

Origin and paleoenvironmental interpretation of aluminum phosphate–sulfate minerals in a Neoproterozoic Baltic paleosol



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ABSTRACT

Aluminum phosphate–sulfate (APS) mineral solid-solutions occur as accessory phases in different sedimentary and hydrothermal deposits. Their composition is a sensitive environmental indicator recording changes in pH, temperature and chemical composition of the weathering, diagenetic or hydrothermal fluids. In this contribution we studied APS mineralization in a Neoproterozoic paleotropical paleosol developed on Paleo–Mesoproterozoic crystalline basement in the Baltic Basin. Small and disseminated APS minerals occur in high abundance (up to 4 wt.% of crystalline phases) in the weathering profile developed on gabbroic rocks rich in magmatic apatite. APS minerals belonging to a goyazite–florencite–svanbergite–woodhouseite solid-solution series occur in the uppermost part of the weathering profile and are replaced down-profile with secondary apatite. The change from APS minerals to secondary apatite precipitates reflects a paleo-pH gradient in the weathering profile from acidic (pH < 6) in the uppermost few meters in the APS precipitation zone, to neutral or near neutral at 4–5 m-depth from the paleoweathered surface where secondary apatite occurs. Typically uniform <5 μm-size APS crystallites suggest rapid precipitation in a highly supersaturated solution, but these crystals show a fine zonal structure whose nature and formation mechanism remain unclear.

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1. Introduction

Aluminum phosphate–sulfate (APS) minerals are minor phases that occur in a range of different geological environments including metamorphic, igneous, hydrothermal, sedimentary–diagenetic and weathering systems (Stoffregen and Alpers, 1987; Dill, 2001, 2003; Gall and Donaldson, 2006; Galan-Abellan et al., 2013). APS minerals are members of the alunite supergroup (Bayliss et al., 2010) and have a wide range of compositional variations. They form complex solid-solutions with more than 20 end-members (Stoffregen, 1993). Composition of the APS minerals is sensitive to changes in the physicochemical conditions during their formation, and can be used as a proxy for pH, temperature and chemical composition of geofluids (Stoffregen et al., 1994a,b; Mordberg et al., 2000; Dill, 2001, 2003; Gall and Donaldson, 2006; Galan-Abellan et al., 2013). APS minerals typically occur in sedimentary sequences as fine, disseminated crystallites (<10 μm) or mineral aggregates with low concentration (ca. 0.05 wt.%), therefore being commonly undetected by conventional mineral analysis techniques such as X-ray diffraction and optical microscopy (Rasmussen, 1996; Gaboreau et al., 2005). Early to late diagenetic or hydrothermal APS mineralization is most commonly associated with sandstone lithologies

(e.g., Rasmussen, 1996; Gall and Donaldson, 2006; Galan-Abellan et al., 2013; Marfil et al., 2013). However, APS minerals are also abundant in weathering environments, specifically in lateritic–kaolinitic soil profiles formed under acid and oxidizing conditions (Dill et al., 1995; Mordberg et al., 2000) and or in weathering of Cretaceous ooidal ironstones (Salama, 2014). Chemical composition of the APS minerals in soil profiles is variable, but is typically represented by the solid solution of the end-members svanbergite, crandallite, goyazite, woodhouseite and florencite (Dill, 2001).

In this contribution we studied an exceptionally rich APS mineralization (up to 4 wt.% of mineral phases) in a Neoproterozoic (Ediacaran) weathering crust (Baltic paleosol sensu Liivamägi et al., 2014) developed on Paleo–Mesoproterozoic crystalline basement in northern Estonia, former Baltica continent. It is a well preserved and unmetamorphosed weathering profile characterized by a mineral alteration sequence topped by up to 7–8 m thick strongly weathered zone composed of kaolinite, Fe-oxyhydroxide and residual quartz. Kaolinite content in the uppermost part of weathering profile can exceed 60% of mineral phases and indicates a strong and deep weathering, possibly under a warm and humid climate (Liivamägi et al., 2014, 2015). APS mineralization in the Baltic weathering crust was found in a profile developed on a postorogenic unmetamorphosed intrusion composed of medium-grained monzogabbro rich in magmatic apatite and titanomagnetite. The aim of this study is to establish the context of APS mineralization in lateritic paleosols and to use APS minerals as an indicator of weathering during paleosol formation.

