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

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Rocks with δ18O 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 δ18Oprecipitation values decrease with increasing latitude, altitude, and toward the interior of continents, the low δ18O values (<5‰) of hydrothermally altered rocks can potentially serve as a proxy for the δ18O 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-δ18O 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 δ18O 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-δ18O rocks exceeds 20,000 km², and is likely 60,000 km² in volume (e.g., Zheng et al., 2008). Similar discoveries in metamorphic rocks from Kazakhstan (~4–6‰; Masago et al., 2003) and more recently Karelia, Russia (~27.5‰; 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-δ18O 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 ultradepth scientific drilling, multimillion-dollar funding, and diverse lines of investigation to estimate the extent of the 18O 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 δ18O determination in the same domain using modern in situ methods. I start here with an explanation on how low δ18O 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 δ18O Mesoproterozoic to Neoproterozoic cores, but (variably) low δ18O Triassic metamorphic rims (Fig. 2), in local isotope equilibrium...
with the host metamorphic assemblage or partial melt. Generally, because the hydrothermal alteration is rarely 100% efficient and rapidly shifts waters to higher δ18O values, it can be expected that the δ18Orock values approach value of altering water only in a small volume of rocks, constantly flushed by fresh and δ18O-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 δ18Owater value prior to metamorphism. It is thus the lowest δ18Omineral value that provides the best estimate for δ18O 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 δ18O values characteristic for ~60,000 km3 volume of rocks. However, to our informed knowledge, these analyses failed to find δ18O values lower than ~11‰, and thus accept the lowest values of ~11‰ ± 2‰ as a good proxy for the δ18O 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 (~6‰ to ~12‰). As OH-bearing hydrous minerals are ~20‰ to 40‰ more negative in δD than waters during hydrothermal exchange, and because metasomatism typically decreases δDrock values through fractional loss of higher-δD fluids, these measured δD values may only provide a lower bound for δDwater, corresponding perhaps to δ18O 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 δ18O values of precipitation lower than ~11‰ (Fig. 1). Thus, any mid-latitude meteoric precipitation (rain or snow) may explain the Dabie-Sulu low δ18O values. Similarly, Kazakhstan’s ~4‰ UHP rock values do not require glaciation. In contrast, values of ~25‰ to ~27‰ in metamorphic mineral assemblages and zircon rims, and ~235‰ in 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 synclinal origin of the Dabie-Sulu low-δ18O anomaly is related to geochronology, and the best argument on that is provided by the igneous low-δ18O zircons, crystallizing from low-δ18O magmas. This is the approach taken by the study of Wang et al. (2011). The likelihood of finding low-δ18O 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 post-dates caldera collapse or rift failure by only 0.1–1.0 m.y., causing the appearance of isotopically zoned zircons with low-δ18O rims (e.g., Bindean, 2008). These time scales would be treated as instantaneous in the Precambrian. Sporadic low-δ18O igneous zircon values of ~+2‰ to ~3‰ and synglacial 756 ± 15Ma 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-δ18O 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 δ18O depletion of 60,000 km3 of crust happened incrementally, over a long time interval in the long-lived rift, as is represented by intermitent low-δ18O A-type magmatism and low-δ18O 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-δ18O 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-δ18O seawater could have caused lower-δ18O continental precipitation, further relaxing any need for a Snowball Earth glaciation.

REFERENCES CITED


