 were taken (Modified from the Fernández-Soler 2002). 1: hornblende andesite breccias and lavas; 2: Tortonian marine sedimentary rocks (limestones, calcarenites, conglomerates and sandstones); 3: layered tuffs; 4: grey tuffs; 5: white dacitic pyroclastic tuffs; 6: the Morrón de Mateo dacite dome; 7: Rodalquilar Complex (rhyo) dacitic rocks; 8: undifferentiated Quaternary sediments; 9: alluvial fans; 10: Pleistocene oolitic sandstones (fossil beach).*

Table 4-6. *The mineral composition of the samples 1-6. Q = quartz, Plag. = plagioclase, K.Fd. = K-deldspar, Amph. = amphiboles, Crist. = cristobalite, Cc = calcite, Dol. = dolomite and T. Ph. = total phyllosilicate.*

	Q [%]	**Plag. [%]**	**K.Fd. [%]**	**Amph. [%]**	**Zeol. [%]**	**Crist. [%]**	**Cc. [%]**	**Dol. [%]**	**T. Ph. [%]**
1.	5	14	4	0.5	1	12	0	0	64
2.	4	1	6	0.5	0	0	31	0	57
3.	5	15	0	0	1	10	19	0	50
4.	5	23	0	1	1	6	10	0	55
5.	2	5	3	0	1	9	0	0	80
6.	1	12	0	0	1	9	27	16	34

Cementation is not observed caused by the hot magma intrusion. This supports the durability of the smectite against the short-term thermal events. The duration of the elevated heat period is unknown which would be essential for more detailed analysis on the long-term stability point of view. Cementation is not observed, but neoformation of minerals has occurred in the precence of sea water heated up to maximum 90 °C (more likely 55-66 °C) during the cooling of the magma intrusion.

4.4.2 San José

San José bentonite (SJ) (Figure 4-9) has been formed by hydrothermal alteration of the originally fractured andesitic rock (Caballero et al. 1985) and it is located in SG area. San José bentonite has been studied as a natural analogue on the bentonite exposed to high saline groundwater because of its location at only 10 m from the Mediterranean shoreline. Karnland et al. (2004) have defined the critical physical properties of the buffer for the San José bentonite on different densities and NaCl concentrations. Also composition of bentonite material has been defined by XRD, ICP/AES as well as CEC. The result show no significant effects of the harsh saline environment on the bentonite and the measured properties show similar values obtained for MX-80. This is a promising result as mineralogically San José bentonite differs from MX-80 (Tables 4-7 a and b). It has a more complex mineral suite and higher Mg and K content than MX-80.

Karnland et al. 2004 conclude that the high initial NaCl content has not affected the favourable physical properties of the bentonite in a significant way, and despite of the differences in materials compared, both have behaved in a similar manner when exposed to short term saline experimental conditions. Swelling pressure results are given in Figure 4-12.

Table 4-7. *Mineralogy of the San José bentonite SJ (bulk) SJw (washed with deionized water) and SJwc (after washing and removing coarse material) compared to MX-80 (bulk) and MX-80c (coarse fraction removed) (Karnland et al. 2004).*

a)

	MX-80	SJw	MX-80c	SJwc
Plagioclase	4	1		1
Cristobalite	3		2	
Gypsum	1	1		
Smectite	87	74	96	83
Muscovite	1	8		6
Pyrite	1		1	
Quartz	3	10	1	1
Chlorite		6		9

b)

	Ca	K	Mg	Na	Sum	CEC Cu-1	CEC Cu-2
SJ	0,20	0,03	0,40	0,46	1,09	0,68	
SJw	0,15	0,01	0,28	0,12	0,56	0,68	
MX-80	0,14	0,01	0,04	0,49	0,68	0,72	0,70
SJc						0,66	0,67
MX-80c						0,85	0,86

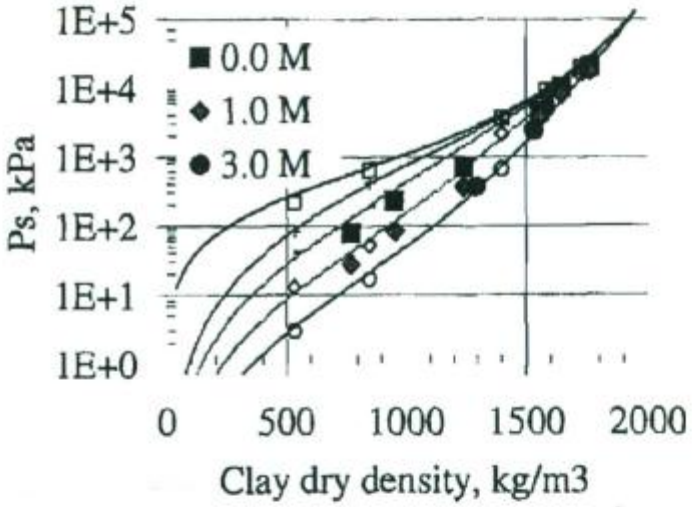


Figure 4-12. *Measured swelling pressure in all San José samples. Lines show theorethical values and non-filled symbols indicate MX-80 results (Karnland et al. 2004).*

4.5 East Slovakian basin

The volcano-sedimentary Neogene East Slovakian basin belongs to the Alpine-Carpathian orogenic belt. It is characterized by 1) an extremely high thermal flow (Q=

82-113 mWm) producing a temperature of ~209 ºC at 4 km depth (Král et al. 1985), 2) the presence of intense syngenetic volcanism of alkali-calcic type (acid to intermediate) (Vass et al. 1988) and 3) occurrence of evaporitic (esp. halite) formations (Rudinec 1978). Bentonite layers are less illitized than the surrounding shales. This difference disappears when temperatures reach about 150 ºC at depth of ~3 km. Illite formation from smectite has been attributed to K fixation and neoformation mechanisms that produce differences in the illitisation rates in shales and bentonites (Šucha et al. 1993). Also microstructural changes are observed as increasing illite particle diameter correlating to decreasing expandability. After sufficient structure change (below 3 km and above 150 ºC) the starting material ceases to influence the course of the smectite-to-illite transition (Šucha et al. 1993). The experimental results of Šucha et al. (1993) are shown in Figure 4-13a.

In the bentonite/shale comparison (Figure 4-13a) the maximum difference I/S is observed around 100 ºC (~1.5 km). Šucha et al. (1993) attributes the retardation of illitisation of buried bentonites to lower tendency of K fixation of volcanic smectites than those of non-volcanic origin (shales). The initial displacement is due to differing initial properties prior to diagenesis. However, the difference in illitisation rates is very small and it follows closely a given smectite (S) %.

Sucha et al. 2000 (unpublished work) have decribed bentonites with saline and non-saline pore waters from the East Slovakian Basin (see Figure 4-13b). In this site bentonites of volcanoclastic origin have been studied in several drill holes down to 4000 m. In Figure 4-13b it is seen that while expandability decreases with depth and thus with increasing temperature, it is even more dependent on the presence or absence of NaCl in the pore water. Because of the high heat flow of up to 120 W/m the whole range of illitisation can be observed at relatively shallow depth. However, the data is rather sparse on the salt bearing bentonites and, more importantly, no data on the geological setting of the samples is given. More detailed investigation would be of interest to establish these controversial results.

When comparing the Figure 4-13 a and b, it seems that the illitisation process is accelerated/retarded in both cases to some extent. In Figure 4-13b the accelerating effect is more pronounced. However, the data is rather sparse and conclusions, especially on the effects at low temperatures and pressures, can not be made. An accelerating effect of the pore fluids on the illitisation rate at deeper parts of the sedimentary sequence (below 1000 m) is seen. No detailed geological data is given how evaporites and bentonites in the study area have been formed, i.e. is there difference in the genesis that would explain the results. And most importantly there is no information on the salinity levels in the bentonite pore fluid.

Figure 4-13c shows new results by Honty et al. (2004) as well as the results of Šucha et al. (1993) (Figure 4-13a). They have concluded that salinity alone does not accelerate illitisation, but when combined with increased burial temperatures and pressures it may have an enhancing effect.

The salinity of the groundwater does not seem to affect illitisation rate at shallow depths (Šucha et al. 2000, Środoń 1984, Honty et al. 2004), but the temperature limit is so far unknown. Based on the results given in Figure 4-13c, one would suggest ~100 ºC, but obviously further study is needed. The actual mechanism that creates these differences is not clear as discussed in Honty et al. (2004), but it seems that crystal growth mechanism probably varies according to the chemistry of the saline environment.

Similar results have been reported by Środoń (1984) from the Carphatian Foredeep in Poland (Upper Miocene). Low temperature diagenesis and evolving salinity trend from abnormally saline to brackish conditions has not affected illitisation rate in shales during the sedimentation at low accumulation rates (max. 80 mm / 10^3 years) (Figure 4-14). Neither is seen change in the illite content versus depth. Also in this sedimentary sequence shales show illitisation (composition interstratified illite-smectite, kaolinite, illite, occasionally minor chlorite) while tuff layers (bentonite) show monomineralic montmorillonite compositions (Wyoming type). Tuff layers occurring in the Goryslawice sequence are shown in Figure 4-15.

In saline (excluding the extreme sedimentation environments, i.e. K-Mg basins) conditions it is concluded that the smectite and smectite-illite are stable in the marine sediments until the high temperatures (~50ºC, usually below 1000 m depth e.g. Perry & Hower 1970) of deep diagenesis are reached (Środoń 1984).

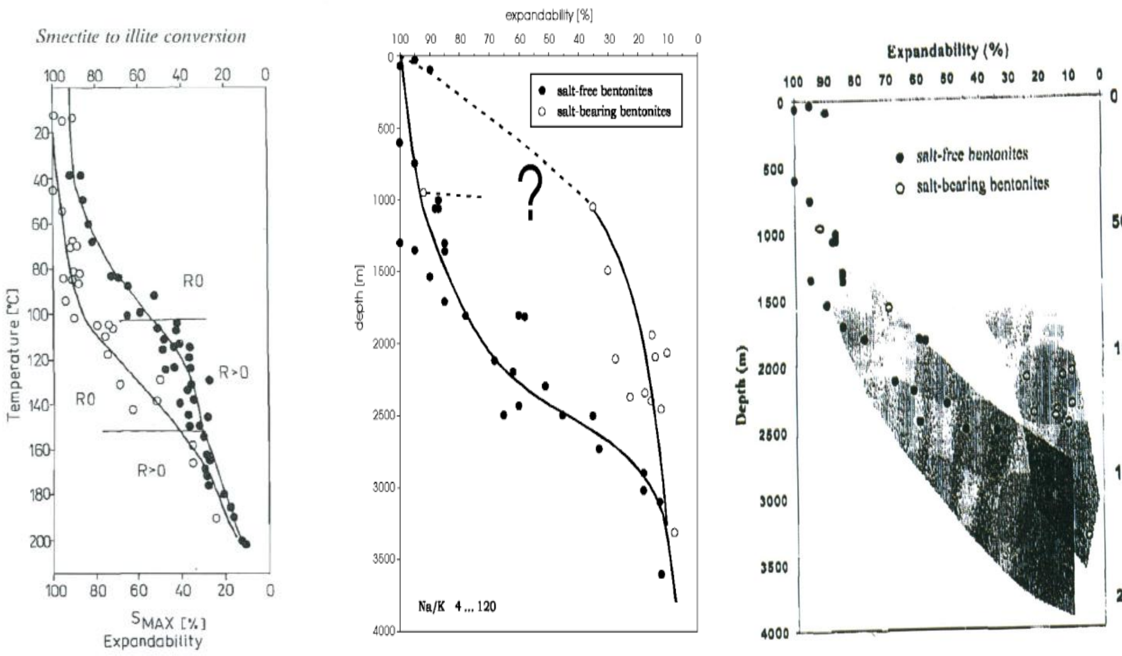


Figure 4-13. *a) Smectite to illite conversion from bentonites (o) and shales (●) in the East Slovak Basin (Šucha et al. 1993) (experimental curve: Środoń et al. 1992) and b) Expandability of bentonites from the East Slovak Basin as a function of depth and salinity of the pore water (Šucha et al. 2000), and c) replot of the results (Šucha et al. 1993, and new results by Honty et al. 2004 (temperatures based on Král et al. 1985).*

