

Wyoming Bentonites

Evidence from the geological record to evaluate the suitability of bentonite as a buffer material during the long-term underground containment of radioactive wastes

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

Summary

In the Swedish programme for the deep, geological disposal of radioactive wastes, bentonite is planned to be used as a barrier material to reduce groundwater flow and minimise radionuclide migration into the geosphere. One of the possible threats to long-term bentonite stability is the gradual incursion of saline water into the repository confines which may reduce the swelling capacity of the bentonite, even to the extent of eliminating the positive effects of mixing bentonite into backfill materials. Important information may be obtained from the study of analogous processes in nature (i.e. natural analogue or natural system studies) where bentonite, during its formation, has been in long-term contact with reducing waters of brackish to saline character. Type bentonites include those mined from the Clay Spur bed at the top of the Cretaceous Mowry Formation in NE Wyoming and demarcated for potential use as a barrier material (e.g. MX-80 sodium bentonite) in the Swedish radioactive waste programme. This bentonite forms part of the Mowry Shale which was deposited in a southern embayment of the late Albian Western Interior Cretaceous sea (Mowry Sea). The question is whether these bentonite deposits show evidence of post-deposition alteration caused by the sea water in which they were deposited, and/or, have they been altered subsequently by contact with waters of increasing salinity?

Bentonites are the product of pyroclastic fall deposits thought to be generated by the type of explosive, subaerial volcanic activity characteristic of Plinian eruptive systems. In Wyoming the overall composition of the original ash varied from dacite to rhyolite, or latite to trachyte. The ash clouds were carried to high altitudes and eastwards by the prevailing westerly winds before falling over the shallow Mowry Sea and forming thin but widespread and continuous horizons on sea floor muds and sands. Whilst bentonites were principally wind-transported, there is evidence of some water transportation as they were forming. Chemical alteration of the ash has occurred in the presence of circulating mineral-rich groundwaters which, in the Mowry Sea environment, were brackish and partially reducing. Under these initial aqueous conditions the newly-formed bentonite appears to have been at equilibrium, and subsequent rapid deposition of impervious mud/silt has served to isolate the bentonite from alteration during the continued palaeoevolution of the Mowry Sea basin.

Based on available evidence, it would appear in general that most of the Wyoming bentonites scientifically studied have undergone no major post-depositional alteration unless exposed to surface/near-surface weathering processes. Moreover, because of their physico-chemical isolation since deposition, it is not possible to study the effects of post-formational alteration of the bentonites under varying aqueous conditions and chemistry during the palaeoevolution of the Mowry Sea basin in Cretaceous times. The bentonites are, therefore, a good natural analogue of long-term stability in a closed system, but there is insufficient information to evaluate their long-term behaviour in an open system in contact with brackish to saline waters.

Sammanfattning

I det svenska programmet för djupförvar av radioaktivt bränsle är bentonit tänkt att användas som barriärmaterial för att minimera radionuklidtransport till geosfären. Ett av de tänkbara hoten mot bentonitens långtidsstabilitet är gradvis inträngande saltvatten i förvaret, vilket kan reducera bentonitens svällbarhet i en omfattning som eliminerar de positiva effekterna av att blanda bentonit i återfyllnadsmaterialet. Viktig information kan erhållas från studier av analoga processer i naturen (dvs naturliga analogier eller naturliga systemstudier) där bentonit har varit i långtidskontakt med reducerande grundvatten med olika saltinnehåll. Tänkbara bentoniter inkluderar dem som bryts i Clay Spur-bädden högst upp i Mowry kritformation i nordöstra Wyoming vilka är tänkbara buffertmaterial (t ex MX-80 natriumbentonit) i det svenska programmet för radioaktiva avfallet. Denna bentonit utgör delar av Mowry-skifferformationen vilken deponerades under sen Albien i en sydlig vik i ”Western Interior Cretaceous sea” (Mowry-havet). Frågan är om dessa bentonitförekomster uppvisar bevis på omvandling som följd av saltinnehållet i bildningsmiljön, och/eller om de har omvandlats vid senare tillfällen genom kontakt med vatten med tilltagande salthalt?

Bentoniten är en produkt av pyroklastiskt material (vulkaniska partiklar), som sorterats genom sedimentation (subaeril; på marken i fria luften), vilket har tillkommit genom explosiv vulkanisk aktivitet. Den övergripande sammansättningen av den ursprungliga askan i Wyoming varierade från dacit (vulkanisk ekvivalent till granodiorit) till ryolit (vulkanisk ekvivalent till granit), eller latit (vulkanisk ekvivalent till monzonit) till trakyt (vulkanisk ekvivalent till syenit). Askmolnet fördes till höga höjder och österut av de rådande västliga vindarna innan det föll ner i det grunda Mowry-havet och formade tunna men vidsträckta och sammanhängande horisonter på havsbottnens slam- och sand-bäddar. Utgångsmaterialet för bentoniten var i huvudsaklig vindtransporterad medan det finns bevis för viss vattentransport då de bildades. Kemisk omvandling av askan har ägt rum vid tillgång på cirkulerande mineralrika grundvatten vilket i Mowryhavets miljö var bräckt och delvis reducerande. Under dessa ursprungliga vattenförhållanden tycks den nybildade bentoniten ha varit i jämvikt, och följande snabb sedimentation av ogenomträngliga slam/silt lager har isolerat bentoniten från omvandling under den fortsatta geologiska utvecklingen i Mowryhavets sedimentationsbäcken.

