

## Sub-aerial rock-inhabiting communities: Role in land colonization and contribution to biogeochemistry of rock surfaces

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Throughout a remarkably long period the biosphere on planet Earth consisted not of multi-cellular macro-organisms, but of mono-layered microbial communities termed biofilms. In the absence of macroorganisms land colonisation has been proceeding by biofilm growth on bare rock surfaces. The very long history of sub-aerial biofilm existence and development resulted in a high degree of their specialisation in different environmental conditions including desert rocks and high mountain altitudes. Presently the interface between the rock substrate and the atmosphere is inhabited by a complex microbial community of chemoorganotrophic and phototrophic microorganisms metabolising under limited water availability and high sun irradiation. Chemoorganotrophic fungi are related to the amount of organic energy-rich compounds contained in the surrounding atmosphere and are the most enduring and important sub-aerial rock dwellers.

It should be pointed out, that (1) these biofilm communities cannot be considered as "primitive" ones regarding the very long history of their development and high degree of their specialized organisation; and (2) bacterial and fungal biofilms cannot be compared to lichen communities, evolving much later than biofilm ecosystems. Our experimental evidence confirms the hypothesis that the colonization of land by eukaryotes was facilitated by a symbiosis between a photosynthesizing organism and a fungus that were equipped to cope with the problems associated with terrestrial existence. Another important issue in studies of sub-aerial epi- and endolithic biofilms is their ability to create and maintain biologically modified environments where mineral solubility and dissolution rates are significantly altered and new metabolic products are deposited on the rock surface. The diverse spectrum of fungal activities on the formation and transformation of minerals will be presented. Further geomicrobiological and biogeochemical role and modifications of biofilm metabolic products on rock surfaces will be discussed.

## High resolution structural and chemical characterisation of framboidal pyrite formed within a bacterial biofilm

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A novel, anaerobically growing microbial biofilm, scraped from the inner surface of a borehole, 1,474 m below land surface within a Witwatersrand gold mine (Republic of South Africa) was found to possess framboidal pyrite. The water flowing from the borehole was measured to be at 30.9°C, pH 7.4, with an Eh = -250 mV.

Focused ion beam sectioning, field emission gun scanning electron microscopy (FIBS/FEG-SEM) of framboids from within the biofilm (Figure 1) supports early theories of framboidal pyrite formation via an organic matrix (e.g., Love, 1957) in this low temperature diagenetic environment.

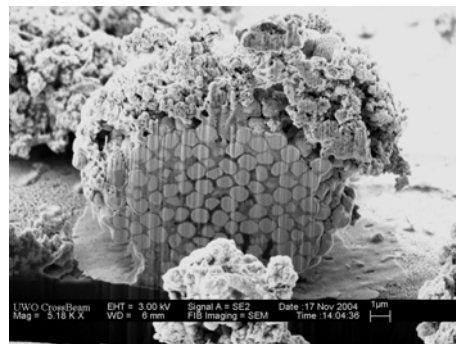


Figure 1: FEG-SEM of a FIB sectioned framboid observed within a microbial biofilm.

Elemental x-ray analysis via energy dispersive spectroscopy (EDS) revealed an extensive carbon matrix encasing individual pyrite crystals within the framboidal structure. While vegetative and fossilized bacterial cells are present throughout the biofilm, no bacterial fossils have been identified within the framboids.

### Reference

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## Photostable $\beta$ -As<sub>4</sub>S<sub>4</sub> produced at low temperature in culture by a novel bacterial isolate from the Alvord Hydrothermal Basin, Oregon

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The Alvord Basin in southeast Oregon contains numerous hydrothermal features never before characterized for their microbiology. Of these, Yellow Pot (61 °C, pH 7.1, [As] 1-4 mg L<sup>-1</sup>) was selected for intensive study because of an unusual flocculent precipitate, outgassing and mixing, a thick sediment layer, and occasional well-developed microbial mats. One goal was to identify microorganisms involved in arsenic cycling. Culturing techniques employed hydrothermal waters amended with yeast extract (0.05%) and 2 mM cysteine acting as a reductant. Inoculation and initial incubation was performed at the site. Several new strains of thermophilic bacteria have been discovered using this approach, including a novel *Caloramator*-like bacterium (designated YeAs-1) capable of reducing arsenic in culture.

