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Corroded hydrothermal quartz in Ordovician altered volcanic ash beds of the Baltoscandian Region

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Abstract. Partly dissolved prismatic quartz crystals have been found in an Upper Ordovician volcanic ash bed of the Vasagård section on Bornholm, Denmark. Similar crystals occur also in a volcanic ash in the Adze Formation of the Aizpute core, Latvia. Although biostratigraphic data are insufficient for the correlation of these findings, the abundant occurrence of this rare form of quartz at Vasagård indicates that it can be reliably used as a correlation criterion in future studies. Partly dissolved prismatic quartz crystals were most likely formed during hydrothermal processes in the volcanic source area.

Key words: quartz, hydrothermal, K-bentonite, Ordovician, Denmark, Latvia, Estonia.

Pyroclastic material in altered Lower Palaeozoic volcanic ash layers (K-bentonites) of Estonia and Latvia is commonly below 0.1 mm in size, rarely larger. Notable exceptions are ash layers of the Keila Stage, containing often pyroclastic material with grain size up to 0.5 mm. Typical pyroclastic minerals are quartz, sanidine, and biotite with minor amounts of zircon, apatite, and other minerals. Broken phenocrysts with sharp angles are found in volcanogenic material.

Elongate quartz crystals (Figs 1–3) with corroded surfaces are numerous in a 7 cm thick K-bentonite of the Vasagård section on Bornholm, in the *Dicellograptus* Shale (Bjerreskov & Stouge 1985). These crystals resemble icicles. Some have preserved (fully or partly) faces and angles of prismatic crystals, while others have been modified by stepwise corrosion of the surface, which has destroyed their original shape. Usually crystals are slightly curved (Fig. 3F, H). They are elongated (diameter 0.07–0.1 mm and length up to 1.0 mm), transparent, and contain only rare inclusions.

We have also found a few crystals of similar quartz in an ash bed at a depth of 1049.35–1049.50 m in the Aizpute-41 drill core in Latvia, in the upper part of the Adze Formation (Fig. 3D). The occurrences at Vasagård and in Aizpute-41 are the only ones among hundreds of Ordovician and Silurian bentonite samples we have investigated during the past ten years. Byström (1956) published photographs of similar quartz forms from Mossen (Sweden). Her sample No. 15, termed as the 'thick bed', was taken from the quarry where bentonite was mined. This thick bentonite was later named the Kinnekulle K-bentonite (Bergström et al. 1995). Byström (1956) also analysed the chemical composition of sanidine phenocrysts in this sample, containing 26 mol% Na-component and 74 mol% K-component. This composition is identical to that of the sanidine in the thick bentonite at the boundary of the Haljala and Keila stages of Estonia (Kiipli et al. 2007), but also of a thin (1 cm) eruption layer in the Aizpute core at a depth of 1052.5 m. Therefore we tentatively correlate the Kinnekulle K-bentonite with the ash bed in the Aizpute core at a depth of 1052.5 m. Other researchers who have studied the mineralogy of pyroclastic grains in bentonites Jürgenson1958; Utsal &

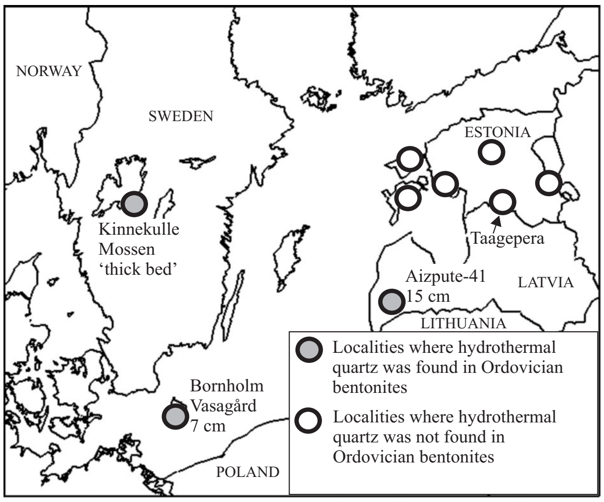


Fig. 1. Location of sections mentioned in text. At each locality thickness of the volcanic ash layers (cm) containing icicle-like quartz crystals is shown. 'Thick bed' is the term used by Byström (1956) for the volcanic ash layer where she found icicle-like quartz grains.

