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Sample-scale carbon isotopic variability and diverse biomass in the Paleoproterozoic Zaonega Formation, Russia

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ABSTRACT

The stratigraphic record of organic matter in the c. 1.97 Ga Zaonega Formation (ZF), Onega Basin, northwestern Russia, exhibits a distinct negative $\delta^{13}C$ excursion ($\delta^{13}C_{org}$ from −25 to −40‰ VPDB), which was previously interpreted either to reflect a disturbance in the global carbon cycle after the Great Oxidation Event, or to have been caused by an increase in basinal methanotrophic activity. In order to assess the nature of primary biomass and the effects of post-depositional alteration, we here report the sample-scale carbon isotopic characteristics of organic matter in two drill cores from the ZF, covering 500 m of stratigraphy, by using secondary ion mass spectrometry (SIMS). The results confirm that the organic matter has to a large extent preserved the primary isotopic signatures, whereas secondary effects are limited (< 4‰). The sample-scale isotopic heterogeneity, defined as the difference between the maximum and minimum $\delta^{13}C$ values obtained by SIMS from every individual sample, increases from typically < 5‰ in the lower part of stratigraphy to systematically larger values (up to 11‰) in the upper part, which coincides with the decreasing trend of $\delta^{13}C_{org}$ of bulk samples from −25 to −40‰. Samples with either relatively high (c. −25‰) or low (c. −40‰) $\delta^{13}C_{org}$ values have small sample-scale isotopic heterogeneities, while samples with intermediate $\delta^{13}C_{org}$ values (between −25 and −40‰) have significantly larger heterogeneities. These observations imply the co-existence of photoautotrophic and methanotrophic biomass during deposition of the upper part of the stratigraphy. Our study provides insight into the carbon isotopic characteristics of organic matter and suggests that the negative excursion of $\delta^{13}C_{org}$ in the ZF is induced by a methanotrophic microbial ecosystem sustained by seepage of thermogenic methane during the deposition of the ZF and contemporaneous igneous activities.

1. Introduction

The global carbon cycle is inferred to have experienced significant perturbations during the Archean-Proterozoic transition as indicated by the carbon isotopic excursions preserved in several sedimentary successions. These excursions include: the negative shift in $\delta^{13}C$ of organic carbon ($\delta^{13}C_{org}$) in the 2.72–2.57 Ga Fortescue and Hamersley Groups in Australia (Hayes, 1994; Eigenbrode and Freeman, 2006), the positive shift in $\delta^{13}C$ of carbonates ($\delta^{13}C_{carb}$) during the 2.2–2.06 Ga Lomagundi-Jatuli Event (Karhu and Holland, 1996; Melezhik et al., 2007; Bekker et al., 2008; Melezhik and Fallick, 2010; Martin et al., 2013a, 2013b; Melezhik et al., 2015) followed by a short-term post-Lomagundi positive $\delta^{13}C_{carb}$ excursion at ca. 2.03 Ga recorded by the Wooly Dolomite (Bekker et al., 2016), the negative shift in $\delta^{13}C_{org}$ in the 2.1 Ga Francevillian series in Gabon (Gauthier-Lafaye and Weber, 2003; Horie et al., 2005), and the negative shift in $\delta^{13}C_{org}$ in the 1.97 Ga Zaonega Formation (ZF) in Russia (Kump et al., 2011; Qu et al., 2012; Melezhik et al., 2015).

