Limits of hydrosphere-lithosphere interaction: Origin of the lowest-known $\delta^{18}O$ silicate rock on Earth in the Paleoproterozoic Karelian rift

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ABSTRACT

Geologic records of Earth's hydrosphere and meteoric precipitation older than 2 Ga are rare, although they provide insight into the past climate, rates of water-rock interaction, and intensity of plate tectonics. Here we report and describe in detail the lowest known $\delta^{18}O$ (–16‰ to –25‰) terrestrial silicate rocks on Earth, found in Paleoproterozoic plagiogneisses from the Belomorian complex, Karelia, Russia. Geochronologic and oxygen isotopic data on zircons (+7‰ to –26‰) and monazite (–17.5‰) imply that the protoliths of these rocks were ca. 2.5 Ga metasediments and metavolcanics that were hydrothermally altered prior to 1.85 Ga within an intracontinental rift zone, and involved ultralow $\delta^{18}O$, <–25‰ meteoric water. Paleogeographic reconstructions indicate that Karelia was at low to middle latitudes throughout the Paleoproterozoic Era. Ultradepleted $\delta^{18}O$ waters outside of polar regions or the interiors of large landmasses provide independent evidence for a moderately glaciated, so called "slushball" Earth climate between 2.45 and 2.4 Ga, in which low- or mid-latitude, mid-size continents were covered with glaciers while the ocean remained at least partially unfrozen to allow for intracontinental isotopic distillation in a large temperature gradient. In addition to these climatic inferences, the data are more readily explained by a depleted –10‰ seawater reservoir during Paleoproterozoic time.

INTRODUCTION

In the modern world, oxygen and hydrogen isotope ratios of <0‰ (Vienna standard mean ocean water) exist only in water that went through the Rayleigh evaporation-precipitation cycle, the most negative values being characteristic of polar regions and continental interiors (e.g., Criss and Taylor, 1986). Interaction of silicate rocks with meteoric water proceeds in hydrothermal systems when temperature exceeds a certain threshold (~100–300 °C) to initiate kinetics of exchange; at these temperatures the isotopic fractionation between rocks and meteoric water is small (0‰–3‰), and thus at high water/rock ratios, rocks may approach, and record, $\delta^{18}O$ and δD values of water.

Reports of anomalously low $\delta^{18}O$ values (Krylov, 2008; Visotskii et al., 2008), in polymetamorphic plagiogneisses from Karelia, Russia, triggered our investigation. Here we present a detailed microanalytical investigation of the Chupa plagiogneisses of the Belomorian belt in Karelia (Fig. 1), and report the lowest (–15‰ to –28‰) $\delta^{18}O$ mineral and rock values ever measured in silicate rocks on Earth.

The Belomorian polymetamorphic complex between Kola and Karelia (Fig. 1) is one of many 1.9–1.8 Ga, Paleoproterozoic mobile belts around the world that collectively indicate accretion of the Nuna supercontinent (Zhao et al., 2002). The Belomorian rift closed via collisional kyanite-grade metamorphism ca. 1.85 Ga, followed by rapid exhumation and subsequent residence near the Earth's surface after 1.75 Ga (Bibikova et al., 2004; Terekhov, 2007). The studied corundum (ruby)-kyanite assemblage of Khitostrov and similar deposits along the Belomorian belt (Fig. 1) record a high-Al Archean metagraywacke protolith (Balagansky et al., 1986; Terekhov, 2007), metamorphosed at ~0.7 MPa (~20 km depth). The large size of minerals in leucosome (pegmatitic or diaphtoresis) bodies (Fig. DR4 in the GSA Data Repository[1]) suggests metasomatic recrystallization with abundant participation of fluid during late Paleoproterozoic exhumation.

