EUG XI

Symposium BG04

Quantifying the Significance of Microbes in Sedimentary Geochemical Processes

Convenors

Derek Lovley
Max Coleman

BG04
Microbes in Sedimentary Geochemical Processes

Tuesday AM Session

BG04 : TUam01 : G1
How Microbial are Microbial Sediments?

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Microbes significantly control sedimentary processes, in particular carbonate precipitation. However, in detail, there are many uncertainities concerning the effect of microbes on precipitation processes. Investigations of modern stromatolite-forming microbial mats indicate that microbial activity can result 1) in the calcification of individual microorganisms by metabolic activities, 2) in the creation of environments by communities of microorganisms in which precipitation preferably occurs, or 3) in the production of extracellular organic compounds that control precipitation in the absence of microorganisms. 1) The mechanism which leads to the calcification of microbes may be related to the ability of microorganisms to concentrate cations such as Ca^{2+}, on their cellular membranes. This concentration is possibly associated with cellular Ca^{2+} antiporter systems, which are pumps to exchange Ca^{2+} for instance with H^+. This exchange allows the microbes to keep the intracellular free Ca^{2+} concentration low in association with a high pH gradient at the cellular membrane. Because of this localized ion concentration microbes can act as nuclei for precipitates and undergo calcium carbonate encrustation. 2) Functional groups of microbes such as sulfate reducing bacteria create conditions in which carbonate precipitation occurs in the presence of sufficient carbonate and ion concentrations. In stromatolite-forming microbial mats such microbes control stratified horizons in the subsurface which can result in the layered stromatolitic structure. However, such processes are only efficient in closed or semi-closed systems. 3) Freshly produced extracellular organic compounds can chelate and concentrate cations and thus, are calcium sinks that prevent carbonate precipitation. With the diagenetic degradation and defunctionalization of such organic matter weak pH-sensitive Ca-bonds form. Under favourable conditions, this results in a Ca^{2+} release associated with carbonate precipitation. Any quantification of microbial activities requires a clear definition of the processes involved. Only then, conclusions in terms of relevance for and impact on sedimentary processes can be drawn.

BG04 : TUam02 : G1
Morphoanalysis of Bacterially Precipitated Calcium Carbonate from Weebubbie Cave, Australia

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Bacterial precipitation of calcium carbonate has been reported in a variety of environments including hot springs, marine and cave environments.

In this paper we present a previously unreported morphology of bacterially precipitated calcite (determined using XRD, FTIR and SAED) occurring in Weebubbie Cave, Australia. Observations using FESEM and TEM revealed spindle-shaped crystals with curved {hk.0} faces lying parallel to the c-axis. Many of the crystals were morphologically polar with one terminus attached to a bacterial filament and the other truncated by three well-defined {10.4} faces. Calcite precipitated under conditions designed to mimic the inorganic solution chemistry of the cave revealed a different morphology. These differences between the crystals suggest that the formation of the cave crystals is a consequence of biological activity.

BG04 : TUam03 : G1
Anaerobic Dolomite and Mg-Calcite Precipitation in Cultures of Sulfate-Reducing Bacteria

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The recognition of widely distributed microbial induced carbonates has led to the realization that this contribution to the global carbonate sedimentary budget has been greatly underestimated. It has long been recognized that dolomite was a common mineral found during the Earth's history but is rarely found in modern environments. The inability to produce dolomite ($CaMg(CO_2)_3$) inorganically under Earth surface conditions led to the hypothesis that anaerobic bacteria are mediate dolomite formation in anaerobic sediments by overcoming the kinetic barrier.

To study the process of microbial-mediated dolomite formation, growth experiments were carried out with selected bacterial cultures under anoxic environmental conditions simulating those found in a hypersaline lagoon, Lagoa Vermelha, Brazil, where dolomite precipitation occurs. Specifically, we report the isolation and the phylogenetic relationship of particular strains (strains LVform1 and LVform6) belonging to the sulfate-reducing bacteria, which apparently promote the formation of nonstoichiometric dolomite (Warthmann et al.; 2000). These bacteria grown in a synthetic liquid medium with an organic substrate produced ~0.1 g/L primary dolomite during 30 days incubation at 30°C. The precipitates have similar dumbbell morphologies, comparable to that observed in Lagoa Vermelha sediment. Our results demonstrate that sulfate-reducing bacteria can influence dolomite precipitation under controlled low-temperature anoxic conditions, implying that anaerobic microorganisms can play an important role in carbonate sedimentation. This process may have been particularly significant in the Earth's earliest history when reducing conditions predominated.

Warthmann R, van Lith Y, Vasconcelos V & McKenzie JA, *Geology*, **28**, 1091-1094, (2000).

BG04 : TUam04 : G1
How Anaerobic Micro-Organisms Induce Carbonate Crust Formation at Seafloor Cold Seeps

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Authigenic carbonate crusts formed through microbial methane oxidation are a common occurrence at seafloor cold seeps world-wide (Ritger et al., 1987; Aloisi et al., in press). Yet, the nature of the micro-organisms involved in their formation is still unknown and the influence of their activity on dissolved carbonate equilibria and carbonate mineralogy are poorly understood. In order to investigate these aspects, we conducted mineralogical, stable isotope, organic geochemical and phylogenetic studies of carbonate crusts formed on submarine mud volcanoes of the eastern Mediterranean Sea.