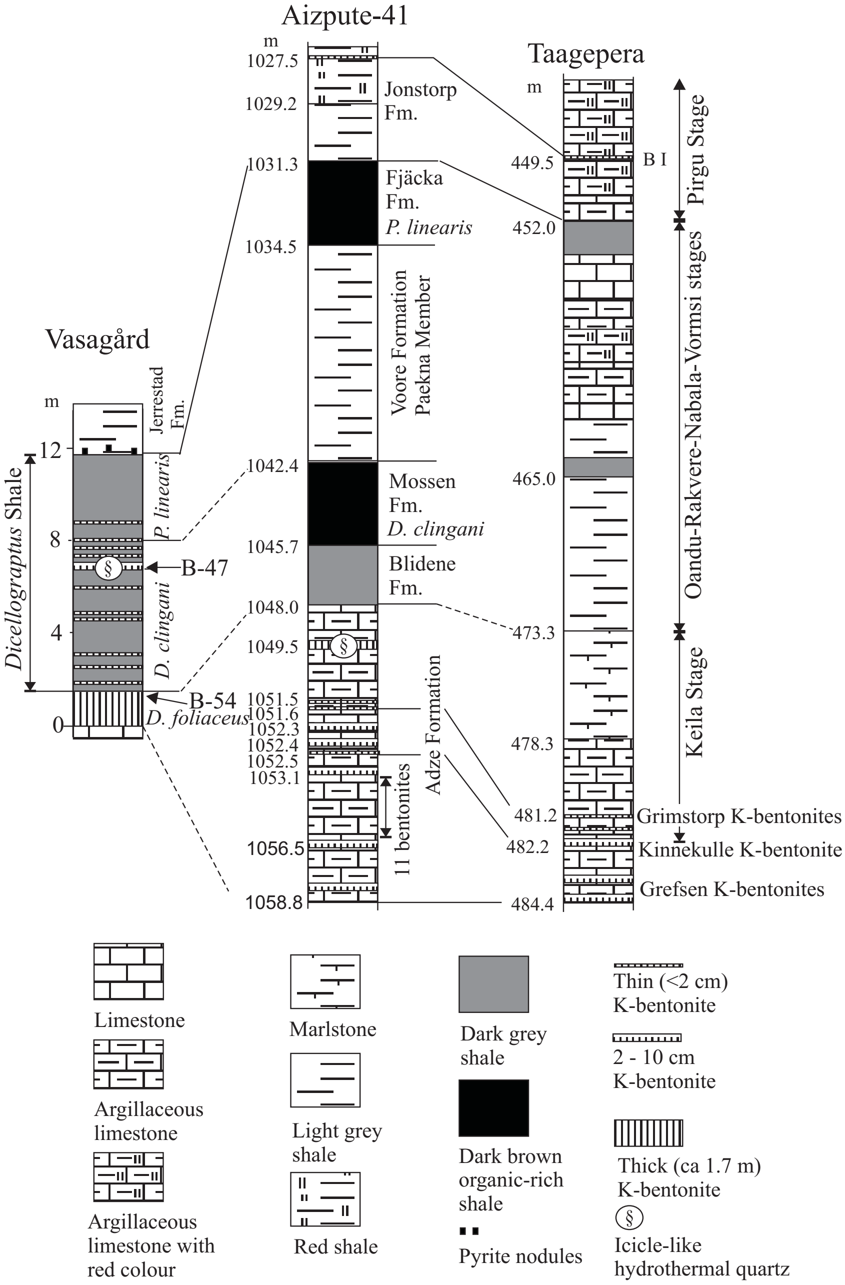
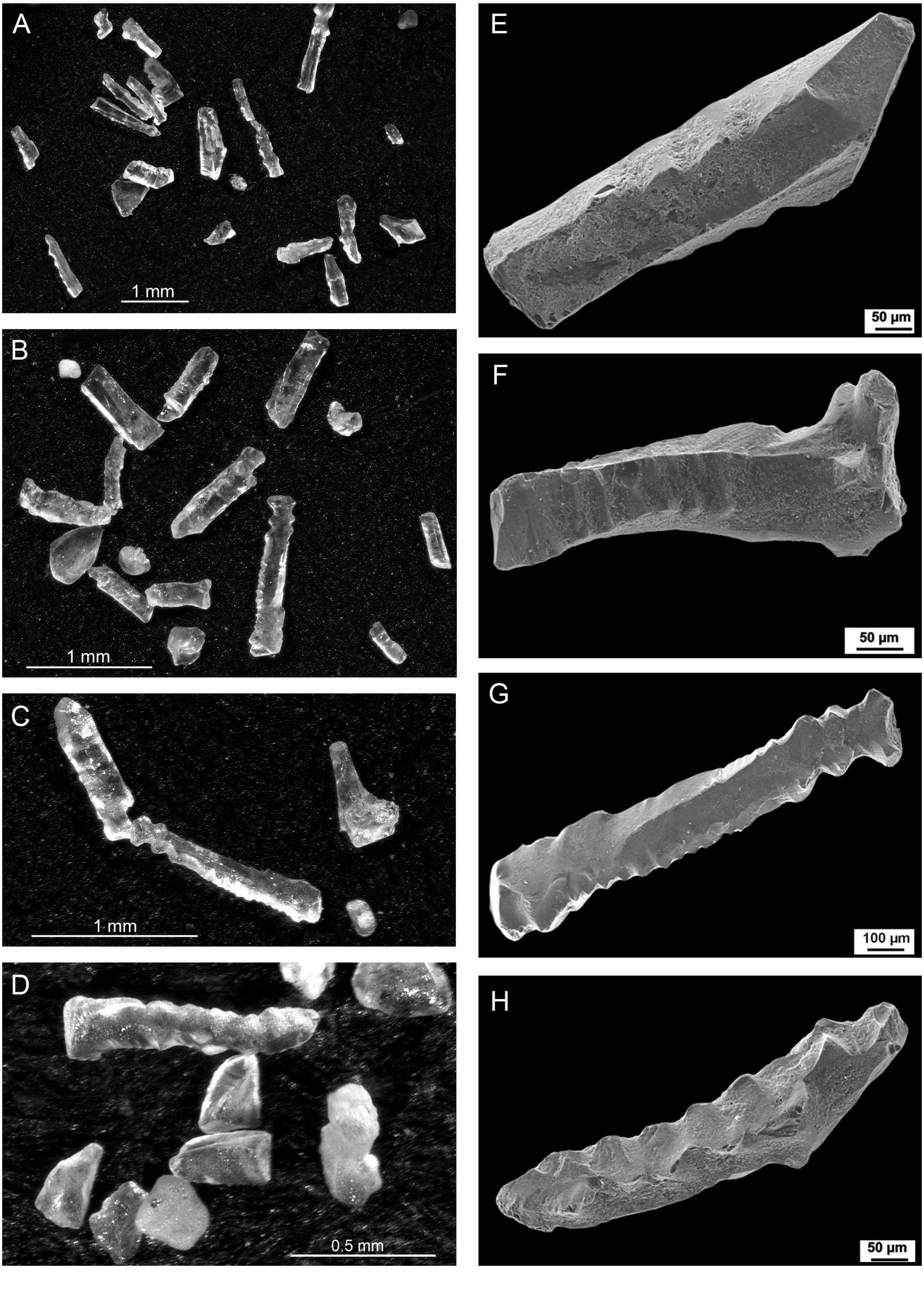


