The Geniai Tuff in the southern East Baltic area – a new correlation tool near the Aeronian/Telychian stage boundary, Llandovery, Silurian

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In three drill cores in Latvia and Lithuania a thin (1 cm thick) altered volcanic ash bed with high concentrations of phosphorus (up to 3%), cerium (1%), lanthanum (0.5%) and strontium (2.5%), has been found close to the Aeronian/Telychian boundary (Llandovery, Silurian, *ca* 438 Ma). Small, millimetre-thick lenses within the ash bed contain up to 12% P and Sr, up to 6% Ce and 3% La. These elements occur as a solid solution of goyazite-florencite mineral. Additionally, authigenic K-feldspar and kaolinite occur in this ash bed. The high concentrations of *REE* elements, strontium and phosphorus suggest a carbonatite source magma, but the strontium isotope ratio contradicts that origin. Such a unique composition in a volcanic ash layer is a good basis for using it as a marker horizon for correlation of sections.
• Keywords: *REE*, goyazite, florencite, K-bentonite, Silurian, East Baltic.

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Thin altered volcanic ashes (bentonites, K-bentonites) in Baltoscandian sedimentary sections, evidencing volcanism at nearby plate margins, have been found from the Upper Ordovician (Bergström *et al*. 1995) through lower Silurian (Bergström *et al*. 1992, Batchelor *et al.* 1995, Batchelor & Jeppsson 1999) to the lower part of the upper Silurian (Snäll 1977). Many Silurian bentonites are recorded also in Early Palaeozoic sedimentary rocks in England (Ray 2007, 2011) and Scotland (Batchelor & Weir 1988). In the East Baltic area ash beds from a total of 51 volcanic eruptions have been identified in the Telychian (Kiipli *et al*. 2008a–c, 2010b) and 50 in the Wenlock (Kiipli *et al*. 2010a). Ash beds in sedimentary sections carry valuable information about the geochemical type of volcanism and can be used as stratigraphical markers for precise correlation of sections.

With the aim of extending correlations of volcanic ash layers southwards, we studied two sections from Latvia, and also some remarkable bentonite interbeds from several sections in Lithuania. Laboratory analyses of these new materials revealed unusually high concentrations of REE elements, Sr, and P in one of these thin volcanic ash layers. Reporting and interpreting this find is the aim of the present article.

Material and methods

Twenty-three altered volcanic ash samples were taken from the Aeronian and lower Telychian of the Ventspils-D3 and Vidale-263 cores, Latvia (Fig. 1). In addition, nine samples were found in the same stratigraphical interval from Lithuanian cores. The thickness of the ash beds varies from 1 mm to 3 cm, which is generally less than in Estonia, where ash beds frequently reach thicknesses of 5–10 cm. The stratigraphical position of the ash beds in Lithuania was established using graptolites (Motuza *et al.* 2002, Paškevičius 1982). In the Aizpute-41 section the graptolite biozonation from the *sedgwikii* to *crenulata* biozones (Loydell *et al.* 2003) was used and correlations with the Ventspils-D3 and Vidale-263 sections were based on the lithology of sedimentary rocks and composition of sanidine in volcanic ash beds. All samples were analysed by

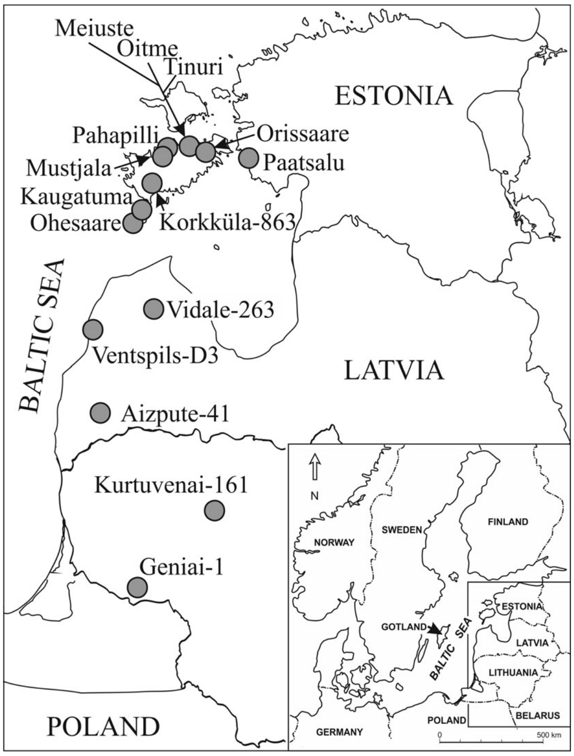

Figure 1. Location of studied drill core sections in the eastern Baltic.

X-ray diffractometry (XRD) for identifying major minerals and determination of magmatic sanidine phenocryst composition. The authors have applied the same methods in their previous works (*e.g.* Kiipli *et al.* 2010a). Samples of sufficient size (at least 8 g) were subjected to standard X-ray fluorescence (XRF) analysis for major and trace elements. Results are available in the database at the http://geokogud.info/git/reference.php?id=1586 (Kiipli *et al.* 2011). XRD and XRF analyses were carried out at the Institute of Geology at Tallinn University of Technology. Ten samples were analysed for trace elements by inductively coupled plasma mass spectrometry (ICP-MS) at the University of Bergen. $^{87}Sr/^{86}Sr$ ratio analyses were performed using ICP-SFMS instruments at the laboratory of ALS Scandinavia AB (see http://www.alsglobal.se for details).

