Phase equilibria in the system $(Ba,Sr,Ra)SO_4 + H_2O$

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Barite-rich solid solitions are assumed to play an important role in controlling Ra(aq) concentrations in various geochemical scenarios. This study is concerned with the effect of Sr on the retention of Ra. Effects of mixing in ternary $(Ba,Sr,Ra)SO_4$ solid solutions were investigated with the aid of first principles based atomistic simulations. The regular mixing interaction parameters increase from W_{BaRa} = 2.4 to W_{BaSr} = 8.4 and W_{SrRa} = 20.0 kJ/mol [1]. Deviations from regular mixing in binary and ternary solid solutions were investigated with a generalized Ising model using the Monte Carlo method, and with the aid of ternary quasi-random structures. Small negative deviations in the excess enthalpy affect predominantly intermediate compositions at which ternary solid solutions are not stable. Therefore, the phase relations can be reliably modelled without introducing a ternary mixing parameter. The ternary solution decomposes at ambient temperatures into a nearly pure celestine and a $(Ba,Ra)SO_4$ phase of variable composition. Our thermodynamic calculations with the GEM-Selector code showed that the mole fraction of $RaSO_4$ in this phase could increase dramatically at high Sr/Ba ratios, even when the total amount of Ra in the system is small. This prediction is entirely consistent with our experimental data on re-crystallization of celestine in the presence of trace amounts of Ba and Ra. Our SEM-EDX investigation showed the formation of a tiny amount of idiomorphic crystals on the surface of celestine, which are simultaneously rich in Ba and Ra. These crystals remained stable for more than 200 days. As the activity of Ra^{2+} in the aqueous phase is linked to the large mole fraction of $RaSO_4$ in the solid, it remains relatively high in a Sr-rich system. This negative effect on Ra retention is compensated, however, by a higher activity of the SO_4^{2-} ion caused by a larger content of $SrSO_4$ in the solid solution.

[1] Vinograd et al. (2013) *GCA*.**122**, 398–417.