Petrography and geochemistry of carbonate rocks of the Paleoproterozoic Zaonega Formation, Russia: documentation of ^{13}C-depleted non-primary calcite.

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Abstract

The ca. 2.0 Ga Zaonega Formation in the Onega Basin of NW Russia represents a deep-water, mixed siliciclastic-carbonate depositional system with voluminous mafic volcanism. It is typified by extremely organic-rich rocks (TOC > 40 wt%) and represents one of the earliest known episodes of oil/asphalt generation. These rocks have been inferred to archive one of the largest negative $\delta^{13}C$ excursions in Earth history, one that followed and/or partially overlapped with the 2.2–2.06 Ga worldwide Lomagundi-Jatuli carbonate carbon isotopic excursion to high values and thought to be linked to the Paleoproteorozoic oxygenation of Earth's surface environments.

In order to assess the post-depositional integrity of the carbonate carbon isotopic signal ($\delta^{13}C_{carb}$) of the Zaonega rocks, we examined in detail the petrography and geochemistry of eight carbonate beds (0.3 to 0.9 m thick) from different stratigraphic levels of the formation. The range of $\delta^{13}C$ values for a single bed can be as much as 17 ‰, with calcite being significantly depleted in ^{13}C relative to co-existing dolomite; the ^{13}C-depleted calcite likely formed by involvement of carbon derived from diagenetic and catagenetic alteration of organic matter possibly abetted by

volcanic CO_2. The presence of calcite ± talc ± phlogopite ± actinolite indicates metamorphic reaction of dolomite with quartz, or possibly K-feldspar, in the presence of water; commonly accompanied by degassing of ^{13}C-enriched CO_2, this caused further ^{13}C depletion of newly formed calcite. The least altered dolomite is documented in central parts of thick dolostone beds with variably calcitized margins. This dolomite is considered as the earliest and possibly primary carbonate phase, potentially recording the $\delta^{13}C$ signal of the ambient seawater. The least-altered dolomite is found in two stratigraphic intervals exhibiting $\delta^{13}C$ values of +8 and +4 ‰ for the middle part of the formation, and $\delta^{13}C$ values of -2 and -4 ‰ for the upper part. All other beds, with $\delta^{13}C$ ranging from -19 to +3 ‰, are considered to have been variably depleted in their ^{13}C content by post-depositional processes and therefore cannot be reliably used for assessing the carbon isotope composition of Paleoproterozoic seawater. Our results emphasise the importance of distinguishing primary versus secondary (or later) isotopic compositions in studies of carbonate rocks used for reconstruction of global environmental change.

Keywords: Paleoproteorozoic, carbon cycle, non-primary calcite, Russia, Great Oxidation Event, Onega Basin

1. Introduction

Ratios of stable carbon isotopes ($^{13}C/^{12}C$ reported as $\delta^{13}C$) in carbonate rocks are widely used for tracking the global carbon cycle and associated environmental conditions as far back in time as the sedimentary rock record exists (Schidlowski, 2001). One of the most profound events of Earth history was the Paleoproteorozoic oxygenation of Earth's atmosphere, beginning around 2.5 Ga (Bekker et al., 2004; Farquhar et al., 2000). This is marked by a worldwide $\delta^{13}C$ excursion to high values in carbonate rocks (Baker and Fallick, 1989; Karhu and Holland, 1996), and known as the Lomagundi-Jatuli isotopic event. Genesis of this event has been explained by intensive burial of organic matter and associated accumulation of oxygen in the atmosphere (Karhu and Holland, 1996), although Melezhik and Fallick (1996) have discussed some problems with this idea. The Zaonega Formation was deposited after or partially overlapping with the Lomagundi-Jatuli Event (Hannah et al., 2008) and contains rocks extremely enriched in

organic matter (TOC > 40 wt%; Melezhik et al., 1999; 2004). The isotopic compositions of reduced and oxidized carbon from the Zaonega Formation have been used in attempts to reconstruct the global carbon cycle for this important interval of Earth history (Kump et al., 2011; Melezhik et al., 1999; Yudovich et al., 1991). The goal of this study is to perform a detailed petrographic and geochemical study of the carbonate-containing rocks of the Zaonega Formation preparatory to an evaluation of their applicability for reconstruction of Paleoproteorozoic sea-water compositions, and consequently, for interpretations of perturbations in the global carbon cycle during Paleoproterozoic time.

The sedimentary and volcanic rocks of the Zaonega Formation in Karelia, NW Russia (Fig. 1) were drilled as part of the International Continental Drilling Program's Fennoscandia Arctic Russia - Drilling Early Earth Project (FAR-DEEP). The Zaonega rocks record a mixed siliciclastic-carbonate depositional system, with much magmatic activity contemporaneous with sedimentation (Črne et al., 2013a,b). They also contain one of the earliest known generations of oil/asphalt and proposed hydrocarbon seeps onto the sea floor (Melezhik et al., 2009; Qu et al., 2012; Strauss et al., 2013). The Zaonega Formation and associated rocks experienced regional greenschist facies metamorphism during the 1.8 Ga Svecofennian episode of orogenesis (Volodichev, 1987).

Previously-reported carbonate $\delta^{13}C$ values from the Zaonega Formation range from -25 to +10 ‰ (Krupenik et al., 2011; Kump et al., 2011; Melezhik et al., 1999; Yudovich et al., 1991). Yudovich et al. (1991) interpreted all the ^{13}C-rich carbonate rocks of the Tulomozero and Zaonega formations to be the result of methanogenesis, whereas low $\delta^{13}C$ values of the Zaonega carbonates were taken as an indicator of both methanotrophy, and a negative isotopic shift in dissolved inorganic carbon due to atmospheric oxidation of biologically produced CH_4. Krupenik et al. (2011) interpreted all the carbonate rocks to be diagenetically altered to some degree such that the range in carbon isotope values between -1 and -20 ‰ was the result of various proportions of oxidized organic matter being incorporated into early diagenetic carbonate minerals. Most investigations of the Zaonega carbonate rocks highlighted the very low $\delta^{13}C$ and/or $\delta^{18}O$ values (Krupenik et al., 2011; Melezhik et al., 1999) and/or an exceptionally low $\Delta^{13}C$ ($\delta^{13}C_{carbonate}$ - $\delta^{13}C_{organic}$; Kump et al., 2011) to conclude that some post-depositional isotopic overprinting had indeed occurred, but a systematic petrographic and geochemical study to substantiate these inferences has not yet been reported. This paper addresses that shortcoming.

The negative $\delta^{13}C$ excursion recorded in the Zaonega Formation, together with assumed coeval strata in the Francevillian Basin, has been interpreted as one of the largest ever perturbations of the global carbon cycle reflecting intense, oxidative weathering of organic-rich rocks as the result of rising oxygen levels in the atmosphere (Kump et al., 2011). This is an important new hypothesis regarding the manner of Earth's transition to an oxygenated planet and underscores the need to carefully assess the potential modification of primary isotopic signals. Post-depositional alteration of the primary $\delta^{13}C$ signal may have occurred during diagenesis driven by respiration of organic matter and also later, during contact and regional metamorphic episodes that the Zaonega rocks have experienced. Within the studied depositional basin, locally generated, syn-sedimentary and/or diagenetic hydrocarbon-rich fluids containing ^{13}C-depleted species, including carbonic acid and CH_4, could have produced secondary carbonates and altered the original carbon isotope composition of primary carbonates. We examined in detail eight representative carbonate beds from cores of the Zaonega Formation, geochemically and petrographically characterizing closely spaced samples within each bed in order to: i) differentiate between early and late carbonate phases and determine their carbon and oxygen isotopic signatures; ii) investigate the potential processes of post-depositional alteration influencing the carbonate carbon isotope record; and iii) estimate the magnitude of any such alteration.

