

EUG XI



Symposium CC04

New and Refined Proxies in Palaeoceanography and Palaeoclimatology

Convenor

Martin Frank

Wednesday AM Session

CC04 : WEam01 : G3

The Chemical Index of Alteration as a Palaeoclimatic Proxy

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Paleoclimatic studies dealing with geological time scales - rocks that are millions to billions of years old - have depended primarily on classical stratigraphic and sedimentological studies. For example, ancient glacial deposits are recognized by the presence of diamictites with striated and faceted clasts and laminated mudstones with isolated clasts (dropstones). Likewise evaporitic deposits, coals and inferences based on metazoan fossils have been used to infer paleoclimatic conditions but these are only common in the upper 10% of the Earth's stratigraphic record. In recent decades much attention has been given to palaeoclimatic proxies that rely on ratios of stable isotopes of various elements, particularly oxygen. Likewise Sr isotope ratios have been linked to tectonic and/or climatic changes (Raymo and Ruddiman, 1992) but there are problems because of variable isotopic composition of source materials. All of these techniques have problems and limitations, especially when they are used to investigate Precambrian sedimentary deposits. A technique developed by Nesbitt and Young (1982; Nesbitt et al., 1996) utilizes The major element geochemistry of siliciclastic sediments and sedimentary rocks has been used in an attempt to quantify the degree of weathering to which they have been subjected (Nesbitt and Young, 1982; Nesbitt et al., 1996). The quantitatively most important weathering reaction at the surface of the earth (the Urey reaction) involves natural acids and feldspars. As weathering progresses, primary Ca-, Na- and K-bearing silicates are leached of these elements and are replaced by newly-formed Al-rich clay minerals. These reactions can be quantified in a Chemical Index of Alteration (CIA) which is calculated as follows:- CIA = $[Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$ where the values are expressed as molar proportions and CaO* is CaO in silicates (as opposed to carbonates or phosphates). This measure provides a way of quantifying the degree of weathering to which soils, palaeosols, sediments and sedimentary rocks have been subjected. It has been successfully applied to 2.3 Ga glacial deposits, to modern sedimentary basins in Arctic and temperate regions, to modern and ancient weathering profiles and to Tertiary-to-Recent oceanic sediment cores. Widely used provenance techniques based on the mineralogy of sediments should take into cognizance the profound changes (particularly in feldspar ratios and quartz feldspar ratios) that accompany the commonly-ignored but all-important intermediate step (weathering) that usually separates sediment from source rock. Caveats in the use of the CIA as a weathering (or paleoclimatic) proxy include grain size (shales should be compared with shales), tectonic influence which can mask climatic effects, presence of carbonates, diagenetic/metamorphic changes, and recycling of materials. Most of these problems can be recognized and appropriate corrections made (Fedo et al., 1995). In many instances the CIA provides a powerful paleoclimatic proxy.

Fedo CM, Nesbitt, HW & Young, GM, *Geology*, **23**, 921-924, (1995).Nesbitt HW & Young GM, *Nature*, **299**, 715-717, (1982).Nesbitt HW, Young GM, McLennan SM & Keays, RR, *Journal of Geology*, **104**, 525-742, (1996).Raymo ME & Ruddiman WF, *Nature*, **359**, 117-122, (1992).

CC04 : WEam02 : G3

Dynamics of the Erosion in the Irrawaddy River Basin during the Last two Climatic Cycles (280 ka)

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Detrital minerals, major elements, Sr-Nd isotopic and grains size analyses have been investigated on sediment of one gravity core (MD77-169) from the Andaman Sea. The stratigraphy of this core has been assessed using 13 AMS ¹⁴C dates and the $\delta^{18}O$ from planktonic foraminifera (*G. ruber*) compared to the SPECMAP reference time scale. This core provides a continuous sedimentary record extending down to climatic stage 8 (280 ka). $\epsilon Nd(0)$ values exhibit a restricted range from -9.5 to -11 which are similar to an Irrawaddy River sample ($\epsilon Nd(0) = -10.7$). This implies no changes of the sediment sources during the last 280 ka and that Irrawaddy River is the main contributor of detrital material to the central Andaman Sea. Quartz/feldspar, kaolinite/quartz, smectite/(illite-chlorite), kaolinite/feldspar ratios and the chemical index alteration (CIA = molar ratio of $[Al_2O_3 / (Al_2O_3 + Na_2O + K_2O)] \times 100$) show a strong precessional periodicity. This indicates that variations in the Indian monsoon is the main process determining mineralogical fluctuations of core MD77-169, rather than sea level changes. Wet periods of summer monsoon reinforcement are characterized by an increase of lowland minerals (kaolinite and smectite) and by a decrease of highland minerals (Quartz, feldspar, illite and chlorite). Two hypotheses can explain this relationship: 1) An increase in the chemical weathering associated with wetter conditions in the Irrawaddy flood plain during periods of reinforcement of the summer monsoon rainfall. This would favor soil development and thus the production of smectite and kaolinite minerals. This process would imply that soil production is sufficiently rapid (<1 ka) to explain the rapid changes observed in the Andaman sediment due to the climatic forcing. 2) An increase in physical erosion of the soils of the Irrawaddy flood plain versus highland areas during periods of reinforcement of the summer monsoon rainfall. However, such a process would be associated with an increase in the river inputs which is not observed in the accumulation rates of the Bay of Bengal and Andaman Sea cores. An increase of forest cover in flood plain areas during wet periods, could explain that no changes have been observed in the detrital input and suggest a important stream bank erosion. These data provide new proxies for weathering/erosion of the Himalayan belt and to reconstruct the activity of the monsoon.

CC04 : WEam03 : G3

Uplift-Related Climate Change in the Southern Patagonian Andes- Evidence from Oxygen Isotope Values of Soil Carbonates

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The main goal of the study presented here is to reconstruct the formation of the orographic rainshadow of the Patagonian Andes using the oxygen isotope signature of pedogenic calcite from paleosols in syn-orogenic foreland deposits.

The up to ~4,000 m high Patagonian Andes form a pronounced topographic barrier to atmospheric circulation in the southern hemisphere westerlies. As a result, they cause a drastic orographic rainshadow; rainfall in the humid W foreland is >3,000 mm/yr, contrasting with only ~300 mm/yr in the semi-arid E foreland. The results of previously published work indicate that this rainshadow

was probably established or significantly enhanced during a relatively young phase of Andean uplift in the late Miocene.

Initial results of our work indicated that the present-day orographic rainshadow is reflected by the oxygen isotope values of surface waters (springs and locally derived streams). The $\delta^{18}O$ values of samples collected along a transect of the Patagonian Andes at 47°30' S latitude show a shift of about -4‰ from W to E across the cordillera. Correspondingly, a similar shift should occur in the isotope signature of pedogenic calcite within syn-orogenic deposits in the E foreland.

To test this hypothesis, we collected pedogenic calcite nodules from the Miocene Santa Cruz Fm., a sequence of terrestrial foreland basin deposits exposed in the E foreland of the southern Patagonian Andes. The Santa Cruz Fm. is a sequence of alternating siltstone and sandstone beds which is ~550-600 m thick in the study area and contains frequent fossil soil horizons. To date, we have analyzed samples from three sections: 1) an almost complete section of the top 500 m, 2) a 320 m thick section near the base, and 3) a section spanning the uppermost 90 m. The $\delta^{18}O$ values of the nodules show a shift of ca. -4‰ towards lighter values in the top 200 m of the formation, implying that the orographic rainshadow of the southern Patagonian Andes formed during the time represented by this stratigraphic interval. Tight chronologic constraints on rainshadow evolution will be provided by ongoing Ar/Ar dating of volcanic tuffs within the Santa Cruz Fm.. From recent studies relating the $\delta^{18}O$ values of authigenic minerals to palaeo-topography, the magnitude of the observed shift indicates that the associated elevation change of the orographic barrier was 1900±250 m.