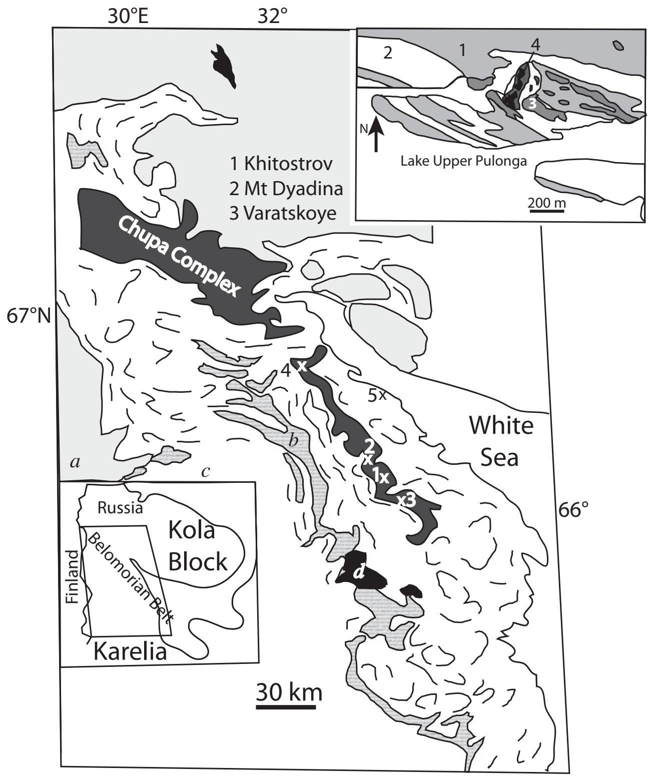

Figure 1. Simplified geologic map of Belomorian belt with structural elements (Balagansky et al., 1986; Bibikova et al., 2004), showing locations of Paleoproterozoic Chupa allochthonous nappe with Khitostrov corundum plagiogneisses (1x), low $\delta^{18}O$ plagiogneiss of Mount Dyadina (2x), and Varatskoye (x3), and two additional localities with similar detrital zircon age distribution (4x, 5x). Map units: *a*—Paleoproterozoic Lapland allochthon; *b*—Archean metavolcanic and metasedimentary rocks; *c*—Other nappes of Belomorian belt; *d*—Gabbro and layered intrusions (2.45–2.4 Ga). Inset, upper right: Distribution of high-Al gneisses in studied locality of Khitostrov (after Serebryakov et al., 2007). 1—kyanite-garnet-biotite plagiogneisses; 2—garnet-biotite plagiogneisses; 3—metamorphosed gabbroids; 4—ruby-bearing corundum gneisses, with large metasomatic pegmatoidal segregations, sampled in this study.

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[1]GSA Data Repository item 2010170, methods, tables, and supplementary figures, is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

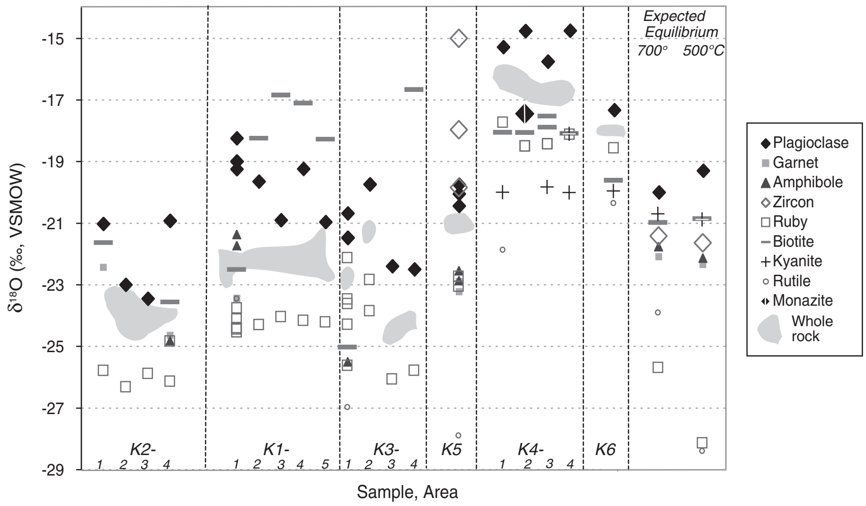

Figure 2. δ¹⁸O values of coexisting single crystals in mineral clusters represented by each vertical array of data points (analyses in Table DR1; see footnote 1). VSMOW—Vienna standard mean ocean water. Each vertical array of data points represents local metamorphic equilibrium that preserves bulk-rock δ¹⁸O value, shown by gray fields. Isotopic equilibrium between minerals is shown on right at 500 °C and 700 °C, inferred temperatures from cation geothermometry (Terekhov, 2007; Krylov, 2008). Note that biotite is higher than equilibrium in samples K1 and K3, which can be explained by 1%–10% retrogressive exchange with higher δ¹⁸O, higher δD magmatic or secondary meteoric fluids (see Fig. DR1). Note significant isotopic heterogeneity among different samples (outcrop scale), and among different mineral clusters in same sample (centimeter scale), explained here to reflect protolith variations.

