

## Microbial biominerals: Role in radionuclide remediation

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Bacteria form a range of biominerals, which can immobilise radionuclides through sorption or precipitation [1, 2]. Biomineralisation can be stimulated *in situ* by injecting nutrients, offering a potential remediation mechanism using indigenous microorganisms. Studies so far have focussed on simplified, pure culture systems. This study is investigating the effect of three biomineralisation processes on radionuclides using natural microbial consortia under complex geological and geochemical conditions, as would be found at contaminated sites. The processes are:

### Carbonate precipitation

Bacterial ureolysis produces  $\text{NH}_4^+$  and  $\text{HCO}_3^-$  and can form biogenic calcite [3].  $\text{Np}^{\text{V}}$  and  $\text{Pu}^{\text{IV}}$  carbonates are insoluble and so could be precipitated through ureolysis, whilst  $\text{Sr}^{\text{II}}$  can be incorporated into biogenic calcite [3]. Calcites have also been found to sorb radionuclides [4, 5].

### Phosphate precipitation

Bacterial hydrolysis of organophosphate can precipitate  $\text{Sr}^{\text{II}}$ ,  $\text{Am}^{\text{III}}$ ,  $\text{Th}^{\text{IV}}$ ,  $\text{Pu}^{\text{IV}}$  and  $\text{U}^{\text{VI}}$  as phosphates [1]. Coupling of phosphate biomineralisation and ureolysis could enhance actinide precipitation by forming highly insoluble ammonium phosphates [6, 7]. In addition, bacterial hydroxyapatite is an effective sorbent for Sr (II) [8].

### Manganese Oxide formation

Mn oxides have high sorption capacities and redox activity, and can immobilise a range of metals and radionuclides [2]. They can sorb significant amounts of Pu [9] and  $\text{U}^{\text{VI}}$  can be incorporated in biogenic Mn oxides [10].

This investigation will be a critical step in the development of novel *in situ* bioremediation technologies.

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## Sulfate standards for *in situ* high spatial resolution SIMS measurements

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Sedimentary sulfates are a valuable proxy for determining the seawater sulfate concentration and isotopic composition of ancient oceans, in particular providing constraints on the redox state of the ocean water. This knowledge is important especially for Precambrian sediments, where the redox state of atmosphere and hydrosphere changed significantly. However evaporites of Precambrian age are rare and often inaccessible with conventional geochemical analytical techniques.

The secondary ion mass spectrometry (SIMS) technique facilitates *in situ* measurements of even small amounts of sulfate minerals with a spatial resolution  $\leq 15$   $\mu\text{m}$ . Application of the method to sulfates is however limited due to the absence of well-documented, homogeneous, matrix-matched reference materials. We present multicollector (three Faraday) SIMS measurements of sulfate  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  for selected Phanerozoic and Precambrian age sulfate minerals (anhydrite, barite and celestine) to test their suitability as potential sulfate reference materials. Replicate conventional S isotope analyses were performed on these minerals prior to the SIMS study to determine their sulfur isotopic composition.

The SIMS study illustrates that the selected sulfate minerals do not exhibit significant heterogeneities in their sulfur isotopic composition, typically yielding external precision of 0.2-0.3 ‰ (1 std. dev.) on both  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  from a  $\leq 15$   $\mu\text{m}$  analysed area. Measurements on several randomly oriented pieces enable us to exclude the possibility of crystallographic orientation effects at this level of precision. The selected minerals thus provide reliable reference materials for *in situ* high spatial resolution sulfur-isotope measurements by SIMS.