2. Zaonega Formation and the FAR DEEP core material

FAR-DEEP drillholes 12A, 12B and 13A targeted the Zaonega Formation in the Onega Basin of central Karelia, northwestern Russia (Fig. 1). Drilllholes 12A and 12B were drilled at the same site, few metres apart (latitude 62.4947 N, longitude 35.2887 E). The reason for the two holes from the same site is that drillhole 12A had to be aborted at the depth of ca. 100 m due to technical problems. Drillhole 12B was drilled without sampling the core for the top 95 m and the correlation between 12A and 12B was made using the lower contact of a large igneous body with the underlying sedimentary rocks occurring at 95.45 m in 12A and 94.56 m in 12B. As these two drillholes provide a continuous rock record, we refer to an integrated drillhole 12AB throughout this article. Drillhole 13A is located approximately 25 km WNW of drillhole 12AB (latitude 62.5891 N, longitude 34.9273 E; Fig. 1). During the Paleoproterozoic, the investigated area was

121 part of the rifted flank of the Karelian craton and formed its continental margin to the
122 Svecofennian Ocean (Lahtinen et al., 2008; Melezhik et al, 1999).
123 The Zaonega Formation is a ca. 1500 m thick succession and consists of interbedded
124 sandstones, siltstones, basalts, limestones, dolostones, cherts, and mafic tuffs all of which are
125 intruded by gabbroic sills (Črne et al., 2013a,b; Galdobina, 1987). It occurs above the 400- to
126 800-m-thick Tulomozero Formation, a shallow marine-sabkha succession dominated by
127 carbonate rocks that preserve the Lomagundi-Jatuli isotopic signature (Brasier et al., 2011;
128 Melezhik et al., 2000). The nature of the contact between these two formations is unresolved and
129 interpretations vary from it being either conformable, or an erosional unconformity (Melezhik et
130 al., 2013), or a tectonic contact (Galdobina, 1987). A minimum age for the Zaonega Formation
131 of ca. 1.98 Ga is constrained by several whole-rock and mineral Sm-Nd and Pb-Pb isochrons on
132 a mafic-ultramafic sill of the overlying Suisari Formation (Puchtel et al., 1998; 1999), which is
133 consistent with a Re-Os age of ca. 2.05 Ga obtained on organic matter from the Zaonega
134 Formation (Hannah et al., 2008). The depositional age of the underlying Tulomozero Formation
135 has been constrained by a Pb-Pb age on dolomite of 2.09±0.07 Ga (Ovchinnikova et al. 2007).
136 Termination of the Lomagundi-Jatuli isotope excursion occurred at 2.06 Ga in Finland and Kola,
137 Russia (Karhu, 1993; Martin et al., 2013; Melezhik et al., 2007), but no definite ages exist for the
138 Karelian succession. Thus the maximum-minimum constraints of 2.09±0.07 and 1.98 Ga for the
139 Zaonega Formation indicate its deposition partly overlapped with and/or post-dated the
140 Lomagundi-Jatuli Event.
141 The presence of lavas and gabbroic sills, some with peperite contacts, throughout the
142 entire Zaonega Formation indicates a tectonically and magmatically active depositional setting.
143 Thick intervals of massive organic-rich rocks, commonly associated with mafic lava flows and
144 gabbroic sills, have been interpreted to result from hydrocarbon generation and migration either
145 within the already deposited succession in the form of diapirs (Filippov, 1994) or as
146 hydrocarbon-rich/asphalt spills on the sea-floor (Melezhik et al., 2004; Qu et al., 2012; Strauss et
147 al., 2013). Cavities associated with migrated hydrocarbons provide evidence for generation of
148 fluids , possibly in the form of SO_2, CO_2, and/or CH_4 (Qu et al., 2012; Strauss et al., 2013).
149 The succession recovered by the FAR-DEEP cores 12AB and 13A (Fig. 2) was divided
150 into four lithostratigraphic units, from bottom to top, the Greywacke, Dolostone-Greywacke,
151 Mudstone-Limestone, and Dolostone-Chert members (Črne et al., 2013a,b). The major facies

change at the boundary between the Mudstone-Limestone and Dolostone-Chert members occurring at 9.3 m in core 12AB and at 76.6 m in core 13A is used for correlating the cores (Črne et al., 2013b). The cored rock represent a deep-water, mixed siliciclastic-carbonate depositional system with voluminous mafic volcanism and turbidity-current deposits represented by flat-laminated, normally graded greywackes interbedded with mudstones, dolostones and limestones; rare debrites are the result of erosion and redeposition within the basin, whereas thick mudstone packages represent background hemipelagic sedimentation (Črne et al., 2013a). Several consecutive intervals of massive organic-rich rocks sandwiched conformably by laminated mudstones (Črne et al, 2013a; 156-133 m in drillcore 12AB; Fig. 2) are interpreted as hydrocarbon-rich/asphalt spills on the sea-floor (Qu et al., 2012; Strauss et al., 2013).

Carbonate beds are present throughout the stratigraphy and their abundance, thickness and textural characteristics are distinctive to each lithostratigraphic member. The Greywacke member contains individual, thin beds of sandy limestone that thicken to several decimeters towards the top of the member, where carbonate concretions were recognized (Črne et al., 2013a). Because it is difficult to identify diagenetic carbonate concretions and layers as such if they have lateral dimensions greater than the width of the core, it is possible that they occur in places in the stratigraphy. The depositional mechanism considered to be most likely for the Zaonega primary carbonates, is the shedding of carbonate from the shallow-water environment into the deeper basin. This is supported by a carbonate bed within the Greywacke member, which contains re-crystallized ooids indicating re-deposition of allochems within the Paleoproterozoic Onega Basin. Above this, dolostones and sandy dolostones of the Dolostone-Greywacke member occur as several-metres-thick, flat-laminated layers, or as metre-thick, massive beds. The carbonate beds of the Mudstone-Limestone member are thinner, a few decimetres-thick and indistinctly laminated or massive. The uppermost part of the stratigraphy is typified by thick-bedded massive dolostone. We chose from one to three carbonate beds from each of the members thereby spanning most of the cored Zaonega Formation (Fig. 2).

3. Sampling and methods

A total of 39 bulk and 29, 1-2 mm diamond-drilled samples were obtained from eight carbonate beds and analyzed at the Geological Survey of Norway (NGU),the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, Scotland, and at the

University of Munster in Germany (Fig. 3; Table A1 in Appendix A). Major and trace elements were analyzed at NGU by X-ray fluorescence spectrometry using a PANalytical Axios at 4 kW and elemental concentrations were determined on acidified extracts (cold 10% HCl acid) by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Thermo Jarell Ash ICP 61. Total sulphur (TS), total organic carbon (TOC), and total carbon (TC) were determined at NGU (16 samples) and at University of Munster (23 samples). At NGU sealed tube combustion using a Leco SC-444 had a total analytical uncertainty of 15%. For measurements of TOC, the samples were reacted with 10% HCl acid before the combustion and inorganic carbon (IC) was calculated from TOC and TC. At University of Munster the IC was determined by reactions with 2 N perchloric acid ($HClO_4$) and TC by combustion of the sample; TOC was calculated from TC and IC. The 29 drilled samples and 39 bulk samples were analyzed for stable carbon and oxygen isotopes at SUERC using conventional procedures. For analyses of stable carbon and oxygen isotopes approximately 1 mg of sample was reacted overnight with phosphoric acid at 70ºC and stable carbon and oxygen isotopes ratios were measured on the purified CO_2 using a SIRA II mass spectrometer. Twenty samples were analyzed for stable carbon and oxygen isotope ratios by sequential extraction of CO_2 in two steps. The first step included reaction of several tens of milligrams of sample with phosphoric acid for three hours in a water-bath at 25ºC. As a second step, the remaining sample was reacted with phosphoric acid overnight in a hot-block at 100ºC. The amount of CO_2 was measured after each step and the carbon and oxygen isotopic composition was measured using a SIRA II mass spectrometer; the precision and accuracy are difficult to specify since they will depend on the efficacy of the sequential extraction procedure and the absolute and relative amounts of different carbonate phases present, but ±0.5 ‰ seems a conservative working estimate (Table A2 in Appendix A). Carbon and oxygen isotopic values are reported and discussed in the conventional delta notation relative to Vienna Pee Dee Belemnite (VPDB).