LOWEST δ¹⁸O AND δD VALUES AND THE ORIGINS OF δ¹⁸O HETEROGENEITY

The large size of the studied minerals made them ideal targets for high-precision and high-spatial resolution, single-crystal, within-cluster study by laser fluorination, and D/H analysis (Bindeman, 2008; see the Data Repository for methods). Six samples of corundum- and kyanite-bearing plagiogneisses were investigated in detail for the oxygen isotopic composition of minerals and hydrogen isotopic composition of biotites and amphibole (Fig. 2). Given the complex metamorphic history of these rocks, a particular emphasis was paid to the minor and accessory minerals, i.e., rubies, kyanites, monazites, zircons, and garnet. Due to their extremely slow solid-state oxygen diffusion (and thus high closure temperatures), these refractory minerals record δ¹⁸O values of the protolith from the time of peak metamorphic initial growth (e.g., Valley, 2001). Such minerals, except zircon, appear to be in overall high-temperature isotopic equilibrium with the rock-forming mineral plagioclase (Fig. 2).

Individual biotites and bulk amphibole crystals from mineral clusters demonstrate highly depleted δD values, as low as –167‰, with variation parallel to the meteoric water line. Other amphiboles (–130‰ to –166‰) and more altered biotite (–83‰ to –189‰; Table DR1 and Fig. DR1 in the Data Repository) are still remarkably low; only the alteration mineral chlorite records higher δD values (–55‰). Isotopic mass-balance calculations require only 1%–20% of high-temperature exchange of an initial –220‰ Paleoproterozoic hydrogen with a variety of younger higher δD metamorphic or secondary waters. These processes have increased δ¹⁸O and δD values of some biotites, but had limited impact on other minerals, and on the major element oxygen. We conclude that the remarkably low δ¹⁸O (and low δD) values characterize the values of the protolith.

Based on single-crystal investigation, we discovered 9‰ δ¹⁸O heterogeneity between studied samples of similar mineralogy and chemistry (Fig. 2) spaced 10–80 m from each other, and as much as 3‰ heterogeneity of rubies within a single 10 cm hand specimen. Furthermore, single large rubies and kyanites exhibit ~1.5‰ isotopic zoning. Given that the amount of retrogressive exchange is limited for these refractory minerals, all these features can be attributed to the initial source heterogeneity prior to mineral growth.

New isotopic values for the Khitostrov corundum deposits (Fig. 2) are the lowest δ¹⁸O values ever measured in silicate materials on Earth. The δ¹⁸O values that we obtained are more negative than values recently reported for Khitostrov and the other two outcrops of corundum "metasomatites" (Mount Dyadina and Varatskoye; Fig. 1; see Krylov and Glebovitsky, 2007). Taken together, these measurements provide a picture of a widespread >50 km linear depletion zone of rocks of similar mineralogy and age within the Belomorian belt. We discount proposed interpretations of low δ¹⁸O values as synmetamorphic or metasomatic, and question their alleged origin as weathering crusts (Krylov, 2008). We infer that high-temperature water-rock exchange can explain the low and heterogeneous δ¹⁸O values. The Karelian δ¹⁸O values are also significantly lower, by more than 10‰–15‰, than those reported for two other localities with strongly depleted δ¹⁸O; i.e., Dabie Shan-Sulu in China (Rumble and Yui, 1998; Zheng et al., 2004) and Kokchetav, Kazakhstan (Masago et al., 2003).

U-Th-Pb AGES AND δ¹⁸O VALUES OF ZIRCONS AND MONAZITE

The electron microprobe U-Th-Pb dating of seven monazite grains in sample K4 (Table DR2) yielded a mean age of 1.89 ± 0.009 Ga (1σ, n = 45) and showed no age zoning or grain-to-grain age heterogeneity. The dated monazites have very low δ¹⁸O values of –17.5‰ that are consistent with overall equilibrium with other minerals (Fig. 2) and published regional metamorphic ages from the Belomorian complex (Fig. 3). Zircons from sample K5 yielded δ¹⁸O values of –20‰ (bulk population), –18‰ (large crystals only), and –15‰ (air-abraded grains); by mass balance we may estimate normal δ¹⁸O (~+4‰ – +8‰) cores, and ~–22‰ to –25‰ rims, values in equilibrium with the host mineral assemblage.

