

## Microbial extracellular polymeric substances modulate the product of uranium biomineralization

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Microbial biomineralization influences the cycling and sequestration of a variety of metals and metalloids in the environment. Uranium biomineralization by *Shewanella oneidensis* MR-1 was shown to produce two distinct U(IV) products under different chemical conditions. Here, we report that the uranium product is modulated by the formation of extracellular polymeric substances (EPS), a biological response that improves cellular resistance to U toxicity. When imaged by cryo-electron microscopy and analyzed by X-ray absorption spectroscopy, the two uranium products have distinct morphologies and atomic environments. This difference is shown to be due to the presence or absence of EPS using a spectro-microscopy method –scanning transmission X-ray microscopy (STXM)– that can differentiate amongst carbon biomolecules and localize U. When EPS is present, U is largely associated with it instead of the cell surface. Furthermore, we show that when the suspected U reductases are removed by mutation, EPS production and cellular viability decrease. Hence, the structure of the product of uranium biomineralization is intricately linked to the formation of EPS. We posit that a single U(IV) product is favored in the subsurface due to the prevalence of biofilms and because EPS are major component of those structures.

## Hydromagnesite reactivity in aqueous solutions

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Hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) is the most common hydrous Mg-carbonate occurring at Earth's surface environments. It usually forms as a secondary phase in alkaline and Mg-rich natural waters where magnesite ( $\text{MgCO}_3$ ) formation is inhibited by the strong hydration of aqueous Mg [1]. Formation of hydromagnesite is commonly mediated by microbiological activity [2], so that its dissolution and growth may be closely coupled to promoting primary productivity in aquatic environments.

A critical factor defining the role of minerals in natural processes is the link between their dissolution and precipitation rates. In accord with transition state theory, precipitation rates should be readily calculated from corresponding dissolution rates using simple functions of chemical affinity. This possibility has proven to be challenging to validate due to the difficulty in measuring the precipitation rates of most minerals in the laboratory. The relative ease to which hydromagnesite precipitates at ambient conditions makes it ideally suited to assess the link between dissolution and precipitation rates.

Hydromagnesite dissolution and precipitation rates have been measured in closed-system reactors from far to near to equilibrium conditions in  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  bearing aqueous solutions at pH from 8.5 to 11.2 and temperatures from 25 to 75 °C. Resulting rates ( $r$ ) have been modeled using:

$$r = k(1 - \Omega^\sigma)^n$$

where  $k$  is the surface area normalized rate constant,  $\Omega$  the saturation degree of hydromagnesite,  $\sigma$  the Temkin's coefficient [3] ( $\sigma = 0.2$ ), and  $n$  the reaction order ( $n = 1$ ). Preliminary data interpretation suggests that the rate constants describing dissolution are from one to two orders of magnitude faster than those describing precipitation. For example, at 25 °C and pH 8.5 dissolution and precipitation rate constants were determined to be  $3.0 \times 10^{-9}$  and  $5.4 \times 10^{-11}$  mol/m<sup>2</sup>/s, respectively. Such differences could be attributable to the changing density of reactive sites on the mineral surface as a function of fluid saturation state.

[1] Lippmann, F. (1973) *Sedimentary Carbonates* Springer (New York). [2] Shirokova *et al.* (2013) *Aquat. Geochem.* **19**, 1-24. [3] Temkin, M. (1963) The kinetics of stationary reactions. *Dolk. Akad. Nauk SSSR*, **152**, 782–785.