Chemical erosion of the bentonite buffer: do we observe it in nature?

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Abstract: It is planned to use bentonites as buffer materials in various types of geological repositories designed to host radioactive waste. For the bentonite materials, the hydrological and hydrogeochemical conditions are two of the main environmental factors affecting their evolution, assessed for a period of up to 1 Ma. Since it has been observed in laboratory tests that smectite, in particular montmorillonite, forms colloids and disperses in very dilute conditions, a scenario for chemical erosion has been discussed at length, especially in relation to geological repositories located in future glaciated terrains and locations otherwise potentially hosting dilute groundwaters. General understanding, based on laboratory experiments, is that bentonite erosion does not occur when the total charge equivalent of cations in groundwater is higher than 4 mM. However, based on current knowledge, it seems that chemical erosion is not observed in repository-relevant natural systems where groundwater conditions are below the given limit. Further investigation is therefore suggested to provide a better scientific understanding of the mechanisms involved in stabilizing smectites in these natural systems.

Bentonite, containing mainly the mineral montmorillonite, is the reference buffer material in the KBS-3V (and KBS-3H) concept for geological disposal of spent nuclear fuel at Olkiluoto, Finland (Posiva 2012*a*, *b*). Montmorillonite is used in the literature both as a synonym for smectite and as a mineral name for a certain type of smectite. Here, 'montmorillonite' is used for the mineral and 'smectite' is used when discussing the mineral group. The longevity of montmorillonite, in particular, and smectites, in general, in current and evolving groundwater conditions is of interest when assessing the long-term performance of the bentonite buffer (cf. Fig. 1). The stability of bentonite is of interest in variable salinity ranges, but especially in relation to potential dilute water intrusion during glacial retreat or to continued dilution due to an extended temperate period (i.e. taking global warming into account). Traditionally, process understanding regarding long-term bentonite EBS behaviour has been acquired from studies performed on bentonite deposits (often called natural analogues: e.g. see Miller *et al.* 2000). To date, detailed behaviour of bentonite deposits in relation to surrounding groundwater systems has been little investigated (see the discussion in Laine & Karttunen 2010). Smectites occur within the crystalline basement in various geological environments: for example, fracture gouge, altered intrusions and some weathering profiles (cf. Marcos 2002; Vartiainen 2005; Laine & O'Brien 2008 for Finnish examples).

Background

Chemical erosion of bentonite is related to conditions where there is dilute enough groundwater to produce, and high enough flow to transport, bentonite colloids away from the repository via water-conducting features. The chemical erosion process is acknowledged in the current requirements set for the repository geochemical environment, especially on the total charge equivalent of cations in groundwater, which should remain above 4 mM (SKB 2011; Posiva 2012*a*). Chemical erosion is often discussed in relation to smectite dispersion only, and depositional processes are not accounted for. Requirements are mainly based on experimental information simulating simplified systems in artificial fractures (see the references given below for details).

The approach for solving this problem has focused on modelling exercises and experiments in the laboratory with bentonite materials (e.g. Neretnieks *et al.* 2009; Schatz *et al.* 2013). Laboratory tests are largely based on small-scale experimental set-ups, including compacted bentonite samples with variable compositions from purified homoionic Na- and Ca- montmorillonites to natural bentonites. Based on experiments (see Schatz *et al.* 2013; Erikson & Schatz 2015 and references therein), the process of chemical erosion is dependent on the initial composition of the smectite or bentonite material, density, aperture of the fracture, fracture inclination and flow rate.

Groundwater–buffer interaction may alter the exchangeable cation composition (ECC) of smectite during repository evolution. In addition, accessory minerals can dissolve and, along with buffer saturation, may affect the cation composition of smectites.

