Geochemical discrimination of the Upper Ordovician Kinnekulle Bentonite in the Billegrav-2 drill core section, Bornholm, Denmark

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Abstract. The content of the trace elements Ti, Nb, Zr and Th has been analysed in 34 Upper Ordovician bentonites from the Billegrav-2 drill core, Bornholm, Denmark. The section contains two 80–90 cm thick bentonites, which potentially may represent the Kinnekulle Bentonite, as well as several rather thick but composite bentonite layers with thin terrigenous shale interbeds. Comparison of the four immobile trace elements with data from the Kinnekulle Bentonite reported from other locations in Baltoscandia indicate that the 80 cm thick bentonite between 88.30 and 89.10 m in the Billegrav-2 core represents this marker bed. The other thick (90 cm) bentonite in the Billegrav-2 core, exceeding the thickness of the Kinnekulle Bentonite, belongs to the Sinsen or uppermost Grefsen Series bentonites. Bentonites in the Grefsen Series frequently contain much higher concentrations of trace elements than the Kinnekulle Bentonite.

Key words: bentonites, Ordovician, Denmark, Kinnekulle.

INTRODUCTION

The lower part of the Upper Ordovician contains numerous altered volcanic ash layers in the Baltoscandian area, amongst them the unusually thick so-called Kinnekulle Bentonite, which represents one of the largest eruptions that has ever taken place during the Phanerozoic (Huff et al. 1992, 1996). After recognition of the volcanic origin of the clay-rich interbeds in the Ordovician of Scandinavia by Thorslund (1945), Hagemann & Spjeldnaes (1955) first applied these layers, in particular the thickest one (XXII), to correlation of sections. In North Estonia Jürgenson (1958) correlated five bentonite layers, including the thickest one (d) at the base of the Keila Stage. Männil (1966) correlated the thickest bentonite (XXII) in Scandinavia with the thickest one (d) in the East Baltic. Using these correlations, Vingisaar (1972) published the first distribution and thickness map of the ‘main metabentonite’ layer across the entire Baltoscandian area. Bergström et al. (1995) applied trace element geochemistry to correlation in combination with palaeontological data and thickness of the beds. Bergström et al. (1995) also named the thickest bed the ‘Kinnekulle’ K-bentonite.

In the Oslo Region, south-central Sweden and Estonia one of the bentonites in the Sandbian Stage (Upper Ordovician) is significantly thicker than the others, supporting correlation, whereas in Latvia and Lithuania all bentonites are thin and, hence, recognition of the Kinnekulle Bentonite is not possible without using chemical or mineralogical fingerprinting. In Scania, southernmost Sweden, the same problem was encountered by Bergström et al. (1997), as more than one thick bentonite occur in Kyrkbäcken and other sections, and identification of the Kinnekulle Bentonite is not straightforward.

In order to identify individual eruption layers, researchers have used phenocryst compositions of apatite (Batchelor 2009; Ray et al. 2011; Sell & Samson 2011), biotite (Batchelor 2003) and sanidine (Kiipli et al. 2007, 2010, 2011, 2012, 2014a; Männik et al. 2014). Separation of phenocrysts for analyses is, however, time-consuming and often phenocrysts are absent or altered to an extent that they cannot be properly identified. Therefore a series of immobile trace elements have been used for correlations (Huff et al. 1998; Inanli et al. 2009; Hetherington et al. 2011; Kiipli et al. 2013; Kaljo et al. 2014).

The aim of the present contribution is to demonstrate the possibilities and problems of geochemical identification of individual volcanic eruption layers and, if possible, to identify the Kinnekulle Bentonite in the Billegrav-2 drill core section on Bornholm, Denmark.
MATERIAL

Seventy-six geochemical samples were collected from the ca 12 m thick Sandbian part of the Billegrav-2 drill core (Figs 1, 2), Bornholm, Denmark. The Sandbian strata are resting unconformably on a thin Komstad Limestone (basal Dapingian) and are in turn overlain by grey and black shales of Katian age; these strata are locally on Bornholm assigned to the *Dicellograptus* Shale. The conspicuous feature of the Sandbian section is that ca 50% of the section is formed by volcanogenic sediment altered to clay, i.e. bentonite. The other 50% of the section is formed by grey, often silicified mudstone. The bentonites contain also much chert. The section includes two thick bentonites (80 and 90 cm) and also thick intervals where bentonite material dominates. These intervals are separated by only thin terrigenous mudstone interbeds.

