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Immobile and mobile elements during the transition of volcanic ash to bentonite – An example from the early Palaeozoic sedimentary section of the Baltic Basin

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A B S T R A C T

In order to check the immobility and mobility of elements during conversion of acidic volcanic glass to bentonites in normal marine environments, we studied the composition of three altered volcanic ash layers from the Palaeozoic of the Baltoscandian Region, correlated through different facies. Regular changes in element concentrations in accordance with loss and gain of material during the transformation of volcanic ash indicate that Al, Nb, Ti, Zr, Sn, Pt, Ta, Hf and Th were generally immobile and can be used for the interpretation of source magma and correlation of ash layers. Cd behaves similarly with immobile elements and this can be explained with preservation only of the immobile portion of Cd that is fixed in phenocrysts. In bentonites in shales during the formation of kaolinite, the data indicate small-scale mobility of Al and Cd. In lime muds where K-feldspar forms from volcanic ash, Ta, Hf and Th reveal some small scale mobility. These slightly mobile elements must be used with caution for interpretation of thin ash layers with thicknesses of <1 cm. Sc, V, Ga, Y and Rare Earth Elements widely used for the interpretation of bentonites have noticeable mobility and can thus be used only semi-quantitatively or qualitatively in the bulk bentonite.

1. Introduction

Distinct chemical signatures of volcanic ash layers in pre-Quaternary sediments, commonly altered to clay-rich materials (bentonites, K-bentonites, Mg-bentonites, tonsteins) or other silicates, allow exceptionally precise correlation of sections (Emerson et al., 2004; Inanli et al., 2009; Kiipli et al., 2011, 2012, 2015; Ray et al., 2011; Sell et al., 2015). Bentonites in sedimentary sections carry information about source magma and tectonic processes in volcanic areas (Huff et al., 1993, 2014; Batchelor and Evans, 2000; Kiipli et al., 2014b; Xing et al., 2015; Huff, 2016) and directions of volcanic sources (Bergström et al., 1995; Kiipli et al., 2013). Isotopic dating of well-preserved phenocrysts can be used for refining the geological timescale (Sell et al., 2013; Cramer et al., 2015; Svensen et al., 2015). Besides the compositions of well-preserved phenocrysts (apatite, biotite, sanidine) (Batchelor, 2009; Sell and Samson, 2011; Kallaste, 2014) trace element contents, analysed from the bulk bentonite, are widely used for interpretations (Inanli et al., 2009; Hetherington et al., 2011; Kiipli et al., 2013, 2014a; Batchelor, 2014a, b). In using trace elements it is most important to know which elements have been immobile and which have been mobile during the alteration processes of volcanic ash. Immobile elements can be used for proving correlations and interpreting source magma, while mobile elements give evidence of diagenetic processes.

In general, large ions with a low valence state (large ion lithophile elements) are mobile in water-rich environments, and smaller ions with high valence (high field strength elements) tend to be less soluble and are often immobile. Mobility depends also on the pH, salinity and redox state of the water environment. pH, being above 7 in the open marine environment, may drop in sediments due to the decay of organic matter. Decaying organic matter additionally changes the Eh of the environment. Elevated temperatures and intrusion of brines during later geological history may also facilitate element mobility and carry elements into and out of the system. Accordingly, lists of immobile and mobile elements vary in different studies, but analysis of element immobility–mobility in the alteration of acidic volcanic ashes in normal marine shelf sea environments has rarely been undertaken (Christidis, 1998; Özdamar et al., 2014). Summa and Verosub (1992) studied mobility of trace elements during alteration of volcanic ash in alkaline lakes. A much greater number of studies of element mobility have been performed on continental weathering profiles (e.g., Middelburg et al., 1988; Nesbitt, 1979; Nesbitt et al., 1980), and palaeosols (Jutras et al., 2015; Xiong et al., 2015). Mobility of elements has been determined in laboratory experiments by Hodson (2002).