Modelling results of the chemical erosion process to date show discrepancies (see Schatz *et al.*

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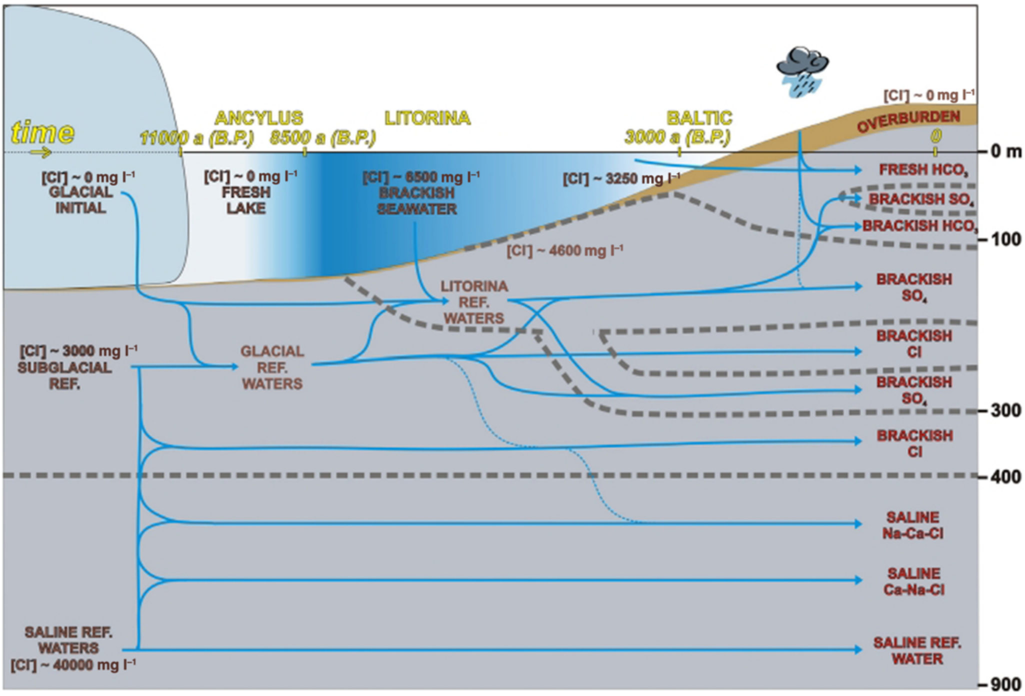

Fig. 1. Schematic representation of interpreted initial and boundary conditions at Olkiluoto since the last glacial period (redrawn from Posiva 2009). Potential salinity (as the Cl content) is shown for recharge waters (in the upper part along the time line) and bedrock groundwaters (on the left) at the initial stage of modelling. Reference waters correspond to figures 7–14 from Posiva (2013*a*). Saline and subglacial reference waters are contemporaneous initial waters (or end members) for the studied time period: that is, their formation dates are prior to the presented timescale. The generalized hydrochemical mixing hypothesis that is solved in detail, using initial waters with mass-balance calculations, is shown with blue arrows for the current groundwater types. Dashed lines between arrows imply minor mixing. Major groundwater types are bounded with grey dashed lines (Posiva 2013*a*).

2013) and, currently, the models are being developed further, along with an attempt to validate the models based on the experimental information (e.g. Moreno *et al.* 2015).

It should be noted that chemical erosion itself is not the only process that has a role in the long-term behaviour of bentonite in relation to mass transfer. Also, accessory minerals, such as quartz, that are of sufficient grain size and relatively insoluble may affect the system by forming filtering layers along the mass transfer path (e.g. fracture) (as suggested by Neretnieks *et al.* 2009). The consequent process of clogging of the water-conducting fractures may then occur, although the significance of this process in inhibiting erosion in unclear.

During the latest review on natural analogues relevant to Posiva's safety case, it was concluded that there are no dedicated natural analogue (NA) studies to support or disregard the chemical erosion process during potential dilute conditions during glacial meltwater intrusion at Olkiluoto (Posiva 2012*c*). The need for further research in relation to chemical erosion and development work has also been acknowledged elsewhere (e.g. see Reijonen & Alexander 2015 and references therein). There is great potential for gathering and interpreting existing information in the literature available on:

- the occurrence of dilute groundwater conditions at repository-relevant depths;
- bentonite/smectite occurrences/deposits where dilute water (e.g. meteoric) is in contact with the clay;
- other localities where smectite occurs in the crystalline basement.

