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Low $\delta^{18}O$ rocks in the Belomorian belt, NW Russia, and Scourie dikes, NW Scotland: A record of ancient meteoric water captured by the early Paleoproterozoic global mafic magmatism

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ABSTRACT

The 2.45–2.38 Ga intrusions and their host rocks in the Belomorian belt of NW Russia and the Scourie dikes of the Lewisian complex in NW Scotland are marked by extremely low $\delta^{18}O$ values. Their isotope signatures reflect high-temperature exchange between rocks and low $\delta^{18}O$ meteoric waters representing a record of active hydrologic cycle early in the Earth's history. Here we explore triple oxygen and hydrogen isotope systematics (δD, $\delta^{18}O$ and $\Delta^{17}O$) of these rocks to evaluate the isotope composition of meteoric water. The new occurrences from Belomorian belt range in $\delta^{18}O$ from −14 to −2‰; combined with previously reported data, ranging between −27 and +3‰, the low $\delta^{18}O$ rocks are traced across 500 km of the Belomorian belt. Based on spatial distribution of the values, hydrothermal alteration driven by the emplacement of the mafic intrusions is the most consistent explanation for the low $\delta^{18}O$ values recorded in the Belomorian belt. The $\Delta^{17}O$ systematics reveals contribution of distinct meteoric waters with $\delta^{18}O$ of −38 and −9‰ recorded at different localities across the belt. We also present new data for the 2.41–2.38 Ga Scourie dikes, with the lowest $\delta^{18}O$ value of −2.5‰ recorded in the amphiboles of Loch na h dike. Unlike the Belomorian belt, the low $\delta^{18}O$ signature of Scourie dikes requires igneous incorporation of low $\delta^{18}O$ hydrothermally altered rocks through contamination of mantle-derived melts. The $\Delta^{17}O$ data analyzed at the Loch na h dike reveals that the incorporated material experienced water-rock interaction with meteoric water that had $\delta^{18}O$ of −35 ± 10‰. The exact mechanism for incorporation of such low $\delta^{18}O$ rocks in the mafic Scourie dike melts is equivocal and could involve subduction or assimilation of low $\delta^{18}O$ hydrothermally altered mafic rocks. These reconstructed isotope compositions of meteoric waters are diverse and comparable to the modern-day precipitation of high-latitude regions (e.g. Greenland, $\delta^{18}O$ = −35‰) and precipitation of mid-latitude regions (−9‰), possibly reflecting spatial $\delta^{18}O$ gradients resulted from an active hydrologic cycle during the cold climate of the early Paleoproterozoic, as depicted by previous isotope-enabled global circulation models of snowball Earth state.

1. Introduction

1.1. Low $\delta^{18}O$ rocks of the early Paleoproterozoic

Between 2.45 and 2.40 Ga, extensive magmatism of the globally distributed Large Igneous Provinces (LIPs) temporally overlapped with the onset of series of snowball Earth glaciations (Evans et al., 1997; Heaman, 1997; Bleeker, 2003; Bleeker and Ernst, 2006; Ernst and Bleeker, 2010; Hoffman, 2013; Gumsley et al., 2017). Since the timing of these events is so close, it is reasonable to consider that the abundant continental magmatism and rifting was accompanied by water-rock interaction induced by hydrothermal circulation of meteoric water. Such interaction is recognized in geological record by low $\delta^{18}O$ values, as, for example, in altered basalts and products of crustal melting in the modern rift system of Iceland (Hattori and Muehlenbachs, 1982). In fact, the 2.44–2.41 Ga rocks from the Belomorian belt of the Karelia craton have been shown to contain very low $\delta^{18}O$ values, between −27 and +3‰, explained by the same style of interaction between glacial meltwaters and rocks induced by numerous intrusions forming in a rifting environment (Bindeman et al., 2010; Bindeman and Serebryakov, 2011; Bindeman et al., 2014; Herwartz et al., 2015; Zakharov et al., 2017). Along with the Paleoproterozoic glacial deposits, these low $\delta^{18}O$ rocks present geochemical evidence for the presence of glacial ice that accumulated in the subaerial portions of ancient continents. They document presence of active hydrologic cycle in the early Paleoproterozoic, in which the isotope signature of meteoric water originates from evaporation of seawater, and subsequent condensation and precipitation over the land. As in modern world, the precipitation $\delta^{18}O$-latitude gradients reflect the dependency between the mean annual temperature, vapor-water fractionation and extent of Rayleigh distillation (Dansgaard, 1964; Bindeman and Lee, 2018). Thus, the isotope values of the early Paleoproterozoic meteoric waters not only provide the evidence for extensive continents exposed above sea level, but they also reflect very low mean annual temperatures during the early Paleoproterozoic. Combined with paleogeographic reconstructions, low $\delta^{18}O$ rocks present a unique way to gain insight into the hydrosphere and paleoclimate of the deep past. Given that they are suitable for precise U-Pb dating, they also provide a temporal

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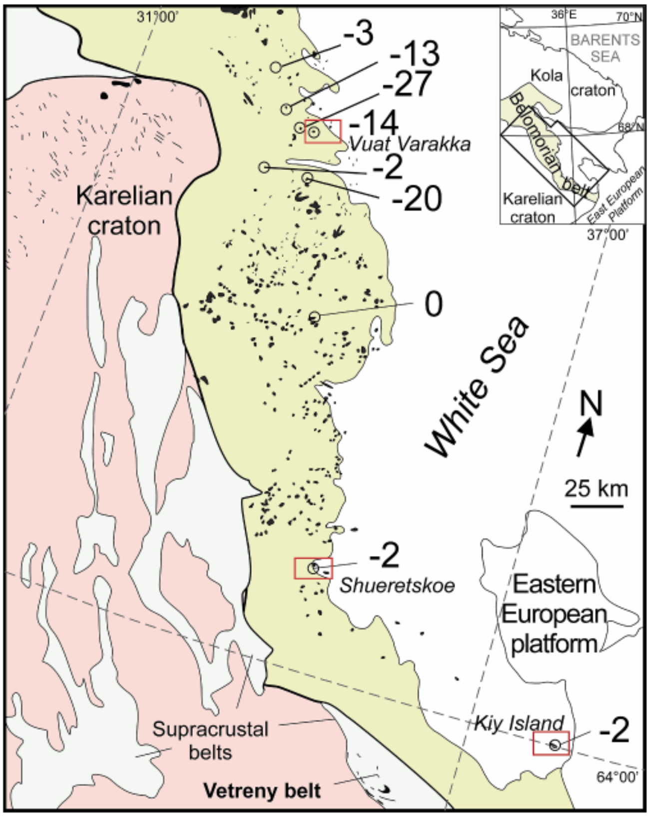

Fig. 1. Generalized geological map of the Belomorian belt and adjacent Karelian craton with Proterozoic supracrustal belts (green) and intrusions (black; modified after Slabunov et al., 2006). The occurrences of low $\delta^{18}O$ rocks are shown with circles. Numbers indicate the lowest $\delta^{18}O$ value measured in garnets at each locality reported in ‰ VSMOW (modified after Bindeman et al., 2014). The samples studied here were collected from the low $\delta^{18}O$ localities outlined with rectangles. Just south of the Belomorian belt, the 2.43–2.41 Ga Vetreny belt contains submarine hydrothermally altered rocks providing a record of nearly contemporaneous seawater with $\delta^{18}O$ close to 0‰ (Zakharov and Bindeman, 2019). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

constraint for the timing of inferred conditions (e.g. Zakharov et al., 2017).

In this study we explore the low $\delta^{18}O$ rocks of the early Paleoproterozoic by providing new measurements from the Belomorian belt and from the low $\delta^{18}O$ Scourie dikes. We focus on documenting recently discovered occurrences of low $\delta^{18}O$ rocks from the Belomorian belt (Fig. 1). This study expands upon those of Bindeman et al. (2010, 2014), Bindeman and Serebryakov (2011) and Zakharov et al. (2017) by providing new H- and triple O-isotope data to further test the hypothesis that these rocks record interactions between low $\delta^{18}O$ glacially derived waters and mafic magmatism during the Paleoproterozoic snowball Earth climate state. These rocks exemplify the water-rock interaction that occurred at low latitudes (c. 30°S; Mertanen et al., 1999; Salminen et al., 2014) induced by extensive rifting and magmatism in the early Paleoproterozoic snowball Earth climate.

We also provide new H- and O-isotope datasets for the Scourie dikes of the Lewisian complex of NW Scotland (Fig. 2). This study expands upon the work of Cartwright and Valley (1991; 1992) and Davies et al., (2015). Unlike the Belomorian belt rocks, the Scourie dikes likely formed as initially low $\delta^{18}O$ mafic magmas with the values as low as −2‰ (Cartwright and Valley, 1991; Davies et al., 2015). To explain their unique O-isotope signature, Scourie dike magmas must have interacted with very low $\delta^{18}O$ rocks, comparable to those from the Belomorian belt. This is potentially one of the earliest documented evidence for generation of low $\delta^{18}O$ mafic magmas reflecting interaction between the low $\delta^{18}O$ continental rocks and mantle-derived melts in the Earth's history. Using the triple O-isotope approach we test for possible incorporation of the Belomorian-belt-like rocks into the melts that produced Scourie dikes. In addition, the Archean-Paleoproterozoic successions of the Baltic Shield and Lewisian complex share several common features beyond having rocks with low $\delta^{18}O$ values: both provinces have similar 2.7 Ga Archean rocks, mafic intrusions have similar geochemical characteristics and both provinces underwent amphibolite-facies metamorphism between 1.9 and 1.7 Ga (Bridgewater et al., 1995; Whitehouse et al., 1997; Hughes et al., 2014; Stepanova et al., 2017). Their potential geographical proximity in the early Paleoproterozoic (Bleeker, 2003) and globally cold climate with prevalence of low $\delta^{18}O$ precipitation (Bindeman and Lee, 2018) provides a motivation to use O isotopes as a new tool for cratonic correlations (see, Park, 1995; Bleeker, 2003; Nilsson et al., 2010; Davies and Heaman, 2014).

1.2. Definition and use of $\Delta^{17}O$

This study utilizes $\Delta^{17}O$ values to derive $\delta^{18}O$ values of meteoric waters from the rock record. To express triple oxygen isotope composition of a sample, the $\Delta^{17}O$ notation is adopted here and defined as $\delta^{17}O - 0.5305 \cdot \delta^{18}O$, where $\delta^{17}O$ and $\delta^{18}O$ values are conventionally expressed as $1000 \cdot ({}^{18\text{ or }17}O/{}^{16}O)_{sample}/({}^{18\text{ or }17}O/{}^{16}O)_{standard} - 1000$. Recent developments in high precision measurements of ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$ have resolved systematic variations in $\Delta^{17}O$ in terrestrial materials presenting a novel way to trace water-rock interaction (Herwartz et al., 2015; Sharp et al., 2018; Zakharov and Bindeman, 2019). Meteoric waters originate by evaporation of seawater and have negative $\delta^{18}O$ values relative to the standard Vienna Standard Mean Oceanic Water (VSMOW). The values of meteoric waters become more negative with progress of condensation and precipitation spanning in $\delta^{18}O$ between −60 and 0‰, while mantle-derived and continental rocks have distinctly high, positive $\delta^{18}O$ values between +5 and +10‰. Governed by small but resolvable differences in mass-dependent fractionations of ${}^{18}O/{}^{16}O$ relative to ${}^{17}O/{}^{16}O$ between coexisting phases (e.g., water vapor and liquid, or olivine and melt), meteoric waters and rocks form fractionation arrays with different slopes (e.g., 0.528 vs 0.530; Miller, 2002; Luz and Barkan, 2010; Pack and Herwartz, 2014; Pack et al., 2016). The $\Delta^{17}O$ values then represent an offset between values measured in a sample and the reference line with slope of 0.5305 in $\delta^{18}O$ - $\delta^{17}O$ space.