CC04 : WEam04 : G3

Towards Quantifying Trace and Nutrient Element Release Rates during Black Shale Weathering

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Anoxic marine sediments efficiently scavenge trace metals, particular oxyanions (e.g. V, As, Se, Mo, Re, Os, and U), from seawater. As a result, sedimentary rocks rich in organic matter [OM] are also rich in nutrients and many trace metals. The weathering of ancient sedimentary rocks and associated release of relatively high concentrations of trace metals may thus have a disproportionate influence on ocean chemistry. The Os isotopic composition of seawater has varied significantly over geologic time. Much of this variation has been ascribed to radiogenic ingrowth of Os from Re decay over millions of years in sedimentary rocks coupled with changes radiogenic Os input to the oceans related to variations in sedimentary rock weathering rates. Thus the potential exists to deconvolute the Os isotope record into a proxy for global organic matter burial and weathering fluxes ultimately yielding a reconstruction of atmospheric composition over geologic time.

A weathering profile developed on ~370 Ma New Albany Shale (Kentucky, USA) has been examined to correlate trace metal and OM release from shales during weathering. Samples were taken from single stratigraphic horizons. Concentrations of OM, Fe₂S₃, and N are low in heavily weathered rocks, while Porg is concentrated in the weathered shale. Thus nutrients are redistributed as oxidation penetrates into initially anoxic shale. Trace metal concentrations (Re, Os, U) decrease with weathering. ¹⁸⁷Re/¹⁸⁶Os ratios fall significantly in progressively more weathered shale, indicating preferential loss of Re over Os. In contrast, ¹⁸⁷Os/¹⁸⁶Os remains roughly constant except in the most weathered sample. This is interpreted as selective mobilization of isotopically distinct Os pools during weathering. Samples plot along a 19 Myr reference line on a Re-Os isochron diagram, suggesting recent mobilization of Re during surficial weathering.

These data are interpreted as mobilization of Re in the recent past from within the anoxic interior of the profile and remobilization in weathered shale, in analogy with Re distributions and U-Th isotope systematics within "burn-down" layers in Madeira Abyssal Plain turbidites. Because U and Re redistributions are similar in the weathering

profile, U-Th disequilibria may provide a time constraint on the rate of penetration of oxygen into black shale during weathering. Using mass loss measurements of trace and nutrient elements across this black shale weathering profile and the rate of oxidation of the shale, mass flux estimates can now be generated for loss of C, N, P, Re, Os and U from black shales during weathering. This will improve quantification of the influence of shale weathering on surficial geochemical cycles of Mo, Re, U and P, as well as the Os isotopic evolution of seawater.

CC04 : WEam05 : G3 Testing the Validity of Dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ as a Proxy for Silicate Weathering in the Himalaya

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Much interest surrounds the potential use of dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ values in Himalayan rivers as a proxy for silicate weathering rates. The existence of such a proxy would establish a persuasive link between uplift of the Himalaya, the contemporary increase in the marine $^{87}\text{Sr}/^{86}\text{Sr}$ record and global cooling resulting from increased uptake of atmospheric CO_2 through the weathering of silicate rocks. Data from river water, bedload and bedrock samples from the Bhoté Kosi river of central Nepal, a Gangetic tributary that traverses the major lithologies of the Himalayan belt, suggest that the dissolved load is firmly controlled by inputs from carbonate and calc-silicate lithologies. This suggests that the indiscriminate use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as a proxy for silicate weathering rates should be critically assessed.

Dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ in the Bhoté Kosi shows a rapid increase (from 0.73 to 0.76) in a 10 km section downstream of the Main Central Thrust (MCT), which separates gneisses and schists of the High Himalayan Crystalline Series from calc-silicates of the Lesser Himalayan Upper Nawakot Unit. Tributaries joining the river in this section are highly radiogenic ($^{87}\text{Sr}/^{86}\text{Sr} > 0.8$). Principal components analysis (PCA) reveals that the key control ($R^2 = 0.86$) on dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ in the Bhoté Kosi is the proportion of Upper Nawakot rock present in a catchment. These calc-silicates have bulk-rock $^{87}\text{Sr}/^{86}\text{Sr}$ values as high as 1.1, which cannot be explained simply through decay of ^{87}Rb , implying isotopic exchange during their 2500 Ma geological history. Strong positive correlation with K^+ concentrations ($R^2 = 0.78$) suggests that much of the radiogenic Sr within the calc-silicates is derived from the incongruent dissolution of mica although it is probable that the bulk of the dissolved Sr derives from weathering of dolomite.

Bedload reflects the same downstream patterns as dissolved load and Nd isotopes are used to constrain the bedload source. Downstream of the MCT the rise in $^{87}\text{Sr}/^{86}\text{Sr}$ is accompanied by a decrease in ϵNd , from -18 to -21 reflecting Lesser Himalayan input (Upper Nawakot bedrock: $\epsilon\text{Nd} = -23$ to -27). High $^{87}\text{Sr}/^{86}\text{Sr}$ tributaries have $\epsilon\text{Nd} = -24$ to -25 confirming the Lesser Himalaya as the dominant input.

CC04 : WEam06 : G3 Sr-Nd Isotope and Geochemical Analysis of Lithic Components in Late Pleistocene Sappropels and Homogeneous Sediments from the Eastern Mediterranean Sea: Implications for Detrital Influx and Climatic Conditions in the Source Areas

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Lithic components of 26 surface sediments and three cores recovered from an east-west transect in the Eastern Mediterranean Sea (MED) have been analyzed for Sr-Nd isotope and element geochemistry. The core material

analysis focuses on sapropel horizons 5 (S5), 6 (S6), homogeneous sediments above and beneath these sapropels as well as the surface sediments of the cores. All Sr-Nd isotopic data in cores derived from southwest and southeast of Crete plot within a narrow and flat hyperbolic envelope between end members Aegean basalt/Nile particulate matters and Saharan dust. Surface and homogeneous sediments from marine isotope stage 5 (MIS5) are characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (average: 0.714544, n=5) and low $\epsilon\text{Nd}(0)$ values (average: -9.5). S5 shows lowest average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.710837) and highest average $\epsilon\text{Nd}(0)$ values (-7.7). Samples from S6 display similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\epsilon\text{Nd}(0)$ values as S5 but are less pronounced. Homogenous sediments from marine isotope stage 6 (MIS6) show intermediate ratios and values but inter-site comparison reveals large differences. In core KL 83, which is located close to Nile cone, all data plot close to the ratios and values of Nile delta sediments. The temporal variations of isotopic composition in KL83 is seen only on the $\epsilon\text{Nd}(0)$ values, while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain fairly constant. A quantitative estimate and temporal variation of Saharan dust and riverine dispersal flux is based on simplified assumptions regarding the source areas of lithic sediment and by applying a general mixing equation. During MIS5 carbonate-free Saharan dust flux was similar to the present situation. During the deposition of S5 and S6, however, the Saharan dust input was drastically reduced. No simultaneous quantitative increase of riverine influx was apparent. Denser vegetation cover under more humid conditions may have reduced physical erosion and sediment removal in the source areas. During MIS 6 (stadial 6.2) a pronounced increase of both eolian and riverine influx is evident and implies more arid conditions. In this phase, inter-site variations are interpreted in terms of their geographic location relative to the sea ways connecting the Aegean and eastern Mediterranean Sea. The width of the straits and hence the amount of sediment entering the eastern basins were probably affected by a sea level low stand which narrowed the gate ways.