Results

Stratigraphy and correlations near the Aeronian/Telychian boundary in the East Baltic

The major, upper part of the Rumba Formation in Estonia, consisting of shallow water nodular limestones, with the brachiopod *Pentamerus oblongus*, corals *Paleofavosites obliquus* and *Calostylis luhai*, stromatoporoid *Clathrodiction variolare*, gastropods *Boiotremus* cf. *longitudinalis* and *Hormotoma* sp. and trilobites *Calymene frontosa* and *Encrinurus rumbaensis* (Kaljo & Einasto 1990) can now be correlated firmly with the lower part of the Telychian ranging from the *Spirograptus guerichi* or *Spirograptus turriculatus* Biozone to the *Streptograptus crispus* or even to the *Streptograptus sartorius* graptolite Biozone (Fig. 2). Formerly the Rumba Formation was correlated with the *Stimulograptus sedgwickii* Biozone, in the upper Aeronian (Nestor 1997). The Aeronian/Telychian boundary corresponds to the boundary of the *Stimulograptus halli* and *Spirograptus guerichi* graptolite Biozones (Loydell 2012). In sections studied by us these species were not found and therefore the position of the Aeronian/Telychian boundary is less constrained between *Stimulograptus sedgwickii* and *Spirograptus turriculatus* biozones.

The "O" volcanic tuff (ID851) – hard layer with high content of authigenic potassium feldspar, having uniquely the most potassic composition of the volcanic sanidine (21.1 ± 0.4 mol% of the Na+Ca component) among Silurian volcanic ashes, forms a perfect marker horizon in the upper part of the Rumba Formation in Estonia (Kiipli *et al.* 2006). Biotite in the "O" Tuff is magnesium-rich (Kiipli *et al*. 2008c). In the Silurian deep shelf area in Latvia and Lithuania the "O" Bentonite (kaolinite and illite-smectite rich variety of the same eruption layer) occurs 4.6–5.9 m above the organic rich shales of the Dobele Formation with *Stimulograptus sedgwickii* in the upper part. In the Aizpute-41 core 10–15 cm below the "O" Bentonite *Spirograptus turriculatus* has been found (Loydell *et al.* 2003). The "O" Tuff in Estonia has been correlated with the Osmundsberg K-bentonite (illite-smectite rich variety of the same eruption layer) in Scandinavia (Bergström *et al.* 1998, Inanli *et al*. 2009). In the Osmundsberget section in Sweden, Loydell & Maletz (2002) identified *Spirograptus turriculatus* both below and above the Osmundsberg K-bentonite.

Study of Lithuanian and Latvian cores has revealed in the interval, barren of graptolites, between the *St. sedgwickii* and *Sp. turriculatus* biozones a new, thin (0.7–1.0 cm) volcanic tuff layer with a unique chemical and mineralogical composition. This layer contains up to 12% phosphorus 6% Ce, 3% La and 11% Sr (Fig. 3). We propose the name Geniai Tuff (tuff, because all known occurrences are represented by hard layers consisting dominantly of goyazite-florencite and potassium feldspar with subordinate clay) and assign the ID number 890 to this layer. The Geniai Tuff has been found in the Geniai-1 core at a depth of 1752.1 m, in the Ventspils-D3 core at 848.5 m and in the Vidale-263 core at 754.4 m (Fig. 2). In the Geniai-1 core this layer occurs 1.1–2.7 m above the Aeronian/Telychian boundary. The Aeronian/Telychian boundary corresponds to the upper boundary of the *St. sedgwickii* Biozone in Lithuania (Paškevičius 1982). *Stimulograptus halli*, index species of the uppermost Aeronian graptolite