This difference in $\delta^{18}O$ - $\Delta^{17}O$ values of meteoric waters and continental crust creates distinctive fields in the triple oxygen isotope space (Fig. 3), with continental hydrothermally altered rocks plotting in between the two. Because of exponential relationship between fractionation factors ${}^{17}\alpha$ and ${}^{18}\alpha$, the $\delta^{18}O$ - $\Delta^{17}O$ relationship is nonlinear resulting in the curvature of meteoric water line that spans over several tens of permil. In Fig. 3 we also consider possible mechanisms for generation of low $\delta^{18}O$ rocks. Hydrothermally altered rocks acquire low $\delta^{18}O$ signature via high-temperature (> 250 °C) equilibrium fractionation between secondary minerals and meteoric water. At this temperature, fractionation is small, around ~2–3‰, resulting in $\delta^{18}O$ and $\Delta^{17}O$ values of hydrothermally altered rocks being very close to that of hydrothermal fluids. At a given temperature and fixed $\delta^{18}O$, $\Delta^{17}O$ values of pristine meteoric water entering a hydrothermal system, the O-isotope composition of rocks are dependent on the extent of isotope exchange with fluids, commonly expressed as water/rock ratios (Taylor, 1977). In these coordinates, an array of water/rock (W/R) ratios is a straight line (Fig. 3). Thus, a set of measurements spanning several ‰ due to variable W/R ratios allows to reconstruct the $\delta^{18}O$ of meteoric water by finding an intersection of the linear regression and meteoric water line. Further, we consider assimilation of hydrothermally altered rocks by mantle-derived melts, which represents simple mixing between low $\delta^{18}O$ component and normal, mid-ocean ridge basalt (MORB) values (Fig. 3). Due to a very small isotope

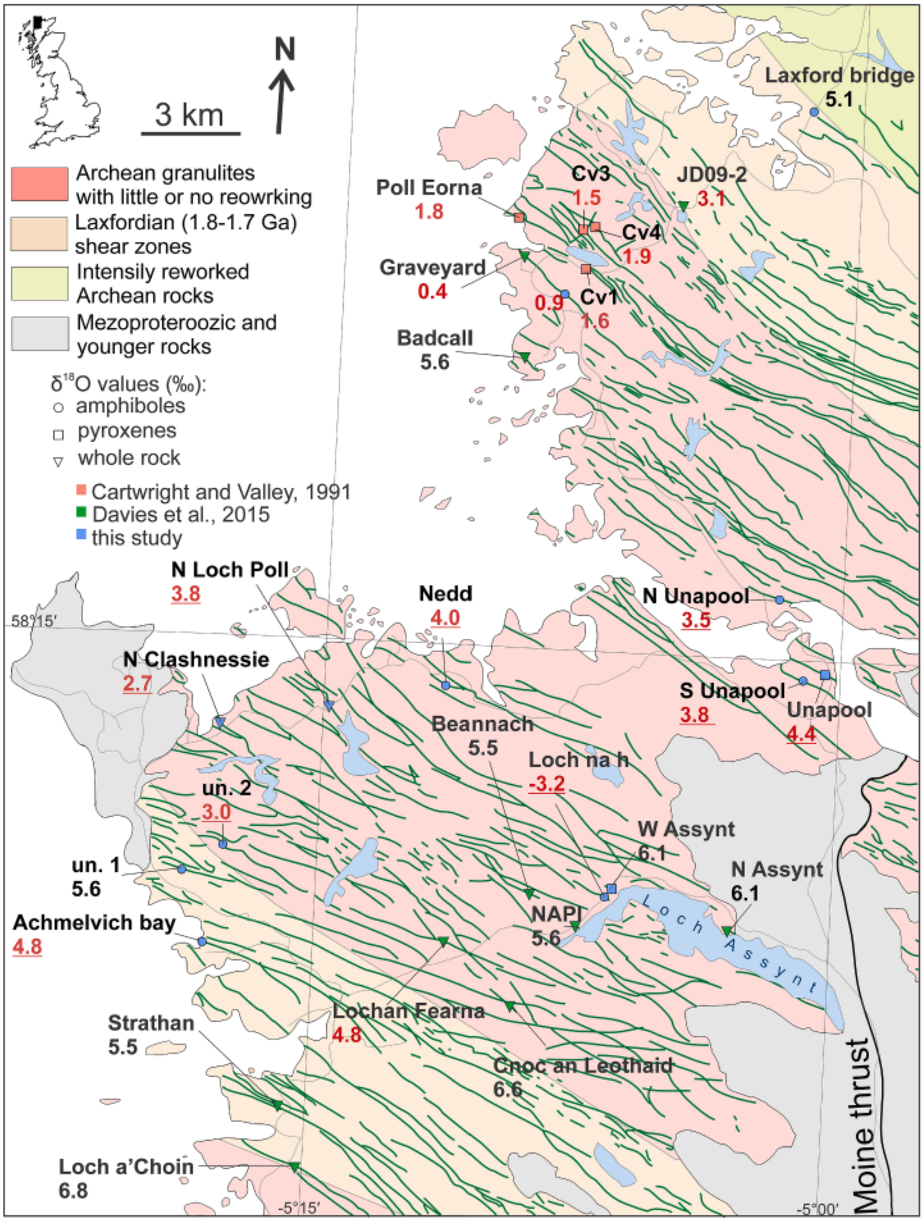

Fig. 2. Geological map of the Assynt terrain, Lewisian complex, NW Scotland with numerous Scourie dikes shown in green (modified after Davies et al., 2015). The $\delta^{18}O$ values are shown with numbers and were measured in amphiboles, pyroxenes and whole rock samples as indicated by different symbols. The low $\delta^{18}O$ values (below the mantle value of 5.6‰) are shown in red and newly discovered low $\delta^{18}O$ values are underlined. The dikes reported in Cartwright and Valley (1991) are labeled as numbered in the paper with prefix "Cv" except Poll Eorna and Graveyard dikes. Two unnamed dikes sampled in this study are labeled "un.". The dike W Assynt could be a continuation of the N Assynt dike (Davies and Heaman, 2014). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fractionation between minerals and melts at solidus temperatures, the $\delta^{18}O$ and $\Delta^{17}O$ values of contaminated magmas forms a linear trend, connecting the assimilated material and primary magma (MORB in Fig. 3). Using these considerations and geologic data, we attempt to constrain the $\delta^{18}O$ values of meteoric waters in equilibrium with low $\delta^{18}O$ hydrothermally altered rocks that were either preserved as is or assimilated by mantle-derived melts. We work under the assumption that the $\delta^{18}O$ value of the early Paleoproterozoic seawater was not significantly different from the range of Cenozoic values (Zakharov and Bindeman, 2019 and references therein). That allows us to explore the relationship between climate, paleogeographic reconstructions and isotope signatures of local precipitation.

2. Geological setting

2.1. The Belomorian belt, Baltic Shield, NW Russia

The Belomorian belt is an assembly of ~2.7 Ga metasedimentary and metavolcanic rocks intruded by 2.44–2.41 Ga high-Mg gabbronorites and, in some cases, by Fe-rich gabbros that are 2.3–2.1 Ga in age (Lobach-Zhuchenko et al., 1998; Balagansky et al., 2001; Bibikova et al., 2004; Stepanova and Stepanov, 2010; Stepanova et al., 2017; Zakharov et al., 2017). Collectively, they are interpreted as a fragmented LIP associated with rifting of the Baltic Shield (i.e. Kola and Karelia cratons; Melezhik and Hanski, 2013; Kulikov et al., 2010) and the entire belt was metamorphosed at 1.89 Ga to amphibolite facies (Skiöld et al., 2001; Bibikova et al., 2004). The low $\delta^{18}O$ values ranging from −27 to +3‰ are hosted in amphibolites, gneisses and high-Al rocks adjacent to the intrusions (Fig. 1; Bindeman and Serebryakov, 2011; Bindeman et al., 2014). The high-Al rocks contain abundant kyanite, staurolite, garnet, gedrite, corundum, and margarite and their protoliths are thought to be hydrothermally altered rocks (see Bindeman et al., 2014).

Here we focus on 3 new occurrences of low $\delta^{18}O$ rocks. *Vuat Varakka* locality is on the northern shore of the Upper Pulongskoe (Verkhneye Pulongskoe ozero, *Russian*), ~5 km away from the Khitoostrov locality described by Bindeman and Serebryakov (2011) with the lowest $\delta^{18}O$ value ever measured in silicate rocks (Fig. 4A). The O-isotope depletion follows a layer of amphibolite and high-Al rocks containing abundant garnet, kyanite, corundum and staurolite in