CC04 : WEam07 : G3 Nd Isotopic Compositions of Terrigenous Detritus and Seawater in the South Atlantic as Inferred from Particles Suspended in Surface Waters

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Nd isotopes and trace elements in suspended particle samples from the Atlantic sector of the Southern Ocean were investigated to delineate the composition of surface water and the origin and distribution of terrigenous material. The particle samples were collected with RV 'Polarstern' during 1997 and 1999. They were separated from up to 7000 liters of seawater and represent average compositions for sampling distances of 30 to 160 km. We inferred the composition of ambient seawater from scavenged Nd (leachate samples), obtained by treating the bulk particle samples with acid. The residues of this procedure were interpreted as the terrigenous component. Altogether ca. 50 particle samples were collected along N-S traverses in the Antarctic Circumpolar Current (ACC), the central and eastern Atlantic Ocean, and the Weddell Sea.

The ϵNd values of -8 to -10 for the majority of the leachate samples indicate a uniform composition of the surface seawater throughout the ACC and the Weddell Sea. On a local scale, seawater south of Africa and in the eastern Weddell Sea may have ϵNd values as low as -18. These very low values indicate partial exchange of Nd from seawater with that from an old terrigenous component.

The ϵNd values of the residue samples can be interpreted as contributions of terrigenous detritus from the adjacent continents: high values up to -1 occur in samples from the western South Atlantic Ocean. They can be explained with presence of detritus from the Antarctic Peninsula and South America. ϵNd values as low as -15 in samples from the eastern Weddell Sea are explained with material derived from East Antarctica. We propose transport of the terrigenous component by icebergs from Enderby Land in East Antarctica. Values as low as -14 in samples collected off South Africa indicate sediment supply via the Agulhas Current. Residue samples from the central Atlantic Ocean yielded uniformly higher ϵNd values of ca. -7, than

measured in ambient seawater (ca. -8) over a distance of ca. 1000 km. We interpret these uniform data as evidence for deposition of dust from South America.

The terrigenous component in the remote South Atlantic Ocean is interpreted as an important source for iron, a limiting nutrient for the growth and blooming of phytoplankton.

CC04 : WEam10 : G3 Rare Earth Element Patterns and Neodymium Signature along the Greenland Slope and in the Denmark Strait

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Seawater neodymium isotopic composition is a tracer of water mass pathways and of their interactions with continental material. It can be used to reconstruct both paleo and present day ocean circulation (Jeandel et al. 1998; Lacan and Jeandel, accepted; Rutberg et al. 2000 and references therein). The main objective of our work is to understand how the North Atlantic Deep Water acquires its neodymium signature in the present day ocean. In this goal, we collected 340 seawater samples throughout the water column in the North Atlantic Ocean : Labrador Sea, Irminger Sea, Iceland Basin, Iceland Sea, Norwegian Sea, Greenland Sea and within the Denmark Strait. Preliminary results on neodymium concentrations in the Denmark Strait and along the Greenland slope show interesting features. For example, neodymium content reaches 100 pmol/kg in the West of the Denmark Strait around 75 m, and decreases progressively eastwards along the same isopycnal down to 32 pmol/kg near the coast of Iceland. This suggests the occurrence of West-East transport and mixing within the East Greenland Current which generally flows southwards. Hydrological data and neodymium concentrations indicate that at least three water masses are necessary to explain this neodymium distribution. Neodymium isotopic ratio should help to identify these water masses and their origins and to confirm and quantify the transport and mixing processes. Neodymium isotopic compositions along the Greenland slope will be presented. Evolution of the isotopic signature of the different water masses composing the East Greenland Current between 77°N and the Denmark Strait will be discussed.

Jeandel C, Thouron D & Fioux M, *Geochim. Cosmochim. Acta*, **62**, 2597-2607, (1998).

Lacan F & Jeandel C, *Earth and Planet. Sci. Let.*, accepted
Rutberg RL, Hemming SR & Goldstein SL, *Nature*, **405**, 935-938, (2000).

CC04 : WEam11 : G3 Vertical and Latitudinal Mapping of the Glacial North Atlantic Deep Water Extent Inferred from Nd Isotopes

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Changes of bottom-water circulation during the Late Quaternary can be inferred by analysing the Nd isotope composition of the Fe-Mn fraction dispersed in marine sediments (Rutberg et al., 2000; Bayon et al., 2000). Application of this new proxy in paleoceanography relies on two properties of Nd: 1) like salinity and dissolved silica, Nd can be regarded as a conservative tracer of the

water masses; 2) during Nd incorporation into Fe-Mn oxides, its isotopes retain the signature of seawater. Rutberg et al. (2000) have demonstrated how powerful this approach may be by showing that North Atlantic Deep Water (NADW) was considerably reduced in the southern Cape Basin during the Last Glacial Maximum (LGM). The use of this proxy is particularly suitable in such high productivity areas where the $\delta^{13}\text{C}$ record of benthic forams is strongly affected by the local productivity signal, limiting any possible paleoceanographic interpretations (Bickert and Wefer, 1999).

Here we present Nd isotope records of the Fe-Mn component from sediment cores taken in the southeast Atlantic during the NAUSICAA - IMAGES II cruise. In the northern Cape Basin, we are investigating the vertical extent of the NADW during the LGM by studying a transect from the upper continental slope to the deep basin. Core MD96-2087 (~ 1000 m water depth) is located at the present-day boundary between the Upper Circumpolar Deep Water (UCDW) and the NADW, whereas core MD96-2086 (~ 3600 m depth) samples the Lower CDW - NADW boundary. Core MD96-2098 (~ 2900 m depth) is situated in the centre of modern-day NADW. These cores therefore are particularly suitable to monitor any vertical variations of NADW during the LGM. Furthermore, in order to better constrain the latitudinal extent of NADW during the LGM, we will also present isotopic results of two other cores from the Angola Basin (MD96-2091, 3600 m) and the central Cape Basin (MD96-2085, 3000 m) along the southward flowing trajectory of present-day NADW.

Rutberg RL, Hemming SR & Goldstein SL, *Nature*, **405**, 935-938, (2000).

Bayon G, German CR, Nesbitt RW & Pierre C, *Goldschmidt Conf. CD Rom*

Bickert T & Wefer G, *Deep Sea Res. II*, **46**, 437-452, (1999).

CC04 : WEam12 : G3

Pb Isotope Data of Authigenic and Detrital Phases of a Deep-Sea Core from Southeastern Arabian Sea – A Record of Climate-Controlled Changes in Weathering Processes and Circulation Pattern?

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Pb isotopes have been analyzed in a deep-sea sediment core (MD-900963) from the southeastern Arabian Sea (05° 04' N, 73° 53' E; 2450 mbsl) in order to investigate if these radiogenic isotopes are suitable as indicator of changes in past ocean circulations in sediments, as demonstrated previously by numerous studies in Fe-Mn crusts. Authigenic and detrital phases were separated from the bulk sediment sample by leaching with 1 N HCl. Pb isotopes in the detrital phases vary for the past 150 kyr in tandem with the $\delta^{18}\text{O}$ record. Various paleoclimate tracers indicate that the strength of the summer monsoon rainfall intensity over the Indian subcontinent and the flux of river water delivered to the Bay of Bengal was reduced during the LGM. Thus it is possible that changes in the riverine input of Pb due to modifications in the weathering and erosion conditions caused the isotope variations of Pb. The Pb isotopic signature of the bulk sediments and the leachates is decoupled from that of the residual phases. Plotted in the Pb-Pb space, the leachates of the deep-sea sediments of core MD-900963, located between the Arabian Sea and the Gulf of Bengal, exhibit a different trend compared to Pb isotope data from Vlastelic et al., 2000 obtained from Fe-Mn-nodules from the northern Indian Ocean. This possibly indicates changes in the ocean current system around the tip of the Indian subcontinent, which is fedded from different continental sources like the Bengal Fan and the Indus Fan.

