When do we need pan-global freeze to explain ^{18}O-depleted zircons and rocks?

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Rocks with $\delta^{18}O$ values of less than 5‰ SMOW (Standard Mean Ocean Water) contain oxygen derived from ~0‰ seawater or meteoric (rain or melted snow, <0‰) waters. As $\delta^{18}O_{precipitation}$ values decrease with increasing latitude, altitude, and toward the interior of continents, the low $\delta^{18}O$ values (<5‰) of hydrothermally altered rocks can potentially serve as a proxy for the $\delta^{18}O$ values of the altering water and as a proxy for climates (Fig. 1). Hydrothermal exchange of rocks with large quantities of meteoric waters presents the most viable opportunity to imprint low-$\delta^{18}O$ water values on the protolith (Fig. 2). Such processes typically require shallow depths of a few kilometers (where water circulates through open cracks and porous rocks), a heat source to drive meteoric-hydrothermal systems, and appropriate hydrogeologic conditions for water refill. These conditions are most commonly found in caldera and rift settings, such as in Yellowstone (Wyoming, United States) and Iceland. Oxygen—as the major element—is not significantly affected by subsequent metamorphism and melting (by more than ~1 ‰), and metamorphism often creates large, refractory metamorphic minerals (garnets, omphacites, zircons) that lock the protolith's oxygen isotopic values permanently in the geologic record.

A remarkable surprise is that low and ultralow $\delta^{18}O$ values (< 0‰) were found in ultrahigh-pressure (UHP) metamorphic rocks from the Dabie (Shan)–Sulu orogenic belt, eastern China (down to –11‰; Rumble et al., 2002; Chen et al. 2003; Zheng et al., 2008), indicating that their protolith was once near the subaerial surface and was altered by meteoric waters prior to metamorphism. New regional investigation and scientific drilling in the Dabie-Sulu orogen have demonstrated that the exposure of low-$\delta^{18}O$ rocks exceeds 20,000 km^2, and is likely 60,000 km^3 in volume (e.g., Zheng et al., 2008). Similar discoveries in metamorphic rocks from Kazakhstan (~–4‰; Masago et al., 2003) and more recently Karelia, Russia (–27.3‰; Bindeman and Serebryakov, 2011, and references therein) pose the question of how common these isotopically extreme rocks are in the geologic record.

Hundreds of publications in the Chinese and international literature attributed the formation of the protolith of the Dabie-Sulu UHP metamorphic rocks to the alteration by low-$\delta^{18}O$ glacial meltwaters under ice. As the South China Block was located at low to mid-latitudes in the Neoproterozoic (Hoffman and Li, 2009), pan-global, Snowball Earth glaciations at ca. 750–780 Ma were proposed by many authors. This bold hypothesis has led to ultradeep scientific drilling, multimillion-dollar funding, and diverse lines of investigation to estimate the extent of the ^{18}O depletion, and to establish its exact timing with respect to one of the known episodes of Neoproterozoic Snowball Earth glaciations (Zheng et al., 2007, 2008; Chen et al., 2011, and references therein). It is this hypothesis that Wang et al. (2011, p. 735 in this issue of *Geology*) seek to challenge.

Dating the timing of hydrothermal alteration in now metamorphic rocks is difficult, and much emphasis is placed on the refractory and alteration-resistant mineral zircon, which permits U-Pb dating and $\delta^{18}O$ determination in the same domain using modern in situ methods. I start here with an explanation on how low $\delta^{18}O$ values in zircons can be used to predict the timing, extent, and origin of past water-rock interaction. Zircon will survive hydrothermal alteration intact (even when its host rock is turned into clays), and indeed Dabie-Sulu zircons display normal $\delta^{18}O$ Mesoproterozoic to Neoproterozoic cores, but (variably) low $\delta^{18}O$ Triassic metamorphic rims (Fig. 2), in local isotope equilibrium

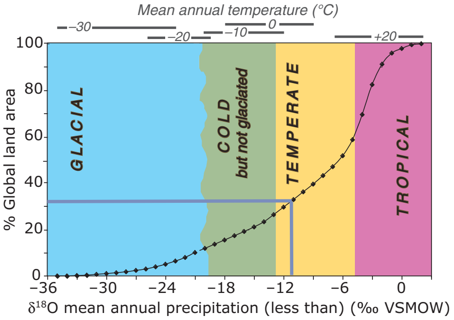

Figure 1. Land area versus $\delta^{18}O$ in precipitation for the modern distribution of land masses (from http://www.waterisotopes.org), showing that $\delta^{18}O_{water}$ <–11‰ is available on 33% of modern land surfaces in temperate climates. Ranges of mean annual temperatures for $\delta^{18}O_{precipitation}$ are from circulation models of Jouzel et al. (1994) for modern and Pleistocene glacial worlds, with ranges due to orography and other factors.

