

EUG XI



Theme BG

Biogeosciences

EUG XI



Symposium BG01

Organic Matter and Transformations in
Sediments and Sedimentary Rocks

Convenors

Paul Farrimond
Emile Pefferkorn

BG01 Organic Matter and Transformations in Sediments

Tuesday PM Session

BG01 : TUpm25 : G1

The Impact of Benthic Biology on Biological Marker Concentrations and Distributions in Deep-Sea Sediments

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The process of feeding and assimilation of organic material by heterotrophic organisms is selective, and can lead to the removal of specific compounds and compound classes during passage through gut systems (Harvey et al., 1987; Bradshaw et al., 1989 and others). Despite this, such processes have often been ignored when considering the role of benthic animals in modifying the relative concentrations and distributions of individual biological markers in the sedimentary record. This is important, because the molecular characteristics of organic material, particularly lipid and pigment biomarkers, are often employed as proxies for environmental conditions of surface waters in palaeoceanographic studies. It is potentially difficult to quantify the effect of benthic feeding on organic matter, as communities are diverse and may process components of organic matter at different rates and in different ways.

Between 1996 and 1999, observations made on the Porcupine Abyssal Plain in the Northeast Atlantic Ocean show that there were significant changes in the organic geochemistry of the sediments. These co-occurred with large changes in the populations of organisms in all size classes (megafauna - > 10 mm; macrofauna - 63 µm to 10 mm; meiofauna - < 63 µm). In particular, the increase in abundance of two species of holothurian, *Amperima rosea* and *Ellipinon* sp., by 4800 individuals per hectare between September 1996 and July 1997 led to the selective removal of sterols and fatty acids, relative to total organic carbon, from surficial sediments (0 - 5 mm; Figure 1). Mass balance calculations show that the sterol required by the holothurian population (deep-sea holothurians apparently do not biosynthesise sterols de novo, Ginger et al., 2000) is equivalent to the flux of sterol to the sea floor during the bloom period. The implications of our observations are considerable. Firstly, the benthic megafauna are capable of extremely rapidly reworking the organic material arriving at the seafloor. Secondly, they selectively remove certain lipid components (particularly the steroids), thus impacting the organic geochemical signature of the sediments. Finally, the sudden bloom of animals that feed exclusively on phytodetritus indicates that quiescent population dynamics cannot be assumed even in the deep sea, so great care must be taken with the interpretation of biomarker distributions in open ocean sediment records.

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BG01 : TUpm26 : G1

Effects of Bioturbation by Polychaete Worms on the Lipid Composition of Detrital *Emiliania Huxleyi*

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The ubiquitous marine alga *Emiliania huxleyi* is one of a limited number of haptophyte species that are responsible for biosynthesising a series of long-chain (nC₃₇) methyl or ethyl ketones. These components have varying degrees of unsaturation dependent on growth temperature (Brassell et

al., 1986). The alkenones are found in Cenozoic and some Mesozoic sediments deposited in all the major ocean basins. They are used in palaeoceanography for reconstructing sea-surface temperatures (most commonly $U^{K_{37}} = C_{37:2}/(C_{37:2} + C_{37:3})$) of the Pliocene-Pleistocene. Most (>95%) algal lipids, including the alkenones, are re-mineralised or bound to non-extractable matrices in the water column and undergo further alteration during sedimentary diagenesis (Harvey, 2000; Prahil et al., 1993; Prahil et al., 2000). The early stages of diagenesis can be significantly accelerated through the process of bioturbation (Conte et al., 1994). Arguably, depositional environments that undergo intensive biological reworking could bias the $U^{K_{37}}$ signal through preferential alteration of the more unsaturated alkenone. Bioturbation is usually limited to oxic sediment-water interfaces and it is possible that where oxidation has been identified as the cause of a $U^{K_{37}}$ bias there may have been a significant contribution from bioturbation.

We have investigated the effects of bioturbation on lipid degradation rates by developing mesocosms containing infaunal burrowers (*Hediste diversicolor*) and epifaunal tube-building (*Eupolyornia nebulosa*) polychaete worms that were fed on senescent cells of cultured *E. huxleyi*. We observed a significant bias to the $U^{K_{37}}$ signal (equivalent to about +1.51/4C) after 40 days in all the mesocosms, including the control. Although this suggests that the feeding habits of the worms did not influence the absolute degree of preferential alkenone diagenesis a sub-sample taken after six days revealed that the polychaete mesocosms had significantly enhanced the rate of $U^{K_{37}}$ bias leading up to day forty. We conclude that it is unlikely that the general bias was caused by bacterial effects (Teece et al., 1998) so there must have been an alternative mechanism by which $C_{37:3}$ was preferentially removed from the solvent extractable pool of lipids relative to $C_{37:2}$. The exact nature of this mechanism is as yet unknown but should be considered when interpreting potential $U^{K_{37}}$ biases solely in terms of oxidation. We also report changes in the relative and absolute abundances of C₃₈ alkenones, alkyl alkenoates, alkenes, fatty acids and sterols.

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Conte MH, Madureira LAS, Eglinton G, Keen D, & Rendall C, *Org. Geochem*, **22**, 679-990, (1994).

Teece MA, Gettiff JM, Lefley JW, Parkes RJ, & Maxwell JR, *Org. Geochem*, **29**, 863-880, (1998).