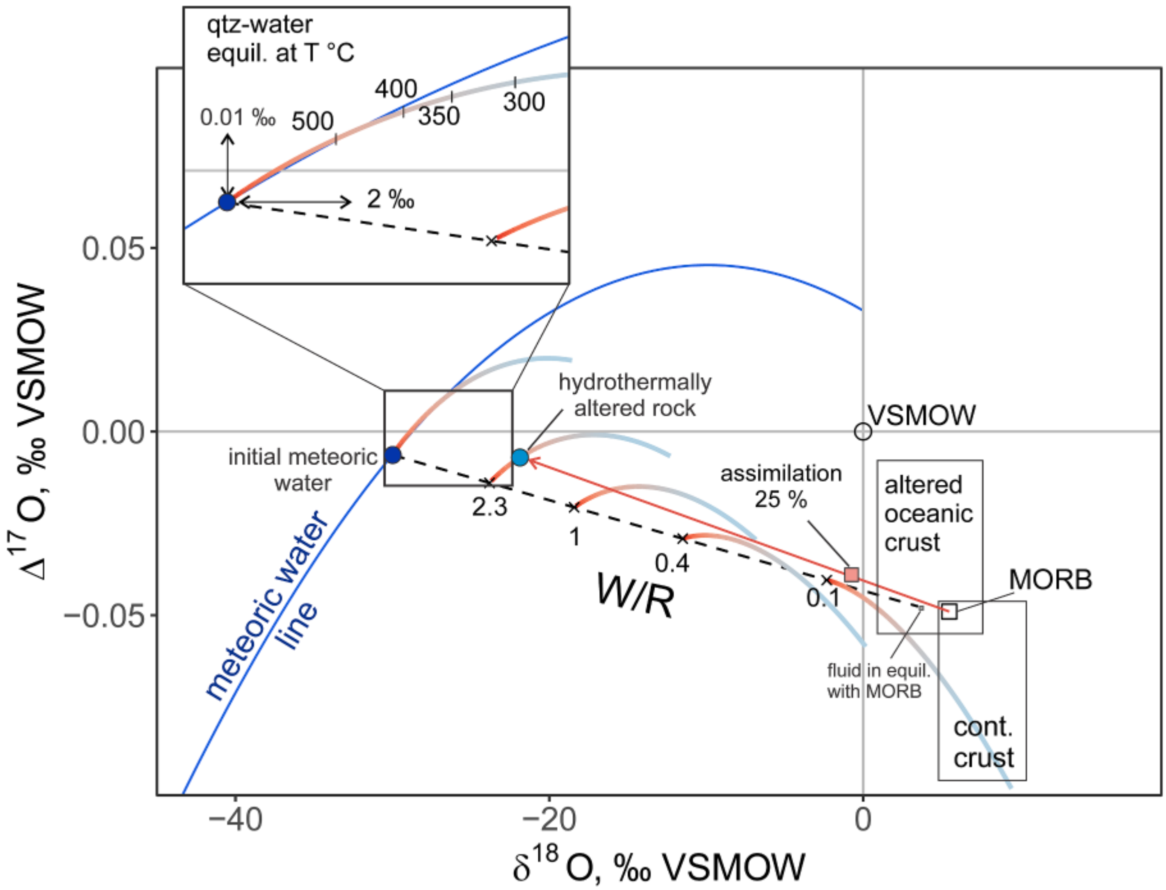

Fig. 3. The triple O-isotope approach used here to trace meteoric water-rock interaction (modified after Herwartz et al., 2015). At a given temperature of water-rock interaction, the $\delta^{18}O$ and $\Delta^{17}O$ composition of minerals are dependent on the water-rock ratio (W/R) as shown for interaction between mid-ocean ridge basalt (MORB) and meteoric water with $\delta^{18}O$ of −30‰. Equilibrium quartz-water fractionation at 200–900 °C (Sharp et al., 2016) is shown with red-blue curves for W/R ratios ranging between 0.1 and infinity, where the red segment corresponds to the temperature > 400 °C representing approximate equilibrium fractionation between fluids and common secondary minerals in hydrothermal systems ($\Delta\delta^{18}O_{rock\text{-}water} \approx$ 2–3‰ for a mixture of amphiboles, chlorite, epidote and albite; Zheng, 1993). The high-temperature segment of fractionation curve is shown in the inset with arrows indicating the range of values attained by high-temperature hydrothermally altered rocks in equilibrium with pristine meteoric water. Igneous assimilation of low $\delta^{18}O$ rocks that were originally altered at W/R ratio of 2.3 is shown with a red arrow. The resultant magma represents a mixture of 25% hydrothermally altered rock and 75% MORB magma. Compositional fields of altered oceanic crust and continental crust are shown after (Bindeman and Lee, 2018; Sengupta and Pack, 2018; Sharp et al., 2018; Zakharov and Bindeman, 2019). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the proximity of the 2.44–2.41 Ga high-Mg gabbro-norite intrusion (Fig. 4B). The core of intrusion is weakly metamorphosed with original igneous pyroxene, plagioclase and olivine crystals preserved. The surrounding amphibolites likely represent metamorphosed and dislocated parts of the same intrusion. *Shueretskoe*, at the southern end of the Belomorian belt, 190 km south from Vuat Varakka, consists of high-Al garnet- and gedrite-bearing biotite gneiss (some are as much as 70 vol% of garnet) and garnet amphibolite (Fig. 5). These rocks can be traced for 15 km (Glebovitsky and Bushmin, 1983) and in many places are intruded by undated gabbros (Antropov and Kratz, 1960). The third locality is *Kiy Island*, a layered mafic intrusion and is the southern-most occurrence of low $\delta^{18}O$ rocks in the Belomorian belt before sedimentary cover of the East European platform overlay the Baltic Shield south of it. The low $\delta^{18}O$ values are hosted in garnet amphibolites and epidosites (Fig. 6). The hosting intrusion consists of differentiated mafic rocks with mostly preserved original igneous minerals and textures, and was dated to 2441 ± 51 Ma using *in situ* U-Pb zircon geochronology (Slabunov et al., 2006).

2.2. The Scourie dikes, Lewisian complex, NW Scotland

The Archean Lewisian complex in northwest Scotland (Fig. 2) consists dominantly of felsic orthogneiss with minor metasedimentary units (Park, 1995) and records a geological history similar to that of the Belomorian belt. The original rocks of the complex were metamorphosed to granulite facies at ~ 2.7 Ga, cut by the 2.42–2.38 Ga mafic Scourie dikes (another set of dikes are 1.9–2.0 Ga in age but these are minor; Tarney and Weaver, 1987a; Heaman and Tarney, 1989; Davies and Heaman, 2014; Hughes et al., 2014; Baker et al., 2019), and then experienced amphibolite facies conditions during the c. 1.7 Ga Laxfordian event (e.g. Park, 1995; Wheeler et al., 2010). The majority of Scourie dikes are quartz tholeiites with minor subsets of them being bronzite picrites, olivine gabbros and norites (Tarney and Weaver, 1987b). They vary in width from a few tens of centimeters to many tens of meters; many of the larger dikes containing coarse interiors with interlocking and ophitic aggregates of plagioclase, pyroxene and iron oxides altered variably to secondary minerals. Their mineralogy, petrography and geochemistry were described with great detail by O'Hara (1961), Tarney (1963), Weaver and Tarney (1981), Tarney and Weaver (1987b), Hughes et al. (2014) and others. Our samples come from the Graveyard, Poll Eorna, Loch na h dikes and other dikes (Fig. 2) in the Assynt terrain of the Lewisian complex, where rocks were least affected by the Laxfordian event and in which low $\delta^{18}O$ values were reported previously (Cartwright and Valley, 1991; Davies et al., 2015). Some of the dikes are locally sheared and turned to amphibolites and thus, the exact effect of metamorphism on the Scourie dikes in Assynt terrain has

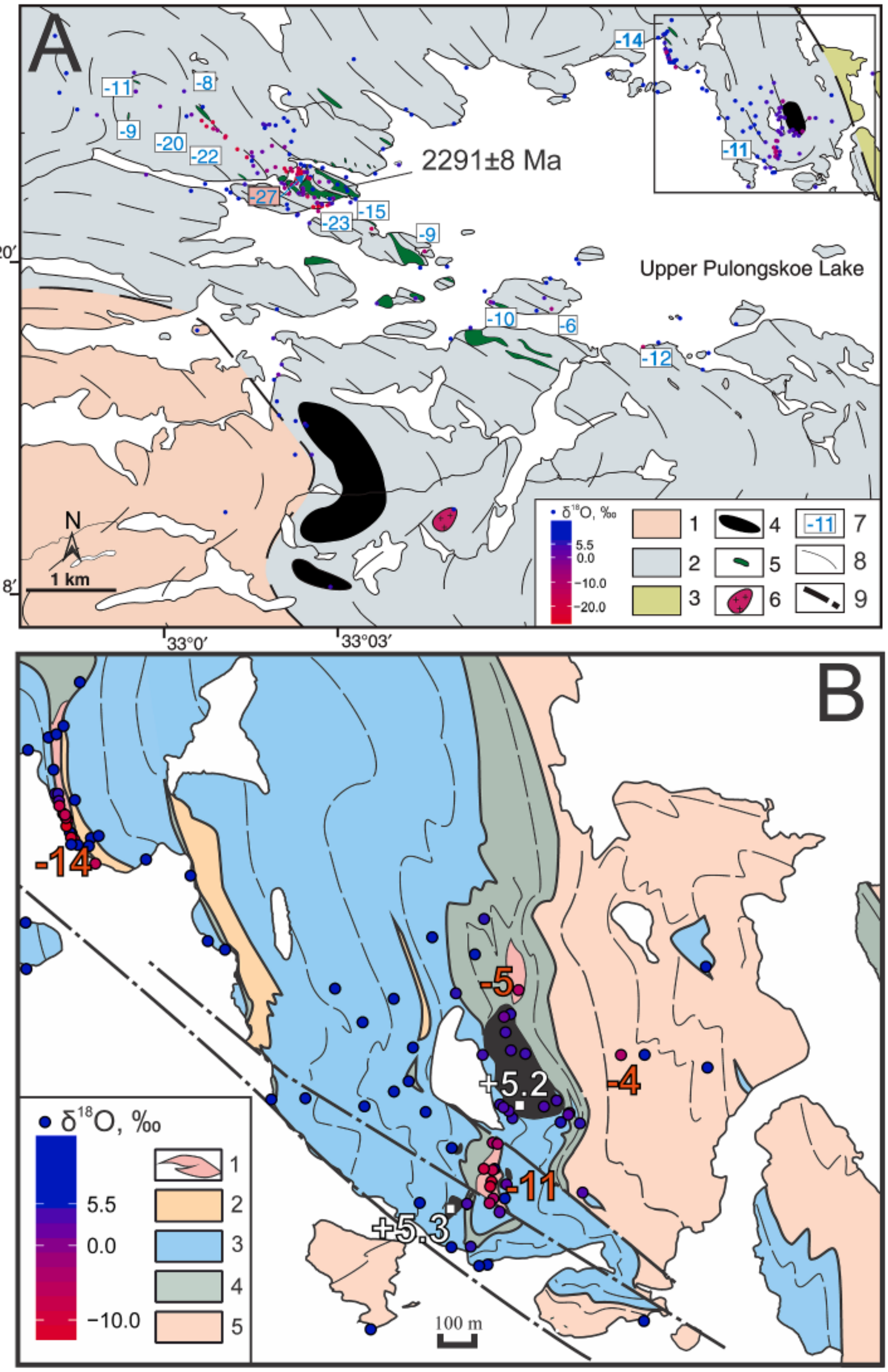

Fig. 4. A – Geological map of the lake Upper Pulongskoe area with the Vuat Varakka locality outlined by solid black rectangular area. The lowest $\delta^{18}O$ value is measured at Khitoostrov locality dated to 2291 ± 8 Ma as labeled (Zakharov et al., 2017). Shown as color coded circles, the $\delta^{18}O$ values are compiled from previous studies (Bindeman et al., 2014) and this study including 200 new values measured dominantly in garnets. Legend: 1 - Kotozero gneiss; 2 – Chupa gneiss; 3 – Khetolambino gneiss; 4 – high-Mg mafic intrusions; 5 – high-Fe gabbro intrusions; 6 - Archean granites; 7 – lowest measured $\delta^{18}O$ value measured at a cluster of measurements; 8 - metamorphic orientation; 9- major faults. B – Detailed map of the Vuat Varakka locality with $\delta^{18}O$ values measured in garnets shown with color coded circles. The lowest $\delta^{18}O$ values (labeled with red numbers) are hosted in amphibolites, gneisses and lenses of high-Al rocks surrounding the 2.44–2.41 Ga high-Mg mafic intrusion shown in black. The two $\delta^{18}O$ values measured in pyroxenes from the gabbro intrusion are shown in white. Legend: 1- high-Al rocks (corundum-bearing); 2 – leucocratic biotite gneiss; 3 – kyanite-garnet-biotite gneiss; 4 – garnet amphibolite; 5 – undifferentiated biotite gneisses and amphibolites. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

not been resolved completely (Beach, 1973; Cartwright and Valley, 1992).

3. Methods

3.1. Sampling and analytical procedures

A total of 270 samples were collected from the Belomorian belt and 60 from the Lewisian complex, and analyzed for $\delta^{18}O$, $\Delta^{17}O$ and δD. The sampling scheme was designed to identify the aerial extent of O-isotope depletion, the variability of $\delta^{18}O$ values along the strike length of units and from the interior to margins of the intrusive bodies. Further, $\Delta^{17}O$ and δD analyses were used to determine the involvement of meteoric water in the protoliths and its original $\delta^{18}O$ value (see Section 1.2). The $\delta^{18}O$ and $\Delta^{17}O$ measurements were done by laser fluorination with a MAT 253 mass spectrometer following conventional procedure with conversion to CO_2 (see Bindeman et al., 2014) and high-precision triple O-isotope analyses as described in Zakharov et al. (2017). Accuracy of conventional $\delta^{18}O$ analysis involving the CO_2-conversion was monitored by routine measurements of University of Oregon garnet (UOG; $\delta^{18}O$ = 6.52‰ relative to Vienna Standard Mean Oceanic Water, hereinafter VSMOW). The measured UOG standards were within 0.3‰ of the nominal value. The unknowns were adjusted for the day-to-day variability of the UOG $\delta^{18}O$ values. Accuracy of the triple O-isotope analyses was monitored by including San Carlos olivine (SCO; $\delta^{17}O$ = 2.677‰, $\delta^{18}O$ = 5.140‰ and $\Delta'^{17}O$ = −0.049‰ VSMOW-SLAP2; Pack et al., 2016) within each analytical session. After Miller (2002), the linearized delta-notation $\delta'^{17/18}O = 10^3 \ln$