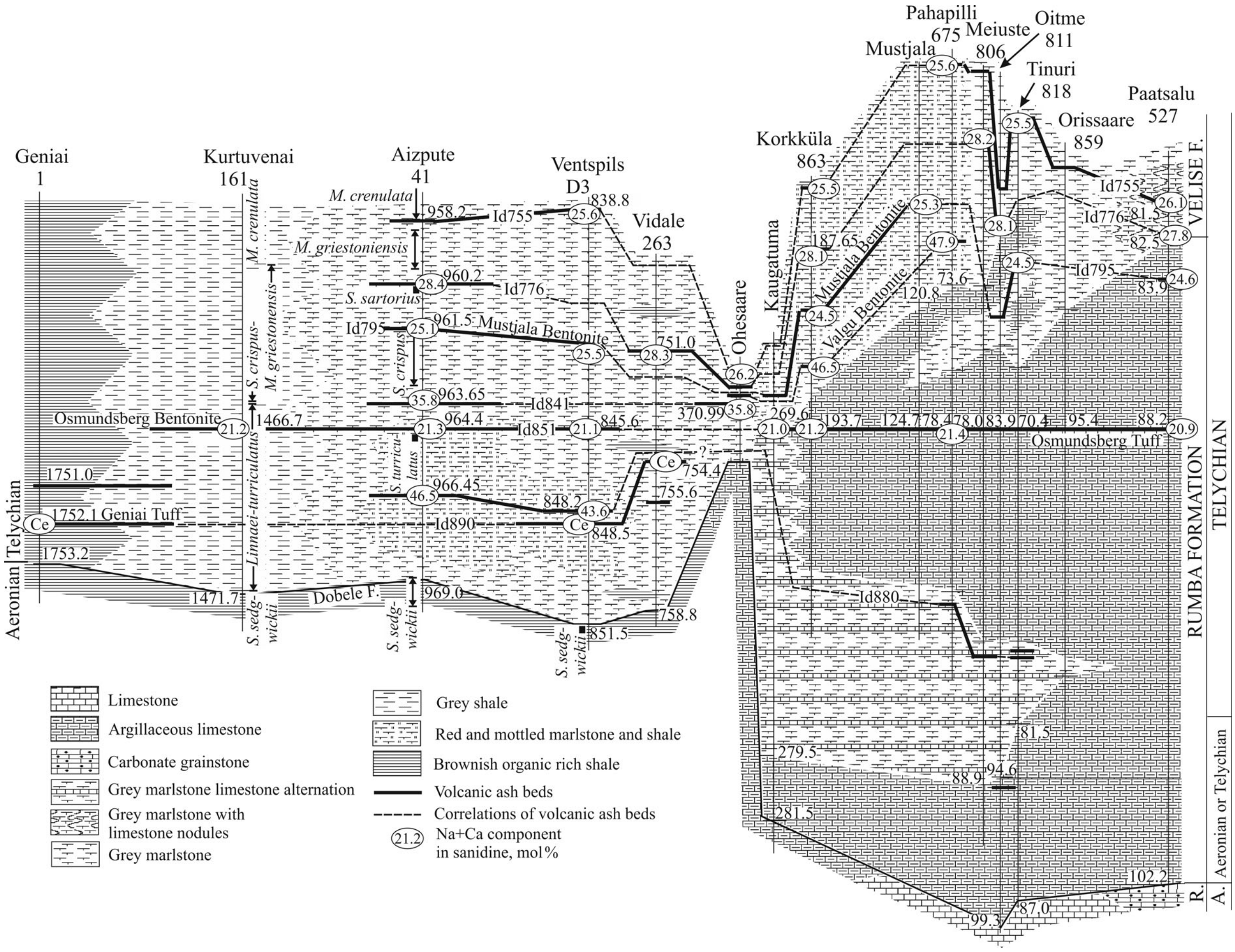

Figure 2. Stratigraphical position of the Geniai Tuff. Correlation of altered volcanic ashes is based on the sanidine phenocryst composition. The Geniai Tuff is marked by Ce (cerium). Numbers near the drill cores represent depths in metres. Graptolite biozonation of the Aizpute core is from Loydell *et al.* (2003).

biozone according to Loydell (2012), was not found in Lithuania. Alike *St. sedgwickii* was not found in the Geniai-1 drill core. The upper boundary of the *St. sedgwickii* biozone is indicated by the last appearance of *Metaclimacograptus hughesi* at a depth of 1754.8 m in Geniai-1. The first graptolite assemblage of the *R. linnaei* and *Sp. turriculatus* biozones was found at a depth of 1753.2 m in Geniai-1. The assemblage comprises *Monograptus marri* and *Streptograptus nodifer*. *Monograptus marri* occurs in the *R. linnaei* and *Sp. turriculatus* biozones in Lithuania (Paškevičius 1997) and in Bohemia (Štorch & Kraft 2009). The interval from 1754.8 m to 1753.2 m is without graptolites or the graptolite rhabdosomes are too badly preserved for identification. The distribution of the Geniai Tuff, spanning over 270 km from South to North, is shown on Fig. 3.

Unfortunately, we have not found the Geniai Tuff in the Rumba Formation in Estonia. The lower part of the Rumba Formation includes three thin feldspathic tuff layers, but none of these contains elevated REE, phosphorus and strontium content. Probably one of these geochemically very similar layers, characterized by the lowest Zr/TiO_2 ratios (0.01–0.03) among Telychian bentonites, correlates with an ash in the Ventspils-D3 core at a depth of 848.2 m (Zr/TiO_2 = 0.019), 30 cm above the Geniai Tuff. Zr/Th ratios varying between 10 and 15 suggest correlation of Ventspils-D3 848.2 m with ash bed ID880 in Estonia. Another two ashes in Estonia revealed slightly higher Zr/Th ratios, varying between 20 and 25 (http://geokogud.info/git/reference.php?id=1586 record numbers 134–139, 251–252, 471–472, 790, 1157). These correlations constrain the position of the Aeronian/Telychian boundary not higher than within the lower 5 m of the Rumba Formation in Estonia.

