Revealing the climate of snowball Earth from $\Delta^{17}O$ systematics of hydrothermal rocks

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The oxygen isotopic composition of hydrothermally altered rocks partly originates from the interacting fluid. We use the triple oxygen isotope composition ($^{17}O/^{16}O$, $^{18}O/^{16}O$) of Proterozoic rocks to reconstruct the $^{18}O/^{16}O$ ratio of ancient meteoric waters. Some of these waters have originated from snowball Earth glaciers and thus give insight into the climate and hydrology of these critical intervals in Earth history. For a Paleoproterozoic [∼2.3–2.4 gigayears ago (Ga)] snowball Earth, $\delta^{18}O = -43 \pm 3‰$ is estimated for pristine meteoric waters that precipitated at low paleo-latitudes (≤35°N). Today, such low $^{18}O/^{16}O$ values are only observed in central Antarctica, where long distillation trajectories in combination with low condensation temperatures promote extreme ^{18}O depletion. For a Neoproterozoic (∼0.6–0.7 Ga) snowball Earth, higher meltwater $\delta^{18}O$ estimates of $-21 \pm 3‰$ imply less extreme climate conditions at similar paleo-latitudes (≤35°N). Both estimates are single snapshots of ancient water samples and may not represent peak snowball Earth conditions. We demonstrate how $^{17}O/^{16}O$ measurements provide information beyond traditional $^{18}O/^{16}O$ measurements, even though all fractionation processes are purely mass dependent.

triple oxygen isotopes | hydrothermal alteration | snowball Earth | climate | paleo-temperatures

Glacial successions deposited near the paleo-equator (≤15°) suggest that the Earth was entirely covered by ice several times during the Precambrian. Such episodes were termed "snowball Earth" climates. Presumably, the concentration of continents at low latitudes enhanced chemical weathering rates and thus removal of CO_2 from the atmosphere (1). Low pCO_2 led to global cooling and formation of polar and continental ice sheets. Once ice caps extended to latitudes below ∼50°, a runaway ice albedo cooling effect occurs (2), global temperatures drop far below zero, and the entire Earth becomes covered with ice (a snowball Earth) (2, 3). At least one "total glaciation" occurred in the Paleoproterozoic era [Makganyene at ∼2.4 gigayears ago (Ga)] (1), and at least two more arose in the Cryogenian (Sturtian at 720 Ma; Marinoan at 635 Ma) (3).

The climatic and hydrologic conditions of these critical episodes are poorly understood because classic paleo-thermometers (e.g., marine carbonates) are not viable for snowball Earth states and ancient water samples are missing. The $^{18}O/^{16}O$ ratio of meteoric water (expressed as $\delta^{18}O_{mw}$) can serve as a proxy for paleotemperature if the hydrogeological context is known (4). A few attempts have been made to reconstruct ancient $\delta^{18}O_{mw}$ (5–8).

Calcite cements that precipitated in methane seeps in the Nuccaleena Formation, Australia, probably sample meltwaters from the ∼635 Ma Marinoan snowball Earth with $\delta^{18}O$ ranging around ∼−29‰ (5). The upper carbonate unit of the Lantian Formation in Anhui, South China, probably formed during the younger, ∼580 Ma Gaskiers glaciation within a meltwater-dominated basin. These carbonates appear to be unaltered, hence low precipitation temperatures imply water compositions of $\delta^{18}O \approx -20‰$ to $-27‰$ (6). Barite- and malachite-associated sulfate from a diamictite in Kaiyang, Guizhou, China, reveals meteoric water compositions of $\delta^{18}O \approx -34 \pm 10‰$, probably representing Marinoan meltwaters (7). Apart from chemical sediments (5, 6) or ancient weathering products (7), it has also been suggested to estimate $\delta^{18}O_{mw}$ from hydrothermally altered rocks that have interacted with meltwater of meteoric origin (8).

