Did thioarsenates start off the early arsenic cycle?

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Arsenic is known as a poison, but there is a diversity of microorganisms that can conserve energy from oxidation or reduction processes in the As cycle. Two inorganic species are commonly thought to exist: Arsenite and Arsenate. Chemolithotrophic arsenite oxidation requires strong oxidants, such as nitrate or oxygen as electron acceptors. That means arsenate production could have only taken place after the onset of oxygenic photosynthesis about 2.5 billion years before present. Dissimilatory arsenate reduction with organic carbon or sulfide as electron donors completes the As cycle.

However, it has been suggested that arsenite could be oxidized in the absence of oxygen, by anoxygenic photosynthesis (1) which is known for Sulfide or Fe^{2+}, but was unsuspected for As. It would enable a full As cycle already 3-3.5 billion years ago. Evidence for anoxygenic As photosynthesis came from two hot springs in Mono Lake, a saline lake in California, USA. The hot springs contain 100-130 μM As, supposedly all arsenite, 5000 μM Sulfide and are dominated by *Oscillatoria*-like cyanobacteria and an *Ectothiorhodospira* strain. Incubations of slurried biofilms showed arsenite oxidation in the light with CO_2 fixation (1).

We re-analyzed As speciation in these hot springs by our IC-ICP-MS method (2) and discovered that arsenite actually is only a minor species (<3%). Instead, thioarsenates ($AsS_nO_{4-n}^{3-}$) dominate (78-95%). The observed anoxygenic production of arsenate (from thioarsenates, instead of arsenite!) could thus be a novel microbial metabolism. An alternative explanation is that there is no anoxygenic arsenic photosynthesis, but arsenite oxidation occurs as an abiotic follow-up to sulfide oxidation. Laboratory experiments show that monothioarsenate forms from arsenite and S^0, an initial product of anoxygenic sulfide photosynthesis. Upon depletion of the S^0 reservoir, monothioarsenate is desulfidized and forms arsenate. Thioarsenates might thus have been key reactive intermediate As species to help kick off a full As cycle before the advent of free oygen by abiotically freeriding the microbially catalzyed S cycle.

(1) Kulp *et al* (2008) *Science* **321**, 967 (2) Planer-Friedrich *et al* (2007) *Environ. Sci. Technol.* **41**, 5245.

Short Timescales of Magma Ascent Recorded in Melt Inclusion Diffusion Profiles

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The rate of magma ascent is a primary proposed control on the eruptive vigor of volatile-rich magmas. Yet, very few quantitative estimates exist, in part because few geochronometers work at such short timescales (minutes to days). Here we present results of two different diffusion clocks, both of which record the minutes prior to and during eruption. The first involves diffusion of volatile species along melt embayments, as the partially-enclosed melt strives to equilibrate with surrounding degassing melt during magma ascent. NanoSIMS analysis (~5 micron spots) provides profiles of H_2O, CO_2 S, Cl and F along 100-300 micron tubes hosted in olivine from the 1974, sub-Plinian eruption of Volcan de Fuego in Guatemala. Fully-enclosed melt inclusions from the same samples constrain the initial volatile contents, and the decompression-degassing path followed by the melt exterior to the embayments. Despite very different diffusivities and solubilities, H_2O, CO_2 and S profiles all yield a consistent ascent rate in three different ash and lapilli samples: 13-16 m/s. Such rapid ascent, 8-9 km in 9-10 minutes, may contribute to the explosivity of this eruption.

Fully-enclosed melt inclusions from the same samples preserve major element profiles (MgO, CaO, Al_2O_3) that derive from olivine-growth on the inclusion rim and diffusion within the inclusion. We fit profiles using a coupled diffusion-growth model, where olivine growth is limited by both the rate of undercooling and the supply of MgO to the interface. While multiple cooling histories are possible, a constant cooling rate of 0.3-0.5K/s fits diffusion profiles across the ~ 50 micron diameter inclusions, with growth of ~ 0.4 microns of olivine in ~ 10 minutes. The similar timescales (~ 10 min) for both chronometers point to rapid decompression and cooling in the run-up to this explosive eruption. Extension of these melt inclusion clocks to other volcanic systems should provide new data on ascent, degassing and cooling rates, and their relationships to eruptive magnitudes.

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