Vlastelic I, Abouchami W, Galer SJG, Galer, Claude-Ivanaj C, Hofmann AW, Claude-Ivanaj, C., Hofmann, A. W., Abouchami, W., Galer, S. J. G., Claude-Ivanaj, C., Hofmann, A. W., *J.Conf.Abs. Goldschmidt*, **5** (2), 1056, (2000).

Claude-Ivanaj, C., Hofmann, A.W.

CC04 : WEam13 : G3

Monitoring the Style and Intensity of Weathering with Combined Hf-Pb-Nd Isotopic Studies on Fe-Mn Crusts

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Dissolved trace metals in the oceans are essentially derived from three main sources: riverine input, eolian provenance and seafloor hydrothermal activity. The isotopic compositions of these trace metals in seawater through time, as recorded by Fe-Mn crusts, may potentially provide information on past changes in continental weathering, hydrothermal input to the oceans and ocean circulation patterns, which are linked to climatic and tectonic events.

Besides the utility of Fe-Mn crust-derived Nd, Pb and perhaps also Hf isotopes as oceanographic tracers, we show that combined Hf-Pb-Nd data can be used to monitor the intensity and style of continental weathering. For the Sm-Nd system there is no evidence of significant fractionation during processes of weathering and sedimentary sorting. In contrast, Lu and Hf tend to be strongly fractionated between muds and sands due to the preferential retention of Hf in chemically resistant zircons. Detrital zircons normally have low Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios, and reside mainly in sands on the continents and continental shelves. Consequently, a more radiogenic, zircon-free fraction, derived from weathering of less resistant minerals, tends to dominate the riverine input to the oceans. These effects of incongruent weathering also occur in the Pb isotope system. The first Pb-fraction, which is released in the initial stage of weathering of fresh granitic rock surfaces is much more radiogenic than their bulk composition. This suggests that the radiogenic Pb isotopes are more loosely bound in the crystal lattice due to radiation damage from the decay of U and Th.

Ferromanganese crust ALV539 from the north-western Atlantic ocean should display a strong connection between isotopic composition and changes in climate and weathering style. Major shifts in Nd, Hf and Pb isotope compositions can be related to the onset of Northern Hemisphere Glaciation around 3 Ma. Dissolved Nd and Hf have become less radiogenic, whereas $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ increase. This is exactly as expected from the mechanical breakdown of zircon and the increasing amount of terrestrial input. Estimated model ages in these zircons, calculated from the Fe-Mn crust data, are consistent with the average crustal ages of surrounding land masses. Moreover, the Pb isotopic signal entering the oceans after the onset of Northern Hemisphere Glaciation, has increasingly been derived from weathering of fresh rock material. Glacial erosion continuously created new outcrops, and therefore favoured the release of radiogenic Pb.

CC04 : WEam14 : G3

NADW Export to the Eastern South Atlantic and Southern Ocean over the Past 14 Myr Deduced from Nd and Pb Isotopes in Ferromanganese Crusts

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The intensity of North Atlantic Deep Water (NADW) production is considered one of the key parameters controlling the global thermohaline ocean circulation and climate. We present a reconstruction of the strength of NADW export over time using Nd and Pb isotopes as water mass tracers, as recorded by ferromanganese crusts and nodules.

Our approach is to compare the variability of Nd and Pb isotope compositions of NADW close to the production sites in the NW Atlantic with those in the eastern south Atlantic and the Southern Ocean.

Pronounced shifts towards less radiogenic Nd isotope composition and more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ of NADW starting between 2 and 3 Ma were recorded in ferromanganese crusts in the NW Atlantic. In marked contrast, six isotope records from the Southern Ocean display basically invariant Nd isotope time series since 14 Ma and a clear trend towards more Pacific-like Pb isotope composition since 3-4 Ma. This increasing difference between the trace metal isotopes in the NW Atlantic and the Southern Ocean, particularly that of quasi-conservative Nd, since the onset of the Northern Hemisphere Glaciation at 3 Ma, provides evidence for an overall reduction of NADW export into the Southern Ocean of 14 to 37%.

New Nd and Pb isotope time series will be presented from the Romanche Fracture Zone which is one of the main pathways for deep water exchange between the western and eastern Atlantic basins. Preliminary data from the Romanche Fracture Zone indicate that the Pb isotope composition of NADW as seen in the NW Atlantic was altered to some extent by local inputs or mixing with water masses from the south before flowing into the eastern basins. There is oceanographic evidence that the deep water of the Angola basin consists mainly of NADW but the renewal rate of deep water masses in the basin is far lower than in the western Atlantic. The available isotope data from the deep Angola Basin show a relatively small variability in Nd and quite pronounced variations in Pb isotope composition over time, comparable with the Southern Ocean records. However, prior to about 1 Ma, the Nd and Pb isotope compositions were lower in Nd isotope composition and higher in $^{206}\text{Pb}/^{204}\text{Pb}$ than those of NADW in the NW Atlantic itself at the same time. Comparison with potential local sources clearly demonstrates the importance of contributions from the Congo River and preclude the use of both Nd and Pb isotopes as quantitative tracers of water mass mixing in the deep Angola basin.

Wednesday PM Session

CC04 : WEpm25 : G3

 $\delta^{44}\text{Ca}$ -Temperature Calibration on Fossil and Cultured *Globigerinoides sacculifer*: A New Paleo Sea Surface Temperature Proxy

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A direct $\delta^{44}\text{Ca}$ -temperature calibration on cultured calcite foraminifera is reported, demonstrating the high potential of Ca-isotopes as new SST-proxy ($\delta^{44}\text{Ca}$ = variation of $^{44}\text{Ca}/^{40}\text{Ca}$ in ‰). In order to avoid species dependent isotope fractionation the investigations are focused on a single planktonic foraminifera species (*G. sacculifer*). Ca-isotope determinations involved the use of a Ca double spike. Ca isotopic compositions were measured on a single cup AVCO mass-spectrometer. Ca isotopic fractionation was calculated based on an exponential fractionation law. The method allows to analyze sub μg amounts of Ca, with a 1 ng blank.

Cultured *G. sacculifer* were analyzed that grew in sea water kept at temperatures of 19.5, 26.5 and 29.5°C. The light and feeding conditions were adjusted to the open ocean environment. It was found that the temperature range of 10°C corresponds to a total $\delta^{44}\text{Ca}$ -variation of ca. 2.5 with a $\delta^{44}\text{Ca}$ -change of 0.24±0.02 per 1°C defined by the weighted linear regression (95% c.l.). Application of this new method to *G. sacculifer* of an equatorial east Atlantic sediment core indicates that the SST difference between Holocene and the Last Glacial maximum (LGM) is identical for both, the Mg/Ca and $\delta^{44}\text{Ca}$ proxies. (3 ±1°C). Because of the use of one species only any vital effects can be ruled out to have influenced our $\delta^{44}\text{Ca}$ record. In addition, variations of the initial seawater $\delta^{44}\text{Ca}$ -ratio can be neglected for Holocene/LGM variations because this time interval is short when compared to the Ca-residence time in the ocean.

Our results indicate that Ca isotopic compositions of a particular species present a SST-proxy complementary to the application of oxygen isotopes and chemical SST-proxies, with Ca isotopes being unaffected by continental ice volume changes, evaporation or freshwater input and potentially less affected by factors like salinity and post-depositional chemical alteration.