Interaction of rocks with meteoric water at hydrothermal conditions (∼350 °C) shifts $\delta^{18}O$ of the rocks ($\delta^{18}O_r$) toward lower values. Modern examples for such shifts are known from volcanically active regions such as Iceland (9) or Yellowstone. Fossil Phanerozoic and Precambrian hydrothermal systems like the Dabie−Sulu ultra-high-pressure terrain (China) (10) or the Belomorian Belt (Russia) (11) are suggested to have formed similarly to their modern analogs. The lowest $\delta^{18}O_r$ values provide an upper limit for the $\delta^{18}O_{mw}$ (8). At full equilibration, rocks have a $\delta^{18}O_r$ that is only 2–3‰ higher than the water they interacted with (12), but the degree of equilibration between a rock and a given water is generally unknown, compromising absolute $\delta^{18}O_{mw}$ estimates (8). Here we present a new approach to reconstruct the absolute $\delta^{18}O_{mw}$ from measuring not only $^{18}O/^{16}O$ but also the $^{17}O/^{16}O$ ratios of hydrothermal low $\delta^{18}O_r$ Precambrian rocks.

Concept of Using Triple Oxygen Isotopes

The $\delta^{17}O_{mw}$ is closely coupled with the $\delta^{18}O_{mw}$ (Fig. S1); a relation hereafter called meteoric water line (MWL). The slope of the MWL is a result of equilibrium-dominated fractionation,

Significance

The snowball Earth hypothesis predicts that the entire Earth was covered with ice. Snowball Earth events were suggested to have occurred several times during the Precambrian. Classic paleo-thermometers (e.g., $^{18}O/^{16}O$ in marine carbonates) are not available from snowball Earth episodes, and only a few reconstructions of $^{18}O/^{16}O$ in ancient meteoric water exist. Here we present a novel approach to reconstruct the $^{18}O/^{16}O$ composition of ancient meteoric waters using the triple oxygen isotopic composition ($^{17}O/^{16}O$ and $^{18}O/^{16}O$) of hydrothermally altered rocks. The inferred $^{18}O/^{16}O$ for waters that precipitated at (sub)tropical paleo-latitudes on a Paleoproterozoic (∼2.4 gigayears ago) snowball Earth are extremely low. Today, similar compositions are observed only in central Antarctica.

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EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

whereas the intercept is due to kinetic fractionation in the exogenic water (see *SI Text* and Fig. S1). Rocks, in general, do not plot on the MWL (13). Rocks that have exchanged to variable degrees with meteoric water will define a mixing trend in a $\Delta'^{17}O$ vs. $\delta'^{18}O$ diagram (Fig. 1). The intersect between the mixing trend and the MWL gives, along with a small offset due to equilibrium hydrothermal water–rock fractionation, the composition of the interacting water (Fig. 1). This allows reconstruction of the $\delta^{18}O_{mw}$ from hydrothermally altered rocks and overcomes the limitation of unknown degree of equilibration, when using $\delta^{18}O_r$ only. Details regarding mass-dependent effects on $\Delta'^{17}O$ in silicates (Fig. S2) and definitions are given in *SI Text*.

Results and Discussion

We first test the new approach on hydrothermally altered low-$\delta^{18}O$ rocks from Iceland, where the $\delta^{18}O$ of the interacting water is approximately known. Icelandic samples are altered basalts from two boreholes (KG7 and KG10) at the Krafla volcano, taken from variable depths between 978 m and 2,100 m below the surface. The samples fall on a mixing array in the $\Delta'^{17}O$ vs. $\delta'^{18}O$ space between the unaltered Iceland basalt and the altered end-member (Fig. 1*A* and Fig. S3*A*). The samples stem from depths where temperatures were mostly ≥300 °C (9) and equilibrium fractionation between water and the alteration product is small [e.g., $\Delta\delta^{18}O_{water\text{-}epidote} \leq 2‰$, temperature ($T$) = 350 °C (14)]. Reconstruction of the pristine meteoric water (see *Methods*) gives a $\delta^{18}O_{mw} = -22 \pm 4‰$ ($1\sigma_{SE}$).

