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 pCO\textsubscript{2} 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 pCO\textsubscript{2} 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 CO$_2$-bearing
fluids, likely at high earth surface temperatures.

Keywords: Travertine, speleothem, carbonate, dissolution, degassing, Paleoproterozoic

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 CO$_2$ primarily originates from interaction of hot rock and CO$_2$-rich fluid (Pentecost and Viles, 1994). The carried CO$_2$ for the precipitation of meteogene travertines is derived from soils and epigean atmosphere (Pentecost and Viles, 1994).

Alternatively, the word “travertine” can be used for thermal/hydrothermal precipitates and the word “tufa” for cool/near-ambient 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 pCO$_2$ soils. These both provide carbonic acid for carbonate bedrock dissolution and provide a contrast with the low pCO$_2$ 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 pCO$_2$ soils existed at that time (see Brasier, 2011). A high pCO$_2$ atmosphere could have caused carbonic acid formation and hence karst formation. Carbon dioxide degassing leading to precipitation of carbonates in high pCO$_2$ atmospheres is possible in certain circumstances (see Brasier,
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 dolomites 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 δ¹³C excursion recorded in sedimentary carbonates (e.g., Baker and Fallick, 1989a, 1989b; 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 travertines have 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, 2013b) and is briefly summarized below.

(Approximate location of Figure 1.)

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 the basaltic andesites 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), 
inferrerd 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, 2013b) 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 Dolostone, Quartzite and Upper Dolostone members. A Fe-picrite dyke (ca. 5 m thick) separates the Arkosic and Lower Dolostone members. Sedimentary carbonates of Drillcore 5A include micritic, sparry and stromatolitic dolostone, dolarenite, micritic limestone and calcarenite. Siliciclastic rocks include arkosic to quartzitic sandstone, graywacke, siltstone, shale and calcareous siliciclastic rocks (marl).
Both Lower and Upper Dolostone members show marks of erosional and dissolution processes. Dolomite crusts, surficial cements and carbonate-filled veins and small dissolution cavities are common (totaling at ca. 18 vol.%) in both of these members (see section 4; Fig. 2; Salminen et al., 2013a). Similar-looking dolomitic crusts and carbonate fills have previously interpreted as hot-spring associated travertines (Melezhik et al., 2004; Melezhik and Fallick, 2001).

The depositional setting of the Arkosic and Quartzite members has been assigned to delta-plain, pro-delta, deltaic environments influenced by tides (Salminen et al., 2013b). The basal part of the Quartzite member has been interpreted as a deposit from a flooding event (Salminen et al., 2013b). The Lower Dolostone member was interpreted to have deposited in a shallow-lacustrine setting and the Upper Dolostone member in a tidally influenced (hence sporadically marine) shallow-lacustrine environment (Salminen et al., 2013b).

3. Materials and methods

Samples for this study were obtained from different depth-intervals of Core 5A. All analyses were performed at the Department of Geosciences and Geography, University of Helsinki using techniques described in Salminen et al. (2013a).

Subsamples were micro-drilled with 1.0 or 1.8 mm diamond grinding bits from carbonate crusts, cements and fills. The number of subsamples from each carbonate type reflects its abundance in the core. All carbonate subsamples were analyzed for the isotope composition...
of C and O. The larger subsamples (those of ca. 10 – 20 mg; drilled with the 1.8 mm bit), were also analyzed for acetic acid-soluble elements by ICP-MS (described below).

In addition, several subsamples were also obtained from the enclosing carbonate rocks, immediately over- and underlying the cavity at ca. 62.1 m. These subsamples were only analyzed for C and O isotopes, to compare/contrast with values obtained from the cavity fills.

Carbonate mineralogy (calcite or dolomite) of the larger subsamples was determined by using Mg/Ca ratios, whereas in the 1–2 mg subsamples it was determined by XRD or through a qualitative acid test (reaction with ca. 3 M HCl).

The acid-soluble Mg, Ca, Mn, Sr, Fe and Ba contents were determined using an Agilent 7500ce/cx ICP-MS. Powdered samples (9 –13 mg) were leached in 5 ml of ca. 0.5 M acetic-acid under room temperature for 16 h. The final results were calculated in relation to the acid-soluble fraction. Including the dissolution step, the average precision (1σ) was 14.6 % for the samples from the depth 79.55 – 81.50 m (excluding the sample from 81.45 m) and 7.5 % for all other samples.

The C and O isotope composition of the samples was determined using a Thermo Finnigan Delta Plus Advantage isotope ratio mass spectrometer in continuous-flow mode. The isotope compositions of ca. 125 – 170 μg powdered samples were measured on phosphoric acid liberated CO₂ gas (in 90°C for ≥1h). The C and O isotope compositions are expressed in conventional δ-notations as a per-mil difference from the international VPDB standard. An in-house dolomite quality standard indicated a long-term reproducibility (1σ) of 0.10‰ for C and 0.22‰ for O (n=59). An in-house calcite standard indicated a long-term reproducibility (1σ) of 0.08‰ for C and 0.17‰ for O (n=7).
Petrography and mineralogy of the carbonate precipitates were investigated in several thin sections under optical microscope and by visual examination of drillcore samples. In addition, selected thin sections were investigated semi-quantitatively (EDS, standardless) with an electron microanalyzer (Jeol JXA-8600 superprobe, accelerating voltage 15 kV, beam current 1 nA, focused beam).

4. Petrography of the precipitates: description and interpretation

Core 5A contains five distinct features. These are (1) cavities, (2) veins, (3) dolomite crusts filling cavities, (4) dolomite crusts precipitated on bedding/erosional surfaces, and (5) dolomite cements encrusting surface rock fragments and uneven surfaces. New petrographic observations and interpretations of these allow us to add substantially to the previously made brief descriptions of the Core 5A rocks (Salminen et al., 2013a, b; Brasier et al., 2013). The general description of the five types of precipitates is provided in Table 1 and the investigated samples are described in Inline Supplementary Table 1.

(Approximate location of Table 1.)

Insert Inline Supplementary Table 1 here.

4.1 Small-scale dissolution cavities (type 1)

Description. Dissolution cavities are found in all types of carbonate. The dolostone immediately surrounding the cavity often appears recrystallized or powdery. The heights of
the cavities vary from a few centimeters to ca. ten centimeters. Cavities are walled with rim(s) of fibrous (radiating), bladed and/or sparitic dolomite; some cavities also contain calcite fills. Carbonate fills show both upwards and downwards growth. Small white stalactites and stalagmites are found in places, e.g. at ca. 60.6 m. These stalactites/stalagmites have concentric bedding-parallel shapes and they are composed of sparitic dolomite, walled with a rim of bladed dolomite. The latest infill is usually quartz and/or dolospar (Figs. 3-4), but in places it is quartz sandstone. Pyrite (Fig 3b) and dolomite ooids have also been identified in some cavities.