Ion microprobe dating coupled with in situ δ¹⁸O measurements in 15 zircons in sample K5 (Fig. 3; Appendix and Table DR2) identified a bimodal population with concordant ages of 2.75–2.45 Ga, +4‰ – +8‰ δ¹⁸O zircons, and 1.9–1.8 Ga, –23‰ to –27‰ zircons and rims; a few analyses of intermediate age and δ¹⁸O are suspected to be due to domain mixing within the spot size of the 20–30 μm ion microprobe beam. The detrital zircon cores (~1000–1500 ppm U and 5–170 ppm Th), and especially younger metamorphic and/or metasomatic rims (~500 ppm U, and <10 ppm Th), have very high U/Th ratios and featureless, dull cathodoluminescence.

Due to very sluggish oxygen isotope diffusion in zircon (Watson and Cherniak, 1997; Valley, 2001), it is the only mineral in the assemblage in which cores survived the Belomorian metamorphism to record protolith age and δ¹⁸O values. Because monazite closes to O-isotope exchange at lower temperatures than zircon (e.g., ~500 °C; Cherniak et al., 2004), the lack of detrital monazite grains and low δ¹⁸O values and ages reflect diffusive exchange and recrystallization during the 1.89 Ga exhumation.

DISCUSSION: ANCIENT METEORIC-HYDROTHERMAL SYSTEM IN A PALEOPROTEROZOIC RIFT

We interpret that heterogeneous and ultralow δ¹⁸O and δD values in minerals from the Belomorian belt record a heterogeneous low δ¹⁸O

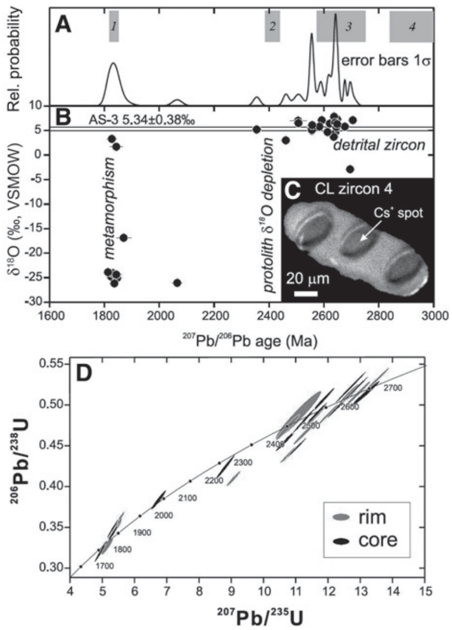

Figure 3. Zircon ages and $\delta^{18}O$ values determined by ion microprobe in sample K5 demonstrating peaks of normal $\delta^{18}O$ (+7‰ – +8‰), concordant zircon ages at 2.7–2.45 Ga representing detrital cores, and low $\delta^{18}O$ (–23‰ to –26‰), ca. 1.85 Ga zircons and rims related to Belomorian metamorphism. A: Age histogram; gray bands denote published ion microprobe zircon ages from other rocks across Belomorian belt (Bibikova et al., 2004; Serebryakov et al., 2007) showing similar age patterns: 1—rims of zircons in similar pegmatites, 2—zircons from regional gabbro, 3—predominant detrital zircons and zircons from metamorphic migmatites and granites, 4—oldest detrital cores. B: $\delta^{18}O$ vs. age diagram; $\delta^{18}O$ analyses were performed on previously dated spots after repolishing. We attribute intermediate ages and $\delta^{18}O$ values due to repolishing and core-rim beam overlap. C: Inset shows dull cathodoluminescence image of zircon 14. D: U-Pb concordia diagram.

protolith that exchanged at high temperatures with ultralow $\delta^{18}O$ meteoric waters prior to metamorphism, and acquired heterogeneity through variable water/rock ratios common to meteoric-hydrothermal systems (Criss and Taylor, 1986). Modern-day shallow meteoric-hydrothermal systems, such as those in calderas of Yellowstone and rift zones of Iceland, are capable of large-scale modification of hundreds of cubic kilometers of crust, and generate highly heterogeneous $\delta^{18}O$ values at centimeter scale (Fournier, 1989). However, because exchange between rocks and water rarely proceeds to completion and requires pervasive water-rock ratios >>1 (Criss and Taylor, 1986), the lowest measured $\delta^{18}O$ value of minerals that we report may correspond to the highest $\delta^{18}O$ value of the altering meteoric water. We estimate that the water that caused Belomorian depletion could have been as low as –30‰ to –35‰, as some of the amphiboles seem to require based on trends in $\delta^{18}O$ and D/H (Fig. DR1). Given the elongated distribution of anomalously low $\delta^{18}O$ corundum-bearing rocks in the Belomorian belt (Fig. 1), an intracontinental rift system would fit the profile well. This inferred intracontinental rift provided favorable magma-driven hydrothermal circulation conditions for removal of ^{18}O and D from rocks by low $\delta^{18}O$, low δD meteoric waters.