Fig. 2. Correlation of the Vasagård (Denmark), Aizpute-41 (Latvia), and Taagepera (Estonia) sections. The Vasagård section is drawn according to Bjerreskov & Stouge (1985) with refinements by M. Bruvo and A. T. Nielsen (unpublished data); the Aizpute and Taagepera sections are drawn according to unpublished descriptions by T. Kiipli. B-47 and B-54 are samples for geochemical analyses (Table 1).

Jürgenson 1971; Vingisaar & Murnikova 1973) have not reported icicle-like quartz from the Kinnekulle K-bentonite or any other Upper Ordovician eruption layer. This likely reflects that Byström separated pyroclastic material from a very large (25 kg) sample and therefore found extremely rare icicle-like quartz crystals in the Kinnekulle K-bentonite.

Quartz shards found in the Lower Ordovician phosphatic sandstones of the Rakvere area are interpreted as being redeposited from volcanic sources (Kurvits 1994). These sediments contain also elongated quartz crystals similar to our icicle-like forms (A. Kleesment pers. comm. 2008).


A
1 mm
B
1 mm
C
1 mm
D
0.5 mm
E
50 µm
F
50 µm
G
100 µm
H
50 µm

DISCUSSION

Bipyramidal β-quartz is commonly formed in high-temperature silicic magmas. However, prismatic quartz crystals are not found among magmatic phenocrysts but tend to occur in hydrothermal veins as druses. Furthermore, prismatic water-clear quartz cannot grow and be corroded in sediments during diagenesis. For example, broken quartz shards, derived from volcanic eruptions, are very common in bentonites, but corrosion of quartz shards has not been recorded. Quartz corrosion during hydrothermal activity has been described by Bignall et al. (2004) and Landtwing et al. (2005).