Some cavities are found in possible surficial dolomite crusts. These include e.g. the cavity at ca. 60.2 m. This cavity is walled with small white stalactites and stalagmites (Fig. 5a), similar to those in the cavity at ca. 60.6 m. The remaining space of the cavity is filled with quartz and patches of fibrous/sparitic dolomite. The cavity is underlain by red, beige and white, banded dolomite crust and overlain by white dolomite crust and a possible silica sinter.

**Interpretation.** Most of the dolomite rims in the cavities are best interpreted as flowstones. However, the small-scale stalactites and stalagmites probably indicate precipitation from dripping water. Dolomite rims are relatively symmetrically walling the cavities. These symmetrically rimmed cavities are interpreted to have been formed in dominantly phreatic conditions.

(Approximate location of Figures 3-5.)

4.1.1 Special small-scale dissolution cavity cases

Cavities at ca. 69.6 m and 72.7 m appear somewhat different to other examples and are therefore described here separately.
The dissolution cavity at 69.6 m has a complex structure, exhibiting three types of carbonate fill (Fig. 3b). The outermost zone includes thin laminae of white dolomite and quartz. The second zone includes yellowish, sparitic calcite, which is followed by thin laminae of white dolomite and quartz. These laminae also form microstalactite-like structures. These laminae are sealed with a thin rim of fibrous dolomite. The remaining space, in the center of the cavity, is filled with quartz, dolospar and pyrite. These three fabrics represent the latest infills of the cavity. The precipitates of this cavity, like the rim of fibrous dolomite, are best interpreted to have precipitated in phreatic to vadose conditions.

The cavity at 72.7 m is filled with siliceous sparitic dolomite with quartz-filled fenestrae-like structures (Fig. 4b). The morphologies of some of these fenestrae resemble sulfate pseudomorphs. The cavity ceiling is composed of white, thinly-laminated, sparitic dolomite, which also forms stalactite-like structures. Similar laminae are not found at the base of the cavity. The non-symmetrical structure of the cavity likely indicates carbonate mineral precipitation in the vadose zone.

4.2 Veins (type 2)

Description. Some structures likely represent veins, rather than filled cavities. These structures include thin (ca. 0.2–2 cm), bedding-parallel vugs (Figs. 6a-b). Some of these have relatively straight borders, whereas others have more curved margins. Veins are walled with rims of sparitic and bladed dolomite. The bladed dolomite shows inward growth. Quartz and/or dolospar represent the latest infills; some veins are almost entirely filled with dolospar.
**Interpretation.** These veins have symmetrical shapes, indicating mineral precipitation within a fluid-filled space (e.g. fracture). In some veins, the flooring is thicker than the ceiling. This could indicate precipitation within a gas- and fluid-filled space.

(Approximate location of Figure 6.)

4.2.1 Special vein case

A vein at ca. 53.7 m shows color and mineralogical zoning (**Fig. 6c**). This vein is larger (with a height of ca. 8-9 centimeters) than other veins in the core. Its outer rim is composed of white dolomite, whereas the outer rim is capped by a grayish calcitic and dolomitic layer. The center of the vein is filled with orange calcite. The color zoning is more pronounced here than in the cavities. Pyrite is also found in this vein. This vein may have formed during burial diagenesis.

4.3 Large cavities with dolomite crust (type 3)

**Description.** The cavities with dolomite crusts are up to ca. 20 cm thick. The flooring in these cavities is thicker than the ceiling. The remaining space between the flooring and the ceiling is filled with dolospar, but cavities often appear as collapsed or deformed. The flooring (red, pink, beige, white, and/or gray) usually consists of banded, laminated or massive dolomitic crust, which is capped with thinly-laminated gray-and-white crust. In places the ceiling is composed of a dolomitic crust (white, gray or yellow) underlain by small thinly-laminated gray-and-white stalactites (**Fig. 5b**), but elsewhere the crust is lacking and there are only stalactites. The thinly-laminated crusts and stalactites are often deformed (**Figs.**
They usually consist of alternating white and/or gray laminae of fibrous, radiating
dolomite (forming cones) and sparitic dolomite.

**Interpretation.** The cavities with dolomite crusts have probably been deposited in vadose
conditions. These cavities have non-symmetrical structure; the cavity flooring is thicker than
the ceiling coating. The basal part of the flooring is often characterized by red coloration,
which possibly implies deposition from an oxidizing fluid.

### 4.3.1 Special large cavity with dolomite crust case

In the cavity at ca. 31.4 m (Fig. 5c), the entire flooring is thinly laminated and also includes
dolospar and quartz filled fenestrae. The stalactites in the cavity consist of laminae of small
(micritic) grain size; the laminae are coloured white, gray, black or reddish (Fig. 5c). This
cavity also shows non-symmetrical structures so its fill probably precipitated in the vadose
zone.

### 4.4 Surficial dolomite crusts (type 4)

**General description and interpretation.** Surficial dolomite crusts were formed on bedding
and erosional surfaces. The crusts are composed of bedding parallel layers with uneven upper
surfaces and contain curved or mound-shaped laminae. Hence, the petrography and
morphology of these carbonate precipitates differs from normal stratified dolostone and
limestone of the KSF. We tentatively interpret such crusts as authigenic precipitates in
surface settings. The red coloration at the base of some crusts may imply deposition from an
oxidizing fluid. Below, different types of the surficial crusts are described in more detail.

**Crust at 30.3 m.** One inferred surficial dolomite crust in the Upper Dolostone member (at ca.
30.3 m, Inline Supplementary Figure 1) shows a reddish lamination at its base, followed by
beige laminated, banded or massive dolomite. This crust includes small vugs/veins, which are
filled with white, grey and black sparry carbonate. The upper part of the crust has a chalky
micritic appearance. The crust is capped with a rim of fibrous dolomite and quartz.

(Insert Inline Supplementary Figure 1 here)

**White dolomite crusts.** There are several inferred surficial dolomitic crusts composed
mainly of white micritic to sparitic dolomite. The crust at ca. 68.3 m shows thin lamination
(Fig. 7). These laminae form mound-like or oncoidal structures. These crusts are capped by a
thin (<1 cm), upwards-growing rim of fibrous dolomite which is sealed with a crystalline
silica sinter (Fig. 7). The crust at 68.3 m is overlain by a sandstone layer (Fig. 7).