Our results show that carbonate crust formation is favoured by specific assemblages of anaerobic methane-consuming archaea co-occurring with a varied population of eubacteria including sulfate reducers. The crusts contain a highly diversified and previously unrecorded set of ^{13}C-depleted archeal lipid biomarkers including diphytanylglycerol diethers (archaeol and *sn*-2- and *sn*-3-hydroxyrchaeol), glycerol dibiphytanylglycerol tetraethers, and saturated and unsaturated C_{20} (crocetane) and C_{25} (PMI) irregular isoprenoids. We also observed analogous C_{30} and C_{40} irregular isoprenoids which have not previously been reported for such settings and a novel C_{35} irregular isoprenoid. Both the diversity and distribution of these biomarkers indicate that methane oxidation is mediated by a highly diversified archaeal community. ^{16}S rRNA gene surveys identified novel archeal groups that potentially comprise both facultative and obligate methanotrophs, confirming that the ability of anaerobic methane oxidation could be phylogenetically more widespread than previously assumed (Hinrichs et al., 1999).

The presence of several ^{13}C-depleted bacterial biomarkers, combined with data from the rRNA gene surveys, demonstrate that diverse eubacterial communities are also involved in the bulk process of anaerobic methane oxidation, possibly by consuming hydrogen and keeping this process thermodynamically favourable (Hoeler et al., 1994). The occurrence of novel non-isoprenoidal ether lipids (Pancost et al., submitted) ascribed to bacteria and their absence in nearby cold seep sediments suggest that the source organisms may play a significant role in carbonate crust formation.

The bulk chemical reactions carried out by micro-organisms produce supersaturation conditions with respect to carbonate minerals by increasing pH and carbonate alkalinity and induce the precipitation of ^{13}C-depleted carbonate minerals. Furthermore, the steep dissolved sulphate gradients produced by methane-based microbial sulphate reduction exert an important control on carbonate mineralogy by affecting the precipitation rates of aragonite and magnesian calcite.

The microbial processes we describe provide the simplest explanation of how micro-organisms control carbonate mineral precipitation and may be dominant at cold seeps world-wide. Highly diverse microbial communities exert these controls supporting recent propositions that micro-organisms play a fundamental role in mineral precipitation (Banfield and Nealson, 1997).

Ritger, S, Carson B and Suess, E, *Geological Society of America Bulletin*, **98**, 147-156, (1987).
Aloisi, G, Pierre, C, Rouchy, J-M, Foucher, J-P, Woodside, Jand the Medinaut Scientific Party, *Earth and Planetary Science Letters*, (in press).
Hinrichs, KU, Hayes, J-M, Sylva, SP, Brewer, PG and De Long, EF, *Nature*, **398**, 802-805, (1999).
Hoeler, TM, Alperin, MJ, Albert, DB and Martens, CS, *Global Biogeochemical Cucles*, **8(4)**, 451-463, (1994).
Parcost, RD, Bouloubassi, I, Aloisi, G, Sinninghe Damsté, JS and the Medinaut Shipboard Scientific Party, *Organic Geochemistry*, (submitted).
Banfield and Nealson, *Geomicrobiology*, (1997).

BG04 : TUam05 : G1
Sedimentary Humic Acid Derived from Bacterial Biomass

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The Be'eri sulfur deposit, in the Mediterranean Coastal Plain of Israel, is characterized by extremely depleted C_{13} values of the organic matter associated with the sulfur (ca. -85%. The origin of the deposit has been ascribed to venting of methane and hydrogen sulfide from underlying Messinian evaporites and oxidation at the surface.

The extractable fractions of the organic matter are predominantly composed of hopanoid derivatives of bacterial origin (alkanes, aromatics, ketones, alcohols and acids). GC and GC-irmMS (δC_{13} of-90%) analysis indicates derivation from hopanoid precursors of methanotrophic bacteria. No evidence was found for contributions of any photosynthetic organisms. The insoluble organic matter in the deposit is composed solely of humic acid (and no fulvic acid) with an isotopic value in the same unusual range as that of the extractable hopanoids, strongly suggesting a common genetic source. Here we present a study of this humic acid that may shed light on a contentious aspect of humic substances: the possibility of formation from bacterial biomass.

The humic acid contains high sulfur (11%) and low nitrogen as compared with other humic acids. The FTIR spectrum differs significantly from published spectra of soil humic acids. Some of the commonly found peaks ascribed to carbohydrates, amides and aromatics are absent. The observed peaks can be assigned mostly to aliphatics and that is also reflected by C_{13} CPMAS-NMR where more then 90% of the peak area is in aliphatic methylene groups. No peaks were observed in the region assigned to o-alkyls carbohydrate-related structures. For comparison, soil humic acids contain on the average 45% o-alkyls, 25% alkyls, 20% aromatics and 10% carbonyls.

Degradation with $HI/LiAlH_4$, yielded a series of hopanes (derived most probably from lipids of methylotrophic bacteria), phytane and cyclized C_{40} biphytane derivatives. The latter most probably correspond to the lipidic part of glycerol tetraethers occurring frequently in acidophilic or thermoacidophilic archaebacteria. The C_{13} values of these lipids (ca. -85%) are similar to the extractable hopanoids, indicating that the carbon source for these archaebacteria is probably biomass of methanotrophic bacteria.

Degradation of the humic acid with RuO_4 yielded hopanoid and 17(21)-secohopanoid acids. Desulfurization reactions released exclusively regular hopanes and 17(21)-secohopanes which were partly, at least, bound to the macromolecular structure via C-S bonds. Bulk EI and CI mass spectrometric analyses of the humic acid showed hopanoid moieties bridged by sulfur, supporting a source from the biomass of methanotrophic bacteria and acidophilic archaebacteria

It was proposed that marine humics might be produced from unsaturated algal fatty acids cross-linked by oxygen. Similar processes may have formed the Be'eri humic acid albeit from bacterial lipidic hopanoids bridged by sulfur. It is conceivable that some sedimentary humics may be formed through a similar route.

