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Experimental and theoretical investigations of stable Sr isotope fractionation during its incorporation in aragonite

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The incorporation of Sr in aragonite was been studied at low degrees of supersaturation of the fluid with respect to aragonite (i.e. $1.1 \leq \Omega_{\mathrm{aragonite}} \leq 2.2$) using a mixed flow reactor setup to quantify the dependence of Sr distribution coefficient (i.e. $D_{Sr,aragonite}$) on aragonite growth rate. Moreover, the stable Sr isotope composition (i.e, $\delta^{88/86}$Sr) of the experimental products was used to constrain stable Sr isotope fractionation between aragonite and the forming fluid ($\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$) and compared with the results of first-principles simulations using Density Functional Theory (DFT). The obtained results allow for an estimation of $\mathrm{D}_{\mathrm{Sr,aragonite}}$ value at thermodynamic equilibrium via extrapolation to $\Omega_{\mathrm{aragonite}}=1$. Under these conditions $D_{Sr,aragonite}$ value is estimated to equal ~2.7. Additionally, for aragonite growth rates $r_p \leq 10^{-8.0\pm0.2}$ (mol/m^2/s), the $\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$ demonstrates a constant value of -0.1±0.05‰, whereas it decreases to -0.40‰ when the growth rate increases to $10^{-7.7}$(mol/m^2/s). The measured $\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$ value under thermodynamic equilibrium conditions comes in excellent agreement with the DFT simulations that yield a $\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$ of -0.04‰ at 25°C. The dependence of $\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$ on mineral growth rate is well described by the surface reaction kinetic model developed by DePaolo (2011) using values of -0.1‰ and -1.2 ± 0.1‰ for the equilibrium and kinetic Sr isotope fractionation factor, respectively. The dependence of $\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$ on mineral growth rate confirms that dehydration of the aqueous Sr^{2+} ion is the mechanism controlling Sr isotope fractionation during its coprecipitation with aragonite. Overall, the experimental results suggest that aragonite growth kinetics affect the distribution and isotope composition of Sr in this mineral phase and should be considered during the interpretation of the isotopic composition of natural samples. Indeed, under equilibrium conditions $\mathrm{D}_{\mathrm{Sr,aragonite}}$ obtain values significantly higher than 1, in contrast to previous experimental studies. But, values >1 have been measured in aragonitic speleothems formed at low $\Omega_{\mathrm{aragonite}}$ values (Wassenburg et al., 2016). Additionally, the dependence of $\Delta^{88/86}\mathrm{Sr}_{\mathrm{aragonite\text{-}fluid}}$ on mineral growth kinetics suggests that fractionation up to -1.2‰ could be observed in natural aragonite samples formed at far from equilibrium conditions.

DePaolo (2011), GCA **75**, 1039-1056
Wassenburg et al. (2016) GCA **190**, 347-367