The upper boundary of the Rumba Formation is often sharp, between argillaceous limestones and marlstones, but in some sections a transitional interval occurs including alternating limestones and marlstones. In the palaeon-

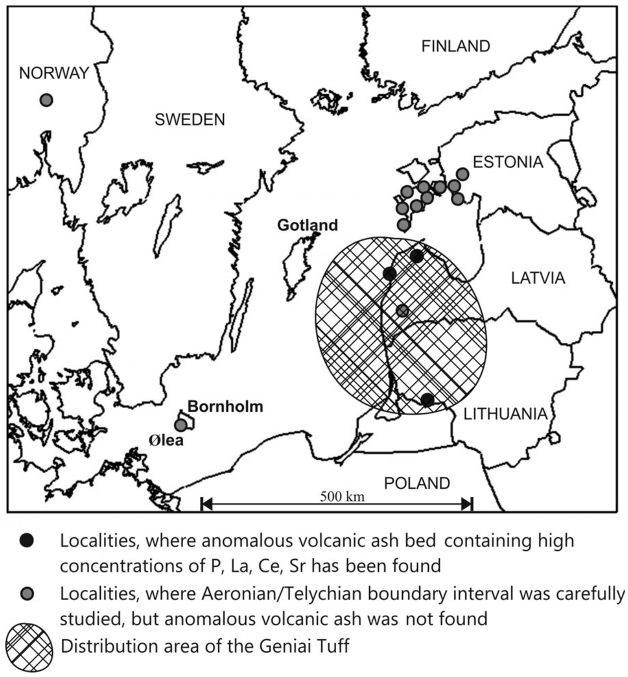

Figure 3. Known distribution area of the Geniai Tuff.

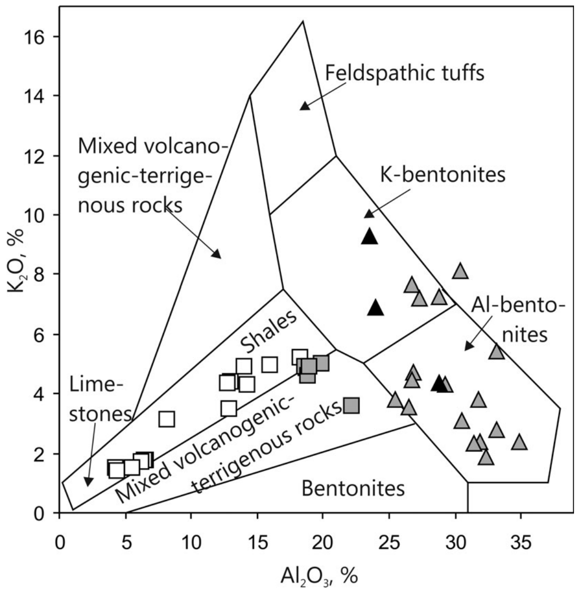

Figure 4. Al_2O_3 and K_2O contents of studied samples. Grey triangles – Al-bentonites and K-bentonites from Latvia and Lithuania. Black triangles – altered volcanic ash beds containing goyazite-florencite. Empty quadrangles – terrigenous shales and marlstones from Latvia. Grey quadrangles – mixed volcanogenic-terrigenous samples. Field boundaries of rock types are from Kiipli *et al*. (2010a).

tologically well studied Paatsalu section (Hints *et al.* 2006) the transition interval is represented by the occurrence of common limestone nodules in the marlstones of the Velise Formation. The Mustjala Bentonite (ID795) has been found in the upper part of the Rumba Formation in the Paatsalu core, while in the Tinuri and Oitme cores it occurs in the transition interval and in the western part of Saaremaa in the Mustjala, Korkküla and Kaugatuma cores it occurs in marlstones of the Velise Formation. Therefore the upper boundary of the Rumba Formation is clearly diachronous over a few tens of kilometres in Estonia: red marlstones of the Velise Formation in the western part of Saaremaa correlate with grey nodular limestones of the upper part of the Rumba Formation on the mainland of Estonia. In the Aizpute-41 core the Mustjala Bentonite was identified in the upper part of the *S. crispus* graptolite Biozone.

Major minerals in altered volcanic ashes

While ash beds in Estonia are composed mainly of illite-smectite and authigenic potassium feldspar (Kiipli *et al.* 2008b), with kaolinite present only in sections near the southern border, in Latvia and Lithuania kaolinite is a common major component besides illite-smectite, whereas K-feldspar is rare. This areal difference has been studied in the Ordovician Kinnekulle ash bed (Kiipli *et al.* 2007) and originates probably from the differences in sedimentary facies. During Palaeozoic times Latvia and Lithuania were located in the deep shelf and Estonia mainly in the shallow shelf area. Hints *et al.* (2008), however, proposed a late diagenetic origin for potassium feldspar in bentonites. Fig. 4 shows this compositional variation in terms of Al_2O_3 and K_2O content.

Three samples of the Geniai Tuff reveal unusual reflections on XRD patterns indicating goyazite-florencite (Sr, Ce, La, Al phosphate) solid solution as one of the major minerals. This mineral occurs as rare grains in Silurian volcanic ashes in the East-Baltic, but as a major component it has not been found previously. Authigenic K-feldspar and kaolinite associate with goyazite-florencite. In some other ash beds apatite is a significant constituent, reaching several percent. A study of the Geniai Tuff by EDS microanalysis showed that concentrations of anomalous elements within the bed form two cycles reaching extremely high values in millimetre-scale horizontal lenses: up to 12% P and Sr, up to 6% of Ce and 3% of La (Fig. 5). These concentrations indicate that the thin lenses within the Geniai Tuff consist almost entirely of the mineral goyazite-florencite. Sharp contacts with the host shale and the content of authigenic K-feldspar and kaolinite together with the absence of terrigenous quartz typical of the numerous volcanic ash beds and not the terrigenous shales in the southern East Baltic demonstrate the volcanic origin of the Geniai Tuff. Further evidence for the volcanic origin comes from the unusually high concentration (2.3–3.0%) of immobile TiO_2. In contrast, the concentration of TiO_2 in carbonate-free host shales in the East Bal-