BG04 : TUam08 : G1
An Experimental "Silicate Surface-Bacteria" Interface to Diagnostic Biotic or Abiotic Processes

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The aim of this work is to determine specific structural and chemical signatures of (1) direct and indirect biotic processes as well as (2) pure abiotic processes recorded by the silicate surfaces. Understanding of the processes involved in surface destabilization requires observations of the bacteria-silicate interfaces at the nanometer scale. In this perspective, bacteria were cultivated on silicate surfaces of single crystals under controlled conditions (see Benzerara et al). Surfaces of various silicate minerals were tested. (001) surface of biotite and muscovite, (010) surface of olivine and (001) surface of pyroxenes (diopside and orthopyroxene) are obtained from natural single crystals of gem quality. Micas are clived. Oriented thin slices of olivine and pyroxene are mechanically polished and HF etched. AT surface of quartz are those of industrial piezoelectric devices. All crystals are sterilized at 120°C and 2 bars during 30 min. Surfaces having a quality amenable to carry on studies of their destabilization at the nanometer scale were selected (see also Lemelle et al. in session J8). The bacterial strain used for these experiments is the TTB310 strain. It has been isolated from Tatahouine meteorite fragments (P. Gillet et al, 2000). Cultures of bacteria are carried on in various media: TSB/10, TSB/50, LB/10 and "minimum" media. We can then prepare bacterial suspensions with controlled bacteria concentrations and fractions of the two forms of the bacterial strain (rod-shaped and spherical). Mineral surfaces are then immersed, vertically or horizontally, in the bacteria suspension. Geometry of the incubator allows impeding a direct contact of the bacteria with the mineral surfaces. Mineral surfaces are also incubated in solutions free of bacteria and constitute an abiotic reference. Incubation is carried at 25°C for run duration ranging between 1 min and 72 hours. The assemblages with alive bacteria are studied by confocal Scanning Optical Microscopy. Cultures are achieved with the addition of glutaraldehyde. Osmium fixatives followed by water baths are applied for Analytical FEG-Scanning Electron Microscopy (SEM) observations. Planar views and transverse cuts are prepared on these samples for Transmission Electron Microscopy (TEM) observations. Quantitative analysis of the SEM and TEM images was performed to analyze the mode of colonization of the silicate surfaces: kind of distribution, size and forms of bacteria. First results concerning the chemical signatures will be presented.

Gillet P, Barrat A, Heulin T, Achouak W, Lesourd M, Guyot F & Benzerara K, *Earth and Planetary Science Letters*, **175**, 161-167, (2000).

BG04 : TUam09 : G1
Bio-Alteration of Basaltic Glass in the Oceanic Crust

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Bio-alteration of Quaternary to Early Cretaceous basaltic glass from pillow lavas of the upper oceanic crust, can be documented in DSDP/ODP samples from shallow to deep drill holes from the north to central Atlantic Ocean, Lau Basin and Costa Rica Rift. Bio-generated textures are rooted in fractures and occur as two main types, a granular type and a tubular type. The granular type appears as individual and/or coalesced spherical bodies, mostly <1-3 mm in diameter, and they are common at all depths within the volcanic pile. The tubular type appears as thin tubular, sometimes branching bodies, mostly 20-30 mm long, and are more common at deeper levels. The degree of bio-alteration shows large within- and between-section variations, related to depth (and temperature), fracture density of the glass, and the age of the crust. Within sections the degree of bio-alteration, representing the latest stage of alteration seen in samples that still contain fresh glass, generally increases from the top of the volcanic basement downwards. The maximum degree biotic of total (biotic + abiotic) alteration, representing optimum conditions for bio-alteration, reaches values of 70 to 90% in the upper 250 m of the oceanic crust, and decreases to c. 10% at a depth of 550 m. Our data further indicates that bio-alteration of the basaltic glass in the upper oceanic crust is nearly completed within the first 6 Ma, and that only insignificant addition of bio-alteration can be detected in 110 Ma crust. Bio-alteration starts at the constructional stage of the crust, but is probably most effective at the near-axis, hydrothermal stage, when effective cooling, due to high water flux through the rocks, creates the most favorable environment for microbes at the deepest levels within volcanic sequences. Thus, the age constraint of 6 Ma for the near-completed bio-alteration may by considerably less.

BG04 : TUam10 : G1
Hematite Mineralized Microfossils from the Gunflint Iron Formation of Ontario Canada: Implications for the Relationship between Iron-Oxide Formation and Microbial Activity

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The 2.0 Ga Gunflint Formation contains a banded iron stromatolite, which was most likely deposited in a shallow water lagoonal environment during the critical period when the oxygen level in the atmosphere reached about 15 percent of its present value. The primary depositional iron mineral was magnetite (Fe_3O_4) and as oxygen fugacity changed, magnetite was oxidized to hematite (Fe_20_3). This multidisciplinary study concentrated on the relationship between iron minerals and the biota within the stromatolite. Methods used to investigate the hematite-rich Gunflint sample, collected in the Mink Mountain region of Ontario, Canada, included optical microscopy, powder x-ray diffraction, electron microprobe analysis, and analytical scanning electron microscopy (SEM).

The sample consists of alternating bands of hematite and chert (quartz), each millimeters thick. Thin section optical microscopy confirmed the presence of fossilized coccoidal and filamentous microorganisms in the chert. An unetched and an etched rock chip, as well as the etched thin section were analyzed by SEM. Samples were etched in the fumes of hydrofluoric acid for 15 or 30 minutes, and then thoroughly rinsed with deionized water.