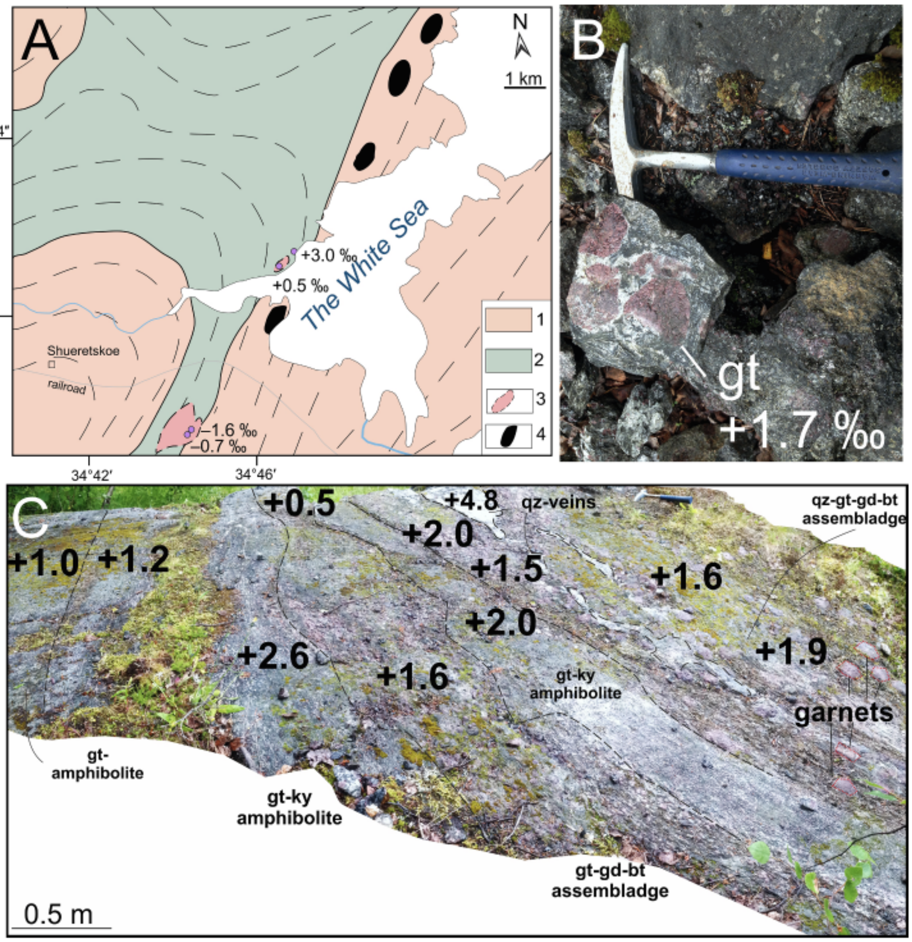

Fig. 5. A – Generalized geological map of the Shueretskoe location with the lowest $\delta^{18}O$ values measured in garnets shown with circles and numbers in ‰. Legend: 1 – biotite and garnet-biotite gneiss; 2 – amphibolites; 3 – outcrops of high-Al rocks with kyanite, gedrite and garnet; 4 –mafic intrusions. B – A representative sample of low $\delta^{18}O$ garnet (red) hosted in gedrite (dark green) matrix. C - Panoramic photo view of the outcrop exposed in an old quarry on the White Sea shore (Elovyi Navolok, *Russian*). Large 10–20 cm across crystals of garnet (pink) hosted in garnet-kyanite amphibolite and massive gedrite-biotite rock. The $\delta^{18}O$ values measured in garnets across the outcrop are shown with numbers in ‰. Minerals abbreviations: bt – biotite, gd-gedrite, gt - garnet and ky - kyanite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$(1 + 10^{-3}\delta^{17/18}O)$ was used for correcting the values using the measurements of SCO within same analytical session. The average values of our SCO during all analytical sessions were $\delta'^{17}O = 2.828 \pm 0.057$‰, $\delta'^{18}O = 5.494 \pm 0.103$‰ and $\Delta'^{17}O = -0.086 \pm 0.004$‰ (mean ± standard error, n = 7) relative to the reference gas, which in turn was calibrated against VSMOW (reference gas values $\delta'^{17}O = 11.970$‰ and $\delta'^{18}O = 23.313$‰). The unknowns were then adjusted to the nominal values of SCO cited above (Pack et al., 2016). The H isotopes were analyzed in amphiboles, biotites, zoisites and epidotes using a high-temperature conversion elemental analyzer (TC/EA) as described in Martin et al. (2017). The $\delta^{34}S$ analyses of three pyrite samples from the Scourie dikes were carried out at the University of Nevada, Reno, USA, using the same procedure as Grassineau et al. (2001). The uncertainty (±1 standard error) of $\delta^{18}O$ values determined by CO_2 conversion method is 0.1‰ or better. For high-precision analyses, the uncertainties of $\delta^{18}O$ and $\Delta^{17}O$ are ±0.010‰ and ±0.015‰, or better, respectively. The precision of δD analysis is ±4‰. Hydrogen and O-isotope values are reported relative to the VSMOW. The $\delta^{34}S$ values were measured at a precision of ±0.2‰ and are reported relative to VCDT (Vienna Canyon Diablo Troilite).

4. Results

4.1. $\delta^{18}O$ values of the Belomorian belt rocks

We here report the new $\delta^{18}O$ values (see Supplementary Table 1) for the three Belomorian belt localities (Figs. 4–6). The $\delta^{18}O$ values were measured in garnets because the mineral is resistant to isotope re-equilibration during metamorphic retrogression due to slow diffusion of oxygen isotopes, and thus they provide the closest analogue to the $\delta^{18}O$ values of protoliths (Kohn and Valley, 1998). Garnet is also resistant to weathering and represents the bulk $\delta^{18}O$ value of the sample, within 1–2‰, due to high temperature equilibrium between coexisting minerals established during the 1.89 Ga high-grade metamorphism. Several samples of amphibole, corundum, epidote, kyanite, pyroxene, quartz, zoisite and whole rock were also measured from different localities and reported in Supplementary Table 1. We found that measurements of amphibole, corundum, garnet, kyanite and zoisite extracted from same samples return $\delta^{18}O$ fractionation (i.e. $\delta^{18}O_{garnet} - \delta^{18}O_{amphibole} \approx 1000\ln^{18}\alpha_{garnet\text{-}amphibole}$) between 0 and 1‰ in all but one sample; S-18A returned 4.6‰ fractionation between amphibole and garnet (coexisting mineral pairs are assembled in Supplementary Table 2). Fractionation of $\delta^{18}O$ between coexisting quartz and garnets ranges from 1.8 to 3.4‰. These fractionations are consistent with high temperature equilibrium (~650 °C; Zheng, 1993) and the metamorphic grade of studied rocks. The $\delta^{18}O$ values measured in garnets at Vuat Varakka scatter between −14 to +8‰. Proximal to the intrusion, high-Al rocks have garnets with $\delta^{18}O$ values between −14 and +4‰ and the adjacent amphibolites also have garnets with low $\delta^{18}O$ compositions, the lowest measured value at −4‰ (Fig. 4A). The high-Mg gabbronorite intrusions sampled in the interior have $\delta^{18}O$ of +5.3‰ measured in pyroxenes (Fig. 4B). At Shueretskoe, the $\delta^{18}O$ values measured in garnets vary between −2 and +5‰ in amphibolites and high-Al rocks hosting large crystals of garnet and gedrite (Fig. 5). At Kiy Island, the ultramafic layers of the intrusion display original igneous textures and minerals and have $\delta^{18}O$ values from +4.6 to +5.1‰ measured in orthopyroxene and amphibole (Fig. 6A). High-Al rocks that contain amphibole, corundum, epidote, garnet, kyanite and zoisite have $\delta^{18}O$ values between −2.1 and +5.7‰ (Fig. 6B, C). The lowest $\delta^{18}O$ values were measured in garnets hosted in a massive epidosite at the contact

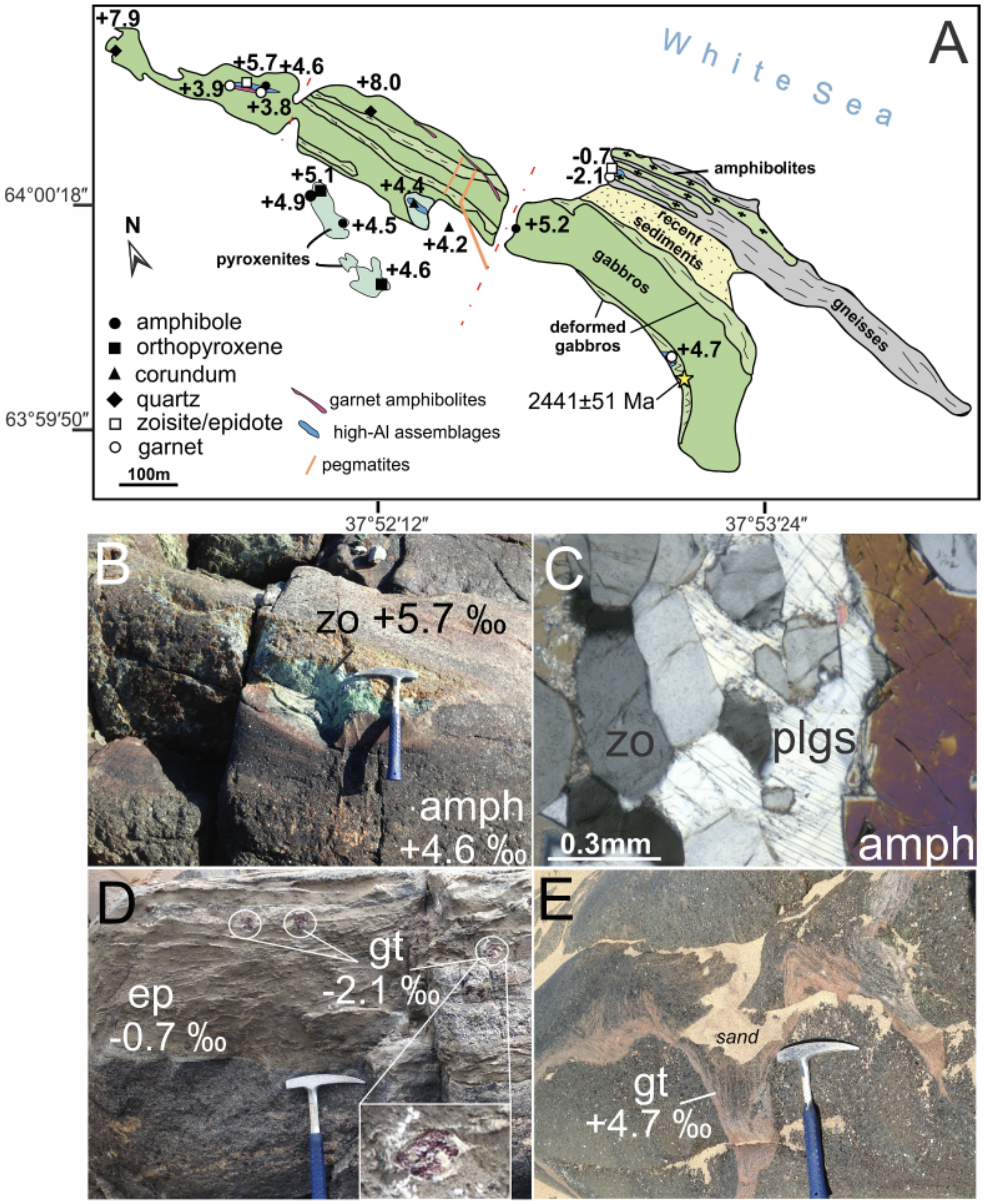

Fig. 6. A – Geological map of the Kiy Island locality (modified after Kulikov and Kulikova, 1990). Most of the island is composed of a large layered mafic intrusion (green) dated to 2441 ± 51 Ma using in-situ U-Pb dating (the sample location is shown; Slabunov et al., 2006). Multiple occurrences of high-Al rocks composed of amphibole, zoisite, garnet, corundum, and epidote are exposed within the intrusion and have $\delta^{18}O$ values ranging between −2.1 and +5.7‰. The lowest $\delta^{18}O$ values were measured in garnets from epidosite at the contact of the intrusion with hosting amphibolite; B – high-Al rock containing green zoisite (zo) and black amphibole (amph) with their $\delta^{18}O$ values shown; C – a microphotograph of the massive zoisite-rich rock shown in B in transmitted cross-polarized light featuring idiomorphic crystals of zoisite (zo), surrounded by plagioclase (plgs) and amphibole (amph); D – the low $\delta^{18}O$ epidosite (ep) with crystals of garnet (gt) hosted at the contact between the gabbros and amphibolites. The inset shows a magnified image of a garnet crystal ~ 5 cm across; E – An outcrop of deformed gabbro with foliated garnet-rich layer. Photograph taken near the sample collected for U-Pb geochronology. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between the intrusion and the host rocks (Fig. 6D).

