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Ca-Sr fractionation between zoisite, lawsonite, and aqueous fluids: An experimental study at 2.0 and 4.0 GPa/400 to 800 °C

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ABSTRACT

The Ca-Sr fractionation between zoisite and, respectively, lawsonite and an aqueous fluid has been determined by synthesis experiments in the presence of a 1 M $(\text{Ca,Sr})\text{Cl}_2$ aqueous fluid at 2.0 GPa/550, 600, and 700 °C and 4.0 GPa/800 °C for zoisite and 2.0 GPa/400 °C and 4.0 GPa/600 °C for lawsonite. Solid run products were characterized by EMP, SEM, and XRD with Rietveld refinement and fluids were analyzed by ICP-OES. Zoisite exhibits notable intracrystalline Ca-Sr fractionation between the A1 and A2 sites and calculated intracrystalline exchange coefficients $K_{D(\text{Sr-Ca})}^{\text{A1-A2}} = 1.5$ to 26 show strong preference of Sr over Ca for the slightly larger A2 site. Calculated individual site-dependent zoisite/aqueous fluid (af, in superscripts)-exchange coefficients for the studied 1 M $(\text{Ca,Sr})\text{Cl}_2$ aqueous fluids are $K_{(\text{Sr-Ca})}^{\text{zo A1-af}} = 3.38$ to 41.08 for the A1 site and $K_{(\text{Sr-Ca})}^{\text{zo A2-af}} = 0.45$ to 6.51 for the A2 site. Assuming $\gamma_{\text{Ca}}^{\text{af}} = \gamma_{\text{Sr}}^{\text{af}}$ and a symmetric mixing model, the thermodynamic evaluation of the site-dependent exchange reactions $\text{Ca}^{2+(\text{af})} + \text{Sr}^{\text{A1}}(\text{M}^{2+})^{\text{A2}}\text{Al}_3[\text{Si}_3\text{O}_{11}(\text{O/OH})] = \text{Sr}^{2+(\text{af})} + \text{Ca}^{\text{A1}}(\text{M}^{2+})^{\text{A2}}\text{Al}_3[\text{Si}_3\text{O}_{11}(\text{O/OH})]$ and $\text{Ca}^{2+(\text{af})} + (\text{M}^{2+})^{\text{A1}}\text{Sr}^{\text{A2}}\text{Al}_3[\text{Si}_3\text{O}_{11}(\text{O/OH})] = \text{Sr}^{2+(\text{af})} + (\text{M}^{2+})^{\text{A1}}\text{Ca}^{\text{A2}}\text{Al}_3[\text{Si}_3\text{O}_{11}(\text{O/OH})]$ yields $\Delta\mu^0 = -29$ kJ/mol and $W_{\text{Sr-Ca}}^{\text{zo A1}} = 5.5$ kJ/mol for the A1 site and $\Delta\mu^0 = -1.1$ kJ/mol and $W_{\text{Sr-Ca}}^{\text{zo A2}} = 0$ kJ/mol for the A2 site at P and T of the experiments. The data indicates ideal Ca-Sr substitution on the A2 site. Lawsonite formed in both the orthorhombic *Cmcm* and the monoclinic $P2_1/m$ form. Calculated lawsonite-aqueous fluid-exchange coefficients indicate overall preference of Ca over Sr in the solid and are $K_{D(\text{Sr-Ca})}^{\text{law } Cmcm\text{-af}} = 1.12$ to 11.32 for orthorhombic and $K_{D(\text{Sr-Ca})}^{\text{law } P21m\text{-af}} = 1.67$ to 4.34 for monoclinic lawsonite. Thermodynamic evaluation of the exchange reaction $\text{Ca}^{2+(\text{af})} + \text{SrAl}_2\text{Si}_2\text{O}_7(\text{OH})_2{\cdot}\text{H}_2\text{O} = \text{Sr}^{2+(\text{af})} + \text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2{\cdot}\text{H}_2\text{O}$ assuming $\gamma_{\text{Ca}}^{\text{af}} = \gamma_{\text{Sr}}^{\text{af}}$ and a symmetric mixing model yields similar values of $\Delta\mu^0 = -9$ kJ/mol and $W_{\text{Sr-Ca}}^{\text{law}}$ $_{Cmcm} = 10$ kJ/mol for orthorhombic and $\Delta\mu^0 = -10$ kJ/mol and $W_{\text{Sr-Ca}}^{\text{law } P21/m} = 11$ kJ/mol for monoclinic lawsonite. Calculated Nernst distribution coefficients for the studied 1 M $(\text{Ca,Sr})\text{Cl}_2$ aqueous fluids are $D_{\text{Sr}}^{\text{zo-af}} = 2.8 \pm 0.7$ for zoisite at 2 GPa/600 °C and $D_{\text{Sr}}^{\text{law } Cmcm\text{-af}} = 0.6 \pm 0.2$ for orthorhombic lawsonite at 4 GPa/600 °C and show Sr to be compatible in zoisite but incompatible in lawsonite. This opposite mineral-aqueous fluid-fractionation behavior of Sr with respect to zoisite and lawsonite on the one hand and the ideal Ca-Sr substitution on the zoisite A2 site in combination with the strong intracrystalline Ca-Sr fractionation in zoisite on the other hand, make Sr a potential tracer for fluid-rock interactions in zoisite- and lawsonite-bearing rocks. For low Sr-concentrations, $x_{\text{Sr}}^{\text{zo}}$ directly reflects $x_{\text{Sr}}^{\text{af}}$ and allows us to calculate Sr-concentrations in a metamorphic aqueous fluid. During high-pressure aqueous fluid-rock interactions in subduction zone settings the opposite mineral-aqueous fluid-fractionation behavior of Sr results in different aqueous fluid characteristics for lawsonite- vs. zoisite-bearing rocks. Ultimately, subduction zone magmas may trace these different aqueous fluid characteristics and allow distinguishing between cold, lawsonite-bearing vs. warm, zoisite-bearing thermal regimes of the underlying subduction zone.

Keywords: Ca-Sr fractionation, zoisite, lawsonite, high-pressure fluids, experimental petrology, subduction zone