

The 'bio' in biominerals — Identification of proteins associated to microbially produced selenium particles

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Selenium oxyanions are frequently encountered in surface waters as result of anthropogenic activities and natural weathering processes, representing a serious ecotoxicological risk due to their high toxicity and bioaccumulation potential. Different microbial groups can reduce water soluble, mobile and toxic selenium forms to elemental selenium, considered less toxic. Such biogenic elemental selenium, however, does not crystallize to large particles and remains dispersed in solution as a colloidal suspension of nanoparticles [1, 2], thus being subject to re-oxidation, uptake and assimilation by biota. The probable reason for the tendency of biogenic selenium to remain suspended in solution is an organic layer modifying the surface, preventing crystallization and conferring the selenium core with physico-chemical properties different from particles without such a layer. Extracellular proteins have been previously shown to determine aggregation and thus dispersal of biogenic chalcogen nanoparticles in the environment [3]. By using Electrospray Ionization (ESI) Mass-Spectrometry we studied biogenic selenium particles formed by phylogenetically different microorganisms (e.g. *Bacillus selenatarsenatis*, *Sulfurospirillum barnesii*, *Rhodospirillum rubrum*), demonstrating that proteins appear to be strongly associated with biogenic selenium nanoparticles of different origin.

[1] Zhang *et al.* (2004) *JEQ* **33**, 559–564 [2] Lenz *et al.* (2008) *JEQ*, **37**, 1691–1700 [3] Moreau *et al.* (2007) *Science*, **5831**, 1600–1603

Global biogeochemical cycle of silicon: sources and fluxes

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The main sources of silicon in its global biogeochemical cycle are very large, as it is the second most abundant element, after oxygen, in the sedimentary and crystalline crust (Figure 1). Si in solution, mostly in the form of $\text{Si}(\text{OH})_4$, is utilized by the land plants and aquatic taxa that incorporate Si in their cell structure and secrete silicate skeletons. Estimates of global primary production show that Si accounts for ~1.5% molar mass of terrestrial primary production and ~4.5% of marine primary production, where it is coupled to the other major nutrient cycles of C, N, and P.

Mean concentration of dissolved SiO_2 in world rivers (10.4 mg SiO_2/L) and river runoff represent a SiO_2 release rate per 1 m^2 of land drainage area of the crustal sources of 0.065 mol $\text{SiO}_2 \text{ m}^{-2} \text{ yr}^{-1}$ or 1.8 g Si $\text{m}^{-2} \text{ yr}^{-1}$. In comparison to the extensively studied dissolution rates of common silicate minerals in sediments and crystalline crust, this release rate corresponds to reactive mineral weathering surface areas of an order of 10^2 m^2 . Studies of the interconnected rock porosity, its surface area, and pore size help determine the weathering layer thickness.

Biological fixation of Si is the main mechanism of its removal from water and storage in sediments, where diagenesis of detrital minerals and neof ormation of clays also contribute to the balance.

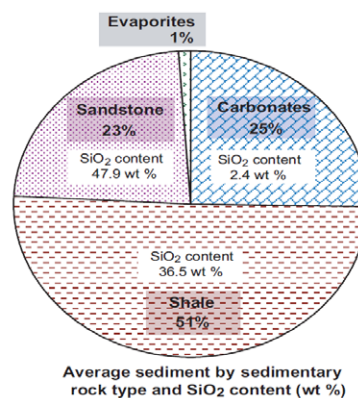


Figure 1: Composition of an average sediment (mass 1.9×10^{24} g) by rock types and their SiO_2 content. Modified from Lerman and Wu (2008).