Baserat på tillgängliga bevis tycks det i allmänhet som om det mesta av Wyomingbentoniterna som studerats vetenskapligt inte har genomgått några större omvandlingar efter sedimentationen såvida de inte har varit exponerade för ytnära vittring. På grund av den fysikalisk-kemiska isoleringen efter deponeringen är det inte möjligt att studera effekterna av omvandling efter bildandet som följd av varierande kemiska förhållanden i grundvattnet under den geologiska utvecklingen av Mowryhavets sedimentationsbassäng under krittiden. Bentoniterna är därför en god naturlig analog till långtidsstabiliteten i ett slutet system, men det finns för otillräckligt med information för att kunna utvärdera bentonitens långtidsutveckling i ett öppet system som är i kontakt med bräckt eller salt vatten.

Contents

1	Introduction	7
2	What is a bentonite?	9
3	Distribution and formation of the Wyoming bentonites	11
3.1	Bentonite distribution	11
3.2	Bentonite formation	12
3.2.1	Palaeoenvironment of the Mowry Sea basin	12
3.2.2	Source material, transportation and deposition	15
3.2.3	Genesis	17
4	Wyoming bentonites; Natural analogues to clay buffer stability	19
4.1	General	19
4.2	Post-formational alteration of bentonite	19
4.3	Conclusions	20
5	Acknowledgement	21
6	References	23
7	Other bibliography	24

1 Introduction

In the Swedish programme for the deep, geological disposal of radioactive wastes, bentonite is planned to be used as a barrier material to reduce groundwater flow and minimise radionuclide migration into the geosphere. In its pure form it is being considered as a buffer material packed around the waste containers, but may also be used as a mixing component in material used to backfill the access galleries following deposition of the radioactive waste canisters. The function of the bentonite buffer is to: a) constitute a mechanical and chemical zone of protection around the canister, b) limit the inward percolation of potentially corrosive substances from the groundwater to the canister surface, c) in the scenario of canister failure, to limit the dispersion of leached radionuclides from the canister out into the bedrock, and d) filter fine particulate and colloidal material that may form during waste leaching. Other important physical properties of bentonite are a reasonable load-bearing capacity to support the weight of the waste package and a relatively high thermal conductivity to dissipate heat generated by the waste. A potential long-term threat to the stability of bentonite is alteration under different physico-chemical conditions that may be encountered in the repository groundwater environment over periods of thousands to hundreds of thousands of years. Alteration may result in the deterioration of the swelling, plastic, permeability and loading properties of the bentonite.

One of the possible risks to long-term bentonite stability is the gradual incursion of saline water into the repository confines; this may originate from the immediate vicinity (e.g. from the surrounding host rock matrix) or from shallower or deeper levels in the bedrock (e.g. during glacial events). Laboratory and *in situ* experimental evidence (e.g. /Karnland, 1997; Karnland et al, 2000/ and references therein) indicate that groundwaters expected at repository depths in the Swedish crystalline bedrock should not detrimentally influence the buffering capacity of the bentonite, even if the waters are brackish to saline in character. However, if incursion of highly saline waters (i.e. brines; normally defined as >100 g/L TDS) should occur then the swelling capacity of the bentonite may well be reduced, even to the extent of eliminating the positive effects of mixing bentonite into backfill materials.

An additional source of information, especially over longer timescales more in tune with the lifespan of a repository, is to study analogous processes in nature (i.e. natural analogue or natural system studies) where bentonite has been in long-term contact with reducing waters of brackish to saline character during its formation. The bentonite tested and proposed for the Swedish programme is the so-called MX-80 sodium bentonite from NE Wyoming, U.S.A. This is a naturally occurring bentonite mined from the Clay Spur bed at the top of the Cretaceous Mowry Formation. The bentonite forms part of the Mowry Shale which was deposited in a southern embayment of the late Albian Western Interior Cretaceous sea (Mowry Sea), believed to have been fresh to brackish in character. At a later stage the sea became increasingly more saline from the south. The question is whether these bentonite deposits show evidence of post-deposition alteration caused by the sea water in which they were deposited, and/or, have they been altered subsequently by contact with waters of increasing salinity?

To answer this and other related questions, a review of published material was carried out to establish the sequence of deposition/formation and alteration of these north American bentonites as an analogy to long-term bentonite stability in a deep repository system for radioactive wastes in Sweden where groundwaters of a brackish to saline character are expected to be present in the repository groundwater system.

2 What is a bentonite?

As reviewed by /Thomas et al, 1990/, there is a degree of confusion surrounding the use of the term 'bentonite'. It has been defined as 'any clay composed dominantly of a smectite clay mineral and whose physical properties are dictated by this clay mineral' /Grim and Guven, 1978/. For example some clays, based on their composition and properties and produced by the hydrothermal or deuteric alteration of igneous material, have been designated as bentonite. However, more widely, bentonite is used as a general term to describe clay formed by alteration of volcanic ash or tuff. Chemical alteration of the ash has occurred in the presence of circulating mineral-rich groundwaters in a variety of sedimentary environments. Shallow marine sequences are the most common source of bentonites, as exemplified from the classic Black Hills region in NE Wyoming (Figure 1) where bentonite was first described and named.