Intrusion of dilute water

Buffering capacity of the bedrock and the nature of infiltrating fluids

In general, at Olkiluoto, the bedrock buffers both the redox conditions and the pH of the groundwaters (Posiva 2013*a*). Dilution of the groundwater can occur via two paths, either by prolonged infiltration of meteoric water during temperate climate conditions or during glaciation (retreat). It is assumed that during the latter, there may be increased flow in the conductive zones in the fractured rock (Posiva 2013*a*) and, hence, the time for water to react with the fracture minerals may be shorter.

Groundwater composition also affects the exchangeable cation composition (ECC) of montmorillonite. Arthur & Savage (2012) suggest that for Forsmark, the available evidence from glacial meltwaters does not support the promotion of chemical erosion. On the contrary, they suggest that the glacial meltwater composition would actually inhibit the erosion. This is based on the fact that the groundwater composition with $(Na^{+})^{2}/Ca^{2+}$ activity ratios <0.05 (as seen in most Forsmark samples) would drive the clay exchanger systems towards a $>90\%$ Ca smectite end member, and thus maintain the bentonite in contact with groundwater in the stability field for gel formation instead of sol. The study of Arthur & Savage (2012) supports the view that the water–bentonite interface should be treated in more precise way in order to be able to describe the processes correctly at the conceptual level.

Local and regional considerations

Geochemical reactions do occur during filtration of the meteoric (or glacial melt) waters in the fractured bedrock system. Based on the current palaeohydrogeochemical knowledge from Olkiluoto (Fig. 1), it can be said that there is no evidence of glacial meltwaters penetrating below 300 m depth (Posiva 2013*a*). However, modelling results suggest that this could be the case in a few canister locations during the long-term evolution of the site (Posiva 2013*b*).

At other coastal and inland sites in Finland, more dilute conditions are observed (e.g. at Palmottu (Smellie *et al.* 2002), and at Hästholmen and Kivetty (Pitkänen *et al.* 1998, 2001)). At these sites, glacial groundwater signatures are present down to a depth of 400–500 m. In the future, when uplift continues at Olkiluoto, meteoric waters will continue infiltrating. This process will cause some dilution in the upper parts of the bedrock: however, its extent in the long term is not clear owing to model uncertainties. Saline groundwaters are present at depth throughout the Fennoscandian bedrock areas, but the depth where more saline conditions exist varies. For example, recently, deep geosphere groundwater chemistry has also been studied at the Outokumpu Deep Drill Hole Project (drill hole depth of 2500 m) (e.g. Kietäväinen *et al.* 2013). This study made at this inland site show no signs of glacial water intrusion. The total dissolved solids (TDS) of the groundwaters here are around $10\ g\ l^{-1}$ down to 1500 m, after which salinity increases. Natural analogue information on the processes near a terminating glacier of the Greenland Ice Sheet has been collected as a part of the Greenland Analogue Project (GAP), but the data are not yet public. This study will provide insight into the groundwater chemistry development near the terminus of a currently existing ice sheet.

Regional knowledge is important in order to understand the overall processes taking place in the crystalline basement areas. To assess the areal information on the groundwater compositions of these locations is beyond the scope of this work, but it has been noted that geological structural controls and local topography are the most important factors controlling the groundwater mixing processes. The only thing that can be concluded is that dilute water intrusion is a process that takes place in fractured bedrock, or any other permeable zone, when conditions favour it. Hence, estimating of the future behaviour of any site must first and foremost rely on an understanding of the site.

Natural analogues of smectite erosion

Bentonite deposits

Puura & Kirsimäe (2010) approached chemical erosion by discussing natural bentonite deposits, but made only cursory suggestions on potential study sites. Reijonen & Alexander (2015) noted that the erosional histories of known bentonite deposits that were impacted by the last glaciation or by meteoric waters could be of interest. Bentonite deposits could provide information, especially in relation to ECC development in contact with groundwater. Kuno *et al.* (2002) conducted a preliminary study of the colloidal dispersion of bentonite in the groundwater of a bentonite mine (Fig. 2), and a similar approach could be used at a more appropriate site and under more controlled conditions (Reijonen & Alexander 2015).