4.2. $\delta^{18}O$ values of the Scourie dikes

The $\delta^{18}O$ values of Scourie dikes from the Assynt terrain are shown in Fig. 2, and reported in Supplementary Table 3; these include new values for dikes analyzed previously (Cartwright and Valley, 1991; Davies et al., 2015) and nine new low $\delta^{18}O$ occurrences. The $\delta^{18}O$ values of coexisting minerals from the lowest $\delta^{18}O$ dike Loch na h are assembled in Supplementary Table 4. In Supplementary Table 5 we also report new $\delta^{18}O$ values for the Archean rocks of the Lewisian complex, including felsic, mafic granulites, metasedimantery units from Stoer area as well as three samples from the South Harris Igneous complex including a sample of hosting metasedimentary gneiss (Cliff et al., 1983). Most Scourie dikes were measured using amphibole and pyroxene separates collected from the freshest portions of the coarse-grained interiors of the dikes. These minerals are abundant in the dikes and are more resistant to secondary exchange and retrogression than other common minerals such as plagioclase and magnetite (Farver and Giletti, 1985; Kohn and Valley, 1998). Cartwright and Valley (1991) showed previously that whole-rock $\delta^{18}O$ values from the Scourie dikes matched closely (< 1‰ difference) those from amphiboles and pyroxenes. We also analyzed several whole rock samples of the dikes' fine-grained chilled margins.

Our work has identified several permil variations within dikes sampled along their strike and large differences between the interiors and chilled margins (Fig. 7). To show variability in each dike and equilibrium fractionations, we compiled previously and newly reported $\delta^{18}O$ values for mineral separates and whole rock values for the Graveyard, Poll Eorna, Loch na h and other dikes in Figs. 7 and 8. We report several new occurrences of low-$\delta^{18}O$ Scourie dikes with values that span between −3 and +6‰. The lowest values are measured in amphiboles and magnetites of the Loch na h dike on the west shore of the lake Loch Assynt (see Fig. 8). Sampled in multiple locations along strike (Fig. 7B), the Loch na h dike returned range of values from −3.68 to −2.22‰ (n = 8) measured in amphibole, −4.78 to −3.27‰ (n = 3) in magnetite, and −0.36 to +3.23‰ (n = 5) in plagioclase. Given compositions of c. 47% amphibole, c. 47% plagioclase and c. 6%

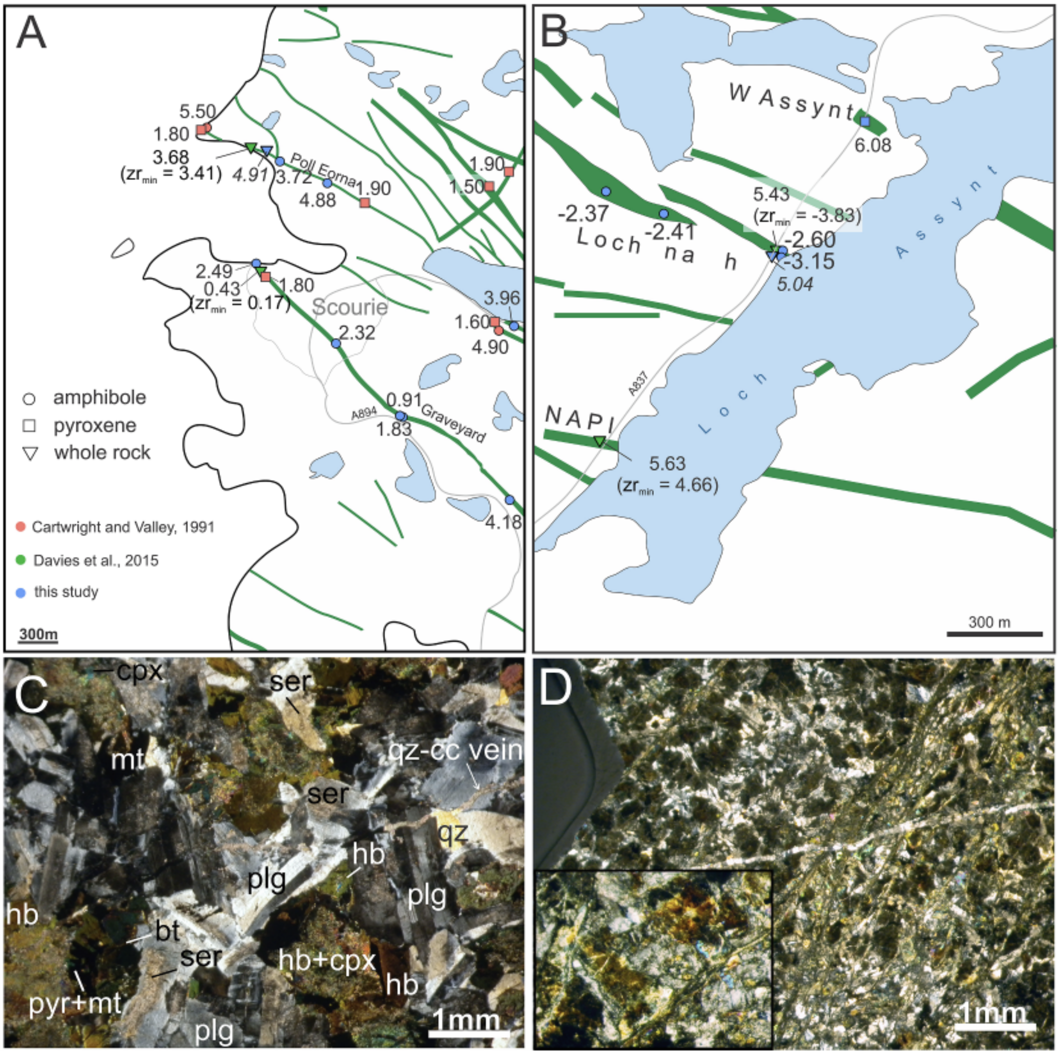

Fig. 7. The $\delta^{18}O$ values analyzed in amphiboles, pyroxenes and whole rock samples in dikes Poll Eorna, Graveyard and Loch na h based on previous studies and this work. The $\delta^{18}O$ value measured in chilled margins are shown in italic. The $\delta^{18}O$ values measured in zircons (zr_{min}) and respective whole rock samples are from Davies et al., (2015). A - The Poll Eorna and Graveyard dikes in the area of Scourie with variable $\delta^{18}O$ values measured along the strike. Large variations were observed in the shear zones and are accompanied by increase in $\delta^{18}O$ of Poll Eorna dike by 4–5‰ as reported previously (Cartwright and Valley, 1991). Smaller variations (1–3‰) were measured in amphiboles from coarse-grained interior even without sign of shearing. B – Location and $\delta^{18}O$ values of analyzed amphiboles from the Loch na h dike. The total range of values measured in amphiboles (n = 8) spans between −3.7 and −2.2‰, much lower than previously reported for the Scourie dikes. C – A cross polarized light microphotograph of the coarse-grained interior of the Loch na h dike showing abundant amphibole almost completely replacing clinopyroxene; plagiolclase is altered to sericite in the cores and magnetite is partially replaced with a rim of biotite. A thin quartz-calcite vein dissects the section indicating fluid-induced alteration. D – A cross polarized light image of the fine-grained chilled margin of the Loch na h dike showing abundance of secondary actinolite, sericite and chlorite almost completely replacing primary pyroxenes and plagioclase. Clay minerals record low-temperature alteration of the chilled margin which is consistent with the $\delta^{18}O$ value of 5.04‰, much heavier than the low $\delta^{18}O$ interior of the dike. The inset shows a magnified portion of the image (~2 times larger).

magnetite, and assuming that the lowest $\delta^{18}O$ values represent original magmatic values (Cartwright and Valley, 1991; Davies et al., 2015), the coarse-grained interior of the dike has calculated whole rock $\delta^{18}O$ value of about −2.5‰. Plagioclase-amphibole (plagioclase composition ~ An_{40}; Davies et al., 2015) pairs exhibit fractionations between 2.0 and 6.2‰, yielding computed equilibrium temperatures between 200 and 560 °C using the diopside-plagioclase fractionation factor (Chiba et al., 1989) as a close approximation for amphibole-plagioclase fractionation (see Supplementary Table 4). Amphibole-magnetite pairs yield fractionations between 1.0 and 2.6‰, corresponding to equilibrium temperatures of above 900 °C (Chiba et al., 1989). The whole rock sample of the chilled margin returned $\delta^{18}O$ value of 5.04‰, significantly higher than the $\delta^{18}O$ values measured in the interior of the dike. The hosting Lewisian gneiss collected about 10 cm away from the intrusive contact has $\delta^{18}O$ value of 7.51‰.

4.3. *Petrography of the Loch na h dike*

To better understand the $\delta^{18}O$ values from the Loch na h dike, we made thin sections from the coarse-grained interior and fine-grained chilled margin. The interior displays original igneous textures with preserved igneous minerals and abundant secondary minerals replacing them (Fig. 7C). Pyroxenes are extensively altered to an aggregate of amphiboles; magnetites are altered to biotite and calcic-rich plagioclase to sericite. The dike contains abundant fine quartz-calcite veinlets (Fig. 7C). Pyrite is found in the dike forming disseminated anhedral grains in spatial association with magnetite. The fine-grained chilled margins are thoroughly altered to an aggregate of sericite, chlorite and actinolite with some relicts of original igneous phases (Fig. 7D). We observed several generations of fine chlorite-actinolite veins and quartz-calcite veins cross-cutting each other indicating pervasive sub-

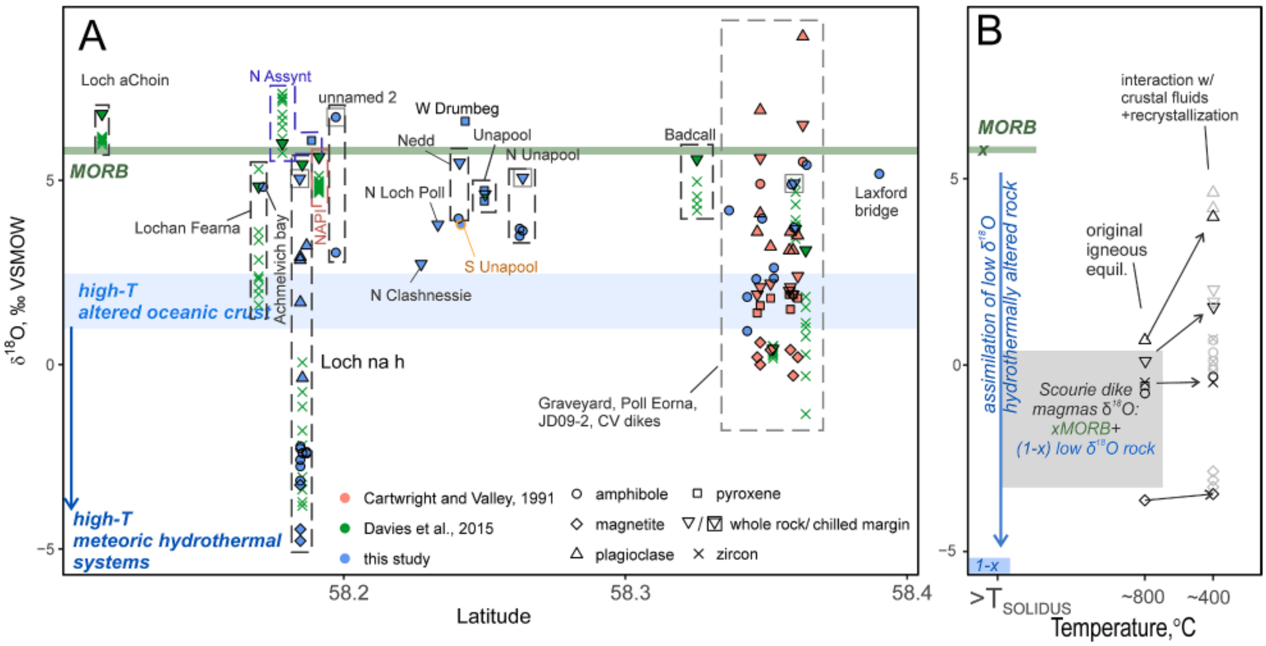

Fig. 8. A - Oxygen isotope values for mineral separates and whole rock samples compiled from the study and from previously published results plotted against their latitude position (see Fig. 2). The $\delta^{18}O$ values of MORB and high-temperature altered oceanic crust are shown with horizontal bands. Shallow meteoric hydrothermally altered rocks have a wide range of values, mostly below 0‰, which indicates that at least a fraction of Scourie dikes originated due to interaction with such rocks. B - A possible origin of low $\delta^{18}O$ signature of Scourie dikes: the initial MORB-like melts were contaminated by low $\delta^{18}O$ hydrothermally altered rocks. Initial high-temperature magmatic O-isotope equilibrium at ~800 °C was attained by crystallized igneous minerals. The effect of post-emplacement alteration via recrystallization and interaction with crustal fluids at 400 °C is shown. Note that due to variable susceptibility of minerals to isotope exchange with fluids, the associated $\delta^{18}O$ shift in different minerals is also variable (shown with arrows). Hypothesized range of values caused by recrystallization is shown with grey symbols.

solidus alteration by aqueous fluids.