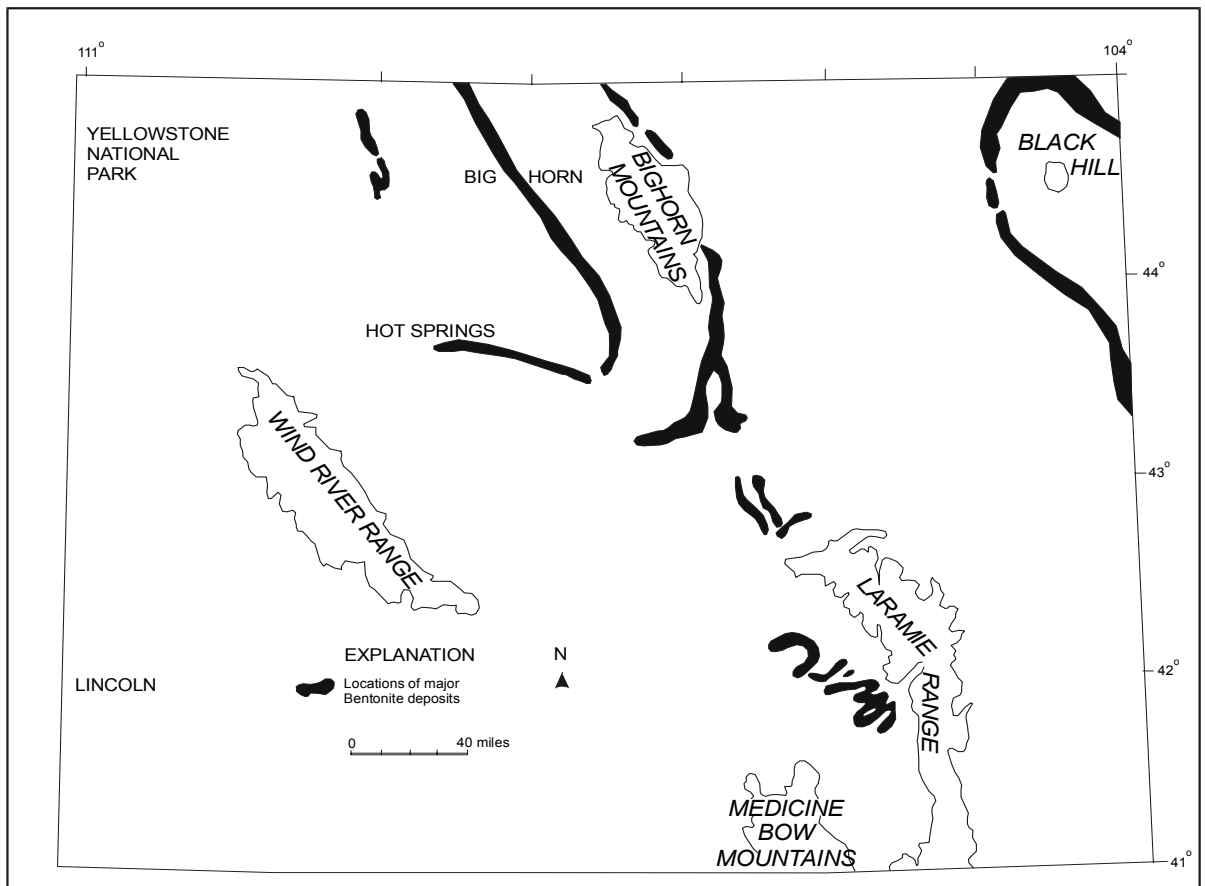


Figure 1. Location of major bentonite occurrences in Wyoming; those of most important economic importance (e.g. Clay Spur bed) are found in the Black Hills region in NE Wyoming /after Rath, 1986/.

3 Distribution and formation of the Wyoming bentonites

3.1 Bentonite distribution

In Wyoming, in common with other western north American deposits, the bentonites are the product of *in situ* alteration of volcanic ash deposits in a shallow marine environment in Cretaceous times (e.g. /Rath, 1986/ and references therein).

Although of explosive volcanic origin, the stratigraphy of the bentonites share a close relationship to the sedimentological and tectonic history of the Cretaceous, rather than representative of incidental volcanism. Major bentonite beds occur in the same cyclic sedimentary sequence which, from bottom to top, comprises shale, coal, bentonite, and finally shale grading to sandstone and conglomerate /Slaughter and Earley, 1965/. These sediments were derived from erosion of an actively rising mountain belt in central Idaho, Utah and Nevada with subsequent river transportation to the Mowry Sea basin.

Outcrops of major bentonite deposits are present in many parts of Wyoming where Cretaceous sediments are exposed at the surface. The most important outcrops are centred in the Black Hills region which borders NE Wyoming, SE Montana and western South Dakota (Figure 1). The most persistent (and historically the most commercial) bentonite occurrence is the Clay Spur bed which characterises the top of the Mowry Formation at the contact with the overlying Frontier Formation. It can be recognised across nearly all of central and northwestern Wyoming, indicating that the Mowry/Frontier contact is essentially an isochronous surface.

Much work has been published on the Clay Spur bentonites (Figure 2) and other bentonites contained in the Mowry and Frontier Formations. Based in these occurrences a typical bentonite can be described as relatively thin and light-coloured; common are pastel shades of blue-green, yellow, green, olive green, cream and white. It may be greasy or soap-like to touch and has been referred to as 'soap clay' and 'mineral soap'. Undisturbed bentonites range in thickness from 1–2 cm to 6–8 m with an average thickness of 30–40 cm. Each bentonite unit is sharply separated from the overlying or underlying unit by a distinct discontinuity in grain size; each unit is coarsest at its base. Many of the Wyoming bentonites contain multiple units each separated by a few cms of shale which can be persistent over distances of 80–200 km and over areas of several thousand square kilometres. Clay is the dominant component at all levels of the bentonite beds but is at a minimum of around 60–80% in the lowest centimetres of any given unit. The uppermost part of the unit is completely gradational into the overlying shales and this transition is very fine-grained /Slaughter and Earley, 1965/.

