First-principles investigation of equilibrium fractionation of O and Si isotopes among crustal minerals

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Equilibrium fractionation factors of Si and O isotopes among silicate minerals is key parameters to understand Si and O isotope data in high temperature rock and mineral samples. Although many works have been done to acquire equilibrium fractionation factors of O isotope among silicate minerals, problems still remain. For example, $\delta^{18}O$ of zircons is widely used to constrain the provenance of their host rocks because the diffusion rate of oxygen in zircon is low and zircon is resistant to secondary alteration. However, fractionation factors of O isotopes between zircon and other minerals are not well determined. Moreover, experimental studies on calibrating Si isotope fractionation factors among silicate minerals are not available in literature.

Here we use first-principles calculation based on DFT to study Si and O isotope fractionation factors among common crustal silicate mineral, including quartz, albite, anthorite, orthoenstatite, clinoenstatite, diopside, olivine, sillimanite, leucite, andalusite, kyanite, and zircon. Our results agree well with natural observations and previous experimental or theoretical works on Si and O isotope fractionation factors [1]. Especially, equilibrium fractionation factor of O isotopes between zircon and quartz obtained in this work is consistent with recent experimental calibration results [2].

Our study reveals that Si isotopes can be significantly fractionated among silicate minerals at high temperature. We estimate Si and O isotope fractionation factors of silicate melts, assuming that the melts have Si and O isotope fractionation factors equal to the weighted sum of those for their normative minerals. Our estimation predicts enrichment of ^{30}Si in more polymerized melt, consistent with observation in Hekla lavas from Iceland[3]. Equilibrium fractionation factors of O isotopes between silicate melts and zircon are strongly controlled by melt composition varying by ~2‰ from basaltic to rhyolitic melt. Thus when $\delta^{18}O$ of zircons are used to constrain the provenance of there host rocks, one must consider the isotope fractionation between zircon and coexisting melt where the zircons crystallize.

[1] Méheut and Schauble, (2014) *GCA*. **134**, 137-154.[2] Trail, et al. (2011) *GCA*. **73**, 7110-7126.[3] Savage et al., (2011) *GCA*. **75**, 6124-6139.