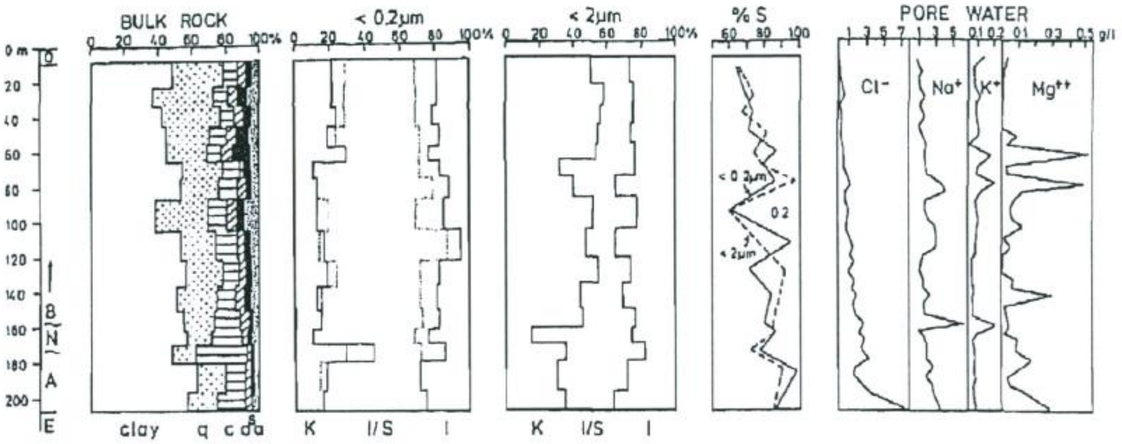


__Figure 4-14.__ Well Baranow: mineral composition of the bulk rock, clay assemblage of <0.2 µm and <2 µm fractions, and porewater composition (from Szczepańska 1982). On extreme left of the figure: Q= Quarternary, E= evaporitic horizon, A,N,B = environments of sedimentation (abnormal salinity, normal and brackish, respectively). Dotted lines in <2 µm fraction column represent simple normalization of measured peak intensity to 100% without correcting for variation of illite-smectite peak intensity (%S = smectite in I/S). Along bottom of figure: q=quartz, c= calcite, d= dolomite, s= siderite, a= albite, K= kaolonite, I/S= illite-smectite, I= illite. (Środoń 1984.)

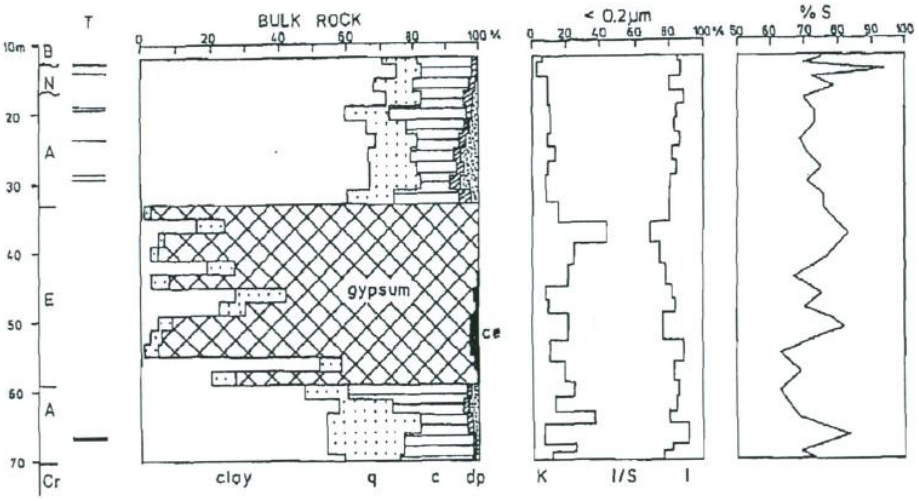


__Figure 4-15.__ Goryslawice well: mineral composition of the bulk rock, clay assemblage of <2 µm and percent smectite in illite-smectite. Cr= Cretaceous, T= tuff horizons, p= pyrite, ce = celestite. Remaining symbols see Figure 4-14 (Środoń 1984).

When comparing the results above, not only salinity is to be taken on account. Obviously, the remarkable difference between bentonite and shale is that shale is considered as half-closed system and bentonite as closed system (Meunier 2005), which has an effect on the hydrogeochemical conditions within the sediment.

Olkiluoto reference waters are compared to salt free bentonite (SFB) leachates and salt bearing bentonite (SBB) leachates (from Honty et al. 2004) in Figure 4-16 a and b. Na and Cl contents in bentonite porewaters calculated for the buffer (BBS and BS) are slightly higher than SBB, but BDB is similar to SFB. The leachates from both SBB and SFB have Mg and K contents are about a decade higher than in Olkiluoto bentonite waters. Mg contents are much lower in SBB/SFB leachates than those of buffer bentonites. As a matter of fact, the presence of Na, Ca and Mg interlayer ions are known to inhibit the illitisation process in hydrothermal experiments (270-350 °C and ~400-9400 ppm K, Na, Ca, Mg solutions) (e.g. Robertson & Lahann 1981).

According to the data presented here, accelerated illitisation seems not probable to occur in the repository.

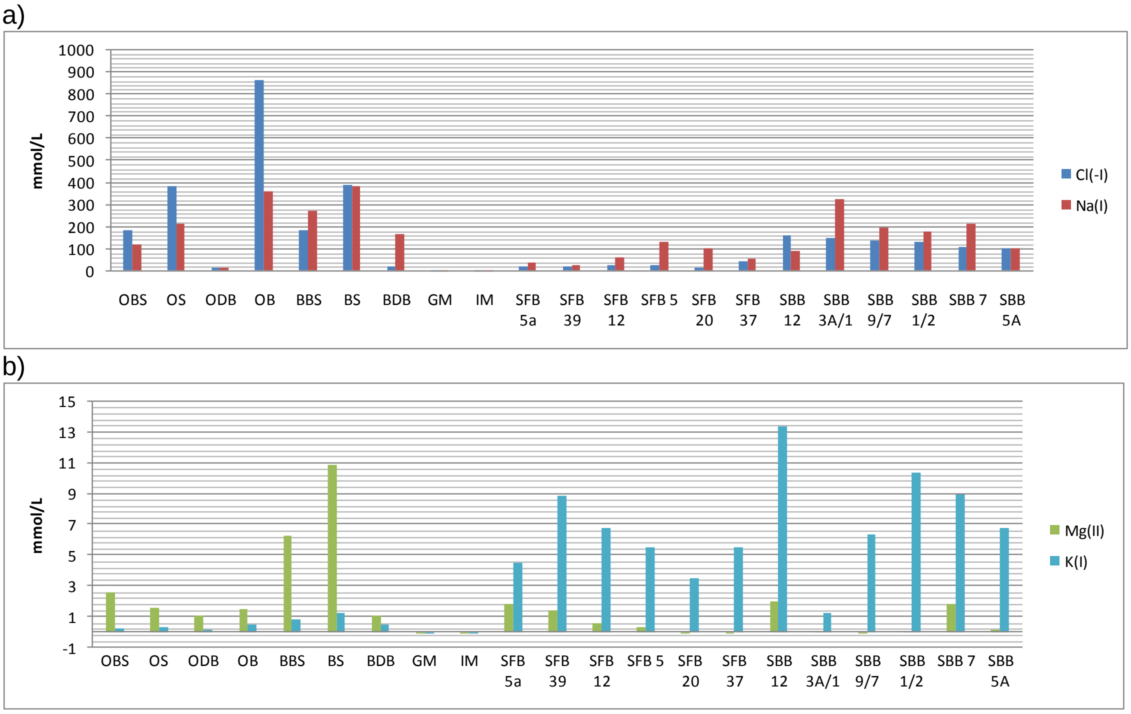


Figure 4-16. a) Na and Cl and b) Mg and K contents in Olkiluoto reference waters (see Table 1-1) and water leachates from the East Slovak basin (SFB=salt free bentonite, SBB= salt bearing bentonite) (Honty et al. 2004). Numbers after SFB/SBB refer to sampled drill hole. ODB=Olkiluoto Dilute Brackish, OBS= Olkiluoto Brackish Saline, OS= Olkiluoto Saline, OB= Olkiluoto Brine, BDB= Bentonite Dilute Brackish, BBS= Bentonite Brackish Saline, BS= Bentonite Saline, GM= Glacial Melt water, IM= Ice Melting water.

4.6 Smectites in Izu-Bonin fore-arc basin

Unusual porewater compositions have been found in the Ocean Drilling Programme (ODP) in the sediment at Izu-Bonin fore-arc basin southwest of Japan (Figure 4-17). Findings on drilling sites 792 and 793 have been reported in Egeberg et al. (1990). In these sediments also smectite is found as a result of alteration, during rapid accumulation of volcanogenic sediments. The porewaters show peculiar composition and are characterized by very large Ca/Na ratios and comparatively small amounts of TDS. Ca/Na rations vary at sites 792 and 793 from sea water 0.022 to 1.77. The water has originated from the sea but depleted almost completely in Mg and K and also SO_4 concentration is reduced by 50 %. Cl concentration is also high, alkalinity and silica contents are low and pH is high, between 7 and 9.

Egeberg et al. (1990) report these peculiar porewaters at two sites reported in detail in Taylor et al. 1990a and 1990b. At site 792 Ca^{2+} concentration in the porewater reaches its highest point of 169.3 mM at 599 m below sea floor (m.b.s.f.). Ca^{2+} concentration increases gradually up to 599 m depth and then gradually decreases down to 114.2 mM at the end of the core at depth 796.51 m. At site 793 Ca^{2+} -concentration in porewater increases similarly down to depth 977 m below sea floor, below which the concentration of Ca^{2+} is settled to about 300 mM.

Smectite is stable within these pore waters (Egeberg et al. 1990) and occurs as an alteration product in the seafloor sediments. According to lithological descriptions (Taylor et al. 1990a and 1990b) a simplified litostratigraphic sheme has been used by Egeberg et al. 1990. The section in focus here includes sediments that deposited during the initial volcanic period. It is observed as sections from 429.3 to 804 m.b.s.f. at site 792 and from 759 m to 1403.9 m.b.s.f. at site 793. These sediments represent Oligocene accumulation and are distinguished from the above Miocene sediments by the sharp decrease in biogenic carbonate and organic carbon and at a time by an abrupt increase in the abundance of zeolites, smectites, palagonite and gypsum. Alteration of the porewaters in these sediments is attributed to reactions taking place in the sedimentary section. Temperature gradient at the site 792 is 54 ºC/km and expected to be higher in the deeper site 793. Higher reaction rates caused by the temperature and depth at site 793 explain the more evolved groundwaters. Alteration has also been favoured by the very low diffusivity. Mass balance considerations supported with mineralogical observations show that 15 to 25 % of the rock matrix has been altered to zeolites, smectites and gypsum.

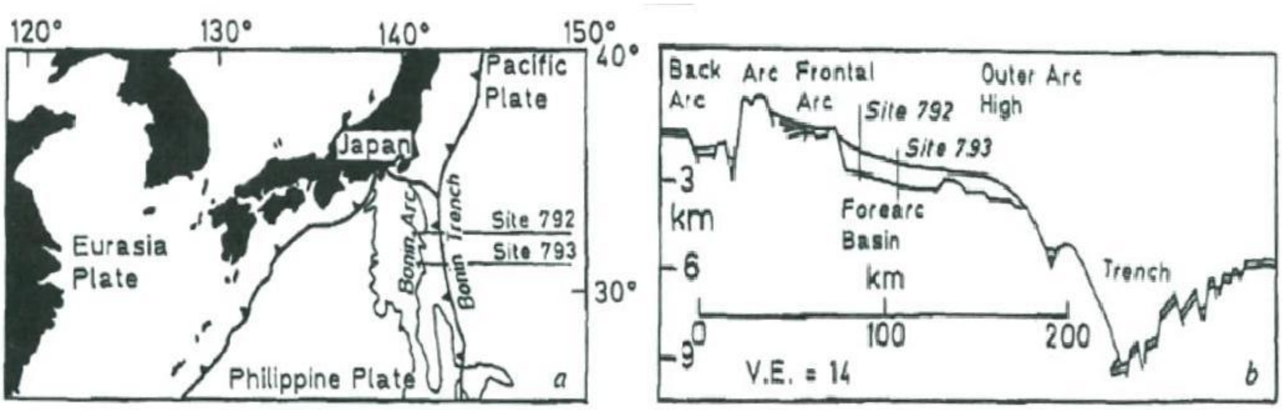


***Figure 4-17**. a) Locations of the drilling sites in the Pacific Ocean, b) Projection of the sites onto a schematic section across the Izu-Bonin Arc (Egeberg et al. 1990).*

In Figure 4-18 Ca/Na ratios are shown against TDS. Izu-Bonin samples are compared to other solutions (see figure details) and Olkiluoto reference waters. Olkiluoto saline waters plot close to those of altered Izu-Bonin waters and are also close to ground waters from Canadian Shield.