The Billegrav-2 well (DGU 248.61) was drilled as part of a shallow drilling campaign conducted by the Geological Survey of Denmark and Greenland (GEUS) on southern Bornholm in August 2010. The well was fully cored and subsequently subjected to an extensive logging programme by GEUS in order to characterize the lithology, the water composition and the flow capacity of the fracture systems (Schovsbo et al. 2011).

LOGSTRATIGRAPHICAL UNITS IN BILLEGRAV-2

Pedersen & Klitten (1990) discerned 6 units (A–F) and 16 subunits based on the gamma-ray log pattern in water wells and scientific wells drilled on southern Bornholm. The log signature of the logstratigraphical units was expanded to also include the formation resistivity and the sonic velocity by Schovsbo et al. (2011). The bentonite-rich interval occurs within log unit D that corresponds to the *Dicellograptus* Shale of traditional Danish terminology (Fig. 2). The log zone is divided into subunits D1–D3 of which the D3/D2 boundary approximates the *Dicellograptus foliaceus/D. clingani* zonal boundary and the D2/D1 boundary approximates the top of the bentonite-rich interval (= Sularp Shale according to the terminology proposed by Lindström 1953; Bergström et al. 1999). This level corresponds to log unit D1 of Pedersen & Klitten (1990). Bergström & Nilsson (1974) correlated this part of the shale with the *D. multidens* [now *foliaceus*] Zone. This unit is much thicker in the Billegrav-2 core (ca 12 m) than at Læså (2.9 m, cf. Funkquist 1919). It is apparently about 1 m thinner in the Sømarken-2 well (see Pedersen & Klitten 1990, fig. 5).

LOG RESPONSE OF BENTONITE BEDS

The log readings of the formation resistivity and gamma ray in the bentonite-rich shale interval clearly indicate that the thick bentonite beds in the mid to upper part are characterized by low formation resistivity and high Gr values (Fig. 2). No clear log signature is seen in the lower part of the interval. This probably reflects that the bentonite–shale intercalations are thin and below logging resolution. The low resistivity of the bentonites probably reflects different clay
Fig. 2. Log data, lithology and sampling depths of the Billegrav-2 core section.
minerals with high cation exchange capacity, such as mix-layer clays compared with the inter-bedded shale that in part is silicified. The formation resistivity appears to be about 17 ohm.m for relatively pure bentonite and 175 ohm.m. for relatively pure shale.

LABORATORY METHOD

X-ray fluorescence analyses for determination of major chemical components and trace elements were made on a Bruker S4 Pioneer spectrometer. The X-ray tube with Rh-anode and maximum working power of 3 kW was used. Eight grams of fine powder (grains not larger than 50 µm) per sample were mixed with eight drops of 5% Mowiol solution and pressed. Pellets were dried for 2 h at 105°C. The samples were measured and preliminary results were calculated by using the manufacture’s standard methods MultiRes and GeoQuant. Ten international and in-house reference materials were used to refine analytical results by up to a few per cent of the concentration. The results are available in an electronic attachment at http://dx.doi.org/10.15152/GEO.6.

The results were compared with published geochemical compositions of the Kinnekulle Bentonite from Scandinavia and the East Baltic (Bergström et al. 1997; Kiipli et al. 2011; Batchelor 2014; Siir et al. 2015).