Microfossils were more easily identified by SEM in the etched samples. Chains of degraded coccoidal bacteria (1-2 µm in diameter), as well as permineralized and hematite-mineralized filaments (1-2 µm in width and up to 200 µm in length) were identified in both thin section and SEM. Collapsed bacteria in the sample characteristically have hematite-rich crusts. The remains of large bacterial sheaths (5-10 µm in diameter) were also identified in both thin section and in the rock chips. Most sheaths do not show evidence of internal structure, (i.e. colonial cyanobacteria). Polymeric substances, substances secreted by bacteria in stressed environments to help them stabilize their surroundings and trap nutrients (Westall et al, 2000), are ubiquitous throughout the sample, and were both iron-mineralized and permineralized by silica.

Microfossils have been identified in both the hematite-rich and chert-rich bands of the banded iron stromatolite. They range from moderately well preserved to badly degraded. The polymeric substances proved to be the most common biogenic structure preserved.

Relationships between the iron oxides and organic components identified in this study include: 1) hematite mineralized microbial remnants, 2) carbon-rich inclusions within the hematite-replaced (magnetite) crystals, and 3) hematite-replaced (magnetite) crystals embedded in polymeric substances. These intimate relationships are interpreted to indicate that bacteria and their polymeric substances could have played a role in the genesis of banded iron formations.

Westall F, Steele A, Toporski J, et al, *Journal of Geophysical Research*, **105, E10**, 24,511-24,527, (2000).

BG04 : TUam11 : G1
Fractionation of Yttrium and Rare Earths by Bacteria

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Although it is well-documented that siderophores released from soil bacteria such as *Arthrobacter* sp. can mobilize Fe in aerobic environments at near-neutral pH, and thereby increase the (bio)availability of this micronutrient, relatively little is known about the effects of siderophores on other trace elements. Recently, however, isotopes of transition elements, such as Fe, Mo and Se, were studied with the aim to find unique biosignatures that may allow to distinguish between biotic and abiotic controls on element behavior. Here, we report first results of experiments in which soil bacteria (*Arthrobacter* sp.) reacted for 28 days with hornblende (hbl) powder in a growth medium at near-neutral pH. As controls, similar experiments were performed with bacteria and medium but without hbl. After separation of the bacteria, the dried cell pellets were decomposed in HNO_3 and analyzed by ICP-MS for Y and REE. The bulk hbl shows a chondritic Y/Ho wt.ratio of 27 and a chondrite-normalized (suffix '$_{CN}$') REE pattern that decreases from the LREE to the HREE. To ensure that the hbl did not host easily soluble accessory minerals, we leached the hbl with distilled water in the presence of an ion exchange resin and with 0.1 M HCl, respectively. Both techniques produced leaching solutions with chondritic Y/Ho ratios and REE patterns parallel to that of bulk hbl, indicating the absence of easily soluble accessory phases. Y and HREE concentrations of the cell pellets that had reacted with hbl were up to more than two orders of magnitude higher than those of the hbl-free controls, indicating Y and HREE release from the hbl. REE patterns of the bacteria pellets are enriched in HREE (Yb_{CN}/Ho_{CN} of 3 compared to 0.9 in hbl) and show super-chondritic Y/Ho ratios of about 42. This is clear evidence for fractionation of the REE and even of the geochemical twins Y and Ho during mobilization from the hbl by (compounds produced by) *Arthrobacter* during "biotic alteration". Although the exact fractionation mechanism is not yet fully understood, the combination of HREE enrichment and super-chondritic Y/Ho ratio is in marked contrast to what has so far been observed during abiotic Y and REE mobilization. Y/Ho ratios that increase with water depth in the upper 400 m of the marine water column and elevated Y/Ho ratios of river waters rich in organic colloids may be due to such a bacterial mobilization of Y and REE.

BG04 : TUam12 : G1
Mineral Magnetic Evidence for the Occurrence of High Concentrations of Bacterial Magnetite in Swedish Varved Lake-Sediments

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Mineral magnetic measurements carried out on four varved lake-sediment sequences in Sweden, which extend from the present day to c. 7000 BC. Comparison of the magnetic properties of the organic rich varved lake-sediments with their respective catchment materials indicate that the magnetic properties of the sediments are dominated by relatively high concentrations of single-domain magnetite magnetosomes produced by magnetotactic bacteria (e.g. Snowball 1994, Snowball et al. 1999). Preliminary results obtained from alternating gradient magnetometry (AGM) and magnetic force microscopy (MFM) of polished section embedded in epoxy indicate that the bacterial magnetite is concentrated into the winter layers. The dimictic nature of the lakes, which help form and preserve the varves due to the weakly oxic or sub-oxic environment, also appear to be suitable for a high-degree of magnetosome productions and perservation. The concentration of the magnetosomes in two of the sequences, as determined by mass specific magnetic measurements, exhibits a positive linear relationship with the total organic carbon (TOC) content. This finding suggests that magnetic measurements reflect lake productivity, via processes of organic matter accumulation and decomposition. Further research should focus on the potential to use the fossil magnetosomes as proxy-climate/environmental change indicators and as recorders of geomagnetic field variations and behaviour.

Snowball I, *Earth and Planetary Science Letters*, **126**, 129-142, (1994).
Snowball I, Sandgren P, Petterson G, *The Holocene*, **9**, 353-362, (1999).

