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

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Abstract: Oscillatory-zoned euhedral single zircons from the upper Sandbian (Upper Ordovician) Kinnekulle K-bentonite at Pääsküla hillock in Estonia and at the type Mt. Kinnekulle in Sweden were dated in grain-by-grain manner by laser-ablation ICP-MS. The U-Pb (weighed mean) ages of the 25 grains from Mt. Kinnekulle and 24 from Pääsküla, are 453.4 ± 4.2 Ma and 454.9 ± 4.5 Ma, respectively. This study first provided ca. 454 Ma (late Sandbian) age for the Ordovician K-bentonite in Estonia and confirmed its correlation with the type Kinnekulle bed on the opposite side of the Baltic Sea within, and also with the Millbrig K-bentonite in eastern USA.

Keywords: K-bentonite, Kinnekulle, U-Pb age, zircon, LA-ICP-MS, Baltoscandia

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 (GOBE) (e.g. Kaygin, 2001; Harper et al. 2006; Servais et al. 2009). Baltoscandia is one of the best places in the world where we can examine non-disturbed, continuous and fossiliferous Ordovician shelf sequences dating (e.g. Bergström et al. 2012). Recent advancements on local graptolite, chitinozoan, and conodont biostratigraphy, in addition to the correlation with the global standard, have been reviewed by Nölvak et al. (2006) for Estonia and by Bergström et al. (2011) for Sweden. The background environmental conditions for the Ordovician biodiversity changes have been analyzed by bio- and chemo-stratigraphic approaches (e.g. Hints et al. 2010; Kaljo et al. 2004; Ainsaar 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-colored mudstone facies in Scania, southern Sweden (Bergström, S. & 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 the Late Ordovician age are well preserved in carbonate rocks of Estonia and western Latvia (Kiipli et al. 2007) and they were utilized as empirical but good stratigraphic markers.

The thickest and most widespread example of the Upper Ordovician K-bentonite in the Baltoscandian region is the Kinnekulle bed (Huff et al. 1992; Bergström et al. 1995; Huff, 2008; **Fig. 1**). This unit was named by P. Thorslund in the mid-20th century for the Kinnekulle Mountain where it was examined both in outcrops and drill core particularly at Mossen in Västergötland (Thorslund, 1948). The Kinnekulle K-bentonite marks the base of the Keila Regional Stage in Baltoscandia (Hints & Nölvak 1999), which is correlated with the uppermost Sandbian Stage of Upper Ordovician in 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 to the eastern extension towards St. Petersburg in Russia. The bulk geochemistry of this K-bentonite suggests an affinity to calc-alkaline (subduction-related) magma series.

The Kinnekulle K-bentonite, sandwiched between the underlying Skagen and the

overlying Dalby limestones in the Mossen area (Jaanusson, 1964), is biostratigraphically assigned to the upper *Amorphognatus tvaerensis* (conodont) Zone, in the upper *Diplograptus foliaceus* (graptolite) Zone (Bergström et al. 2011), and in the *Spinachitina cervicornis* (chitinozoan) Zone (Nölvak & Grahn, 1993). The rare and very short-ranged, but stratigraphically valuable chitinozoan *Angochitina multiplex* (Schallreuter) appears just above the K-bentonite bed, offering a good opportunity to trace this level in Sweden and Estonia (Grahn & Nölvak 2010; Hints & Nölvak 1999).

In Estonia, the Kinnekulle bed still retains a considerable thickness (up to 60 cm in the 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 (Fig. 1). Possible volcanogenic hazards 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 in 444–457 Ma (Huff, 2008; **Fig. 2**). Despite the modernization of dating techniques, no new age data were added for the Kinnekulle K-bentonite during the last decade.

By utilizing laser-ablation induced-coupled-plasma mass spectrometer (LA-ICP-MS), 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. 3**); one from the old bentonite quarry at Mossen on Kinnekulle (MK) in southern Sweden, and the other from Paasküla Hillock at Tallinn (PH) in northern Estonia. Although these two localities are currently separated for 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 & Nölvak, 2010) ensure their correlation across the Baltic Sea.

Sample MK: The type locality of the 180 cm thick Kinnekulle K-bentonite at the old bentonite quarry at Mossen on the eastern slope of Kinnekulle, Sweden (58° 35.555'N, 13° 25.263'E; collected by L. Holmer from the top of the Kinnekulle K-Bentonite

(Bergström et al. 1995, fig 4). Details of this locality were described by Bergström (1995; see also Thorslund 1948).

Sample PH: Paasküla Hillock, Tallinn, Estonia (collected by Y. Isozaki from tunnel wall of the underground bunker, Shelter no. 1 in Tallinn; Hints et al., 1997). Details of this outcrop were described by Hints et al. (1997). The K-bentonite is 27 cm thick, mostly plastic and light yellowish grey colored. The base of the K-bentonite bed has a sharp contact with underlying argillaceous limestones while the upper boundary is transitional.

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. By cathodoluminescence (CL) visual imaging, we selected micro-domains of zircon crystals with oscillatory zoning that is unique to igneous zircon (Corfu et al., 2003). The U–Pb isotope analyses of these micro-domains were performed one-by one on the LA-ICP-MS at the Kyoto University. Ablation was done using a pulsed 193 nm Ar Excimer laser with fluence of $\sim 2.72 \text{ J/cm}^2$ and irradiance of $\sim 0.54 \text{ GW/cm}^2$ at a repetition rate of 8 Hz and pit size of 15 μm in diameter. See Iizuka & Hirata (2004) for detailed analytical procedures. Among the all measurements, 24 for MK and 25 for PH are plotted on the Concordia diagram. Figure 2 summarizes the $^{206}\text{Pb}/^{238}\text{U}$ age population of the detrital zircons as probability age frequency curves, according to the *Isoplot /Ex 3* (Ludwig, 2003).