Surficial bentonite deposits are often vast, and erosional processes occurring are mostly controlled by meteoric water drainage, resulting in instability of the slopes. Thus, in most outcropping bentonites, the amount of historical erosion due to colloidal transport would be difficult to assess (Fig. 3).

Other smectite occurrences

As mentioned earlier, in addition to bentonites, smectites have been observed in various geological environments, including crystalline basement areas, such as in the Fennoscandian Shield. Smectites also occur in soils (e.g. Righi *et al.* 1997), as fracture- and fault-gouge-filling minerals (e.g. Pearson *et al.* 2003; Gehör 2007; Sandström *et al.* 2008; Koroleva *et al.* 2009), in general as an alteration product of,

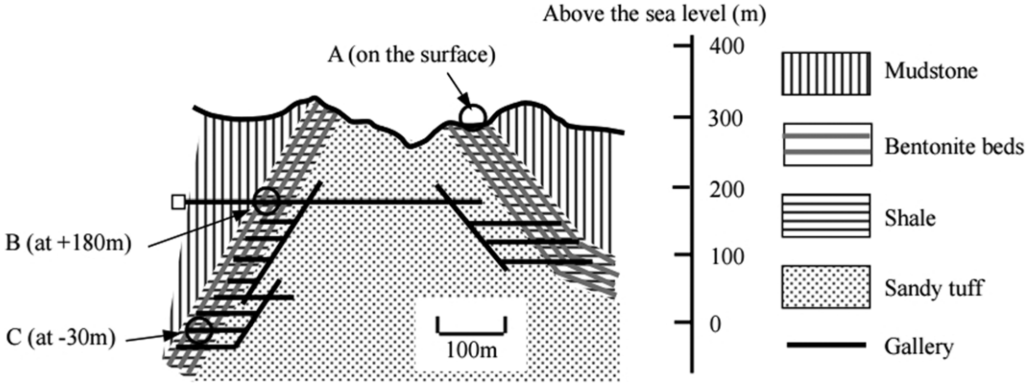

Fig. 2. Example of a situation where natural bentonite erosion could be studied. Schematic cross-section through the Tsukinuno bentonite mine, northern Japan. Locations of sampled groundwater (A–C) and their depths (above the sea level) are indicated (Kuno *et al.* 2002).

for examples, intrusive rocks (e.g. Laine & O'Brien 2008) and within bedrock weathering zones (e.g. Vartiainen 2005). In Table 1, a few examples of smectite occurrences in Fennoscandia are presented; smectite is widespread in many surficial and shallow bedrock environments, where formation of smectite is related to processes that have been active in timescales of hundreds of millions of years. It is worth noting that in crystalline basement areas (e.g. the Karelian craton, eastern Finland), intrusions of basic and ultrabasic rocks occur. In some cases, these intrusive rocks, with volumes usually comparable to a bentonite-filled repository tunnel, have altered to clays, including smectites, but to date these occurrences have not been studied in relation to deep geological repositories. However, several other examples will be discussed here: Hyrkkölä, Olkiluoto and other sites included in the Finnish site selection process (e.g. see McEwen & Äikäs 2000).

Hyrkkölä. A good example of a site where smectite has been observed as a fracture-filling mineral in water-conducting fractures is at Hyrkkölä, Finland (Fig. 4). Marcos (2002) reported smectite occurrences at the site. For example, at a depth of approximately 80 m, smectite is found at a location where current groundwater conditions are relatively dilute (*c.* 1.5 mM; TDS 116 mg l^{-1}: Marcos & Ahonen 1999) (Fig. 5; Table 2) and, hence, under the 4 mM limit of concern. Despite this, it seems that the smectite persists, so more detailed analyses of the smectite properties (e.g. ECC, smectite mineralogy and swelling properties) would be of great interest.

Olkiluoto and other repository (candidate) sites. The potential for using naturally occurring host-rock smectites to assess the longevity of industrial EBS bentonite has been previously raised by Apted *et al.* (2010) and Arthur & Savage (2012) when reviewing information on the Forsmark site for the Swedish regulator (SSM) (see also Savage 2012). Arthur & Savage (2012, p. 307) noted that:

> Site mineralogical data (SKB 2011) show that smectite and calcite occur at all depths in Forsmark fractures, with no evidence for removal/dissolution by previous glacial episodes. This natural analogue implies that these minerals may not have been dissolved/eroded during previous glacial episode.