Porewaters from the selected sites at Izu-Bonin fore-arc basin are compositionally close to Olkiluoto reference waters Olkiluoto Brackish Saline, Olkiluoto Saline and Olkiluoto Brine (Figure 4-19). Smectites are stable at the Izu-Bonin site in the similar groundwater compositions that are expected to occur in Olkiluoto deep repository at least in cases of Olkiluoto Brackish Saline (current groundwater at repository level) and deeper saline groundwater that could upcone up to repository level in the early stages of evolution or in the long term.

Smectite seem to be stable in the environment described above, but no exact compositional data is available for the specific smectite mineralogy. A detailed mineralogical study would be needed to better apply this occurrence as an analogue for montmorillonite stability.

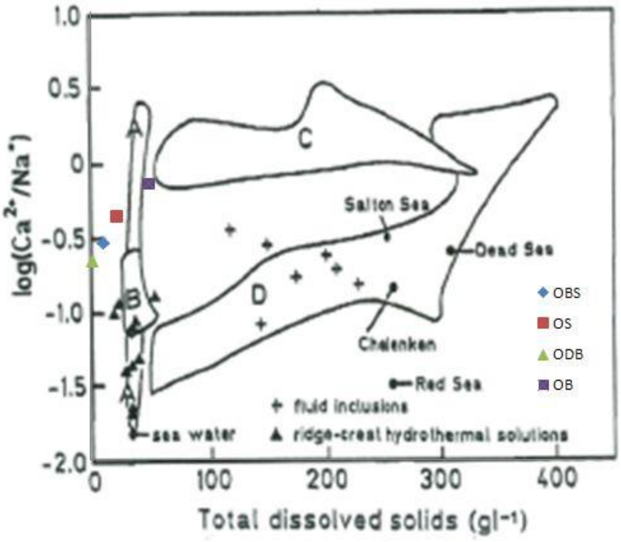


Figure 4-18. *Ca/Na ratios plotted against TDS for sites 792 and 793 (field A), hydrothermal waters from Iceland (field B) (Bjørnsson et al. 1972), groundwaters from Canadian Shield (field C) (Frape et al. 1984), formation waters from the Illinois and Michigan basins (field D) (Graf et al. 1966), the geothermal fields Chelenken (Lebedev & Nikitina, 1968) and Salton Sea (Muffler & White 1969), the Dead Sea (Livingston 1963), the Red Sea (Miller et al. 1966), fluid inclusions from hydrothermal minerals (Roedder et al. 1963, Hall & Friedman, 1963)) and ridge-crest hydrothermal solutions (Edmond et al. 1979, Van Damm et al. 1985, Campbell et al. 1988) (from Egeberg et al. 1990). Olkiluoto groundwaters plotted on top in the same scale in colour. See abbreviations in the text of the figure below Figure 4-21).*

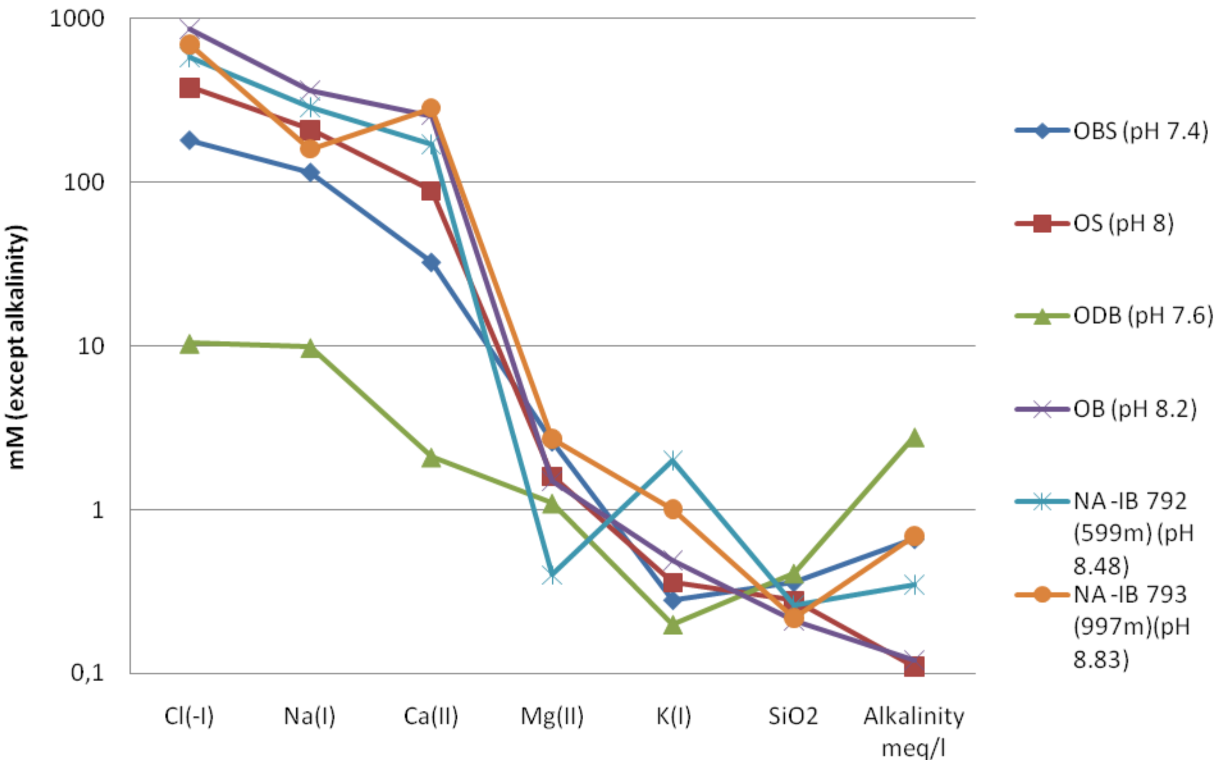


Figure 4-19. *Porewaters analysed from Izu-Bonin fore-arc basin at 599 m (NA-IB 792) and 997 m (NA-IB 793) depths below sea floor (Taylor et al. 1990a, Taylor et al. 1990b and Egeberg et al. 1990) compared to Olkiluoto reference waters. ODB=Olkiluoto Dilute Brackish, OBS= Olkiluoto Brackish Saline, OS= Olkiluoto Saline, OB= Olkiluoto Brine (Grive et al. 2007); pH is given in the legend.*

4.7 Sedimentary sequences and the Lake Chad system

A well known study of the smectite distribution has been done also from Paris Basin (France), which has shown clearly that in sediments the smectite composition changes progressively from palaeosols and moderately leached continental material to marine evaporates of confined areas (Trauth 1977). Based on the previous study a comprehensive sedimentary sequence has been produced (Table 4-8).

Table 4-8. *Sequence from detrital (mostly beidellite) to evaporite (mostly stevensite) sediments in Paris Basin. Structural formulas and octahedral occupancies are after Trauth (1977).*

Mineral	Structural formula	Octahedral occupancy
Beidellite:	$Ca_{0.133}(Al_{1.327}Fe^{3+}_{0.5}Mg_{0.24})(Al_{0.267}Si_{3.733})O_{10}(OH)_2$	2.09
Smectite, Wy:	$Ca_{0.06}K_{0.5}\ (Al_{1.44}Fe^{3+}_{0.3}Mg_{0.3})(Si_4)O_{10}(OH)_2$	2.04
Smectite, Cheto:	$Ca_{0.12}K_{0.16}\ (Al_{1.18}Fe3+0.24Mg_{0.6})(Si_4)O_{10}(OH)_2$	2.02
Saponite:	$Ca_{0.12}K_{0.13}\ (Al_{0.80}Fe^{3+}_{0.24}Mg_{1.35})(Al_{0.21}Si_{3.79})O_{10}(OH)_2$	2.39
Stevensite:	$Ca_{0.08}Na_{0.08}K_{0.15}\ (Al_{0.21}Fe^{3+}_{0.07}Mg_{2.4})(Si_4)O_{10}(OH)_2$	2.68

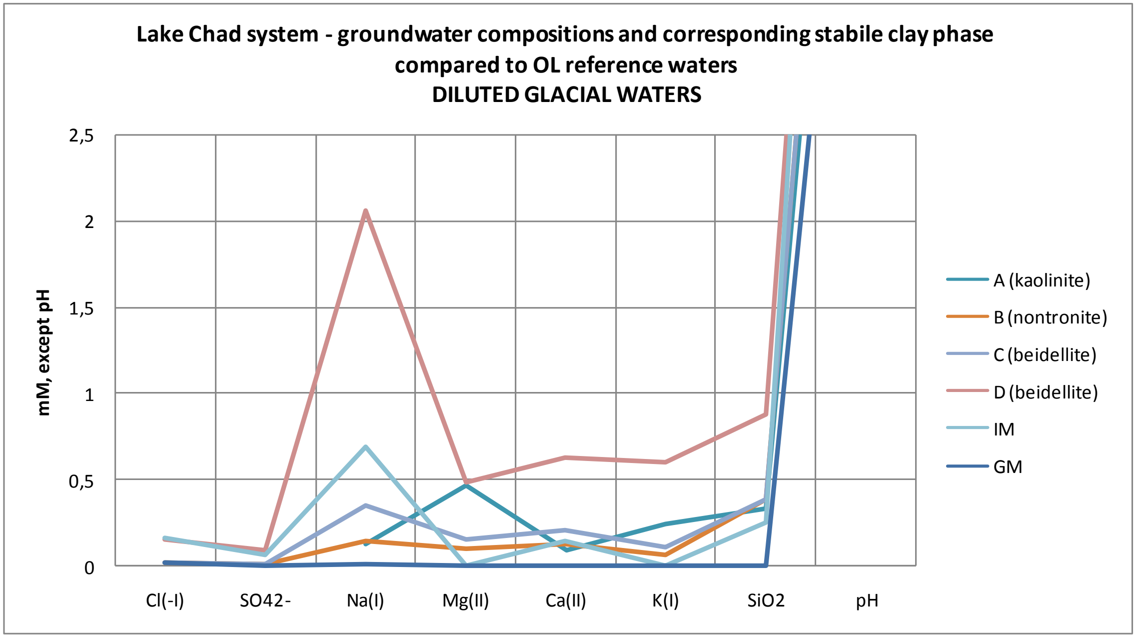
In general, it can be said that a continental effect is seen as a formation of aluminous minerals where as evaporitic smectites are enriched in Mg. In the middle the smectites are progressively enriched in magnesium and depleted in Al and Fe. Similar profiles are produced also in weathering horizons of ultramafic and basic rocks that show saponitization in the more concentrated environment and nontronite formation is common in the more diluted ones (e.g. Wildman et al. 1968, 1971).

Lake Chad is situated in central Northern Africa (Figure 4-20). A similar profile as the one described above has been found also in the sediments of this lake system, extensively studied by Lemoalle & Dupont (1973), Carmouze (1976), Gac (1980) and Gac & Tardy (1980).