This estimate is lower than modern Icelandic meteoric waters with $\delta^{18}O_{mw} \approx -12‰$ (14, 15) but agrees with exchange with meteoric water from the Last Glacial Maximum (LGM). Such "ice age" waters are components of modern fumaroles [$\delta^{18}O$ values down to −19.3‰ (15)] and epidote-forming hydrothermal fluids [$\delta^{18}O_{hf} \approx -16‰$ (14)] at Krafla. The $\delta^{18}O_{hf}$ of any hydrothermal fluid in Iceland must be higher than the oxygen isotopic composition of the pristine meteoric water (i.e., $\delta^{18}O_{mw} < \delta^{18}O_{hf}$), because water–rock interaction drives the initial meteoric water to higher $\delta^{18}O$. Hence the $\delta^{18}O_{hf}$ reconstructed from epidote [∼−16‰ (14)] will be systematically higher than the pristine $\delta^{18}O_{mw}$ reconstructed by our novel approach (−18 to −26‰). The $\delta^{18}O_{hf}$ would only be equal to $\delta^{18}O_{mw}$ if water/rock ratios (W/R) were infinitely high, because the $\delta^{18}O_{hf}$ is a function of W/R whereas our approach is independent of W/R.

At W/R > 10, the initial water composition would change by less than 10%, implying that the Icelandic basalts had been altered to ∼40–65% (Fig. 2*A*). However, the respective samples are to 100% mineralogically reconstituted to secondary minerals (clay, chlorite, epidote); hence a W/R = 2 (Fig. 2*B*) seems more realistic. The water composition would be altered from −22‰ (initial $\delta^{18}O_{mw}$) to −14.5‰ ($\delta^{18}O_{hf}$) along a mixing line between the initial meteoric water and water in equilibrium with the unaltered basalt. Apparent degrees of alteration (up to 95%; Fig. 2*B*) are then more consistent with the rock mineralogy. If W/R ≈ 2 (Fig. 2*B*) are representative for other samples from Krafla, the $\delta^{18}O_{hf} = -16‰$ for the epidote precipitating fluid (14) is several permil higher than the respective initial $\delta^{18}O_{mw}$. We therefore propose that the role of ice age fluids at Krafla has been underestimated and W/R ratios have been overestimated. However, because the water mixing line is parallel to the rock mixing line, estimates of pristine $\delta^{18}O_{mw}$ are independent from assumed W/R ratios. Collectively, the data from Iceland demonstrate that $\delta^{17}O$ along with $\delta^{18}O$ can be used to infer the composition of the pristine meteoric water from hydrothermally altered rocks.

Neoproterozoic samples are eclogites (omphacite, garnet, quartz, rutile) from the Dabie–Sulu ultra-high-pressure terrain, eastern China. The $\Delta\delta^{18}O$ between the metamorphic minerals of these eclogites imply Mesozoic (240–220 Ma) isotopic equilibrium at 500–900 °C (10), well after the Neoproterozoic hydrothermal alteration (16). However, the metamorphic petrology, the age, the mineral equilibration temperatures, and even the rock type are unimportant for our approach. Despite the later metamorphic overprint, the bulk samples are still low in $\delta^{18}O_r$; hence part of the samples' oxygen still originates from the meteoric waters that had interacted with the samples. All hydrothermally altered samples (whole-rock estimates; Table S1) fall on a mixing trend between the unaltered and the fully altered end-members. This mixing trend crosses the MWL and implies a $\delta^{18}O_{mw} = -21 \pm 3‰$ (Fig. 1*B*). If the protolith exchanged oxygen not at hydrothermal, but at lower temperatures, a water composition of −22 ± 3‰ is suggested (see *Supporting Information*).