As-sulfide precipitates form rapidly at 60 °C once As-containing growth medium is inoculated with YeAs-1. The precipitates appear as a bright yellow flocculant material. FT-Raman spectra of precipitates formed in cultures not exposed to light and processed under 725 nm illumination indicate they are  $\beta$ -As<sub>4</sub>S<sub>4</sub>, typically only stable at temperatures above 260 °C. Realgar and its  $\beta$ -polymorph are photosensitive, transforming to pararealgar upon exposure to sunlight or artificial light. Wavelengths <550 nm induce rapid transformation (Muniz-Miranda *et al.*, 1996). Following 24 h exposure to ultra violet light, very little phototransformation of the YeAs-1-formed  $\beta$ -As<sub>4</sub>S<sub>4</sub> was observed spectroscopically. Difference spectra indicate formation of pararealgar, but even after 14 days exposure to sunlight, approximately equal mixture of both the  $\beta$ -phase and pararealgar is observed. Thus, the precipitates formed by YeAs-1 are conferred atypical photo- and thermal stability by some, as yet, uninvestigated mechanism.

### Reference

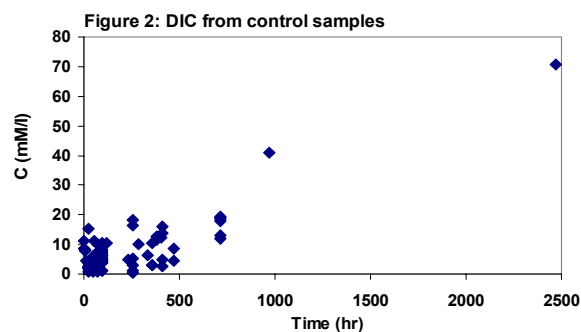
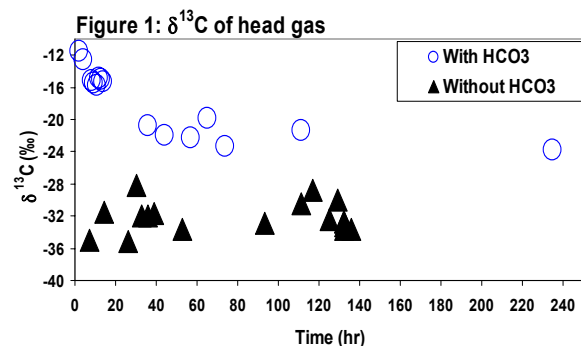
Muniz-Miranda M., Sbrana G., Bonazzi P., Menchetti S. and Pratesi G. (1996) *Spectrochim. Acta A* **52**, 1391-1401

## Stable carbon isotope fractionation during anaerobic microbial reduction of metals

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Experiments have been conducted using the Fe (III) reducing bacterium *Shewanella Putrefaciens* (200R), to understand stable carbon isotope fractionation during dissimilatory Fe (III) reduction. Ferric citrate and sodium lactate ( $\delta^{13}\text{C}$ , -25‰) were used as electron acceptor and donor respectively. Sodium bicarbonate ( $\delta^{13}\text{C}$ , -3‰) or potassium phosphate was used as buffering agent.  $\delta^{13}\text{C}$  of the head gas suggested that bicarbonate not only enhanced iron reduction but also was a source of carbon in the reduction process (Figure 1). During the course of the experiments, consistent production of DIC in all the control samples was observed (Figure 2), very likely produced abiotically. The  $\delta^{13}\text{C}$  of this DIC had a range of -30 to -38‰. These are the initial results of an ongoing research involving different metals, microbial species, electron donors and acceptors.