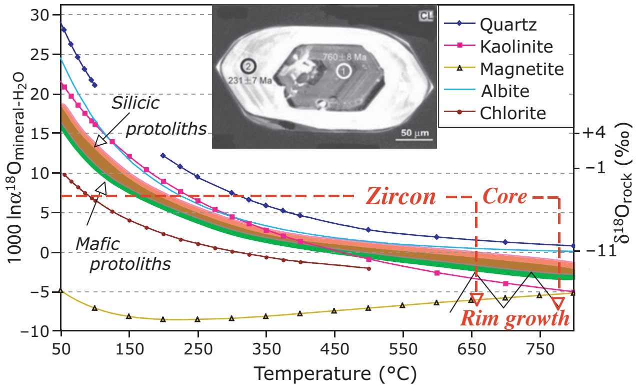

Figure 2. Equilibrium water-rock oxygen isotope fractionation between water and typical secondary alteration minerals, and 1000 ln$\alpha^{18}O_{rock-water}$ for generic basic and silicic lithologies, estimated using the fractionation factors of their constituent minerals in respective proportions. Notice that at temperature (T) > 350 °C, 1000 ln$\alpha^{18}O_{rock-water}$ is close to 0‰. Shown on the right axis are the $\delta^{18}O_{rock}$ values in equilibrium with –11‰ unshifted water at different temperatures of exchange. Such water, in equilibrium with the lowest measured, –11‰ rock values is widely available at mid-latitudes (Fig. 1), and is not necessarily glacial in origin. Inset shows a typical Dabie Shan zircon with normal $\delta^{18}O$ Neoproterozoic core and 231 Ma rim (Liu et al. 2005). Zircon is not affected by hydrothermal alteration and retains its original age and ~+7‰ $\delta^{18}O$ value (dashed horizontal arrow). Only at a high temperature of metamorphism will zircon recrystallize to yield a low-$\delta^{18}O$ rim, in equilibrium with the local metamorphic mineral assemblage. In nature, hydrothermal alteration generates a protolith that is diverse in $\delta^{18}O$ due to incomplete and variably intensive water/rock ratios (shown as a zigzag pattern); upon metamorphism, the $\delta^{18}O_{zircon\ rim}$ values will inherit this heterogeneity but be in isotopic equilibrium on a centimeter scale with the local mineral assemblage. Finally and paradoxically, the lowest $\delta^{18}O$ zircon rim values provide the best record of the initial $\delta^{18}O$ values of water, which altered the protolith hundreds of millions of years before metamorphism.

Geology, August 2011; v. 39; no. 8; p. 799–800; doi: 10.1130/focus082011.1.

with the host metamorphic assemblage or partial melt. Generally, because the hydrothermal alteration is rarely 100% efficient and rapidly shifts waters to higher δ^{18}O values, it can be expected that the $\delta^{18}O_{rock}$ values approach value of altering water only in a small volume of rocks, constantly flushed by fresh and δ^{18}O-unshifted waters at high temperatures (Fig. 2). Each local analysis of a metamorphic assemblage or a zircon domain will thus provide an independent probe into the past water-rock interaction, water-rock ratios, and the $\delta^{18}O_{water}$ value prior to metamorphism. It is thus the lowest $\delta^{18}O_{zircon}$ value that provides the best estimate for δ^{18}O of altering water.

By now, thousands of in situ (secondary ion mass spectrometry; SIMS) and bulk (laser fluorination) oxygen isotope analyses have been performed on surface samples and drill cores of Dabie Shan, and have revealed both normal and negative δ^{18}O values characteristic for ~60,000 km^3 volume of rocks. However, to our informed knowledge, these analyses failed to find δ^{18}O values lower than –11‰; we thus accept the lowest values of –11‰ ± 2‰ as a good proxy for the δ^{18}O value of the altering meteoric water (Fig. 2). Complementing that are the δD values reported for Dabie-Sulu rocks (Zheng et al., 2008), which are only moderately depleted (~–60‰ to –126‰). As OH-bearing hydrous minerals are ~20‰–40‰ more negative in δD than waters during hydrothermal exchange, and because metamorphism typically decreases δD_{rock} values through fractional loss of higher-δD fluids, these measured δD values may only provide a lower bound for δD_{water}, corresponding perhaps to δ^{18}O values of ~–5‰ to –13‰ in original altering waters along the meteoric water line.