The Dabie–Sulu is located on the northern margin of the South China block that was drifting between ∼35°N (at 750 Ma) (17) and ∼15°N (at 600 Ma) (18) in the Neoproterozoic. A $\delta^{18}O_{mw}$ of −21 ± 3‰ at such low latitude is probably related to either the Sturtian (∼720 Ma) or the Marinoan (∼635 Ma) glaciation (3), but an origin from one of the smaller events (e.g., the Gaskiers glaciation) is also plausible. Published lower $\delta^{18}O_{mw}$ estimates of ∼−29‰ (5), ∼−20‰ to −27‰ (6), and −34 ± 10‰ (7) differ from ours in space and time. Some estimates are likely related to other Neoproterozoic glaciations; hence large variations between individual studies are expected. Because the hydrological cycle becomes sluggish at very low temperatures (3), it seems plausible that most $\delta^{18}O_{mw}$ estimates do not represent water that had precipitated during the peak of a snowball Earth episode. Maybe none of them does. Therefore, all estimates should be rated as maximum values with respect to peak snowball Earth conditions.

Paleoproterozoic samples from the Belomorian Belt (Hetoostrov Island, Karelia, northwestern Russia) are Al-enriched mafic schists, composed of plagioclase, amphiboles (pargasite and gedrite), biotite, garnet, rutile, staurolite with corundum, or kyanite (11, 19). Coexisting mineral $\Delta\delta^{18}O$ suggest equilibration temperatures between ∼450 °C and 700 °C (11, 20) that relate to the Svecofennian orogeny at ∼1.9 Ga. The regional concentric $\delta^{18}O_r$ zoning around vents are interpreted as signs for a fossil high-temperature hydrothermal system that probably formed at low paleo-latitudes (≲35°) during a Paleoproterozoic snowball Earth around 2.3–2.4 Ga (8). The whole rocks define an array in the $\Delta'^{17}O$ vs. $\delta'^{18}O$ diagram that intersects with the MWL and gives $\delta^{18}O_{mw} = -43 \pm 3‰$ (Fig. 1*B*). If the alteration occurred not at high but at low temperatures, a $\delta^{18}O_{mw}$ of ∼−49‰ is suggested (Fig. S3*C*). The maximum $\delta^{18}O_{mw} \approx -30‰$ estimate that can be derived from the lowest measured $\delta^{18}O_r$ = −27.3‰ (8) from the same locality is considerably higher, illustrating the value of additional $\delta^{17}O_r$ measurements.

Our reconstructions of $\delta^{18}O_{mw}$ are based on a $\delta^{18}O$ of seawater ($\delta^{18}O_{sw}$) similar to today (21). Higher (8) or lower (22) $\delta^{18}O_{sw}$ values would shift the MWL (Fig. 1*C*). If $\delta^{18}O_{sw}$ were high, our $\delta^{18}O_{mw}$ estimate would also increase to the same extent. Lower $\delta^{18}O_{sw}$ (22) would not affect $\delta^{18}O_{mw}$ estimates because the position of the MWL would remain similar to today's (Fig. 1*C*; see *Supporting Information* for the effects on temperature estimates). Such low $\delta^{18}O_{sw}$ are vigorously debated and are implausible if plate tectonics worked in broadly similar ways to today (21).

Today, $\delta^{18}O_{mw}$ bear information on mean annual temperature (MAT) (4). The only place on Earth where mean annual $\delta^{18}O_{mw}$ values are as low as −43 ± 3‰ is central Antarctica distal from the sea. Using a modern $\delta^{18}O_{mw}$ vs. MAT relationship (8) [e.g., $\delta^{18}O_{mw}$ = 0.69*MAT − 13.6‰ (4)], a $\delta^{18}O_{mw} = -43‰$ would translate into a MAT estimate of −42.5 °C. However, the hydrology of a fully frozen Earth close to the equator certainly differs from present-day conditions near the poles. Even today, local $\delta^{18}O_{mw}$ vs. MAT relationships show significant deviations from the global trend (23–25). Spatial slopes for Antarctica are generally steeper [e.g., 0.8‰/°C (25)], while ice core $\delta^{18}O$ from the LGM reveal shallow temporal relationships [e.g., ∼0.4‰/°C