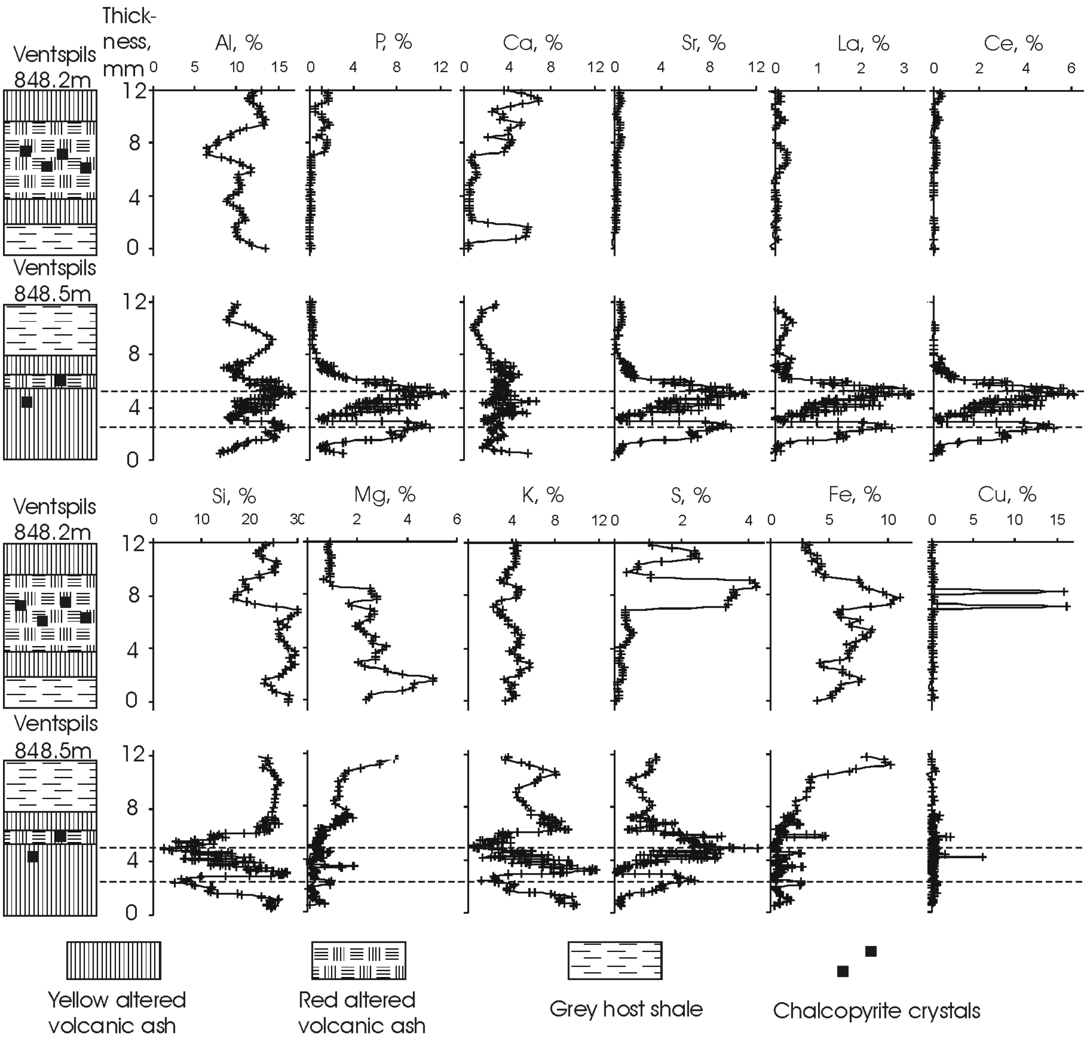

Figure 5. Distribution of chemical elements within two thin lower Telychian ash beds. Ventspils 848.5 m is the Geniai Tuff. The Geniai Tuff is characterised by very high contents of REE, Sr and P. Ash bed only 30 cm higher in a section do not contain any high concentrations of these elements. This indicates, that REE, Sr and P in the Geniai Tuff originated from the volcanic ash of specific composition and not from the diagenetic processes.

tic is very stable, ranging between 0.7–0.9% (Kiipli *et al.* 2008b).

Red patches in the host rock and also in the Geniai Tuff in the Ventspils core indicate an oxic sedimentary environment (Kiipli *et al.* 2000a). Silurian red sedimentary rocks and volcanic ashes in the East Baltic often contain early diagenetic chalcopyrite (Kiipli *et al.* 2000b). The same has been found also in the Geniai Tuff and other ash beds in the Ventspils core (Fig. 5). The Geniai Tuff in the Geniai and Vidale cores formed in anoxic sediments, indicated by the grey colour of rocks caused by the occurrence of dispersed pyrite.