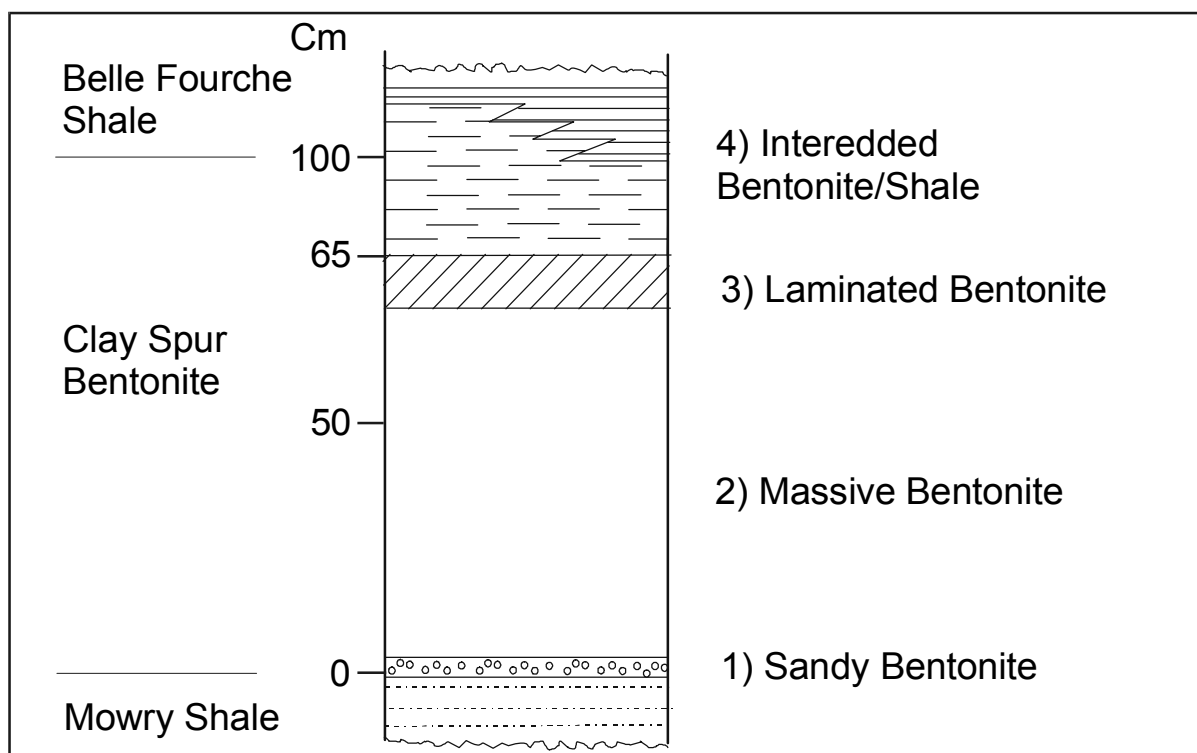


Figure 2. Profile through the Clay Spur bed showing the four main lithological units: 1) thin sandy bentonite layer, 2) thick layer of massive bentonite, 3) zone of interlaminated organic-rich and organic-poor bentonite, and 4) zone of interbedded bentonite and bentonitic shale (based on /Elzea and Murray, 1990/ and reproduced after /Keto, 1999/).

3.2 Bentonite formation

3.2.1 Palaeoenvironment of the Mowry Sea basin

During Late Albian to early Cenomanian times the Mowry Sea consisted of a semi-restricted elongate basin closed to the south and periodically open to the north (Figure 3); it was shallow, partially reducing and chemically stratified /Davis, 1970; Byers and Larson, 1979/. As discussed by /Byers and Larson, 1979/ at least three Mowry palaeoenvironments have been identified in Wyoming (see Figure 4) and there is a consensus that the sea became increasingly saline, deeper and anaerobic towards the southeast. /Byers and Larson, 1979/ referred to these environments as: a) vital heterostrate (agitated, fully aerobic and less than 15 m deep), b) vital isostrate (quiet, marginally. Agitated and extending to 150 m depth), and c) lethal isostrate (quiet, anaerobic and deeper than 150 m). The depositional topography of the Mowry basin shows that the thickest accumulation of sediment occurred along the western margin, where the water was shallowest, thinning eastwards to the deepest waters.