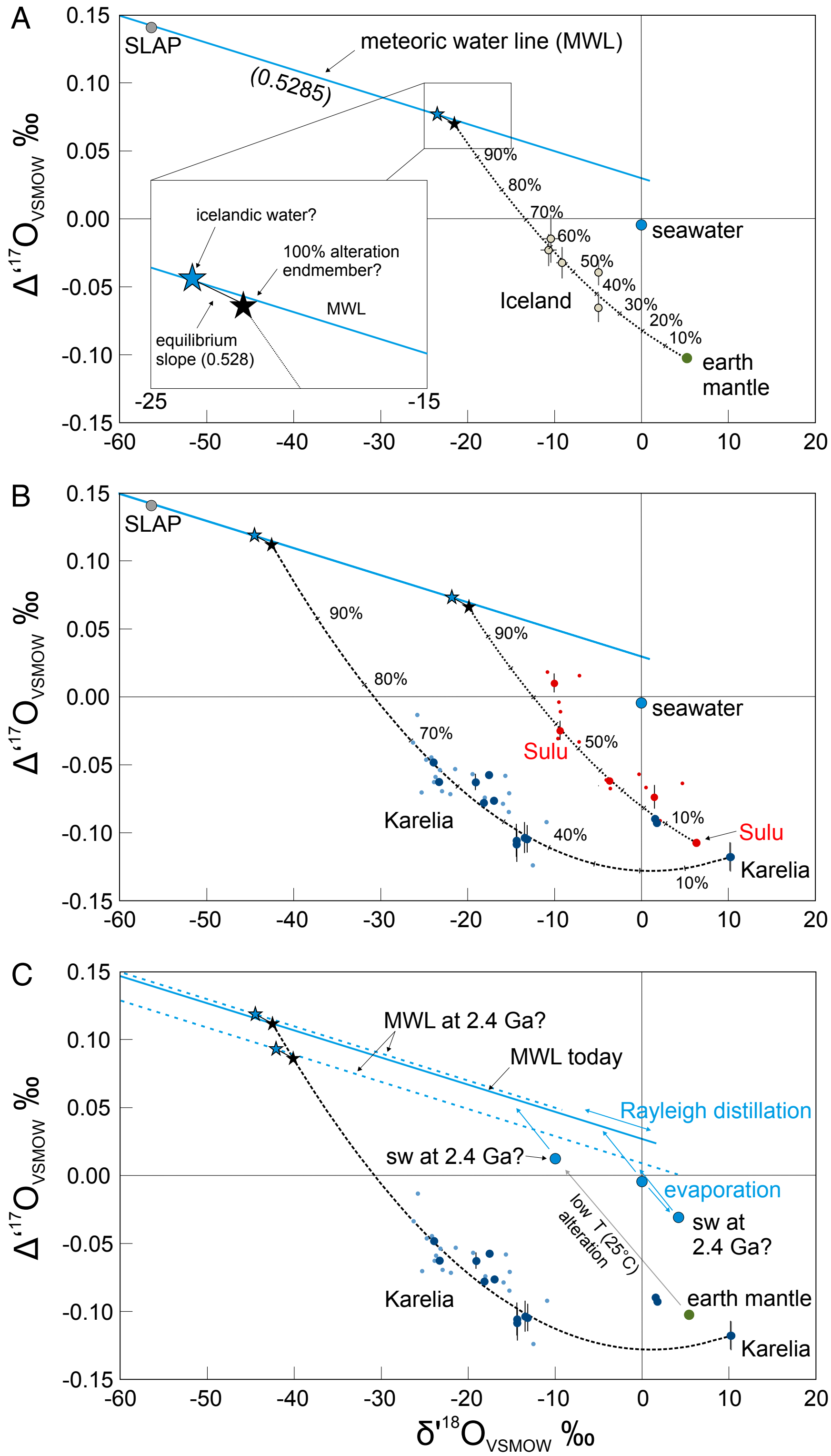

Fig. 1. Triple oxygen isotopic compositions of hydrothermally altered samples. (*A*) Samples from Iceland plot on a mixing line between the Earth mantle and a 100% alteration end-member close to the MWL (assuming infinite W/R). Literature data of meteoric waters mostly plot above the MWL with a slope of 0.5285 (Fig. S1). (*B*) Samples from the Sulu and Karelia also plot on mixing lines between the predicted composition of meteoric water from snowball Earth events and their unaltered end-members. (*C*) Estimated compositions for Paleoproterozoic seawater and respective MWLs (stippled lines). The relative offset of the MWL from seawater remains constant. Large points are whole-rock averages with error bars showing 1σ SEM ($1\sigma_{SE}$). Small points represent individual mineral analysis (no error bars shown).

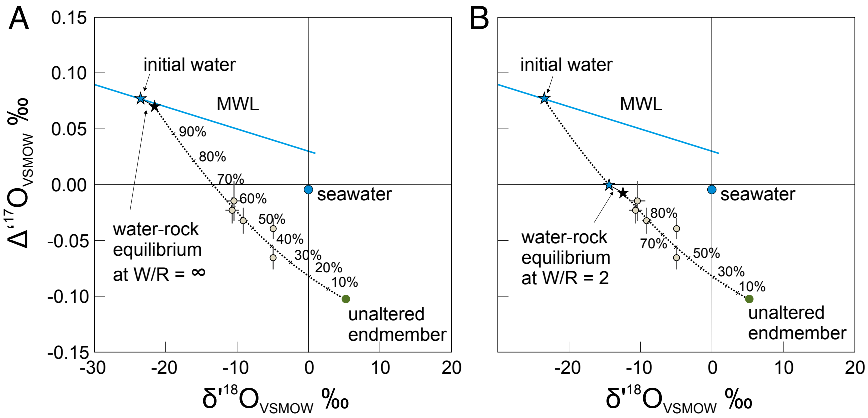

Fig. 2. Estimates of pristine $\delta^{18}O_{mw}$ are independent from W/R ratios. (*A*) At infinite W/R, the composition of the hydrothermal fluid is identical to the pristine meteoric water. Because the degree of sample alteration are underestimated (see *Results and Discussion*), this end-member scenario does not apply. (*B*) Lower W/R ratios (batch model) give more realistic estimates of sample alteration. The $\delta^{18}O_{hf}$ will evolve along a mixing line parallel to the rock mixing line. Therefore, estimates of pristine $\delta^{18}O_{mw}$ are independent of W/R and for simplicity, infinite W/R are assumed for Sulu and Karelia.