POLAR POSITION, SUPERCONTINENT GLACIATION, OR LOW $\delta^{18}O$ SEAWATER?

The occurrence of <–25‰ meteoric water is limited on modern Earth to the Greenland (–25‰ to –45‰) and Antarctic ice sheets (–25‰ to –60‰) (http://www.waterisotopes.org). If one accepts arguments of constancy of $\delta^{18}O$ value of seawater at 0‰ ± 2‰ buffered by nearly constant plate tectonic recycling and/or hydrothermal alteration rates (Muehlenbachs, 1998), then the only way to explain ultradepleted $\delta^{18}O$ values is for the Belomorian rift to be deep within the interior of a large landmass close to the pole, or under an ice cap at polar latitude.

However, paleomagnetic data from Kola and Karelia (Evans and Pisarevsky, 2008) indicate low to moderate paleolatitudes for the Belomorian region at 2.45, 2.06, and 1.88 Ga (Fig. 4), and the most parsimonious interpolation from these data precludes an excursion of the Belomorian region to polar latitudes at any time during the Paleoproterozoic (Fig. 4). Additional constraints can be applied indirectly if one assumes that Kola and Karelia were joined with the Superior craton between initial consolidation ca. 2.7 Ga and separation ca. 2.05 Ga. This reconstruction satisfies both the distribution of precisely dated mafic dike swarms and paleomagnetic data (Mertanen et al., 2006), the latter specifically if it is assumed that the paleomagnetic result shown for 2.45 Ga in Figure 4 is primary. The Superior craton has a much richer data set of demonstrably primary paleomagnetic poles in the 2.45–1.88 Ga interval (references in Fig. 4); this likewise restricts paleolatitudes of its once-juxtaposed cratons to low-moderate latitude throughout that time. Although the original extent of continental continuation between Kola and Karelia and other cratons is unknown (Bleeker, 2003), the rift architecture of sedimentary basins at 2.45 Ga suggests that the Belomorian belt was not deep within the interior of a large supercontinent, thus disallowing the possibility of prolonged intracontinental vapor distillation.

If –30‰ to –35‰ intracontinental waters were to be explained by temperate climate conditions and local alpine glaciation, then an initially depleted seawater of <–10‰ would be required, as more than 15‰–20‰ depletion would be difficult to achieve solely by Rayleigh distillation in the interior of a small to medium-size continent. The initially depleted seawater and Rayleigh distillation would collectively produce <–25‰ alpine snow. Our isotopic and geochronologic data are more consistent with formation of the