4.4. $\Delta^{17}O$ values

The results of high-precision triple O-isotope analyses of the Belomorian belt rocks and Scourie dikes are listed in Supplementary Tables 6 and 7, and are displayed in Fig. 9. The values adapted from previous investigation of the Belomorian rocks (Herwartz et al., 2015; Zakharov et al., 2017) were recalibrated to San Carlos olivine (SCO) standard with $\Delta^{17}O = -0.053$‰ (Pack et al., 2016). The compositions of reference materials used here are reported in Supplementary Table 8. Ranging from −14 to −8‰ in $\delta^{18}O$, the Vuat Varakka garnets have $\Delta^{17}O$ values between −0.10 and −0.05‰, similar to other low and ultra-low $\delta^{18}O$ localities Khitoostrov, Varatskoe, Height 128 (see Zakharov et al., 2017; Fig. 9A). Grouped together with these localities, the linear regression line yields an intersection with meteoric water at $\delta^{18}O$ of −38 ± 3‰ (Fig. 9). The Shueretskoe and Kiy Island garnets have distinctly different values compared to those from Vuat Varakka: $\Delta^{17}O$ values vary between −0.05 and 0‰ and yield an intersection at −9 ± 5‰ for the $\delta^{18}O$ of the meteoric water (Fig. 9A). The Scourie dikes were measured using pyroxenes and amphiboles that range in $\Delta^{17}O$ from −0.10 to −0.02‰. The $\delta^{18}O$ and $\Delta^{17}O$ values in amphiboles of Loch na h dike plot between the mantle and meteoric waters, indicating incorporation of a component similar to the low $\delta^{18}O$ rocks from the Belomorian belt (Fig. 9).

4.5. δD values

The δD values as well as H_2O wt. % are reported in Supplementary Table 9. The δD values are plotted against $\delta^{18}O$ values in Fig. 10. Most δD analyses were done on amphiboles; a few on epidote, zoisite, staurolite and whole rock samples (see Supplementary Table 9). The δD values for the Belomorian belt are between −185 and −24‰ and those for the Scourie dike amphiboles are between −92 and −65‰. The hosting Lewisian gneisses and metasedimentary rocks yield whole-rock values between −52 and −36‰.

4.6. $\delta^{34}S$ values

Three analyses of pyrites from the Scourie dikes returned $\delta^{34}S$ values between 1.2 and 1.8‰; these, along with their $\delta^{18}O$ values, are reported in Supplementary Table 10. These results show that sulfur was likely sourced from the mantle-derived melts, not providing an additional insight into the interaction with meteoric water or seawater. Thus the $\delta^{34}S$ values are not regarded in subsequent discussion.

5. Discussion

5.1. Origin of $\delta^{18}O$ values in the Belomorian belt

The low $\delta^{18}O$ values in the Belomorian belt are concentrated around mafic intrusions dated at c. 2.4 Ga. The central parts of intrusions have mantle-like $\delta^{18}O$ values (c. 5.6‰) whereas low $\delta^{18}O$ values occur in host rocks adjacent to and along the contacts of the intrusions. We interpret this as due to hydrothermal alteration of the Archean protoliths induced by intrusion of the early Paleoproterozoic mafic magmas, with the high-Al rocks near the contacts related to chemical alteration of the protoliths. The O-isotope signatures were likely attained while the intrusions were still hot enabling low $\delta^{18}O$ meteoric water to interact with the host rocks at high temperature when the fractionation between most minerals and water is minimal (about 1–3‰; Zheng, 1993). Such process is well known and has been documented elsewhere where intrusions interacted with low $\delta^{18}O$ meteoric waters at high temperatures (300–500 °C; e.g. Taylor, 1971). Later metamorphism is unlikely to have generated these O-isotope values because during solid-state recrystallization the $\delta^{18}O$ values of metamorphosed rocks are largely governed by that of the protoliths (Taylor, 1974; Valley, 1986; Hoefs, 2018 and references therein). This is further supported by the $\delta^{18}O$

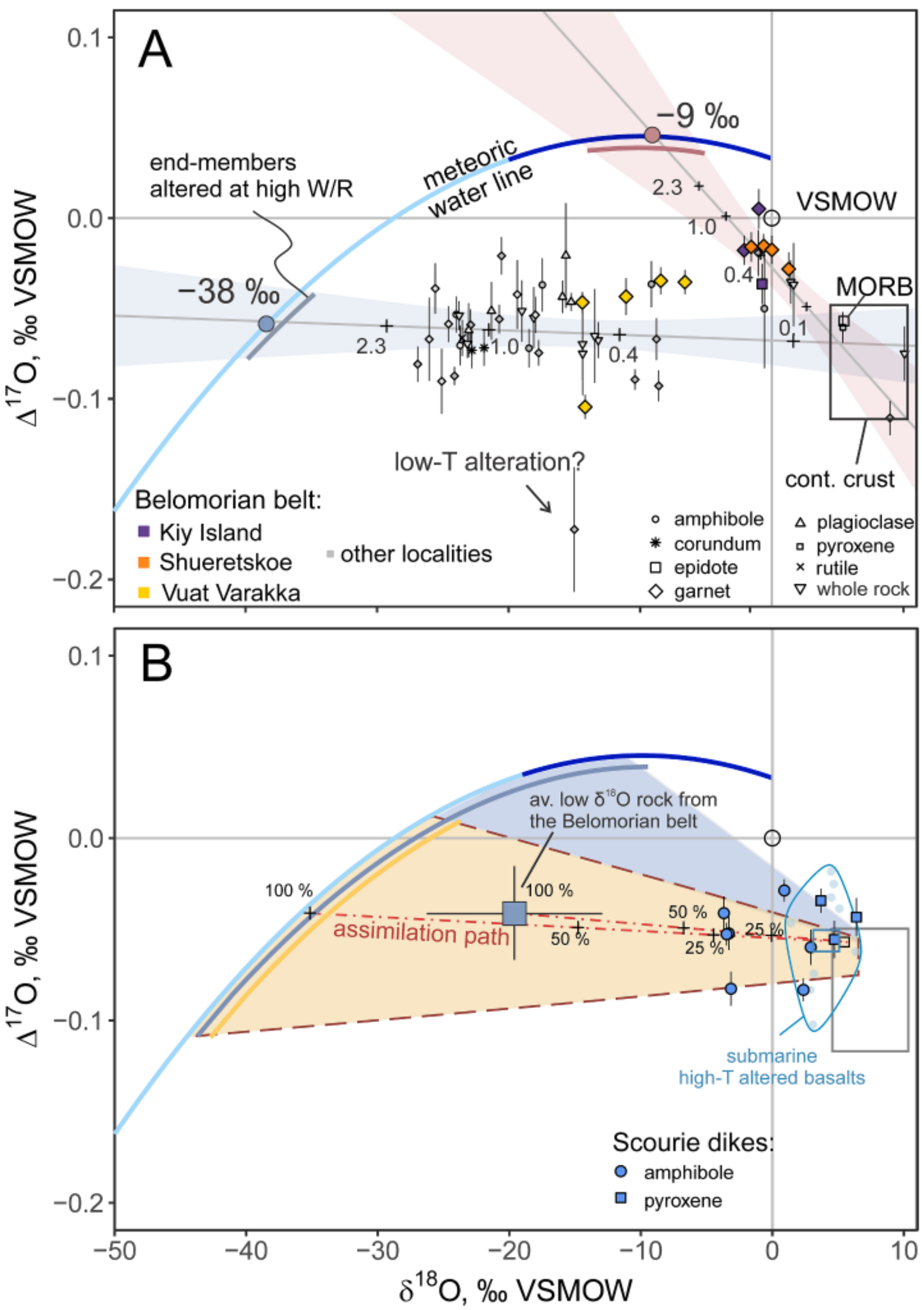

Fig. 9. Triple O-isotope composition of the low $\delta^{18}O$ rocks from the Belomorian belt (A) and Scourie dikes (B) with linear regression and 95% confidence intervals shown. Meteoric water line is shown with the blue curve (Luz and Barkan, 2010). Values of modern glacial ice ($\delta^{18}O$ below −20‰) are depicted by the cyan-blue segment. A - The samples from Vuat Varakka are consistent with involvement of meteoric water with $\delta^{18}O$ value of −38‰, plotting together with in other low- and ultralow $\delta^{18}O$ localities in the Belomorian belt. Samples from Shueretskoe and Kiy Island indicate that meteoric water with $\delta^{18}O$ of −9‰ is recorded in some hydrothermal systems. Small grey squares represent samples from previous studies (light grey – Herwartz et al., 2015; dark grey – Zakharov et al., 2017). See Supplementary Fig. 1 for the list of localities from the previous studies. Compositions of hydrothermally altered rocks in equilibrium with pristine meteoric water are shown with curves next to the meteoric water line. They represent end-member compositions altered at infinite W/R ratios (ratios 0.1–2.3 are shown with crosses and numbers). One sample with $\Delta^{17}O$ value close to −0.2‰ was likely altered at low temperature (< 200 °C) or undergone weathering. B - The $\delta^{18}O$ and $\Delta^{17}O$ values of the Scourie dikes are shown along with possible compositions of hydrothermally altered rocks that can produce the signature of analyzed samples through assimilation (dark shaded regions). For dike localities shown here see Supplementary Fig. 1. High W/R ratio end-members are shown with curved segments parallel to the meteoric water line. A subset of samples (Loch na h dike) with values < 0‰ plotting in the dark-yellow shaded region outlined by dashed lines require involvement of extremely low $\delta^{18}O$ hydrothermally altered rocks, similar to the samples from Belomorian belt. Two possible trajectories of magmatic assimilation of such rocks by mantle-derived magmas are shown with the red dash-dotted lines. The numbers in percent denote the mixing fraction of incorporated material. About 30% of assimilated material with isotope signature of Belomorian belt samples ($\delta^{18}O$ = -20‰, $\Delta^{17}O$ = -0.05‰) is required to reproduce the lowest $\delta^{18}O$ samples from Loch na h dike. It can be achieved by addition of smaller amount (~20%) of hydrothermally altered end-member at high W/R with $\delta^{18}O$ = −35‰. The encircled blue area represents submarine hydrothermally altered basalts which were previously suggested as the source for Scourie dike magmas (values from Sengupta and Pack, 2018; Zakharov and Bindeman, 2019). The assimilation paths for the dikes with modest O-isotope depletion ($\delta^{18}O$ = 0–2‰) are difficult to constrain due to limited range and scatter of values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

values and ages of zircons from these rocks: the Archean or Paleoproterozoic cores have normal $\delta^{18}O$ values while metamorphic rims have low $\delta^{18}O$ values which formed at 1.89 Ga by crystallization from the low $\delta^{18}O$ hydrothermally altered protoliths (see data in Bindeman et al., 2014). Consequently, we interpret our low $\delta^{18}O$ and $\Delta^{17}O$ values as due to hydrothermal alteration occurring close to the time of emplacement of the mafic bodies.