**Crust at 27.4 m.** The layer at ca. 27.4 m has a complex internal structure (Fig. 8). Its basal
part is composed of beige, laminated, micritic dolomite and contains some quartz-filled
fenestrae. The basal part is overlain by a partially vuggy interval. The latter contains several
small vugs, which are surrounded by beige, laminated, micritic dolomite and grayish
(siliceous), structureless, sparitic dolomite. The vugs are walled by white (inner) and yellow
(outer) laminae of fibrous dolomite. The remaining space in the vugs is filled with dolospar
and quartz. The yellow and white laminae also form small (ca. 1 cm) mounds. The vuggy
interval is sealed with a rim of white sparitic dolomite. These vugs probably formed
simultaneously with the surrounding dolomites. The uneven surface of the entire layer is
capped with a thin siliceous film (interpreted as a sinter or a silcrete layer). The overall
structural pattern suggests a surficial dolomite crust.
4.5 Dolomite cements (type 5)

Dolomite cements are found in the Lower Dolostone member (Fig. 9), chiefly at ca. 76-78 m and at 83 m. These cements consist of white feather-shaped (Figs. 9a-c), fibrous, radial, bladed and/or sparitic dolomite. Dolomite cements do not form distinct bedding-parallel layers (in contrast to the surficial dolomite crusts), but they are found on uneven surfaces and capping or corrosively replacing sandstone fragments. Sometimes they form mound-like accumulations (Figs. 9a-b), which often have exhumed upper surfaces. There are also thinly-laminated cements (Fig. 9b). Dolomite cements usually show upward growth and appear as syn-depositional precipitates. Sometimes they are also found filling space between the sandstone fragments, showing downward growth (Fig. 9d); quartz or dolospar is the latest infill.

Although the dolomite cements and quartz also fill void spaces between sandstone fragments, the cements are best interpreted as syn-depositional precipitates, as these precipitates are usually cementing surface rock fragments and uneven erosional surfaces.

5. Geochemical results
5.1 Electron microprobe data

Carbonate cavity fills, crusts and cements were analyzed semi-quantitatively with an electron microanalyzer to determine mineralogies. The reddish dolomite crust in the cavity flooring at ca. 81.5 m includes mainly dolomite but also calcite, quartz, talc, phlogopite, muscovite, Fe-poor chlorite, potassium feldspar and fluorapatite. Calcite was found filling the remaining space between dolomite crystals. Dolomite and minor calcite and talc were identified in the cavity at ca. 60.6 m. The quartz-filled fenestrae in the layer at ca. 72.7 m contain calcite and dolomite inclusions. Apatite and potassium feldspar were also identified in that layer. No traces of evaporite minerals were found in the investigated fenestrae. Two samples from the dolomite cements are composed of mainly dolomite with minor calcite, quartz and talc. Several minor minerals were also identified in the dolomite cements, including fluorapatite, potassium feldspar and chlorite. Possible sulfate pseudomorphs (now dolomite and calcite) were recognized in a secondary electron image (Inline supplementary figure 2) in the dolomite cement at ca. 76.9 m.

(Insert Inline Supplementary Figure 2 here.)

Both the electron microprobe and the microscope investigations suggest that dolomite is a primary mineral. There are no petrographic indications for dolomitization. Instead, the presence of talc could indicate that the minor calcite has been formed via de-dolomitization.

5.2 Acid-soluble elemental contents (ICP-MS)
The acid-soluble elemental contents and the Mg/Ca and Mn/Sr ratios of the carbonate fills, crusts and cements are presented in Inline Supplementary Table 2.

(Insert Inline Supplementary Table 2 here.)

The Mg/Ca ratios vary from 0.01 to 0.71 (n=65). Based on the Mg/Ca ratios, most of the subsamples were dolomitic. Two subsamples were calcitic. Two subsamples were mixtures of dolomite and calcite.

On the core scale, the Mn and Fe contents show subtle upwards decreasing trends. The Mn contents vary from 42 to 3900 ppm (average 640 ppm, n = 65, Fig. 10). The abundances of Fe range between 110 and 9600 ppm (average 1600 ppm, n = 65, Fig.10). The Fe concentrations correlate strongly with the Mn concentrations (r = 0.57, n = 65, Fig. 11).

The Sr contents show an upwards increasing trend in the core, varying from 30 to 310 ppm (average 96 ppm, n=65, Fig. 10). The Sr and Mn contents do not show co-variation in the investigated carbonate precipitates (Fig. 11). The Ba contents do not show any clear stratigraphic trend, varying from <0.48 to 51 ppm (average 6.2 ppm, n=65, Fig. 10).

(Approximate location of Figures 10-11.)

5.2.1 Detailed investigations of distinct cavities and crusts

Several subsamples from the cavities at ca. 79.6 m and ca. 81.4 m were analyzed for elemental contents. In the cavity at 79.6 m (Fig. 12), the highest Mn and Fe contents were obtained from a stalactite and stalagmite in the cavity center. TheFe contents show a subtle
upwards increase in the upper part of the cavity (in the ceiling). The Mn, Sr and Ba concentrations do not exhibit any clear trends. In the cavity at 81.4 m (Fig. 13), the Mn and Fe contents show generally upwards increasing (cyclical) trends. The Sr concentration is variable, demonstrating no clear trend across the cavity, whereas the Ba content shows a subtle upwards decrease.

(Approximate location of Figures 12-13.)

The vein at ca. 53.7 m shows mineralogical and color zoning. The orange infill in the center is composed of calcite (Mg/Ca = 0.01), whereas the grayish rim surrounding the orange infill has a mixed dolomite-calcite composition (Mg/Ca = 0.20). The white outermost rim consists of dolomite (Mg/Ca = 0.64). The Mn and Ba concentrations decrease from the calcitic infill towards the dolomitic rim. The highest Fe and Sr contents were obtained from the mixed calcite-dolomite sample. All analyzed carbonate phases have a high Mn content (750–2700 ppm), whereas the Sr abundances (62–150 ppm) are higher or similar to those obtained from other carbonate phases from similar depths.

The cavity at ca. 72.7 m includes silica filled fenestrae. As mentioned earlier, some of these fenestrae morphologically resemble sulfate pseudomorphs, although no traces of sulfates have been detected. High Mn (3900 ppm) and Fe (9600 ppm) contents were measured from this interval. In contrast, the Sr (35 ppm) and Ba (0.82 ppm) contents are relatively low.

5.3 Carbonate C and O stable isotopes
The δ¹³C and δ¹⁸O values of all analyzed samples are presented in Inline Supplementary Table 2.

In cavity fills, crusts and cements (n = 139), the δ¹³C values vary from 4.0 to 8.0‰ averaging at 6.8‰ (Fig. 2). The δ¹⁸O values range from -15.1 to -8.4‰, with an average value of -12.6‰ (Fig. 2). In general, cavity/vein fills, surficial crusts and cements show similar variations of δ¹³C and δ¹⁸O values.

The δ¹³C and the δ¹⁸O values show moderate positive correlation (r = 0.50, n = 139, Fig. 11) in the carbonate fills, crusts and cements. Lower δ¹³C values are often linked to higher Mn concentrations (Fig. 11). The Sr contents of the precipitates do not show correlation with the δ¹³C or δ¹⁸O values (Fig. 11). No significant co-variation is observed between the δ¹⁸O values and the Mn contents (Fig. 11).

