

Nanocrystallization of rare earth phosphate using extracellular substances derived from *Saccharomyces cerevisiae*

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Rare earth elements (REEs) have been used as a surrogate of trivalent actinide in laboratory experiments owing to their similarity in chemistry, and the mobility in subsurface environments greatly depends on geochemical and microbiological processes due to the ubiquitous occurrence of microorganisms. In order to understand the role of extracellular substances (ES) derived from microorganisms in biomineralization processes, we have conducted laboratory-scale experiments of nanocrystallization using ES separated from microorganisms.

Saccharomyces cerevisiae X-2180 incubated in YPD medium was exposed to 1 mM NaCl solution at pH 3 or 5 for 72 h to obtain ES released from cells. The ES solution was separated from cells. Subsequently, 0.2-0.9 M Ce³⁺ was added at pH of 3-8 and reacted for 72 h at room temperature. The suspensions were filtered with 0.1 μm membrane filter to obtain precipitates. In addition, the same experiments were performed using ribonucleic acid (RNA) and adenosine triphosphate (ATP) instead of ES to investigate the effects of organic P. The supernatants were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The precipitates were analyzed by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and fourier transmission infrared microscopy (FT-IR).

The released ES mainly consists of 72.3±19.5 ppm of total organic C, 0.157±0.069 mM of total P, and 0.489±0.032 mM of K⁺. Approximately 80 % phosphorus was inorganic orthophosphate. Precipitates formed after reaction are identified to be rhabdophane structure, REEPO₄•nH₂O, P₆Z₂₂, Z=3. Organic P as well as inorganic P in the ES was removed from the solution. The Ce/P ratio in the initial solution did not affect the crystallographic properties. The pH dependence of crystal shape and size is same as the case for inorganic synthesis of CePO₄; the size decreases as pH increases. The FT-IR diagram of the precipitates that formed at pH 3-8 showed absorption peaks at 1541-1576 cm⁻¹ and 1200 cm⁻¹, indicating the occurrence of proteins and nucleic acids in the aggregates of CePO₄. The experiments using RNA and ATP as P source also revealed the formation of Ce phosphates, although the shape and structure are different from that formed by the interaction with ES. Hence, our results suggest that ES derived from microorganisms can form nanocrystals of REE phosphates even without cells and the organic substances contained in the ES can co-precipitate.