These carbon isotopic anomalies are usually correlated to other geochemical and geological records during the Neoarchean-Paleoproterozoic time interval, and interpreted as episodes of global environmental changes, such as the variations of oceanic redox

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conditions and ocean-atmosphere oxygen level (Asael et al., 2013; Schrag et al., 2013; Fru et al., 2016), the increased activity of methanotrophs (Hayes, 1994; Eigenbrode and Freeman, 2006), the enhanced primary production and burial rate of ^{13}C-depleted organic carbon due to increased nutrient supply from oxidative weathering after the Great Oxidation Event (Karhu and Holland, 1996; Campbell and Allen, 2008; Bekker and Holland, 2012; Papineau et al., 2013), the oxidation of atmospheric methane and the subsequent global glaciations (Brasier et al., 2013), the expansion and contraction of the seawater sulfate reservoir (Planavsky et al., 2012; Scott et al., 2014; Blättler et al., 2018; Ossa et al., 2018), and the ^{13}C-depletion in the atmospheric CO_2 and marine dissolved inorganic carbon (DIC) due to extensive weathering of organic-rich rocks and assimilation of ^{13}C-depleted inorganic carbon by photoautotrophs (Kump et al., 2011; Canfield et al. 2013).

The ZF in Karelia, Russia, recorded geobiological processes in the final stage of the Neoarchean-Paleoproterozoic carbon cycle perturbations (Kump et al., 2011; Qu et al., 2012; Lepland et al., 2013; Melezhik et al., 2015). It contains organic-rich rocks with extremely high concentrations of total organic carbon (TOC) up to 98% (weight percent), representing lithified oil reservoirs (Melezhik et al., 2004). The stratigraphic succession of the ZF records an upward decreasing trend in $\delta^{13}C_{org}$ from approximately −25 to −40‰ (VPDB), which has been interpreted to reflect a global ^{13}C-depletion in atmospheric CO_2 and marine DIC, either due to CH_4 oxidation (Yudovich et al., 1991) or due to enhanced weathering of organic-rich rocks after the Great Oxidation Event (Kump et al., 2011). Alternatively, this negative shift in $\delta^{13}C_{org}$ is proposed to record a basinal methanotrophic event, stimulated by seepage of thermogenic methane that was generated due to the interaction of magmatic intrusions with organic matter-bearing strata, coeval with sedimentation (Qu et al., 2012).

All the above interpretations rely on the prerequisite that the carbon isotopic compositions found in these successions faithfully record the signatures from primary biomass. The ZF experienced a complex geological history (Qu et al., 2012; Melezhik et al., 2012), which could have modified the primary carbon isotopic composition of organic matter. It is therefore important that more detailed studies are carried out on organic matter preserved in the ZF.

In this study, we focus on the sample-scale carbon isotopic characteristics of organic matter preserved in the ZF, combining isotopic data with petrographic features, and investigate stratigraphic variations along the 500-metre lithological sequence. The objectives are: 1) to investigate the post-depositional processes that could have affected the carbon isotopic composition of organic matter; 2) to evaluate to what extent the organic remains preserved information from primary biomass; 3) to reconstruct the microbial ecosystem during deposition of the ZF and assess if the carbon isotopic excursion reflects local methanotrophy or global variation of the carbon cycle.

2. Geological setting

The ZF, at the south eastern margin of the Fennoscandian Shield, in central Karelia (Fig. 1), north western Russia, forms part of a supracrustal succession that accumulated in the Paleoproterozoic Onega Basin. This basin developed on the rifted margin of the Karelian craton at the continental edge in the Svecofennian Ocean (Galdobina, 1987; Melezhik et al., 1999). The ZF consists of a c. 1500 m-thick deep water succession of interbedded organic-rich siliceous calstic and carbonate sediments, mafic lava flows, tuffs and magmatic intrusions (Melezhik et al., 1999, 2004; Črne et al., 2012a, 2012b). The presence of several packages of lava flows and magmatic intrusions throughout the ZF indicates the sedimentary deposition occurred in a magmatically- and hydrothermally-active setting. The underlying carbonate rocks of the Tulomozero Formation recording the Lomagundi-Jatuli Event indicate a shallow-water, evaporitic environment in a mixed non-marine and carbonate shelf (Galdobina, 1987; Melezhik et al., 2005; Campbell and Allen, 2008; Brasier et al., 2011; Blättler et al., 2018).

