

Solid solution formation and uptake of Radium in the presence of barite

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The phase relations in the $\text{BaSO}_4\text{-RaSO}_4\text{-H}_2\text{O}$ system may determine the solubility of radium in natural waters due to the formation of a solid solution. In the near-field of nuclear waste repositories for spent fuel, radium may enter a system in which barite is in equilibrium with the aqueous solution. Thermodynamically, a $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ solid solution is expected to form as solubility controlling phase rather than RaSO_4 . However, due to a lack of reliable data, the solid solution system $\text{RaSO}_4\text{-BaSO}_4\text{-H}_2\text{O}$ is currently not considered in long term safety assessments for nuclear waste repositories. The solubility product of the pure RaSO_4 endmember is poorly constrained between $\text{p}K_{\text{RaSO}_4} = 10.26$ to 10.41 by only very few experimental data [1,2]. Published interaction parameters W_{BaRa} of the $\text{RaSO}_4\text{-BaSO}_4\text{-H}_2\text{O}$ system varies in different studies [3, 4] between 0.9 and 3.9 - 6.5 kJ/mol.

In this study we have combined experimental data, atomistic calculations and thermodynamic modeling to study in detail how a radium containing solution will equilibrate with solid BaSO_4 under repository relevant conditions. Batch sorption experiments at close to equilibrium conditions indicate the formation of a $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ solid. Our first principles calculations based on the single defect method [5] indicate a value of $W_{\text{BaRa}} = 2.5 \pm 1.0$ kJ/mol, implying a non-ideal solid solution. Thermodynamic assessment calculations indicate that the final experimental Ra(aq) concentration at room temperature and 90 °C can be matched with $W_{\text{BaRa}} \approx 1.5$ kJ/mol and $\text{p}K_{\text{RaSO}_4} \approx 10.41$.

[1] Lind, S. C., *et al* (1918). *J Am Chem Soc* **40**, 465-472. [2] Paige, C. R. *et al.* (1998). *Geochim. Cosmochim. Acta* **62**, 15-23. [3] Zhu, C., 2004. *Geochim. Cosmochim. Acta* **68**, 3327-3337. [4] Curti, E., *et al.* (2010). *Geochim. Cosmochim. Acta* **74**, 3553-3570. [5] Sluiter & Kawazoe (2002) *Europhys Lett.* **57**, 526-532.

The co-ordination of Boron in foraminiferal calcite

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The analysis of boron in foraminiferal calcite is a burgeoning palaeo-proxy for past ocean-acidification events [1]. This is particularly relevant to today's 'carbonated ocean' [2]. However, considerable uncertainty surrounds the mechanisms of boron incorporation into the shell. Foraminiferal calcite is known to be highly chemically heterogeneous [3], and understanding how boron fits into this complex structure is central to our understanding of, and confidence in, this important proxy.

We have applied synchrotron NEXAFS spectroscopy to examine the distribution and coordination of boron in foraminifera at the nm length scale.

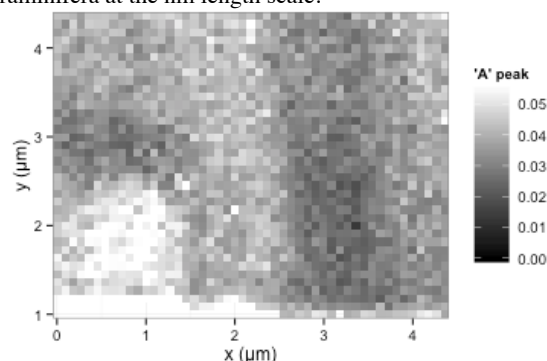


Figure 1: A Scanning Transmission X-ray Microscope (STXM) image of a section of foraminifera test at the trigonal B edge, showing variations in the concentration of B [4].

STXM results reveal clear homogeneity in boron concentration, which appears to be uniformly hosted in a trigonal coordination in the calcite crystal lattice (BO_3 groups). Analysis of boron coordination is ongoing.

[1] Spivack, *et.al.* (2002) *Nature* **363**, 1-3 [2] Elderfield (2002) *Science* **296**, 1618-1621 [3] Erez (2003) *Rev. Min. Geochem.* **54**, 115-149. [4] Fleet & Muthupari (2000) *Am. Min.* **85**, 1009-1021.