



Prediction of Equilibrium Isotopic Fractionation of the Gypsum/Bassanite/Water System using ab initio Calculations

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The equilibrium isotopic fractionation factors (α) for $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ and $2\text{H}/1\text{H}$ (or D/H) have been calculated from first-principles using density functional theory and within the harmonic approximation for the system of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and water. Our theoretical results for $\alpha^{18}\text{O}$ and αD of gypsum/water are in good agreement with previous experimental results. We predict that the $^{18}\text{O}/^{16}\text{O}$ fractionation factor for bassanite/water is similar to that of gypsum/water in the temperature range of 0 oC and 60 oC. Temperature has a small effect on $\alpha^{18}\text{O}$ of gypsum/water, of about 0.0006 per 50 oC. Theta (θ), the triple oxygen isotope fractionation factor of gypsum/water also agrees with experimental values. Moreover, we found that the value of θ for gypsum/water shows a weak temperature dependence (0.0013 between 0 oC and 60 oC). The hydrogen isotope fractionation factor (αD) for bassanite/water is predicted to be 0.0205 lower than αD of gypsum/water at 0 oC, and 0.0090 lower at 60 oC. The temperature dependence for αD of bassanite/water (0.0189 per 50 oC) is much greater than that of gypsum (0.0089 per 50 oC). The fact that oxygen isotopes are enriched in gypsum hydration water relative to the fluid ($\alpha^{18}\text{O} > 1$) and hydrogen isotopes are depleted ($\alpha\text{D} < 1$) is explained by phonon theory, without needing to assume that different water molecular sites are involved.