Indeed, further investigation since has shown that the smectites occur throughout the host rock (Sandström *et al.* 2008). Dating of the fracture systems suggests that the smectites have been present since at least the Palaeozoic (i.e. 540–250 Ma BP), with the deep brines that are in contact with the smectites having been stable for at least several million years, if not longer (Smellie *et al.* 2008).

As discussed by Reijonen & Alexander (2015), montmorillonite has been reported from the fracture gouges sampled at Olkiluoto (e.g. Front *et al.* 1998), as well as in other Finnish site investigation reports (e.g. for Hästholmen (Gehör *et al.* 1997*b*; Front *et al.* 1999), Kivetty (Gehör *et al.* 1997*a*) and Romuvaara (Kärki *et al.* 1997)), suggesting smectite to be present at most depths.

The above-mentioned locations vary from inland (e.g. Romuvaara and Kivetty) to coastal (e.g. Olkiluoto and Forsmark). Deep groundwater systems in the Fennoscandian bedrock have been thoroughly studied in relation to site investigations, and these data provide both the salinity range for conditions where smectites occur and the spatial and temporal evolution of the groundwater salinities (e.g. see Posiva 2013*b*). As such, an assessment of likely

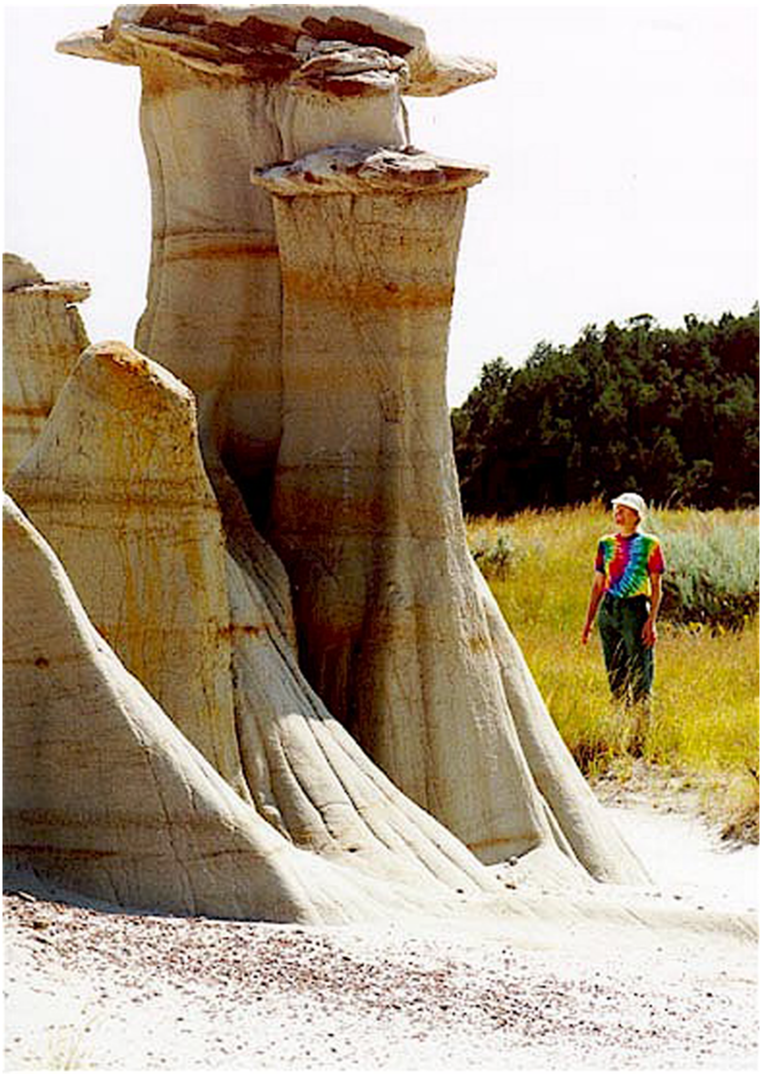

Fig. 3. Bentonite pillars protected by caprocks in North Dakota, USA (Bluemle 1991).

previous groundwater salinities at any given borehole depth can be conducted, meaning that by analysing the associated smectite minerals, in particular their paragenesis and mode of occurrence, their long-term stability could be assessed.