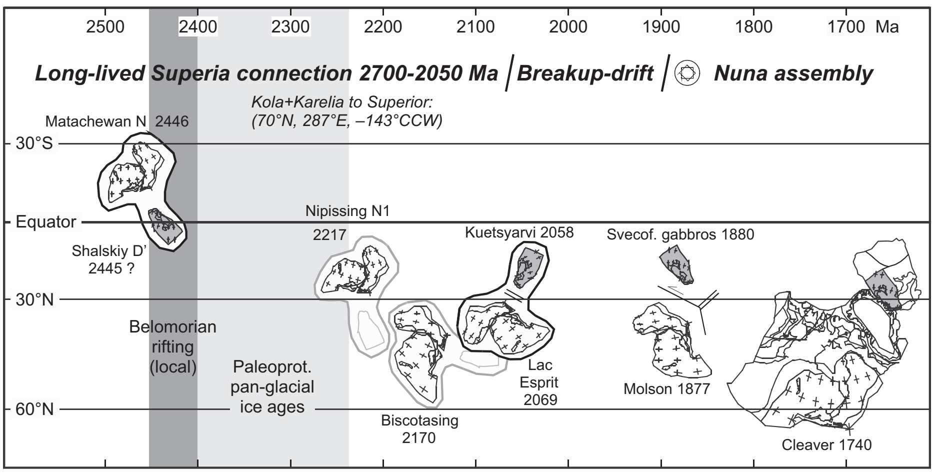

Figure 4. Paleogeographic setting of Belomorian belt. Superior craton (gridded, unshaded) and Kola and Karelia (gridded, shaded) are reconstructed through time, to paleolatitudes (Mercator projection) and orientations according to named paleomagnetic poles (ages in Ma) (Mertanen et al., 2006; Pesonen et al., 2003). Double-line segments schematically indicate rifting; arrow indicates relative transform motion. Long-lived supercraton Superia connection, which likely included other cratons not shown (e.g., Bleeker and Ernst, 2006), is presumed valid throughout interval 2.70–2.05 Ga, permitting paleolatitude assignments for Kola and Karelia inferred by data from Superior craton. Gem symbol indicates metamorphic age of Belomorian gneisses. Reconstruction at 1740 Ma shows Kola and Karelia joined to newly consolidated Laurentia craton (Evans and Pisarevsky, 2008) as part of Nuna supercontinent. Most parsimonious interpolation of Kola and Karelia paleolatitudes precludes any polar excursion between Belomorian rifting (ca. 2.45 Ga) and metamorphism (ca. 1.89 Ga). Svecof.—Svecofennian.

protolith of Chupa gneiss in a ca. 2.45 Ga cold climate period extending to low latitudes in a so called "slushball" regime (Hoffman, 2009). If glaciers reached shores at low latitudes, significant $\delta^{18}O$ and δD gradients inland could have existed by analogy with Greenland (–15‰ to –35‰), aided by the glacial flow supplying lowest $\delta^{18}O$, high-altitude ice to the seashore. Seawater would need to have remained unfrozen to allow for effective evaporation-precipitation cycles inland, thus favoring a "slushball" versus the "hard" snowball model ca. 2.45 Ga. Then, the basalt-generating Belomorian rift zone could have been active in low-latitude, low-altitude, subglacial conditions ca. 2.45 Ga to fit the regional geochronology, amid the recognized global cold climate period (Fig. 4). The 2.45–2.35 Ga stratigraphic record for Kola and Karelia includes abundant mafic rocks and immature sediments of the Sumian and Sariolian successions, indicating rifting accompanied by glaciation (Ojakangas et al., 2001). The presence of a 2.20–2.05 Ga carbonate-evaporite platform with enriched $\delta^{13}C$ and $\delta^{18}O$ values (Melezhik et al., 1999) disallows attainment of the ultralow $\delta^{18}O$ Belomorian values during that interval.

Seawater values of ~–10‰ have been proposed specifically for ca. 2.0 Ga (Burdett et al., 1990), consistent with an overall trend toward decreasing values with increasing age (Jaffres et al., 2007). Such depleted oxygen isotopes in Precambrian carbonate rocks have been interpreted as representing a secular change in either ocean chemistry or temperature (Knauth and Kennedy, 2009; Jaffres et al., 2007). Absolute temperature of the Paleoproterozoic ocean is irrelevant to our conclusions, as long as zonal temperature and precipitation/evaporation gradients remain constant regardless of the global mean. Nonetheless, agreement of the carbonate isotope depletion between Precambrian and Ordovician, the latter time hosting modern-like marine animal ecosystems, favors the model of secular chemical change (Jaffres et al., 2007). We propose that the ultralow, yet heterogeneous, $\delta^{18}O$ values from the Belomorian basic metasediments are best explained by three combined effects: regionally cold glacial climate conditions at low to moderate paleolatitudes, hydrothermal alteration within an early Paleoproterozoic subglacial intracontinental rift, and an initially $\delta^{18}O$-depleted Paleoproterozoic seawater value. While questions remain as to whether a "slushball" Earth is a stable climate state (e.g., Bendsen, 2002), the observations presented here may provide empirical support for it.

ACKNOWLEDGMENTS

We thank two anonymous reviewers for careful reviews, and Paul Hoffman in particular for suggestions leading us to favor a "slush-ball" rather than "snowball" interpretation of our data. This work was supported by National Science Foundation (NSF) grant EAR-CAREER-0844772 and NSF I&F 0732691.

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Manuscript received 15 December 2009
Revised manuscript received 16 December 2009
Manuscript accepted 11 February 2010

Printed in USA