BG01 : TUpm27 : G1

Alteration of the Nitrogen and Carbon Isotope Composition of Residual Organic Matter during Experimental Oxic and Anoxic Microbial Degradation

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The nitrogen and carbon isotope composition of organic matter (OM) has been widely used as a tracer for studying nitrogen and carbon cycling and as a proxy of past changes in degree of nitrate utilisation and primary productivity in marine and lacustrine environments. However, the isotopic composition of bulk OM is not only determined by the inorganic source material and any related isotopic fractionation during biosynthesis, but also by degradational processes in the water column and during early diagenesis in the sediments. In order to reconstruct past environmental changes recorded by OM, it is crucial to consider potential alteration of the primary isotopic signal by bacterial degradation. To simulate oxic degradation of phytoplankton, a natural sample of biomass was collected in the photic zone of Lake Lugano and incubated for 110 days. It was kept in suspension in 5l culture vessels that were continuously aerated. Anoxic culture experiments were also conducted. After oxygen removal, the vessels were purged with N₂ to maintain anaerobic conditions. Anoxic lake bottom water was added to the vessels as an inoculum to provide a natural anaerobic microbial consortium. Particulate matter samples were withdrawn from each vessel for isotope analysis at distinct intervals. The degradation can be described as first-order decay with rapidly decreasing organic nitrogen and carbon concentrations within the first days. The refractory nitrogen and carbon fractions after stabilisation are about 14% for the oxic exper-

iment and 31% for the anoxic experiment. The evolution of $\delta^{15}N$ values for residual OM shows a fundamentally different pattern during oxic and anoxic decomposition. During anoxic decay, the $\delta^{15}N$ values are continuously decreasing to 3.5‰ below the initial value. In the oxic experiment, $\delta^{15}N$ values for residual material increase by more than 3‰ before decreasing to a value indistinguishable from the initial isotopic composition. High OM loss does not necessarily coincide with large changes in isotopic composition. Both anoxic and oxic decay result in a qualitatively similar evolution of the $\delta^{13}C$ values for the residual OM. Within 3 months of incubation the $\delta^{13}C$ of collected OM decreased by 1.8‰ (oxic) and 2.7‰ (anoxic) with respect to the initial value. Our results are not consistent with the widely accepted hypothesis that OM becomes enriched in the heavier isotope during decomposition. The decrease in delta values might be attributed to bacterial growth using soluble organic compounds. Although they only approximate natural conditions, we can conclude from our incubation experiments that microbial activity in the water column and in sediments has a high potential to alter the isotopic composition of bulk OM towards lower delta values. The different impact of oxic versus anoxic decomposition on the $\delta^{15}N$ of residual OM may allow for an improved reconstruction of past changes in redox conditions.

BG01 : TUpm28 : G1

Organic Matter Trapped in Sedimentary Dolomite: A Potential Tracer to Recognize Microbial Dolomite

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The microbial dolomite model was proposed based on the study of a hypersaline lagoon, Lagoa Vermelha (Brazil), where dolomite presently precipitates. This model suggests that sulphate-reducing bacteria mediate dolomite precipitation by increasing the pH and removal of the inhibitor sulphate (Vasconcelos and McKenzie, 1997). Lagoa Vermelha is a natural laboratory, which can serve as an analogue to understand the process of microbial dolomite formation in the geologic record, particularly during times when dolomite precipitation was much more abundant than today. Understanding this process may provide clues about the peculiar distribution of dolomite in the geologic record. The stable carbon isotopic composition of dolomite has been used as an indicator of microbial activity in its depositional environment, but it does not demonstrate the involvement of bacteria in dolomite precipitation. An additional analytical tool is needed to recognize and trace microbial dolomite through time and estimate the contribution of microbial dolomite to the global dolomite budget.

In laboratory experiments, pure cultures of sulphate-reducing bacteria produced dolomite with a remarkable dumbbell shape, similar to the morphologies found in Lagoa Vermelha sediment (Warthmann et al., 2000). Bacteria were observed sometimes attached to the dumbbell shaped minerals, suggesting that bacteria or their outer membrane constituents may influence the mineral shape. This implies that the dumbbell morphology may be an indicator of microbial dolomite. In addition, in Lagoa Vermelha sediments, bacterial shapes were observed coated with a fine-grained mineral precipitate, suggesting that bacteria could be entombed in the growing mineral phase.

To test this hypothesis, the organic matter locked up inside the dolomite mineral structure was extracted by extensive bleaching and dissolution of the dolomite crystals and analyzed for its molecular composition. The intra-crystalline extractable organic matter did not contain exclusively bacterial-derived compounds, such as those found in the cultures that precipitated dolomite minerals, but it was significantly enriched in fatty acids and hydroxy fatty acids. This indicates that fatty acids are preferentially occluded in the dolomite crystals. Our results do not demonstrate the entombment of bacteria inside dolomite minerals. However, more specific biomarkers, such as branched or saturated fatty acids, and their stable carbon isotopic composition or other compounds, such as proteins, are potential biomarkers to trace microbial dolomite formation through geologic time.

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BG01 : TUpm29 : G1 Sedimentary Transformations of Diatomaceous Highly Branched Isoprenoid Alkenes

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Numerous C₂₅ highly branched isoprenoid alkenes (HBIs) are found in sedimenting marine particles and marine sediments from diverse parts of the globe and have been proposed as 'chemical fossils' of diatoms. A body of evidence shows that HBIs are produced by benthic diatoms, but these cannot be the source of the HBIs in the particles and to date only one planktonic diatom source of one HBI has been reported. The HBIs undergo rapid isomerisation and cyclisation reactions in the presence of clay, complicating the interpretation of geological data from the distributions.

The present study reveals previously unreported planktonic algal sources of HBIs, including rigorous chemical (MS, NMR) and microscopy (EM, optical) characterisation data for new HBI isomers. The likely diagenetic reactions of these are discussed by comparison with the results of laboratory simulation studies with pure isolated HBIs and clays and MM computer models of the most stable products.

Belt, S.T., Allard, W.G., Rintatalo, J., Johns, L.A., van Duin, A.C.T. & Rowland, S.J., *Geochimica Cosmochimica Acta*, **64**, 3337-3345, (2000).