Petrographic characterization of 19 polished thick sections (ca. 200μm in thickness), at least two from each carbonate bed, involved backscattered electron imaging with a scanning electron microscope (SEM-BSE) and the use of cathodoluminescence (CL). SEM-BSE work was done at NGU using an SEM Leo1450VP in low vacuum mode at 16 Pa, an acceleration voltage of 15 kV and a beam of 80 μA. The CL work was done at Karst Research Institute at Postojna, Slovenia, using a CL8200 Mk4 instrument operating at 15 kV beam energy and a 400 mA beam.

3.1. Carbon and oxygen isotope analyses of carbonates by sequential extraction

Twenty samples from beds #1 to #7 were analyzed for carbon and oxygen isotopes by sequential extraction of CO_2 in two steps. $\delta^{13}C$ and $\delta^{18}O$ values were measured for each step of the reaction, after 3 hours at 25ºC and after an overnight reaction at 100ºC, and marked as $\delta^{13}C_1$, $\delta^{18}O_1$ for the first and $\delta^{13}C_2$, $\delta^{18}O_2$ for the second step. Due to differences in reaction rates of calcite and dolomite (Al-Aasm et al., 1990), we expected the $\delta^{13}C_1$, $\delta^{18}O_1$ and $\delta^{13}C_2$, $\delta^{18}O_2$ to correspond to the isotopic composition of calcite and dolomite, respectively. In order to evaluate whether the data from the two steps can be reasonably considered to correspond to calcite and dolomite, we compared the amounts of calcite and dolomite determined by ICP-AES for each sample with the measured amount of CO_2 extracted after each step.

The majority of the calcite-dominated (Mg/Ca<0.1) and dolomite-dominated (Mg/Ca>0.5) samples of the Zaonega Formation show relatively small, up to 2.5 ‰ differences of $\delta^{13}C$ between the two steps of extraction (Fig. 4; Table A2). Exceptions are the calcite-dominated sample in bed #6 (difference in $\delta^{13}C$ between the two steps is 5 ‰) and two dolomite-dominated samples from the bed #1 (difference in $\delta^{13}C$ between the two steps is 4 ‰). The relatively large differences in $\delta^{13}C$ between the two steps within the samples, where geochemical data suggest a single carbonate phase of either calcite or dolomite, might be due to the extraction-related kinetic isotopic effect but more likely to isotopic heterogeneity of the sample. During dissolution of dolomite-dominated samples, when a small amount of sample reacts during the first step, anomalously ^{13}C-depleted CO_2 could be produced due to an extraction-related kinetic effect, the result being a lower $\delta^{13}C_1$ value in comparison to the $\delta^{13}C_2$. For the calcite-dominated samples a large amount of sample dissolves after the first step (ca. 60 % of the whole sample reacts in 3 hours, Al-Aasm et al., 1990) and therefore the kinetic effect appears unlikely to be the reason for the differences between $\delta^{13}C$ of the two steps. Differences between $\delta^{13}C_1$ and $\delta^{13}C_2$ can also occur in either a dolomite- or calcite-dominated sample, if isotopic heterogeneities are coupled with differences in dissolution rates, e.g. an Fe-poor calcite/dolomite has a different isotopic composition than Fe-rich calcite/dolomite.

Based on our dataset and published reaction rates for calcite and dolomite at different temperatures (Al-Aasm et al., 1990), we conclude that the results of the two-step sequential extraction method may be used as an approximation of carbon and oxygen isotope signatures of

calcite and dolomite for those samples that contain significant relative amounts of each mineral phase (>5 wt% of all carbonate). Predominance of either of the two mineral phases results in a mixed signal in either of the two steps, complicating the determination of the isotopic differences between calcite and dolomite. We have therefore interpreted the $\delta^{13}C_1$, $\delta^{18}O_1$ and $\delta^{13}C_2$, $\delta^{18}O_2$ to represent calcite and dolomite respectively for the samples with the following characteristics: i) general correspondence between amounts of calcite and dolomite determined by ICP-AES and the measured amount of CO_2 extracted at each step; and ii) presence of a significant relative amount of each mineral phase (>5 wt% of all carbonate). Other results of the sequential extraction method on the Zaonega samples can be used for determination of isotopic homogeneity of the samples and/or for assessment of the applicability of the method for the Zaonega carbonates. Large differences in $\delta^{13}C$ between the two steps for the samples containing either pure calcite or pure dolomite imply a limited applicability of the sequential extraction method for all the samples of the Zaonega Formation such that an isotopic variability a few per mil of needs to be taken into account.

4. Results

The aims of detailed sampling, geochemical analyses and petrographic characterization were: i) assessment of $\delta^{13}C$ variability within single carbonate beds; and ii) determination of mineralogy and textures of carbonate phases and associated minerals. Geochemical results include analyses of 39 samples for stable carbon and oxygen isotopes, TOC/IC, ICP-AES, and XRF for eight carbonate beds, together with the 29 additional closely spaced samples analyzed only for carbon and oxygen isotopes. The textural characterization of carbonate minerals is based on SEM-BSE and CL images of thin sections. Individual samples represent 12-cm-long quarters of the core taken continuously along the whole thickness of carbonate beds, while one bed (#5) was sampled from core to top. The positions of sample points in Figures 3 and 4 correspond to the tops of individual 12-cm-long samples. The response of carbonate beds to 5 % HCl was monitored during core logging: blue-colored lithologies in Figures 3 and 4 mark intensive reactions whereas violet-coloring indicates lithologies that did not react to the acid (in Figs. 3 and 4).

4.1. Geochemistry

Selected geochemical parameters plotted along eight carbonate beds are presented in Figure 3, and results from the carbon and oxygen analyses by sequential extraction are shown in Figure 4. Beds #1 to #6 are described together because they show similar within-bed $\delta^{13}C$ variability of several per mil, with middle portions having relatively higher $\delta^{13}C$ values compared to the margins (exception is bed #3). Beds #7 and #8 have low within-bed variation of $\delta^{13}C$ (≈2 ‰), hence their geochemical characteristics are described separately.

Beds #1 to #6

The $\delta^{13}C$ variability within these six, single beds ranges from 4 ‰ (bed #3) to 17 ‰ (bed #6; Fig. 3). All beds, except #3, display a decline in $\delta^{13}C$ values from their central parts (from -9 to +8 ‰; Table 1) outward to their margins (from -19 to -4 ‰; Table 1). For bed #3, the lowest $\delta^{13}C$ values occur at the base (-8 ‰) and increase consistently upward through the middle (-5 to -6 ‰) and to the top (-4 ‰). $\delta^{18}O$ values only show minor variation throughout the beds, with beds #1 and #6 having $\delta^{18}O$ a few per mil higher in their middle parts relative to their margins. Middle parts of all beds contain higher wt% of carbonate (IC=10–11 wt%), and therefore lower wt% of siliciclastic material in comparison to the bed margins. The main carbonate mineral in the central part of the beds is dolomite, which is Fe-Mn-rich in beds #2 to #5 but Fe-Mn poor in beds #1 and #6 (Fig. 3). Calcite prevails at the margins of all beds (exception is lower margin of bed #1), coinciding with relatively low IC and $\delta^{13}C$ in comparison to the centres of the beds. Calcite contains higher amounts of Sr, up to 320 ppm, in comparison to dolomite with Sr content below 100 ppm; an exception is dolomite in bed #3 with Sr values up to 160 ppm.