This would be of interest for understanding the situation at the Olkiluoto site, but, even more importantly, these sites with proven dilute deep groundwater conditions could be used as analogues for deep dilute water infiltration and interaction with smectites in general. In this regard, of great importance is that, at sites such as Kivetty and Romuvaara, smectites are present in conditions that show more dilute conditions than those noted in the national programme requirements (see earlier). Why these minerals remain here and in numerous surficial occurrences (e.g. weathering horizons) in seemingly too dilute conditions (see Table 2) would need further clarification. The mineralogical data currently available unfortunately does not allow a thorough assessment of this.

Other potential areas of research

In addition to the chemical erosion process, the formation of filter cakes was mentioned by Apted *et al.* (2010) as a topic that has not been backed up with any observations from nature. This process is

Table 1. *Examples of smectite occurrences in Fennoscandia*

Type	Locality	Geology	Smectite content	Age and genesis	Reference
Weathered profile	Mätäsaapa, Pelkosenniemi, Lapland, Finland	Weathering zone in crystalline basement (up to 20 m in depth), current overburden from 10 to 45 m	16–17 drill core samples contained 5–15% smectite. Smectite content in the fine fraction (<20 µm) is 30–40% higher than in bulk samples	Definite ages unknown, but ages between Precambrian and 360 Ma are likely. Related to kaolinization during warm and humid climate conditions	Vartiainen (2005)
	Vitikko, Salla, Lapland, Finland	Weathered (originally albite carbonate rock) profile (2–6 m thick)	Large smectite content reported, in the fine fraction (<20 µm) over 50%		Vartiainen (2005)
	Vitsaoja, Salla, Lapland, Finland	Weathered zone of crystalline basement, current overburden 14–16 m	In some samples, up to 60% smectite		Vartiainen (2005)
	Lapioaapa, Rovaniemi mlk, Lapland, Finland	Weathered zone in the crystalline basement (quarzites, vulcanites and dolomite)	X-ray diffraction (XRD) results show smectite as a weathering product down to depths of 70 m. The current overburden is tens of metres		Vartiainen (1996)
Altered alkaline intrusion	Helsinki, Finland Sewage water tunnel site (tunnel collapse site due to smectite swelling)	Altered lamprophyre	Smectitization reported for a lamprophyre dyke	Age unknown, probably hydrothermal alteration of lamprophyre	Suominen (1997)
	Kaavi, Finland	Altered kimberlite	Thorough saponitization of kimberlite	Age of the alteration unknown	Laine & O'Brien (2008)
Fault	Stuoragurra, Norway	Post-glacial fault with clay gouges	Smectite as a fracture-filling mineral		Kukkonen *et al.* (2010)
Fractured crystalline rock	Hyrkkölä, Finland	Crystalline basement	Smectite as a fracture-filling mineral		Marcos (2002)
	Olkiluoto, Finland	Crystalline basement	Smectite as a fracture-filling mineral		Front *et al.* (1998)
	Hästholmen, Finland	Crystalline basement	Smectite as a fracture-filling mineral		Gehör *et al.* (1997*a*), Front *et al.* (1999)
	Kivetty, Finland	Crystalline basement	Smectite as a fracture-filling mineral		Gehör *et al.* (1997*b*)
	Romuvaara, Finland	Crystalline basement	Smectite as a fracture-filling mineral		Kärki *et al.* (1997)
	Forsmark, Sweden	Crystalline basement	Smectite as a fracture-filling mineral	Palaeozoic (likely)	Sandström *et al.* (2008)