The $\Delta^{17}O$ approach is used here to reconstruct the meteoric water values involved in the ancient hydrothermal systems and to account for the unknown extent of isotope exchange with rocks (as described in Section 1.2). In the Belomorian belt, the Vuat Varakka locality (and other ultra-low $\delta^{18}O$ occurrences such as Khitoostrov and Varatskoe; see Fig. 1) indicate involvement of meteoric water with $\delta^{18}O$ of about −38‰, which in the modern world corresponds to the $\delta^{18}O$ value of high-latitude glacial ice and snow (Fig. 9A). The triple O-isotope composition of rocks from Shueretskoe and Kiy Island indicates involvement of much heavier $\delta^{18}O$ value of meteoric water, around −9‰, characteristic of near-coastal regions in the modern world and generally, precipitation at low latitudes (Dansgaard, 1964; Bowen, 2010). Thus, the original meteoric water was, from place to place, variable in its $\delta^{18}O$ composition and this is recorded in the observed differences in the Belomorian belt rocks that span about 40‰ in $\delta^{18}O$. The triple O-isotope composition of these rocks allows to reconstruct the extent of isotope exchange within the ancient hydrothermal systems: the W/R mass ratios varied from 0.1 to 2.3 (see Fig. 9). We should acknowledge that these are minimum estimates of W/R ratios since the rocks likely interacted with metamorphic fluids. Interaction with metamorphic fluids is registered in these rocks using H-isotope values (see

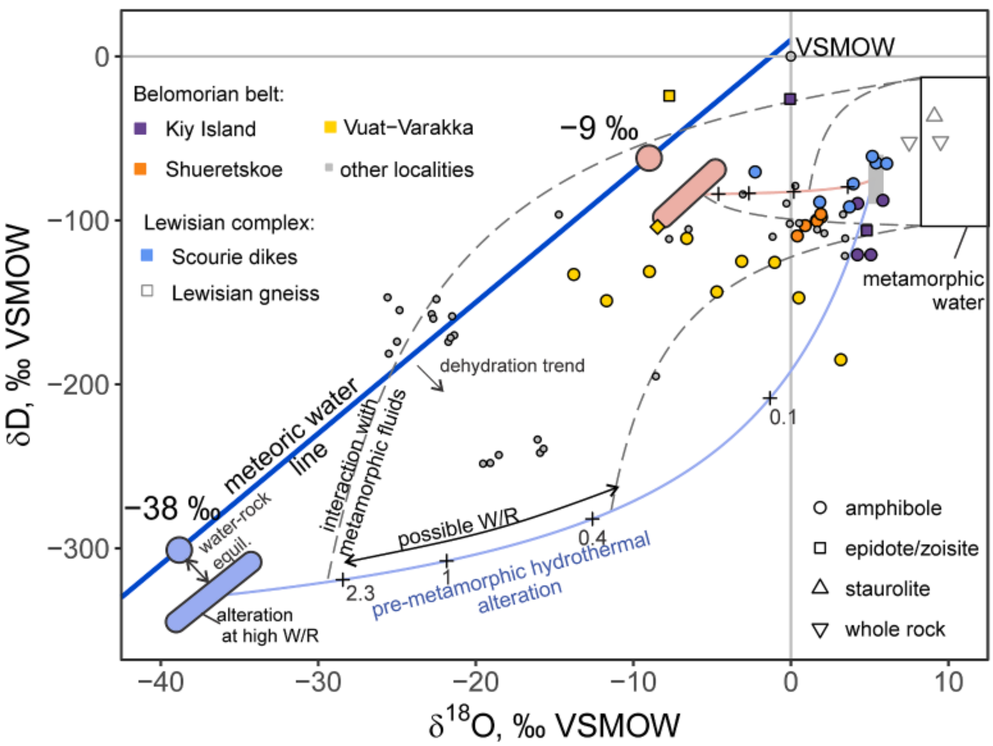

Fig. 10. Hydrogen and O-isotope compositions of the Belomorian belt rocks and the Scourie dikes including the hosting Lewisian gneiss. The low $\delta^{18}O$ rocks from the Belomorian belt described here are color coded as shown in the legend. Grey-filled circles plotted after analyses published in Bindeman and Serebryakov (2011). See Supplementary Fig. 2 for the list of localities from previous studies shown here. In the Belomorian belt, the measured δD values represent a mixture of inputs from the original hydrothermally altered rocks (shown as solid colored curves with crosses at different W/R ratios) and interaction with metamorphic fluids (dashed grey curves). The initial pre-metamorphic range of possible values is shown with curved arrows at W/R ratios as indicated by the triple O-isotope approach, between about 2.3 and 0.4. The compositions of original hydrothermally altered rocks at infinitely high W/R ratios are shown with oval shapes. Equilibrium meteoric waters computed from the $\Delta^{17}O$ data are shown with red and blue circles. The contribution of dehydrating reactions is shown with the arrow and is likely small due to high-temperature fractionation between minerals and water. In the Scourie dikes, the extent of preservation of original δD values and metamorphic overprint is unresolved, however some amphiboles have δD values slightly lower than accepted δD range of mantle-derived rocks shown with grey rectangle (Hoefs, 2018), and about 60‰ lower than the δD values of hosting Lewisian gneiss indicating possible presence of meteoric component in the dikes. For dike localities shown here see Supplementary Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Section 5.3); thus the O-isotope values could have been shifted only a few per mil (if at all) due to abundance of oxygen in rocks (Taylor, 1974). Bindeman et al. (2014) attributed ~+ 3‰ $\delta^{18}O$ shifts measured *in situ* within single grains of corundums and zircons to interaction with metamorphic fluids in the Belomorian belt. Due to high temperature fractionation between minerals and fluids during high-grade metamorphism, the $\Delta^{17}O$ values would likely shift towards the values of continental crust rocks (see Fig. 9). However, the registered shifts constitute only a small fraction of the total range of observed values in the Belomorian belt localities spanning over about 40‰ in $\delta^{18}O$. We consider that the $\delta^{18}O$ values of the rocks within each locality dominantly reflect the effect of variable W/R ratios, while $\delta^{18}O$ values across the belt also reflect differences in the compositions of meteoric water.

5.2. Origin of low $\delta^{18}O$ values in the Scourie dikes

The range of $\delta^{18}O$ values measured in Scourie dikes is consistent with the previous investigations (see Fig. 8; Cartwright and Valley, 1991; Cartwright and Valley, 1992; Davies et al., 2015). Magmatic origin of low $\delta^{18}O$ values in the Scourie dikes (Cartwright and Valley, 1991; Cartwright and Valley, 1992; Davies et al., 2015) was originally suggested based on preservation of small high-temperature, magmatic (600–800 °C) O-isotope fractionation recorded by mineral pair measurements from unsheared, coarse-grained parts of dikes and absence of low $\delta^{18}O$ values in the host rocks. In addition, our measurements of hosting Archean orthogneisses, mafic granulites, metasedimentary units of the Assynt terrain and younger rocks from the South Harris Igneous complex returned values above +5.4‰. Based on the new insights offered by the combined $\delta^{18}O$-$\Delta^{17}O$ measurements presented here, we attempt to explain the origin of isotope signature of the lowest $\delta^{18}O$ Loch na h dike, and possibly the other Scourie dikes too. We should first note that the comparatively high $\delta^{18}O$ values measured in sheared zones (up to +6‰; Cartwright and Valley, 1991) and variable $\delta^{18}O$ values measured along strike likely represent complex post-emplacement interaction with crustal fluids during subsequent metamorphic events, e.g. Laxfordian event (see Fig. 8B). Conforming to this is the fact that we did not find any $\delta^{18}O$ values lower than those measured in low-Ca zircons that experienced least amount of radiation damage (Davies et al., 2015). Similar to interpretation of the O-isotope data measured in zircons, we consider the lowest $\delta^{18}O$ value measured within the same dike to be the most reflective of the original magmatic signal. This suggests that the $\delta^{18}O$ values of +5.0–5.4‰ measured by us and Davies et al. (2015) in the chilled margin of the lowest $\delta^{18}O$ Loch na h dike is due to subsequent interaction with fluids, which is also now supported by the petrographic evidence (Fig. 7). Below we outline possible mechanisms that could have generated the low $\delta^{18}O$ signature in the Scourie dikes rocks.

Original studies (Cartwright and Valley, 1991) identified dikes with values 3‰ lower than the $\delta^{18}O$ expected for mantle-derived magmas (c. 5.6‰), interpreting this as a result of melting of low $\delta^{18}O$ hydrothermally altered oceanic crust. However, the range now extends to negative values recorded in amphiboles, magnetites and in zircons of the Loch na h dike (Davies et al., 2015), corresponding to $\delta^{18}O$ value of equilibrium melt of about −2.5‰. Generation of such low $\delta^{18}O$ magmas is not compatible with melting of lower oceanic crust and requires an addition of hydrothermally altered component that experienced high-temperature isotope exchange with isotopically negative meteoric water in subaerial environment. The lowest value that can be achieved by altered oceanic crust is ~ +2‰; this constraint is derived from high temperature fractionation between pristine seawater ($\delta^{18}O$ = 0‰) and secondary minerals at infinitely high W/R ratios. Such values are sparsely present in the oceanic crust. The overall range of seafloor high-temperature hydrothermally altered rocks is between +2 and +5‰, with average values of about +3–4‰ (Alt and Teagle, 2000). Much lower $\delta^{18}O$ of Archean seawater and thus, possibly much lower $\delta^{18}O$ values of altered oceanic crust, presents a possible explanation for the low $\delta^{18}O$ values of the Scourie dikes, however all known examples of submarine altered basalts of Archean and early Paleoproterozoic age exhibit $\delta^{18}O$ values comparable to modern-day oceanic crust (e.g., Holmden and Muehlenbachs, 1993; Furnes et al., 2007; Hodel et al., 2018; Zakharov and Bindeman 2019).

We thus suggest that contamination of mantle-derived melts by low $\delta^{18}O$ hydrothermally altered rocks is a more probable explanation. Based on the new $\Delta^{17}O$ data and insights from the Belomorian belt rocks, we explore the possibility of reconstructing $\delta^{18}O$ value of the protoliths assuming that the igneous isotope signature was generated by mixing between isotope composition of hydrothermally altered rocks and mantle-derived mafic magmas. If the uncontaminated magmas had $\delta^{18}O$ values of MORB, the values recorded in the Loch na h dike reflect contribution of very low $\delta^{18}O$ component which experienced alteration by meteoric water with $\delta^{18}O$ values in a broad range, between −45 and −25‰ (Fig. 9B). The relationship between $\delta^{18}O$ and $\Delta^{17}O$ in meteoric waters (Luz and Barkan, 2010) was likely similar to the modern (Bindeman and Lee, 2018), constraining the amount of hydrothermally altered rock incorporated into the mantle-derived melts to about 20–30% (Fig. 9B). This number would be higher if the protoliths were altered at lower water-rock ratios and vice versa. This explanation is based on the lowest $\delta^{18}O$ Loch na h dike, assuming that it records the highest fraction or/and the lowest $\delta^{18}O$ value of assimilated component. It is possible that other dikes, with higher $\delta^{18}O$ values (+2‰) were produced by assimilation of smaller amounts of such low $\delta^{18}O$ component or by melting of the high-temperature altered oceanic crust, or both (Fig. 9). The limited range of $\delta^{18}O$ values in these dikes does not allow us to constrain the fraction of the $\delta^{18}O$ value of assimilated material.