Whole-rock content of Ca is mostly stable throughout bed thickness, the exception being the upper margins of beds #3 and #6, which are considerably lower in Ca abundance. Mg whole-rock content decreases either significantly (beds #3, #4, #5, #6) or slightly towards the bed margins (beds #1 and #2), broadly matching the trend of IC and $\delta^{13}C$ (exceptions are margins of beds #1 and #3). The majority of beds with Fe-Mn-rich dolomite in the centres, (beds #2 and #5), contain Fe-Mn-rich calcite at the bed-margins; Fe-poor, Mn-rich calcite is present at the margin of bed #4 and Fe-Mn-poor calcite at the margin of bed #3. Beds #1 and #6, having Fe-Mn-poor dolomite in their centre, also contain Fe-Mn-poor calcite at their margins.

Beds #7 and #8

The main characteristic of these two beds is that there are no significant differences in geochemical compositions from their centres to margins (Fig. 3). The $\delta^{13}C$ variability is 2 ‰ in bed #7 and 0.3 ‰ in bed #8. The $\delta^{18}O$ values are stable in both beds (ca. -17 ‰ in bed #7 and -18.5 ‰ in bed #8). Amounts of carbonate and siliciclastic material are stable in bed #8 and inversely proportional in bed #7, ranging from 7 to 10.4 wt% IC and from 7 to 21 wt% SiO_2. The main carbonate phase in both beds is calcite with Sr content below 110 ppm, which is significantly lower than the Sr content of calcite in beds #1 to #6. Whole-rock content of Mg is low, only a few wt%.

4.2. Textural properties of carbonate minerals

Petrographic studies were performed to identify the carbonate components, characterize their microtextures and interrelationships, and assess genetic associations with other mineral phases. At least two thin sections were studied from each of the eight beds, one from the centre of the bed and the other close to the margin of the bed. Samples were characterized by SEM-BSE (hereafter BSE) imaging and cathodoluminescence (Figs. 5, 6 and 7). The beds with common textural properties are described together: i) beds #2 to #5 contain zoned Fe-Mn-rich dolomite; ii) beds #1 and #6 contain homogenous Fe-Mn-poor dolomites; iii) beds #7 and #8 contain low-Sr calcite.

Beds #2 to #5

The middle parts of these beds contain zoned dolomite crystals ca. 20 μm in size, either in tightly intergrown indistinct rhombohedric shapes and zones (beds #2 to #4; Figs. 5a, 5d and 5g) or rather loosely packed but well-defined rhombohedra with distinct zones; the latter is cemented by dolomite (bed #5; Fig. 5j). Using CL, dolomite is nonluminescent in all samples (e.g. Fig. 5f), only in bed #5 do rhombohedric rims and very few cores show bright red luminescence (Fig. 5l). A significant amount of calcite, in places intergrown with quartz (bed #3; Fig. 5d) and overgrowing dolomite or infilling spaces in partially dissolved dolomite, is present in the middle parts of beds #2 to #4; these beds also contain abundant mica (mostly phlogopite; talc is present in bed #2) and pyrite formed at different stages of diagenesis/metamorphism (Figs. 5b and 5d).

The margins of these beds contain mostly calcite occurring as smaller (beds #2 and #4) or larger (bed #3), irregularly shaped patches usually intergrown with either quartz (bed #2 and #3; Figs. 5b and 5e) or albite (bed #4; Fig. 5h). Albite occurs also as larger grains/patches, which could be of detrital origin or a product of albitization of older grains, for example plagioclase or sulfide. Dolomite is only present in the margin of bed #5 which contains mostly Ca and Fe-rich dolomite as cement around the dolomitic rhombohedra and some calcite (Fig. 5k). Under CL, calcite luminesces orange with a moderate to bright intensity (e.g. Figs. 5c and 5i). Micas in beds #3 to #5 and talc in bed #2 are more abundant near bed margins than in the centre of the beds.

Beds #1 and #6

The middle parts of these two beds show large, tightly intergrown dolomite crystals ca. 70 μm in size (Figs. 6a and 6e); in bed #6, the crystals are so tightly packed that their shapes are difficult to recognize, and only in places are rhombohedra observed. Dolomite crystals are mostly homogeneous in BSE imagery with slightly darker cores in comparison to the outermost parts (the transition is gradual). The contacts between crystals are straight to sutured (Fig. 6e). Under CL most dolomite crystals show very dull red luminescence, some have dull luminescent cores and bright rims, and in bed #1 a few crystals show bright-dull-bright zoning (Fig. 6c). Calcite, mica and talc are present, but in minor amounts in comparison to the margins of the same beds.

The lower margin of bed #1 mostly contains dolomite, whereas calcite is the dominant carbonate mineral at the margin of bed #6. The former displays large dolomite crystals ca. 70 μm in size and mostly tightly intergrown with recognizable rhombohedral shapes (Fig. 6b). Inner parts of the crystals are brighter in BSE images in comparison to their outer parts (Fig. 6b). Under CL, dolomite crystals are mostly zoned (dull-bright-dull luminescence), but many are dull with bright rims (Fig. 6d). Where dolomite crystals are less tightly packed, micas and organic matter occur in the interstices. Minor amounts of calcite are present. The margin of bed #6 contains calcite intergrown with quartz (dolomite is not observed, Fig. 6f). Talc and phlogopite are more abundant at the margin than at the centre of the bed.

Beds #7 and #8

Bed #8 contains large (ca. 100 μm in size) patches of irregularly shaped calcite with numerous embayments, tightly intergrown with albite (Fig. 7d). The middle part of bed #7 contains ca. 20 μm-large BSE homogeneous calcite crystals with albite intercalations; boundaries between the crystals are straight and undulate (Fig. 7a). Albite, micas (phlogopite, chlorite) and titanite are present in both beds, with albite occurring as spherical inclusions within calcite and as rectangular grains in bed #7 (Fig. 7a) and as a mineral phase intergrown with calcite in bed #8 (Fig. 7d). Micas overgrowing calcite are more abundant in bed #8. Disseminated titanite is present in both beds. Actinolite is only present in bed #8, overgrowing all mineral phases. Under CL, calcite in both beds has medium-dull red luminescence, but a few small areas are bright red (Fig. 7c).

The upper margin of bed #7 contains up to 0.5 mm large rhombohedra having a calcitic core and an outer rim of calcite (Fig. 7b). The calcite forming the core is homogenous in BSE images and contains spherical inclusions of albite of a few μm in size (Fig. 7b). The calcitic rim contains spherical inclusions of quartz a few μm in size. Numerous inclusions of quartz mark the sharp, but undulated boundaries between the core and rim (Fig. 7b). The outer boundary of the calcitic rim to the surrounding quartz matrix is irregular with numerous embayments. Titanite occurs predominantly together with micas in the quartz matrix, but also in the calcite rims and in the cores of the rhombohedra. Micas overgrow all mineral phases.

5. Discussion

5.1. Primary and secondary carbonate precipitates – textural and geochemical indications

On the basis of geochemical data, four main carbonate phases have been identified: i) Fe-Mn-poor dolomite (bed #1 and centre of bed #6) and; ii) Fe-Mn-rich dolomite (centres of beds #2 to #5); iii) calcite, relatively rich in Sr (hereafter Sr-rich calcite; margins of beds #1 to #6); and iv) calcite relatively poor in Sr (hereafter Sr-poor calcite; beds #7 and #8). Geochemical and textural properties of these four carbonate phases, relevant to their relative order of formation, are discussed below (overview of textural properties is shown in Figs. 8a-n).

