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Travertine precipitation in the Paleoproterozoic Kuetsjärvi Sedimentary Formation, Pechenga Greenstone Belt, NE Fennoscandian Shield



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ABSTRACT

Precambrian travertines, tufas and speleothems either formed rarely or they have not been identified in previous studies. In the absence of high pCO₂ soils in Paleoproterozoic, karst solution and speleothem formation occurred by processes distinct from those commonly found in present-day low temperature karst environments. However, the high pCO₂ atmosphere could itself have encouraged karst formation. The Paleoproterozoic Kuetsjärvi Sedimentary Formation of the Pechenga Greenstone Belt, NW Russia, includes abundant terrestrial carbonate precipitates. These precipitates were sampled from a drillcore representing a complete section of the ca. 120-m-thick formation and were investigated for C and O isotopes, acid-soluble elemental contents and petrography. The newly obtained results were used to constrain the origins of the precipitates and to illuminate different terrestrial carbonate types. The investigated drillcore includes abundant small-scale cavities and veins, which are commonly filled with dolomite and quartz. Dolomite crusts are found both in the cavities and on bedding/erosional surfaces. Dolomite cements coat uneven surfaces and surficial rock fragments. The surficial dolomite crusts form distinct and discrete layers, whereas the cements do not. The cavity and vein fills are likely post-depositional in origin, whereas the surficial dolomite crusts and dolomite cements are likely syn-depositional precipitates. The investigated precipitates often show $\delta^{13}C$ values lower than those reported from their host rocks, suggesting the influence of an external carbon source. Petrographic features and geochemical data suggest dissolution and precipitation of carbonate material originating from deep-sourced CO₂-bearing fluids, likely at high earth surface temperatures.

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1. Introduction

Reports of Precambrian travertines, tufas and speleothems are rare because they either rarely formed or have not been identified (see Brasier, 2011; Brasier et al., 2013). Identifying these deposits in drillcore can be problematic as examples may be mistaken for signs of post-depositional alteration. Distinction between travertines, tufas and speleothems is also challenging and perhaps unnecessary (e.g. Brasier, 2011; Rogerson et al., 2014).

Travertine and tufa have been classified in many ways. The word "tufa" was originally used for both volcanic ash and soft, poorly consolidated freshwater carbonate, but later "calcareous tufa" was

used for freshwater carbonates (e.g. Pentecost, 1993; Pentecost and Viles, 1994). Today, many sedimentologists use "calcareous tufa" or "tufa" for the softer varieties (unsuitable for building), whereas the word "travertine" is used for harder freshwater carbonates (e.g. Pentecost and Viles, 1994). However, travertine and tufa have also been classified according to their fabrics, morphology, geochemistry and water temperature at time of deposition (e.g. Ford and Pedley, 1996; Pentecost and Viles, 1994).

In some cases the word "travertine" is used for both thermal (above ambient) and ambient water temperature chemical carbonate precipitates, and can be divided into (i) thermal or thermogene travertines and (ii) meteogene travertines (e.g. Pentecost and Viles, 1994). Thermal travertines are normally precipitated from hot waters and their carrier CO₂ primarily originates from interaction of hot rock and CO₂-rich fluid (Pentecost and Viles, 1994). The carried CO₂ for the precipitation of meteogene travertines is derived from soils and epigean atmosphere (Pentecost and Viles, 1994).

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Alternatively, the word "travertine" can be used for thermal/hydrothermal precipitates and the word "tufa" for cool/nearambient water precipitates (e.g. Ford and Pedley, 1996; Pedley, 1990; Riding, 1991). In modern environments macrophytes can be used to distinguish between travertine and tufa: travertines lack macrophyte remains, but tufas are commonly characterized by macrophytes (e.g. Ford and Pedley, 1996). As there were no plants during Precambrian, distinguishing between travertine and tufa is difficult or even impossible (Brasier, 2011).

Modern speleothems are usually formed under high pCO₂ soils. These both provide carbonic acid for carbonate bedrock dissolution and provide a contrast with the low pCO2 of the cave atmosphere that enables degassing of drip-waters causing carbonate mineral precipitation (e.g. Fairchild et al., 2000; Frisia and Borsato, 2010). Paleoproterozoic karst and speleothem probably formed in some other way, as there is no convincing evidence that high pCO₂ soils existed at that time (see Brasier, 2011). A high pCO₂ atmosphere could have caused carbonic acid formation and hence karst formation. Carbon dioxide degassing leading to precipitation of carbonates in high pCO₂ atmospheres is possible in certain circumstances (see Brasier, 2011). One of the most appealing explanations for Paleoproterozoic karst and speleothem formation is the common-ion effect, involving dissolution of Ca sulfate (e.g. Calaforra et al., 2008; Wigley, 1973a) or incongruent dissolution of dolomite (e.g. Wigley, 1973b). Explanations may alternatively involve deep-sourced CO2 (e.g. Duliński et al., 1995; Pentecost and Viles, 1994), possibly connected to hydrothermal activity.

In this paper, we use the term "travertine" in a collective way for the ancient deposits we describe. The term "speleothem" is here used for cavity fills and the word "cement" for dolomite binding or coating surface rock fragments and erosional surfaces.