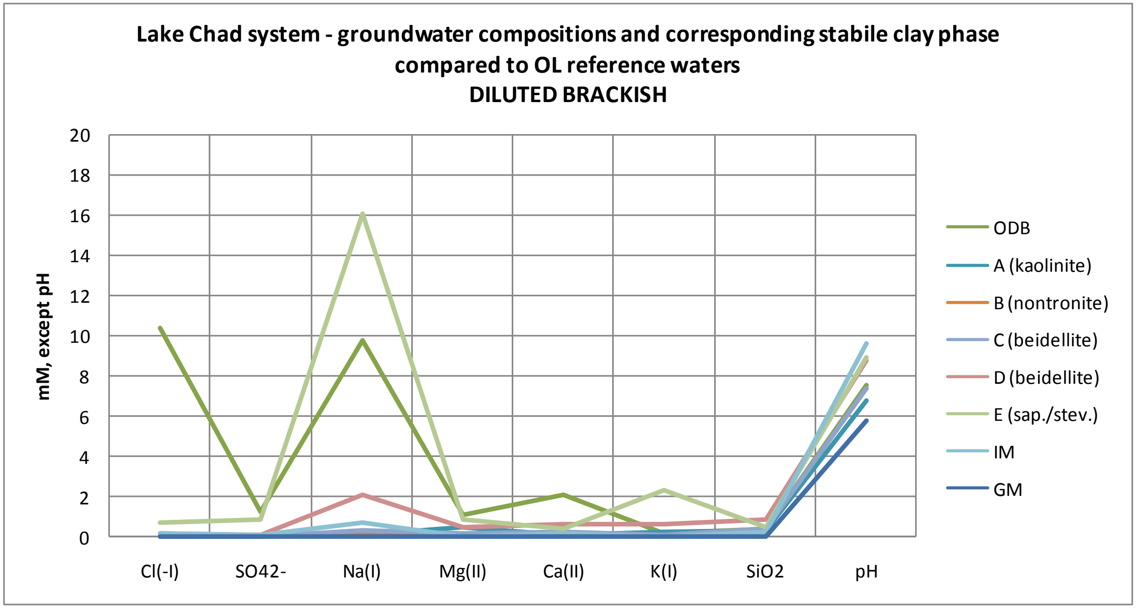
Porewater compositions in the sediments correspond to the smectite abundance and have allowed determination of the stability fields for different smectites and kaolinite (Gac 1980). Water compositions have been compared to Olkiluoto reference waters in Figure 4-21. In the Lake Chad system the most stable clay phase depends on the groundwater composition. For the minerals presented corresponding salinity TDS (millimoles/kg H_2O) are: Kaolinite (A) 61.0, Nontronite (B) 76.0, Beidellite (corresponding montmorillonite) (C,D) 76.0 and 548.3 and Saponite/Stevensite (E,F) 1759.2 and 5567.5. The pH rises from 6.8 to 9.9, respectively. As the waters are examples of sediment pore waters, the comparison has been made with groundwaters, not pore waters. In case of diluted glacial melt water (IM) the composition is close to sediment porewater of nontronite and beidellite stability fields (more diluted environment) (Figure 4-21a). Olkiluoto diluted brackish groundwater has quite close composition to that of water occurring with saponite (more diluted alternative) and it is not that far either from the water composition observed at the beidellite stability field (Figure 4-21b). Saponite/stevensite groundwater compositions envelope the Olkiluoto brackish saline to saline compositions quite nicely, except that the $CaCl_2$ composition is obviously higher in the Olkiluoto waters that what is found in the lake system (Figure 4-21c). Smectites are stable phases in also diluted environments and this information may be used to evaluate the effects of the glacial melt waters possibly penetrating the repository during the future glaciations.

Figure 4-20. *Location of the Lake Chad. (Map from: http://www.news.wisc.edu/5846).*

a)



b)



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c)

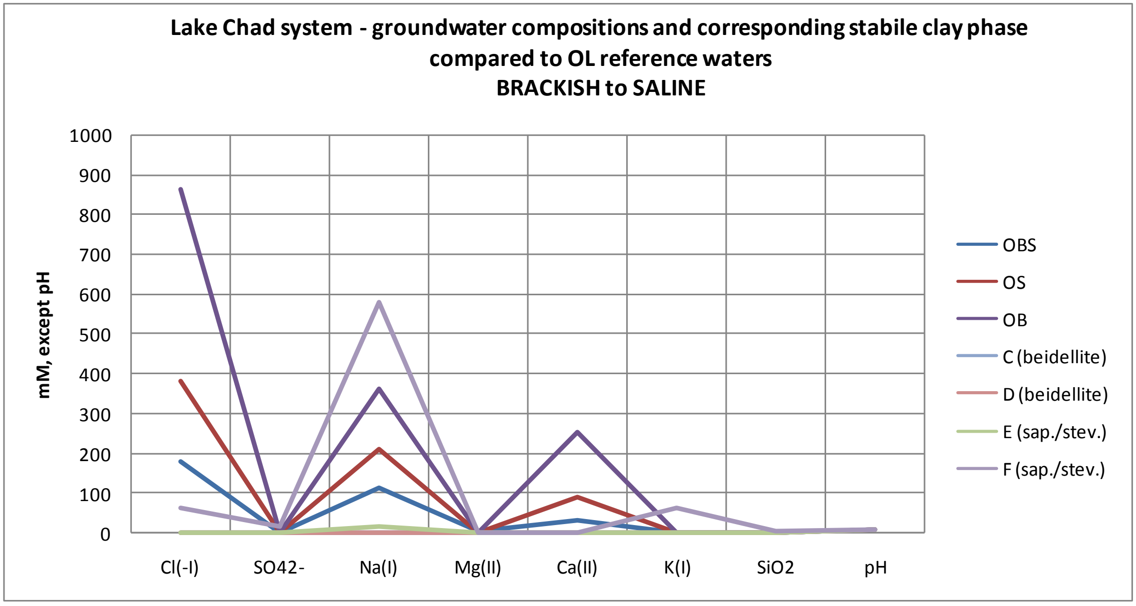


Figure 4-21. *Lake Chad groundwaters compared to Olkiluoto reference groundwaters a) diluted glacial melt waters, b) diluted brackish and c) brackish to saline. See B) for detaild pH. Abbreviations: ODB=Olkiluoto Dilute Brackish, OBS= Olkiluoto Brackish Saline, OS= Olkiluoto Saline, OB= Olkiluoto Brine, BDB= Bentonite Dilute Brackish, BBS= Bentonite Brackish Saline, BS= Bentonite Saline, GM= Glacial Melt water (Grive et al. 2007).*

4.8 Fraser River delta (Canada)

Smectite occurs in the sediments collected from the modern Fraser river delta (<10000a) near Vancouver (Canada). Porewaters collected from sediments at different depths of show mixing of meteoric and marine waters that have been preserved as “connate” in the sediments (Simpson & Hutcheon 1995). Deviation from simple mixing is observed for Ca, Mn, Fe, SO_4 and HCO_2 suggesting diagenetic modification, but not for Na. Salinity increases with depth from dilute to composition close to that of modern sea water. In this environment sediments, both clay rich and sandy, contain 5-10 % smectite in the < 2µm fraction. Bulk composition of the sediments is: quartz 50-60 %, feldspar 30-40 %, mica/illlite <15 %, chlorite <2 %, amphibolite <2 %, pyrite <2 % and calcite as commonly detected (max 11 %).

The Fraser river delta has been formed after the last glaciation on the top of glacial till (~10000 a). Diagenetig features have not been observed from the sediments apart from precipitated calcite and pyrite. Thus, illite is most likely from sedimentary origin. The porewater of the lower most unit directly above the till has anomalously low Cl content representing the meteoric source after glaciation, which has been preserved in the sediment.

Smectite is observed in all samples in the clay fraction. Selected pore water samples that have been taken from the sediments logged as clay rich are compared with Olkiluoto reference waters. Water compositions from the Faser river delta overlap those of Olkiluoto reference waters (Grivé et al. 2007). Examination of reactions between clay minerals and water suggest that porewaters are in cation exchange equilibrium with smectite. Smectite was modelled as a micture of Ca-, Na-, Mg- and K- beidellite end member components. Activities of each component was estimated with marine and freshwater (compositions given in Simpson & Hutcheon 1995). Clustering of the activity ratios around the exchange reaction suggests that an exchange reaction between Ca-beidellite and Na-beidellite is occurring in the sediments.

Porewaters from the Fraser river delta sediment have lower Ca but higher Mg and K contents compared to those of Olkiluoto reference waters (Figure 4-22). pH ranges from 5.7 to 8.7 in Fraser river delta (shallow samples have lower pH) sediments and the samples O,P and Q (deeper samples) that are the most close to Olkiluoto reference samples (OBS, OS and OB) have pH ~7.5, which is close to those of Olkiluoto pH values.

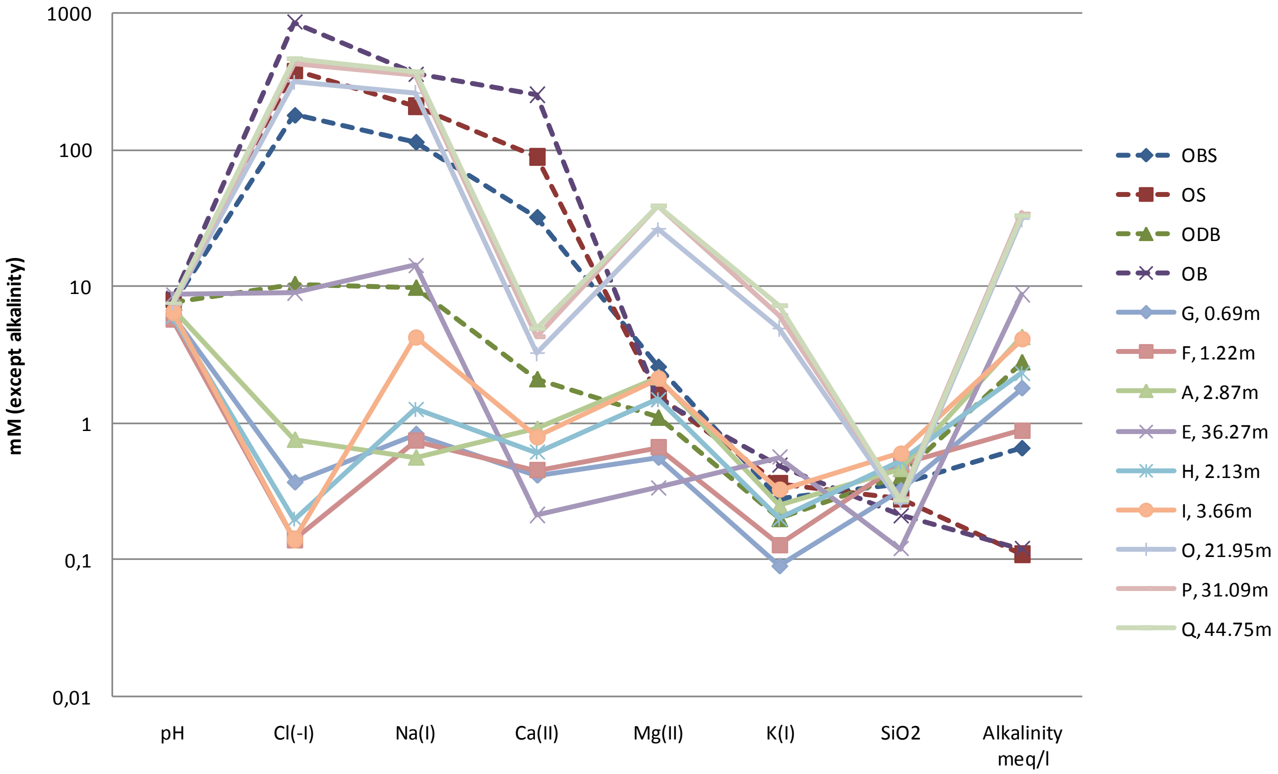


Figure 4-22. *Olkiluoto Brackish Saline (OBS), Olkiluoto Saline (OS), Olkiluoto Dilute Brackish (ODB) and Olkiluoto Brine (OB) reference waters (dashed lines) compared to porewaters extracted from the clay rich sediments (Fraser river delta). Smectite occurs as a stable phase in all of these sediments in similar amounts (5-10 %) of the clay fraction.*

4.9 Searles Lake (California, USA)

As discussed above high pH is related to the dissolution of smectite. Previously this phenomenon has been studied in laboratory (e.g. Nakayama et al. 2004, Yamaguchi et al. 2007, Karnland et al. 2007) and by means of modelling (e.g. Savage et al. 2002; Gaucher et al. 2004) but evidence from natural systems has been very limited.