The Fe-Mn-poor dolomite consists mostly of ≈70 μm-large homogenous crystals, which are very tightly intergrown and have a dull red luminescence under CL; only a few crystals (middle part of bed #1) have clearly distinguishable dull red cores and bright red rims under CL (Fig. 6c). Homogenous textures of the Fe-Mn-poor dolomite crystals imply stable conditions

during their precipitation in the sedimentary/early diagenetic environment and/or during burial recrystallization. Tight crystal intergrowth, likely developed during burial, could have prevented intensive infiltration of later fluids. The Fe-Mn-poor dolomite is overgrown by texturally later Sr-rich calcite.

The Fe-Mn-rich dolomite consists of ≈20 μm large, zoned rhombohedric crystals, which are mostly nonluminescent under CL; only a few crystals (bed #5) show bright red luminescent rims and very few of them possess also luminescent cores. Nonluminescence under CL is presumed to be due to quenching by iron in these cases (Machel, 2000). Zoned crystals indicate variable geochemical conditions during precipitation, either due to a closed system as the pore waters are progressively depleted in certain species, or due to infiltration of fluids with a different geochemical signature. The Fe-Mn-rich dolomite is overgrown by the Sr-rich calcite, indicating relatively early formation of Fe-Mn-rich dolomite in relation to the calcite.

The Sr-rich calcite in beds #1 to #6 forms irregular patches containing either albite or quartz inclusions and overgrows both types of dolomite in the centres of the beds; this calcite thus formed relatively late with respect to dolomite. The amount of Sr-rich calcite varies along the thickness of each bed, being least at the centres of the beds and greatest at the bed-margins: at the margins of beds #2, #3, #4, and #6, we find only calcite. While the timing of calcite precipitation is more difficult to verify at the bed margins because only one carbonate phase is present, we interpret the calcite at the centres and at the margins of the same beds as an identical phase due to textural similarities (Figs. 5-7). The $\delta^{13}C$ values of Sr-rich calcite in the studied beds are between -19 ‰ and -4 ‰ (samples with Mg/Ca<0.1 in Fig. 8a), which is as much as 17 ‰ lower in comparison to the dolomite-dominated samples occurring within the same beds (Figs. 3, 4, 8a). Significantly different carbon isotope composition, and relatively late formation of Sr-rich calcite in comparison to dolomite implies different conditions for the dolomite and Sr-rich calcite formation. This, together with the co-occurrence of calcite with secondary albite and quartz, suggests that the Sr-rich calcite formed later in the post-depositional history of these rocks than the dolomite.

The Sr-poor calcite does not occur in conjunction with any other carbonate phase, making it difficult to assess its place in the paragenetic sequence. Texturally, however, the Sr-poor calcite in beds #7 and #8 is comparable to the Sr-rich calcite on the outer margins of beds #1 to #6; i.e. mostly irregularly shaped calcite patches inter-grown with either quartz or albite. Further,

the Sr-poor calcite is associated with actinolite in bed #8, which is located 20 m above a 70-m-thick mafic intrusion (Fig. 2). It is most probable that the Sr-rich and Sr-poor calcite formed under similar conditions, the Sr-poor calcite probably at higher temperatures as indicated by the presence of actinolite, implying precipitation of the Sr-poor calcite later than the dolomite. Rhombohedral calcite patches in bed #7 (Fig. 7b) could have formed through complete calcitization of dolomite rhombohedra. The large size of the former suggests their initial formation, or recrystallization, during burial and a later formation of Sr-poor calcite. Small Sr-poor calcite crystals in the centre of bed #7 have well preserved crystal boundaries and likely represent the least altered sedimentary calcite. The $\delta^{13}C$ and $\delta^{18}O$ values of all Sr-poor calcite, however, are low and fall within the range of the $\delta^{13}C$ and $\delta^{18}O$ values of the Sr-rich calcite (Fig. 8d), inferred to reflect post-depositional formation or alteration of earlier carbonates. It is therefore most probable that the small calcite crystals in bed #7 are also of post-depositional origin, or at least their carbon and oxygen isotopic composition have been reset. There may be some primary calcite in bed #7, but the carbon isotope composition of this bed ($\delta^{13}C$ = -11 ‰) and co-occurrence of calcite with albite or quartz is similar to the clearly post-depositional calcite in other beds.

In summary, dolomites of both types likely represent primary or early diagenetic carbonate precipitates within the Zaonega Formation, whereas calcite mostly formed as a relatively late carbonate phase precipitating under variable post-depositional, including hydrothermal conditions. This latter interpretation is based on the observation that, within the same samples, calcite overgrows dolomite and has textural association with secondary quartz and albite.

5.2. Formation of secondary carbonates

The calcite ± talc ± phlogopite ± actinolite paragenesis observed in carbonate beds indicates that the following volatilization reactions could have been the pathway influencing $\delta^{13}C$ and $\delta^{18}O$ composition of residual dolomite and newly formed calcite (Bucher and Frey, 2002; Shieh and Taylor, 1969):

Eq. (1): $6[Ca, Mg(CO_3)_2] + 8SiO_2 + 2H_2O \rightarrow Mg_6[Si_8O_{20}](OH)_4 + 6CaCO_3 + 6CO_2$ (1)

Eq. (2); $3[Ca, Mg(CO_3)_2] + KAlSi_3O_8 + H_2O \rightarrow KMg_3AlSi_3O_{10}(OH)_2 + 3CaCO_3 + 3CO_2$ (2)

460 The CO_2 produced by such reactions can be enriched in ^{13}C and ^{18}O in comparison to the original
461 dolomite due to equilibrium isotopic fractionation between CO_2 and dolomite (Shieh and Taylor,
462 1969; Valley, 1986), and in high-temperature greenschist metamorphic conditions the $\delta^{13}C$ of the
463 calcite produced was found to be up to 4 ‰ lower than the co-occurring dolomite (e.g. Melezhik
464 and Fallick, 2003; Melezhik et al., 2003). The mineralogy of carbonate beds #1 to #6 is
465 consistent with such alterations, containing reactants (dolomite, quartz) and all the products
466 (phlogopite, talc, and calcite). The reason for the lack of K-feldspar in carbonate beds could be
467 its initial absence, or could be due to complete reaction of K-feldspar with the co-occurring
468 dolomite. Mineral associations together with ^{13}C-depletion of calcite imply that Sr-rich calcite
469 formed as a metamorphic reaction product as described by the equations above. The magnitude
470 of $\delta^{13}C$ depletion of calcite relative to dolomite is as much as 17 ‰. This cannot be due to
471 volatilization alone and requires a ^{13}C-depleted fluid to explain the low $\delta^{13}C$ values of the calcite
472 (Valley, 1986). It is known that large changes in the carbon and oxygen isotope compositions of
473 carbonate rocks can be due to extensive fluid-rock interaction at low metamorphic temperatures
474 (e.g. Guerrera et al., 1997). As the deposition of the Zaonega rocks was accompanied by
475 contemporaneous vigorous magmatic activity, formation of peperites, oil generation and seeping
476 and spilling of hydrocarbons (Črne et al., 2013a,b; Melezhik et al., 2009; Qu et al., 2012), it is
477 reasonable to infer that intense hydrothermal fluid circulation supplied water, silica, CO_2 (likely
478 as carbonic acid) and CH_4 to the depositional system (Strauss et al., 2013).
479 There are abundant possible ^{13}C-depleted sources within the Zaonega Formation:
480 volcanic CO_2 with assumed $\delta^{13}C$ ca. -5 ‰, ample organic matter with $\delta^{13}C$ between -25 and -42
481 ‰ (Filippov and Golubev, 1994; Kump et al., 2011; Qu et al., 2012) and its catagenetic products
482 (including organic acids and biogenic methane), and inferred thermogenic methane (Qu et al.,
483 2012) with $\delta^{13}C$ likely between -20 and -50 ‰ (for precursor organic carbon at -25 ‰)
484 (Whiticar, 1999). Although volcanic CO_2 might have played an important role in hydrothermal
485 fluids, it does not in any clear way facilitate precipitation of calcite with $\delta^{13}C$ values lower than -
486 5 ‰. Oxidation of organic matter forming CO_2 or bicarbonate must have occurred in order to
487 explain the very low $\delta^{13}C$ values of the secondary calcite. No measured $\delta^{13}C$ of secondary
488 carbonate demands the involvement of oxidized CH_4, although we recognize that it is
489 geologically reasonable that both biogenic and thermogenic methane were available at various
490 times. Sedimentary rocks within the drilled succession are rich in TOC; mudstones, which are by