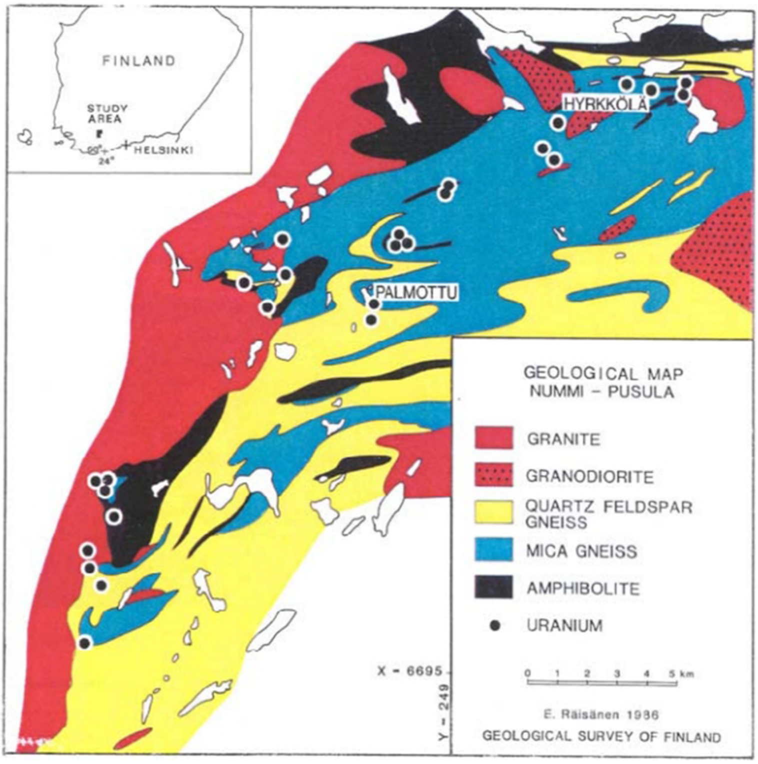

Fig. 4. Geological map of the Hyrkkölä area (Marcos & Ahonen 1999).

coupled with erosion, as when the smectite can be chemically eroded away in dilute enough conditions by the groundwater flow, other minerals initially bound in bentonite can remain in place/or build up in small aperture fractures This is because the grain size of these minerals (such as quartz) is larger and, owing to their other mineralogical properties, cannot be eroded in the repository conditions. This

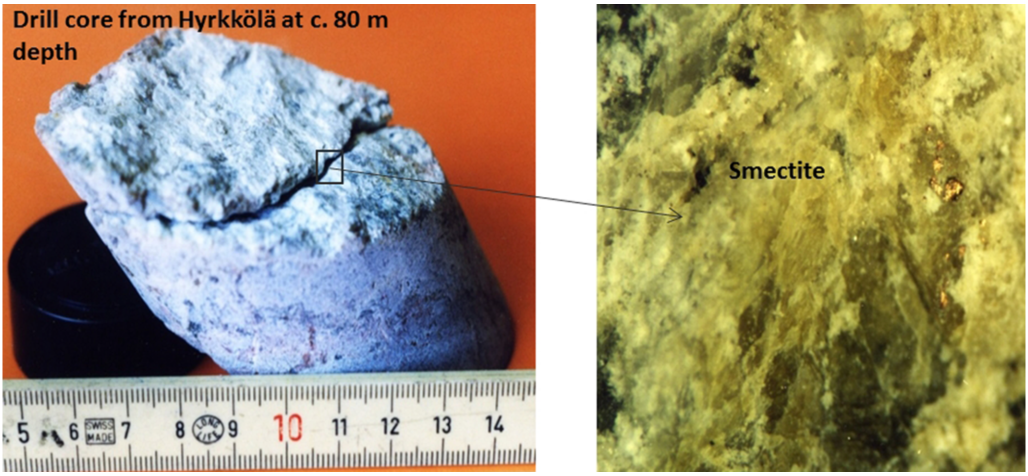

Fig. 5. Smectite from the Hyrkkölä study area drill core (photographs by Nuria Marcos).