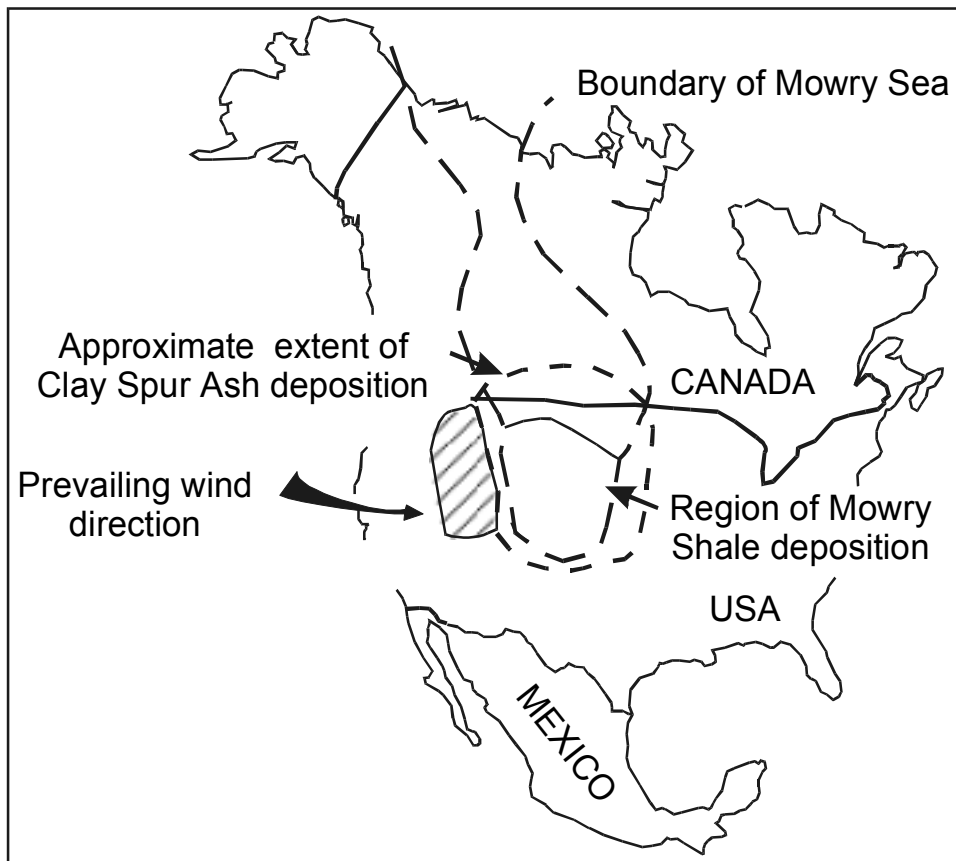


Figure 3. Palaeogeography of North America and the western interior seaway (Mowry Sea) during Albian times /after Elzea and Murray, 1990/.

A simplified evolutionary sequence /after Slaughter and Earley, 1965/, can be summarised as:

- High Mowry Sea basin with moderate height sediment source to the west;
- Volcanic activity to the west; deposition of bentonites;
- Uplift of the sediment source area and coincident subsidence in the Mowry Sea basin;
- Continuation and intensification of uplift/subsidence;
- Abrupt uplift of Mowry Sea basin with cessation of source uplift; end of cycle.

During the major sedimentation from the west, there was only a diffuse sedimentary source to the east of the basin (present-day Iowa) characterised by kaolinite which progressively disappeared as the proportion of sediment from the west increased.

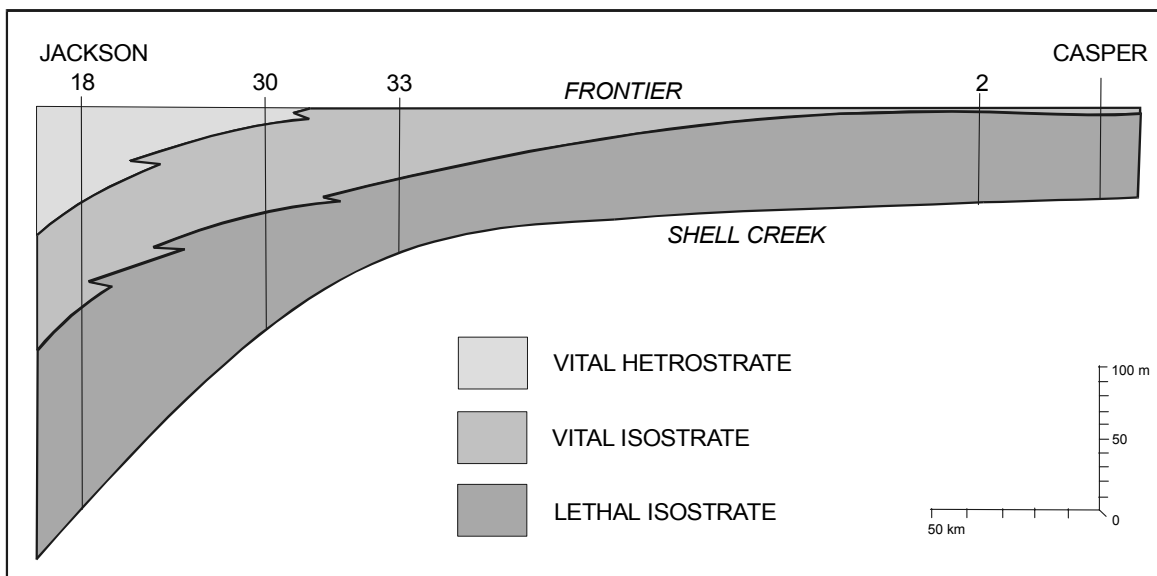
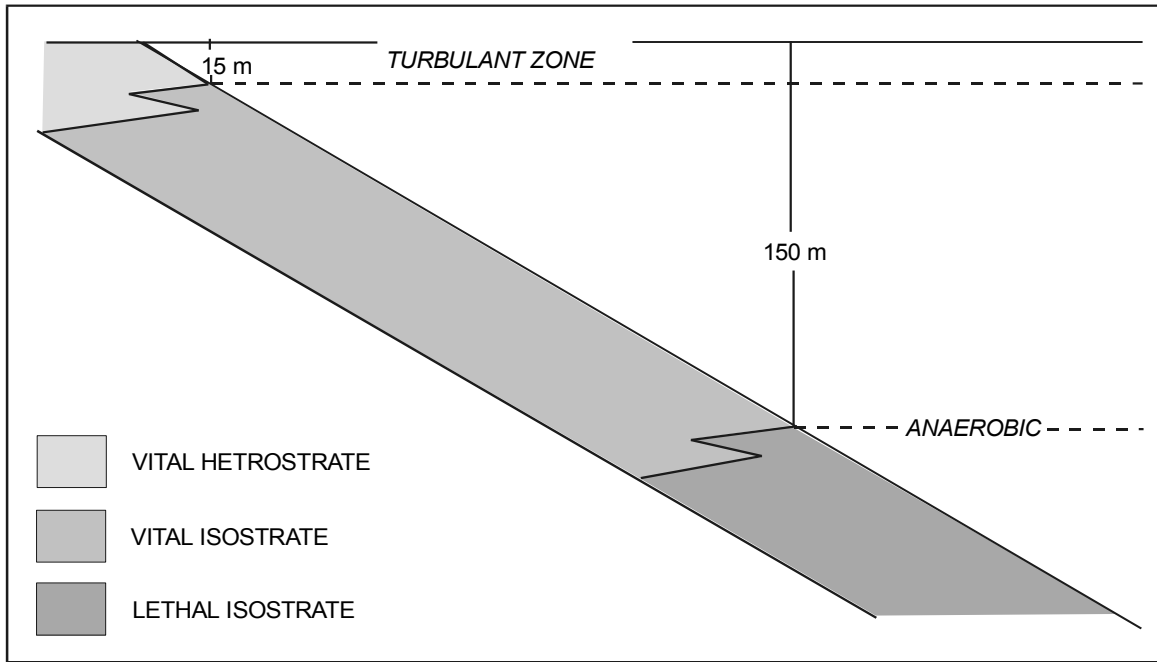