(24)]. General Circulation models (GCMs) predict such shallow temporal $\delta^{18}O_{mw}$ vs. MAT slopes mainly due to (*i*) low source and precipitation temperatures and (*ii*) a more dominant summer over winter precipitation combined with a stronger drop in summer than in winter temperatures (24). To our knowledge, GCMs have not been examined for the extreme conditions of a snowball Earth, but more simple Rayleigh-type models also predict shallower temporal slopes for a simultaneous drop in source and precipitation temperatures (23). On a snowball Earth, at least the source temperature would be lower than in the LGM, implying that shallow temporal slopes [e.g., 0.4‰/°C (24)] may extrapolate to even colder climates. If so, a modern-day $\delta^{18}O_{mw}$ vs. MAT relationship will overestimate paleo-temperatures not only for the LGM (23–25) but likely also for snowball Earth climates. A robust translation of $\delta^{18}O_{mw}$ into an absolute temperature scale could resolve debates about the extension of ice sheets (3, 26, 27) and sea ice thickness (28) during a snowball Earth (see *Supporting Information*). Extensive (sub)tropical glaciers on the continents are widely accepted for snowball Earth climates, but it remains a matter of debate whether the entire oceans were also covered by thick ice (3, 28). Climate models predict far lower equatorial temperatures for a “hard” snowball Earth (−45 °C to −20 °C) compared with a “slushball” Earth state (0−10 °C) (3, 26, 27). Thick sea ice > 100 m requires temperatures between −25 °C and −12 °C (28).