Savage et al. (2010) have reported clay alteration in natural system controlled by salinity and pH at Searles Lake, California (Figure 4-23). Lacustrine mudstones (almost 700 m thick) of continuous sedimentation over last 3.2 Ma show variation in amounts of detrital minerals. Three different diagenetic zones have been identified (Figure 4-24):

1) Upper zone with alkaline pore fluids (pH 9-10) and variable salinity (28 % TDS used in modelling based on Gale 1915; see Table 4-9), in which detrital montmorillonite has been largely consumed,
2) Middle zone with pore fluid pH > 9, but moderate salinity (28 % TDS used in modelling based on Gale 1915; see Table 4-9), showing considerable amount of unaltered detrital montmorillonite, and
3) Lower zone with moderate pore fluid pH (7.5-8) and moderate salinity (~3.5 % TDS according to Hay & Guldman 1987), in which detrital montmorillonite is unaltered.

Detrital montmorillonite (currently lacking among the upper zone authigenic minerals, see figure 4-27) is thought to be the principal reactant in the formation of authigenic minerals (Fe-illite, Mg-smectite, K-feldspar and analcime; Hay et al. 1991). This is based on the occurrence of montmorillonite in the sedimentary source areas Searles Lake sediments (Droste 1961). Also dry climate and a stable Lake drainage system of the area suggest that montmorillonite should have been the major clay mineral in sediment supply during sedimentation (Hay et al. 1991). Isotopic studies show that several substantial downward groundwater flow events (rather than dissolution) have taken place when brines formed in lake have moved down through the salt and mud deposits (Friedman et al. 1972). Temperature in the formation has been estimated to have reached 48 ºC at its maximum and the mean lake temperature has been estimated to have been ~20 ºC (Smith et al. 1983).

Savage et al. (2010) have also performed modelling using reactive-trasport module of the generic modelling code QPAC (Quintessa 2008). Pore fluid compositions used in the modelling are given in Table 4-9. Pore fluid compositions have been derived based on the studies by Hay & Guldman (1987), Hay et al. (1991), Gale (1915) a.o. and is described in detail in Savage et al. 2010. Porefluid compositions are representative of those of different diagenetic zones.The model reproduces the observed mineralogy relatively well, though not exactly. Improvments to the modelling are presented in the study, which concern also previous studies made for radioactive waste repositories (e.g. Wanner et al. 1992).

However, the main observation from the nature is made that suggest that montmorillonite is relatively inert in pH conditions of <9, but could be reactive under mildly alkaline conditions (pH 9-10) over long time scales. However, salinities between these two types of groundwaters vary apparently from 3.5 % TDS to 28 % TDS, respectively.

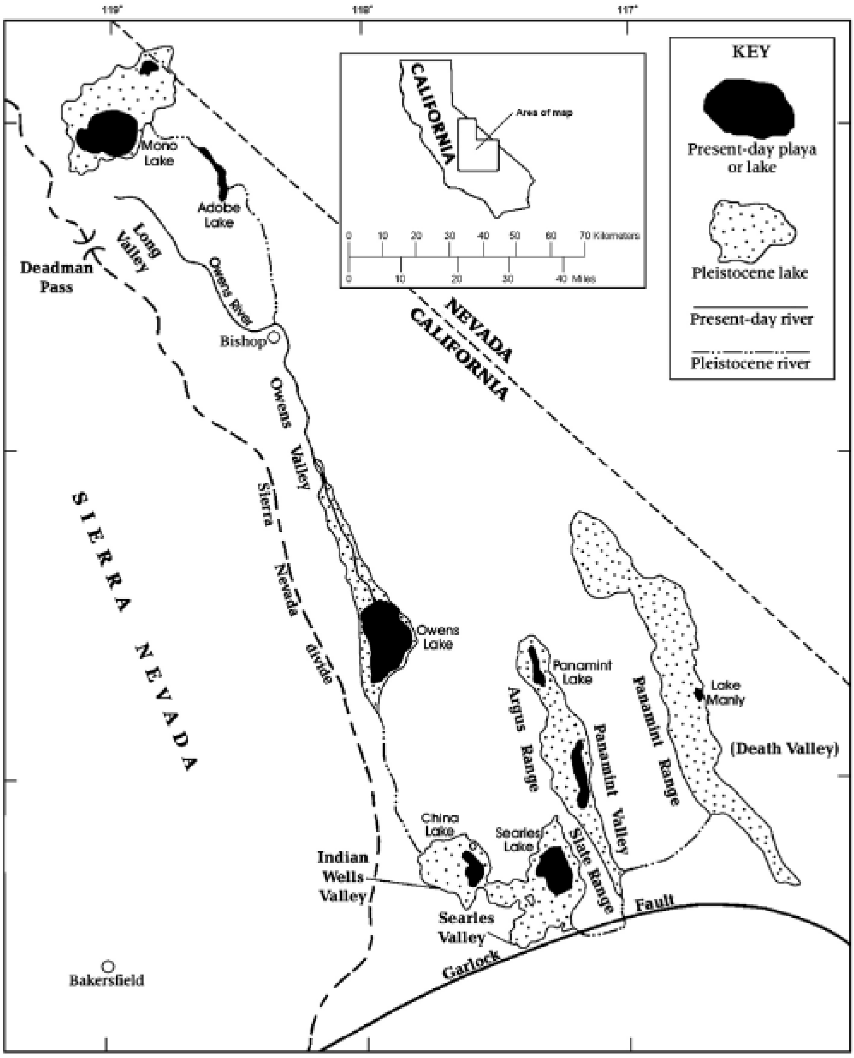
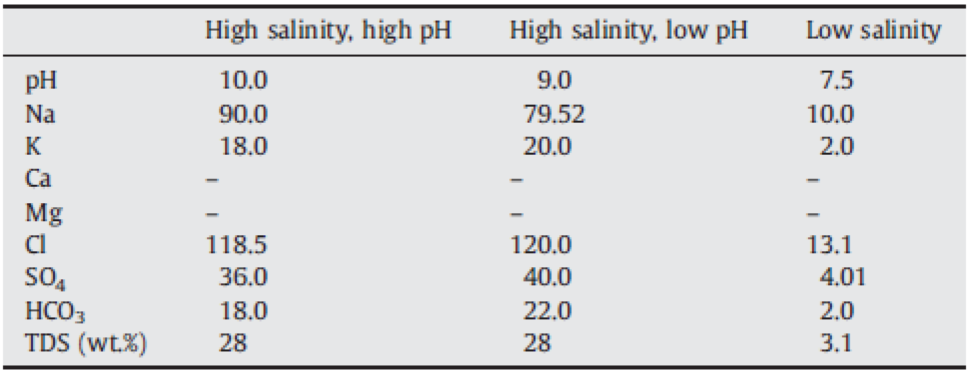


Figure 4-23.*Location of the Searles Lake, California (Savage et al. 2010).*

Table 4-9. *Compositions of pore fluids used in the modelling (g/l).*



	High salinity, high pH	High salinity, low pH	Low salinity
pH	10.0	9.0	7.5
Na	90.0	79.52	10.0
K	18.0	20.0	2.0
Ca	–	–	–
Mg	–	–	–
Cl	118.5	120.0	13.1
SO_4	36.0	40.0	4.01
HCO_3	18.0	22.0	2.0
TDS (wt.%)	28	28	3.1

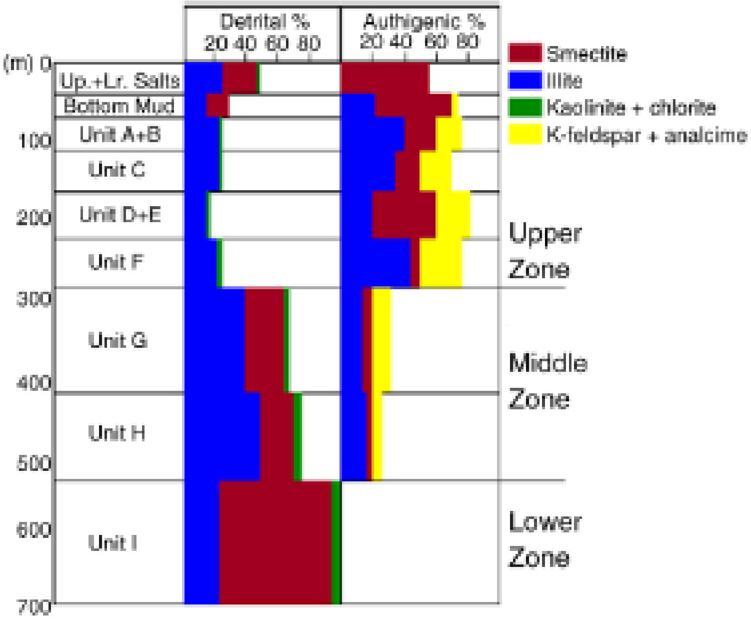


Figure 4-24. *Variation of amounts of detrital and authigenic minerals in mudstones with depth from Searles Lake (Savage et al. 2010).*

4.10 Clay Spur bentonite, Wyoming (MX-80)

MX-80 bentonite is mined in NE Wyoming (USA) among others from the Clay Spur bed at the top of the Cretaceous Mowry formation (Figure 4-25). The deposition of bentonites is part of the sedimentary history of the Mowry shale that took place more than 65 Ma ago (Slaughter & Earley 1965) in the southern embayment of the late Albian Western Interior Cretaceous sea (Mowry sea), which is thought to have been fresh to brackish in character. At later stage during genesis the sea became increasingly saline (Byers & Larson 1979). Volcanic ash, rhryolitic (Slaughter & Earley 1965) that deposited in the shallow sea has been altered in situ in Wyoming area (in common with other western American bentonite deposits; Rath 1986). The ash is considered to have been chemically homogenous (Elzea & Murray 1989).

The Mowry shale has been divided in three palaeoenvironments based on the biogenic and sedimentologic structures. Different paleoenvironments are seen as variation in trace element chemistry of smectites collected from Clay Spur bentonite, which explains that the smectite composition varies both stratigraphically and laterally (Elzea & Murray 1989; Figure 4-26). Differences in weathering conditions overprints the chemical signatures related to palaeoenvironment in some places (Elzea and Murray 1990). Also major element chemistry of smectite follows the northwest-southeast geographic trend showing for example total average Fe decrease from 4.51 to 3.88 wt.% and Mg increase from 1.98 to 2.34 wt.% respectively (Elzea & Murray 1990).

The most important bentonite deposits in Mowry shale occur in the same cyclic sedimentary sequence consisting from bottom upwards of shale, coal, bentonite and finally shale grinding to sandstone/conglomerate (Slaughter & Earley 1965).

The deposit of the Wyoming bentonite MX-80 provides a natural analogue for the long term stability of bentonite in a closed system and thus it can not be used as a direct analogue for the repository, which is considered to be an open system (Smellie 2001). The Wyoming bentonites have remained unaffected by the continued palaeoevolution of the Mowry sea basin since the deposition, due to rapid deposition of the overlying mud/silt that isolated the formation rapidly after deposition (Cadrin et al. 1995). The most of the scientifically studied bentonites (see Smellie 2001) seems to have not undergone significant post-depositional alteration. However, as shown by Cadrin et al. (1995) bentonites from other localities than Wyoming show chemical variation that can be explained by postformational processes. Bentonite sampled at e.g. Pueblo, Colorado represents the same bentonite formation as bentonite mined in Wyoming (MX-80) and shows neoformation of smectite due to exposure to basinal fluids during burial down to ~2 km. In Manitoba (Canada) the stable isotope results from bentonite suggest contact with ^{18}O rich basinal brines at 20-25 ºC. Unfortunaltely no groundwater compositions are given in this work, but it seems that at least in these two locations mentioned above the montmorillonite content has been sustained 100 % (clay mineralogy) thus suggesting smectite stability in the given circumstances. Neoformation of smectite is seen as fibrous smectite that is concentrated in <0.2 µm fraction and has higher ^{18}O values. Interaction with basinal brines seen in ^{18}O values correlates in the Ca (interlayer) and Mg contents in montmorillonite. Diagenetic alteration is also reported in Cadrin et al. (1995).