We propose the following hypotheses for the origin of these rare quartz forms:

1. formation of fissures in the volcanic cone under pressure from the magma chamber;
2. incursion of silica-rich hydrothermal fluids into the fissures in the volcanic cone and precipitation of quartz druses;
3. rise of temperature in fluids before eruption and start of the corrosion of quartz crystals;
4. volcanic eruption destroying the volcanic cone and distributing ash and partly dissolved quartz grains to wide areas.

Hydrothermal processes in volcanic systems are well known and can form significant gold, silver, lead, zinc, and copper deposits like the gold ores in Round Mountain Mine in Nevada (John 2008). A very large flux of gold capable of forming the largest known hydrothermal deposits was measured in the fluids of the Taupo Volcanic Zone in New Zealand (Simmons & Brown 2007). Therefore, indications of hydrothermal processes in volcanic ash beds can point to important mineral resources in the volcanic source areas. In this context it is interesting to mention that the geochemical reference sample (Es-15) prepared from the Kinnekulle K-bentonite contains 38–43 ppb gold (Kiipli 2005). This concentration exceeds the average crustal abundance by about 10 times. However, XRF analyses of K-bentonites from Bornholm (Table 1) do not show any unusual concentrations of other elements.

Considering the rare occurrences of elongated, partly dissolved quartz crystals in most volcanic ash beds and their abundance in the Vasagård section, this type of quartz combined with biostratigraphy could be used as a correlation criterion for this eruption layer. For example, a 6 cm thick bentonite is found in the *D. clingani* Zone at a depth of 53.58 m in the Lindegård drill core, Scania (Glimberg 1961). Possible identification of icicle-like quartz grains in this bentonite would corroborate such correlation.

Table 1. XRF analyses of the Ordovician K-bentonites of Bornholm

	B-54	B-47
Major components, %		
LOI_{920}	9.20	8.30
SiO_2	55.30	49.21
TiO_2	0.46	0.77
Al_2O_3	21.70	26.75
Fe_2O_3	3.77	5.25
MnO	0.00	0.06
MgO	2.19	2.67
CaO	0.56	1.47
Na_2O	0.05	0.03
K_2O	5.06	6.52
P_2O_5	0.11	0.07
Cl	0.03	0.03
S	0.14	0.66
Trace elements, ppm		
As	20	25
Ba	284	331
Br	6	<5
Ce	80	39
Cr	<20	21
Cu	<20	28
Ga	26	22
La	34	<20
Mo	<5	<5
Nb	14	12
Ni	6	22
Pb	7	24
Rb	134	158
Sc	14	13
Sr	25	11
Th	16	17
U	<10	<10
V	27	78
Y	42	12
Zn	18	52
Zr	435	295

Fig. 3. Photographs of corroded hydrothermal quartz crystals from bentonites. **A–C**, crystals from the K-bentonite in the Vasagård section, optical microscope. **D**, a crystal from the Aizpute-41 section, depth 1049.35–1049.50 m, optical microscope. **E–H**, electron microscope photos of crystals from the Vasagård section. E, crystal with partly preserved faces; F, quartz crystal with the thicker end indicating fixing of the crystal to the substrate (wall of the fissure) before the volcanic eruption; G, elongated prismatic crystal with strongly corroded surfaces; H, strongly corroded and curved crystal.

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Osaliselt lahustunud hüdrotermaalne kvarts Ordoviitsiumi vulkaanilise tuha kihtides Baltoskandia regioonis

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Ülem-Ordoviitsiumi vulkaanilise tuha kihist Vasagårdi läbilõikest Bornholmi saarelt Taanist leiti hulgaliselt prismalisi osaliselt lahustunud kvartsikristalle. Ka vulkaanilisest kihist Aizpute puuraugust Adze kihistu ülaosast leiti selliseid kristalle. Kuigi biostratigraafilisi andmeid pole piisavalt, et neid leide korreleerida, annab sellise haruldase kvartsivormi massiline esinemine Vasagårdi läbilõike vulkaanilises kihis lootust kasutada seda korrelatsiooni kriteeriumina tulevastes uuringutes. Prismaline osaliselt lahustunud kvarts moodustus tõenäoliselt hüdrotermaalsetes protsessides vulkaani koonuses.