Besides low absolute temperatures, large degrees of Rayleigh-type distillation are required to reach such low $\delta^{18}O$ in precipitation. For example, ~80% condensation of the initial vapor at temperatures of −40 °C is necessary to reach $\delta^{18}O_{mw}$ values ≤ −40‰ (Figs. S4 and S5). The main source of atmospheric water vapor on a hard snowball Earth is sublimation in equatorial regions (≤10°; Fig. S6) (3) where temperatures are highest. A large degree of distillation thus implies glaciers deposited at some distance from this water source. Empirical correlations from Antarctica imply a decrease of 3‰/1,000 km (25); hence vapor transport over thousands of kilometers (over land or over sea ice) would be required to reach the observed low $\delta^{18}O_{mw}$. Initial precipitation at high altitudes with subsequent transport to the (presumably low-elevation) rift setting suggested for Karelia (8) is also feasible. Presently, $\delta^{18}O_{mw}$ decreases by *ca.* 2‰ per kilometer in temperate regions (29) and by 7‰ per kilometer in Antarctica (25). This increase in isotopic lapse rate (permil per kilometer) for colder regions is predicted by the thermodynamic model of Rowley et al. (30). Colder and drier climates are expected to yield increased lapse rates (30). For a slushball Earth, with evaporation temperatures ~5 °C at the equator (3, 26, 27), an altitude of ~5 km is sufficient to reach $\delta^{18}O_{mw} \approx -40$‰. At this lapse rate (8‰ per kilometer), an elevation of only 2.5 km would be required to reach our Neoproterozoic $\delta^{18}O_{mw}$ estimate of ~−21‰.

On a fully frozen but tectonically active Earth, cryovolcanism (as observed on the icy Jupiter moon Europa) is another potential source of atmospheric water that may help to decrease the overall $\delta^{18}O_{mw}$ compositions at low latitudes. Most of the erupted seawater and vapor would immediately resublimate and freeze in the cold atmosphere with only a small fraction being transported farther away from the source (distillation). Such waters would also have low $\delta^{18}O$ despite short distillation pathways.

Conclusions and Outlook

Our approach offers a way to reconstruct pristine $\delta^{18}O_{mw}$ from samples that had not been isotopically equilibrated with meteoric water. This example demonstrates how measurements of $^{17}O/^{16}O$ expand the traditional $\delta^{18}O$ scheme by another dimension. Being able to discriminate between kinetic fractionation vs. equilibrium fractionation vs. mixing will help quantify individual processes (e.g., diagenesis) or parameters (e.g., temperature). The basic theory is well developed, but applications are mainly restricted to the hydrogeological cycle (see *Supporting Information*). In principal, these systematics are applicable to all isotope systems with at least three stable isotopes. The sole limitation is currently set by the required high precision of isotope analysis.

Methods

The oxygen isotope ratios of anhydrous whole rock samples and minerals separates were measured using a high-precision laser fluorination technique (13). The hydrous samples from Iceland that could not be analyzed by laser fluorination were conventionally reacted with BrF_5 in Ni bombs. Samples were measured relative to tank O_2 that was calibrated against O_2 released from Vienna Standard Mean Ocean Water (VSMOW). The $\delta^{17}O$ and $\delta^{18}O$ are therefore reported on VSMOW scale (13).

To estimate equilibrium water–rock fractionation in triple-isotope space, we used a $\theta_{water\text{-}rock} = 0.528$ [corresponding to $T \approx 350$ °C; see Pack and Herwartz (13)]. Uncertainty in θ has a negligible effect, because fractionation in $\delta^{18}O$ is small (Fig. 1*A*). For fossil sites (Sulu and Karelia), the temperature of water–rock interaction is uncertain. At lower temperatures, $\theta_{water\text{-}rock}$ would decrease. As illustrated in Fig. S3, such low T alteration would slightly reduce $\delta^{18}O_{mw}$ estimates.

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