Composition of the goyazite-florencite

According to the XRF and ICP-MS analyses, aluminous phosphate in the Geniai Tuff of the Geniai-1 core, depth 1752.1 m, contains 61% goyazite $SrAl_3(PO_4)_2(OH)_5{\times}(H_2O)$ and 39% florencite $(\mathit{REE})Al_3(PO_4)_2(OH)_6$ component in a solid solution (Table 1). Unit cell dimensions (trigonal a = 6.986 Å and c = 16.418 Å) calculated from XRD reflections are in good accordance with such a composition. Composition of the aluminous phosphate in the Ventspils and Vidale cores is similar. In total, composition of the goyazite-florencite in the Geniai Tuff varies between 57–65% of the goyazite component and correspondingly 35–43% of the florencite component. A small (7–14%) crandallite $CaAl_3(PO_4)_2(OH)_5{\times}(H_2O)$ component is also possible, although cannot be proved by geochemical data because XRD reflections indicate the presence of some apatite; therefore some CaO and P_2O_5 certainly belong to this mineral.

In the florencite component Ce, La and Nd comprise about 88% of the total *REE* content and the remaining 12% is formed by Pr and heavier *REE*.

Table 1. Major and trace elements in the Geniai Tuff and other volcanic ash beds.

Core		Ventspils-D3			Vidale-263	Geniai-1	Geniai-1
Depth, m		845.6	848.2	848.5	754.4	1752.1	1751.0
ID		851	880	890	890	890	860
XRF analyses							
SiO_2	%	51.0	46.9	43.2	49.6	38.7	49.7
TiO_2	%	0.36	1.63	2.32	2.40	2.97	3.08
Al_2O_3	%	26.9	23.8	23.9	23.2	28.4	27.3
Fe_2O_3T	%	5.55	4.48	1.49	1.34	0.52	2.65
MnO	%	0.016	0.009	0.008	0.007	0.003	0.006
MgO	%	2.20	1.47	0.65	0.66	0.45	0.6
CaO	%	0.41	4.59	3.32	1.54	1.49	1.63
K_2O	%	4.70	5.46	7.20	9.62	4.33	7.2
Na_2O	%	1.1	1.4	0.6	0.6	< 0.1	< 0.1
P_2O_5	%	0.052	2.92	5.10	3.12	7.86	1.05
S	%	0.06	0.30	0.27	0.58	0.50	0.56
Cl	%	0.36	0.71	0.27	0.09	0.04	0.020
LOI	%	7.0	6.8	6.4	5.0	9.2	6.6
Ce	%	< 0.006	0.04	0.72	0.36	1.19	0.06
La	%	< 0.004	0.01	0.36	0.23	0.47	0.03
Sr	%	0.01	0.02	1.17	0.87	2.59	0.06
As	ppm	5	3	5	12	2	15
Ba	ppm	280	393	528	675	482	357
Br	ppm	17	29	10	4	0	4
Cr	ppm	8	6	32	25	39	14
Cu	ppm	481	1,907	783	418	90	446
Ga	ppm	21	11	4	6	5	10
Nb	ppm	14	19	38	13	15	24
Ni	ppm	11	86	8	24	16	10
Pb	ppm	4	27	23	24	4	3
V	ppm	14	123	116	198	279	331
Y	ppm	–1	393	356	77	77	108
Zn	ppm	25	15	11	11	18	14

Trace element geochemistry of the altered volcanic ash layers: distinguishing the Geniai Tuff from other lithologies and volcanic ashes

According to the shale-normalised *REE* patterns (Fig. 6) the analysed samples are divided into four groups:

1. The host terrigenous shale from Ventspils 846.0 m. *REE*s form a flat pattern very similar to the average Post-Archean Australian Shale (PAAS) (McLennan 1989).

2. The Osmundsberg Bentonite from Ventspils 845.6 m reveals very low concentrations of *REE* showing also a flat pattern. A specific feature is a significant positive Eu anomaly evidencing source magma generation through preferential melting of feldspars (Rollinson 1993).

3. Volcanic ash beds with moderately elevated concentrations of REE, *e.g*. Geniai 1751.00 m, Aizpute 966.45 m, Ventspils 848.20 m, and Vidale 755.60 m. Concentrations of Ce vary between 300 and 600 ppm. These layers contain a few percent of P_2O_5 and XRD indicates the presence of apatite. Shale-normalised *REE* patterns show enrichment in middle *REE*, forming so-called "hat"-like patterns.

4. The Geniai Tuff with high concentrations of *REE*, *e.g*. Geniai 1752.1 m, Ventspils 848.5 m and Vidale 754.4 m. The Ce content varies between 0.4 and 1.3%. These layers contain goyazite-florencite as a main carrier of *REE*. *REE* patterns show strong enrichment of light *REE* and a distinct positive Er anomaly.

Discussion

Mineralogy and geochemistry of the Geniai Tuff

Goyazite-florencite (grandallite mineral group) solid solution minerals, $(Sr,Ce,Nd,La)Al_3(PO_4)_2(OH)_6$, have been