5.3.1 Detailed investigations of distinct cavities and crusts

A series of subsamples was obtained from some cavity fills. In individual crusts and cavities, the δ¹³C and δ¹⁸O values show moderate or even strong positive correlation (Fig. 14). Clearly decreasing δ¹³C and δ¹⁸O trends from the walls towards the centers were found in the cavities at ca. 83.0 m (Fig. 15) and ca. 79.6 m (Fig. 12). In the cavity at ca. 81.4 m (Fig. 13), the lowest δ¹³C and δ¹⁸O values were obtained from the upper part, which included thinly-laminated gray-and-white crust and stalactites. The δ¹³C and δ¹⁸O values show subtle upwards decreasing trends in the flooring of that cavity, followed by subtle upwards increasing δ¹³C and δ¹⁸O trends.

(Approximate location of Figures 14-15.)

The cavity fills at ca. 62.1 m show similar or lower δ¹³C values (6.1 – 7.5‰, average 7.0‰) than those (7.3 – 7.8‰, average 7.6‰) in the carbonates enclosing the cavity (Fig. 16).
These rocks over- and underlying the cavity show a subtle, symmetrical decrease in their $\delta^{13}C$ values towards the cavity. The $\delta^{18}O$ values are relatively similar or slightly higher in the cavity fills (from -12.5 to -9.2‰, average -11.5‰) than in the rocks enclosing it (from -12.3 to -11.3‰, average -11.9‰) (Fig. 16).

(Approximate location of Figure 16.)

In the surficial crust at ca. 30.3 m (Fig. 17), the $\delta^{13}C$ values first show a cyclic, upwards decreasing trend (in the lowermost third of the crust), followed by a subtle tendency towards higher values. The $\delta^{18}O$ values show an increasing trend in the lowermost part of the crust, followed by a decreasing trend, and after that, variable $\delta^{18}O$ values. The upper half of the surficial dolomite crust at 68.3 m shows a small (ca. 0.5‰) increase in $\delta^{13}C$ and $\delta^{18}O$ upwards in the section (Fig. 18); the lower half of the crust was not investigated. These crusts at 30.22 m and 68.26 m are different in their petrography.

(Approximate location of Figures 17-18.)

Carbonates in the vein at 53.7 m vary in their $\delta^{13}C$ and $\delta^{18}O$ values. The calcitic phase (from the central orange zone of the vein) shows a $\delta^{13}C$ value of 5.2‰ and a $\delta^{18}O$ value of -12.7‰. The subsample representing a mixture of calcite and dolomite (from the grayish zone) shows a $\delta^{13}C$ value of 5.9‰ and a $\delta^{18}O$ value of -13.5‰. The dolomitic subsample (from the white zone) shows a value of 7.6‰ and a $\delta^{18}O$ value of -12.0‰. Thus, the $\delta^{13}C$ values increase from the central calcitic zone outwards, towards the dolomitic zone. In contrast, the lowest $\delta^{18}O$ value was obtained from the mixture of dolomite and calcite.

6. Discussion
6.1 Petrographic aspects

Many of the precipitates studied in Core 5A are post-depositional phases, including cavity and vein fills (types 1-3). The term speleothem could be appropriate for the cavity fills. Whether the waters from which they precipitated were thermal (e.g. Corbella et al., 2004; Djidi et al., 2008; Dublyansky, 1995) or at ambient temperature remains to be substantiated.

The thinly-laminated crusts and stalactites in the type 3 cavities (Fig. 5a, c) are similar to carbonate crusts coating modern travertines (e.g. Jones and Renaut, 2008). Moreover, some of the studied carbonates (e.g. type 4) resemble the ~1.8-Ga-old Baker Lake Group laminar crust travertines of Canada briefly described by Rainbird et al. (2006); those travertines are associated with volcanic rocks.

All surficial dolomite crusts (type 3) are capped with a thin siliceous sinter or silcrete (e.g. Fig. 7). This silica layer distinguishes such dolomite crust from “normal” stratified dolostones of the KSF. Silica sinters in modern travertines are usually precipitated through rapid cooling and/or evaporation (e.g. Jones et al., 1996; White et al., 1956; Rimstidt and Cole, 1983), and do not form if surfaces are continually bathed in hot-spring water (Jones et al., 1996).

Melezhik and Fallick (2001) noted that the silica sinters in the travertines of the KSF may have not been formed in a similar manner to the sinters in modern travertines. Rather, they suggested that the silica was derived from quartz-rich carbonate rocks underlying the travertines, and (hot?) silica-saturated fluids were transported by capillary rise, allowing sinter to be subaerially precipitated by evaporation and cooling.

The investigated dolomite cements (type 5; Fig. 9) are often composed of feather-shaped dolomite crystals. Crystals with feather-like shapes are well known in modern travertines (e.g. Fouke et al., 2000; Guo and Riding, 1992; Rainey and Jones, 2009).
Corbella et al. (2004) reported hydrothermal calcite and sulfide stalactites, which outwardly resemble some of the type 3 thinly-laminated crusts and the thicker crusts underlying them. Corbella et al. (2004) described a model of karst and stalactite formation by (i) dissolution of carbonates and (ii) precipitation of sulfides and later carbonates. Their model is based on the mixing of two calcite-supersaturated hydrothermal fluids with different salinities, Ca and bicarbonate ion concentrations and pH levels. They concluded that dissolution and precipitation occur in separate but adjacent zones; dissolution occurs in the zone dominated by brine-rich mixtures and precipitation takes place where low ionic strength groundwaters dominate. A similar model might explain several of the KSF carbonates, whereby brines generated through dissolution of evaporites mixed with low ionic strength groundwaters, causing both cavity formation and carbonate precipitation.

### 6.2 A comparison to the host carbonates

The background sedimentary dolostones and limestones sampled in Core 5A were studied by Salminen et al. (2013a). Below, their data are compared to the newly obtained isotopic and geochemical results from the cavity fills, crusts and cements.

At the core scale, cavity fills, cements and crusts show in overall similar $\delta^{13}C$ variation (from 4 to 8‰) to that (from 5 to 8‰) reported by Salminen et al. (2013a) from the host carbonates (Fig. 2). However, the carbonate fills, crusts and cements often show lower $\delta^{13}C$ values compared to the host rocks from comparable depths (Fig. 2).

The $\delta^{18}O$ values obtained from cavity fills, crusts and cements show a somewhat different range (from -15 to -8‰) compared to that reported from the host rocks (from -18 to -10‰; Salminen et al., 2013a). This difference could be explained by different depositional
conditions or different fluids. For example, evaporation or a down-flow trend of rising water
temperature could explain increasingly higher $\delta^{18}$O values in the precipitates.

At hand-specimen scale, the cavity fills, crusts and cements show more variation in the $\delta^{13}$C
and $\delta^{18}$O values than that reported from their host carbonates (Salminen et al., 2013). For
example, within a distance of 10 cm, the carbonate fills, crusts and cements show up to 2‰
variation in their $\delta^{13}$C values and up to 4‰ variation in their $\delta^{18}$O values.

The investigated carbonate precipitates show coupled $\delta^{13}$C and the $\delta^{18}$O trends (Figs. 11, 14)
In host rocks, only carbonates near contacts with magmatic rocks show statistically
significant correlations between the $\delta^{13}$C and $\delta^{18}$O values, whereas the bulk carbonates do
not, hence suggesting overall good preservation of the C isotope composition (Salminen et
al., 2013a).