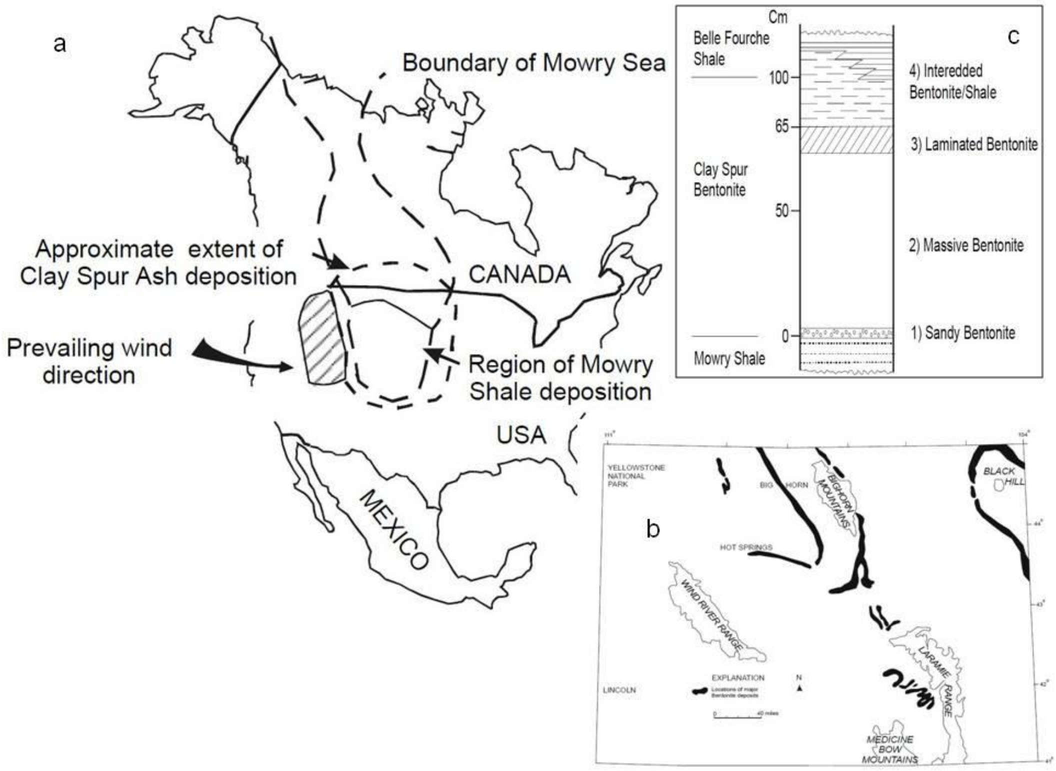


Figure 4-25. *Occurrence of Wyoming bentonites. a) palaeogeography of North America and the westrn interior seaway (Mowry sea) during Albian times (after Elzea & Murray, 1990), b) close up of the Wyoming bentonite deposits (the most important economic deposits (such as Clay Spur bed are found in the Black Hills region) (after Rath 1986), c) profile through the Clay Spur bed showing the four lithological units [(based on Elzea & Murray (1990) and reproduced by Keto (1999)].*

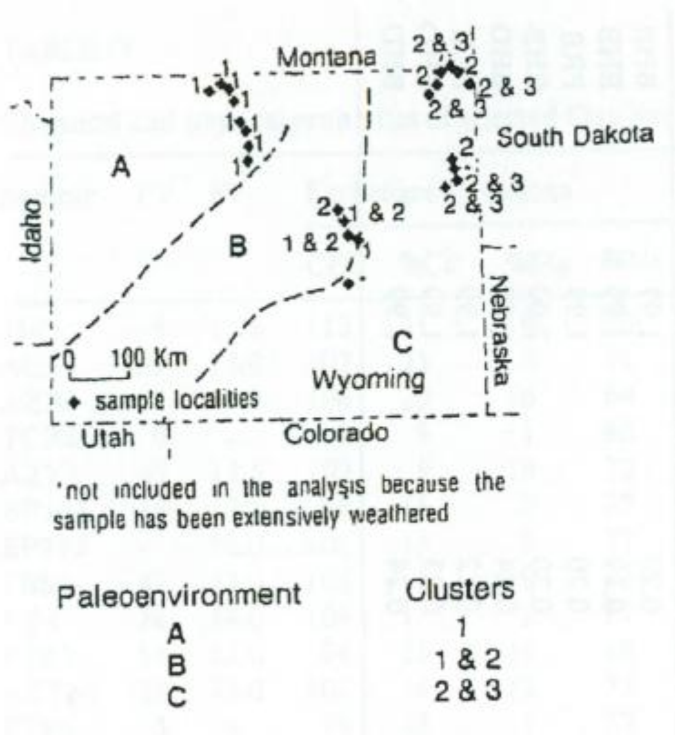


Figure 4-26. *Paleoenvironments of the Mowry Sea and corresponding smectite sample localities and alteration clusters. A= Big Horn Basin, B= Powder River Basin, C= Black Hills District.*

The studies mentioned above consider smectite data acquired from surficial deposits of the Clay Spur bed. However, a notable feature of the Clay Spur bed is that it occurs at different depths around in different areas. The Mowry shale is commonly a known source also for oil and gas deposits, which are constrained by the local deeper sedimentary basins (e.g. Anna & Cook 2008, Burtner & Warner 1986). Oil and gas is generated at elevated temperatures of about 50-175 ºC and 175-260 ºC, respectively. Oil and gas formations have been located both above and below the Clay Spur bed. Differences in thermal conditions would then be expected and its effects on the bentonite could be studied in more detail. As an example the burial history of the Mowry shale in Powder River basin next to Black Hills (Figure 4-27) is shown in Figure 4-30. At the location marked in Figure 4-28 the same bentonite hosting formation that is excavated for MX-80 is found buried at ~12000 feet corresponding to ~3650 m.

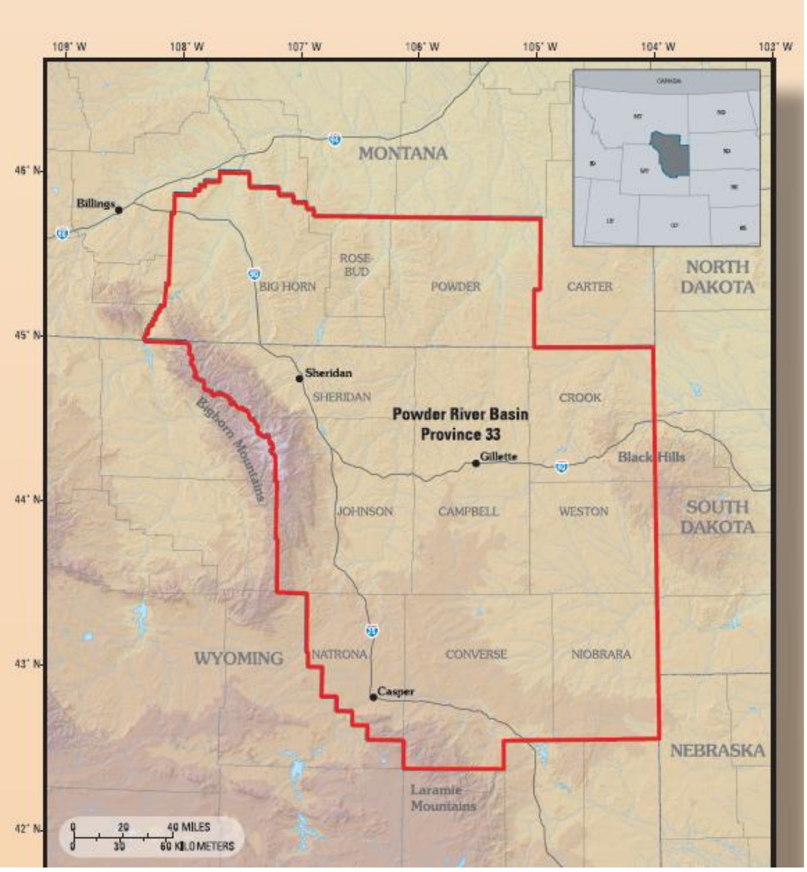


Figure 4-27. *Map showing boundary of Powder River Basin Province (red line) (Anna & Cook 2008).*

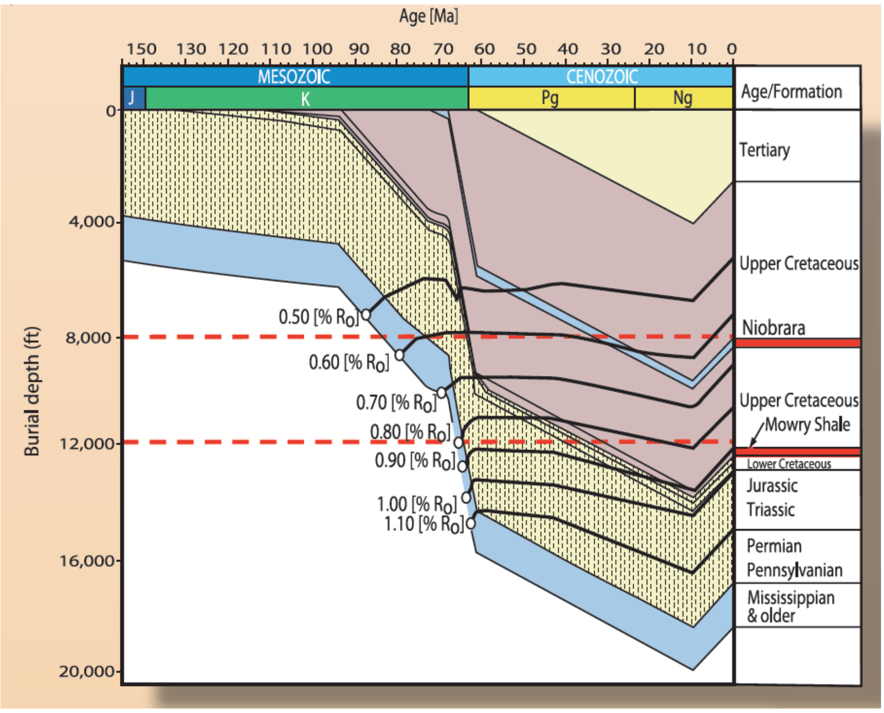


Figure 4-28. *Burial history curve for the Mowry Shale on west side of the Powder River Basin (Anna & Cook 2008).*

Sedimentary environment of the bentonite deposits in the Blackhill district was investigated in detail by Knechtel & Patterson already in the 60's. This is the region where MX-80 is excavated. According to Knechtel & Patterson (1962) the following is reported, which may be of interest for this report:

- Moisture content in the bentonites in the northern Black Hills district ranges from about 10% to several times the weight of the dry bentonite
- Average moisture content assumed by the operators has been about 30 % (also Clay Spur)
- Drying and wetting cycle is repeated in most outcropped areas
- Weathered surfaces of the bentonite swells only slightly and are characterised by polygonal shrinkage-crack patterns
- Clay Spur Bed and two other bentonites in the Mowry Shale are Na type, but also Ca-, Ca/Mg- and Ca/Mg/Na type bentonites occur at different stratigraphic levels.

Clay Spur bed:

- Chemical analyses are close to those presented in Table 2-2.
- In addition to Ca^{2+}, also H^+ is analysed as an exchangeable cation in some samples. Na^+ is the dominating cation. H^+ is seen as low $pH < 5$, but this is observed only in few localities.
- Similar montmorillonite compositions and minerlalogical descriptions as given in Table showing a good level of homogeneity of the Clay Spur material.

The data available shows that while the Clay Spur bed provides relatively homogenous deposits of bentonite for production it also occurs at different depths and may show variation that could be used in the long-term safety evaluation of the material. The samples in Elzea & Murray (1990) study come from the surface pits and provide useful information on the properties of the MX-80 material.

I/S expandability and organic indices of the Mowry Shale have been studied by Burtner & Warner (1986) related to hydrocarbon generation in the northern Rocky Mountain area including the Powder River Basin next to Black Hills district. The maturation degree was studied by selecting smectite samples (exluding bentonite beds as they show less alteration) that were studied using clay mineral, TOC and Rock-Eval analysis. Smectites of the Mowry shale show expandable I/S contents as low as about 20 % at depth of ~4 km in Powder River basin. Down to ~2.5 km depth the I/S remains at ~80 %, showing the sudden decrease in expandability as seen also e.g. Gulf Coast of Texas (see references in Burtner & Warner 1986). Burtner & Warner (1986) report today's temperatures of about 82-88 ºC for the Mowry Shale at 2499 m and 2621 m (start of oil generation).