## Microbial mineral transformations in the Fe(II)-Fe(III)-H<sub>2</sub>O system

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The Fe(II)-Fe(III)-H<sub>2</sub>O system is of particular geomicrobiological interest owing to the behavior of iron in energy metabolism, depending on oxidation state, as either an electron donor or an electron acceptor. This means that iron is not only subject to intense biogeochemical cycling in nature, but also plays a critical role in the cycling of other elements such as carbon and oxygen. Apart from redox stability in Eh-pH space, another important feature of iron biogeochemistry is the limited solubility of Fe(II) and Fe(III). Of the two redox species, Fe(III) is particularly sensitive to hydrolysis and precipitation, which contributes to its behavior as a strong oxidant (i.e., electron acceptor) under reducing conditions. On the other hand, in anaerobic sulfide-rich environments Fe(II) tends to form insoluble sulfide phases (e.g., pyrite, mackinawite), or mixed oxide phases (e.g., hematite, green rust) under non-sulfidogenic conditions. These solubility constraints promote a wide range of mineral transformations owing to metabolic exploitation of the Fe(II)-Fe(III) redox couple by bacteria. Interesting examples include the oxidative dissolution of Fe(II)-sulfides in mine wastes by bacteria, which gives rise to Fe(III)-hydroxy sulfates such as jarosite, and formation of green rust in response to reductive dissolution of hydrous Fe(III)-oxide. More recent studies have focused on oxidation of dissolved Fe(II) at circumneutral pH where bacteria must compete efficiently with chemical oxidation to generate energy for growth. In most situations the Fe(II)-Fe(III) mineral transformation reactions proceed in association with bacterial cell surfaces. This frequently results in the preservation of fully mineralized, structurally intact cells that resemble microfossils in ancient sedimentary rocks. The implication is that microbial mineral transformations in the Fe(II)-Fe(III)-H<sub>2</sub>O system have contributed to biogeochemical cycling over a considerable period of Earth history.

## Microbial transformation of AQDS, Fe(III), Cr(VI), and U(VI) by a novel *Clostridiales*, Strain UFO1

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The activities of metal-reducing microorganisms offer potential bioremediation strategies for the immobilization of toxic metals in the environment. Strain UFO1 was isolated under strictly anaerobic conditions from an enrichment established with pristine sediment from the NABIR Field Research Center in Oak Ridge, TN on acetate and 2-line ferrihydrite. Strain UFO1 appears to be a novel genus within the bacterial order *Clostridiales*. Direct reduction of Fe(III)-nitrilotriacetic acid occurred in the presence of lactate. Additionally, strain UFO1 reduced the humic acid analog anthraquinone-2,6-disulfonate (AQDS) to its reduced form, AH<sub>2</sub>DS, using a variety of electron donors including lactate and H<sub>2</sub>. Ferrihydrite was not directly reduced in the absence of an electron-shuttling moiety. Synchrotron-XPS spectra revealed the mineral transformation of ferrihydrite from Fe(III) to Fe(II) by a culture of UFO1 containing lactate and AQDS, suggesting that the reduction of insoluble Fe(III) was shuttle-mediated. Reduction of 1, 3, and 5 ppm Cr(VI) occurred within 24 hours using lactate; in the presence of 1 mM AQDS, 3 and 5 ppm Cr(VI) were reduced to 0.1 ppm within 2 hours. Whereas Cr(VI) was directly reduced by UFO1, results suggest that UFO1 cannot directly reduce U(VI) in the absence of AQDS. U(VI) and phosphate profiles suggested however that UFO1 could immobilize U(VI) as uranyl phosphate. Fluorescence microscopy using exopolysaccharide (EPS)-specific probes showed colonization of ferrihydrite by UFO1, with copious EPS, suggesting an EPS-mediated cell-mineral association. The reduction of AQDS, Fe(III), and Cr(VI) and precipitation of U(VI) suggest a potentially important role for strain UFO1 in the biogeochemistry of pristine and contaminated geologic media at the Field Research Center.