Figure 4. Upper: Schematic diagram of relations between Schäfer biotope, depth and oxygenation in stratified oxygen-deficient basin. Lower: Cross-section of Mowry Shale from NW to central Wyoming showing the distribution of lithologies according to the Schäfer classification /after Byers and Larson, 1979/.

3.2.2 Source material, transportation and deposition

During ash deposition the western margin of the Mowry Sea was brackish and dysaerobic due to high river input and restricted circulation. The source of the volcanic ash was explosive volcanoes in western Wyoming and Idaho associated with regional tectonics and emplacement of the Idaho batholith /Slaughter and Earley, 1965/. In the bentonite deposits in southern Alberta /Thomas et al, 1990/ it has been suggested that the pyroclastic fall deposits were probably generated by the type of explosive, subaerial volcanic activity characteristic of Plinian eruptive systems. Bentonite studies in Wyoming show that the overall composition of the original ash varied from dacite to rhyolite, or latite to trachyte; latite or low quartz latite group was the most common. The ash clouds were carried to high altitudes and eastwards by the prevailing westerly winds before falling over the shallow Mowry Sea and forming thin but widespread and continuous horizons on sea floor muds and sands. It has been hypothesised by /Slaughter and Earley, 1965/ and /Slaughter and Hamil, 1970/ that most of the Wyoming bentonites were formed from explosive ash clouds which extended to heights of 20–25 km, and the depositional distribution pattern was controlled by high altitude (10–13 km) wind directions with mean velocities of near 50 kilometres per hour. Whilst the finest particles extended far to the east parallel to the wind direction, the larger diameter, heavier particles, tended to settle somewhat perpendicular to the wind direction. Over a very short period of time (hours to days to weeks as proposed for the southern Alberta ash falls /Thomas et al, 1990/), this resulted in a depositional succession of partly coalescing bentonite horizons of tongue or lobate character extending eastwards (Figure 5). This distribution pattern is very similar to recent volcanic deposits, for example, in Alaska (Mt. Katmai), Chile (Mt. Quizapú) and USA (Mt. St. Helens).

Whilst the bentonite source material was principally wind-transported, there is evidence of some water transportation. Many bentonites show that at least part of the bed was either water transported from a land source or from some point at which the original ash settled out in water. Such evidence is usually restricted to the uppermost layers of the bentonite beds which exhibit bedding laminations, lack of graded bedding and intercalations of organic-rich shale /Slaughter and Earley, 1965/.