Coupled $\delta^{13}$C and the $\delta^{18}$O trends in carbonate precipitates could indicate metamorphic
alteration (Valley, 1986). As the host rocks have generally retained their primary C isotope
compositions, it is unlikely that the C isotope composition of the carbonate fills, crusts or
cements was significantly affected by metamorphism. A linear correlation between the $\delta^{13}$C
and $\delta^{18}$O values could instead indicate mixing between two chemically different fluids
(Banner et al., 1988; Banner and Hanson, 1990; Lohmann, 1988) or a thermal origin (e.g.
Chafetz and Guidry, 2003).

In some cavities, the $\delta^{13}$C and $\delta^{18}$O values decrease from the cavity walls towards the cavity
center. This could result from the progressively decreasing degree of fluid/bedrock-
interaction. Thus higher $\delta^{13}$C and $\delta^{18}$O values could indicate more interaction with the host
rocks. Alternatively, in some modern speleothem precipitation, kinetic isotope fractionation
of C and O results in correlations between the $\delta^{13}$C and $\delta^{18}$O values (e.g. Mickler et al.,
2006). However, in the modern speleothems of Mickler et al. (2006), the $\delta^{13}C$ and $\delta^{18}O$
values increase from the rim towards the center – and this is not the case in the KSF.

The surficial dolomite crust at ca. 30.3 m and the possible surficial crust at ca. 27.4 m both
show lower $\delta^{13}C$ values and generally lower $\delta^{18}O$ values compared to their host carbonates
(Fig. 2). In contrast, the similar crust at ca. 68.3 m shows slightly higher $\delta^{13}C$ and $\delta^{18}O$ values
than its host carbonates (Fig. 2). This latter crust also shows a subtle trend of upwards
increasing $\delta^{13}C$ and $\delta^{18}O$ values in its upper half (Fig. 18). This pattern might conceivably be
related to evaporation (e.g. Stiller et al., 1985). Alternatively, it might be related to
temporally (even seasonally?) increasing carbonate precipitation (causing progressive $^{12}CO_2$
loss) upstream of the site of crust deposition, from progressively cooler waters. This is seen
in some modern tufa and speleothem systems where mineral precipitation is driven by $CO_2$
degassing, since subterranean cave ventilation, $CO_2$ degassing and calcite precipitation, is
greater in the winter than the summer (e.g. Matsuoka et al., 2001). However the high p$CO_2$ of
the Paleoproterozoic atmosphere probably argues against such a degassing precipitation
mechanism for the KSF precipitates.

The investigated cavity fills, crusts and cements often show higher Mn contents than those in
their host carbonate rocks, whereas their Sr contents are similar (Fig. 10). High Mn contents
could imply a thermal origin for the waters, as hot-spring travertines are often characterized
by high Mn and Fe contents (e.g. Tanaka et al., 1994; Pentecost, 2005, pp.118). The
investigated precipitates show upwards decreasing Mn and Fe trends at the core scale (Fig.
10), This could indicate decreasing concentrations of soluble iron and manganese in the
carbonate mineral precipitating waters through time, consistent with a temporal change to a more oxidizing environment (e.g. Pentecost, 2005: pp.116; Kah et al., 2012).

In the Upper Dolostone member, the precipitates are slightly less Fe rich than their host rocks (Fig. 10). In contrast, the Mn contents are similar to or higher than those in the host rocks (Fig. 10). This is perhaps explained by divalent Mn (which can be incorporated into the carbonate mineral lattice) persisting longer in oxidizing travertine-depositing conditions than Fe$^{2+}$ (Pentecost, 2005, pp. 116).

The upwards increasing Sr contents might imply a transition to a more saline environment and opening of a connection to the ocean. This idea is supported by published interpretations of the depositional setting as Melezhik and Fallick (2005) and Salminen et al. (2013b) suggested sea-water invasion during the deposition of the upper part of the KSF. Higher Sr contents could also imply dissolution of the calcitic host rocks in the uppermost part of the succession. Calcite in general contains less Mn and more Sr than dolomite (e.g. Gaucher et al., 2007).

Samples distribute into four groups according to the co-variation plots (Fig. 11). (I) Majority of the samples is plotted in the group, which is characterized by relatively high δ$^{13}$C values (ca. 6–8 ‰), moderate to low δ$^{18}$O values (ca. -10 to -15‰), relatively low Mn contents (up to 1000 ppm) and Sr contents (<200 ppm). (II) Another group includes some cavity and vein fills (chiefly dolospar representing the latest infill) with high δ$^{18}$O values (ca. -9 to -8 ‰), high δ$^{13}$C values (ca. 7-8 ‰), and low Mn (<500 ppm) and Sr contents (<120 ppm). (III) Second minor group includes different types of samples with low δ$^{13}$C values (<6 ‰), low δ$^{18}$O values (<11 ‰), high Mn contents (> 1000 ppm) and low to moderate Sr contents. (IV) One more minor group consist of a few samples (cavity and vein precipitates and one
subsample from a surficial crust) from the Upper Dolostone member with high $\delta^{13}C$ values, moderate $\delta^{18}O$ values, **high Sr contents** and low Mn contents.

Samples in the group I likely show also geochemical characteristics of the dissolved dolomitic host rocks, whereas the group IV probably indicates dissolution of calcitic (and dolomitic) host rocks. Group III samples perhaps represent “pure” deep-sourced fluid, as implied by the low $\delta^{13}C$ values and high Mn contents. Group II represents the last dolomite generation/phase.

6.3 Comparison to previous investigations of the KSF travertines

Some carbonates investigated in Core 5A (e.g. the cavity at ca. 81.4 m) resemble the travertines studied by Melezhik and Fallick (2001) and Melezhik et al., (2004) from other locations in the KSF. Melezhik and Fallick (2001) reported $\delta^{13}C$ values from 0.8 to 7.2‰ and $\delta^{18}O$ values from -12.4 to -9.8‰ in a travertine crust. They also reported a much greater range of $\delta^{13}C$ and $\delta^{18}O$ ratios (from -6.1 to 7.7‰ and from -18.3 to -9.1‰, respectively) in a travertine mound. Even the lowest $\delta^{13}C$ values found in the current study are several per-mils higher than the lowest $\delta^{13}C$ values reported by Melezhik and Fallick (2001). They explained the observed $\delta^{13}C$ and $\delta^{18}O$ variations and trends by invoking initial $CO_2$ out-gassing at the hot-spring orifice, down-flow trends of thermal waters (following modern examples e.g. Friedman, 1970; Chafetz et al., 1991; Chafetz and Lawrence, 1994), mixing with ambient
waters, and possible evaporation. The travertine crusts were suggested to be precipitated in shallow distal pools, periodically fed by the thermal springs (Melezhik and Fallick, 2001).