Four elements, Ti, Nb, Zr and Th, were used in searching for the Kinnekulle Bentonite as these have been shown to be immobile during conversion of volcanic ash to authigenic silicates (Kiipli et al. 2008, 2014b). Element ratios vs Al₂O₃ are used for comparison in order to eliminate the effects of different residual enrichment of immobile elements during conversion of volcanic ash to authigenic silicates (Kiipli et al. 2013).

HOMOGENEITY OF THE KINNEKULLE BENTONITE COMPOSITION

The most reliable average composition of the Kinnekulle Bentonite, based on analytical results from 13 laboratories worldwide (reference sample Es-15), is published by Kiipli et al. (2000). Sample Es-15 originates from the upper part of the Kinnekulle Bentonite in the Pääsküla exposure, North Estonia. There the Kinnekulle Bentonite contains abundant authigenic K-feldspar and 18–19% Al₂O₃. More frequently the Kinnekulle Bentonite consists predominantly of illite–smectite and contains 20–26% Al₂O₃, even up to 31% in a kaolinite-rich variety from the Valga core (Kiipli et al. 2007). In Scandinavia bentonites often contain some carbonate or chert diluting the immobile elements and in these cases the Al₂O₃ content may be as low as 14–17% (Batchelor 2014).

Average immobile element/Al₂O₃ ratios in the Kinnekulle Bentonite, calculated on the basis of 46 analyses from the East Baltic and Scandinavia, are as follows:

\[
\begin{align*}
\text{TiO}_2 \times 10^4/\text{Al}_2\text{O}_3 &= 122, \\
\text{Nb} \times 10^4/\text{Al}_2\text{O}_3 &= 0.595, \\
\text{Zr} \times 10^4/\text{Al}_2\text{O}_3 &= 8.26, \\
\text{Th} \times 10^4/\text{Al}_2\text{O}_3 &= 0.648.
\end{align*}
\]

Data from the Fjäcka and Vasagård exposures are excluded from these calculations because they are deviating from the main data cluster (Fig. 3). These average values are used for comparison in Fig. 3. All element ratios in particular samples are divided by the average values for the Kinnekulle Bentonite. Figure 3A shows that the composition of particular samples of the Kinnekulle Bentonite in the East Baltic mostly does not differ from the average more than 1.2 times. In Scandinavian sections the deviation from the average can reach 1.4 times and in the Fjäcka and Vasagård sections the differences are 1.6–2.6 times.

IDENTIFICATION OF THE KINNEKULLE BENTONITE IN THE BILLEGRAV-2 SECTION

The comparison of Sandbian bentonites with the Kinnekulle Bentonite shows that other bentonites mostly have higher concentrations of Ti, Nb, Zr and Th (Fig. 3B). Zr concentrations are often especially high in the lower part of the Sandbian section in the Billergrav-2 core, showing up to 3.5 times higher values than in the Kinnekulle Bentonite. High contents of Zr characterize many bentonites of the Grefsen Series (Batchelor 2014), so the lower bentonites in the Billergrav-2 core likely belong to this series. Lower concentrations of elements compared with the Kinnekulle Bentonite are less frequent.

Eight of a total of 34 separate bentonite layers show geochemical similarity with the Kinnekulle Bentonite. Starting from below, the depths of these samples are: 93.88, 93.84, 92.75 and 91.90 m, inside the lower 90 cm thick bentonite at 90.0 and 90.45–90.60 m, inside the upper 80 cm thick bentonite at 88.55–88.95, 89.05–89.10, 87.5 and 87.25–87.35 m (Fig. 3B). Four layers in the lower part of the section are thin (1–4 cm) and alternate with high Zr layers and, hence, likely belong to the Grefsen Series. A relatively small part of the overlying thick bentonite between 89.95 and 90.85 m (25% e.g. five samples of a total of 20) is similar to the Kinnekulle Bentonite. The most likely candidate for the Kinnekulle Bentonite is the 80 cm thick bentonite between 88.30 and 89.10 m, revealing in nine of 13 samples closely similar compositions with the Kinnekulle Bentonite. Higher up the upper part of the thick composite bentonite layer between 87.25 and 88.00 m also exhibits some similarity with the Kinnekulle Bentonite.
Fig. 3. Geochemical comparison of Ti, Nb, Zr and Th immobile element concentrations in the Kinnekulle Bentonite in the East Baltic and Scandinavia. A, reference data of the Kinnekulle Bentonite (Bergström et al. 1997; Kiipli et al. 2009, 2011; Batchelor 2014); B, comparison with bentonites from the Billegrav-2 section. All element/Al₂O₃ ratios are divided by the average of the Kinnekulle Bentonite. In the vertical scale 1 is the average value of the Kinnekulle Bentonite. Samples from the same bentonite bed are connected with a line.
DISCUSSION
Possibilities and problems of using immobile elements for proving correlations