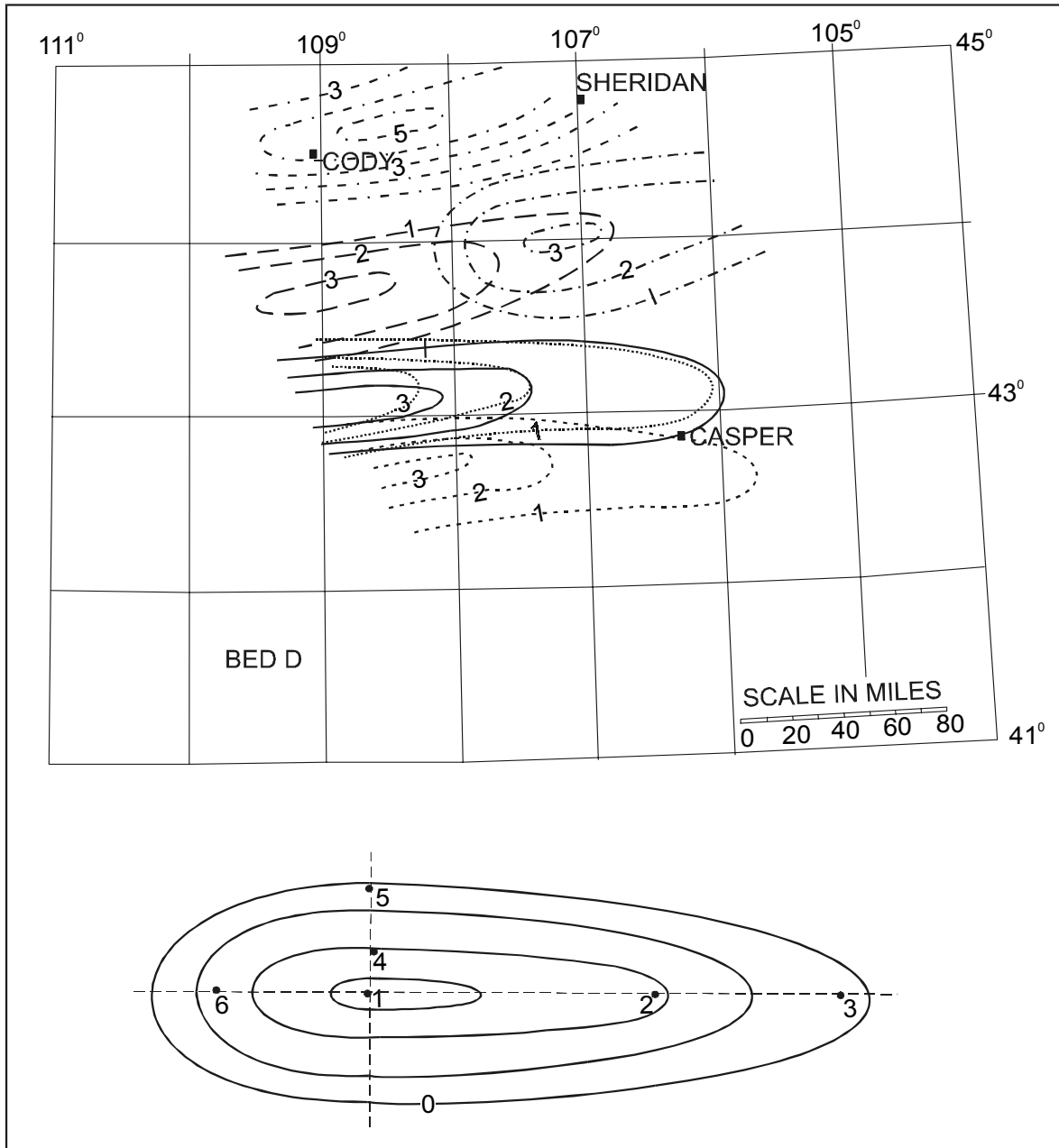


Figure 5. Upper: Schematic isopach maps of individual groups of bentonite units of bed D; portions are schematic and thicknesses in feet are approximate. Lower: Idealised isopach map of a single bentonite unit /after Slaughter and Earley, 1965/.

3.2.3 Genesis

As described above, based largely on Mowry Shale studies in NE Wyoming, at the time of bentonite formation the western margin of the Mowry Sea, which existed from Late Albian to early Cenomanian, is believed to have been shallow, of restricted circulation, brackish and partially reducing. It is generally accepted that the airborne volcanic ash produced by the volcanic activity in what is now western Wyoming and Idaho began to alter immediately on contact with the sea water and continued as the ash particles filtered down to the sea floor. The degree of water circulation and off-shore currents probably played a role in the dissolution process, with the volcanic glass dissolving quickly freeing the elements necessary to form montmorillonite. The heavy insoluble constituents of the ash settled faster and are concentrated toward the bottom of the sediment. The initial dissolution of water-soluble salts coating the ash particles may well have altered the chemistry of the sea water /Rath, 1986/. Immediate glass dissolution to form bentonite is strongly supported by the trace element chemistry of smectite separated from the bentonite /Elzea and Murray, 1989/ and also from laboratory leaching studies of similar ash-types from the recent Mt. St. Helens' eruption in 1980 /Smith et al, 1982/. /Elzea and Murray, 1990/ also report that smectite formed under such environmental conditions proposed for the western margin of the Mowry Sea basin is depleted in Sr, enriched in Zn and contains higher concentrations of octahedral iron than Mg relative to smectites altered in the more normal marine environment (i.e. higher salinity and anaerobic conditions) of the central and eastern portions of the Mowry Sea basin which show enriched Sr and Y and depletion of Zn.

/Slaughter and Earley, 1965/ discussed at length the alteration of ash to bentonite. They pointed out that if alteration occurred soon after deposition then the physical conditions supposed for the glass-water system, i.e. permeable sand and silt, would leave a fairly open system to the overlying sea water. However, the impermeable fine-grained muds covering the sea floor prior to deposition would allow little downward migration of fluids from the ash. If post-depositional alteration should take place after a thin accumulation of fine mud or very fine ash covered the ash bed, permeation by fluids would be hindered and alteration would have to take place in a restricted system. The actual conditions prevailing during deposition of the Wyoming bentonites are not known with certainty.

Most of the eastern Mowry Sea basin bentonites have been deposited in a deep marine environment whilst, in contrast, many of the western basin bentonites (i.e. Mowry Formation/Frontier Formation) are associated with shallow water-laid sediments. In common, however, both were formed under aqueous conditions and alteration of the volcanic glass according to /Slaughter and Earley, 1965/ has been by hydrolysis according to the reaction:



The chemistry of the bentonites would therefore be expected to show enrichments in silica and zeolite. In reality, the bentonites suggest a significant loss of the silica during alteration. That conditions were generally alkaline is indicated by the significant presence of zeolites adjacent to the bentonite proper and only small amounts of precipitated silica and kaolinite. Interestingly the loss of silica in the Wyoming bentonites has not, as might be expected, resulted in silica-rich concentrations at their base (although thin layers of glassy to cherty material has been reported in cases by /Rath, 1986/), but rather the opposite; overlying beds some metres above the bentonites are sometimes silica-rich /Slaughter and Earley, 1965/. This has been interpreted as suggesting that the system undergoing alteration had at least some access to the overlying body of water, and that large quantities of silica were carried upward and dispersed into the basin.

To summarise, segregating the processes into convenient steps /after Slaughter and Earley, 1965/ the sequence is:

- extraction of cations;
- solution of portions of the silica-alumina framework;
- reconstitution of residual material to montmorillonite; minor kaolinite in some instances;
- precipitation of zeolite or kaolinite from solution; minor montmorillonite in some instances;
- removal or precipitation of silica.

