New U-Pb zircon ages of the Sandbian (Upper Ordovician) “Big K-bentonite” in Baltoscandia (Estonia and Sweden) by LA-ICPMS

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New U–Pb zircon ages of the Sandbian (Upper Ordovician) “Big K-bentonite” in Baltoscandia (Estonia and Sweden) by LA-ICPMS

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Abstract: Oscillatory-zoned euhedral single zircons from the upper Sandbian (Upper Ordovician) Kinnekulle K-bentonite exposed in a hillock at Pääsküla in Estonia and at the type locality on Mt Kinnekulle in Sweden were dated in a grain-by-grain manner by laser ablation-inductively coupled plasma mass spectrometer. The U–Pb (weighed mean) ages of the 25 grains from Mt Kinnekulle and 24 grains from Pääsküla are 453.4 ± 6.6 and 454.9 ± 4.9 Ma, respectively. This study provides the first ca. 454 Ma (late Sandbian) age for the Ordovician K-bentonite in northern Estonia and confirmed its correlation with the type Kinnekulle bed across the Baltic Sea.

Keywords: K-bentonite; Kinnekulle; U–Pb age; zircon; laser ablation-inductively coupled plasma mass spectrometer; Baltoscandia.

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1. Introduction

Immediately following the major biotic turnover called the Cambrian explosion, the Ordovician Period was characterized also by major biotic events lately referred to as the Great Ordovician Biodiversification Event (e.g. Kanygin 2001; Harper 2006; Servais et al. 2009). Baltoscandia is one of the best places in the world where non-disturbed, continuous and fossiliferous Ordovician shelf sequences (e.g. Bergström et al. 2012) can be examined. Recent advancements on local graptolite, chitinozoan and conodont biostratigraphy, in addition to correlation with the global standard, were reviewed by Nõlvak et al. (2006) for Estonia and by Bergström et al. (2011) for Sweden. Background environmental conditions for changes in Ordovician biodiversity also have been analyzed by bio- and chemostatigraphic approaches (e.g. Kaljo et al. 2004; Ainsaar et al. 2010; Hints et al. 2010).

The Ordovician succession in Baltoscandia intercalates numerous K-bentonite (altered volcanic ash) beds; more than 150 beds are hosted in deep-water grey-to-black-coloured mudstone facies in Scania, southern Sweden (Bergström & Nilsson 1974). The majority of these K-bentonite beds in Scania, in particular thin ones, are missing in the coeval shallower marine carbonate facies elsewhere in Baltoscandia. Nonetheless, a few K-bentonite beds of Late Ordovician age are well preserved in carbonate rocks of Estonia and western Latvia (Kiipli et al. 2007), and they are utilized as empirical but good stratigraphic markers.

The thickest and most widespread example of an Upper Ordovician K-bentonite in the Baltoscandian region is the Kinnekulle bed (Huff et al. 1992; Bergström et al. 1995; Huff 2008). This unit was named by P. Thorlind in the mid-20th century after Kinnekulle Mountain, where it was examined both in outcrops and by drill core, particularly at Mossen in Västergötland (Thorlind 1948). The Kinnekulle K-bentonite marks the base of the Keila Regional Stage (Fig. 1) in Baltoscandia (Hints & Nõlvak 1999), which is correlated with the uppermost Sandbian Stage of Late Ordovician age in the global time scale (Bergström et al. 2009). The thickness of the Kinnekulle bed is the greatest in south-central Sweden (over 2 m; Bergström et al. 1995), and it pinches out eastward towards St Petersburg in Russia. The bulk geochemistry of this K-bentonite suggests an affinity with the calc-alkaline (subduction-related) magma series.

Sandwiched between the overlying Skagen and the underlying Dalby limestones in the Mossen area (Jaanusson 1964), the Kinnekulle K-bentonite is biostratigraphically assigned to the upper *Amorphagnostus tvaerensis* (conodont) Zone, coeval with the upper *Diplograptus foliaceus* (graptolite) Zone (Bergström et al. 2011) and in the *Spinachitina cervicornis* (chitinozoan)
The rare and very short-ranged, but stratigraphically valuable chitinozoan species *Angochitina multiplex* (Schallreuter) appears just above the K-bentonite bed, offering a good opportunity to trace this level in Sweden and Estonia (Hints & Nõlvak 1999; Grahn & Nõlvak 2010).

In Estonia, the Kinnekulle bed still retains a considerable thickness (up to 60 cm on Hiiumaa Island, western Estonia), and it is intercalated within the sequence of the variably argillaceous rocks of the Kahula Formation in northern and central Estonia. Possible volcanogenic hazards of this ancient volcanic ash fall to benthic fauna were discussed by Hints et al. (2003) and Perrier et al. (2012).

According to the latest time scale (Cooper & Sadler 2012), the Keila stage is calibrated roughly to 453–455 Ma; nonetheless radiometric ages previously reported from the Kinnekulle bed ranged widely from 444 to 457 Ma (Huff 2008). Recently, new zircon U–Pb ages by thermal ionization mass spectrometry (TIMS) for the correlatable bentonites from Denmark and western Estonia were reported: 454.41 ± 0.17 and 454.65 ± 0.56 Ma (Sell et al. 2013).

By using a laser ablation-inductively coupled plasma mass spectrometer (LA-ICPMS), we dated single-grain zircon U–Pb ages for the Kinnekulle K-bentonite from Pääsküla Hillock for the first time from Estonia, and also from Mossen, the type locality of the bed, near Kinnekulle Mountain in southern Sweden for comparison. This short note reports the result of the U–Pb zircon dating.