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BG01 : TUpm32 : G1 Sequestration of Biomarkers through Natural Sulfurisation during Early Diagenesis

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Biomarkers (or chemical fossils) can provide a wealth of information on past environmental conditions, especially during periods of black shale deposition where often carbonate microfossils have not been preserved (e.g. Kuypers et al., 1999). For a proper identification of the sedimentary biomarker record, however, a detailed knowledge of the diagenetic reactions altering the chemical structure of characteristic biolipids is essential. Under the anoxic conditions where black shales are formed, natural sulfurisation (i.e. the reaction of organic matter with reduced inorganic sulfur species during early diagenesis) is often an important diagenetic reaction, modifying the structure and mode of binding of specific biomarkers. Recently, we have established that this process takes place in the first thousands of years of burial (Werne et al., 2000; Kok et al., 2000). Depending on the structure of the precursor biolipid, biomarker skeletons may in this way be sequestered in higher molecular weight sedimentary organic matter fractions (i.e. via "cross linking" reactions) for millions of years. Although these biomarkers skeletons thus escape conventional biomarker analyses, specific chemical degradation techniques can be applied to obtain this information and compound-specific ¹³C analysis of the released biomarker skeletons often results in the retrieval of important palaeoenvironmental information (e.g. Kuypers et al., 1999).

Three examples to illustrate the importance of sulfur sequestration of biomarkers and the use of these bound biomarkers in palaeoenvironmental reconstruction of black shales will be discussed. Highly branched isoprenoid (HBI) alkenes are specific biomarkers for certain species of diatoms. They are often found in marine surface sediments but absent in slightly deeper sediments. For example, the diatom *Rhizosolenia* sp. has been proposed to play an important role during the deposition of the Pleistocene S5 sapropel (Kemp et al., 1999) but conventional biomarker analyses do not support this contention. However, desulfurisation of higher molecular weight fractions releases high amounts of the C₂₅ HBI. Obviously, HBI alkenes react readily with reduced inorganic sulfur species during early diagenesis. Other examples to be discussed are the pigment, isorenieratene, characteristic for anaerobic photosynthetic green sulfur bacteria and often applied for the

assessment of euxinic conditions in the photic zone (Passier et al., 1999), and 2-methyl hopanoids, characteristic components for cyanobacteria (Summons et al., 1999).

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Summons RE, Jahnke LL, Hope JM & Logan GA, *Nature*, **400**, 554-557, (1999).

Werne JF, Hollander DJ, Behrens A, Schaeffer P, Albrecht P & Sinninghe Damsté JS, *Geochim. Cosmochim. Acta*, **64**, 1741-1751, (2000).

BG01 : TUpm33 : G1 Organic Cyclicality of the Upper Jurassic Kashpir Oil Shales (Russian Platform): Depositional and Early Diagenetic Origin of Contrasted OM Features

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During the Middle Volgian, large amounts of organic matter (OM) were deposited on the Russian Platform. The resulting formation shows decimetric to metric alternating levels of gray clayey marlstones and black shales. Rock-Eval analyses revealed very large variations in TOC (0.5 to 45%) and HI values (50 to 700 mg HC/g TOC) in this formation. A relatively high mean TOC value is noted, although bioturbations are present in most part of the oil shale unit and some levels exhibit both large TOC values and extensive bioturbation. This formation was studied at Gorodische section, located along the Volga river, in order to determine the processes of OM sedimentation and preservation. Palynological observations indicated that the kerogens are dominated by amorphous organic matter (AOM) and that TOC and HI variations are not due to differences in relative contributions of terrestrial and marine OM. On the basis of morphological and bulk geochemical features, the kerogens were divided into three groups: (i) dominated by grey AOM, poorly aliphatic and Sorg-poor samples of lowest TOC contents, (ii) dominated by heterogeneous orange AOM, relatively aliphatic and Sorg-containing samples of middle to high TOC contents, (iii) dominated by pure orange AOM, aliphatic and Sorg-rich samples of very high TOC contents. The detailed geochemical study (spectroscopy and pyrolysis) of three kerogens representative of each group revealed a phytoplanktonic origin for the OM. A weak bacterial contribution is also noted. Different OM preservation processes are observed: pure orange AOM was mainly formed by natural sulphurisation of lipids and carbohydrates under anoxic conditions; grey AOM was mainly formed by the degradation-recondensation pathway with a minor contribution of selectively preserved algal cell walls under mainly oxic conditions; heterogeneous orange AOM appears in between the other two groups and is constituted of melanoids (from the degradation-recondensation pathway) and sulphurised material, formed under changing oxygenation conditions, mainly dysoxic. The three kerogens also show an important contribution of lipids incorporated by oxidative reticulation. This study (1) reveals the role of early diagenetic conditions on OM preservation pathways and (2) shows that differences in early diagenetic conditions and OM preservation pathways account for the large variations in TOC and HI observed along Gorodische section.