491 far the most abundant lithology encompassing the studied carbonate beds in FAR-DEEP cores
492 12AB and 13A, may contain more than 20 wt% of TOC (Črne et al, 2013a,b).
493 Decomposition of organic matter can be facilitated by thermochemical and bacterial
494 processes of sulfate, iron, or manganese reduction, all plausibly sourced from minerals within the
495 Tulomozero and Zaonega formations, and from seawater; H_2O itself is a likely source of oxygen
496 once the oil window is reached. The sulfur isotope data from the Zaonega (Shatsky, 1990) and
497 Pilgujarvi Formations (Melezhik et al., 1998), the latter a unit on the Kola Peninsula that is
498 broadly correlative to the Zaonega Formation (Hannah et al., 2006), indicate presence of sulfate
499 in contemporaneous sea-water enabling sulfate reduction during deposition (Reuschel et al.,
500 2012). Sulfate may have also been supplied from the underlying Tulomozero Formation
501 containing abundant calcitized sulfates (Brasier et al., 2011; Melezhik et al., 2005) and even
502 thick anhydrite beds (Morozov et al., 2010). As the formation of ^{13}C-depleted calcite occurred
503 relatively late in comparison to the earlier formed dolomite (that was probably of sedimentary
504 and/or early diagenetic origin), it is likely that low ^{13}C carbon was supplied from different depths
505 during burial of the Zaonega sediments (cf. Irwin et al., 1977), followed by metamorphic
506 reactions and possible hydrothermal alterations. Whatever the source of the oxidants and
507 whatever the processes of oxidation, the solid organic matter or fluid hydrocarbons of the
508 Zaonega Formation had ample opportunity to be oxidized and supply ^{13}C-depleted CO_2 to the
509 post-depositional fluids.
510 The isotopic uniformity of carbonate beds #7 and #8, located in proximity to thick mafic
511 bodies, is tentatively interpreted to be the result of homogenization of $\delta^{13}C$ and $\delta^{18}O$ due to
512 pervasive post-depositional fluid infiltration associated with those intrusions. A somewhat
513 similar isotopic effect was reported by Frauenstein et al. (2009) from dolostones in near contact
514 with the Bushveld intrusive complex. The absence of talc within beds #7 and #8 could reflect the
515 actions of pervasive CO_2-rich fluid flow and/or high temperatures (>450 ºC) within the lower
516 part of the succession, hindering talc formation and preservation (e.g. Bucher and Frey, 2002).
517 Alternatively, bed #7 may represent either a sedimentary layer or an early diagenetically formed
518 concretion with an original calcitic mineralogy, though (as with all carbonates here) now likely
519 recrystallised.
520 We interpret the pervasive calcitization of the margins of carbonate beds #1 to #6 as
521 caused by: i) reactions between quartz-rich mudstone and dolomite in the presence of

hydrothermal fluids; and ii) potential early lithification of the carbonates relative to the organic-rich mudstones resulting in differences in permeability between the two lithologies, thus channeling fluid flow at lithological boundaries. A larger amount of secondary calcite at the bed margins fits a hypothesis of flow of post-depositional fluids along lithological contacts. The intensity of rock-fluid interaction can be approximated by differences in composition between newly formed calcite and its presumed dolomite precursor, up until the point of total resetting. In beds #3 and #4, the calcite is Fe-Mn-poor even though the dolomite within the same bed is Fe-Mn-rich. This can be interpreted as due to greater fluid mobilization in this part of the stratigraphy: both beds are located in close proximity to asphalt spills (Fig. 2; bed #3 is also closer to the magmatic body). High amounts of Fe and Mn in dolomite and calcite in beds #2 and #5 suggest a partly inherited geochemical signature of calcite from its dolomite- precursor and therefore imply less intense fluid mobility and/or interaction in this part of the succession. Less prone to secondary overprints were those carbonate beds that: i) contain tightly intergrown dolomite crystals that inhibited pervasive fluid infiltration; and ii) have the highest initial carbonate content, thereby buffering the carbon isotopic system to a larger degree ($\delta^{13}C$ is correlative to IC, see Fig. 8c). Noteworthy, though, is that all studied samples show variable signs of alteration as evidence that even the 'best' samples (in terms of preserving original/primary carbonate geochemical signatures), contain secondary calcite (e.g. BSE image of the sample from the centre of bed #6 shown in Fig. 6e).

Regional greenschist metamorphism at 1.8 Ga could have additionally altered the geochemistry of the Zaonega carbonate rocks. The Zaonega Formation as a whole underwent low- to middle-temperature greenschist-grade regional metamorphism with temperatures of 300 to 350°C (Volodichev, 1987); the presence of actinolite (bed #8) indicates locally higher temperature conditions close to the mafic intrusions. Secondary actinolite and albite-calcite intergrowth in proximity to contacts with peperites implies formation of these minerals in relation to mafic intrusions and therefore prior to complete lithification. It is therefore likely that some calcite formed locally as a secondary mineral of hydrothermal/metasomatic origin before the regional metamorphic event, while some might have formed earlier, perhaps during early (syn-sedimentary?) diagenesis (e.g. bed #7), and we do not entirely exclude a possible initial calcitic mineralogy of some carbonate beds.

In summary, the lower part of the Zaonega succession might have experienced extensive fluid circulation causing complete calcitization of carbonate beds, although their original calcite mineralogy cannot be excluded. In the upper part of the succession calcitization was restricted to bed-margins. Samples in centres of beds, containing largely dolomite and little calcite, are most easily interpreted as belonging to the least-altered carbonate samples of the Zaonega Formation, and as the most likely to have preserved the $\delta^{13}C$ signal of ambient sea-water.

5.3. Preliminary implications for the Zaonega $\delta^{13}C$ record and global Paleoproterozoic events

Our results show that all studied carbonate samples have been to varying degrees affected by post-depositional alteration. The least altered carbonate samples are in the centres of carbonate beds composed mainly of dolomite in a tightly intergrown crystal texture and containing little calcite. One current approach to identify the best-preserved carbonates within the Zaonega Formation is identifying those with the highest amount of dolomite, as these are the samples with the highest carbon isotope buffering capacity against secondary and subsequent alterations. We have therefore used (Mg/Ca)*IC (Mg/Ca ratio multiplied by inorganic carbon) as an approximation of the amount of dolomite to identify the best-preserved samples from this study and those in the study of Kump et al. (2011) on the same drill core (Fig. 8b). Using our (Mg/Ca)*IC metric, samples were categorized into four groups of assessed apparent alteration: minor/moderate, significant, extensive, and complete (arbitrary boundaries at (Mg/Ca)*IC = 6; 3.5; 1; see Fig. 8b). Altogether 7 samples were found to belong to minor/moderately altered caltegory: 5 samples from the set of 39 samples of this study and 2 samples from the dataset of Kump et al. (2011). We acknowledge that such a discriminatory classification is inherently biased against the possibility that a few of the calcites could have well-preserved carbon isotope signatures, but our aim here is solely to ascertain the samples we can be most confident about.