2. Samples

Two samples were collected from central Baltoscandia (Fig. 2): one from the old bentonite quarry at Mossen on Kinnekulle (MK) in southern Sweden, and the other from Pääsküla Hillock at Tallinn (PH) in northern Estonia. Although these two localities are currently separated by a distance of ca. 650 km, the high-resolution bio- and lithostratigraphic data on the Baltoscandian Ordovician (e.g. Bergström et al. 1995; Huff 2008; Ainsaar et al. 2010; Grahn & Nõlvak 2010) ensure their correlation across the Baltic Sea.

2.1 Sample MK

The type locality of the 180-cm-thick Kinnekulle K-bentonite is the abandoned bentonite quarry at Mossen on the eastern slope of Kinnekulle, Sweden (58°35.555’N, 13°25.263’E). The study sample was collected by L. Holmer from the top part of the Kinnekulle K-Bentonite (Bergström et al. 1995, see fig. 4). Details of this locality were described by Bergström (1995); see also Thorslund (1948) and Jaanusson (1964).

2.2 Sample PH

The study sample PH was collected by H. Bauert and Y. Isozaki from a tunnel wall of the underground bunker, Shelter no. 1 in Tallinn (Hints & Nõlvak 1999; see fig. 3). The K-bentonite is 27 cm thick, mostly plastic and light yellowish grey in colour. The base of the K-bentonite bed has a sharp contact with underlying argillaceous limestones, whereas the upper boundary is transitional. Details of this outcrop were described by Hints et al. (1997).

3. Analytical procedures

Individual zircon grains were easily separated, because both K-bentonite samples of MK and PH were soft/plastic. Euhedral ca. 120-μm-long single grains were hand picked, 25 grains from MK and 30 from PH, respectively. Using cathodoluminescence visual imaging, we selected micro-domains of zircon crystals with oscillatory zoning that is unique to igneous zircons (Corfu...
The U–Pb isotope analyses of these micro-domains were performed one by one on the LA-ICPMS at Kyoto University. Ablation was done using a pulsed 193-nm Ar Excimer laser with fluence of \(2.72 \text{ J/cm}^2\) and irradiance of \(0.54 \text{ GW/cm}^2\) at a repetition rate of 8 Hz and pit size of 15 \(\mu\text{m}\) in diameter. See Iizuka & Hirata (2004) for detailed analytical procedures. Among all measurements, 24 for MK and 25 for PH are plotted on the Concordia line; see DD-Figs. 1 and 2 of data depository in Supplementary Material. Fig. 3 and DD-Tables 1 and 2 of data depository in Supplementary Material summarize the \(^{206}\text{Pb}/^{238}\text{U}\) age population of the zircons as probability age frequency curves, according to the Isoplot/Ex 3 program (Ludwig 2003).

### 4. Results and discussion

As all the laser-ablated spots for measurements were targeted in the oscillatory zoned part of any given zircon grain, they represent the primary age of crystallization from magma. The 24 measured U–Pb ages of the single-grain zircons from the sample MK vary by 433.9–490.1 Ma, and the 25 measured U–Pb ages from the sample PH vary within 428.6–483.0 Ma, respectively (DD-Tables 1 and 2, Supplementary Material). The weighted mean age for the MK zircons is 453.4 \(\pm 6.6\text{ Ma}\) and that for PH zircons is 454.9 \(\pm 4.9\text{ Ma}\). The location and shape of the peak are almost identical between the two diagrams (Fig. 3). The slight age difference between them is within the error range (2 standard deviation). These ages around 454 Ma correspond to the late Sandbian of early Late Ordovician, as the ages of the base and top of the Sandbian are calibrated at 458.4 \(\pm 0.9\text{ Ma}\) and 453.0 \(\pm 0.7\text{ Ma}\), respectively (Cooper & Sadler 2012).

Compared with the previously reported radiometric ages (Fig. 4), the present age data from the studied localities agree with the Ar–Ar age of biotite (454.8 \(\pm 2.0\text{ Ma}\)) reported by Min et al. (2001) and the U–Pb ages of zircons (454.41 \(\pm 0.17\text{ Ma}\)) reported by Sell et al. (2013).

The newly obtained zircon age of ca. 454.9 \(\pm 4.9\text{ Ma}\) for PH provided the first direct measurement of the Kinnekulle K-bentonite from northern Estonia. The almost identical ages around 454 Ma from the type section in Sweden and Estonia (this study) as well as from the Island of Bornholm, Denmark (Sell et al. 2013), confirm not only the previous ages but also the assumed correlation of the major K-bentonite bed on the opposite sides of the Baltic Sea.

In contrast, regarding the plausible correlation between the Kinnekulle bed in Baltoscandia and the Millbrig K-bentonite in the Appalachia Mountains of the USA, some doubt was expressed as to the basis of the differences in biotite and apatite chemistry (Haynes et al. 1995; Sell & Samson 2011) and zircon U–Pb ages (Sell et al. 2013). As the composite nature of the so-called Kinnekulle K-bentonite should be checked (Huff et al. 2004; Huff et al. 2010), further high-resolution age dating in a bed-by-bed manner is needed for identifying the age and location of the multiple-staged volcanism(s) on both sides of the proto-Atlantic ocean.

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