These observations alone suggest that glacial meltwater may not necessarily be required to explain Dabie-Sulu depletions. If the modern, multi-continent world is taken as an analogy for Neoproterozoic, then 33% of Earth's land surface has δ^{18}O values of precipitation lower than –11‰ (Fig. 1). Thus, any mid-latitude meteoric precipitation (rain or snow) may explain the Dabie-Sulu low δ^{18}O values. Similarly, Kazakhstan's ~–4‰ UHP rock values do not require glaciation. In contrast, values of –25‰ to –27.3‰ in metamorphic mineral assemblages and zircon rims, and –235‰ δD values of Paleoproterozoic rocks in Karelia, Russia (Bindeman and Serebryakov, 2011) do indeed require glacial meltwater, because only ice is that isotopically low (Fig. 1).

The second argument that may "falsify" a synglacial origin of the Dabie-Sulu low-δ^{18}O anomaly is related to geochronology, and the best argument on that is provided by the igneous low-δ^{18}O zircons, crystallizing from low-δ^{18}O magmas[1]. This is the approach taken by the study of Wang et al. (2011). The likelihood of finding low-δ^{18}O igneous zircons coeval to rifting, hydrothermal alteration, and remelting processes, in a detrital record is high. The reason is that in caldera settings and rift zones, hydrothermal alteration, burial, and remelting occur side by side, and melting postdates caldera collapse or rift failure by only 0.1–1.0 m.y., causing the appearance of isotopically zoned zircons with low-δ^{18}O rims (e.g., Bindeman, 2008). These time scales would be treated as instantaneous in the Precambrian. Sporadic low-δ^{18}O igneous zircon values of ~+2‰ to ~3‰ and synglacial 756 ± 15Ma age in the least metamorphosed granites were attributed to the remelting processes of silicic rocks happening during the Kaigas glaciation (Zheng et al., 2007), and these results are quoted as "smoking gun" evidence for a Dabie-Sulu protolith origin during subglacial rifting under Snowball climate conditions.

The study by Wang et al. (2011) demonstrates that the low-δ^{18}O magmatism and igneous zircons are not limited to a synglacial ca. 756 Ma time interval. Instead, they found evidence that the rifting episode(s) lasted >100 m.y., since ca. 870 Ma. Thus, the ^{18}O depletion of 60,000 km^3 of crust happened incrementally, over a long time interval in the long-lived rift, as is represented by intermittent low-δ^{18}O A-type magmatism and low-δ^{18}O detrital zircons. In summary, the study by Wang et al. (2011) challenges the long-rooted argument of a synglacial origin of the Dabie-Sulu protolith, and opens up more realistic and general scenarios of depletions happening in a long-lived intracontinental rift zone, and shows that invoking the Neoproterozoic glaciation may not be necessary.

Finally, we would like to entertain the possibility of variably low-δ^{18}O seawater in the Neoproterozoic (~–10‰; Jaffres et al., 2007). While we are not aware that seawater caused a direct imprint on Dabie Shan protolith (e.g., Fu et al., 2002), the hypothetical low-δ^{18}O seawater could have caused lower-δ^{18}O continental precipitation, further relaxing any need for a Snowball Earth glaciation.

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[1] True low-δ^{18}O igneous rocks are typically higher in δ^{18}O than their parental hydrothermally altered rocks, because the magma segregation process averages-out large volumes of variably and less extremely ^{18}O-depleted protoliths, here perhaps represented by the average δ^{18}O value of a Chinese drillcore (i.e., Chinese Continental Scientific Drilling Project [CCSD], >4000 m deep). The distinction between the true low-δ^{18}O magmas and hydrothermally altered Dabie Shan metamorphic rocks is often confused, and many authors refer to the Dabie Shan–Sulu terrain as the largest "low-δ^{18}O magma" province on Earth, which is not correct, except for small-volume migmatites.

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