

## 石膏与水溶液中硫酸根之间的氧及硫同位素分馏

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Some non labile oxyanions such as sulfate ( $\text{SO}_4^{2-}$ ) or nitrate ( $\text{NO}_3^-$ ), do not exchange O atoms readily with O in water at ambient temperatures. They often behave like a single atom during mineral precipitation, dissolution, adsorption, and even microbial transport. Considering the many different isotopologues these oxyanions usually possess, for example  $\text{SO}_4^{2-}$  has  $^{32}\text{-}^{16}\text{-}^{16}\text{-}^{16}\text{-}^{16}$ ,  $^{34}\text{-}^{16}\text{-}^{16}\text{-}^{16}\text{-}^{16}$ ,  $^{32}\text{-}^{18}\text{-}^{16}\text{-}^{16}\text{-}^{16}$ ,  $^{34}\text{-}^{18}\text{-}^{16}\text{-}^{16}\text{-}^{16}$ , etc., the behaviour of isotope fractionation for different elements in the oxyanions (e.g., O and S) may lead to certain degrees of coupling during different physical, chemical and biological processes. Here we use an aqueous sulfate - solid gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) system to illustrate a first-principle approach to calculating the isotope fractionation factors and their coupling for O and S in sulfate during gypsum precipitation.

Using Urey model or Bigeleisen-Mayer equation in combination with quantum chemistry calculations

(at BLYP/6-311+G(2df,p) level), we have calculated equilibrium isotope fractionation factors  $\alpha^{18}$  and  $\alpha^{34}$  for tens of isotopologues of  $\text{SO}_4^{2-}$ . We use a time-consuming yet explicit solvent model (i.e. "water droplet") to precisely evaluate solvation effects for aqueous sulfate species. A large and partially fixed cluster model is used for simulating gypsum mineral surface. Our results show that the equilibrium fractionations at 25 °C between solid gypsum and aqueous sulfate are ~ 2.5 and 1.6 permil for the  $\Delta \delta^{18}\text{O}$  and  $\Delta \delta^{34}\text{S}$  respectively. Without considering ion-pair effect on sulfate anion in solution, however, the corresponding  $\Delta \delta^{18}\text{O}$  and  $\Delta \delta^{34}\text{S}$  become ~ 4.4 and 2.8 permil respectively. Our work presents a new approach to predicting isotope fractionation behaviour for non-labile species at equilibrium and lays the ground for evaluating kinetic effects. The results also shed lights on the mechanism and model for gypsum crystal growth at molecular level.