Carbonate rocks extremely enriched in ¹³C were deposited world-wide during the Paleoproterozoic (ca. 2200-2060 Ma), marking a global positive $\delta^{13}C$ excursion recorded in sedimentary carbonates (e.g. Baker and Fallick, 1989a,b; Karhu and Holland, 1996). The Kuetsjärvi Sedimentary Formation (KSF) of the Pechenga Greenstone Belt (NW Russia) records this excursion (e.g. Karhu, 1993; Karhu and Melezhik, 1992; Melezhik et al., 2005; Salminen et al., 2013a). The KSF exposures and cores are excellently preserved, and provide an opportunity for studying Paleoproterozoic carbonate rock environments and precipitation processes. In addition to stratified dolostone and limestone, hot-spring associated travertine has previously been interpreted from the KSF (Melezhik and Fallick, 2001). Carbonates associated with dissolution surfaces and small-scale cavities (epikarst) have also been found in the KSF (Melezhik et al., 2004), along with calcrete (caliche) and dolocrete (e.g. Melezhik et al., 2004; Melezhik and Fallick, 2003). These calcrete and dolocrete instances were interpreted to have formed by capillary rise and evaporation (Melezhik et al., 2004; Melezhik and Fallick, 2003). Moreover, Melezhik and Fallick (2005) reported probable CaSO₄ pseudomorphs in the KSF sabkha- or playa-carbonates.

In this study, discrete morphologies of carbonate precipitates were investigated from a drillcore of the KSF. These included dolomite crusts, dolomite cements, and carbonate fills in small-scale cavities and veins. A detailed petrographic picture of the precipitates was constructed. Several samples were analyzed for the isotope composition of C and O and acid-soluble abundances of selected elements. Results were compared to those of the more common stratified dolostone and limestone rocks from the same drillcore (Salminen et al., 2013a).

The goals of this research were to (1) identify and characterize different kinds of Precambrian terrestrial carbonates, (2) decipher the origins of the investigated carbonate precipitates, and (3) provide additional information on the depositional setting of the KSF.

2. Geological background

2.1. Geological setting

This investigation is based on the samples from Core 5A, which was drilled by ICDP (International Scientific Continental Drilling Program) FAR-DEEP (Fennoscandia Arctic Russia-Drilling Early Earth Project) from the KSF of the Pechenga Greenstone Belt, NW Russia (Fig. 1). The geological setting of the core has previously been described by Salminen et al. (2013a,b) and is briefly summarized below.

The Pechenga Greenstone Belt is a section of a larger (ca. 1000 km long) belt in the north-eastern part of the Fennoscandian Shield (e.g. Melezhik and Sturt, 1994). This larger belt has been interpreted as an intracontinental rift developed into an intercontinental rift with a subsequent aborted oceanic phase and arc-continent collision (e.g. Melezhik and Sturt, 1994). More extensive opening followed by oceanic floor subduction and arc-continent collision has also been suggested (Berthelsen and Marker, 1986). The Pechenga Greenstone Belt has been divided into the North and South Pechenga groups (e.g. Melezhik and Sturt, 1994). The KSF belongs to the North Pechenga Group, which is composed of four paired sedimentary-volcanic cycles (e.g. Melezhik and Sturt, 1994).

The Pechenga Greenstone Belt rocks underwent metamorphic alteration ranging from prehnite-pumpellyite to amphibolite facies (Petrov and Voloshina, 1995). Core 5A was drilled from biotite-actinolite phase of the greenschist facies. The KSF has also been exposed to epigenetic alteration (Melezhik, 1992).

The thickness of the KSF varies from 20 to 120 m. Its thickness in Core 5A is ca. 117 m. The KSF was deposited on a paleo-weathering crust developed on basaltic andesite of the Ahmalahti Formation and its depositional top is defined by the first basalts of the Kuetsjärvi Volcanic Formation (Predovsky et al., 1974).

The minimum depositional age (U–Pb) of the KSF is 2058 ± 2 Ma (Melezhik et al., 2007), inferred from detrital zircons in volcaniclastic conglomerate within the Kuetsjärvi Volcanic Formation and the overlying Kolosjoki Sedimentary Formation. Martin et al. (2013) obtained a depositional age (U–Pb) of 2056.6 ± 0.8 Ma for the Kolosjoki Sedimentary Formation. A robust maximum depositional age (U–Pb) is 2505.1 ± 1.6 Ma, obtained from the Mount Generalskaya gabbronorite intrusion (Amelin et al., 1995). This intrusion is unconformably overlain by basal conglomerate of the Neverskrukk Formation, which is the lowermost formation of the North Pechenga Group.

Travertines of probable hot-spring origin were reported from the KSF by Melezhik and Fallick (2001) and Melezhik et al. (2004). Melezhik and Fallick (2001) reported two types of travertines from the KSF: (1) laminated crusts formed on a pure carbonate substrate and capped by stratified, stromatolitic dolostone, and (2) small-scale mounds formed on a carbonate substrate and buried under red siltstone and sandstone. In addition to travertines, several other kind of subaerial exposure surfaces have been reported from the KSF (Melezhik et al., 2004; Melezhik and Fallick, 2001, 2003). These include dissolution surfaces and epikarst, erosional surfaces, calcrete/caliche, dolocrete, silica sinters. Dissolution surfaces and epikarst included voids and small-scale cavities.

2.2. Core 5A: lithostratigraphy and depositional setting

A detailed lithostratigraphic description of Core 5A and an interpretation of its depositional setting can be found in Salminen et al. (2013a,b) with a brief summary provided below. The lithostratigraphy of the core is presented in Fig. 2.

Salminen et al. (2013b) divided the KSF in Core 5A into four informal members. From oldest to youngest these are the Arkosic, Lower

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