Post-depositional alteration of the Zaonega carbonate rocks is also likely indicated by cross-plots of $\delta^{13}C$ and $\delta^{18}O$, as decreasing $\delta^{18}O$ values correspond to lower $\delta^{13}C$ values within single beds (beds #1 and #6 in Fig. 8d). The non-primary calcites show a trend of decreasing $\delta^{18}O$ values with depth, whereas the dolomites have $\delta^{18}O$ values slightly above the calcite $\delta^{18}O$ values (Fig. 9). Well-defined stratigraphic trend of $\delta^{18}O$ implies that the oxygen isotope composition of calcite represents complete homogenization or formation during post-depositional alteration and that the alteration is successively stronger down the stratigraphy (Fig.

9). Oxygen isotope compositions can show complete homogenization as per those beds with relatively low $\delta^{18}O$ values overlapping with those of non-primary calcite (beds #2 to #5, #7, #8 in Fig. 8d), or they can show less modification including distinctly higher $\delta^{18}O$ values than the calcite, as per beds #1 and #6 (Fig. 8d). We have therefore used values of $\delta^{18}O$ for additional screening of those samples, that were found to be minor to moderately altered on the basis of (Mg/Ca)*IC metric. Minor to moderately altered samples were further subdivided such that those with the highest $\delta^{18}O$ were interpreted to be least altered and most likely to be archiving $\delta^{13}C$ values closest to the initial composition (Fig. 8d). Two out of eight studied beds contain minor to moderately altered samples: the line perpendicular to the $\delta^{13}C$ vs. $\delta^{18}O$ alteration trend defines the least altered sample within each carbonate bed. Both minor to moderately altered samples from the data-set of Kump et al. (2011) on the basis of (Mg/Ca)*IC metric are here considered as least altered carbonate samples.We have linked all the samples to the Zaonega stratigraphy (Fig. 9) and these show a negative $\delta^{13}C$ shift with amplitude larger than 20 ‰ (Fig. 9). Comparing screened to unscreened samples shows that the difference in values between the least- to most-altered is larger than 10 ‰ within the same bed or within a 20–m-thick stratigraphic interval. Hence, using our selective criteria, the amplitude of the $\delta^{13}C$ shift based on un-screened samples cannot be straightforwardly interpreted as a result of changes in the global carbon cycle.

Examining all data, those in this study and those reported by Kump et al. (2011), only four carbonate samples from two stratigraphic intervals can be considered convincingly in the category least altered. These samples have $\delta^{13}C$ values of +8 ‰ and +4 ‰ in the middle part of the section (at 250 m and 239 m in core 12AB), and -4 ‰ and -2 ‰ at the top (at 2 m in 12AB and at 58 m in 13A, respectively; Fig. 9). Thus, using our admittedly strict screening criteria, least-altered $\delta^{13}C$ values define a stratigraphic profile that is considerably different from the one reported previously by Kump et al. (2011) (Fig. 9). If the least altered carbonates formed in equilibrium with the $\delta^{13}C$ of the global CO_2, we can make the following conclusions about the $\delta^{13}C$ of marine and atmospheric carbon at the time of deposition of the Zaonega sediments: i): i) stratigraphically lowermost least-altered samples (250 and 239 m in core 12AB) have $\delta^{13}C$ values of +8 and +4 ‰, which are higher from that of the present; ii) among so far studied carbonate samples, none is in the least-altered category in the stratigraphic interval between 239 m and 2 m in drillcore 12AB; conclusions about the changes in the global carbon cycle during the time of deposition of this stratigraphic interval are currently not possible; and iii) the top of

614 the section is typified by $\delta^{13}C$ values of -4 ‰ and -2 ‰, which are lower from that at the present.
615 (Fig. 9).
616 Environmental conditions specific to the Paleoproterozoic Onega Basin, such as ample
617 organic matter, petroleum generation and seepage (Melezhik et al., 1999; 2009; Qu et al., 2012;
618 Strauss et al., 2013) could have influenced and lowered the $\delta^{13}C$ of the local dissolved inorganic
619 carbon pool. If the primary carbonates formed in such restricted conditions, they could reflect
620 more of a basinal than global $\delta^{13}C$ signal, whereas the non-primary carbonates should provide a
621 proxy to $\delta^{13}C$ of burial and metamorphic fluids. However, the inferred restricted basinal
622 conditions should not directly affect the isotopic composition of carbonate shedded to the
623 Zaonega basin from the shallow-water environment, which we infer as the main mechanism of
624 primary carbonate deposition based on sedimentological evidence. Much of the Zaonega
625 stratigraphy shows signs of post-depositional alteration and few least-altered samples were
626 convincingly recognized. This suggests that some primary carbonate supplied from the
627 environmentally decoupled shallower settings site might have experienced post-depositional
628 alteration in organic-rich environments in their final depositional location. We should therefore
629 apply caution when using non-discriminated $\delta^{13}C$ data of the Zaonega carbonate rocks to infer
630 functioning of the Paleoproterozoic global carbon cycle. Given these caveats, further detailed
631 sedimentological and geochemical investigations of the Zaonega rocks, as well as carbonates and
632 organic matter of other sedimentary units of similar age elsewhere, are required to corroborate
633 the existence of a major perturbation of the global carbon cycle at this time (e.g. Kump et al.
634 2011).
635
636 **6. Conclusions**
637 Based on detailed textural and geochemical characterization of representative samples from the
638 carbonate rocks of the Paleoproterozoic Zaonega Formation, Karelia, Russia,we conclude:

639 i) Dolomite is the early, most primary carbonate phase preserved within the
640 Zaonega Formation whereas the majority of the calcite formed during progressive
641 burial accompanied by possible hydrothermal alteration and metamorphic
642 carbonate-silicate reactions.

ii) While many studied carbonate samples have been affected by post-depositional alteration, the samples most easily interpreted as least-altered contain high amounts of dolomite represented by tightly-intergrown crystals, and are located in the central parts of thicker carbonate beds. These yield values of $\delta^{13}C$ of 8 ‰ in the middle part of the succession and decline to -4 ‰ in the topmost part.

iii) Extensive fluid circulation has permeated through the Zaonega succession causing secondary calcitization of carbonate bed-margins and apparent complete calcitization of some thin carbonate beds in the lowermost parts of the stratigraphy close to the gabbro sill.

iv) Calcite-talc±phlogopite±actinolite mineral paragenesis suggests calcitization occurring through reactions of dolomite with quartz, or possibly K-feldspar, in the presence of fluids. The possibility of an initial calcitic mineralogy of carbonates that might represent sedimentary layers and concretions needs further assessment.

v) When calcite and dolomite occur within the same carbonate bed, and the former is significantly depleted in ^{13}C in comparison to the dolomite, this suggests the formation of calcite due to infiltration of ^{13}C-depleted fluid probably sourced from volcanic CO_2 and oxidation of organic matter.

vi) In most intervals, the $\delta^{13}C$ signal of the primary carbonate lithologies has been variably modified such that previously published carbon isotopic profiles of the Zaonega Formation based on whole rock analyses should be viewed cautiously with respect to their utility in assessing the Paleoproterozoic carbon cycle.

vii) The apparent scarcity of least-altered carbonate rocks highlights the need for additional study of all such units used to track the Paleoproterozoic carbon cycle during the Paleoproterozoic oxidation of the Earth and the importance of careful assessment for post-depositional alteration on the basis of geochemical and petrographic properties.

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676

677 **Appendix A. Supplementary data**

678 Supplementary data, Table A1 and A2, can be found at…

679

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Figure captions

Fig. 1. Geological map of the Lake Onega area in central Karelia showing locations of the FAR-DEEP drillholes that targeted the Zaonega Formation. The Tulomozero Formation preserves the Lomagundi-Jatuli isotopic signal.