## Investigation of iron oxyhydroxides reduction and associated metals release in soils using an *in-situ* iron-coated support

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Iron oxyhydroxide dissolution and precipitation are important control of element such as metal and organic matter solubilization and immobilization in soil solution. Knowledge of iron biogeochemistry is thus essential to understand soil behaviour. Dissolution of iron oxyhydroxides under reductive conditions have been extensively studied in the laboratory, (i) either in simplified batch experiments that have synthetic iron oxide mixed with a chemical reducer (hydroxylamine, ascorbic acid) or (ii) by performing anaerobic incubation of natural soil samples. However, both approaches are faced with several problems. In the simplified systems, the role of other soil phases such as clays and/or organic matter is not taken into account. In soil incubation experiments, the chemistry and crystallography of the iron oxides is little known since it is difficult to separate them from the soil matrix. In the present study, a new and original *in situ* methodology is proposed. Several iron oxides -amorphous: ferrihydrite, mixed: lepidocrocite or well crystallized: goethite- spiked with metals (Cd, Pb, Cu and As) were fixed on an inert polymer support and directly inserted in a controlled way in selected soil profiles. They were then recovered after definite time intervals. Such conditions allow the whole mineral surface to be exposed and to interact with the surrounding soil solution and organic or mineral components. This technique allows the study of the iron oxide surface after a long-term *in-situ* exposure to natural soil without any difficulty to isolate the mineral from the matrix. The first experiment was set up in controlled conditions in the laboratory. The iron coated supports were mixed in batches with a suspension of an organic-rich soil recovered in a previously studied wetland. Reductive conditions were induced under anaerobic conditions, either by the autochthon biomass, or by chemical reducers. In the second experiment, iron coated supports were inserted directly in the field into lysimetric cases where reductive conditions are forced by imposed storage of stagnant water above the studied soil sequence. Water samples were collected under a nitrogen pressure to preserve the anaerobic conditions. Fe(II) and associated released trace-metal concentrations were controlled in the soil solution. Supports were collected under inert atmosphere to allow the analysis of the mineral phases. The iron oxides on the support were then analysed to: (i) study their alteration and development of new mineral phases using XRD and TEM and (ii) to allow the dynamics of the metals possibly associated to these secondary phases be constrained.

## Microbially controlled selenate reduction in nutrient limited systems

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### Introduction

The widespread contamination of aquatic ecosystems with selenium has led to growing concern regarding the factors that control the distribution, fate, and bioavailability of selenium in these settings. Of specific concern is the more mobile anionic species which have a relationship with mortality and teratogenic mutations in many aquatic species.

In this study we provide evidence that *Shewanella putrefaciens* mediates the reduction of selenate and selenite in experimental systems devoid of nutrients. Considering the ubiquity of microorganisms in near-surface geological environments and that many of these systems are considered nutrient poor this mechanism may have important implications for Se cycling and bioavailability in these settings.

### Results and Discussion

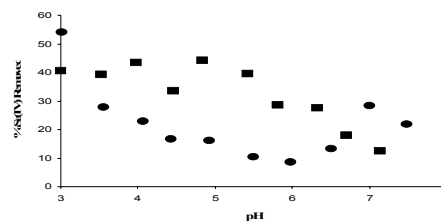


Figure 1: Reversibility of selenate removal as a function of pH. After 2 hours reaction time (squares) at pH 3 samples were readjusted to their final pH. Also presented here are the results of 2 hour adsorption experiment (circles).

Our preliminary results from batch kinetics, reversibility and adsorption experiments at multiple ionic strength and pH conditions indicate that *S. putrefaciens* irreversibly (Fig 1) removes some selenate from our reactors. Analysis of the reaction products via XANES techniques indicate that the irreversible Se fraction is reduced selenate in the form of elemental selenium associated with the cell wall of *S. putrefaciens*.

### Conclusions

Results from this study indicate that *S. putrefaciens* is capable of both dissimilatory reduction of Se and reduction via other pathways which do not utilize a carbon substrate.