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The widely cited classic study by Winchester and Floyd (1977) uses Ti, Zr, Y, Nb, Ce, Ga and Sc for the interpretation of altered volcanic rocks. Their Nb/Y-Zr/TiO_2 ratio diagram and the Y-Nb diagram of Pearce et al. (1984) have repeatedly been applied to the interpretation of bentonites (Batchelor and Clarkson, 1993; Huff et al., 1993, Pearce, 1995; Histon et al., 2007). Comparing the compositions of tonsteins (kaolinite-rich altered ashes) with potential source rock, Zielinski (1985) concluded that Al, Ti, Ga, Zr and Hf have been immobile. Huff and Kolata (1989) considered Sc, Ti, Zr, Th, Hf, Ta, Fe, Co, Sb and Rare Earth Elements (REE) useful for the correlation of Ordovician bentonites. Zhou et al. (2000) considered Sc, V, Zr, Hf, Nb, Ta, Th, U, Co, Cr and REEs to be relatively immobile in surficial alteration processes during the formation of tonsteins. According to Dai et al. (2011), Sc, Zr, Nb, Hf, Ta and Th were immobile and REEs had low mobility. Batchelor (2014a,b) used Ti, Zr, Nb and Th in the interpretation of Palaeozoic bentonites. Among major components aluminium has been considered immobile (Huff et al., 1996, 1998; Kiipli et al., 2013, 2014a,b). Christidis (1998), studying alteration of Quaternary volcanics in Aegean islands, concluded that Al, Ti, Nb, Zr, V and Ni were immobile. Barrett et al. (2001) impressively discriminated source rock types in strongly hydrothermally altered rhyolites using binary plots of Al-Ti-Zr. Alteration lines in their study converge to the origin of the chart, indicating the immobility of these elements. Inanli et al. (2009) used Ti, Zr, Th, Sc, Hf, Ta, V and REEs for the correlation of bentonites. REEs have often been used for the estimation of source magma, e.g., presuming their immobility or low mobility (Histon et al., 2007; Dai et al., 2011). From the study of the alteration of volcanic ash in an alkaline lake in Tanzania, McHenry (2009) concluded that only Nb and Ta were immobile, whereas Zr and Ti commonly believed to be immobile exhibited noticeable mobility. Siir et al. (2015) registered the mobility of Nb to a distance of a few centimetres from bentonite to the host rock. Thus, depending on the particular sedimentary environments and later history of sediments, elements can behave differently.

In the present paper, we analyse the results of the geochemical study of three well-correlated Ordovician–Silurian volcanic eruption layers through different open shelf sedimentary facies. Our aim is to distinguish immobile from mobile elements. Ordovician and Silurian rocks are represented by shallow-water carbonate rocks in Estonia and by deep-water marlstones and shales in Latvia. The depositional assemblages form a monocline slightly dipping (ca. 3 m/km) to the south. Rocks crop out in North-Central Estonia and occur at depths of about 1 km in Latvia. Maximum burial palaeotemperatures did not exceed 50 °C (Kirsimäe et al., 1999).

2. Materials

Altered volcanic ash samples were collected from several Estonian and Latvian drill cores and from a temporary exposure at Pääsküla, on the Tallinn–Pärnu road (Fig. 1). Samples from the Kinnekulle Bed of the Billegrav-2 core of Bornholm were used, after Kiipli et al. (2014a). Three samples from the Vollen exposure in Norway were studied for comparison. In total 85 samples were studied. Samples were taken from the following three bentonite beds:

1. The Kinnekulle Bed, Ordovician Sandbian age, the *Diplograptus foliaceous* graptolite zone. Its stratigraphic name was assigned by Bergström et al. (1995) after the exposure at Kinnekulle mountain in Southern Sweden. The thickness of this layer reaches 0.7 m in Estonia (Kiipli et al., 2007), 2 m in Sweden, 1.4 m in Norway (Bergström et al., 1995) and 0.8 m in Denmark (Kiipli et al., 2014a). It is the most important stratigraphic marker horizon that has been used through decades starting from Hagemann and Spjeldnæs (1955). Besides the remarkable thickness of the layer, its sanidine phenocryst composition has been used as a correlation criterion in the East Baltic sections (Kiipli et al., 2007; Siir et al., 2015). Sanidine is homogeneous, containing 25 ± 0.5 mol% of small cations (Na + Ca). Samples were taken mostly from the middle of the bed; only in the Pääsküla exposure and Billegrav-2 drill core, several samples covering the full section of the ash layer were collected. In total 44 samples were studied from the Kinnekulle Bed.