Upwards (within cavities/crusts) increasing or decreasing $\delta^{13}$C and $\delta^{18}$O trends and cyclical variations of $\delta^{13}$C and $\delta^{18}$O values were found in the investigated precipitates from Core 5A. Such fluctuations could be explained by the model of Melezhik and Fallick (2001). The upward $\delta^{13}$C increase would then be explained by a down-flow trend, possibly connected to evaporation and some mixing with ambient water in the depositional basin. The upwards decreasing $\delta^{13}$C and $\delta^{18}$O trends could be explained by a resurgence in supply of hot-spring water to the point of travertine precipitation (such as a distal pool). The cyclical $\delta^{13}$C pattern in the crust at ca. 30.3 m could indicate pulsed supply of the thermal waters, connected to intervals of intense evaporation.

Melezhik and Fallick (2001) and Melezhik et al. (2004) found that travertines and the stratified dolostone of the KSF plot along two entirely different lines in a $\delta^{13}$C-$\delta^{18}$O cross-plot. Melezhik et al. (2004) found that travertines show positive correlation between the $\delta^{13}$C and $\delta^{18}$O values, whereas no significant correlation between them is found in the stratified dolostone. Like the travertines investigated by Melezhik et al. (2004), the cavity fills, crusts and cements in Core 5A show positive co-variation between the $\delta^{13}$C and $\delta^{18}$O values (Fig. 14), while only the contact-altered host carbonate show co-variation between $\delta^{13}$C and $\delta^{18}$O values (Salminen et al., 2013a). Thus, the investigated carbonate precipitates of Core 5A also plot differently on a $\delta^{13}$C-$\delta^{18}$O cross-plot to their host rocks.

Melezhik and Fallick (2003) reported variable $\delta^{13}$C and $\delta^{18}$O values from dolospar/dolomicrospar cements and fills in fenestrae and voids. They did not find significant differences between the $\delta^{13}$C values of such cements and fills and their host dolomicrite. They did find that the $\delta^{18}$O values in the dolospar/dolomicrospar were somewhat lower to
those in the host dolomicrite, hence were explained by syn-depositional/early diagenetic alteration processes. In Core 5A, the $\delta^{13}C$ values are commonly lower in the cavity fills, crusts and cements than in their host carbonate rocks, suggesting that an external lower $\delta^{13}C$ carbon source is required. It is plausible that all the investigated carbonate precipitates from Core 5A could have been precipitated from $^{13}C$-depleted fluids.

### 6.4 The origin of the cavity fills, crusts and cements in the KSF

An external carbon source would explain the lower $\delta^{13}C$ values in the cavity fills, crusts and cements compared to the surrounding host rock. That source could be (i) CO$_2$-bearing meteoric water, (ii) CO$_2$ derived from oxidation of organic carbon, or (iii) deep-sourced CO$_2$. As the sedimentary rocks in the KSF are devoid of organic carbon (e.g. Melezhik and Fallick, 2005), it seems unlikely that the external carbon comes directly from an organic source. A meteoric water with low $\delta^{13}C$ dissolved inorganic carbon is a possibility, though this would have implications for the record of life in Paleoproterozoic terrestrial environments. The external carbon could also be derived from deep-sourced CO$_2$, as magmatic carbon commonly has $\delta^{13}C$ values around -5 to -7‰ (e.g. Anderson and Arthur, 1983; Deines, 2002).

Several possible mechanisms could be invoked to explain how these carbonate rocks formed under a high pCO$_2$ atmosphere and without high pCO$_2$ soils (Brasier, 2011). Paleoproterozoic speleothem may have been formed (1) under an ice cover due to warming of waters (Dreybrodt, 1982), and alternatively (2) freezing of water could have caused carbonate precipitation in caves (e.g. Aharon, 1988). However, no petrographic or structural evidence for glaciation is present in the KSF and these two models cannot explain the observed $\delta^{13}C$ and $\delta^{18}$O trends.
Precipitation may have been aided by (3) cyanobacteria and microbes (e.g. Merz, 1992; Spiro and Pentecost, 1991). As stromatolites are found in the KSF, it is possible that cyanobacteria influenced precipitation of crusts. However the formation of the cavity fills and veins cannot be explained by photosynthetic cyanobacteria.

Carbonates are today usually dissolved by fluids rich in carbonic acid (H$_2$CO$_3$). However, fluids rich in other acids may also cause carbonate dissolution. For example, (4) sulfuric acid (H$_2$SO$_4$) has been reported to cause dissolution (e.g. Atkinson, 1983). Local H$_2$SO$_4$ production in the Paleoproterozoic was likely increased due to the oxygenation of the atmosphere and the oxidation of sulfides (Bekker and Holland, 2012; Brasier, 2011). But sulfuric acid dissolution alone could not itself explain the precipitation of the cavity fills.

Karst and speleothem-like precipitates can also be formed by local (5) calcite supersaturation due to a common-ion effect: extra calcium is supplied e.g. from dissolution of evaporites (e.g. Calaforra et al., 2008; Wigley, 1973a) or incongruent dissolution of dolomite (e.g. Wigley, 1973b). This leads to calcite precipitation when the solution becomes supersaturated with respect to calcite. The common-ion effect is found in polymineralic systems (calcite and gypsum, or calcite and dolomite) that are initially calcite saturated (see Brasier, 2011). Such a common-ion effect causes precipitation in some modern hot springs (Pentecost, 1995) and in cold (~6.5°C) springs (Omelon et al., 2006) in the presence of gypsum. It can also explain the precipitation of lake tufas (Dunn, 1953). Thus, the common-ion effect could also explain the formation of the surficial crusts and cements in the KSF.

The common-ion effect caused by dissolution of evaporites (5a) may explain the formation of the small-scale cavities and the precipitation of the carbonate fills and the surficial precipitates in the KSF. Probable sulfate pseudomorphs have previously been reported from the KSF (e.g. Melezhik and Fallick, 2005), and they were also found in this study. The
common-ion effect due to dissolution of Ca-evaporites (e.g. gypsum) results in precipitation of calcite (e.g. Wigley, 1973a). Calcite, however, is only a minor constituent in the cavities of the KSF, and there is no clear evidence of calcite recrystallizing to dolomite. Dolomites could have been precipitated due to a common-ion effect caused by dissolution of Mg-rich evaporites. However, pseudomorphs after Mg-rich evaporites have not been found in the KSF.

The common-ion effect caused by dissolution of dolomite (5b) is a possible explanation, as the host carbonates in the formation are mainly dolostones. However, Wigley (1973b) noted that the incongruent dissolution of dolomite leads to the precipitation of calcite prior to dolomite. Incongruent dissolution of dolomite is an unlikely explanation for the formation of the precipitates. Thus, the common-ion effect could explain the karst solution in the KSF, but does not obviously explain the precipitation of chiefly dolomitic precipitates.