BG04 : TUam13 : G1
Factors Limiting Iron Oxide Reduction in Tidal Freshwater and Deep Sea Sediments

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Under anaerobic conditions organic carbon can be mineralised by iron oxide reducing bacteria. Iron-oxide reduction is determined not only by the characteristics of the bacterial community but also by factors like the amount of reactive iron oxides and labile organic carbon in the sediment. Slurry experiments were performed to determine the factors limiting iron-oxide reduction.Two sites were studied: a tidal freshwater site with muddy, organic-carbon rich sediment and an oligotrophic deep-sea site in the eastern Mediterranean. The slurries were kept anaerobic and consisted of sediment and anaerobic bottom water. Freshly precipitated iron oxides and/or glucose were added in different amounts. In a time series, samples were taken, filtered and analysed to determine the rates of mineralisation and several anaerobic bacterial processes. At the freshwater site, higher amounts of reactive iron oxides result in faster iron oxide reduction rates with no effect on carbon mineralisation. Addition of labile carbon and reactive iron also stimulated iron reduction rates. Methane formation was inhibited by the addition of extra iron oxides. Samples from the deep-sea site still are being analysed but initial results clearly show an increase in the rate of mineralisation and iron oxide reduction after addition of glucose and iron oxides.

BG04 : TUam14 : G1
Isotopic Evidence for Microbial Reactions in the Biogeochemical Sulfur Cycle of Sediments from the Landsort Deep (Baltic Sea): Influence of Reactant Limitations

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Two sediment cores, taken from the deepest part of the Landsort Deep (459 m water depth) and from its eastern slope (221 m water depth) were investigated for sulpur and carbon stable isotopic biogeochemistry. The sediments were deposited during post-glacial Yoldia Sea, Ancylus Lake and Littorina Sea stages of the Baltic Sea history. In both cores, the stable isotopic composition of total sulfur was analyzed as a function of depth with high resolution. Phase specific isotopic measurements were preformed on pyrite (FeS_2), greigite (Fe_3S_4), MnS and baryte ($BaSO_4$) fractions, separated from the selected samples. Besides main and minor elements (including: sulfur, iron, manganese, and organic carbon), mineral composition was studied by XRD and SEM, and pyrite textures were analyzed by SEM-EDS and optical microscopy.

The sediments corresponding to brackish and freshwater stages can clearly be separated in studied cores by the contents and stable isotopic composition of TOC. Microbial reactions associated with the oxidation of organic matter resulted in characteristic assemblages of authigenic (thermodynamically stable and metastable) sulfide minerals. The sulfur isotopic compositions of the brackish water Littorina Sea sediments in two cores differ significantly (slope: between -40 and -27 per mil; deep: between -16 and +15 per mil vs. V-CDT). This dissimilarity between two cores is mainly determined by different sedimentation rates and the influence of the fluctuating chemocline in the basin. Additional factors are the abundance of sulfur (transport processes of dissolved sulfur species versus rates of microbial reactions; bioturbation) and reactive iron and manganese. The upper part of the Ancylus Lake sediments in the slope core, for instance, is sulfidized by downward diffusing H2S and/or microbial in-situ reduction of downward diffusing sulfate.

Anoxic basins of the Baltic Sea are the only known localities where authigenic manganese sulfide has been identified. The material analyzed within present study evidenced the occurrence of mm-scale MnS concretions in organic rich sections of the deep core. In these sections H_2S has locally exceeded the reactive iron availability facilitating MnS precipitation .The extreme internal isotopic zonation of concretions (e.g., center: -9 per mil; rim: +15 per mil) indicate that MnS formation took place in a closed system diagenetic environment. Besides hexagonal MnS, which is the most common variety in the Baltic Sea sediments, partial transformation into the cubic modification (alabandite) was also observed. The minor concretionary barite formation in the fresh water sediments of the slope core is most likely due to the reaction of pore water sulfate diffusing downward from brackish water sediments with barium desorbed from limnic sediments.

Tuesday PO Session

BG04 : TUpo01 : PO
Estimating the Microbial Activity in the Deep Layers (Catothelm) of an Ombrotrophic Peat Bog

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The deeper part of peat bogs - the catothelm - is often considered to be in a dormant state with relatively low biological activity. This study (see also Eilrich and Steinmann, 2001) investigates the biological - especially methanogenic - activity of a thick (ca. 6 m) ombrotrophic peat bog (Etang de la Gruère - EGR, Jura Mountains, Switzerland). We assessed the microbial diversity across a vertical peat profile at EGR using 16S rDNA gene analyses of Bacteria and Archea (physical extraction of DNA, PCR amplification, and TTGE analyses). The observed DNA patterns reveal clear differences between the microbial communities found in the near surface layers and those found at depth. Evidently, there is a specific microbial activity in the catothelm, the extent of it, however, cannot be reckoned from these microbiological analyses alone. Further evidence for microbial activity in the catothelm is provided by the pore water concentrations of methane and dissolved inorganic carbon (DIC) and their isotopic composition (Eilrich et al., 2000). Methane and DIC concentrations are highest in the deep layers of the bog with an isotopic signature pointing clearly to microbial origin probably methanogenesis via CO_2 reduction. BUT, the catothelm is not a closed compartment. It is linked via pore water advection, diffusion of solutes in the pore water and escaping gas bubbles with the surface of the bog and its base. This physical mixing must be carefully evaluated before interpreting methane and DIC concentrations and isotopic composition in terms of microbial reactions. It is the purpose of this paper to summarise the evidence of microbial activity in the catothelm of the EGR bog and to estimate its quantitative importance.