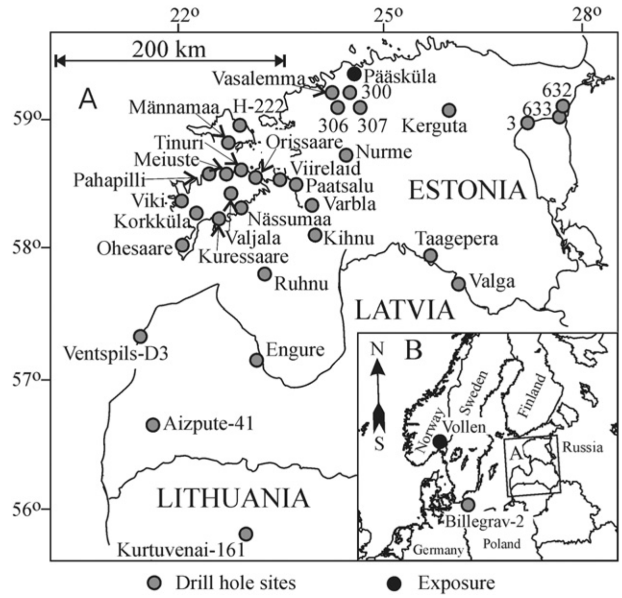

Fig. 1. Location of the studied drill-holes and exposures. A – East Baltic, B – wider area.

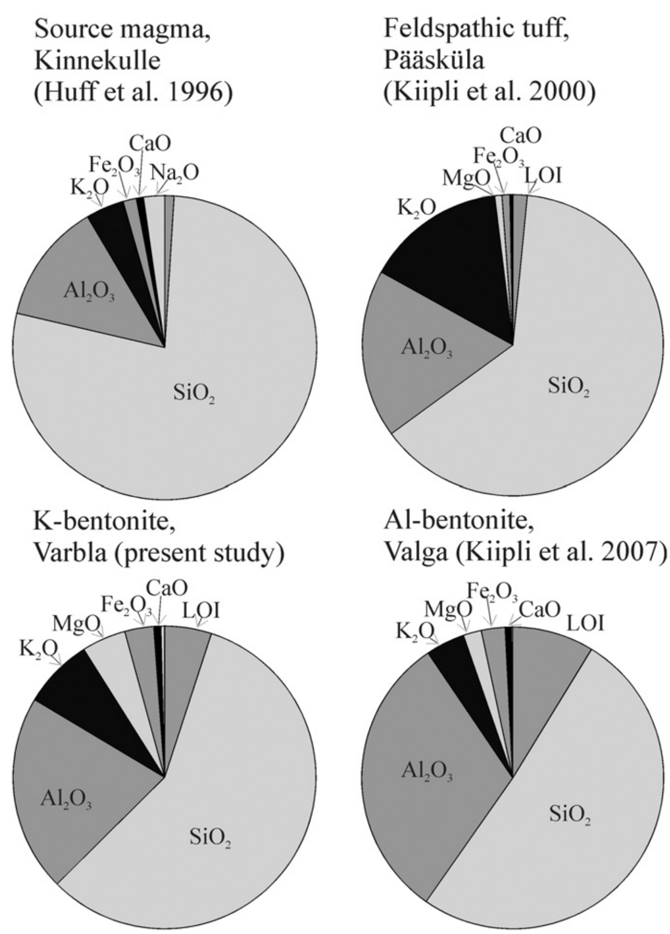

Fig. 2. Various Kinnekulle volcanic ash alteration products and source magma composition. Source magma composition, analysed from glass inclusions in quartz phenocrysts is given after Huff et al. (1996).