

Re-checking of the B isotope paleo-pH indicator

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Based on the study of Hemming and Hanson (1992), the stable B isotopic composition ($\delta^{11}\text{B}$) of carbonate has been used as pH-indicator to reconstruct paleo-pH value of seawater and the paleo- CO_2 in the atmosphere (e.g. Palmer and Pearson, 2003; Sanyal *et al.* 2000; Pearson and Palmer, 1999; Palmer *et al.* 1998; Sanyal *et al.* 1995; Spivack *et al.* 1993). However, there are arguments recently occurred for questioning the base of such proxy. Rustad *et al.* (in press) recently found that various density functional theory (DFT) methods could not produce the fractionation factor (1.030) between boron acid (B3) and borate (B4) suggested by experiments (Byrne *et al.* 2006, Klochko *et al.* 2006) and previous quantum chemistry studies (Liu and Tossell 2005, Zebee 2005, Rustad and Bylaska 2007), putting doubts on this important value. Several other experimental studies also suggested that during the precipitation, instead of B4, part of B3 will also be incorporated into the carbonates. These findings have weakened the base of using B isotopes as the paleo-pH indicator which is a common practice in the geochemistry field now.

In this study, we first verify the DFT calculation issues by employing the water-droplet explicit solvent model to precisely evaluate the solvation effect on the fractionation between aqueous B3 and B4. We also use methods beyond harmonic approximation level to confirm whether B isotope systems are with large anharmonic corrections or not. These checking have clarified the issues of DFT calculations. Then, we find that there is an anion-paired intermediate structure if B3 would be incorporated into the mineral structure. Such anion-paired B3 intermediate complex will have very similar beta value compared to that of B4. In another word, no matter how many B3 are incorporated into the carbonate by the form of such intermediate complex, the isotopic composition of incorporated B4 won't be affected. The B isotope composition of precipitated carbonate will be the one like with pure borate. Our study will justify the use of B isotopes as paleo-pH proxy.

Li isotopic fractionation in the refertilized lithospheric mantle beneath the North China Craton

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Lithium isotope compositions of mantle materials may be affected by diffusion processes due to the exceptionally high diffusivity of Li and faster diffusion of ^6Li than ^7Li . High-temperature diffusive fractionation has been invoked to account for striking $\delta^7\text{Li}$ variations in country rocks of pegmatite [1], within individual phenocrysts [2] and intra-granular, inter-granular and inter-sample scales in mantle-derived rocks [3]. Despite major advances in Li isotopic geochemistry, the processes responsible for Li isotope fractionation in mantle peridotites, such as diffusion of Li during melt/fluid-peridotite interactions, are still poorly understood.

Peridotite xenoliths investigated in this study were collected from the Hannuoba and Fanshi on the North China Craton. High-degree enrichment of Li in cpx (2.4-24 ppm) relative to coexisting opx (1.4-7 ppm) and olivine (1.4-4 ppm) indicates that the peridotites experienced metasomatism by mafic silicate melts. The mineral $\delta^7\text{Li}$ values vary greatly, with olivine (+1.2‰ to +5.4‰) isotopically heavier than coexisting opx (-4.4‰ to -23‰) and cpx (-3.3‰ to -20‰) in most samples. The dominant low $\delta^7\text{Li}$ in pyroxenes are considerably lower than normal mantle values (+1‰ to +6‰), and show negative correlation with their Li abundances, likely due to recent diffusive ingress of Li. Olivine in one sample has $\delta^7\text{Li}$ down to -7.9‰, which is close to that of coexisting cpx (-8.4‰). This may indicate the existence of low $\delta^7\text{Li}$ domain in the mantle, which could be generated by meter to kilometer-scale diffusion of Li during melt/fluid-peridotite interaction in the mantle.

- [1] Teng, McDonough, Rudnick & Walker (2006) *Earth Planet. Sci. Lett.* **243**, 701–710. [2] Parkinson, Hammond, James & Rogers (2007) *Earth Planet. Sci. Lett.* **257**, 609–621. [3] Aulbach & Rudnick (2009) *Chem. Geol.* **258**, 17–27.