Ca-Sr distribution among amphibole, clinopyroxene, and chloride-bearing solutions

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ABSTRACT

The distribution of Sr between a 1 M (Ca,Sr)Cl solution, (Ca,Sr)-tremolite and (Ca,Sr)-diopside was determined at 750 °C and 200 MPa. The synthesized crystals of (Ca,Sr)-tremolite (2000 × 30 µm) and (Ca,Sr)-diopside (1500 × 20 µm) were large enough for accurate electron microprobe analysis. The experimental results indicate that CaSr2+ can be replaced completely by Sr2+ on the M4-site in tremolite and on the M2-site in fluid. The compositions of the product fluid were analyzed by atomic absorption spectroscopy. In both the (Ca,Sr)-tremolite-fluid and (Ca,Sr)-diopside-fluid systems, Sr strongly fractionated into the fluid. For bulk compositions having low Sr concentrations, mineral/fluid partition coefficients, $D_{\text{mineral}/\text{fluid}}$, of 0.045 for (Ca,Sr)-tremolite/fluid and 0.082 for (Ca,Sr)-diopside/fluid were derived. The experimental results were evaluated thermodynamically assuming Henry’s law and simple mixing properties for SrCl2 and CaCl2 in the fluid. The mixing energies of the solids were calculated using a regular solution model. In the (Ca,Sr)-tremolite–(Ca,Sr)Cl2 system, $\Delta\mu^o$ is 59.0 kJ and $W_{\text{Ca}}^{\text{min}}$ = 9.8 kJ. In the system (Ca,Sr)-diopside–(Ca,Sr)Cl2, $\Delta\mu^o$ is 30.8 kJ and $W_{\text{Ca}}^{\text{min}}$ is 11.7 kJ. The high $\Delta\mu^o$ values and, to a much lesser extent, the $W_{\text{Ca}}^{\text{min}}$ values cause the strong fractionation of Sr into the fluid. The moderate values for $W_{\text{Ca}}^{\text{min}}$ and $W_{\text{Sr}}^{\text{min}}$ strongly suggest that complete solid solution exists for (Ca,Sr)-tremolite and (Ca,Sr)-diopside at experimental run conditions. However, for the (Ca,Sr)-tremolite and (Ca,Sr)-diopside joins, limited miscibilities were calculated below 316 and 430 °C, respectively.

The experimentally derived thermodynamic properties were used to determine Ca/Sr ratios of Sr-rich metasomatic fluids that penetrated a metaeclogite in Børkedalen, southwest Norway. The derived Ca/Sr ratios from amphibole-fluid equilibria are in good agreement with those calculated from plagioclase-fluid equilibria.

INTRODUCTION

In most rock-forming minerals, Sr occurs as a minor or trace element and is preferentially incorporated in Ca-bearing phases. Because both Sr and Ca belong to the alkaline earth group of elements, they have a similar chemical behavior. The ionic radius in eightfold coordination is 1.12 Å for Ca2+ and 1.26 Å for Sr2+ (Shannon 1976).

Strontium enrichment in rocks is commonly induced by fluid-rock interactions (Grapes and Watanabe 1984; Theye and Seidel 1988). An example of extreme Sr metasomatism has been reported in a metaeclogite from Børkedalen, southwest Norway, by Brastad (1985) in which whole-rock SrO concentrations ranged up to 2.4 wt%. It is clear that information about trace element distribution between fluids and minerals is required for the reconstruction of such metasomatic processes.

Experimentally determined partition coefficients for Sr as a trace element between fluids and minerals have been reported for apatite (Ayers and Watson 1993), olivine (Brenan and Watson 1991), garnet (Brenan et al. 1995), clinopyroxene (Brenan et al. 1995; Adam et al. 1997; Ayers et al. 1997), and amphibole (Brenan et al. 1995; Adam et al. 1997). The distribution of Sr as a major element between fluids and minerals has been determined experimentally for (K,Sr)-feldspars by Kotelnikov and Chernysheva (1995), and Kroll et al. (1995) and for (Ca,Sr)-plagioclase by Kotelnikov and Chernysheva (1995), Kotelnikov et al. (1989), and Lagache and Dujon (1987). Thermodynamically relevant distribution coefficients and mixing models are not available for Sr-bearing amphiboles and pyroxenes. Although Sr-rich amphiboles and pyroxenes are only observed rarely in nature, both structures are flexible enough to incorporate significant Sr. Della Ventura and Robert (1990) and Robert et al. (1993) synthesized (K,Sr)-richterites with Sr2+ completely replacing Ca2+ on the M4-site. Benna (1982) and Benna et al. (1987) synthesized Sr-rich pyroxenes with at least 30 mol% of the Sr-diopside component.

Besides the geochemical interest in the quantification of Sr substitution in amphiboles and pyroxenes and the corresponding fluids/melts, there are questions of mineralogical importance. First, how much Ca2+ can be replaced by Sr2+ in the tremolite and diopside structure? Second, how can this substitution be described structurally and thermodynamically? An appropriate mixing model along the whole composition range provides the activity coefficients at low Sr concentrations (Henry’s law constants), which are required for the geochemical applications.

The aim of this study is to determine the mixing behavior of Ca and Sr in amphibole and in pyroxene by considering the