## Active bacterial Mn(II)-oxidation accelerates Cr(III) oxidation compared to abiotic oxidation by Mn oxide minerals

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Bioremediation through reduction has been suggested as a cost-effective and non-invasive way to immobilize and detoxify Cr(VI) contamination. However, the long term immobilization of environmental Cr(VI) contamination by reduction to Cr(III) may be hindered by the presence Mn oxides, the only known environmental oxidants of Cr(III). Previous work has used rates of Cr(III) oxidation by well-characterized Mn oxide minerals to predict the potential for Cr(III) re-oxidation. Because bacteria are known to catalyze the rapid oxidation of Mn(II), forming reactive amorphous oxides, we hypothesized that Mn(II)-oxidizing bacteria would accelerate Cr(III) oxidation.

*Bacillus sp.* strain SG-1 is a marine bacterium whose spores oxidize Mn(II) to Mn(IV) via a multicopper oxidase-like enzyme located on its spore coat. Previously this bacterium has been shown to oxidize Mn(II) through two sequential one-electron transfers, resulting in an Mn(III) intermediate before formation of Mn(IV). Additionally, the Mn(II)-oxidizing enzyme is thought to be somewhat non-specific, leading to the possibility that Cr(III) could be directly oxidized by Mn(II)-oxidizing bacteria.

Incubation experiments with SG-1 showed that rates of Cr(III) oxidation during active Mn(II) oxidation by this bacterium are much faster than those by either biologically formed or abiotic Mn oxides. These results indicate that the process of bacterial Mn(II) oxidation may be more important in Cr(III) oxidation than the Mn oxide minerals that are produced. Although it acts competitively at higher amounts, our experiments show that some Mn is required for Cr(III) oxidation, ruling out direct oxidation by the Mn(II)-oxidizing enzyme. Abiotic experiments with Mn(III) compounds did not result in Cr(III) oxidation, while incubations with a colloidal Mn oxide resulted in rapid Cr(III) oxidation, suggesting that it is likely the Mn(IV) immediately produced by bacteria that is reacting with Cr(III). Possible explanations for the reactivity of the Mn(IV) product may be that the smaller particles are more reactive, or that the Mn oxide minerals are quickly passivated by sorption of other chemicals to their surfaces.

## Dependence of microbial dissimilatory U(VI) reduction on U(VI) chemical speciation

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Predicting how bacteria in natural systems can influence uranium (U) biogeochemistry depends on an accurate understanding of how the enzymatic reactivity of U(VI) varies according to its chemical form. In this study we present the results of laboratory experiments demonstrating the dependence of microbial dissimilatory reduction rates on the speciation of U(VI) both in aqueous solution and as U(VI) surface complexes on selected metal oxides. The facultatively aerobic bacterium *Shewanella putrefaciens* was used as a model metal-reducing organism, and U(VI) was supplied as sole terminal electron acceptor in a defined minimal medium under strictly anaerobic conditions. Uranium was provided either in the form of dissolved organic complexes with a series of low-molecular weight organic ligands (oxalic, malonic, succinic, glutaric, adipic, pimelic, citric, NTA, EDTA, tiron, and humic acid), or as adsorbed surface complexes on amorphous silica (SiO<sub>2</sub>), corundum, (Al<sub>2</sub>O<sub>3</sub>) and anatase (TiO<sub>2</sub>). Experimental results illustrate that the reductive bioavailability of U(VI) to *S. putrefaciens* depends strongly on the structure and stability of available U(VI) species. Rates of microbial U(VI) reduction under the experimental conditions varied systematically as a function of the stability of aqueous U(VI) complexation, with more stable aqueous U(VI)-organic complexes resulting in slower rates of U(VI) bioreduction. Strong aqueous chelation of U(VI) effectively suppresses bioreduction. If U(VI) is supplied in the form of adsorbed surface complexes, the properties of the adsorbing surface and the resulting adsorbed complexes has a governing effect on microbial reductive availability. For example, adsorption of U(VI) onto silica severely limits bioreduction rates (relative to aqueous U(VI)), while adsorption onto corundum does not. The experimental data suggest that under natural conditions, microbial U(VI) reduction will tend to be limited by coordination with available ligands, mineral surfaces, and organic matter.

