Resonance photoionization mass spectrometry for determination of isotope ratios of krypton in extraterrestrial samples

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Analysis of samples returned by e.g. the Genesis and Stardust NASA missions requires instrumentation with extremely high sensitivity (~1000 atoms). Information about krypton isotope ratios of primitive meteorites or individual SiC grains can help to better understand the irradiation history of the early solar system [1,2] and to study the physics (e.g. s-process temperature and neutron flux) of nucleosynthesis sites [3].

A time of flight mass spectrometer with pulsed resonant laser ionization system capable to perform the measurements at ultra trace level has been developed in our laboratory. The first TOF spectra acquired can be seen in Fig.1.

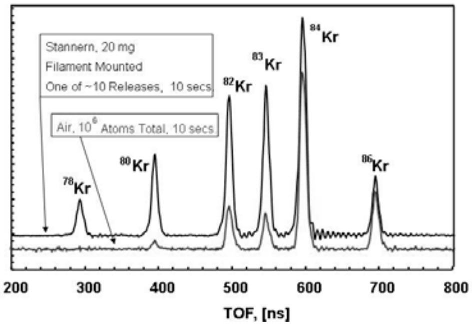

Figure 1: TOF spectra of Krypton measured for air samples and Stannern meteorite. In both cases the total Kr content was 10^6 atoms. In the air spectrum the ^{84}Kr peak corresponds to 5.7×10^5 atoms and ^{80}Kr peak to 2.3×10^4 atoms.

[1] Eugster *et al.* (2002) *MAPS* **37**, 1345-1360. [2] Polnau *et al.* (2001) *GCA* **65**, 1849-1866. [3] Lewis *et al.* (1994) *Geochim.Cosmochim.Acta* **58**(1) 471-494.

Sulfur cycle mediated microbial reduction of ferric iron

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Ferric iron oxides represent the globally most widespread electron acceptors for anaerobic respiration. Unlike other electron acceptors, the availability of iron oxides is strongly limited by their extremely low solubilities. Therefore, the reduction of iron oxides is a surface process requiring direct contact between reductant and iron surface sites. Some prokaryotes overcome this constraint by utilizing dissolved electron shuttling molecules. Observations in freshwater enrichment cultures under ferric iron-reducing conditions indicated that ferrihydrite was reduced to ferrous iron via sulfur cycling with sulfide as the reductant. Our laboratory observations are in good accordance with geochemical data from marine sediments suggesting an important role of sulfur cycle mediated reduction of ferric iron oxides. To explore this indirect mechanism of ferric iron reduction in more detail, experiments were conducted with a pure culture of *Sulfurospirillum deleyianum*. This prokaryote was isolated as sulfur-reducing bacterium unable to reduce ferric citrate or ferrihydrite directly. However, with low thiosulfate concentrations, growth with ferrihydrite was possible via sulfur cycling. Due to the low concentration of thiosulfate only little sulfide was produced by *S. deleyianum*. In addition, spatially distant ferrihydrite that was embedded in 1% agar was available as electron acceptor. The low concentration of sulfide evidently allowed the delivery of electrons to ferrihydrite with no or only little formation of ferrous sulfides. Ferrous iron and sulfide oxidation products (most likely elemental sulfur species) were produced instead, and the latter served again as electron acceptor for *S. deleyianum*. We suggest that these diffusible sulfur species can act as electron shuttles between bacterial cells and ferric iron oxides in natural environments. Particularly in freshwater habitats with small pools of available sulfur, bacteria may funnel electrons to abundant reservoirs of ferric iron oxides by means of sulfur cycling. Preliminary results of microcosm experiments inoculated with freshwater sediments indicated that the addition of low concentrations of sulfur compounds can indeed stimulate reduction of ferrihydrite. However, the ecological importance of sulfur-cycle mediated ferric iron reduction *in situ* still needs to be demonstrated