BG01 : TUpm34 : G1 Survival of Proteinaceous Material in an Ancient (140 My Old) Kerogen: Role of the Encapsulation Process

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The non-acid polar fraction obtained upon 400°C off-line pyrolysis of a kerogen, termed "f top", from the Kashpir oil shales (Russia, Volgian) shows substantial O-, S- and N-contents (9.7, 7.2 and 1.5%wt respectively). To retrieve structural information on f top kerogen, these NSO compounds (accounting for 25%wt of the total pyrolysate) were examined via a combination of methods including Raney-Ni desulphurization and conventional and TMAH-assisted Curie point pyrolysis-gas chromatography/mass spectrometry (CuPy-GC/MS) at 650°C. Though an almost complete removal of S was achieved, the GC trace of the desulphurized polar fraction still showed an extensive hump of co-eluting, hardly identifiable, products. Moreover, conventional CuPy-GC/MS only resulted in further thermal cracking that released O- and S-containing compounds previously identified in the less polar fractions (Riboulleau et al., 2000). It thus appeared that the structure of f top kerogen is not only based on alkyl skeletons cross-linked by O- and S-bridges. Cleavage of O-bonds and methylation was achieved through TMAH-assisted thermochemolysis and afforded methylated C₆-C₁₈ fatty acids A strong even-over-odd carbon number predominance and the presence of unsaturated compounds were noted for these acids, thus reflecting a low level of alteration. In addition, amino acids (glycine, alanine, aspartic acid and phenylalanine) were identified, for the first time to the best of our knowledge upon TMAH thermochemolysis of ancient material. Similar results were recently reported but they were concerned with recent sediments (Knicker and Hatcher, 1997; Garcette-Lepecq et al., 2000). In contrast, the present observations provided evidence for the survival of proteinaceous moieties in the case of a 140 million years old kerogen. As recently suggested for recent materials (Knicker and Hatcher, 1997), and in agreement with the co-occurrence of amino and fatty acids in the thermochemolysate, the unexpected preservation of such moieties is likely related to physical protection through encapsulation within a refractory, aliphatic, organic matrix. The conspicuous survival observed for proteinaceous moieties in f top was also possibly favoured by the abundant presence of O- and S-bridges in the macromolecular structure of the kerogen.

Garcette-Lepecq A. *TMAH thermochemolysis of kerogen-like organic matter in recent sediments off the Danube delta. 14th International Symposium on Analytical and Applied Pyrolysis, Séville*, 48, (2000).

Knicker, H. *Survival of protein in an organic-rich sediment: possible protection by encapsulation in organic matter. Naturwissenschaften*, **84**, 231-234, (1997).

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BG01 : TUpm35 : G1 Solvation Effect on Organic Compound Interactions in Soil Organic Matter

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Sorption of pyridine by model soil organic matter (SOM) from n-hexadecane, acetonitrile, acetone, and n-hexadecane-solvent mixtures was compared on an activity basis to sorption from water. Sorption from n-hexadecane and acetone was very comparable and much less than sorption from acetonitrile and water. Increasing the amount of acetonitrile in n-hexadecane-acetonitrile mixtures up to 80% of acetonitrile solubility resulted in increased pyridine sorption. There was no apparent competition despite the fact that acetonitrile and pyridine are capable of specific interactions. Pyridine sorption from n-hexadecane-acetone mixtures was also non-competitive. In general, pyridine uptake was assisted by polar solvent molecules rather than suppressed due to competition. An explanation for this behavior is tendered on the basis of our earlier hypothesis of water-assisted disruption of polar SOM contacts. Certain polar moieties of dry SOM are unavailable for compound

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sorption due to strong interactions between them. By penetrating SOM structure, solvent molecules (and water) solvate (hydrate) polar moieties creating new sorption sites. Solvent molecules must solvate both moieties of the polar contact, such that the driving force for solvent-assisted sorption is solvation of the partner of the disrupted contact that does not directly interact with the sorbate.

BG01 : TUpm36 : G1 Mobility of Pb in Topsoils Assessed via Temporal Changes in Concentrations and Isotopic Compositions

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As a result of increasing constraining policies, the heavy metal content in the European atmosphere has considerably decreased in the last twenty years, particularly for lead which was progressively phased out from the gasoline. However, the problem is not definitely fixed because all these pollutants have been accumulated at least since 3000 years BP in soils and they may become harmful to ecosystems. Understanding the mobility of these elements is therefore one of the great challenge for the next years.

Paces (1999) recently proposed a simple predictive model allowing the calculation of a 'critical load', which corresponds to the input of heavy metals that would yield steady-state concentration in soils not yet harmful to the ecosystems. The 'critical load' was calculated for Pb and Cd on the basis of their toxicity in ecosystem, and from an atmospheric input considered as constant. Although clever, this model suffers from the debatable hypothesis. It is obvious that the atmospheric inputs have considerably varied during the past, and that they may vary again following the next environmental policies.

In the present study, we maintained the basic structure of the model which was proposed by Paces for Pb, but we operated some modifications. The fate of lead content in topsoil is now described by the combination of two flux functions: (i) the atmospheric input, variable with time and, (ii) the output function related to the mobility of the anthropogenic component. The model is also constrained by a second equation taken into account the Pb isotopic compositions. Knowing the evolution of the atmospheric fluxes as well as their isotopic compositions, one can compute, for different mobilities, what should be the temporal evolution of Pb contents and Pb isotopic compositions observed in soils. These data are compared to what is actually measured on the field, then providing an estimation of the mobility factor. Data coming from an experimental field plots maintained since 70 years at Versailles (INRA) are used for simulation. The advantages and the limits of this new model are discussed.

Paces, T. *Geochemistry of the earth surface. conf abstr. 5th int. symposium on geochemistry of the earth surface, Reykjavik, Iceland*, 143-147, (1999).

BG01 : TUpm37 : G1 Organic Matter Composition and Phosphate Retention in Sediments of a Littoral Wetland of the Seine Estuary (The Vernier Marsh, France)

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The Vernier marsh is located in a former meander and has been gradually isolated from the river's influence. Thus, the northern section is a polder while the southern section is a mosaic of natural environments with various ponds. This

study focused, on these ponds : a main one (the « Grand-Mare ») and 2 smaller ones (the « Crevasse » and the « Petite Mare »), which are being filled by sediments. This filling can be explained by the consequence of natural evolution of eutrophication and also by an input of minerogenic particles from the Seine transported through a canal, the « St Aubin » canal. It has been regularly opened during dry season, to maintain sufficient water level.