Organic matter in the ZF experienced local contact metamorphism from the mafic intrusions and lava flows, and also regional greenschist-facies metamorphism. Organic matter occurs as autochthonous kerogen residues and allochthonous (migrated) pyrobitumen. Numerous pyrobitumen veins, usually with quartz and lesser amounts of mica and carbonate, can be observed throughout the ZF as well as in the overlying sedimentary and volcanic rocks (Melezhik et al., 1999, 2009). Pyrobitumen-rich intervals are found in the contact zones of magmatic bodies as interlayers in sedimentary rocks. The association of pyrobitumen-rich intervals with mafic lava flows and contemporaneous intrusions is consistent with a contact-heat-induced hydrocarbon generation and migration (Rankama, 1948), coeval with or shortly postdating sedimentation. Isolated pyrobitumen-rich intervals that are not associated with magmatic bodies are typically massive and exhibit cryptic fluidal textures and signs of multiphase, syndepositional microbrecciation. These intervals appear to represent organic-rich mushes generated during the course of hydrocarbon migration that have been injected into the host sediment or expelled onto the sea-floor as a type of mud-volcano (Melezhik et al., 2004).

Determinations of the depositional age for the ZF have been based on the whole-rock Sm-Nd, Pb-Pb and Re-Os isochrons on volcanic, carbonate and organic-rich rocks, respectively, that collectively yielded dates between c. 2.09 and 1.96 Ga (e.g. Puchtel et al., 1998, 1999; Ovchinnikova et al. 2007; Hannah et al. 2008). Most recently, U-Pb TIMS dating of zircons obtained from a purported lava near the base of the ZF and detrital zircons from an overlying unit suggest that deposition of the Zaonega sediments occurred between 1975.3 ± 2.8 and 1967.6 ± 3.5 Ma (Martin et al. 2015).

3. Materials and methods

The materials were sampled from two overlapping drill cores 12A and 12B (hereafter referred to as drill core 12AB) intersecting c. 500 m of the ZF in the Onega Basin (62°29.711 N, 31°17.460 E; Fig. 1). These cores were obtained during the International Continental Scientific Drilling Program (ICDP), Fennoscandian Arctic Russia-Drilling Early Earth Project (FAR-DEEP). The petrographic analyses were performed on polished thin sections using an Olympus BX41 optical microscope at the Centre for Geobiology, Bergen, Norway. Based on this petrographic characterization, the specific areas relevant for *in-situ* carbon isotope analysis by secondary ion mass spectrometry (SIMS) were selected. Rectangular rock chips with a side length of 4 to 12 mm for SIMS analysis were isolated from the thin section off-cuts. These rock chips were embedded in round epoxy resin molds (25 mm in diameter) and the obtained discs were subsequently polished. Scanning electron microscopy-back scattered electron (SEM-BSE) images were obtained from the polished surfaces of these discs using a Leo1450VP of Oxford Instruments in low vacuum mode (16 Pa) with an acceleration voltage of 15 kV, beam current of 80 µA and working distance of 8–13 mm, at the Geological Survey of Norway in Trondheim. These SEM-BSE images were used for navigation and locating targets in the SIMS sessions.

The *in-situ* carbon isotopic analysis of organic matter was performed using the Cameca IMS 1280 of the NordSIM-facility at the Swedish Museum of Natural History in Stockholm. A section of the sample was cut from a polished disc and mounted together with the graphite standard of pyrolytic graphite ('C-pyr' which has $\delta^{13}C = -31‰$, VPDB; G. D. Layne, personal communication). The samples were coated with a c. 30 nm gold layer to provide conductivity. A 20 kV impact energy Cs^+ beam was focused to a 5–10 µm spot, and a low energy electron flooding gun was used to compensate for charge build-up. Measurements were made in high transmission transfer mode with simultaneous determination of the ^{12}C and ^{13}C signals in a Faraday cup and low-noise ion counting electron multiplier, respectively, the latter of which was operated at high mass resolution (M/DM ~ 3000) to separate $^{13}C^-$ from $^{12}C^1H^-$. Carbon isotopic data were calibrated using the graphite standard and are reported as ‰ deviation from VPDB.