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Reaction controlled kinetic inter-mineral Ca isotope fractionation between orthopyroxene and clinopyroxene

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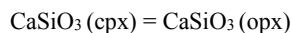
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Ca isotope fractionation between orthopyroxene and clinopyroxene ($\Delta^{44/40}\text{Ca}_{\text{opx-cpx}} = \delta^{44/40}\text{Ca}_{\text{opx}} - \delta^{44/40}\text{Ca}_{\text{cpx}}$) is up to 1.7‰ as revealed in mantle xenoliths [1-3]. $\Delta^{44/40}\text{Ca}_{\text{opx-cpx}}$ shows a negative correlation with $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe})$ in opx and a positive correlation with $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe})$ in cpx. Whether the correlation reflects equilibrium or kinetic fractionation is not clear. Here, in order to better understand the fractionation between orthopyroxene and clinopyroxene, we report Ca isotopic data of 11 co-existing pyroxene pairs in 10 lherzolites and 1 harzburgite collected from Hainan igneous province, southeastern Asia.

Ca isotopes were measured using Triton-TIMS double spike method at Guangzhou Institute of Geochemistry, CAS. The data are reported relative to NIST SRM 915a ($\delta^{44/40}\text{Ca}(\text{‰}) = \frac{^{44}\text{Ca}/^{40}\text{Ca}_{\text{SAMPLE}}}{^{44}\text{Ca}/^{40}\text{Ca}_{\text{SRM915a-1}}} - 1$). Seven out of eleven co-existing pyroxene pairs show small equilibrium fractionation with $\Delta^{44/40}\text{Ca}_{\text{opx-cpx}}$ ranging from 0.00 to 0.15‰. Other four samples show large kinetic fractionation from 0.82 to 1.23‰. Ca distribution between the two pyroxenes in peridotite is controlled by the solid solution equilibrium:



Since the zero-point vibrational energy and the mean molecular velocity of light isotopes are higher than those for heavy isotopes, the light isotopes react faster than heavy isotopes, leading to kinetic isotope fractionation. We argue that the compositional related inter-mineral Ca isotope fractionation can be explained by the reaction induced kinetic effect during Ca-redistribution between the two pyroxenes.

[1] Huang et al (2010) EPSL 292 [2] Kang et al (2016) GCA 174 [3] Zhao et al (2017) GCA 208