The purpose of this study is to discuss the influence of organic matter on phosphate mobility. Thus it combines a geochemical composition of organic matter with those of the particulate organic phosphate.

Surficial sediments have been sampled at 19 stations randomly distributed on the ponds. Geochemical analyses which comprise C/N/P determinations, Rock-Eval pyrolyses, chemical fractionation of phosphate, neutral carbohydrate identification and quantification, were performed on the top 10 cm of sediments.

All of these results show that the ecosystem is divided into two areas: Sediments from the « Grand-Mare » are weakly organic (C/N/P : 10/1.3/0.13% ; organic P : 128 µg/g Total sugars : 9 mg/g) whereas those of the 'Crevasse' and the 'Petite Mare' are highly organic (C/N/P : 46/1/0.11% organic P : 235 µg/g Total sugars : 62 mg/g).

According to the neutral carbohydrate analyses, sediments of the main pond mainly contain hemicellulosic sugars (86% of Tot. Sugars) whereas those from the smaller ponds are dominated by mainly cellulosic glucose (53%).

Results of the fractionation of particulate organic phosphate gave the following distribution : biodegradable particulate organic phosphate (ASOP 'Acid soluble Organic Phosphate') in the 'Grand-Mare' pond instead of a refractory particulate organic phosphate (AH-P 'acid-humic-bound-phosphate') in the southern ponds ('Crevasse' and 'Petite Mare').

So the organic matter quality (sugars) might be related to the bioavailability of particulate organic phosphate in sediments. The strongest concentration of ASOP (a bioavailable particulate organic P) is located in sediments containing high concentration of hemicellulosic sugars (labile sugars, easily removed). Instead of the refractory particulate organic P found in sediments enriched with cellulosic sugars (refractory compounds). Organic matter quality influence the retention of particulate organic phosphate in sediments.

BG01 : TUpm38 : G1 Adsorption of Polyacrylic or Humic Acids on Aluminium Oxide and Kaolinite in the Presence of Aluminium Ions

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Understanding of adsorption phenomena involving humic acids and clays constitutes a difficult challenge due to their complex nature. Thus, to progress in the study of such systems, attempts were done to replace natural systems by polyacids and oxides of simpler chemical and morphological structure (1). Since the present investigation was dedicated to determine some characteristics of acidic soils which contain traces of aluminium ions, these ions were put to the adsorbent/ polyacid systems as trace constituents at pH 5.0. Phenomena related to the interactions of humic or polyacrylic acids with aluminium oxide and kaolinite clay have been investigated and the well differentiated interfacial behaviour of the oxide and kaolinite were determined and discussed. Humic and polyacrylic acids were found to exert very comparable interactions with the aluminium oxide surface as shown by the aluminium ion transfer on addition of the macromolecule to the oxide suspensions and behave like amphoteric polyelectrolytes. The major difference in the adsorption behaviour is attributable to the adsorbent surface characteristics. Surface charges of the aluminium oxide results from the presence of aluminium sites belonging to the solid. These ions combine with the carboxylic acid groups of the macromolecules and this complexation leads to the formation of neutral ion-pairs having a hydrophobic character. This surface generates hydrophobic interactions with the adsorbed macromolecules. Surface charge arise on the lateral face of the kaolinite from the protonation of aluminol sites leading to the formation of Al-(OH₂)⁺ sites. Surface charge on the charged basal face results from the isomorphous substitution and

aluminium ions exert the role of counter ions. No complexation by carboxylic acid groups was determined to occur and the surface thus exert long ranged electrostatic interactions. Results of electrophoretic mobility measurements demonstrated the huge time dependent effect of polymeric layers adsorbed on oxides and modified clays.

Pefferkorn E. *Adv. Colloid Interface Sci.*, **73**, 127-200, (1997).

BG01

Organic Matter and Transformations in Sediments

Tuesday PO Session

BG01 : TUpo01 : PO Unexpected Preservation Process of Sedimentary Organic Matter in an Euxinic Upwelling-Influenced Basin: The Cariaco Trough (Venezuela)

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The Cariaco basin, a structural depression on the northern continental shelf off Venezuela is the largest anoxic marine basin in the world after the Black Sea. Combination of an extensive oxygen demand created by upwelling-induced high surface productivity and limited exchange with open sea, results in the development of anoxic conditions below 300 m depth. Despite an intense bacterial remineralisation, the Cariaco basin has been characterised by a marked accumulation of sedimentary organic matter since the Younger Dryas (12600 yBP). In this basin anaerobic processes induce high concentration in sulphide within bottom water and sediment that are a priori highly favourable conditions for preservation of organic matter through intense sulphurisation. Six sediment samples were collected from a section core at ODP site 1002 located on the central saddle of the Cariaco basin at a water depth of 893 m. These samples span a late Pleistocene to Holocene age interval, including the transition from oxic to anoxic bottom conditions. TOC contents range from 0.4% to 5.6% and HI values from 180 to 390 mg HC/g TOC. The kerogen-like material was isolated from the youngest sample (30 cm bsf). Its chemical structure, source organisms and formation pathway were investigated using a combination of microscopic, spectroscopic and pyrolytic methods, the latter included Curie point pyrolysis-gas chromatography-mass spectrometry and thermochemolysis with tetramethylammonium hydroxide (TMAH). Parallel examination of bitumen by GC/MS was performed. It appears that this kerogen-like material is mainly derived from the degradation-recondensation of planktonic organic matter and that selective preservation and, unexpectedly, natural sulphurisation only played a minor role in its formation. The possible causes of such a limited role for the sulphurisation pathway will be discussed.