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BG04 : TUpo02 : PO
Seasonal Variation of Acetate Concentration and Implications for Methanogenesis in a Deep Peat Bog (Jura Mountains, Switzerland)

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Acetate is a key-metabolite in order to assess different methanogenic pathways in peat bog environments. We report acetate concentration patterns in the pore water of an ombrotrophic bog (Etang de la Gruère, Jura Mountains, Switzerland). Pore water samples were obtained in situ using diffusion chambers ("peepers") down to a depth of nearly 6 m for a period of one year. Acetate concentrations increase with depth from well below 100 ppb at 0.5 m to up to about 6.7 ppm at 5 m but then decline again in the bottom layer of the bog. The presence of two concentration maxima at approximately 3.2 and 5 m depth is confirmed by most measurement series. Since the temperature is rather constant in the deeper part of the bog, these maxima rather reflect differences in the established microbial communities and/or the available substrate. Over the measured period significant seasonal variations occurred with highest acetate concentrations in spring and early summer and lowest in late autumn and early winter. The observed acetate patterns are discussed in relation with methane and dissolved inorganic carbon concentrations and other pore water parameters, as well as physical parameters (such as advective and diffusive transport).

BG04 : TUpo03 : PO
Signatures of Microbial Mats in Modern Sediments Monitored by Element Assemblages

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Oligotrophic quartzsandy sediments can be fertilized by cyanobacteria-dominated microbial mats. As a result, the geochemical conditions are completely changed. In the present study, we focus on chemical elements characteristic of microbial mats. In analogous subfossil and fossil deposits, similar element assemblages may be indicative of the former presence of microbial mats, even if the microbial community itself would not be preserved. Sediment samples were obtained from modern coastal environments of the North Sea and Tunisia. The element distribution was comparatively studied in microbial mat layers and siliciclastic interlayers. Both lamina types are distinguishable by the concentrations of elements. Samples obtained from microbial mats were more frequently enriched in (i) Al, K, Na; (ii) Ca, Mg and Sr, typical of authigenic mineral formation; (iii)occasionally Zr and Ti and certain heavy metals; and (iv) P and S. The paragenetic formation of selected elements may be connected with the following microbial mat attributes: (i) Biomass production preferentially proceeds during intervals of low or zero sedimentation and low hydroenergy. During these intervals, the mat-forming populations grow, overprint and stabilize sedimentary surfaces. Their extracellular polymeric substances (EPS) act as “fly papers” for suspended material. Several species are also able to erect tufts into the supernatant water. Due to these processes, suspended detrital clay and other fine material may be deposited by trapping and baffling. These processes facilitate the enrichment of Al, and probably also Na and K in microbial mats. (ii) The biochemical environment which favours the enrichment of specific elements is triggered by an interactive process of microbial primary production of organic matter and microbially induced decay of the organic matter. Such a precondition is prominent for authigenic mineral precipitation already proceeding during earliest diagenetic stages and facilitating the enrichment of Ca, Mg and Sr. (iii) Due to their “fly paper” attributes, microbial mats sometimes are even traps for heavy minerals. This is reflected by increased contents of Ti and Zr. In the samples from the North Sea coast, the geochemical and mineralogical traces of microbial life seem to be less unequivocal than compared to those from the subtropical arid Tunisia coast. In the temperate humid area, biogenic carbonates authigenically formed in situ are rather unstable, quickly reoxidized or microbially degraded. On the contrary, the mats in the subtropical arid coastal zone contain high amounts of syngenetic and early diagenetic carbonates. The studies presented here encourage to look at further occurrences of microbial mats of different climate zones. However, the fact that certain elements such as Al can also be transformed in situ during diagenesis, shows that one should be cautious not to rely on only a few positive examples, but to base interpretations on more extensive studies of similar deposits.

BG04 : TUpo04 : PO
Bacterial Mediation of Dolomite Formation in Deep-Sea Hemi-Pelagic Sediments

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The mechanism of dolomite formation has remained controversial because it involves a large number of interacting factors, such as hydrologic, thermodynamic, kinetic, etc. Recent culture experiments, using sulfate-reducing bacteria (SRBs) derived from a hypersaline coastal lagoon (Lagoa Vermelha, Brasil), have demonstrated that an additional microbial factor must be considered to explain dolomite precipitation under Earth’s surface conditions (Vasconcelos and McKenzie, 1997; Warthmann et al., 2000). The growth of dolomite layers or nodules within the anoxic sediments of Lagoa Vermelha indicates that microbial activity continues with depth below the sediment/water interface. In a similar fashion, in situ dolomite formation in deep-sea hemi-pelagic sediments on continental margins is often associated with SRB activity. Strong evidence for microbial activity is based on the carbon isotope composition of authigenic carbonates. We proposed to test if a common microbial process might be active in both Lagoa Vermelha and deep-sea environments. As a first step, we selected dolomite samples from a number of locations with elevated productivity in the overlying surface waters and, hence, organic carbon-rich sediments [e.g., Gulf of California (DSDP Leg 64), Oman Margin (ODP Leg 117), Japan Sea (ODP Leg 128) and Namibian Margin (ODP Leg 175)]. We extracted the organic matter locked up in these deep-sea dolomites to seek specific organic tracers or biomarkers, which might be indicative of microbial activity. Phospholipids were selected for evaluation because the lipid composition is taxonomically characteristic for different bacterial strains. Our hypothesis was that these biomarkers might be potentially preserved in the mineral phase providing evidence of specific microbial mediation during dolomite precipitation. Our first results show that, besides the presence of some long chained fatty acids (FA’s), characteristic of diatoms, short chained FA’s (C_{12} - C_{20}) of bacterial origin are enriched in the dolomite. Typical biomarkers for specific SRBs were also found preserved in the dolomite. Further investigations will focus on how these SRBs are related to the dolomite formation. Systematic sampling will be combined with a multivariate statistical analysis of the FA-profiles. In addition, the $^{13}C/^{12}C$ ratios of the specific fatty acids of bacteria, cultured with ^{13}C-labelled substrates, will provide information about the substrate usage, metabolic processes and biosynthetic products of the organisms mediating the precipitation of dolomite.

