

## Reducing the uncertainty of spent nuclear fuel dissolution: an investigation of UO<sub>2</sub> analogue CeO<sub>2</sub>

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In the safety case for the geological disposal of nuclear waste, the release of radioactivity from the repository is controlled by the dissolution of the spent fuel in groundwater. Therefore, to assess the performance of the repository after infiltration of groundwater and contact with spent fuel, the dissolution characteristics must be determined. In spent nuclear fuel, high energy sites occur at grain boundaries and within the material as naturally occurring surface defects. Current studies of spent nuclear fuel dissolution have not considered the effect of high energy surface sites within the material structure.

In this investigation, CeO<sub>2</sub> analogues, which approximate as closely as possible the characteristics of fuel-grade UO<sub>2</sub>, were characterised after dissolution under a wide range of conditions. Samples were powdered to three different size fractions to investigate high energy surface site density on dissolution rates, while monolith samples were monitored for development of surface defects as pores, steps and dissolution pits. These samples were subject to a range of aggressive and environmentally relevant alteration media with different solubility controls, including 2M HCl, a simplified groundwater of dilute NaCl (10mM) buffered to pH 7.5 by NaHCO<sub>3</sub> (2mM) and 0.01M NaOH, and reacted at a range of temperatures from 90°C to 150°C. Dissolution was monitored through analysis of the coexisting aqueous solution, and morphological changes at the surface using atomic force microscopy, confocal profilometry and scanning electron microscopy. Dissolution rates were found to be greater in high pH solutions, and at higher temperatures, and greatest for samples with the highest reactive surface area. Chemical analysis of additional monolith samples reacted in <sup>18</sup>O-enriched aqueous solutions was conducted using TOF-SIMS. The data demonstrate re-precipitation of Ce-hydroxide species on the sample surface, which may form a passivating barrier to dissolution.

## Nanometer scale characterization of fossil bacteria in an Eocene phosphorite sample

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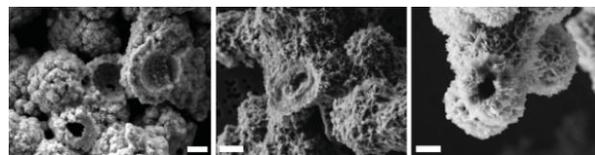
A great number of microstructures described as fossilized microbial bodies have been described in phosphorites of all ages in the past years (e.g., [1]). Most of these putative fossils have been identified based on their morphology (sizes and shapes) using SEM observations only. However, this approach might be misleading since micrometer-sized calcium phosphate globules resembling bacteria can also be produced by abiotic processes, as we will show here.

Here, we will present the study of an Eocene phosphatic coprolite from Morocco containing numerous purported bacterial fossils. We characterized the mineralogical structure and chemical composition of these objects down to the nano-meter scale using a combination of FIB-SEM, TEM and STXM.

The fossils are composed exclusively of francolite (Ca<sub>10</sub>(PO<sub>4</sub>,CO<sub>3</sub>)<sub>6</sub>(F,OH)<sub>2</sub>). However, some variations in electron density outlining these fossils could be evidenced. Based on TEM and STXM analyses, we interpret them as variations of mineralogical texture and chemical composition, resulting from the precipitation of francolite in the cell wall of the bacteria during their fossilization.

We compare these fossils with modern bacteria calcified in the laboratory on the one hand, and with bacteria-free and enzymatically-produced hydroxyapatite globules on the other hand. We will show that although they present great morphological similarities at the SEM scale (Figure 1), these different objects can be discriminated unambiguously at greater spatial resolution.

This study provides new signatures for identifying microbial activity in past and present phosphorites and illustrates the importance of using high resolution analytical tools for the search of biosignatures in terrestrial and extraterrestrial rocks.



**Figure 1:** SEM images of the fossils in the Eocene phosphorite (left), bacteria calcified in the laboratory (middle) and bacteria-free, enzymatically-precipitated hydroxyapatite globules (right). Scale bars: 1 µm.

[1] Zanin & Zamirailova (2011) *Russian Geology and Geophysics* **52**, 1134-1139.