

Equilibrium oxygen isotope fractionation in $\text{Mg}(\text{OH})_2\text{-Ca}(\text{OH})_2\text{-H}_2\text{O}$: Insights from in situ high-temperature and high-pressure vibrational spectroscopy

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ABSTRACT

Equilibrium oxygen isotope fractionations have been extensively studied between H_2O and minerals, such as brucite-type hydroxides, in isotope geochemistry. In this study, pure ^{18}O -enriched hydroxides were synthesized through reactions between $M_3\text{N}_2$ ($M = \text{Mg}$ and Ca) powders and H_2^{18}O water. In situ high-temperature (T) and high-pressure (P) Raman and Fourier transform infrared (FTIR) spectra were systematically collected for these phases. The observed ^{18}O - ^{16}O effect on the frequency shifts aligns with the theoretical model and has little impact on the anharmonic O-H potential well. The calculated intrinsic anharmonic parameters (a_i) for both lattice and OH-stretching modes are essentially identical between $M(^{16}\text{OH})_2$ and $M(^{18}\text{OH})_2$, satisfying the classical limit for the Helmholtz free energy at extremely high temperature. Based on the measured vibrational data, the equilibrium oxygen isotope fractionation $\beta(T,P)$ factors were modeled for both hydroxides. Both the intrinsic and external anharmonic contributions are smaller than the experimental uncertainties, and this model is also validated by ab initio calculation. Next, the $10^3 \cdot \ln \alpha(T)$ profiles were computed between brucite/portlandite and H_2O , which are consistent with the reported oxygen isotope exchange measurements above 200 °C. Additionally, the discrepancy between this equilibrium model and the precipitation experiment below 120 °C provides useful information for investigating the mechanism of kinetic isotope fractionation. The predicted $10^3 \cdot \ln \alpha_{\text{brucite-portlandite}}(T)$ curve also agrees well with points inferred from the ^{18}O - ^{16}O exchange measurements, while the pressure effect can be ignored for ^{18}O - ^{16}O fractionations. Therefore, vibrational spectroscopic measurements, including Raman and infrared spectroscopy have valuable applications in studying equilibrium non-metallic isotope fractionations in minerals.

Keywords: Brucite, portlandite, Raman spectroscopy, FTIR, oxygen isotope fractionation, anharmonicity, high temperature, high pressure