CC04 : WEpm26 : G3

Determination of $\delta^{44}\text{Ca}$ -ratios on *G. bulloides* (ODP Leg 183 Site 1138) using a New TIMS Multicollector Technique

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During the last years the precision of calcium isotope measurements ($\delta^{44}\text{Ca}$) has considerably improved due to technical improvement in mass spectrometer instrumentation, and the application of the double spike technique. Recent progress in Ca-isotope measurements showed that calcium isotopic variations can be used in order to reconstruct past sea surface temperature variations (Nägler et al., 2000) and past global fluctuations of continental weathering fluxes (De La Rocha & DePaolo, 2000). Here we present a rapid method for the determination of calcium isotope compositions by thermal ionisation mass spectrometry (TIMS). The main improvement is the use of a multicollector analyser and the use of a $^{43}\text{Ca}/^{46}\text{Ca}$ double spike. The analyses were performed on a MAT262 RPO+ using a two step dynamic mode. In the first step masses 40, 41, 42 and 43 are measured simultaneously and in the second step masses 44 and 48 are measured simultaneously.

Interferences of ^{40}K are monitored on mass 41 and can generally be neglected. Comparison of the result from this new method to results from simple peak jumping indicate that the new method show comparable and precision. Measured ratios are corrected for the double spike by an external numerical algorithm using an iterative approach (Compston & Oversby, 1969). The $\delta^{44}\text{Ca}$ -ratios are normalised to the $^{44}\text{Ca}/^{40}\text{Ca}$ ratio of NIST SRM 915a (pure CaCO_3). The long term reproducibility was determined by repeated measurements of this standard and amount to ±0.08‰ (δ -units). The new technique has been applied to $\delta^{44}\text{Ca}$ variations of planktonic foraminifera (*G. bulloides*) from ODP Leg 183 Site 1138 (Kerguelen Plateau). The results show that the $\delta^{44}\text{Ca}$ ratios vary during the last 22 Ma within a range of about 1‰. The $\delta^{44}\text{Ca}$ values decrease from the present to a $\delta^{44}\text{Ca}$ -minimum at about 16 Ma. This observation can be interpreted in terms of global SST-cooling or an increase of ocean calcium concentration due to enhanced rates of continental weathering.

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Compston W & Oversby V, *J. Geophys. Res.*, **74**, 4338-4348, (1969).

CC04 : WEpm27 : G3

Using $\delta^{44}\text{Ca}$ - and $\delta^{18}\text{O}$ -Isotopes as Proxies for SST and Salinity Changes during the Closure of the Central American Gateway

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During the Pliocene, the emergence of the Central American Isthmus led to a restricted surface water mass exchange through the Panama Strait. This is indicated by diverging trends in planktonic $\delta^{18}\text{O}$ (*G. sacculifer*) between the Caribbean Sea (Site 999) and the equatorial East Pacific (Site 851) since about 4.6 Ma and more clearly since 4.2 Ma. The Caribbean $\delta^{18}\text{O}$ values increase by about 0.5 ‰ with respect to the Pacific values. This can be interpreted either as an increase in Caribbean sea surface salinity and/or a decrease in Caribbean sea surface temperatures (SST). In order to evaluate this problem we measured the $\delta^{44}\text{Ca}$ ratios on *G. sacculifer* (Site 999) because recent investigations (Nägler et al., 2000) indicate that $\delta^{44}\text{Ca}$ ratios reflect SST variations and are presumably independent from salinity variations. In contrast to a possible Caribbean temperature decrease that can be inferred from the $\delta^{18}\text{O}$ -signal, the $\delta^{44}\text{Ca}$ record suggests a temperature increase of about 2°C from 4.3 to 4.05 Ma. By correcting the $\delta^{18}\text{O}$ record for this temperature change, the planktonic $\delta^{18}\text{O}$ -salinity signal would increase to about 0.9 ‰, if changes in ice volume were negligible. On average this would correspond to a Caribbean salinity increase of about 1.8 ‰ in response to the emergence of the Isthmus. Additional support for the validity of the planktonic $\delta^{44}\text{Ca}$ data, is the positive correlation with the benthic $\delta^{18}\text{O}$ record of *C. wuellerstorfi*. In contrast to the oxygen isotope composition of planktonic species the $\delta^{18}\text{O}$ of these benthic foraminifera is not significantly affected by salinity changes of the surface water and shows therefore more likely a global temperature signal.

Nägler T., Eisenhauer A., Müller A., Hemleben C., and Kramers J., *G3*, **1**, 000091, (2000).

CC04 : WEpm28 : G3

Oxygen and Carbon Isotopic Compositions of Coral Skeleton at Micrometer Scale

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Oxygen isotopic compositions of coral skeletons are often used as proxies for seawater paleotemperature. But the temperature dependence of fractionation between seawater and coral remains not fully understood. The analysis at micrometer scale with an ion probe of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ could help to better understand this fractionation. The spatial resolution of this method is 30 μm and the precisions obtained on the carbonate standards are 0.45 and 0.65 ‰ for oxygen and carbon, respectively.

The studied coral is a modern *Porites lutea* from New Caledonia. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of this coral measured at intervals of 1 mm using the H_3PO_4 digestion vary by about 1 ‰ from 26.16 to 27.18 ‰ for oxygen and from -3.79 to -2.63 ‰ for carbon. This variation in $\delta^{18}\text{O}$ corresponds to a variation in temperature of 5.8°C which is in good agreement with the amplitude of temperature recorded at the sample location.

At the micrometer scale, the variation of $\delta^{18}\text{O}$ is about 10 ‰ from 19.97 (below the expected "vital effect") to 30.65 ‰ (value of aragonite isotope equilibrium with seawater). The $\delta^{13}\text{C}$ at micrometer scale vary from -2.16 ±0.67 to -4.43 ±0.65 ‰ and so is in the range of $\delta^{13}\text{C}$ measured by bulk method. Thus, whereas the $\delta^{18}\text{O}$ data show variations up to 10 ‰, the $\delta^{13}\text{C}$ data show no variation. Therefore the μm scale data prevent the model of kinetic fractionation as the explanation of the "vital effect" (McConnaughey, 1989) and imply that two different mechanisms are necessary to explain the records of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.

For calcification of coral skeleton, the major source of carbon is metabolic CO_2 (70-75%) while only 25-30% originate directly from the seawater. The $\delta^{13}\text{C}$ of the metabolic CO_2 is lower than the $\delta^{13}\text{C}$ of seawater CO_2 . If the aragonite precipitation is too fast to permit the total establishment of carbon isotopic equilibrium with the calcifying fluid, then the aragonite crystals would have the fingerprint of the sources and would be depleted in ^{13}C relative to the equilibrium value. This mechanism does not affect the $\delta^{18}\text{O}$ because H_2O buffers all the solution. The lower values in $\delta^{18}\text{O}$ exceed the maximum disequilibrium which could be expected from kinetic effects in the calcifying fluid. Therefore other mechanisms such as pH variation is needed to account for the amplitude of variation. This variation in pH does not influence the $\delta^{13}\text{C}$ because the difference in carbon isotopic composition is small between HCO_3^- and CO_3^{2-} .

McConnaughey T, *Geochim. Cosmochim. Acta*, **53**, 163-171, (1989).

CC04 : WEpm29 : G3

Paleotemperatures Reconstructed from Mg/Ca in Foraminifer Tests: Correcting for Dissolution Effects using Calcite Crystallinity and Other Dissolution Proxies

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Since the work of Delaney et al. (1985), many authors have shown that Mg/Ca ratio in foraminifer tests is strongly dependent upon the temperature at which the shells developed. Among its advantages as a paleotemperature proxy, the Mg/Ca ratio is quick to measure on new ICP-AES apparatus and can be obtained on the same material as the one used for stable isotopic measurements (specific foraminifer species).