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2. Geological setting

A Neoproterozoic, ca. 560–600 Ma old Baltic paleosol buried under Paleozoic sedimentary cover is found on the peneplanated Paleoproterozoic crystalline basement at the northern and north-western part of the Russian platform in the Baltic Basin (Estonia, Latvia and Lithuania), and in north-western Russia (Kuuspalu et al., 1971; Puura et al., 1983; Brangulis, 1985; Vanamb and Kirs, 1990; Koistinen et al., 1996; Meshcherskii et al., 2003). The weathered crystalline basement is overlain by a transgressive series of marine alternating sandstone–claystone Ediacaran sequence in eastern and central parts, and Cambrian claystone–siltstone–sandstones in western parts of the area (Mens and Pirrus, 1997a,b).

The Paleoproterozoic crystalline basement in northern Estonia is composed of 1.8–1.9 Ga volcano–sedimentary sequence and is regionally metamorphosed in amphibolite–granulite facies conditions and intersected by 1.63–1.58 Ga anorogenic plutons. The rock types in the western part of the area are migmatized amphibolites, biotite and quartz–feldspar gneisses, and in the east are predominantly high-alumina pelitic gneisses (Haapala et al., 2005; Kirs et al., 2009). A small (ca. 2 km wide and 5 km long) unmetamorphosed Sigula monzogabbroic intrusion (Fig. 1) represents, together with small stocks of porphyritic alkali–granites in northern Estonia and a large Riga composite rapakivi batholith in southwestern Estonia and Latvia, a bimodal anorogenic rapakivi magmatism in conditions of extensional tectonics (Rämö et al., 1996).

3. Materials and methods

Rocks of the Sigula massif are recovered in the lower part of the F124 (Sigula) drillcore section. Samples for petrological, mineralogical and geochemical studies were collected from a 322 m deep F124 (Sigula) drillcore (Fig. 1). The studied rock section in the F124 drillcore is nearly 100 m long and consists of greenish-gray ophitic monzogabbro–norites topped with strongly weathered reddish-to-greenish gray rocks at depth 223–230 m below the ground surface. The lowermost part of the core (depth interval 223–322 m) under the Ediacaran–Paleozoic sedimentary cover intersects the crystalline basement upon which a weathering profile was developed. For analysis, samples from fresh to highly weathered rock were selected (Fig. 2). Whole rock chemical and mineral composition of this weathering profile was earlier reported in Liivamägi et al. (2015) and is adapted from there. For detailed analysis of APS mineralization, 23 samples from the uppermost part of the weathering profile in the depth interval 223–230 m were inspected.

The mineralogical composition of whole rock samples was studied by X-ray diffractometry (XRD). Samples were pulverized in a planetary mill and unoriented preparations were made. Preparations were scanned using Bruker D8 Advance diffractometer with CuK α radiation and LynxEye positive sensitive detector in 2°–70° 2 θ range. The quantitative mineralogical composition of the samples was interpreted and modeled by using the Rietveld algorithm-based program Siroquant-3 (Taylor, 1991). The chemical composition of whole-rock samples were analyzed using X-ray fluorescence (XRF). The samples were homogenized, diluted with Li tetraborate and melted at 1200 °C into beads and directly measured.

