

Iron isotope systematics of the Baima magmatic Fe-Ti(V) oxide deposit, SW China

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The Baima oxide-bearing mafic-ultramafic layered intrusion, SW China, provides an excellent opportunity to examine the controls of high temperature fractionation of Fe isotopes. The intrusion consists of a Lower zone of net-textured and disseminated oxide ores, a Middle zone of olivine gabbro and an Upper zone of gabbro. Fe isotopes (IRMM-014-normalized) have been measured by high-resolution MC-ICPMS (Neptune Plus) at the CRPG-Nancy, with a 2 sigma reproducibility of $\leq 0.08\text{‰}$ [1]. Olivine has $\delta^{56}\text{Fe}$ values ranging from -0.01 to $+0.11\text{‰}$, clinopyroxene from $+0.11$ to $+0.22\text{‰}$ and titanomagnetite from $+0.20$ to $+0.51\text{‰}$. In $\delta^{56}\text{Fe}_{\text{Cpx}}-\delta^{56}\text{Fe}_{\text{Ox}}$ diagram, Baima samples plot on the primitive mantle end member of the mantle metasomatism trend, indicating the parental magma of the Baima intrusion is the partial melting equivalent of the mantle rocks. Fe isotopes of titanomagnetite-clinopyroxene and titanomagnetite-olivine pairs do not display linear correlations, strongly against simple fractional crystallization model.

Positive correlations of whole-rock TFe_2O_3 vs. $\delta^{56}\text{Fe}$ values of olivine, roughly constant $\delta^{56}\text{Fe}$ values of titanomagnetite from net-textured and disseminated oxide ores and an abrupt break of TFe_2O_3 content and $\delta^{56}\text{Fe}_{\text{Mt}}$ between oxide ores and mafic rocks would indicate that mechanisms for the Fe-Ti oxide ore genesis depend on the oxidation state of the magma chamber. Oxygen fugacity variations inferred from V contents of titanomagnetite indicate that the crystallization of low $\delta^{56}\text{Fe}$ titanomagnetite occurred firstly from a high $f\text{O}_2$ liquid, followed by the $f\text{O}_2$ dropped to the lowest with crystallisation of high $\delta^{56}\text{Fe}$ titanomagnetite on olivine gabbro and gabbro.

These results indicate the strong control of redox state of the magma on Fe isotopic signatures.

[1] Johanna (2011), *Chem. Geol.* **285**, 50-61

Anharmonic effects of equilibrium clumped isotope signatures for H_2O , H_2S , SO_2 , NH_3 and CH_4

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Geological application of clumped isotope techniques has been broadened, but the studied objects mainly remain CO_2 , or O_2 . There is an urgent need to include other species into the inventory of clumped isotope geochemistry. In this study, we provide equilibrium Δ_i values of several common gaseous molecules which can be potential targets for the clumped isotope study in future. For improving the calculation accuracy, theoretical treatments beyond the harmonic level by including several higher-order corrections to the Bigeleisen-Mayer equation are used. We have evaluated contributions from many higher-order corrections (e.g., AnZPE, AnEXC, VrZPE, VrEXC, QmCorr and CenDist) to calculate the anharmonic effects of vibration, vibration-rotation coupling, quantum mechanics and centrifugal distortion for rotation, etc., which are ignored in the Bigeleisen-Mayer equation for the calculation of reduced partition function ratios. All calculations are performed at MP2/aug-cc-pVTZ level and no frequency scale factor has been used. The computational details of these higher-order corrections can be found in [1].

Our results provide detailed temperature dependencies of clumped isotope signatures of those molecules. We also find AnZPE is the most significant correction at room temperature. VrZPE plays second important role at room temperature, but may contribute equally important to AnZPE at higher temperature. Other corrections can contribute a little only if hydrogen atom is involved. With the increase of temperature, contributions of AnEXC, VrEXC and CenDist will become larger; contributions from AnZPE and QmCorr will become smaller. Our results suggest anharmonic corrections can significantly improve the estimation of clumped isotope signatures especially when hydrogen atom is in the clumps (e.g., H_2O , H_2S , NH_3 and CH_4). Higher-order anharmonic corrections are therefore recommended to the theoretical study of clumped isotope fractionations.

[1] Liu, Tossell and Liu (2010) *Geochim. Cosmochim. Acta* **74**, 6965-6983.