Table 2. *Groundwater compositions in connection with the occurrences of fracture smectite*

Locality	TDS (mg l^{-1})	Total charge equivalent of cations (mM)	Cl (mg l^{-1})	SO_4 (mg l^{-1})	Na (mg l^{-1})	K (mg l^{-1})	Ca (mg l^{-1})	Mg (mg l^{-1})	HCO_3 (mg l^{-1})	Fe (mg l^{-1})	O (mg l^{-1})	pH
Olkiluoto meteoric (PVP)	567	*c.* 7	60	48	24.6	6.7	92.3	15.6	291			
Grimsel water	83	*c.* 1	5.7	5.9	15.9	0.2	5.2	0.015	27.45	0.0002		9.6
Kivetty (minimum)	133	*c.* 0.8	1	0.1	4.7	0.2	11.2	0.9	82.4	0	0	7.2
Kivetty (maximum)	240	*c.* 3.6	5.8	3.5	27	2.4	33	8.6	158.6	1.4	0.4	8.5
Hyrkkölä	116	*c.* 1.5	3.8	10	7.1	2.8	14.4	4.3	57	0.05	4	6.6
Romuvaara (minimum)	62	*c.* 0.3	0.9	1	4.3	0.7	2.7	0.1	0	0	0	6.8
Romuvaara (maximum)	190	*c.* 3.6	7.4	6.5	43.2	3	23	5.3	123.3	3	1.1	9.3

Data for Hyrkkölä from Marcos & Ahonen (1999), Kivetty and Romuvaara from McEwen & Äikäs (2000). Olkiluoto reference compositions for Olkiluoto meteoric water and glacial meltwater (Grimsel) are given for comparison (Hellä *et al.* 2014).

phenomenon is mentioned, for example, by Schatz *et al.* (2013), who called for further experimental work to be undertaken as major uncertainties currently exist in the understanding of this process.

In addition to fracture smectites observed at a wide range of sites to date, post-glacial faults could provide useful targets for smectite stability research as smectite has been reported, for example, in the Stuoragurra Fault in northern Norway (Kukkonen *et al.* 2010 and references therein).

Discussion

The palaeohydrogeochemical evolution of the Olkiluoto site is well understood and supports the view that glacial meltwater has not intruded into the repository depths. However, current modelling of the groundwater processes during repository evolution cannot rule out the presence of dilute conditions in some waste canisters (Posiva 2013*b*). It is acknowledged that the models are far from perfect and, owing to uncertainties, very conservative assumptions have been employed.

Multiple lines of arguments are needed in order to assess the performance of a repository system. Knowledge that has been, and can still be, obtained by looking at the bentonite and smectite longevity in geological formations can help reduce the over-conservative treatment of repository processes and lead the way to more realistic assessments. Whilst many of the processes, such as ECC changes and the overall erosion pattern, can be seen in bentonite deposits themselves, fracture smectites and other smectite occurrences of relevance within the crystalline basement can provide information where bounding conditions are closer to the repository conditions (present and evolving). Regarding the Olkiluoto site, smectite occurrences above the assumed maximum depths of dilute water penetration support the likely longevity of smectite during future glaciations, while even more convincing support comes from other sites where the current groundwater salinity in smectite-hosting formations is below the requirements set for smectite stability.

Conclusion

Bentonite erosion in surficial natural deposits is mainly controlled by weathering and physical erosion, which makes observation of the process of chemical erosion within these difficult to assess.

However, smectite persists in widespread locations regardless of the presence of glacial meltwaters in the past, suggesting that the waters were not dilute and already buffered in the upper bedrock or that the limit set for the erosion is very conservative. Smectites are observed in localities where current groundwater composition is below the 4 mM limit given in the requirements. Many targets exist that could be investigated as potential analogues, although currently available information is not sufficient to assess their relevance with respect to repository conditions. Detailed studies would be required to assess the mode-of-occurrence of fracture smectites or other smectite bodies that occur in current and future repository-relevant hydrogeochemical and hydrogeological conditions.

The answer to the question, ‘do we observe chemical erosion in nature?’, would be ‘no’ – or ‘unproven’. The natural analogues presented here do not support the widespread occurrence of chemical erosion and, thus, would support the stability of smectites in dilute conditions over geological timescales, something that cannot be investigated in the laboratory. However, further research is needed to provide a sound basis for this statement at the level of detail needed in the safety case.

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