The compositional effect on Ca-Mg isotope fractionations among carbonates: First-Principles Investigations

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The compositional effect on the equilibrium isotope fractionation has been found in previous work [1]. Ca concentration of orthopyroxene significantly influences fractionation between orthopyroxene and clinopyroxene especially when Ca/Mg ratio in orthopyroxene is below 1:15. The isotope fractionation is sensitive to the local chemical environment of the element such as the bond lengths, which depend on the element's concentration. The variation of the element's concentration of the minerals in natural samples is ubiquitous. These works suggest that the concentation effect on isotrope fractionation is a phenomenon worthy of specail study.

Natural carbonates ($Mg_xCa_{(1-x)}CO_3$) have wide variations in Mg/Ca ratio, which can modify local chemical environment of these minerals. Equilibrium Ca and Mg isotope fractionations among carbonates with various Mg/Ca ratio were calculated using density functional perturbation theory. The results indicate that dolomite (x=0.5) is enriched in ^{26}Mg but depleted in ^{44}Ca relative to the other carbonates. Mg concentration significantly affects Mg and Ca isotope fractionations among the carbonates. At 300 K, Mg isotope fractionation is ~ -4.5‰ betweeen $Mg_{1/24}Ca_{23/24}CO_3$ calcite and dolomite, and Ca isotope fractionation is ~ 6‰betweeen $Mg_{23/24}Ca_{1/24}CO_3$ and dolomite. Therefore, Mg/Ca ratio in carbonate should be taken into account when appling the isotope fractionation coefficients to understand Earth processes such as deep carbon cycle.

[1] Feng, C., Qin, T., Huang, S., Wu, Z., Huang, F., 2014. Geochim. Cosmochim. Acta143, 132–142.