Degassing can also happen due to (6) boiling (in addition to high temperature) in springs (e.g. Arnósson, 1989). Temperatures well below the boiling point cause travertine precipitation today (e.g. Fouke et al., 2000), but meteoric waters can also be heated when percolating through the bedrock (e.g. Dublyansky, 1995; Djidi et al., 2008). Boiling meteoric waters could cause carbonate precipitation, but might not explain all the observed $\delta^{13}$C and $\delta^{18}$O trends. Moreover, heating of meteoric waters could be connected to supply of deep-sourced CO$_2$ (Djidi et al., 2008).

Deep-sourced CO$_2$ (7) could explain the formation of the cavity fills, surficial dolomite crusts and dolomite cements in the KSF (e.g. Duliński et al., 1995; Pentecost and Viles, 1994; Yoshimura et al., 2004). Deep-sourced CO$_2$ could be either volcanic or produced by metamorphic reactions, and is usually associated with hydrothermal activity (e.g. Pentecost and Viles, 1994; Pentecost, 1995). Deep-sourced CO$_2$ can increase the dissolution rates as
well as carbonate precipitation even in ambient water temperatures (Yoshimura et al., 2004), but some of the investigated precipitates have physical and geochemical characteristics (e.g. veins that could have been fluid conduits; mound morphologies; feather-shaped crystals, high Mn contents, co-variation and trends of $\delta^{13}$C and $\delta^{18}$O) that are at least consistent with deep-sourced fluids and hot-spring travertine.

The isotope results from Core 5A samples do not show unambiguous evidence of a deep-sourced origin or deposition in close vicinity to hot-spring vents. However, the carbonate precipitates in the KSF could have precipitated from thermal waters distally from the vents, as suggested by Melezhik and Fallick (2001).

The most likely explanation for the formation of the carbonate precipitates in the KSF is apparently deep-sourced CO$_2$, connected to hydrothermal activity. Boiling may have contributed to the carbonate precipitation and deep-sourced fluids may have mixed with meteoric waters. Thus, the cavity and vein fills in the KSF could represent hydrothermal karst (“cave travertine”). Dolomite cements and some of the surficial crusts are likely travertine, although some dolomite crusts could represent evaporite layers. The Mn/Sr ratios, elemental contents and their patterns in the vein at 53.7 m in Core 5A could suggest formation during burial.

If pseudomorphs or relicts of Mg-rich evaporites were later found in the KSF, the common-ion effect connected to dissolution of evaporites could also explain the formation of the cavities and the cavity fills, crusts and cements.

6.5 The depositional setting of the KSF
Salminen et al. (2013b) interpreted the depositional setting of Core 5A as deltaic and lacustrine, but tidally influenced. Melezhik and Fallick (2005) concluded that the depositional setting of the KSF was deltaic and shallow lacustrine. This new investigation supports the previous interpretations of the depositional setting of the KSF.

Melezhik and Fallick (2001) pointed out that the modern travertines are only found in terrestrial settings. Most of the investigated cavity fills, crusts and cements are likely travertine or “cave travertine”. We infer they precipitated in terrestrial settings.

Melezhik et al. (2004) investigated various subaerial exposure surfaces in the KSF. Findings of this study also support occasional subaerial exposure during the deposition of the KSF. The red color in the dolomite crusts likely indicates oxic conditions, possibly in a subaerial environment. Likely evaporitic sulfate pseudomorphs were also found.

The question of how the deep-sourced CO2 was supplied to the carbonate sediments in the KSF is open. One possibility is through the veins (now cemented up); another is through syndepositional faulting, as the KSF was likely deposited in an intracontinental rift setting (Melezhik and Sturt, 1994). Melezhik and Fallick (2005) provided a reconstruction of the Kuetsjärvi rift-related lake, which includes hydrothermal springs and transverse faults. Eruption of later volcanic rocks of the Kuetsjärvi Volcanic Formation may also have provided a source for the formation of cavity and vein fills, which are apparently secondary precipitates. However, this cannot explain the deposition of the surficial precipitates.

7. Conclusions
Core 5A was obtained from the Paleoproterozoic Kuetsjärvi Sedimentary Formation. Drilled stratified carbonate rocks contain dolomite crusts, dolomite cements and abundant small-scale cavities and veins. These cavities and veins are mainly filled with dolomite and quartz. Dolomite crusts occur in the cavities and on bedding/erosional surfaces. Dolomite cements are found on uneven surfaces encrusting sandstone fragments. Dolomite crusts, cements and carbonate fills were analyzed for $\delta^{13}C$ and $\delta^{18}O$ values and selected acid-soluble elements. The newly obtained results were compared to the published results from the host carbonates. The investigated carbonate precipitates show lower or similar $\delta^{13}C$ values to their host carbonates. The lower $\delta^{13}C$ values suggest the presence of an external carbon source, which was likely deep-sourced/hydrothermal CO$_2$. Dolomite cements and the dolomite crusts on bedding/erosional surfaces are likely thermal travertines. This is supported by the petrographic and geochemical observations. In the absence of organic carbon rich soils, deep-sourced/hydrothermal CO$_2$ also provides a very plausible explanation for the formation of the cavities, veins and carbonate fills. Cavity fills may be interpreted as “cave travertine”. Some veins may represent burial veins, or could have been conduits through which the travertine-precipitating fluids passed.

The $\delta^{13}C$ and $\delta^{18}O$ values show positive correlation. Both upwards increasing and decreasing $\delta^{13}C$ and $\delta^{18}O$ trends were found in the dolomite crusts. These trends could be explained by down-flowing thermal water possibly affected by evaporation and/or modified due to mixing with the ambient waters. Dolomite crusts showing only upwards increasing $\delta^{13}C$ trends could represent dolomitized evaporite layers. The $\delta^{13}C$ and $\delta^{18}O$ values commonly show increasing trends from the middle of the cavity towards the cavity walls, probably indicating different degrees of mixing with the host rocks and thermal waters.
Few reports have been published on Precambrian travertine or speleothem. The above new
detailed geochemical data and petrographic analyses of what may be Earth’s earliest
travertines provide a glimpse of complexity in textures and facies likely quite similar to that
found in modern hot-spring settings. Consideration of several possible depositional
mechanisms leads to the conclusion that these are two billion year old hot-spring travertines
likely formed by similar processes to those of the modern world.

Acknowledgements

PES was supported by Väisälä Foundation (Finnish Academy of Science and Letters) and the
Finnish Doctoral Program in Geology. This is a contribution (paper) to the ICDP FAR-DEEP
project.

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**Figure captions**

**Figure 1.** (a) The location of the KSF and the Pechenga Greenstone Belt. (b) The location of Core 5A in the Pechenga Greenstone belt. Modified from Melezhik and Fallick (2005)

**Figure 2.** Lithostratigraphic profile of Core 5A (modified from Salminen et al., 2013a) and the C and O isotope composition of the surficial dolomite crusts and cements and carbonate fills in cavities and veins. The C and O isotope compositions of the host carbonates (micro-drilled samples; Salminen et al., 2013a) are shown for comparison. In addition, the estimated proportion of the carbonate crusts, cements and fills (Salminen et al., 2013a) is shown in the figure.