Important research efforts were devoted in the mid 90's to get regression equations linking Mg/Ca (measured on ICP-AES) to temperature for different foraminiferal species (i.e. Nurnberg, 1995; Elderfield and Ganssen, 2000). However, confirming early observation made by Savin and Douglas (1973), Rosenthal and Boyle (1992) have shown that calcite dissolution on the sea floor results in the preferential dissolution of Mg, leading to a decrease of the Mg/Ca ratio. We recently showed (Levi et al., 2000) that Mg/Ca in *Globigerinoides ruber* decreases by about 0.6 mmol/mol in core top samples retrieved along a transect ranging from 2700 m to 4250 m in the eastern Atlantic Ocean. Such a Mg/Ca depth-related evolution in core tops translates into a temperature difference comprised between about 1.5 and 2.0°C if we apply the published regression equations.

In order to correct Mg/Ca for dissolution effects, we have analyzed Mg/Ca and different dissolution proxies along two depth transects : Sierra Leon (eastern equatorial Atlantic) and Ontong Java Plateau (western equatorial Atlantic). We have paid a special attention to a possible new proxy for dissolution quantification: calcite crystallinity. In this presentation, we will discuss the possibilities of correcting Mg/Ca and other paleoceanographic proxies for carbonate dissolution.

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Rosenthal Y & Boyle EA, *Geochim. Cosmochim. Acta*, **57**, 346-355, (1992).

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CC04 : WEpm30 : G3

Interspecies Variability in Foraminiferal Sr/Ca Ratios over Glacial-Interglacial Cycles

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Glacial-interglacial changes in foraminiferal Sr/Ca have now been recorded at several sites and appear to be ubiquitous [Martin et al., 1999; Stoll et al., 1999]. However, there is some controversy as to whether they record changes in the Sr/Ca ratio of sea water or whether they reflect a "vital effect" such as changing foraminiferal calcification rate. In order to investigate this phenomenon, a piston core from a site of major monsoonal upwelling in the western Arabian Sea has been analyzed for Sr/Ca ratios of several species of planktonic and benthic foraminifera. Work on other sites is in progress. Analysis of Sr/Ca from three species of planktonic foraminifera (*Globigerina bulloides*, *Globigerinoides ruber* and *Neogloboquadrina dutertrei*), together with stable isotopic evidence from the same species allows an evaluation of the various chemical and physical controls on the uptake of Sr into foraminiferal calcite. The single species variation in Sr/Ca is in the order of 10%, unrealistically high compared with modeled predictions of changes in seawater Sr/Ca [Stoll and Schrag, 1998]. Sr/Ca ratios in the tests of *Neogloboquadrina dutertrei* and *Globigerina bulloides* reveal a lagged, linear relationship with variations in $\delta^{18}\text{O}$ whereas the Sr/Ca record for *Globigerinoides ruber* reveals an inverse relationship with $\delta^{18}\text{O}$. Such phase differences in Sr/Ca between species are similar to those recorded in the northeast Atlantic. These data clearly establish that factors other than seawater Sr/Ca must be implicated.

Martin PA, Lea DW, Mashioita TA, Papenfuss T & Sarnthein M, *Geochemistry Geophysics Geosystems* (**G3**), **1**, (1999).

Stoll HM, Schrag DP & Clemens SC, *Geochim. Cosmochim. Acta*, **63**, 3535-3547, (1999).

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CC04 : WEpm31 : G3

Sclerosponges: New Proxy Recorders of Environmental Data

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The sclerosponge *Ceratoporella nicholsoni* is a slow growing organism that builds a dense, laminated aragonitic skeleton. It occurs in tropical reef caves and at the deeper slopes of the Caribbean and Bahamas down to water depths of 150 m. It's skeleton grows very slowly at rates of 0.1-0.4 mm/y. Thus, as an advantage over reef corals, proxy records from *Ceratoporella* skeletons cover time intervals of decades to centuries, expanding the time frame back to the Middle Ages. Because sclerosponges do not depend on photosynthesis, they live as deep as the upper thermocline. Therefore, these seldom studied materials greatly extend and complement proxy records derived from reef corals.

We have studied *Ceratoporella nicholsoni* skeletons from the Caribbean, collected alive at Jamaican reefs (20 m) and at Pedro Bank (125 m). Based on the ²³⁰Th-²³⁴U dating method, our sclerosponges are between 200 and 600 years old. We have investigated oxygen, carbon, boron and calcium isotopes and Ca, Na, Sr, B, Ba, U, Mn, V and Pb concentrations. Isotope values and element ratios are compared to published data from corals, ooids and inorganic aragonites.

Most parameters measured show that the sclerosponge skeletons differ significantly from corals but have a very similar composition as ooids and inorganic aragonite. Boron concentrations and isotope ratios of C. nicholsoni demonstrate the biomineralization from a fluid with a pH very similar to seawater and more acidic than in corals. Ooids may crystallize at a slightly higher pH than C. nicholsoni. Ca isotope values from C. nicholsoni are in the same range as values from planktonic foraminifers. However, unlike the foraminifera we cannot detect a temperature effect on the Ca isotopic composition of the sclerosponge skeletons. Oxygen and carbon isotopes are very close to predicted equilibrium with ambient waters. Distribution coefficients of Sr, Pb and probably Mg of the sponge aragonite are similar to those of inorganic aragonite. The uranium concentrations are enriched by a factor of 2-3 in sclerosponge skeletons compared to corals.

In conclusion carbon and oxygen isotopes, boron isotopes and boron concentrations in sclerosponge skeletons have a high potential, uranium and strontium are promising candidates as proxies for environmental changes.

CC04 : WEpm34 : G3

Global Calibration of *Gephyrocapsa* Coccolith Abundance and Morphology for Paleotemperature Assessment during the last Glacial Maximum in the Canary Islands Region

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This study presents a new coccolith-based proxy to estimate absolute sea surface temperature, which was used for the paleoceanographic reconstruction of the Canary Islands region during the Last Glacial Maximum (LGM). Off NW Africa, extensive studies exist on the glacial-interglacial variability of coastal upwelling processes and related (primary) productivity, coupled with atmospheric circulation patterns. During the LGM, coastal upwelling was generally enhanced due to the increased strength of the Trade Winds. However, this general view of high glacial productivity seems limited to the northernmost latitudes of the NW African upwelling system (at 25°N). This study

extends our knowledge of the Eastern Boundary Current system to the north of the Canary Islands (29-32°N), in an area that includes both the oligotrophic waters of the eastern North Atlantic subtropical gyre and the productive, seasonal coastal upwelling zones off Morocco.

In Holocene sediments, the morphology of coccoliths belonging to the genus *Gephyrocapsa* is closely correlated with sea surface temperature and fertility patterns. Based on this relationship, a temperature transfer function was established using a set of 85 globally distributed Holocene deep-sea sediments covering a temperature range from 7°C to 29°C. This transfer function was then used to reconstruct the paleotemperature during the LGM in the Canary Islands region and off Cape Blanc (at 21°N), in the center of the perennial upwelling system.

Using this approach, absolute mean sea surface temperature for a given location can be calculated from the relative abundance of *Gephyrocapsa* morphotypes as well as from the mean morphology of *Gephyrocapsa* coccoliths with a standard deviation of $\pm 1.8^\circ\text{C}$ and 2.1°C , respectively. If a regional data set is used the error can be reduced to $\pm 1.5^\circ\text{C}$.

This method revealed that temperatures during the LGM were up to 6°C colder than today in the Canary Islands region. A consistent pattern exists with distance from shore where the greatest $\Delta T_{\text{today-LGM}}$ (5-6°C) are found about 200 km offshore, with gradually decreasing ΔT towards the outer oceanic domain (4°C). These values are consistent with estimates from the CLIMAP Project (1981) and other paleotemperature reconstructions in the same region. In contrast, offshore Cape Blanc our temperature estimate for the LGM is significantly warmer ($\Delta T < 4^\circ\text{C}$) than proposed by CLIMAP (ΔT 6-10°C). Similarly, temperature reconstructions based on alkenones also indicate smaller temperature changes (ΔT 3°C) in this area.