BG01 : TUpo02 : PO The Composition of Organic Matter and Paleoenvironment Conditions of Oil Shales Deposit of Sysola Region (Mezen Basin, Russia)

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Upper Jurassic deposits outcropping in the Sysola region are present by upper part of Tithonian stage (ammonitic zones Dorsoplanites panderi and Dorsoplanites maximus). Rocks of the section are present by oil shale, clayey oil shale, kerogene clay, gray clay and clay-marl. A content of TOC in studied section ranges from 0.52 to 18.6%, and yield of extractable OM varies from 1.3 to 61.4 mg/g TOC.

Organic matter of oil shales was studied using several analytical methods. TOC and bitumen contents were measured. Isolated bitumen was separated by LC. Aliphatic and aromatic fractions were GC and GC-MS analyzed. Polar fraction was subjected to Ni-Raney desulphurization, and sulphur-bound biomarkers were GC and GC-MS analyzed. Kerogen was isolated from a number of rocks that characterized by different TOC content. Elemental analysis and off-line pyrolysis of kerogen were performed.

Organic matter of oil shales, that we studied, has a very low degree of thermal maturation. We suppose mainly marine source of OM, but terrestrial input is not excluded. Presence of the isorenieraten derivatives makes us suppose that anoxia was an important geochemical factor during oil

shales deposition. Increasing of thiophenes concentration in the pyrolysis products of kerogen with increasing TOC content in rock permits us to suggest that sulphur incorporation into OM during early stages of diagenesis played an important role in OM preservation.

BG01 : TUpo03 : PO Bulk and Molecular Isotope Organic Geochemical Record of the Permian-Triassic Boundary in the Idrija Valley (Slovenia)

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Drastic redox and compositional changes in sea water and terrestrial and marine sediments led to the most extensive biomass extinction in the PTB. Elemental and isotopic composition of the marine carbonates records the nature and extent of the PTB changes. Few organic geochemical data and to our knowledge no molecular isotope data of organic fractions from PTB sections are available. Combined molecular and isotope geochemical study of the organic matter of the PTB limestones in the Idrija Valley (Slovenia) provides new insight into the PT biotic crisis in this part of the Tethys. The $\delta^{13}\text{C}$ values of the carbonates (P: $+3.3\pm 1.5\%$, T: $+0.4\pm 0.3\%$), the TOC (P: $-26.7\pm 0.8\%$, T: $-26.2\pm 0.9\%$), the kerogens (P: $-27.0\pm 0.6\%$, T: $-27.4\pm 2.9\%$), the extracted bulk bitumen (P: $-26.9\pm 0.3\%$, T: $-26.7\pm 2.2\%$) and the saturated hydrocarbons (P: $-25.7\pm 1.2\%$, T: $-26.2\pm 0.2\%$) indicate a general negative excursion at the transition from Permian to Triassic. These isotopic shifts combined with the decrease in TOC contents record a drop of the biological productivity and degradation of the organic matter. The boundary is characterized by an unusual increase of the $\delta^{13}\text{C}_{\text{KER}}$ value from -27.9% in the Upper Permian to -25.4% 3 cm above the PTB. This increase of the $\delta^{13}\text{C}_{\text{KER}}$ ratio is synchronized with a drop of $\Delta^{13}\text{C}_{\text{CAR-KER}}$ of 3.9‰. Both are interpreted as a bloom of the biological productivity. The molecular parameters, such as Pr/Ph, Pr/n-C₁₇, Ph/n-C₁₈ and the isotopic composition of the individual n-alkanes and isoprenoids record a preferential degradation of the hydrocarbons near the PTB. The increase of the concentration of n-C₂₀ at the PTB and in the Triassic reflects an increased contribution of the terrestrial organic matter imputed to the Griesbachian transgression. The variations of the contents of n-C₁₉₋₂₀ in the Permian and n-C₁₈ in the Triassic suggest two distinct palaeoenvironments: a mainly planktonic biomass in the Permian, and a predominant bacterial contribution in the Triassic. Volcanism, marked by a level rich in sulfur 50 cm below the PTB, and the PTB regression caused the decrease of the biological bloom. These changes of the environment are marked by a high amount of n-C₂₃, which may characterize hypersaline environments where only one type of bacteria survives and proliferates. The ratios Pr/Ph > 1 (1.5 ± 0.2) in the PTB and < 1 (0.8 ± 0.1) in the Triassic confirm the oxic character of the boundary and the anoxia of the Triassic. The Permian sediments are enriched in pristane (Pr/Ph = 1.2), probably suggesting a contribution of zooplankton biomass. The organic molecular and isotopic geochemistry provide further insights into the changes of depositional environments, changes of organic facies, and biomass extinction and recovery in the PTB of the Idrija Valley.

BG01 : TUpo04 : PO Chemical Structure and Morphological Features of the Insoluble Organic Matter from Boom Clay Formation (Belgium): Model Site for Deep Geological Disposal of Nuclear Waste

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Clay formations take a prominent place between the candidate geological formations for the deep geological disposal of long-lived radioactive waste and spent fuel. In this respect, extensive studies are being carried out on the Boom Clay (Belgium), so as to test the suitability of clay for such a disposal and its effectiveness as a barrier for migration of radionuclides. In addition to clay minerals, quartz and pyrite, substantial levels of organic matter occur

in the Boom Formation which may influence the mobility of radionuclides through the clay. Although mineralogical and physicochemical features of the Boom Clay have been extensively studied, no analysis of the chemical structure of the insoluble organic matter has been performed so far. Moreover, this organic matter will be submitted to thermal stress during long-term disposal and the kerogen fraction may therefore generate some mobile (liquid and gaseous) compounds with complexing properties. It is therefore important to characterise the structure of the insoluble macromolecular organic matter. We have thus studied the kerogen isolated from a Boom Clay sample with a TOC of 1.5% by a combination of complementary techniques. Scanning and transmission electron microscopy observations were performed on the kerogen to examine its morphological features, and on the whole rock to study the spatial relationship between mineral matrix and organic matter. Spectroscopic methods (FTIR and solid-state ¹³C NMR) allowed to determine the nature and the relative abundance of the main functional groups present in the kerogen. Pyrolysis, combined with gas chromatography-mass spectrometry, afforded information on the chemical structure at a molecular level. Taken together, these results provided detailed information on the chemical structure of kerogen in the Boom Clay Formation. Moreover, implications of these results in terms of kerogen origin and formation pathway will be discussed.