Fig. 2. Lithostratigraphic columns of the FAR-DEEP drillholes 12AB and 13A (after Črne et al., 2013a,b) with marked stratigraphic positions of the carbonate beds selected for this study.

Fig. 3. Selected carbonate beds with lithological information and geochemical parameters. Beds #1 and #2 are from drillhole 13A; beds #3 to #8 are from drillhole 12AB.

Fig. 4. Carbon and oxygen isotope profiles of carbonate beds #1 to #7.

Fig. 5. SEM-BSE and CL images of samples from the centres (left column) and margins (right column) of carbonate beds #2 to #5 from drillholes 13A and 12AB. All scale bars show 100 μm. (a) SEM-BSE image of large dolomite crystals, as much as 20 μm in size, which are zoned and tightly intergrown. Overgrowing the dolomite are calcite, mica and talc; calcite occurs as irregular patches of different size (centre of bed #2; sample 13A-144.27 m). (b) SEM-BSE image showing calcite containing a few μm-scale rounded intercalations of quartz (marked by white arrows). Also present are pyrite grains, partly overgrown by calcite. Mica is overgrowing both calcite and pyrite (margin of bed #2; sample 13A-144.39 m). (c) CL image showing bright and dull red luminescence of calcite (margin of bed #2; sample 144.39 m). (d) SEM-BSE image of dolomite rhombohedra as large as 20 μm, which are zoned and tightly intergrown. Quartz is present as dark, irregular patches in places overgrown by calcite containing spherical intercalations of quartz. Calcite, mica and pyrite overgrow the dolomite (centre of bed #3; sample 12B-126.88 m). (e) Large, irregular patches of calcite containing spherical intercalations of quartz are overgrowing the quartz-mica matrix. Small, irregular grains of pyrite are disseminated throughout the sample (margin of bed #3; sample 12B-126.52 m). (f) CL image showing red luminescence of calcite, whereas dolomite, micas and pyrite are non-luminescent (centre of bed #3; sample 12B-126.88 m). (g) Homogenous dolomite rhombohedra overgrown by mica and calcite, the latter containing intercalations of quartz (centre of bed #4; sample 12B-162.99 m). (h) Calcite, with spherical intercalations of albite (marked by white arrows), overgrowing mica. Large either rectangular or irregular patches of albite overgrow mica and calcite. Pyrite is present as small grains and large cubes, the latter overgrowing mica, calcite and albite (margin of bed #4; sample 12B-163.13 m). (i) CL image of dull to bright red luminescent calcite and dark, non-luminescent pyrite, mica and albite (margin of bed #4; sample 12B-163.13 m). (j) SEM-BSE image of zoned dolomite rhombohedra cemented together by dolomite cement and in places surrounded by organic-matter (black) (centre of bed #5; sample 12B-183.4 m). (k) SEM-BSE image of dolomite rhombohedra composed of a dark core and a bright rim, cemented by large amount of homogenous dolomite cement. Some calcite containing intercalations of quartz is overgrowing the dolomite. Mica overgrows both, dolomite and calcite (margin of bed #5; sample 12B- 183.11 m). (l) CL image showing mostly red luminescence of rims of the

dolomite rhombohedra, but also some luminescent cores. The bulk of the dolomite is non-luminescent (centre of bed #5; sample 12B-183.4 m).

Fig. 6. SEM-BSE and CL images of samples from the centres (left column) and margins (right column) of carbonate beds #1 from drillhole 13A and #6 from drillhole 12AB. All scale bars show 100 μm. (a) SEM-BSE image of mostly homogenous dolomite crystals, which are tightly intergrown, with straight boundaries between the crystals. Margins of the dolomite crystals are slightly brighter than the crystal cores. Minor amounts of calcite and mica are present, calcite mostly occurring as irregular patches (centre of bed #1; sample 13A-58.16 m). (b) SEM-BSE image of rhombohedral dolomite crystals, mostly tightly intergrown with straight contacts, but also loosely packed and surrounded by organic-matter (black). A few irregular calcite patches are present either overgrowing dolomite rhombohedra (lower right part of the photo) or as precipitates along the dolomite crystal boundaries (margin of bed #1; sample 13A-58.45 m). (c) CL image showing dull red luminescence of dolomite crystals and some bright red luminescence of crystal-margins (centre of bed #1; sample 58.16 m). (d) CL image of dolomite with dull and bright red zones (margin of bed #1; sample 58.45 m). (e) SEM-BSE image of homogenous dolomite crystals, very tightly intergrown as indicated by sutured crystal boundaries, recognizable due to their darker colour. Some mica and a few small patches of calcite are present, calcite mostly along the dolomite crystals but clearly overgrowing dolomite (centre of bed #6; sample 12B-249.5). (f) SEM-BSE image of quartz-rich sample containing patches of calcite with spherical intercalations of quartz (margin of bed #6; sample 12B-248.7 m).

Fig. 7. SEM-BSE and CL images of samples from the centres (left column) and margins (right column) of carbonate beds #7 to #8 from drillhole 12AB. All scale bars show 100 μm. (a) SEM-BSE image of calcite consisting of homogenous crystals of various shapes and as much as 30 μm in size, in places rhombohedra can be recognized. Albite occurs mostly as rectangular grains (?replacing pyrite) but also as small intercalations of spherical shape. Some mica and small titanite crystals are also present (centre of bed #7; sample 12B-283.02 m). (b) Up to 0.5 cm large rhombohedra are composed of calcitic core and calcitic rim, the boundaries between the two are marked by spherical intercalations of quartz; rhombohedra cores contain intercalations of albite (margin of bed #7; sample 12B-282.65 m). (c) CL image of dull red to bright red luminescent calcite and nonluminescent albite (centre of bed #8; sample 12B-283.02 m). (d) SEM-BSE image of large, irregular calcite patches having undulating contacts with surrounding albite. Much mica and some titanite are also present. Actinolite needles overgrow all minerals phases (margin of bed #8; sample 12B-394.30 m).

Fig. 8. (a) Cross-plotted values of $\delta^{13}C$ and Mg/Ca ratio with separate symbols for each of the studied beds. (b) Cross-plotted values of $\delta^{13}C$ and (Mg/Ca)*IC, a product between the Mg/Ca ratio and inorganic carbon (IC) content, with separate symbols for each of the studied beds. Also plotted are data points for samples analysed for $\delta^{13}C$ by Kump et al. (2011). Thresholds of (Mg/Ca)*IC are used for approximation of sample alteration. (c) Cross-plotted values of $\delta^{13}C$ and IC with separate symbols for each of the studied beds. (d) Cross-plotted values of $\delta^{13}C$ and

939 $\delta^{18}O$ with separate symbols for each of the studied beds. The two minor to moderately altered
940 samples from Kump et al. (2011), recognized on the basis of (Mg/Ca)*IC (Fig. 9b), are also
941 plotted. The $\delta^{13}C$ vs. $\delta^{18}O$ alteration trends for the samples located in the two beds, which
942 contain minor to moderately altered samples, are parallel and indicated by the thick grey arrows.
943 The line cutting off the least altered samples, on the basis of the data presented, is oriented
944 perpendicular to the $\delta^{13}C$ vs. $\delta^{18}O$ alteration trend.

945 **Fig. 9.** $\delta^{13}C$ and $\delta^{18}O$ values of samples from this study and the study of Kump et al. (2011)
946 plotted along the combined lithostratigraphic column of drillholes 12AB and 13A. The samples
947 are divided into four groups with different alteration grades, which correspond to the amount of
948 dolomite within the sample. The least altered carbonate samples have the largest symbols with a
949 thick black line and are denoted with an asterisk.

950