The critical step appears to be the cation extraction which allows the glass structure to break-up. This is most easily accomplished by hydration of cations and proton-cation exchange.

Despite the certainty that the Wyoming bentonites formed from the alteration of volcanic material, there is little direct evidence of volcanic ash and glass since alteration has been so complete. There is, however, abundant indirect evidence such as zeolite alteration products which have preserved the original textures of glass shards and other glass particles.

4 Wyoming bentonites; Natural analogues to clay buffer stability

4.1 General

As described and discussed above, the Wyoming bentonite material, which may be used as an engineered buffer material in the Swedish radioactive waste programme to radionuclide migration into the geosphere, has formed mostly *in situ* from the rapid alteration of airborne volcanic ash on contact with the shallow, brackish waters of the Mowry Sea basin in early Cretaceous times. The interest to the Swedish programme is that during the expected lifespan of a radioactive waste repository (thousands to hundreds of thousands of years), will there be a deterioration in the exceptional physical properties of the bentonite for which it was chosen in the first place? In particular, would a gradual incursion of brackish to saline groundwaters into the near-field engineered confines initiate this deterioration?

To answer these questions it is important to know the chemistry of the sea water in the Mowry Basin during, and subsequent to, bentonite formation. Furthermore, has rapid accumulation of fine sediments over the bentonite beds effectively preserved the physico-chemical properties of the bentonite? Finally, is there later evidence of reworked bentonite deposits associated with more saline marine waters?

4.2 Post-formational alteration of bentonite

From available data, the bentonites have been formed under shallow, brackish and partially reducing aqueous conditions. Under these initial conditions the newly-formed bentonite appears to have been at equilibrium, and subsequent rapid deposition of impervious mud/silt has served to isolate the bentonite from alteration during the continued palaeoevolution of the Mowry Sea basin. How true is this statement?

The work of /Cadrin et al, 1995/ is highly relevant. The basic rationale behind their study was to select a so-called Middle Cenomanian 'X' bentonite dated to 95 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ /Obradovich, 1993/, of thickness 3–100 cm, and traceable over 3200 km within the Western Interior seaway (i.e. southern extension of the Mowry Basin to link-up with the Gulf of Mexico seaway). Samples have been taken from Colorado, Kansas, Wyoming, Montana, Nebraska, S. Dakota, Oklahoma, New Mexico and Manitoba. In Wyoming, the 'X' bentonite is equivalent to the Clay Spur bentonite occurring at the top of the Mowry Shale in the Mowry Formation and directly relevant to this report. /Cadrin et al, 1995/ used the following paragenetic sequence of formation: 1) volcanic ash deposition, 2) devitrification of volcanic glass, 3) initial clay formation (submarine weathering), and 4) subsequent clay neoformation (burial diagenesis). Neoformation of clays results from alteration by waters that post-date initial clay crystallisation.

An extensive sampling campaign of these 'X' bentonites was carried out and separated smectites were mineralogically characterised and analysed for the stable isotopes ^{18}O and ^2H . As reviewed by /Cadrin et al, 1995/, empirical investigations of clay minerals indicate that smectite does not undergo subsequent oxygen-isotope exchange with post-formational water at temperatures of less than 80–100°C for several millions of years. Therefore, smectite that has been at low temperatures since formation and not greatly exposed to post-formational waters should have stable isotopic values representative of the waters in which it was originally formed. The authors defined post-formational waters as including meteoric rainwater, evolved pore water and basinal formation water that is not the original seawater which reacted with the ash to form the bentonites. That smectites can preserve the initial stable isotopic signature of the waters from which they have been formed had been shown earlier by /Henderson et al, 1971/. However, /Cadrin et al, 1995/ went one step further by correlating smectite isotopic values with the stable isotope signatures of well-preserved fossil remains which are stratigraphically of the same age.

Results from the South Dakota and Wyoming montmorillonites showed δD and $\delta^{18}\text{O}$ values compatible with formation from a fluid with an oxygen-isotopic composition near -6‰ and a hydrogen-isotopic composition near -40‰ , which is the value calculated from fossil remains for the Greenhorn Sea during Middle Cenomanian time and from the relation between $\delta^{18}\text{O}$ and δD values for meteoric water. The data indicate that these studied bentonites at least, have not been subject to a sufficient flux of post-formational meteoric water to have resulted in a preferential hydrogen-isotope exchange. To have retained the original isotopic signature of the Cenomanian seawaters, reflects that the Wyoming and South Dakota bentonites were deposited in a thick, relatively impermeable sequence of shales, characteristic of the central part of the Mowry Sea basin. Other indicators include the absence of diagenetic, fibrous smectites in the $<0.2\ \mu\text{m}$ fraction, which otherwise is an indication of post-formational interaction with basinal brines. Furthermore, the Wyoming bentonites comprise 100% montmorillonite which contain Al, Mg and Ca consistent with a sea water origin.

4.3 Conclusions

Based on the evidence presented and discussed above, it would appear in general that most of the Wyoming bentonites scientifically studied, and possibly commercially mined, have undergone no significant post-depositional alteration. Moreover, because of their physico-chemical isolation since deposition, it is not possible to study the effects of post-formational alteration of the bentonites under varying aqueous conditions and chemistry during the palaeoevolution of the Mowry Sea basin in Cretaceous times. The bentonites are, therefore, a good natural analogue of long-term stability in a closed system, but there is insufficient information to evaluate their long-term behaviour in an open system.

5 Acknowledgement

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