BG01 : TUpo05 : PO Organic Markers as Witness of the Dynamic Features of the Mangrove Coast in French Guyana

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The coastline of the French Guyana is a highly dynamic environment, mostly composed by fine-grained sediment. This muddy coastline results from the huge mud discharge of the river Amazon, partly deflected Northwestward by the current of the Guyanas. The mudbanks, being eroded on their windward side and accreting on their lee side, move rapidly (1 km/year) along the coast. A dense recruitment of mangrove propagules (predominantly Avicenia germinans) follows this phase within months. Subsequently, a mature to senescent mangrove forest develops up to a moment, about 30 years later, when the windward end of the mudbank reaches the considered location and erosion location kills the trees.

The aim of this study is to understand and to quantify the relationship between the organic composition of the sediment, the evolution of the Avicenia germinans-dominated mangrove forest, and therefore the dynamic feature of the coast. In addition, we wish to define the influence of environmental conditions on the sedimentary record. For this, 12 two-meters deep cores were collected under mangrove at different stages of evolution and one core in shoreface sediment as a reference. The relative forest ages were determined using Spot images (Vega, 2000) and sorted in five stages of evolution: pioneer forest, mature forest, senescent forest, dead forest and "recolonized" dead forest.

This work includes geochemical datas obtained from Rock-Eval and LECO CNS pyrolyzers, optical observations and countings, and physico-chemical parameters (salinity, redox potential and pH). As expected, the content of organic matter in the sediment rises up with the mangrove age, the TOC content ranges from 1 to 18%. This trend is also underlined by the optical results; i.e., an increase in ligno-cellulosic degraded debris. However for the youngest mangrove forest, sedimentary organic matter mainly derives from algal mats with low C/Nat. (5-8), the higher plant debris being exported by the tides. In the case of the oldest mangrove (50 years old), the C/Nat. ratio rises to 19. Whatever the stage of mangrove evolution, the influence of the forest on the sediment occurs between the surface and 30 cm deep. Below this depth, the characteristics of the sediment are those of the shoreface ones. The efficient decomposition by sulfate-reducing bacteria superimposed to the youth of the mangrove are responsible for this rapid decrease in organic matter content. In addition, some positive gradients of organic markers in the dead forest sediments underline previous phases of erosion and accretion.

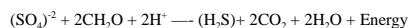
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BG01 Organic Matter and Transformations in Sediments

BG01 : TUpo06 : PO Hydrogen Sulfide Occurrences in the Surface Water of The Golden Horn, Istanbul, Turkey

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The Golden Horn, an estuary in the European part of Istanbul, is heavily affected by anthropogenic activities and the uncontrolled discharge of pollutants. Streams, called by Ka_thane and Alibeyköy, land runoff, urban wastes, industrial discharge and atmospheric wet and dry depositions are all sources of pollutions to the estuary. The aim of this study decipher the occurrences of H₂S in the surface water of the Golden Horn and determine the sulphate reducing bacteria. Twenty water samples were analysed for (SO₄)²⁻, (NO)²⁻, (NO)³⁻, (NH₄)⁺, pH, Eh and dissolved oxygen (DO). Sulphate reducing bacteria were tested in the special incubator. The growth of anaerobic sulphate reducing bacteria cause the formation of black iron sulphide. Iron sulphides occur FeS_{0.94}, FeS_{1.1}, Fe₂S₃, FeS₂ in the tube, respectively (Perdue, 1997). Hydrogen sulphide produced by sulphate reducing bacteria is harmonious with the anoxic conditions, having 0.2 mg/l dissolved oxygen and -374 Mv Eh, is in the study area (Çelik, 1997). Sulphate, the average 200 mg/l in the shallow part of the region, is reduced biologically under anaerobic conditions to sulphide, with the following generalized reactions.



The more than 90 percent of hydrogen sulphide in the study area is produced as stated above. The remaining occur due to the fact that the material with protein are decomposed. In suitable conditions bacteria can produce hydrogen sulphide 3 gr per litre (Balman, 1984). The optimum pH ranges for sulphate reducing bacteria are neutral and slightly basic conditions. As a result of detailed pH measurements, it is shown that pH range of the study area is between these intervals. The average dissolved oxygen concentration of the region is 0.62 mg/l. All these parameters are suitable to occur H₂S. The quantity of H₂S occurrences in the region ranges between 3,14 mg/l and 8,94 mg/l (Göçmen, 1983). Sulphate coming from sewage and urban waste water is reduced by biologically as cited reaction so the dissolved oxygen concentration of the region decrease. The average sulphate concentration in the shallow part of the region, having depth 40 cm, is 200 mg/l and that in the deeper part of, 42 m at the mouth of sea water, is 1600 mg/l.