CC04 : WEpm35 : G3

Planktic Foraminiferal Distribution Across the Azores Front

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The population dynamics and sedimentation of planktic foraminifers is significantly influenced by the hydrography of the Azores Front-Current System, south of the Azores Islands. During seasonal cruises across the Azores Front, planktic foraminifers and pteropods have been sampled from the water column and record the temporal and spatial scale of hydrographic and faunal dynamics within the studied region. In comparison, the planktic foraminiferal test assemblage from surface sediments reflect the distribution of the living fauna and, consequently, the average position of the modern Azores Front. All of the surface sediment samples which have been investigated contain pteropod shells (aragonite), indicating full preservation of CaCO₃ and, therefore, little alteration of the planktic foraminiferal test assemblages (calcite). Consequently, most of the seasonal and spatial variability of the Azores Front can be deduced from the planktic foraminiferal assemblages within the surface sediment. In particular, the deep-dwelling species *Globorotalia truncatulinoides* and *Globorotalia scitula* display fine-scale changes across the frontal area, along a north-south transect, and may serve as a paleoceanographic tool to reconstruct the ancient Azores Front. Since the Azores Front-Current System is the distal southern branch of the Gulf Stream, its variability may provide information on glacial/interglacial changes of the Quaternary current system not only of the Azores region but of the entire North Atlantic Ocean.

CC04 : WEpm36 : G3

Paleovegetation Conditions in the Equatorial Indian Ocean between 300 and 500 ka B.P

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In order to study bottom water conditions in the equatorial Indian Ocean during isotope stages 10 to 12, we measured Cd/Ca-ratios of benthic foraminifera *Uvigerina* spp. and *C. wuellerstorfi* from core MD900963 (5°N/73.5°E). This ratio is closely correlated to bottom water phosphate concentration and commonly used as a nutrient proxy. Cd- and Ca- measurements were performed with a VG-54 Thermo Ionisation Mass Spectrometer, using a double spike solution (¹¹⁶Cd, ⁴⁸Ca). Cd/Ca ratios range between 0.087 μmol/mol at 371 ka and 0.308 μmol/mol at 441 ka, with a mean of 0.161 μmol/mol during stages 10 and 12 and 0.194 μmol/mol during stage 11 (disregarding 2 extreme values of 0.445 and 0.386 μmol/mol at 428 and 354 ka based on single measurements). The mean phosphate estimations of 2.3 and 2.6 μmol/kg derived from Cd/Ca do not vary significantly and indicate only slightly better-ventilated bottom water masses during isotope stages 10 and 12 when compared to stage 11. From these data, the glacial/interglacial change in oxygen concentration can be estimated to roughly 1 ml/l. Based on the modern interglacial oxygen concentration of about 3.2 ml/l at the core location, it can be concluded that it has always been exposed to oxic bottom water conditions, and, consequently, the high organic carbon content measured in this core cannot be due to enhanced preservation linked to anoxia.

CC04 : WEpm37 : G3

Determination of Isotopic Variations of Zinc in the Biogenic Fraction of Marine Sediments: A Potential Tool for Paleoproductivity Reconstruction

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Productivity is an important component in the climate system because it accounts for the partitioning of CO₂ between ocean and atmosphere by the mechanism of the 'biological pump'. It is now admitted that trace metals play an important role in biological cycles. For instance, Zn is, used in the enzymatic carbonic anhydrase reaction to convert HCO₃⁻ to CO₂. Considering that biological activity preferentially affects chemical bounds of lighter isotopes, a fractionation of Zn isotopes is likely to occur. The amplitude of this fractionation will be related to the biological activity in the surface water. Therefore determination of isotopic Zn variations could potentially be used as a paleo-productivity proxy.

We have investigated a new method to analyze the isotopic variations of Zn which are linked with the biological activity, by analyzing the carbonate fraction in a sample of approximately 70 mg of bulk sediment, using MC-ICP-MS (Plasma 54). The method we developed is inspired from a foraminifer cleaning procedure previously proposed by Boyle & Keigwin [1]. The entire procedure is run under a laminar flow hood to avoid external contamination. It consists of several water rinses and a methanol rinse to remove the small particulate fraction of the sediment, mostly clays, and the salt coming from pore water. Then, organic matter is destroyed with an oxidizing step, which is followed by a reduction step, notably to reduce iron hydroxides. Finally, the carbonate fraction is dissolved in 1N acetic acid, which was previously purified twice on an anionic resin to remove the Zn coming from the acid. For the chemical extraction of Zn from the biogenic fraction and the mass spectrometry procedure we used the method published by Marechal et al. [2].

First results on core MD97-2138 (1.42N, 146.24W, 1900 m water depth) from the Western Pacific Warm Pool show ⁶⁶Zn variations ranging from 0.08‰ to 0.25‰, which is much greater than the overall external precision estimated to be 0.04‰ (2σ). Values from the last glacial period (average of 0.14‰) are lower than Holocene values (average 0.19‰). Two values at the transition between isotopic stages 5 and 4 show the same trend with a decrease of the ⁶⁶Zn signal, from 0.27‰ to 0.19‰. ⁶⁶Zn variations

have been previously inferred to be due to variability in the amplitude of the seasonal productivity [3]. However, the studied core is located in a region characterized by low seasonal amplitudes. Therefore if this low seasonal contrast persists through it is likely that the ⁶⁶Zn variations we observe are a results of variability in productivity. These preliminary observations are in good agreement with the (²³¹Pa/²³⁰Th)_{ss,0} measurements in core MD97 2138, which could be taken as a productivity proxy [4] in the studied area [5].

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CC04 : WEpm38 : G3

Reconstructing Paleosalinities of the Baltic Sea from Oxygen Isotopic Composition of Authigenic Mn-Carbonates: Applicability and Limitation

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The oxygen isotopic composition of Baltic Sea waters shows a linear relationship with its salinity content (Fröhlich et al 1988). Paleosalinities were calculated from ¹⁸O values of authigenic Mn-carbonates formed syndimentary at the sediment surface during deepwater renewal. Calculated paleosalinities from Mn-carbonates, which have formed during the last 100 years, vary from 14 to 19 PSU, which is significantly higher compared to about 13 PSU measured by oceanographers within this time period. This difference is too large to be accepted for paleoreconstructions and the applicability of ¹⁸O values in Mn-carbonates as a quantitative paleoproxy becomes uncertain. Based on isotopic mass balance calculations, we suggest that the initial oxygen isotopic composition of water (¹⁸O = -5.4 ‰ VSMOW) was modified during Mn-reduction, when MnO₂ with ¹⁸O of +8.9 ‰ (VSMOW) released oxygen enriched in ¹⁸O into the anoxic porewaters of the uppermost sediment column. Mn-carbonates that formed in these waters display heavier ¹⁸O values as expected solely from the initial water composition. This explains the discrepancy between the calculated paleosalinities and the oceanographic observations and shows that deepwater renewal processes do not fully control the oxygen isotopic signature of authigenic Mn-carbonates. In the Baltic, the effect of Mn-reduction even exceeds the modification of the oxygen isotopic composition of the water by deepwater renewal processes.

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Wednesday PO Session

CC04 : WEpo01 : PO

Artemisia as a Climatic Proxy? Morphometry of Selected Artemisia Species Pollen Grains (REM- and Spectral Confocal Microscopy Study)

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Plant/plant cover is a body sensitive to a complex of conditions. Out of all, the climatic conditions play a major part. Based on this premise, studies on vegetation pattern shifts in geological time are used as a helpful tool able to reflect the palaeoclimate shifts/conditions. Palaeo-climatic interpretations/reconstructions are based on comparison with climatic requirements of 'nearest living analogs'. The taxonomical level of species of modern plant is taking in consideration.