## Bio-extraction of REE and other valuable elements from red mud left after alkaline processing of gibbsite bearing sediments, Sinai, Egypt

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The use of microbial uptake for trace elements was tested on gibbsite bearing sediments from southwestern Sinai, Egypt as well as red mud left after alumina extraction using Bayer process. The red mud slurry contains valuable elements such as Mn, Ni, Co, Cu, Zn and REE. The alkalinity of the slurry was adjusted to pH 4 - 5 before subjecting to microbial culture. The microorganisms could not tolerate high aluminum content in the original samples mainly due to the effect aluminum toxicity.

The SEM-EDX investigations show the effect of colonized microorganisms in perturbing red mud chemistry via selective dissolution and re-precipitation in biological active layer. The most frequent elements that accumulated in the biomass layer, which may serve as energy source, are K, Na, Mg, Ca, Mn, Zn, Cu, Co, S, P and REE. The REE enrichment in LREE or MREE differ quietly according to experiment conditions (Fig.1).

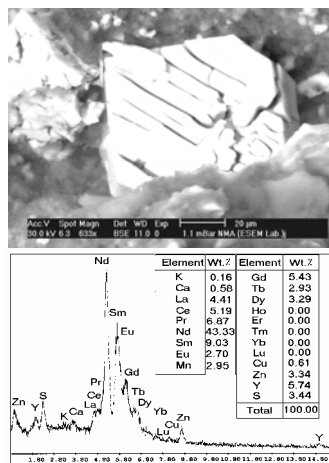


Fig. (1): SEM image shows REE bio-extraction in crystal like habit from red mud slurry.

Fig. (2): EDX analysis of the biologically precipitated REE in crystal like form.

## Microbial selenate reduction in a selenium-contaminated watershed

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Selenium continues to be a persistent environmental problem as a result of human activities such as irrigation of seleniferous soils, pesticide applications and mining operations. The oxyanions selenate and selenite are most prevalent in the environment and their toxicity is a function of their analogy to sulfur compounds. Mining operations in southeastern Idaho over the past 80 years have led to extensive leaching of selenium oxyanions from seleniferous overburden resulting in selenate contamination of waters and soils within the region. As part of a larger study of the controls on the biogeochemical cycling of selenium within this environment, the microbial reduction of selenate was investigated. Several selenate-reducing microorganisms were enriched and isolated from seleniferous shales. Isolates were identified and further characterized. Cores taken from the watershed region were used to quantify total numbers of selenate reducers within sediments as a function of depth. Denaturing gradient gel electrophoresis was used to compare the microbial diversity within sediments having high numbers of selenate reducers. The results of the study will provide information regarding which microorganisms affect the transport and mobility of selenium oxyanions in the environment, and may be beneficial towards the design of strategies to prevent selenium dispersal.

## **Stimulated migration of arsenic and uranium by reductive transformation of iron**

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Arsenic and uranium are redox active toxins that can have severe impacts on environmental quality and human health. One of the principal phases controlling dissolved concentrations and transport of both elements within aerobic environments is Fe (hydr)oxides. As a consequence, reductive transformation of Fe will have pronounced influences on the partitioning of these toxins. A transition from aerobic to anaerobic conditions appears to be the major means by which As is displaced from solids. Reductive transformation, inclusive of dissolution and recrystallization, invokes a displacement of As(III) and As(V). However, desorption and transport of As(V) is transitory whereas As(III) undergoes prolonged and pronounced desorption. Moreover, desorption of As(III) occurs independent of iron reduction. Thus, although As(III) has a greater binding capacity on iron (hydr)oxides than As(V), surface complexes of the reduced species, arsenite, are appreciably more labile than for the oxidized counterpart. Contrasting the behaviour of arsenic, uranium undergoes minimal gross transport under anaerobic conditions owing to reductive precipitation of uraninite (UO<sub>2</sub>) by dissimilatory bacterial reduction. Although gross transport is not observed, uranium does undergo a micro-scale redistribution within physically heterogeneous systems, migrating to points of microbial activity. Using constructed reaction cells having a distribution of advective and diffusive pore-domains, in combination with micro- X-ray fluorescence and absorption spectroscopies, we reveal the repartitioning of uranium during a transition from an aerobic to anaerobic state.