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BG01 : TUpo07 : PO Characterization of Waters and Soils in Vineyards Combining Geochemical Data and Ultrasounds Measurements

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The economy of the Lavaux region in canton of Vaud, Switzerland, is highly dependent on the wine production. The main factor affecting the yield of vine grapes in this region is iron chlorosis disease (yellowing of leaves), which has been proven to be highly dependent on carbonate content of soils and chemistry of the waters. The latter varies in time and space by multiple water-water mixing and water-mineral interaction processes. There is thus a strong need for understanding the origin and compositional changes of the vineyard waters, and for effective means of their control. The development of iron chlorosis and of other environment dependent factors affecting wine yields can be early detected using a highly sensitive physico-chemical instrumentation, such as ultrasounds. In this communication we present the first results of a geochemical study of Lavaux vineyards combining chemistry of

soils and waters, and ultrasounds. The main goal of this study is to evaluate the ultrasounds as a new alternative technique for rapid non-destructive geochemical surveys.

Eight water samples were collected every two months during a year and were analyzed for deuterium and oxygen isotopes, and major anions and cations (Na, K, Mg, Ca, HCO₃, Cl, NO₃, SO₄) concentrations. Assuming a partial preservation of the original isotope fingerprint, these data provide the basis for understanding of the origin and mixing processes of the soil-interstitial waters. Sound velocity was measured in the same samples using a Cygnus Ultrasound Velocity Meter UVM 1 with Panametrics 2 MHz probe and their density measured with a Paar Density Meter DMA 58. The sound velocity and water density allows calculation of compressibility of specific electrolytes in the waters. Soil analysis reference methods were used to characterize the chemical composition of the various soil types.

The isotopic results (-9.35±0.68‰ δ¹⁸O and -70.5±4.3‰ δD) close to the mean value of precipitation suggest a recharge of the waters from the vineyards by local precipitations. Their altitude of infiltration should not exceed 900 to 1000 meters according to the regional topography and local precipitations water line. The total ions contents of the water samples (572.2±37.9 ppm) are similar throughout the studied area. The concentrations of Na, K and Cl show statistically significant seasonal variations. The waters K, Mg, Ca concentrations are correlated (R²=0.82) with the composition of the various soil types. The same trends in space and time are observed in the sound velocity measurements. Having established that ultrasounds techniques serve to trace geochemical changes, further studies using a similar approach on different environmental liquid and solid matrixes are in progress.

BG01 : TUpo08 : PO Water Adsorption: A Parameter to Evaluate Heavy Metal Adsorption on Sediments and Soils?

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Soils and sediments are an important trap for heavy metals, due to both their adsorption (by complexing and ion exchange) and their temporary storage capacity. Lithogenic input from different geological backgrounds in the catchment area causes differences in metal concentrations due to changing adsorption mechanisms, which are influenced by elements derived from the geological background.

Metals are bound and remobilised mainly as a result of changing chemical conditions, such as the pH-value, redox-potential and electric conductivity. The sorption of metals comprises a wide range of reactions (complexation, ion exchange, physio- and chemisorption) with organic matter (humic acids), clay minerals, Fe-, Mn-, Al oxyhydroxides, biogenic silica (diatoms) and calcite. Some of the metal scavengers are able to adsorb water by the same mechanisms, due to differences in charges on the water molecules. Previous investigations (Kralik, 1999) showed that water and heavy metal adsorption can be compared in some cases.

Therefore the adsorption of water and heavy metals onto the fine fraction (<0,04 mm for sediments; <2 mm for soils) was compared, to determine if the amount of water adsorption and metal adsorption show any correlations. Lead ('immobile' metal) and cadmium ('mobile' metal) have been used in our adsorption studies as key metals with various soil- and sediment-samples.

The batch experiments were carried out with river water (sediments) from the sampling site and distilled water (soils) at neutral pH to resemble natural conditions. During the contact time (maximum: two hours) the pH, electric conductivity, redox potential and temperature were recorded. The water adsorption was measured on dried (90°C) sediment samples, which were held under 70% relative humidity for three days and then dried again to obtain the specific water content.

Generally cadmium and lead adsorptions show different correlations with the water uptake by sediments: The samples from a crystalline background had a higher amount

of metal scavengers and therefore a higher adsorption of cadmium and water compared to the carbonate dominated samples, indicating a positive correlation.

The main factor controlling the water adsorption as well as the metal uptake in the sediment samples was the content of organic carbon (particulate and dissolved).

In the sediment samples the adsorption of lead was higher in the carbonate dominated background, where the water adsorption was significantly lower. This might be due to precipitation of lead carbonates, a mechanism which does not influence the water adsorption. Hence the parameters cannot be compared concerning lead adsorption in carbonate catchment areas. The applicability in crystalline dominated backgrounds is not fully confirmed here, but may be possible.

However, soil samples (green land and forest) of the same areas indicate negative trends for both cadmium and lead with the water adsorption.

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BG01 : TUpo09 : PO Utilization of the Stream Sediments and Geology of the Kargi River Drainage Basin, Fethiye, Turkey

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Geology map of approximately 30 km² of the study area at the research realize with reference to the sediments existing in the Kargi River (Fethiye / Mugla) has been taken out and 3 samples of the stream sediment have been received from the Kargi River. According to the mineralogical and petrographic evaluations performed for the stream sediments, it has been determined that the stream sediments have consisted of calcite, serpentine, quartz, dolomite and pyroxene minerals and have included heavy minerals such as chromite and magnetite.

In addition, there are not any minerals which can effect the features of the aggregates, any alteration conditions in mineral grains, any straight, long and thin minerals and chemicals and any non-demanding contaminants specified in The Turkish Standarts 10088 in the stream sediments. Any substance That will be able to damage the solidification or hardening of concrete to be made by means of the samples of the stream sediments in the Kargi River, will be able to reduce its resistance and will be able to cause its shattering or will be able to risk the protection of the concrete against corrosion has not been involved.

Finally, It's determined that the mortar sands can be classified as 'medium sand' according to the biggest grain size and finness modul values of RP3 numbered stream sediment sample without subjecting to sieving treatment and this can be used in the construction sector as a coarse sand.