Detailed mineralogical data or groundwater data related to Clay Spur or other bentonites in the Mowry shale was not found in the literature. Energy companies have drilled the area quite extensively but no relevant published data on the detailed sedimentology was found. On the long-term evaluation point of view, such data would provide valuable information.

To be able to make a reliable comparision between bentonite in its natural state and the compacted buffer in the disposal hole, a more detailed investigation would be needed where the water conductivity properties of the adjacent rocks of the Wyoming deposit would be defined. This would provide an estimate about groundwater availability in the deposit. Also burial history and more detailed mineralogical studies of the Wyoming bentonite would be of great interest. Smellie (2001) conclude that the Wyoming bentonites have not gone through post-depositional alteration because of physico-chemical isolation. Also surrounding shales are considered impervious, but in general, shales are considered half-closed systems, in which few elements are controlled by the external environment (Meunier 2005). As shales commonly show more evolved alteration than bentonites at the same strata, the preservation of bentonite may not be due to isolation of the surrounding shales, but to the “closed” nature of the bentonite itself.

4.11 Greek bentonite Deponit Ca-N

The Greek bentonite (Deponit Ca-N) is quarried in the north-eastern of the island of Milos, where some of the currently economically most important bentonite deposits in Europe are concentrated (Figure 4-29a). The charge compensating cations are dominated by calcium, which is referred to in the commercial name IBECO Deponit Ca-N, also Mg is a major cation component. The island of Milos in the Aegean Sea is part of the Hellenic Arc volcanic province. Pyroclastic tuffs and lavas of andesitic to dacitic compositon are the main parent rocks of the bentonite, which forms irregular bodies with a thickness of 10–40 m within the pyroclastics (Figure 4-31b).

The volcanic rocks have yielded K-Ar ages in the range 3 .5–0.09 million years (Fytikas et al. 1986). Based on C, D and O isotope data, (Decher et al. 1996) conclude that the bentonite formation is a result of hydrothermal reactions between the permeable volcanic rocks and percolating groundwater heated to below 90 °C during volcanic activity, although there is some disagreement about the genesis e.g. Christidis et al. (1995). Bentonitization is assumed to be driven by either marine or meteoric fluids.

Hydrothermal alteration is ubiquitous through the entire island of Milos within and in close vicinity of bentonites. Gypsum and barite veins, stockwork textures characterized by sulphur-metasomatism, silicification and still active solfatara thermal springs are observed and the type of alteration is controlled by structural criteria and is superimposed to stratiform bentonites (Christidis 1992).

The formational temperatures are below the 100 ºC limit set for the buffer material which should support the stability of the bentonite in the repository conditions. Information on the chemical composition of the altering fluids would be of interest but were not found in the literature.

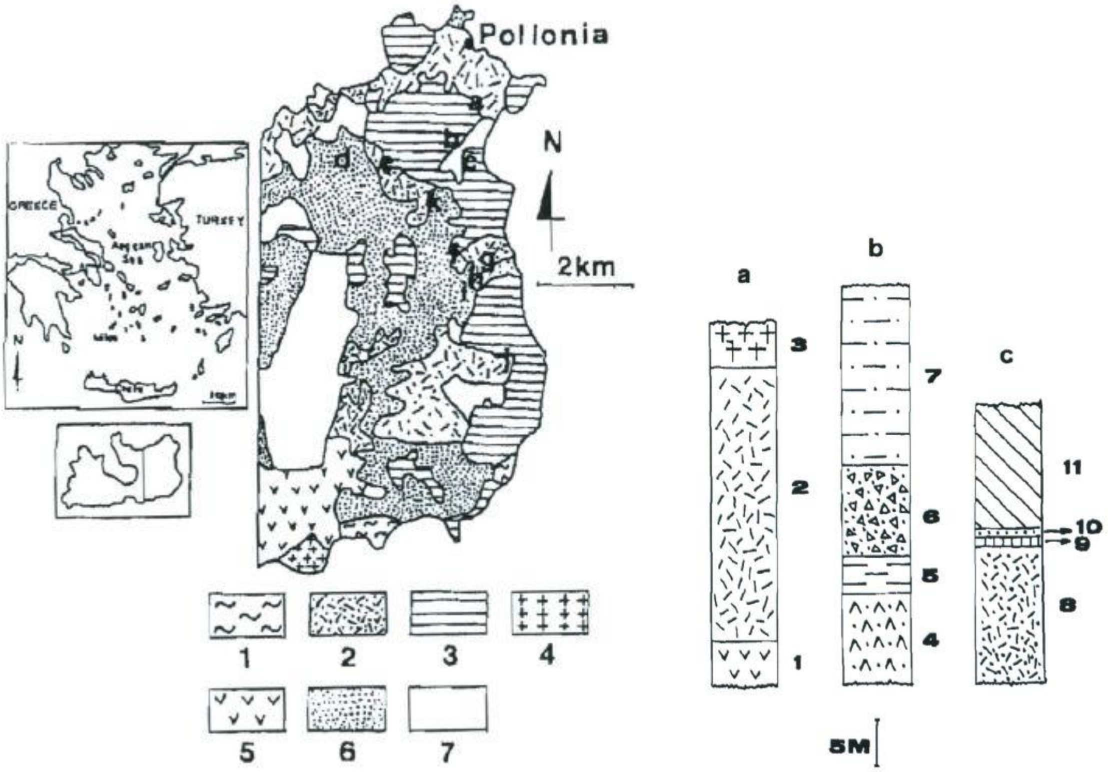


Figure 4-29. *a) The island of Milos (map modified after Fytikas et al. 1986) (key: 1. Basement, 2. Protoliths of bentonites, 3. Lower Pleistocene lava domes, 4. Lava dome of Halepa, 5. Rhyolitic complex, 6. Products of phreatic activity of Quarternaty, 7. Quarternary sediments, a. Zoulias, b. Aspro Horio, c. Tsantili) and b) a schematic sections of representative Miloan bentonite deposits (Christidis et al. 1995) (key: a. Koufi deposit, 1. Green basal bentonite derived from a lapilli tuff, 2. Blue-green bentonite with porphyritic texture, 3. Yellow bentonite, b. Ankeria deposit, 4. Blue green plastic bentonite, 5. Bright yellow bentonite, 6. Yellowish bentonite with beds of opal-CT, 7. grey bentonite, c. Aspro Horio deposit, 8. Blue-green bentonite with "brocken tuff" texture, 9. Pink-reddish bentonite, 10. Grey bentonite, 11. Yellowish bentonite with opalini silica beds in the upper parts.)*

Cryptic variation has been observed in Milos bentonites (Christidis & Makri 2007). This variation is seen as systematic compositional variation in layer charge, which increases towards the top of the formation accompanied with increase in beidellitic component. Also CEC is increased along with the layer charge. Quite similar variation is also observed from Charente (France; Meunier et al. 2004). This phenomenon is invisible to the naked eye and further research is needed to better describe the phenomenon. Cryptic variation may contribute to the optimization of the Na-activation processes of commercial bentonites. This process is attributed to microenvironment during the formation of bentonite. Whether this affects the behaviour or the properties of the commercial product is unclear. However, experimental studies have been done using the actual bentonite materials and therefore there is no reason to expect that this variation should have effects on the buffer behaviour as long as the quality control of the bentonite material is at sufficient level during the manufacturing of the buffer for the deep repository.

4.12 Summary of evidences from natural occurrences

The basic information of the natural occurrences dicussed to address the issue of cementation in Sections 4.1-4.4 is collected in Tables 4-10 and 4-11. In natural occurrences cementation is generally a consequence of smectite/illite conversion (see Section 3.1), in which silica is first released and further precipitated as the conditions have changed favourable for it. However, the temperature conditions are quite different compared to the repository conditions: temperature of magma intrusions have been generally between 800-900 ºC, while the canister surface temperature is below 100 ºC. Also the duration of the heating effect in many cases is in order of millions of years or unknown. In the repository the elevated temperature (87.5°C to 30.5°C, unsaturated state, see Figure 1-3) period is relatively shorter (about 10000 years or even less), as described in Chapter 1. However, for some natural occurrences shorter time periods and lower temperatures have been suggested. Several studies have concluded that cementation is quite unlikely at temperatures below 130ºC. In the natural occurrences considered in this study the cementated aureole width varies from 20 cm to 90 m. If the wideness of the aureole is dependent on the temperature of the heat source, the wideness of the cementation zone in the repository is probably much smaller than in natural formations. In natural occurrences the exact composition of hydrothermal solutions is not very well known, so it is difficult to estimate on these bases the width of the possible cementated area in repository conditions.

Thus the cementation information from natural bentonite occurrences may not be directly applicable to the repository conditions, but they show, anyhow, that though much larger temperatures have affected the bentonites and for even larger periods of time than the transient thermal phase last in the repository, there is still unaltered bentonite in those deposits.

According to the data available, accelerated illitisation due to saline conditions is not probable in the expected repository conditions (see Section 4.7). Salinity effect on the bentonite has been also studied at San José, Cabo de Gata (Section 4.4). Critical physical properties of the bentonite have been retained despite of the harsh saline environment.

Illitisation even in the oldest (Ordovician) bentonites is not thorough and it seems that in general smectite contents remain higher in the middle parts of the bentonite beds which may be due to the potassium source from the adjacent rocks (see Section 4.1). As well, if the bentonite is reheated the changes are often located in the restricted area at the edge closest to the heat source (see Section 4.2). Thus, the effect of the thermal event is strongly affected by the chemical environment.

Slight illitisation has been taken place also in the Clay Spur bed from which MX-80 is excavated. This is seen in the mineralogical analysis. The closed nature of the Clay Spur bed has been attributed as responsible for the good preservation of the high smectite content. The same bentonite is found also in deeper diagenetic environments and comparative studies from varying conditions of the same bentonite would be informative (see Section 4.10).

It also seems, that the rheological properties of some natural bentonites are quite similar even when comparing completely different bentonites (see Section 4.4). This was observed at least for differing Mg, K, and Na contents in the smectite. However, the expected Olkiluoto groundwater conditions do not favour these cations.

Very little data was found on the porewater/groundwater composition in bentonite occurrences and more investigations on this area would be needed better to evaluate the long-term stability of the buffer in the disposal hole. Stability of smectite in different porewater (sediment) compositions has been discussed as well as some bentonite leachates. The simplified compositions of the groundwaters discussed in this report are given in Table 4-12. This table contains data presented as ranges and any further use of this data shoud be made by using the original references given in the table. However, as seen in the table smectites occur as stable phases in similar groundwater compositions as what are expected in Olkiluoto (see Sections 4.6, 4.7 and 4.8). Though it should be noted, that detailed mineralogical data is sparse in many cases, as smectite mineralogy is not further reported. On the other hand, the extreme conditions (alkaline) for example in Searles Lake are drastically different (Section 4.9).

Alkaline conditions (pH 9-10) has been observed to increase smectite reactivity in natural conditions at Searles Lake (Section 4.9) in relevant (repository evolution) time scales and to cause mineral transformation at variable salinities (28 wt.% TDS by Gale 1915). Alkaline conditions have been studied extensively in laboratory and by means of modelling but the examples in nature have been sparse. It is suggested that under these mildly alkaline conditions (pH 9-10) up to 70 % of the detrital clay may be replaced by authigenic minerals such as Fe-illite, analcime, and K-feldspar over timescales < 100 ka. Montmorillonite has been considered to be relatively inert at pH < 9. Smectite is completely unaffected at pH 7.5 and 3.5 wt.% TDS at the lowermost and thus the oldest sedimentary zone.

The impact of alkaline leachates on bentonite buffer is being studied currently according to the plans presented in Posiva 2009a and more information should be available in the near future.

One of the best natural analogue for the long-term stability of the bentonite buffer could be the Clay Spur bed itself from which the MX-80 is mined (Section 4.10). Unfortunately the hydrogeochemical data from this formation is sparse and more detailed investigation would be needed to evaluate the actual circumstances in which the bentonite has been preserved, especially to be able to evaluate the groundwater conditions as well as physical conditions (e.g. density and pressure). At the area of the Clay Spur deposition the sedimentary conditions vary depending on the location. At the bottom of the basinal areas there are known source areas of hydrocarbon (gas and oil) both above and below the Clay Spur indicating elevated temperatures. However, no information of the geological/hydrological details from these locations was found. Also other bentonite source formations should be studied especially focusing on groundwater chemistry to gain better understanding of the stability fields of bentonites in nature.