Table 1 – continued

Core		Ventspils-D3			Vidale-263	Geniai-1	Geniai-1
Depth, m		845.6	848.2	848.5	754.4	1752.1	1751.0
ID		851	880	890	890	890	860
ICP-MS analyses							
Ba	ppm	349	413	565	854	481	416
Co	ppm	5.1	24.6	2.8	8.4	4.0	3.9
Cs	ppm	14.1	2.7	0.5	1.1	1.5	1.6
Cu	ppm	711	4,022	1,146	312	107	446
Hf	ppm	5.0	8.6	6.2	8.4	9.1	9.3
Mn	ppm	111	69	70	89	29	53
Pb	ppm	6.0	24.5	29.7	37.4	7.0	13.6
Sc	ppm	7.9	20.5	17.6	13.2	13.4	12.7
Sr	ppm	112	259	12,821	9,612	29,913	668
Th	ppm	37.5	21.0	18.8	30.6	30.0	24.1
Ti	ppm	2,476	12,121	17,259	14,792	21,904	22,658
U	ppm	0.9	8.4	15.9	42.8	34.8	40.9
V	ppm	27	123	124	161	278	268
Y	ppm	2.6	364	372	93	138	100
Zr	ppm	142	332	255	384	406	385
La	ppm	3.7	175	4,121	2,782	5,452	194
Ce	ppm	10.3	606	8,161	4,229	13,546	431
Pr	ppm	1.0	66	508	312	1,629	52
Nd	ppm	4.3	374	1,579	973	7,641	254
Sm	ppm	0.8	95.1	157.4	110.6	906.2	62.4
Eu	ppm	0.3	24.6	31.7	24.7	118.7	15.1
Gd	ppm	0.8	100.1	176.1	114.7	731.7	52.8
Tb	ppm	0.1	16.1	29.0	16.6	104.7	8.0
Dy	ppm	0.7	78.8	82.9	31.9	54.9	31.4
Ho	ppm	0.1	14.5	15.4	4.8	7.5	5.1
Er	ppm	0.4	39.2	56.7	24.8	142.8	14.1
Tm	ppm	0.1	4.5	4.6	1.3	1.7	1.4
Yb	ppm	0.4	29.0	28.9	9.8	19.0	9.9
Lu	ppm	0.1	3.8	3.8	1.1	1.6	1.2

found in sedimentary rocks as early diagenetic trace minerals in Australia (Rasmussen 1996). In other works florencite has been interpreted as a hydrothermal alteration product (Lefebvre & Gasparrini 1980), as metamorphic, associated with monazite (Nagy *et al*. 2002), and as a weathering product of apatite and monazite in alkaline carbonatites from Brazil (Ribeiro *et al*. 2005). Grandallite has been found also in kaolinite-rich altered volcanic ash layers in coal formations (Rao & Walsh 1997, Ward 2002).

In the East-Baltic volcanic ash layers goyazite-florencite could originate in the volcanic ash only through submarine weathering (halmirolysis) of volcanic ash on the seabed and/or early diagenetic processes in sediments. The sedimentary rocks in the East Baltic are not metamorphosed and have not been subjected to hydrothermal alteration. Our samples were taken from deep drill-cores – consequently the rocks had not been subjected to subaerial weathering in exposures. The most critical prerequisite for formation of goyazite-florencite is the availability of major elements of this mineral, most of which are characterized by low solubility in Earth surface environments and cannot migrate for long distances. Reactive Al is always available in abundance in dissolving and crystallizing amorphous volcanic ashes. Commonly this process results in the formation of Al-rich clay minerals. This is the case also in many ash layers close to the Geniai Tuff in core, often lying only 0.3–1.5 m vertically separate from it. This leads to the conclusion that Sr, *REE* and P were incorporated into goyazite-florencite from the specific volcanic material with a high content of these elements, and not from the sedimentary environment.

Comparing Zr/TiO_2 and Ce/Al_2O_3 ratios from Geniai Tuff with common silicate volcanic rocks and carbonatites reveals a similarity with carbonatites (Fig. 7). The $^{87}Sr/^{86}Sr$ isotope ratio determined in a sample of the Geniai Tuff

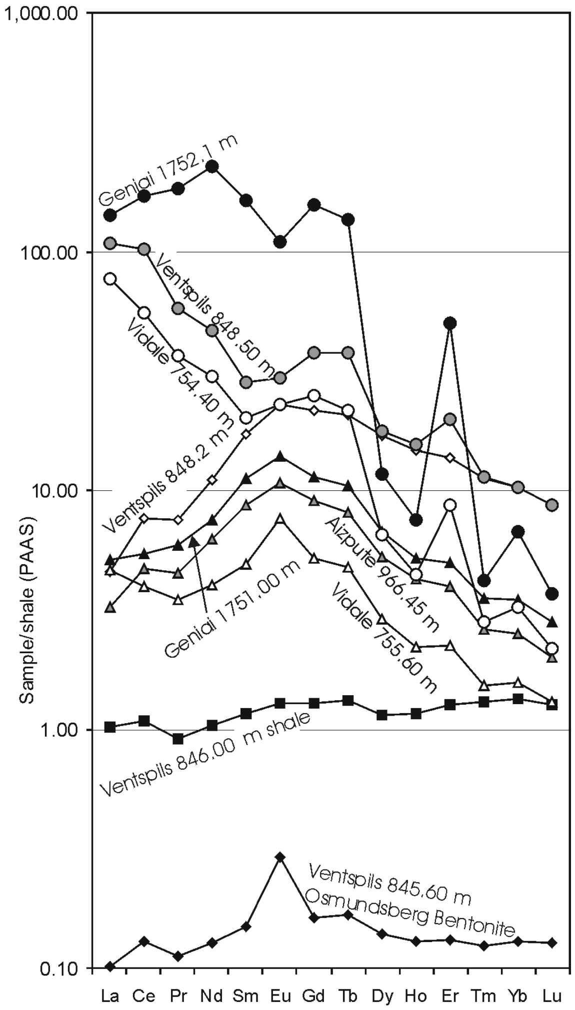

Figure 6. REE element patterns of altered volcanic ashes from the Aeronian/Telychian boundary interval. REE contents are normalised relative to the Post-Archean Australian Shale (PAAS). Geniai 1752.1 m, Ventspils 848.5 m and Vidale 754.4 m represent the Geniai Tuff.

