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

AXEL LIEBSCHER,1,2,* GUIDO DÖRSAM,2 GERHARD FRANZ,2 BERND WUNDER,1 AND MATTHIAS GOTTSCHALK1

1German Research Centre for Geosciences GFZ Potsdam, Telegrafenberg, D-14473 Potsdam, Germany
2Fachgebiet Mineralogie-Petrologie, Technische Universität Berlin, Ackerstrasse 76, D-13355 Berlin, Germany

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 (Ca,Sr)Cl2 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 \( K_{A1\text{Ca},A2}^{\text{Ca,Sr}} = 1.5 \) 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 (Ca,Sr)Cl2 aqueous fluids are \( K_{\text{ZC}(\text{Si} \text{O}_{4}) \text{O} \text{H}}^{\text{Ca,Sr}} = 3.38 \) to 41.08 for the A1 site and \( K_{\text{ZC}(\text{Si} \text{O}_{4}) \text{O} \text{H}}^{\text{Ca,Sr}} = 0.45 \) to 6.51 for the A2 site. Assuming \( a_{\text{Ca}}^{\text{af}} = a_{\text{Sr}}^{\text{af}} \) and a symmetric mixing model, the thermodynamic evaluation of the site-dependent exchange reactions \( \text{Ca}^{2+} + \text{Sr}^{2+} \text{Sr}^{2+} \text{(M}^{2+})^{4} \text{Al}_{2} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} + \text{Ca}^{2+} \text{(M}^{2+})^{4} \text{Al}_{2} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} \text{Sr}^{2+} \text{Cl}^{2-} \text{Sr}^{2+} \text{(M}^{2+})^{4} \text{Al}_{2} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} + \text{Sr}^{2+} \text{(M}^{2+})^{4} \text{Al}_{2} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} \text{Sr}^{2+} \text{(M}^{2+})^{4} \text{Al}_{2} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} \) yields \( \Delta \mu_{\text{Sr}}^{\text{af}} = –9 \text{kJ/mol} \) and \( W_{\text{af}}^{\text{Sr}} = 11.32 \text{kJ/mol} \) for the A1 site and \( \Delta \mu_{\text{Sr}}^{\text{af}} = –11 \text{kJ/mol} \) and \( W_{\text{af}}^{\text{Sr}} = 0 \text{kJ/mol} \) 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 \( \text{Cmcm} \) and the monoclinic \( \text{P2}_{1}/m \) form. Calculated lawsonite-aqueous fluid-exchange coefficients indicate overall preference of Ca over Sr in the solid and are \( K_{\text{LW}(\text{Si} \text{O}_{4}) \text{O} \text{H}}^{\text{Ca,Sr}} \text{Cmcm} = 1.12 \) to 11.32 for orthorhombic and \( K_{\text{LW}(\text{Si} \text{O}_{4}) \text{O} \text{H}}^{\text{Ca,Sr}} \text{P2}_{1}/m = 1.67 \) to 4.34 for monoclinic lawsonite. Thermodynamic evaluation of the exchange reaction \( \text{Ca}^{2+} + \text{Sr}^{2+} \text{Sr}^{2+} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} + \text{Sr}^{2+} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} + \text{Sr}^{2+} \text{Si}_{3} \text{O}_{9} (\text{OH})_{5} \text{Cl}^{2-} \) assuming \( a_{\text{Ca}}^{\text{af}} = a_{\text{Sr}}^{\text{af}} \) and a symmetric mixing model yields similar values of \( \Delta \mu_{\text{Sr}}^{\text{af}} = –9 \text{kJ/mol} \) and \( W_{\text{af}}^{\text{Sr}} = 11.32 \text{kJ/mol} \) for monoclinic lawsonite. Calculated Nernst distribution coefficients for the studied 1 M (Ca,Sr)Cl2 aqueous fluids are \( D_{\text{af}}^{\text{Sr}} = 2.8 \pm 0.7 \text{ for zoisite at 2 GPa/600 °C and } D_{\text{af}}^{\text{Sr}} = 0.6 \pm 0.2 \text{ 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, \( x_{\text{Sr}}^{\text{af}} \) 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

INTRODUCTION

The concentration of strontium and especially its enrichment in metamorphic rocks and minerals is potential tracers of metamorphic fluid-rock interactions and metasomatic processes (Grapes and Watanabe 1984). An extreme example of such fluid-induced Sr metasomatism is, e.g., reported by Brastad (1985) from a metagneissite from Bjørkedalen, Norway. Because the

ionic radii of Ca\(^{2+}\) (=1.06 Å) and Sr\(^{2+}\) (=1.21 Å; both for sevenfold coordination; Shannon 1976) are quite similar, Sr readily substitutes for Ca. Besides carbonates, the Ca-silicates plagioclase and members of the epidote and lawsonite groups are, therefore, the most important carriers of Sr in typical metamorphic rocks. In high- and ultrahigh-pressure metabasites and metagreywackes, minerals of the epidote and lawsonite groups, which replace the anorthosite component of plagioclase in protoliths, may control more than 75% of the whole-rock Sr budget (Tribuzio et al.

* E-mail: alieber@gefz-potsdam.de