Table 4-10. *Summary of the essential information of the natural bentonite formations.*

Location	Cause of thermal effect	T_{max} magma	Intrusion, years ago	T_{max} bentonite	Temperate period	Pressure max. in situ	Time of maximum pressure	Hydro-thermal effect	Cementation	Aureole, width	Reference
Kinnekulle (Sweden) (Section 4.1)	Intrusion	1 100	450 Ma	140	200 days	20 – 30 MPa	Quaternary	Possible	Yes (silica and calcite)	> 95 m	*Pusch et al. (1998)*
Busachi (Sardinia) (Section 4.2)	Intrusion	700-800	Not known	800-500	1-7 days	0.05 – 0.2	Miocene - present	Yes	Yes	> 0.7 m	*Pusch & Karnland (1988a)*
Morrón de Mateo (Spain) (Section 4.4)	Intrusion	820	10.5-12 Ma	55-66				Yes			*Caballero et al. (1985)*
Ishiri (Libya) (Section 4.3)	Intrusion	830-900	20.3 Ma					Yes	Yes (silica)	20 cm	*Kolaříková & Hanus (2008)*

Table 4- 11. *Summary of the essential properties of the natural bentonite formations.*

Location	Water content, in situ[%]	Density [kg/m^3]	Porosity [%]	Clay fraction content [%]	Smectite content in clay fraction [%]	Swelling pressure [MPa]	Hydraulic conductivity [m/s]	Cation exchange capacity [meq/100 g]	Reference
Kinnekulle (Sweden) (Section 4.1)	22-35	2000-2200*	30-40	35-40	60-45 (smect.+I/S)	15-3.8			*Pusch et al. (1998), Muller-Vonmoos et al. (1994)*
Busachi (Sardinia) (Section 4.2)	6 – 36	1800*, 1250**		75-90	60 -90 (montm.)	0.48-0.51	10^{-11} - 3 x 10^{-11}	90-103	*Pusch & Karnland (1988a)*
Morrón de Mateo (Spain) (Section 4.4)		2000*	26					77	*Caballero et al. (1985)*
Ishiri (Libya) (Section 4.3)					90			35-90	*Kolaříková & Hanus (2008)*

**=density in water saturation, **=dry density*

Table 4-12. *Simplified composition of the porewaters discussed in this report. Main cation, chloride and* SiO_2 *compositions are given as mmol/dm*^{3}*. For more details see section given in brackets.*

Location	**Cl**	**Na**	**Mg**	**Ca**	**K**	**SiO_2**	**pH**	**Water type**	**Occurrence of smectite**	**Reference**
Olkiluoto dilute brackish to brine (Section 1.3.3.)	10-863	10-360	1,1-2,6	2,1-255	0,2-0,49	0,21-0,41	7,4-8,2	Groundwater at Olkiluoto	-	*Grivé et al. 2007*
Izu-Bonin fore arc sedimentary basin (Section 4.6)	579-700	160-285	0,4-2,7	169-285	1-2	0,22-0,26	8,5-8,8	sediment porewater	marine sediment	*Egeberg et al. 1990*
Lake Chad system B to F (stabilitiy fields from nontronite to saponite) (Section 4.7)	0,02-63	0,1-580	0,1-0,9	0,1-0,6	0,06-64	0,4-2,3	7,4-9,9	sediment porewater	lake sediment	*Tardy et al. 1987*
East Slovak Basin Salt free bentonites (Section 4.5)	12-39	25-131	0,04-1,84		3,5-9			bentonite leachate	bentonite	*Honty et al. 2004*
East Slovak Basin Salt bearing bentonites (Section 4.5)	98-157	90-322	0,06-2,04		1,3-13,4			bentonite leachate	bentonite	*Honty et al. 2004*
Fraser river delta shallow (Section 4.8)	0,14-0,76	0,57-4,26	0,56-2,18	0,41-0,79	0,09-0,32	0,32-0,6	5,7-6,9	sediment porewater	delta	*Simpson & Hutcheon 1995*
Fraser river delta deep (Section 4.8)	9-463	14-376	0,3-39	0,2-4,9	0,6-7,2	0,1-0,27	7,5-8,7	sediment porewater	delta	*Simpson & Hutcheon 1995*
Searles Lake modelling High Salinity, High pH (Section 4.9)	3342	3915			460		10	modelled porewater	lake sediment,	*Savage et al.2010*
Searles Lake modelling High Salinity, Low pH (Section 4.9)	3385	3459			512		9	modelled porewater	lake sediment	*Savage et al.2010*
Searles Lake modelling Low Salinity (Section 4.9)	370	435			51		7,5	modelled porewater	lake sediment	*Savage et al.2010*

5 CONCLUSIONS

This literature review summarises the available information on the long-term thermodynamic stability and possible mineralogical changes of the bentonite buffer in the evolving chemical, thermal and hydrological conditions in Olkiluoto. Experimental results and theoretical considerations on the smectite stability have been discussed in Chapter 3 including mineralogical changes that may have an effect on the bentonite buffer (such as cementation/illitisation, other mineral transformations and changes in the exchangeable cation composition in the montmorillonite interlayer space). The other focus has been on indentifying natural occurrences providing evidence on the long-term stability of bentonite in the expected repository conditions, especially with respect to mineral transformation due to thermal effects (i.e. cementation) and smectite stability in varying geochemical conditions (Chapter 4). The processes seen in nature can be used in the evaluation both, the short-term (hydrothermal) and long-term (hydrogeochemical) stability of the bentonite buffer.

As the temperature in the repository will be relatively low (<100 °C) in the beginning of the evolution and the decrease will occur relatively fast (after 1000 years the expected maximum temperature is 45.5 °C in saturated case and after 10000 years 20.5 °C), it is likely that the chemical environment will dictate the buffer evolution in case of mineral alteration/transformation.

According to the reviewed literature it seems that illitisation and (silica) cementation of bentonite in the Olkiluoto repository is very unlikely in the current and expected natural groundwater conditions and due to the expected temperature evolution. However, this may change due to the foreign materials and structures of the repository (e.g. plugs, backfill, cement based construction materials, etc.). The release of K^+ and SiO_2 and the pH are the most important factors controlling cementation/illitisation processes. Elevated pH and salinity accelerate illitisation (at pH <13 the effects are rather unclear) and also promote other transformations. For example zeolite formation is suggested to occur already at pH<11. The repository evolution due to introducing foreign materials as well as pH should be and is being further evaluated. The alkaline leachates in the repository are expected to have pH 10.5-11.5, but, how these initial leachates evolve (i.e. dilute) in the repository in uncertain. Also other mineral alteration types than cementation/illitisation has been proposed to possibly occur in the repository. Experimental studies suggest that mineral transformation could lead more likely to saponitization and/or beidellitization, which can be faster reactions than illitisation. Saponitization of the buffer is not neccessartily harmful as saponite is also a swelling clay and has been considered suitable for buffer material in preliminary studies, which beidellite is not. Kaolinitisation/pyrophyllitisation with Si accumulation has been suggested to be more probable than illitisation at least in case of high saline and cementitious systems, but this is not observed in salinities similar to Olkiluoto conditios. However, this should be taken into account when evaluating cement-bentonite interaction.

A general assumption is that the higher the solid/liquid ratio the slower the mineralogical changes should be in the expected repository conditions. However, is has been suggested that also water vapour could act in the illitisation/cementation process.

The disposal hole may be dry for long periods of time and saturation times of the disposal holes may vary considerably depending on their location in the repository. Differing saturation conditions (Olkiluoto conditions) in relation to mineral transformation have not been studied in detail.

Salinity increase affects also smectite stability by causing loss of swelling ability. For Ca-type montmorillonite already a 115 g/l concentration of NaCl has been observed to cause significant swelling pressure decrease at initial dry density conditions (1.65 kg/m^3). More detailed studies using Olkiluoto specific mixed (Ca/Na) solutions are ongoing.

It seems that cation exchange in montmorillonite interlayer composition will occur in the expected groundwater conditions in the repository. Na type montmorillonite will change towards Ca dominant composition, but the actual rate and extent has not been evaluated explicitly. Natural bentonite have also Mg- and K- cations that are not so easily affected by the saturation process (cation exchange) as are Ca and Na. MX-80 has all these cations at initial state, and thus, a monocationic composition seems not possible to achieve in the Olkiluoto environment. Consequently it is important to notice this, when using the results from experiments that concern monocationic variants. The behaviour of a monocationic bentonite can be very different from that of bentonite that has only a dominance of a certain cation. Exchange process may lead to demixing of cations that may cause Na cation segregation to individual layers that may decrease the mechanical strength of the buffer. It is also clear that cation exchange affects some microstructural properties of the buffer at least the Cl incorporation in the interlayer space. In general it seems that the transformation towards Ca-dominated composition would favour the long-term stability of the buffer as Ca-dominated smectite has larger water retention capacity and anion incorporation to the interlayer space of montmorillonite is more extensive for divalent cations and it is not as easily dissolved in case of diluted groundwater or in case of high pH.

Natural occurrences provide information on the themal effects on bentonite as well as on the chemical stability of smectite giving positive prospects on the long-term stability of bentonite in repository conditions.

Thermal effects on bentonite are seen in nature in wide variety caused from short term magma intrusions to slow diagenetic formations. The attempt in this report has been to search for such locations where a relatively short term thermal effect would be seen. Several such locations were found, but the initial temperatures or the time scale or both are commonly not in the range expected in the repository. No such cementated or othervise transformed bentonite occurrences were located that would suggest cementation or mineral alteration in the current Olkiluoto conditions caused by the thermal effects. However, it should be noted that there is often lack of data and more precise studies are needed to better evaluate the cementation phenomenon as well as mineral alteration. Specific information on the hydrochemical conditions is usually sparse or lacking as well as estimates on the duration of the thermal event. Thus, the cementation information from natural bentonite occurrences may not be directly applicable to the repository conditions, but they show anyhow that though larger temperatures have affected the bentonites and for larger periods of time, there is still unaltered bentonite in those deposits.

According to natural occurrences the salinity seems not to accelerate transformation or cementation. Illitisation, even in the oldest (Ordovician) bentonites, is not thorough and it seems that in general smectite contents remain higher in the middle parts of the bentonite beds which may be due to the potassium source from the adjacent rocks (see Section 4.1). Especially in the occurrences where the temperatures have been relatively low during the cementation (see Section 4.1) the cemented bentonite is located at the bentonite-rock interface both at the closest and the further from the heat source, emphasising the effect of the hydrochemical environment (i.e. potassium content). Bentonites in nature behave mostly as closed systems and the mineralogical changes are located at or close the surfaces of the formation often leaving the middle parts unaffected.

The available information on the stability of smectite in the natural chemical conditions (without the thermal event) support the buffer stability in the disposal hole, although in these occurrences the mineralogical information is commonly too general and more detailed investigation on the porewater chemistry within bentonites would be of interest. Groundwater composition in natural bentonites is not very well studied topic according to the literature available. Such studies together with a careful mineralogical and formational study would provide a better possibility to evaluate the long-term stability of bentonite in the disposal hole in more precice way.

Highly saline (280 g/l TDS) and mildly alkaline conditions (pH 9-10) favour mineralogical transformations in natural sedimentary ocurrence, but there is evidence that in pH conditions of 7.5 and TDS ~35 g/l (mainly NaCl, K ~2 g/l) provide conditions where the smectite has remained unaffected (see Section 4.9). This supports very well the smectite stability at the current Olkiluoto conditions.

Natural occurrences provide information on the bentonite behaviour in varying conditions. How to adapt this information in the predicting the buffer behaviour is a challenging task. The evolution of thermal and hydrological conditions in the repository is quite well established. More concern is related to the foreign materials brought into the facility e.g. cementitious materials. Water/rock ratio plays important role also in mineral transformation affecting reaction rates. To be able to make a direct comparison between different natural occurrences and the buffer, more detailed information would be needed on density/compaction rate, saturation degrees, pressure conditions, chemical conditions, and duration of the thermal events for the natural bentonites as these are well known for the buffer.

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