from Ventspils core, depth 848.5 m is 0.70891 ± 0.00002. This value differs significantly from the late Llandovery seawater value (Brand *et al.* 2006). The absence of a negative Ce anomaly on shale-normalised *REE* patterns (Fig. 6) characteristic of oxic seawater (Shields & Stille 2001) also indicates a source other than marine. $^{87}Sr/^{86}Sr$ in the Geniai Tuff differs even more significantly from most mantle values, excluding Sr derivation from common sources in the mantle as well. High $^{87}Sr/^{86}Sr$ values are typical for the continental crust and only rarely occur in the mantle. In these cases, it is possible that continental crust has been subducted (Rollinson 1993).

High concentrations of REE and phosphorus in magmatic rocks are commonly associated with alkaline carbonatite intrusions (Hoernle *et al.* 2002, Ribeiro *et al.* 2005). The problem is that almost all carbonatites originated from a deep mantle source with low values of $^{87}Sr/^{86}Sr$ (Bell & Simonetti 2010). Therefore the geochemical type of the

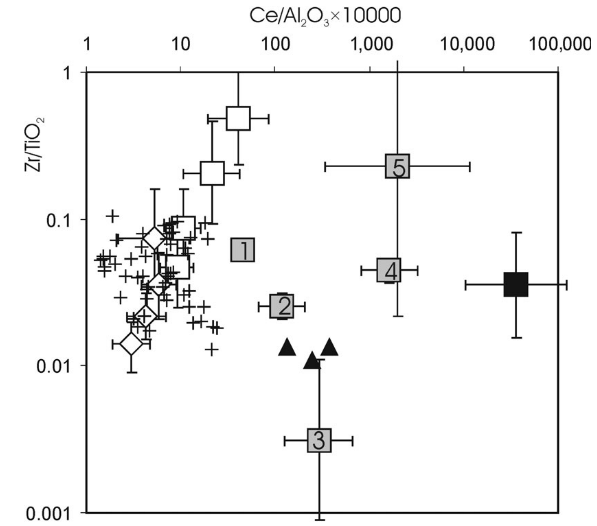

Figure 7. Immobile element Zr/TiO_2 and Ce/Al_2O_3 ratios in the Telychian ash beds of the eastern Baltic. Crosses – Telychian bentonites from Estonia. Black triangles – Geniai Tuff. Empty rhombs with error bars (one standard deviation) – Italian subalkaline volcanic rocks and empty quadrangles with error bars – alkaline volcanic rocks (data from Peccerillo 2005). Grey quadrangles – some carbonatites of the world: 1 – Italy, 2 – Uganda, 3 – China, 4 – Cape Verde extrusive, 5 – Cape Verde intrusive (Peccerillo 2005, Mourão et al. 2010, Nelson Eby *et al.* 2009, Xu *et al.* 2008). Black quadrangle – Ol Donio Lengai natro-carbonatite (Zaitsev & Keller 2006). Chart shows extreme compositional variation of carbonatites, exceeding significantly the variation in silicate rocks and shows the Geniai Tuff falling into the field of carbonatites.

magmatic source of the Geniai Tuff cannot be demonstrated conclusively and remains under discussion.

Possible mechanism for increasing element concentration in a sedimentary environment

Although the possible source for the Geniai Tuff – a carbonatite magma – contains high concentrations of *REE* compared with rocks common in the Earth's crust, concentrations reaching as high as several percent are not common. Therefore we propose that the majority of the carbonate portion of the carbonatite source magma was dissolved and removed in the marine environment. As a result, components characterized by lower solubility were concentrated strongly in a residue that forms the thin tuff layer.

Time of the anomalous high-REE event

According to the correlation with the established graptolite zonation, an anomalous magmatic *REE* event occurred close to the Aeronian/Telychian boundary, with ash beds being found in the lowermost layers of the Telychian. The Aeronian/Telychian boundary is currently dated at 436 ± 1.9 Ma (Ogg 2004). The Osmundsberg K-bentonite, lying directly above the anomalous volcanic layer within *Spirograptus turriculatus* Biozone, was dated from zircons as 438.7 ± 1.0 Ma using the $^{207}Pb/^{235}U$ method (Bergström *et al*. 2008). These dates suggest that the anomalous magmatic *REE* event occurred at approximately 438 Ma.

Conclusions

Considering all of the geochemical and mineralogical data, we propose that the Geniai Tuff originated from a volcanic eruption *ca* 438 Ma. The high content of *REE*, Sr and P suggest a carbonatite source magma, but the strontium isotope ratio contradicts this. So the source magma type of the Geniai Tuff remains under discussion. Dissolution of supposed major carbonate material in the sedimentary environment may have caused extreme residual enrichment of immobile elements in the ash bed. A volcanic ash bed of such an anomalous composition forms a perfect marker horizon for stratigraphy.

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