Replacement of barite by $(Ba,Ra)SO_4$ at T = 25 - 90 °C

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In some scenarios for the direct disposal of spent nuclear fuel, ^{226}Ra dominates the dose after 100,000 years. Radium has a high affinity to barite ($BaSO_4$) which is also likely to form as a result of the reaction between sulfate bearing ground waters and Ba present as a fission and decay product in spent fuel. Several recent studies have shown that upon contact with radium, original pure barite is replaced by $(Ba,Ra)SO_4$ solid solutions even under close-to-equilibrium conditions expected for this system in a nuclear waste repository. At ambient conditions it was shown that this lowers the radium solubility by several orders of magnitude, depending on the amount of $BaSO_4$ present in the system and that a full equilibrium of the system is approached within less than 1000 days [1]. Here, we have extended the study of this replacement reaction to the temperature range 25 to 90 °C. Batch experiments with two different types of barite in the presence of radium in aqueous solution were performed at room temperature and elevated temperatures. For this purpose pure $BaSO_4$ was equilibrated at room temperature, 70 °C and at 90 °C with an aqueous solution containing 0.1 mol/L NaCl and $5 \cdot 10^{-6}$ mol/L radium. Depending on the solid/liquid ratio and on the temperature, a constant radium concentration in the aqueous phase was reached after a few hundred days and was attributed to equilibrium between solid and aqueous phase. From the final radium concentrations and the known $BaSO_4$ solubility [2] solubility constants of $RaSO_4$ for 70 and 90 °C were calculated based on Lippmann theory [3] using interaction parameters derived from atomistic calculations [4]. New values for S^o_f, H^o_f, Cp^o for $RaSO_4$ were obtained, providing a reasonable model predicting the behavior of the $Ba\text{-}Ra\text{-}SO_4\text{-}H_2O$ system in the range from 25 to 90 °C for the first time.

[1] Brandt et al. 2015, *Geochim. Cosmochim. Acta*, **in press**. [2] Brown P. L et al., In: Uranium Past and Future Challenges. Springer International Publishing. pp. 553–564. [3] Lippmann, 1980. *N. Jb. Miner. Abh* **139**, 1–25. [4] Vinograd et al., 2013, *Geochim. Cosmochim. Acta* **122**, 398-417.