Finding of negative δ^{18}O zircon from metagranite in eastern Sulu, China: Implications for local paleoclimate

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Since finding of extremely low δ^{18}O eclogite at Qinglongshan in the western end of the Sulu orogen (Yui *et al*., 1995; Zheng *et al*., 1996), much efforts have been devoted to unraveling of not only more lithologies of this δ^{18}O anomaly surrounding the Qinglongshan outcrop, but also more localities of low δ^{18}O metamorphic rocks along the Dabie-Sulu orogenic belt (Zheng *et al*., 2003, and references therein). This study reports our new finding of unusually ^{18}O-depleted zircons in granitic gneiss in the eastern end of the Sulu orogen Low δ^{18}O values as negative as −7.8 to −3.1‰ occur along a profile of 60 m length at Zuobuzhen. They are close to extremely low δ^{18}O values of −9.0 to −5.9‰ for metagranite at Qinglongshan and adjacent areas. CL imaging shows that the low δ^{18}O zircons at Zuobuzhen are primarily of igneous origin, but underwent different degrees of metamorphic modification by recrystallization and overgrowth. SHRIMP U-Pb dating yield mid-Neoproterozoic ages of 751±27 Ma for the igneous zircons and Triassic ages of 232±4 Ma for the metamorphic zircons. They are respectively interpreted to represent timing of protolith emplacement and ultrahigh-pressure metamorphism.

The variably negative δ^{18}O values for the zircons indicate considerable O isotope heterogeneity in its granitic protolith. The low δ^{18}O zircons are interpreted as crystallizing from low δ^{18}O magma due to melting of meteoric-hydrothermally altered low δ^{18}O rocks in an active rift setting at the mid-Neoproterozoic. The metagranites at Zaobuzhen and Qinglongshan, about 450 km apart, are two known occurrences of the unusually low δ^{18}O zircons below −6‰ so far reported in the Sulu orogen. They are similar to each other in both protolith and metamorphic ages, so that they share the same nature of both Neoproterozoic protolith and Triassic metamorphism. Therefore, the locally negative δ^{18}O zircons may register centers of low δ^{18}O magmatism during the advance from supercontinental rifting to breakup, with the negative δ^{18}O fluid deriving from the meteoric water of cold paleoclimate (or continental glacial meltwater) prior to the snowball Earth event. Thus the negative δ^{18}O rocks may provide a geochemical proxy for local deglaciation on rifted continental margin in response to the Rodinia breakup along the northern margin of the South China Block.

References

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Re-evaluation of the equilibrium Fe isotope fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ in aqueous solution

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We have used high level *ab initio* quantum chemistry methods to re-evaluate the equilibrium Fe isotope fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ in water. The calculated equilibrium fractionation $\Delta_{Fe(III)\text{-}Fe(II)}$ is 3.7‰±0.4 at 22°C, which is quite different from previous theoretical or experimental results.

Because it is an important and basic fractionation to govern the Fe isotopic fractionation extent between different redox states, many researchers have previously studied this. Schauble *et al*. (2001) first used a semi-empirical method (MUBFF) to calculate this fractionation as about 5.5‰. The experimental result suggested by Johnson *et al*. (2002) and Welch *et al*. (2003) is a much smaller fractionation (~2.9‰). Meanwhile, the DFT & PCM calculation result suggested by Anbar *et al*. (2005) and Jarzecki *et al*. (2004) is even smaller (i.e. ~2.5‰). Since there are several possible error sources in the experimental process (e.g. possible Fe-Cl or Fe-OH complexation,etc..) and the DFT & PCM calculation also has a weak point (e.g. PCM methods can poorly handle the salvation effects with strong H-bonding situations), we re-evaluate this fractionation by using a larger basis set and a better way to handle the solvation effects other than the PCM method. Our method is using up to 40 water molecules to form various supermolecules or so-called “water-droplets” surrounding the Fe^{2+} or Fe^{3+} ion, then do the geometry optimization and frequency calculations at B3LYP/6-311G* level. This method can treat the interactions between solute and solvent molecules explicitly and hence provides more accurate results when there is strong H-bonding existing. We also check the possible contributions from the complexation of Fe^{3+}, Cl^- and OH^- in the solution. It turns out to form the Fe-Cl or Fe-OH species will let the experimental fractionation value become smaller. We conclude that the fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ will be larger than 2.9‰ and our calculated fractionation (3.7‰ ± 0.4) is very reasonable if those previously ignored errors have been included in.