We should note that this interpretation is independent of the exact mechanism by which the mantle-derived melts were able to incorporate low $\delta^{18}O$ rocks. Assimilation of solid rocks, partial melting and mixing, or even subduction of low $\delta^{18}O$ hydrothermally altered rocks in the melting region, all would lead to almost identical triple O-isotope signature of the resulted magma due to minimal isotope fractionation at temperatures of magmatic solidus. Given that the estimated erosion level in the Assynt terrane corresponds to the lower crustal levels (5–7 kbar; ~500 °C; O'Hara, 1961; Tarney, 1963; Zirkler et al., 2012), assimilation of low $\delta^{18}O$ hydrothermally altered rocks that originated in the near-surface environment presents a puzzling explanation. Moreover, no low $\delta^{18}O$ rocks were found in the area, including the numerous analyses published previously (Cartwright and Valley, 1992) and this study, where we searched for hydrothermally altered rocks within metasedimentary units near Stoer area all of which returned values +7‰ and higher (Supplementary Table 5). Subduction of low $\delta^{18}O$ rocks into the melting region (i.e. contamination of the mantle source; Hughes et al., 2014) would be consistent with emplacement of dikes in the lower crust, however, low $\delta^{18}O$ hydrothermally altered rocks overall do not provide volumetrically significant reservoir of O-isotopes compared to the crustal and mantle reservoirs that participate in subduction and partial melting. Alternatively, we suggest that the low $\delta^{18}O$ signature of rather thick Scourie dikes, a least partly, might have originated during closely spaced syn-eruptive alteration and partial remelting of the mafic dikes. This would explain occurrence of somewhat diverse $\delta^{18}O$ values in zircons with homogenous U-Pb ages (Davies et al., 2015), variations in $\delta^{18}O$ values along strike measured within coarse-grained interiors and high MgO content of the dikes. Similar processes occur in modern LIPs and areas of extensive rifting, for example in the Columbia River Basalt province of North America or fissure basalts in Iceland, where heat derived from storage of large volumes of magmas promotes hydrothermal alteration, remelting and assimilation of low $\delta^{18}O$ crust (Bindeman et al., 2012; Colón et al., 2015).

5.3. Hydrogen isotopes

Because hydrogen is only a minor element weakly bonded in silicates, its isotope composition is often reset due to subsequent interaction with crustal fluids. Given that both the Belomorian rocks and Scourie dikes underwent variable extent of metamorphism, hydrogen isotopes likely experienced a wide variety of changes including interaction with metamorphic fluids and dehydrating reactions (Fig. 10). Consequently, we view the δD values as recording a mixed input from dehydration of the original protoliths and from the later reaction with metamorphic fluids. At the estimated temperatures of metamorphism in the Belomorian belt (600–700 °C), fractionation between amphiboles and water is around 10‰ for δD (Suzuoki and Epstein, 1976), thus, amphiboles closely reflect the δD of metamorphic fluids. Dehydration reactions involving preexisting minerals likely contributed to negative shifts of δD values. The lowest δD values were probably inherited from dehydration of those photoliths because secondary processes involving crustal fluids would only increase the δD values. This interpretation is supported by finding the correlation between the lowest δD values and the lowest $\delta^{18}O$ values (down to −235‰ δD and −27‰ in $\delta^{18}O$ reported by Bindeman et al., 2014). In this study, the Vuat Varakka locality contains δD values as low as −190‰ with $\delta^{18}O$ of −14‰, whereas the lowest $\delta^{18}O$ samples (−2‰) from the Shuereskoe and Kiy Island localities returned the lowest δD value of −100‰.

Compared to the Belomorian rocks, the low $\delta^{18}O$ Scourie dikes have higher δD values; these fall at the low end of the range for MORB, which is −90 to −60‰ (Fig. 10; Hoefs, 2018). Such values generally fit the proposed model above; the H-isotope composition indicates the dominant input from the mantle, allowing for a small addition of hydrothermally altered rocks. However, it is likely that dehydration during melting and post-emplacement alteration (as seen in thin sections) occurred, in combination obscuring the H-isotope signature of original melts. Clearly, the δD values of studied here rocks were significantly altered during subsequent interaction with crustal/metamorphic fluids. Hence, the triple O-isotope approach undertaken here provides a more robust record of interaction with ancient meteoric waters.

5.4. Implications for paleoclimate: Paleolatitude and age constraints

This study relates two early Paleoproterozoic provinces that recorded interaction with very low $\delta^{18}O$ meteoric waters. Such record provides evidence for substantial portions of continental crust exposed above sea-level allowing for active hydrologic cycle to exist. The O-isotope ratios in precipitation vary largely as a function of mean annual surface temperature which in turn depends on the latitude position of the region (Dansgaard, 1964). For example, meteoric waters with $\delta^{18}O$ of −38 ± 3‰, as recorded in the Belomorian belt rocks, precipitate in cold, high-latitude regions such as Greenland and Antarctica, whereas precipitation of warm mid-latitude, near-costal climate zones have values of −9 ± 5‰; such are recorded at Shueretskoe and Kiy Island. To investigate the $\delta^{18}O$ of precipitation in the early Paleoproterozoic snowball Earth climate state with a narrow strip of ocean remaining unfrozen (Jormangand state; Abbot et al., 2011), Bindeman and Lee (2018) applied an isotope-enabled Global Circulation Model. Their results indicated following: (i) the relationship between mean annual temperature and $\delta^{18}O$ of precipitation is very similar to that in the modern-day climate, (ii) snowball-Earth-derived meteoric waters have sharp $\delta^{18}O$ gradients such that the $\delta^{18}O$ of precipitation at low- and mid-latitudes could vary between −60 and −10‰. Given that the rocks comprising the Belomorian belt were very likely located at low-latitudes at 2.44–2.41 Ga (Mertanen et al., 1999; Bindeman et al., 2010; Salminen et al., 2014), our $\delta^{18}O$ data are consistent with model predictions for steep $\delta^{18}O$ gradients in low latitudes. We acknowledge that the dearth of precise age constraints hinders our ability to provide precise temporal resolution for the hydrothermal alteration across the Belomorian belt but, given that analogous Neoproterozoic snowball Earth episodes lasted for tens of millions of years (e.g. Rooney et al., 2015), this shortcoming is not overly limiting. For the Scourie dikes, the reconstructed value of $\delta^{18}O$ of assimilated material is also indicative of

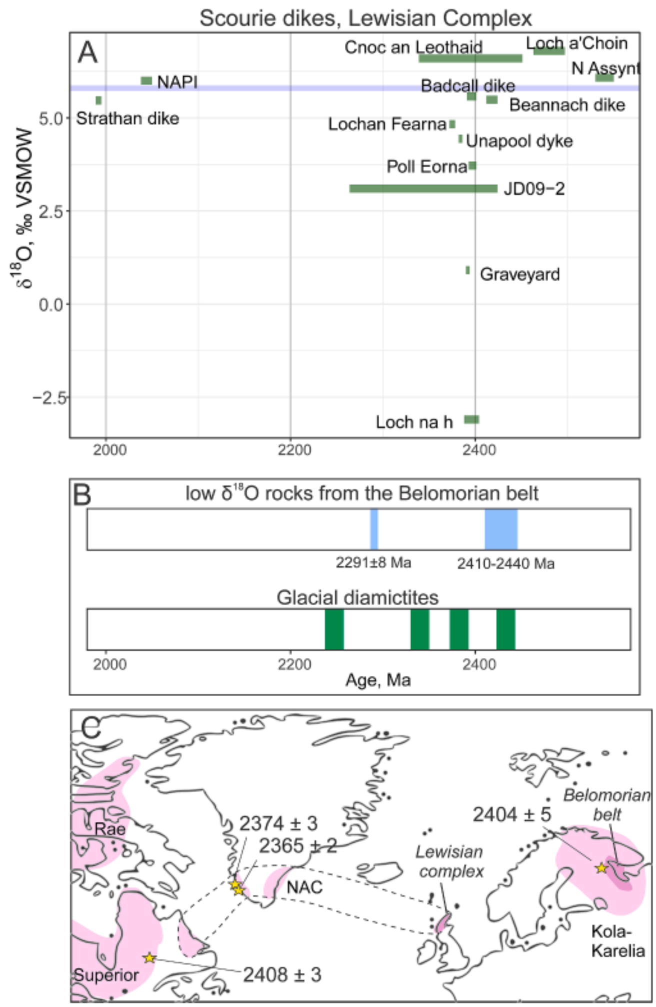

Fig. 11. The ages of Scourie dikes (A), low $\delta^{18}O$ rocks from the Belomorian belt and Paleoproterozoic glacial diamictites (B). The map of the North Atlantic region (C) shows the areal extent of exposed Archean cratons (North Atlantic craton = NAC) and some previously dated dike swarms (Superior craton dates from Krogh, 1994; NAC dates from Nilsson et al., 2013; Karelia craton dates from Stepanova et al., 2017) that could be coeval with the low $\delta^{18}O$ Scourie dikes of the Lewisian complex. Measuring their $\delta^{18}O$ values could assist paleogeographic reconstructions of the early Paleoproterozoic. The bar width for Scourie dikes corresponds to the error in U-Pb age (Heaman and Tarney, 1989; Davies and Heaman, 2014).

meteoric waters in cold regions, which is similar to the triple O-isotope composition of the low $\delta^{18}O$ rocks from the Belomorian belt. The close paleogeographic position of the two (Bleeker, 2003; Ernst and Bleeker, 2010) would be consistent with possible generation of low $\delta^{18}O$ rocks and their incorporation into mantle-derived melts during the rifting and intrusion of massive amount of mafic magmas in the early Paleoproterozoic during globally cold climate.

Given our results, we encourage further O-isotope characterization of magmatic and hydrothermally altered rocks that span the time interval to potentially overlap with the known episodes of early Paleoproterozoic glaciations. Similar to modern Iceland, magmas stored in the shallow crust initiate abundant hydrothermal systems that should leave an O-isotope imprint of contemporaneous meteoric water in the host rocks, which then could be remelted or recycled to produce new low $\delta^{18}O$ magmas (Taylor, 1971; Hattori and Muehlenbachs, 1982; Wotzlaw et al., 2012). Further, we suggest O-isotopes of dikes as a predictive tool for cross-cratonic correlations based on coeval low $\delta^{18}O$ rocks associated with magmatism, i.e. similar to "bar coding" of mafic dike swarms (e.g. Bleeker and Ernst, 2006). The $\delta^{18}O$ values of possible coeval analogues of Scourie dikes found in the fragments of North Atlantic craton (Fig. 11) could provide an effective tool to "bar code" connection between continental cratons in the early Paleoproterozoic. We thereby suggest sampling 2.44–2.38 Ga mafic dikes across Canada and Greenland using the coarse-grained interiors and their encasing host rocks, especially if mineralogical and textural relationships suggest contemporaneous hydrothermal alteration.

6. Summary

Pervious work identified a record of the early Paleoproterozoic glaciations imprinted in the low $\delta^{18}O$ rocks of the Belomorian belt, Baltic Shield, Russia (Bindeman et al., 2010; Bindeman and Serebryakov, 2011; Bindeman et al., 2014; Herwartz et al., 2015; Zakharov et al., 2017). It has been proposed that these rocks reflect the environmental conditions at low latitudes, where meteoric waters with $\delta^{18}O$ of ca. − 40‰ participated in hydrothermal systems induced by the voluminous magmatism and rifting of the Baltic Shield between 2.44 and 2.41 Ga. In this study we support this hypothesis with a new set of triple oxygen isotope measurements from the new occurrence of very low $\delta^{18}O$ rocks at Vuat Varakka (as low as −14‰) that reveals involvement of meteoric waters with $\delta^{18}O$ of −38‰. We also show that localities Kiy Island and Shueretskoe in the southern Belomorian belt record meteoric waters with $\delta^{18}O$ value of around −9‰. These estimated values of meteoric waters are diverse and reflect temporal or/and geographic variations of the early Paleoproterozoic precipitation consistent with previous modeling results (Bindeman and Lee, 2018).

A possible connection between the low $\delta^{18}O$ Belomorian belt rocks and the Scourie dikes, Lewisian complex is investigated here using the triple oxygen isotope approach. We found that the $\delta^{18}O$ values of Scourie dikes extend as low as −2.5‰ recorded by amphiboles as they are more resistant to secondary alteration compared to the whole rock samples or plagioclase. This value is most consistent with involvement of very low $\delta^{18}O$ material in the generation of Scourie dike magma as previously suggested based on the $\delta^{18}O$ values of igneous zircons (Davies et al., 2015). The exact mechanism of incorporation of such material is inconclusive, however, the reconstructed triple oxygen isotope composition of the assimilated material is strikingly similar to the isotope signature of the Belomorian belt rocks. This serves as a potential evidence for the connection between the Lewisian complex and the Baltic Shield in the early Paleoproterozoic and for the presence of an active hydrologic cycle that promoted generation of such low $\delta^{18}O$ signature imprinted in the rock record.

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Appendix A. Supplementary material

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