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BG04 : TUpo05 : PO
A New Bacterial Model for Silicate Weathering and Calcite Precipitation

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Quantification of microbial processes in sedimentary environments requires the knowledge of the mechanisms of interaction between microorganisms and minerals. In this work, we present a new bacterial model of interest concerning the precipitation of calcite in dry environments and the weathering of silicates. We used the strain TTB310, whose 16S rDNA was sequenced and deposited in the GenBank database (N° AF144383). This strain belongs to a new species closely related to Acidovorax and two different forms (ovoid and rod-shaped forms) occur during its life cycle. It was isolated from Tataouine (Tunisia) desert soil (P. Gillet et al, 2000) and is well suited to our study as it was observed in association with pyroxene dissolution pits and calcite precipitation. The isolation of TTB310 was performed by culturing in a Tryptic Soy Broth (TSB) medium.

To get a better understanding of the involvement of strain TTB310 in calcite precipitation, this bacteria was cultured on solid media enriched in calcium carbonate. Rosettes of calcite appear systematically and exclusively above the colony spots. In liquid media, we compare the rates of saturation leading to calcite precipitation in abiotic and biotic conditions. Moreover paracrystalline layers of proteins (S-layers) were evidenced on the outer surface of the spheric form of the bacteria. Refined Transmission Electron Microscopy (TEM) observations were carried out on these cell-wall structures because as for other bacteria (i.e. cyanobacteria Synechoccus), they can be preferential nucleation sites for calcite.

The strain was also cultured in a TSB/10 liquid medium containing 20 g/l of a very fine orthopyroxene powder (<10 mm) at 30°C. TEM and SEM observations of both bacteria and minerals were performed. We showed that only one bacterial form (ovoid-shaped) appearing during the complex cellular cycle of the bacteria can form biofilms embedding submicron pyroxenes and secondary alteration phases which were characterized by transmission electron microscopy. The nature of the extracellular slime gluing both bacteria and pyroxenes is under investigation, in order to better characterize the local environment where pyroxene grains weather. Altogether, these observations could constitute an example of mineral-induced selective pressure among bacterial species as well as among different active forms within one given species.

Finally, as TSB is a chemically and mineralogically complex culture medium, we try to adjust a “minimal medium” where bacteria can grow but where no chemical species is superfluous. This will help to understand which nutritional parameters are critical for TTB310 growth and the potential role of calcium, magnesium, silicium and iron (all contained in calcite and pyroxene) in bacterial growth.

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BG04 : TUpo06 : PO
Microbes in Ocean Floor Basalt and their Relation to Alteration Textures and Geochemical Composition of Palagonite

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Samples of recent lava flows from the rift valley of the Mohns Ridge and Knipovich Ridge have been studied by electron microscopy, epifluorescence microscopy, cultivation and biomolecular methods, aimed at describing the microbial population in the basalt and the influence of microbes on the dissolution and alteration of the basaltic glass (Thorseth et al., 1995; Torsvik et al., 1998). The samples were collected at 2000-3500 m below sea level and the ambient seawater temperature was measured to -0.7 °C. Along fractures in the glassy margins of the lava flows, yellow brown to red brown alteration rims (palagonite) are developed. The thickness of the alteration rims vary from 80 µm at the outer surface of margins to < 1 µm in the interior. The alteration rims has a zoned texture where porosity and chemical composition differ. The glass surface at the alteration fronts vary from regular and smooth to irregular with multiple spherical pit marks of different sizes (<1-10 µm in diameter). Irregular alteration fronts are most strongly developed in the interior of the glassy margins. In most fractures a microbial community of various types of coccoid, rods and stalked cells is associated with the alteration product. The microbes are observed both at the outer surface of the altered rims and at the alteration front, where they attach to the fresh glass. Irregular alteration fronts without microbial cells indicate that the development of pit marks may not be directly related to the microbial activity. Some irregular pit marks with shape and size as microbial cells may however have formed by microbial etching (direct bio-dissolution) of the glass. In all samples fossilized cells are observed as hollow subspherical, rod-shaped and filamentous structures, due to precipitation of alteration products around the different morphological forms of microbes. Accumulation of Fe and Mn in some morphological forms may indicate utilization of these elements in energy metabolic processes. Results from cultivation, PCR, DGGE and 16S-rDNA sequencing show that iron oxidizing, iron reducing and methanotrophic bacteria and metanogenic archaeae are present in the rock samples. The microbial population is unique for the rock and differed from the populations found in sediment and seawater samples.

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Torsvik T, Furnes H, Muehlenbachs K, Thorseth IH & Tumyr O, *Earth Planet. Sci. Lett*, **162**, 165-176, (1998).

BG04 : TUpo07 : PO
Morphological and Spectral Investigation of an Exceptionally Well Preserved Bacterial Biofilm from the Enspel Formation, Germany

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In this communication we discuss the results of the investigation of an exceptionally well preserved fossil bacterial biofilm, attempting to marry morphological information with spectral data for in-situ biomarker detection. We investigated the fossil remains of the soft body of a tadpole and a possible coprolite from the Oligocene Enspel Fossillagerstätte, Germany. A multi-disciplinary approach was designed mainly using Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray analysis (EDX), High Resolution Transmission Electron Microscopy (HRTEM), and Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS analysed samples remain virtually undamaged so that samples can subsequently be SEM imaged allowing the combination of molecular and morphological information.