Immobile trace elements, analysed easily by the X-ray fluorescence method (Ti, Nb, Zr, Th and major element \( \text{Al}_2\text{O}_3 \)), can be confidently used for the correlation of bentonites. However, volcanic ash compositions from repetitive eruptions from the same volcanic source may exhibit similar compositions. A favourable situation for volcanic stratigraphy is when ashes from different volcanoes alternate regularly (Kiipli et al. 2010). Using the thickness of bentonites for correlation is unreliable as a thick eruption layer can be thin in other areas.

Bentonites from single eruptions and composite layers from several eruptions

Internal compositional variations of two thick bentonite layers in the Billegrav-2 core indicate that the composition of magma can vary during long-lasting eruptions. The absence of terrigenous shale interbeds suggests that it was the same continuous eruption. Compositional variations can be caused by involving the lower layers from a stratified magma chamber during the eruption or differentiation of ash material during air transport or redeposition. Somewhat larger variations in the composition of the Kinnekulle Bentonite in Scandinavia (Fig. 3) compared to the East Baltic may indicate a change in wind directions during the eruption. The maximum power of the eruption is likely represented by the middle part of the Kinnekulle Bentonite in the Billegrav-2 core and at this time the ash cloud reached the most distant areas including the East Baltic. Initial and final stages of the eruption reached mostly Scandinavia, creating different compositions in the lower and upper parts of the bentonite layer. Thin shale interbeds in the interval between 87.25 and 87.82 m in the Billegrav-2 core indicate that this thick bentonite formed from several volcanic eruptions.

Causes of geochemical differences of the Fjäcka and Vasagård bentonites compared with the Kinnekulle Bentonite

The bentonites from these two localities were not used for calculating the average composition of the Kinnekulle Bentonite due to large deviation from the other data at hand, although these sections were previously believed to represent this bed. The compositional difference of the Fjäcka bentonite (Batchelor 2014) may be caused by mixing with terrigenous material as indirectly indicated by the high carbonate content. Terrigenous material commonly contains significantly higher contents of trace elements than is typical of the Kinnekulle Bentonite. The bentonite from Vasagård has only a significantly higher content of Ti, whereas the other immobile elements occur at low levels. This may indicate that bentonite from Vasagård (or at least the sample taken in 2003 from the poor outcrop and analysed by Kiipli et al. 2009) does not belong to the Kinnekulle Bentonite.

CONCLUSIONS
The study suggests with high probability that the 80 cm thick bentonite in the Billegrav-2 core section between 88.30 and 89.10 m represents the Kinnekulle Bentonite. Bentonites above it belong to the Grimstorp Series and those below to the Sinsen and Grefsen series. One of the Sinsen or uppermost Grefsen Series bentonites is 90 cm thick, thus exceeding the thickness of the Kinnekulle Bentonite. Bentonites in the Grefsen Series frequently show much higher concentrations of trace elements than the Kinnekulle Bentonite.

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REFERENCES


Vingisaar, P. 1972. On the distribution of the main metabentonite stratum (d, XXII) in the Middle Ordovician of Baltoscandia. Eesti NSV Teaduste Akadeemia Toimetised, Keemia, Geologia, 21, 62–70 [in Russian, with English summary].