3. Results and Discussion

As all the laser-ablated spots for measurements were targeted in oscillatory zoned part of 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 in 433.9–490.1 Ma, and the 25 measured U-Pb ages from the sample PH within 428.6–483.0 Ma, respectively (**Fig. 4**). The weighted mean age for the MK zircons is $453.4 \pm 4.2 \text{ Ma}$, and that for PH zircons is $454.9 \pm 4.5 \text{ Ma}$, respectively. The

difference between them is within the error range (2 standard deviation). These ages around 454 Ma correspond to the late Sandbian of Early Upper Ordovician, as the ages of the base and top of the Sandbian are calibrated at 458.4 ± 0.9 Ma and 453.0 ± 0.7 Ma, respectively (Cooper & Sadler, 2012).

Among the wide variation in previously reported radiometric ages, the present age data from the 2 localities agree with the Ar-Ar age of biotite 454.8 ± 2.0 Ma by Min et al. (2001). In addition, the U-Pb ages of zircons (452 ± 2 and 456.9 ± 1.8 Ma calculated with older decay constants) are also in a close age range (Compston & Williams, 1992; Tucker & McKerrow, 1995).

The newly obtained zircon age of ca. 454.9 ± 4.5 Ma for PH provided the first direct measurement of the Kinnekulle bed in Estonia. The similar age of 453.4 ± 4.2 Ma for MK confirmed not only the previous ages from the same area but also the correlation of the major K-bentonite bed on the opposite sides of the Baltic Sea. In addition, the Kinnekulle K-bentonite in the Baltoscandia is safely correlated with the Millbrig K-bentonites in eastern North America (Huff, 2008) across the modern Atlantic Ocean.

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Captions to figures

Fig. 1. Stratigraphic chart showing the horizon of the Kinnekulle K-bentonite bed (modified from Bergström et al., 2012; names of lithostratigraphic units in Sweden and in Estonia after Jaanusson 1964 and Meidla et al., 2008).

Fig. 2: List of radiometric ages previously reported for the Kinnekulle K-bentonite in Sweden (compiled by Huff, 2008).

Fig. 3: Index map of the sample localities in southern Sweden and northern Estonia.

Fig. 4: Frequency diagrams of U-Pb zircon ages of the Kinnekulle K-bentonite.
A: Mossen in southern Sweden; B: Paasküla in northern Estonia

GLOBAL DIVISION Series Stages	Stage slices	REGIONAL DIVISION Series Stages	GRAPTOLITE ZONES	CHITINOZOAN ZONES	CONODONT ZONES	MAIN LITHOSTRATIGRAPHIC UNITS (FORMATIONS)	
						MT. KINNEKULLE / SKÖVDE AREA	NORTH ESTONIA
LATE ORDOVICIAN	KATIAN	VIRU	Oandu	<i>Dicranograptus clingani</i>	?	Mossen	Rägavere
			Keila	<i>Spinachitina cervicornis</i>	<i>Amorphognathus tvaerensis</i>	Skagen	Hirmuse
			Haljala	<i>Belonech. hirsuta</i> <i>Lagenoch. dalbyensis</i> <i>Angoch. curvata</i> <i>Armonioch. granulifera</i>	<i>B. alobatus</i> <i>B. gerdae</i> <i>B. variabilis</i>	Kinnekulle K-bentonite	Kahula
	Sa2		Kukruse	<i>Nemagraptus gracilis</i> <i>D. vagus</i> <i>(Hustedograptus teretiusculus)</i>	<i>Laufeldochitina stentor</i>	Dalby	Tatruse
MID ORD.	DAR. SANDBIAN		Uhaku		<i>Pygodus anserinus</i> <i>Pygodus serra</i>	Ryd Gullhögen	Viivikonna
		DW3					Kõrgekallas

Fig. 1. Stratigraphic chart showing the horizon of the Kinnekulle K-bentonite bed (modified from Bergström et al., 2012; names of lithostratigraphic units in Sweden and in Estonia after Jaanusson 1964 and Meidla et al., 2008).

Location	Formation	Age (Ma)	Method	Reference
Kinnekulle	Dalby	453.4±4.2	U–Pb	this study
Tallinn	Kahula	454.9±4.5	U–Pb	this study
Kinnekulle	Dalby	454.8±2.0	Ar–Ar	Min, et al 2001
Kinnekulle	Dalby	456.9±1.8	U–Pb	Tucker & McKerrow 1995
Kinnekulle	Dalby	456.8±1	U–Pb	Tucker 1992
Kinnekulle	Dalby	452±2	SHRIMP	Compston & Williams 1992
Kinnekulle	Dalby	455.6±3.7	Ar–Ar	Kunk, et al 1985
Kinnekulle	Dalby	455±3	Ar–Ar	Kunk & Satter 1984

Fig. 2: List of radiometric ages previously reported for the Kinnekulle K-bentonite in Sweden (compiled by Huff, 2008).

Fig. 3: Index map of the sample localities of MK and PH from Mossen at Kinnekulle in southern Sweden and Paasküla Hillock at Tallinn in northern Estonia.

Fig. 4: Frequency diagrams of U-Pb zircon ages of the Kinnekulle K-bentonite. A: MK from southern Sweden; B: PH from northern Estonia

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