Preliminary SEM investigation on both samples revealed the presence of sub-micron sized spherical bacteriomorphs. Remarkably, the ca. 4 mm thick material of the supposed coprolite purely consisted of those spheres. In both cases, the spheres showed features characteristic for bacterial biofilms such as arrangement and spatial distribution and the presence of extracellular polymeric substances (EPS). Tentative evidence of cell division and preservation of double-layered cell walls could also be observed. As the samples could clearly be shown to be mineralised, we interpret the observed structures as lithified bacterial biofilms (Westall et al., 2000). EDX and HRTEM investigations supported this interpretation as HRTEM showed the spherical structures to be electron dense and EDX analyses revealed a peak distribution clearly indicating a mineral composition.

ToF-SIMS analyses revealed a variety of organic molecules in the atomic mass unit (AMU) range from 0 to 1000 AMU. Preliminary peak identifications indicate the presence of aromatic and polycyclic aromatic hydrocarbons (PAH's) (Stefan et al., 1999), alkanes, alkenes, saturated and unsaturated fatty acids, pyrrols and pyridyls (Brown et al., 1988) and possibly C30 triterpanes (Peters & Moldowan, 1993). Subsequent SEM analysis of the ToF-SIMS analysed coprolite showed that the material purely consists of fossil cells and polymeric substances. This is thus the first successful effort to combine spectral data with morphological information, which provides insight in the fate of bacterial cells and their organic constituents. The advantages of highly sensitive non-destructive in-situ analysis techniques for biomarker detection are invaluable, particularly with respect to envisaged Mars sample return missions, as it may allow us to identify remains and traces of former microbial life in terrestrial and extraterrestrial materials.

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BG04 : TUpo08 : PO
Detection of Life In Extraterrestrial Materials

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The announcement of potential biogenic fossils in Martian meteorite ALH84001 led to a spate of research which was meant to disprove this hypothesis. Indeed many techniques used to refute the McKay (1996) hypothesis are considered to be the mainstay of the techniques that would search for life on samples from other planets. However, these techniques failed to conclusively detect the presence of a terrestrial organism living within this meteorite (Steele et al., 1999, 2000a, 2000b). Since analysis of ALH84001 a further seven meteorites have been examined and all seven including Nakhla, Murchison and Allende have been found to be contaminated with terrestrial microbiota (Steele et al., 1999 2000a,b, Toporski 2000). This is not a surprising situation given the resident time of these meteorites on Earth.

What this research shows however is that the techniques that are used to detect life sometimes are not sufficient. The parameters that make each technique fail in life detection are poorly understood and are only just coming to light (Steele et al., 1999). With this in mind we have tested a suite of techniques for their ability to detect meteoritic contamination, ie life in extraterrestrial materials.

Among the suite of techniques used thus far are; · Light Microscopy · Epifluorescence microscopy · Scanning Electron Microscopy (SEM) · Atomic Force Microscopy · Culturing studies · Direct DNA extraction and analysis · Flow Cytometry · Raman spectroscopy · Time of Flight Secondary Ion Mass Spectrometry coupled with SEM · Two step Laser Ablation Mass Spectrometry

The results of these investigations will be presented and the advantages, disadvantages and detection sensitivity of each technique will be summarised.

Future approaches to life detection in these materials include the development of an immunological approach to life detection. Immunoglobulins represent one of the main techniques in microbiology for the detection and characterisation of micro-organisms. Thus far these techniques have not been applied to extraterrestrial materials. An approach to use these techniques both in contaminated meteorites, laboratory experiments and within a potential Mars lander (NASA Mars 2005) will be presented.

The contamination of meteorites by terrestrial microbiota is a double edged sword. On the one hand separating this contamination from the indigenous material, which appears to be being respired by the contaminating microbes, is a potential nightmare. On the other hand these materials represent a natural group of analogues to home the techniques to find life on. This resource should be further exploited and tested.

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BG04 : TUpo09 : PO
Quantifying Impact of Ant and Termite Activities on Soil Chemical Compositions

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Termites and ants are common biological agents, especially in soils of tropical and subtropical regions, that can induce significant physical and chemical modifications of soils. The present study was made to document whether or not significant amounts of amorphous or microcrystalline neoformed material could be recognized in soils affected by termite or ant activities, and also whether or not significant changes occurred in the mobilities of various elements other than the biochemically common nutrient elements such as K, Ca, Fe, Mg, C, N and P for which some adequate information exists. The soil samples came from the experimental Nsimi basin (Cameroon). The ant and termite related soils consist mainly of clays, quartz and probably some iron oxides. The chemical investigations on these soils revealed that ant and termite activities were dominated by developments of Fe-Mn-oxihydroxides, especially Mn-oxihydroxides with relatively minor amounts of calcite and even a minute amount of phosphate minerals in the termite related soils and minor amounts of Mg-carbonate in the ant related soils. The neoformed oxihydroxides in the ant and termite related soils potentially fixed some K and also some Mg and Al. The content of amorphous material was about 10.68 mg/g for the soil without any visible termite activity, and about 10.81 mg/g for the soil affected by termites. While in the soil without ants, the total content of amorphous material was 11.15 mg/g. In the soil activated by ants, this content was about 9.05 mg/g.

Chemical restructuration of the soil by termite activities resulted in some Si (14%) loss, and significant gains in Ca (4750%), Mn (350%), K (76%) and REE (70%), relatively smaller gains of Al and Fe (25%), whereas other elements such Na and Ti remained unchanged. Chemical restructuration of the soil by ant activities evolved in some losses of REE (6%), Si (9%), Al (17%) and Fe (20%), as well as significant amounts gains of Ca (600%), whereas the content of Mg, Mn, Ti, K and P remained unchanged. A fractionation of the REE with an enrichment of LREE and a slight enrichment of the HREE seem have been induced by termite and ant activities, respectively. Heterogeneous chemical reactions have been observed from analyses of leachates derived from water- and HCl- sediment reactions.