

Silica cycle: The land-ocean connection

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Silicon (Si) is the second most abundant element in the Earth's crust after oxygen. Despite its high abundance, only a minor fraction of Si takes part in biogeochemical cycling. Weathering of the earth's crust is the ultimate source of dissolved silicate (dSi), which is an essential nutrient for numerous organisms, both on land and in the oceans. The biological fixation of dSi under the form of structural elements composed of amorphous biogenic silica (bSiO₂) initiates the biological cycle of Si and links the Si cycle to those of carbon and other nutrient elements. This presentation will highlight a number of implications of Si fixation on the continents for the global biogeochemical Si cycle.

Because of the relatively fast dissolution of bSiO₂ in soils compared to the chemical weathering of silicate rocks, a significant fraction of the reactive Si reaching the oceans has undergone prior biological cycling on land. Recent work further indicates that a significant portion of the reactive Si load in rivers may be under the form of bSiO₂ produced by land plants and freshwater diatoms [1]. Upon arrival at the land-ocean interface, changes in salinity and pH enhance the dissolution of the land-derived bSiO₂ [2], hence releasing dSi that supports biosiliceous productivity of nearshore marine ecosystems.

Biological Si fixation on land couples the continental and marine biogeochemical cycles of Si. The rise of land plants during the Paleozoic may therefore have played a significant role in accelerating the radiation of Si-fixing organisms in the oceans. Ongoing alterations of the riverine delivery of dSi and bSiO₂ by human activities may similarly cause long-lasting changes in the structure and functioning of marine ecosystems, particularly in the coastal zone.

[1] Laruelle *et al.* (2009) *Global Biogeochem. Cycles* **23**, GB4031, doi:10.1029/2008GB003267. [2] Loucaides *et al.* (2008) *Limnol. Oceanogr.* **53**, 1614–1621.

In situ measurement of CH₃SH on Earth and Mars

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As a biomarker, methyl mercaptan (CH₃SH) may be key for detecting life on Mars and in exoplanet atmospheres [1]. The molecule is implicated in the origin of life at sites of low-temperature serpentinization-driven hydrothermal activity [2]. Serpentinization may be occurring on Mars [3, 4, 5] and in other small wet bodies to a greater extent than on Earth, with important implications for life (Vance *et al.* 2007; Vance and Hand, *in prep.*). We recently detected absorption features in pure laboratory samples of CH₃SH and CH₃DH using the Methane Carbon Isotope Laser Spectrometer (CH₄-CILS), an infrared (3.27 μm) tunable diode laser spectrometer with capabilities nearly identical to those of the TLS instrument on the Mars Science Laboratory. The molecule is detectable at the ppm level. Global methane thiol production on Earth is estimated at one thousandth of biological CH₄ production [1]. Biogenic methane occurs in some serpentinizing systems on Earth at the percent level [7]. The present measurements therefore create the possibility for using methyl mercaptan as an *in situ* biosignature for Earth-based and extraterrestrial exploration.

[1] Pilcher (2003) *Astrobiology*, **3**, 471–486. [2] Martin & Russell (2007) *Phil. Trans. Royal Soc. B*, **362**, 1887–1925. [3] Ehlmann, *et al.* (2008) *Science*, **322**, 1828. [4] Ehlmann *et al.* (2009) *JGR-Planets*, **114**, E00D08, doi:10.1029/2009JE003339. [5] Mumma *et al.* (2009) *Science*, **323**, 1041–1045. [6] Vance *et al.* (2007) *Astrobiology*, **7**, 987–1005. [7] Morrill *et al.* (in revision) *Geochem. Cosmochim. Acta*.