**Figure 3.** Cavities. (a) Dissolution cavity at the depth of 62.1 m. The cavity is mainly filled with dolospar. Dolostone immediately surrounding the cavity is recrystallized and has a powdery appearance. (b) Dissolution cavity at the depth of 69.6 m with complex internal structure. The outer zone of the cavity fill includes (1) thin laminae of dolomite and quartz (also forming “mounds”) and (2) yellowish sparitic calcite. These are sealed with (3) a thin rim of fibrous, inward-growing dolomite. Quartz with some dolomite and (4) pyrite represent the latest fills in the cavity.

**Figure 4.** Cavities. (a) Scanned image of a cavity at the depth of 83.0 m. The cavity is lined with several rims of sparitic dolomite, capped with a rim of fibrous dolomite. The remaining space is filled with dolospar and minor quartz. (b) Cavity (at the depth of 72.7 m) includes
quartz-filled fenestrae, some of them appearing as sulfate pseudomorphs (e.g. in the circled area).

Figure 5. Cavities with stalactites. (a) Quartz-filled and carbonate-walled cavity at the depth of 60.2 m. Note small white stalactites at the roof of the cavity. (b) Scanned slab showing gray-and-white, thinly-laminated crust (at the bottom) and stalactites in a cavity at a depth of 81.4 m. (c) Gray, white and yellow thinly-laminated dolomitic crust (at the bottom) and stalactites (in the middle), overlain by pinkish dolomite, at a depth of 31.4 m.

Figure 6. Veins. (a) A thin section showing a vein above a stromatolitic layer at the depth of 35.1 m. (b) A thin section showing a vein in sandy micritic dolostone at the depth of 62.7 m. (c) A probable burial vein in dolarenite overlying a sandstone-filled cavity (at the bottom). The vein shows coloration and mineralogical zoning. The innermost, reddish part is calcite. It is lined with a mixture of gray calcite and dolomite. The outermost white rim is composed of dolomite. The depth is 53.7 m.

Figure 7. A surficial dolomite crust at the depth of 68.3 m. (a) Thin-section of the crust. (b) Thin-section image of the crust (stereo microscope). The micritic/sparitic crust at the base (grayish color in the photo) shows upward growth and thin lamination. This part of the crust is overlain by a rim of fibrous dolomite (black colored in the photo). The entire crust is sealed with a silica sinter (bright colored in the photo) and overlain by a sandstone layer (at the top of the photo).

Figure 8. A probable surficial dolomite crust at 27.4 m. The crust is over- and underlain by sandy dolarenite. The basal part of the crust is composed of beige dolomitic bands overlain
by partially vuggy interval. The crust is capped with white rim of sparitic dolomite and a thin
film of siliceous precipitate (a sinter or a silcrete). (a) A photo of the crust. (b) Scanned slab.

**Figure 9.** Dolomite cements. a) Scanned slab showing dolomite cement with feathery
crystals, forming a mound-like structure at the depth of 76.4 m. b) Dolomite cements in a thin
section. Fibrous dolomite cement forms thin crusts/mounds at the depth of 76.0 m. c) A thin
section image of feathery dolomite cements (stereo microscope) at the depth of 76.0 m. d) A
thin section image showing surficial cement (stereo microscope) at the depth of 76.9 m.

**Figure 10.** Acid-soluble elemental contents (ICP-MS) of the carbonate fills, cements and
crusts. The elemental contents of the host carbonates (micro-drilled samples) have been
adopted from Salminen et al. (2013a); the Ba contents for the host rocks have not been
published.

**Figure 11.** Cross-plots of selected variables in carbonate fills, crusts and cements.

**Figure 12.** The C and O isotope composition and acid-soluble elemental compositions of
micro-drilled subsamples from the cavity at 79.6 m. The subsamples were obtained from the
circular spots shown in the slabs photo aside. The width of the slabs is ca. 2.5 cm.

**Figure 13.** The C and O isotope composition and acid-soluble elemental compositions of
micro-drilled subsamples from the cavity at 81.4 m. The subsamples were obtained from the
circular spots shown in the slab photos aside. The width of the slabs is ca. 2.5 cm.

**Figure 14.** A δ¹³C–δ¹⁸O cross-plot of the subsamples from the cavities at 79.6 and 81.4 m and
the surficial dolomite crusts at 30.3 and 68.3 m.
Figure 15. The C and O isotope composition of the micro-drilled subsamples from a cavity at 83.0 m. The subsamples were micro-drilled from the circular spots shown in the slab photo aside. The width of the slab is ca. 2.5 cm.

Figure 16. The C and O isotope composition of the dolospar fill from the cavity at 62.1 m. The C and O isotope composition of the dolostone immediately over- and underlying the cavity is also shown in the figure. The subsamples were micro-drilled from the circular spots shown in the slab photo aside. The width of the slab is ca. 2.5 cm.

Figure 17. The C and O isotope composition of the subsamples from the surficial dolomite crust at 30.3 m. The subsamples were obtained from the circular spots shown in the slab photo aside. The subsamples A-C were also analyzed for the acid-soluble elemental composition (results not shown in this figure). The width of the slab is ca. 2.5 cm.

Figure 18. The C and O isotope composition of the subsamples from the surficial dolomite crust at 68.3 m. The subsamples were micro-drilled from the circular spots shown in the slab photo aside. The width of the slab is ca. 2.5 cm.

Inline Supplementary Figure 1. Dolomite crust at the depth of 30.3 m. The crust starts with reddish dolomitic bands overlain by beige dolomite bands (the lower half), then followed by a crust with clotted microfabrics (the upper half). The dolomite crust contains small vugs filled with white, gray or black sparitic dolomite. There are also reddish fills in the vugs. (a) A photo of the crust. (b) Scanned slab of the crust showing also position of the micro-drilled subsamples.

Inline Supplementary Figure 2. A secondary electron image showing possible sulfate pseudomorphs (not visible in a back-scatter image) in dolomite cement at the depth of 76.9 m.
Host carbonates (Salminen et al., 2013)

- Cavity/vein
- Dolomite cements
- Surficial dolomite crusts
- Probable surficial dolomite crust
δ¹⁸O (VPDB,%o) vs δ¹³C (VPDB,%o)

δ¹⁸O (VPDB,%o) vs Mn/Sr

δ¹³C (VPDB,%o) vs Mn/Sr

Sr (ppm) vs Mn (ppm)

Sr (ppm) vs Fr (ppm)

Mn (ppm) vs Fr (ppm)

Carbonate fills
Dolomite cement
Surficial dolomite crust
Probable surficial dolomite crust
$\delta^{13}$C (VPDB, $\%$)

$\delta^{18}$O (VPDB, $\%$)

- Cavity at ca. 79.6 m
- Cavity at ca. 81.4 m
- Surficial crust at ca. 68.3 m
- Surficial crust at ca. 30.3 m