

## Recrystallization of Barite in the presence of Ra at elevated temperatures up to 90 °C

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The uptake of Radium by Barite via solid solution formation is an important process controlling the solubility of Ra in aqueous systems. Recent studies have focused on ambient conditions (Bosbach et al., 2010; Curti et al., 2010). Here, we have focused on the understanding of kinetics and uptake mechanisms at elevated temperatures.

New experimental data of batch recrystallization experiments at room temperature (RT) and 90 °C are presented. A pure barite solid was put into contact with an aqueous solution (0.1 n NaCl) with an initial Ra/Ba ratio of 0.3 ( $5 \cdot 10^{-6}$  mol/L Ra) and neutral pH. The solid/liquid ratio was 5 g/L. A barite which consists of blocky crystals with a particle size of  $> 10 \mu\text{m}$  and a specific surface area of  $0.17 \text{ m}^2/\text{g}$  was used for the recrystallization experiments at close to equilibrium conditions. The evolution of the Ra and Ba concentration in solution with time was monitored via Gamma spectrometry and ICP-MS. Furthermore, the morphological evolution of the barite crystals was investigated by SEM.

A faster decrease of the Ra concentration in solution is observed at 90 °C compared to room temperature. A steady state of the Ra concentration is reached at  $3 \cdot 10^{-8}$  mol/L for experiments at 90 °C after 30 days and after 70 days at  $3.5 \cdot 10^{-9}$  mol/l for experiments at room temperature.

Our results agree with the thermodynamic data of the  $\text{RaSO}_4$  and  $\text{BaSO}_4$  endmembers. At room temperature,  $\text{RaSO}_4$  is less soluble than  $\text{BaSO}_4$  whereas estimated solubilities indicate that  $\text{RaSO}_4$  is more soluble than  $\text{BaSO}_4$  at 90 °C. As a consequence, a lower retention capacity for Ra can be expected for 90 °C.

Electron microscopy results of the crystal morphology show a distinct influence of the presence of Ra on recrystallization at close to equilibrium conditions and 90 °C. In the presence of Ra, the crystals show plain crystal faces. In the absence of Ra rough surfaces and deep holes in the crystals are observed. These differences clearly indicate different recrystallization mechanisms.

TEM studies will be carried out to achieve a nanoscopic system understanding of micro structural evolution and Ra incorporation into the barite crystal as well as its spatial distribution in the crystal.

Bosbach, D.; Böttle, M. & Metz, V. (2010) *Waste Management, Svensk Kärnbränslehantering AB*  
Curti, E.; Fujiwara, K.; Iijima, K.; Tits, J.; Cuesta, C.; Kitamura, A.; Glaus, M. & Müller, W. (2010) *Geochimica et Cosmochimica Acta*, **74**, 3553-3570

## Prebiotic selection of D-ribose on mineral surfaces

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Pentose sugars are major biochemical building blocks. Prebiotic syntheses have been proposed leading to complex mixtures including 4-, 5-, and 6-carbon sugars [1,2]. However, the pentose sugar D-ribose has the greatest biological importance because it is the sugar found within modern nucleic acids. We are investigating whether this is due to some exceptional characteristic of ribose associated with its interaction with mineral surfaces.

Some studies have shown that D-ribose can be stabilized in the presence of borate [3] or silicate [4] minerals. Recent study of the adsorption of nucleosides and nucleotides on rutile [5] indicates that adjacent OH-groups on the ribose part of these molecules play a critical role in the attachment to mineral surfaces. The four pentose sugars ribose, xylose, lyxose and arabinose differ only in the arrangement of the OH-groups and their stereochemistry in solution. This suggests that the different structures of these sugars might lead to selective adsorption on mineral surfaces.

The present study is focused on interactions of pentose sugars on rutile ( $\alpha\text{-TiO}_2$ ,  $\text{pH}_{\text{PZC}} = 5.4$ ,  $\text{BET} = 18.1 \text{ m}^2/\text{g}$ ) in the presence of light: in pure water; and in the dark: in pure water, 10 and 100 mM NaCl solutions over a wide range of pH conditions (5-11).

In the presence of light, the results of our batch adsorption experiments indicate an occurrence of a photocatalytic reaction between rutile surface and four pentoses. Xylose and lyxose form threose via loss of an aldehyde group. The reaction product of ribose or arabinose and rutile has not yet been identified.

In dark conditions, batch adsorption experiments of the four sugars individually and in mixtures indicate that adsorption increases with increasing pH and salt concentration of the solution. The salt effect and pH dependancy of adsorption is more pronounced for ribose. Ribose adsorption is the strongest among the pentose sugars, suggesting that ribose's cis diol OH-groups play a critical role in the attachment to mineral surfaces. Overall, our results are consistent with the hypothesis that mineral surfaces could potentially have played a role in selecting ribose relative to the other pentose sugars.

[1] Springsteen and Joyce (2004) *J. Am. Chem. Soc.* **126**, 9578-9583. [2] Shapiro (1988) *Origin Life Evol. Biosphere* **18**, 71-85. [5] Ricardo et al. (2004) *Science* **303**, 196. [4] Vazquez-Mayagoitia et al. (2011) *Astrobiology* **11**, 115-121. [5] Cleaves et al. (2010) *Astrobiology* **10**, 311-323.