

## Deciphering the early fossil record of cyanobacterial mats based on their mode of mineralization

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Archean traces of life are vague and confusing due to poor preservation. Identifying traces of life in early geological record requires understanding the mode of fossil formation. Carbonaceous matter, although abundant in many Archean deposits, does not *per se* prove presence of life. Key to decipher earliest life forms could be their mode of mineralization. Etching of Neoproterozoic carbonates (Nauga Fm, South Africa) revealed coccoid cyanobacterial mats preserved as web-like structures composed of pits, mineralized with CaCO<sub>3</sub>, and walls permineralized with Al-Fe-Mg-K silicates [1, 2].

Similarly permineralized web-like structures commonly occur in modern coccoid cyanobacterial mats. Studies on such mats from Lake Van (Turkey), Niuafu'ou Island (Tonga), and Satonda (Indonesia) showed that after death the mats undergo mineralization. The type of mineral phase(s) and the rate of mineralization depend chiefly on geochemical conditions within the degraded biomass. First to decompose is the cellular content and the thin mucilage sheaths surrounding individual cells and smaller groups of cells. Therefore cells are only exceptionally preserved. The most durable parts of the mat are the thicker outer web-like mucilagenous sheaths, which due to early permineralization with CaCO<sub>3</sub> and silicates, are fossilized.

Early diagenetic calcification and silicification is associated with post mortem activity of heterotrophic bacteria. Bacteriolysis liberates cations complexed during cyanobacterial lifetime in their EPS. This process enhances mineral precipitation in the bacterially degraded mucilage sheaths and preserves their web-like texture. Morphology and mineral composition of Neoproterozoic web-like structures resemble those of modern mineralized cyanobacterial mats and can therefore be regarded as biosignatures of benthic coccoid cyanobacterial mats.

[1] Kazmierczak, J. Altermann, W. (2002) *Science* **298**, 2351.

[2] Kazmierczak, J. *et al.* (2009) *Precambrian Research* **173**, 79–92.

## Density functional study of uranyl adsorption on solvated surfaces of clay minerals

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Actinide adsorption on clay mineral surfaces represents an important retardation mechanism for these metal ions. With the topical issue of safe disposal of radioactive waste in mind, it is important to gain comprehensive knowledge of the environmental chemistry of radioactive elements and their compounds, where the interaction of actinides with mineral surfaces in general plays an important role. Various experimental techniques are being used to examine these issues, and these results are favorably complemented by computational chemistry studies.

We explored uranyl adsorption on solvated clay minerals with the plane-wave based projector augmented wave approach as implemented in the program VASP. Neutral 1:1 layered kaolinite was considered as a simple model clay mineral. We focused on (001) basal aluminol and (010) edge surfaces. Solvation plays a crucial role when modeling the latter type of surfaces. These effects were approximated by including a mono- or bi-layer of adsorbed water in the quantum mechanical models.

We mainly explored bidentate inner-sphere adsorption complexes on deprotonated sites representing neutral or slightly higher pH. Uranyl adsorption on kaolinite edge surfaces commonly leads to a deprotonation of aqua ligands of uranyl, resulting in monohydroxide as adsorbate. Aluminol adsorption sites are preferable for uranyl adsorption compared to mixed aluminol-silanol sites. The geometry of adsorption complexes is compared to available experimental results. Overall, complex formation energies suggest that several adsorbed species may simultaneously be present at kaolinite surfaces.