Phosphorus rich rock slabs of selected samples for micromorphological analysis were cut and polished using wet grinding and argon plasma ion-milling as a final step for scanning electron microscopy and microprobe analysis. Polished samples were coated with carbon prior to analysis using a Zeiss EVO 15MA instrument equipped with Oxford AZTEC X-MAX energy dispersive detector (EDS) system, and a Wave700 wavelength dispersive spectrometer (WDS). Standardization was performed using natural reference minerals: apatite for P and Ca, celestite for S and Sr, albite for Al and Na, orthoclase for K, quartz for Si, olivine for Fe, sylvite for Cl, barite for Ba and monazite for La, Ce, Pr and Nd. Operating conditions during WDS analysis were 15 kV acceleration voltage, 20 nA emission current and spot size 1 μ m. Owing to very small

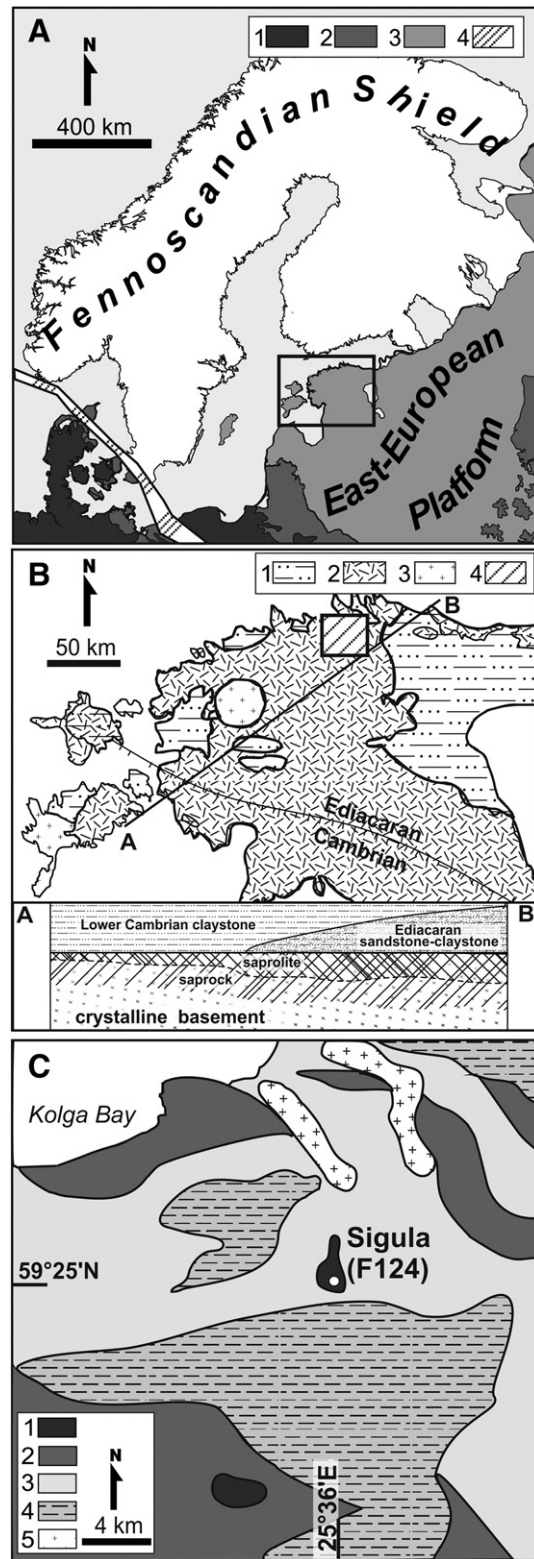


Fig. 1. (A) Location of the study area, 1 – Cenozoic; 2 – Mesozoic; 3 – Paleozoic; 4 – Tornquist line. (B) Simplified geological setting of the crystalline basement of Estonia and schematic cross-section (not in scale) of the buried Baltic paleosol and the overlying sediments, 1 – Metasediments; 2 – Metavolcanics; 3 – Rapakivi granites; 4 – Sigula intrusion shown in C. (C) Geological setting of the crystalline basement and location of the Sigula drillcore (F124) on the Sigula gabbroic intrusion, 1 – Gabbroic rocks, 2 – Amphibolites and amphibole–gneisses, 3 – Quartz–K–feldspar gneisses, 4 – Mica (Biotite) gneisses, 5 – Migmatite granites.

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