A great deal of palaeo-vegetation studies are carried out using pollen grain analysis. Taxonomical level of identifications of fossil pollen grains reach generally genus level and seldom species level. Therefore, the following palaeoclimate interpretation/reconstruction - using either comparison with "nearest living analog" climatic requirements of species (comparison proceed on unequal level), or the range of climatic requirements of whole genus (lac of precision) - may lead to some mis-interpretation.

Poster presented here shows a study on Artemisia pollen group. The scientific issues stem from the point, that Artemisia abundances in pollen diagrams are used as an indicator/proxy of glacial phasis (Plio-Pleistocene); this can be correct for west mediterranean/nord european regions (Zagwijn, 1960, Suc et al.1995), but the studies located in east Mediterranean yield the Artemisia pollen abundances coeval with interglacial phasis (Cheddadi and Rosignol-Strick, 1995, Subally et al., 1999). This discrepancy arouses our attention to study morphological features of Artemisia pollen grains with connection to ecological requirement of Artemisia plants. The aim of study is to discriminate at means two morphological pollen groups linked to ecological requirements. Results of Raster Electron Microscopy and Spectral Confocal Microscopy studies applied on 20 Artemisia species will be illustrate. Although the review of ecological conditions of representative Maghrebian Artemisia species shows large ranges of temperature and humidity, the pollens of Artemisia species show only soft differences in their pollen morphology. Therefore the palaeoclimatic interpretations based only on Artemisia s.l. abundances in pollen diagrams require caution and cannot be regarded as an a priori climate hallmark.

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CC04 : WEpo02 : PO

First Results on the Miocene Palaeoaltitude of Southern Tibet using the CLAMP Palaeoclimate Proxy

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Over 400 leaf fossils from two Late Miocene (12 Ma) lake sequences were recovered from the Namling Basin near the settlement of Wang Dui in south central Tibet. The sites are separated by 300 m of vertical distance and the lower one is at an altitude of 4.3 Km. From these specimens 35 leaf morphotypes (species) were identified and scored for the Climate Leaf Analysis Multivariate Program (CLAMP). This technique quantifies the physiognomy of woody dicotyledonous angiosperm leaves in terms of a range of thermal and hydrological climate parameters such as mean annual temperature (MAT), warm month mean temperature, and enthalpy. 31 leaf character states were scored and analysed using three modern comparison datasets: 103, 145 and 173 sites. Climate vectors were positioned in axes 1-4 space which gave a standard deviation (σ) of residuals about the second order polynomial regression for MAT of 1.1°C for the 103 dataset and 1.73°C for the 173 dataset. This is a marked improvement over previous regressions in 2D space.

Using estimates for the Miocene lapse rates and sea level yields an altitude of 2.8 km \pm 700 m (2 σ) with the 173 set and 2.6 km \pm 470 with the 103 data. Enthalpy-based altitude estimates are virtually the same for both datasets and indicate an altitude of 2.9 km \pm 100 m.

These results suggest this part of Tibet has risen approximately 1.5 km in the last 12 Ma compared to only 3 km in the previous 35-40 Ma. Such an acceleration in uplift is consistent with models of lithospheric detachment.

CC04 : WEpo03 : PO

Lake-Level of Closed Basins as a Proxy for Past Atmospheric Changes- Seismic Stratigraphy of Lago Cardiel, (49°S, Argentina)

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Lake level fluctuations of closed basins, as demonstrated in the study by a lake in Southern Patagonia, is a useful proxy to reconstruct the evaporation/precipitation ratio in former times. This ratio is a crucial element in palaeoclimatology to constrain earlier atmospheric circulation patterns. In the past, the southern part of South America has been affected several times by changes in the strength and the latitudinal extent of the Southern Westerlies - the main moisture source in this area. Our study site, Lago Cardiel (49°S), is a hydrologically closed, deep lake, located within the modern track of the Southern Westerlies. Therefore, it provides a unique opportunity to reconstruct past environmental conditions. Old shoreline deposits have been dated in previous studies constraining time periods of wetter conditions. However, a complete record with lower lake-level than modern can only be recognized with subaqueous geology. A seismic survey with a high-resolution 3.5 kHz single-channel, as well as a stronger boomer source, permits the partitioning of the sedimentary record into 6 major seismic sequences. The paleowater depth can be reconstructed according to the sequence geometries. A

preliminary age model was obtained by combining AMS C-14 and tephrochronology in a series of long cores. An unconformity at the top of the lowermost seismic sequence implies that a total desiccation of the basin likely occurred around 21,000 years B.P. A shallow, playa-like lake with variable water depth probably persisted until 11,220 ¹⁴C yr. B.P., at which time the lake was again desiccated. These dry conditions indicate a weakening of the hydrologic cycle that promoted enhanced dust transport to the Atlantic sector of the Southern Ocean and Antarctica during the Late Glacial Maximum. The early Holocene was characterized by a rapid and massive lake level rise of at least 80 m. A shoreline 55 m higher than present, previously dated around 9,500 years. B.P., suggests a total lake level rise of over 135 m within a few hundred years. No seismic evidence points towards any significant drop in lake-level below the modern shoreline during the entire Holocene. The occurrence of drift-deposits since the Mid-Holocene, however, indicates the onset of a strong circular current caused by increasing wind stress. The ongoing multidisciplinary analysis of the sedimentary cores may further identify small-scale changes and, combined with water balance modeling, paleoclimatic conditions can be quantitatively reconstructed.

CC04 : WEpo04 : PO

Stable Isotopic and Geochemical Proxies for the Palaeoenvironment of Organic Rich Eocene Maar Lake Sediments

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The Eocene Maar lake sediments of Eckfeld (Rhemish massif, Germany) are a valuable source of information about the palaeoecological situation of a 44-45 Ma old Eocene Maar lake and its environment. The well preserved laminated organic rich sediments were formed under subtropical conditions. Samples were taken from a drilling core and from an excavation site where parts of the lake sediments are exposed to the surface. Because of the complexity of the lake system a multi-proxy approach is used concentrating on the stable isotopic composition of siderite, of the organic material and of diatomaceous silica. Additionally the amount of total organic carbon and total nitrogen of the organic matter was determined. For selected samples hydrogen and oxygen indices were measured using Rock-Eval pyrolysis.

The stable carbon isotopic composition of siderite can be used as an indicator for the extent of methanogenesis at the sediment/water boundary layer. A trend towards higher $\delta^{13}\text{C}$ -values of siderite can be explained by the development of meromictic conditions within the lake, leading to permanent anaerobic conditions at the sediment/water boundary layer accompanied by methanogenesis. Variations in $\delta^{18}\text{O}$ -values of siderite reflect changes in the ratio of freshwater input to evaporation (Bahrig, 1989). Interpretation of the $\delta^{18}\text{O}$ -values is complicated by the stratified water column of the lake. The stable isotopic composition of the organic material ($\delta^{13}\text{C}$) and its C/N ratio provide information about the origin of the biomass. Although the signal might be influenced by various processes taking place within the lake, e.g. CO₂-recycling and variations in bioproductivity (Freeman et al., 1990), the important role of allochthonous land plant input becomes obvious.

The oxygen isotopic fractionation between the SiO₂ of the diatom frustules and the lake water is temperature dependent. Therefore, the attempt was made to gain information about the temperature variations of the lake water by determining the $\delta^{18}\text{O}$ -values of separated diatom-frustules (Labeyrie et al., 1982). Certain assumptions had to be made to calculate a temperature variation curve. The validity of the assumptions will have to be checked in the future to improve the reliability of the method.

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CC04 : WEpo05 : PO

Use of Isotopic Determinations from Brachiopod Shells as Environmental Indicators

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The shells of fossil brachiopods have been used extensively as environmental indicators using stable isotope determinations (Lowenstam, 1961, Veizer et al. 1986, Marshall & Middleton, 1990). This popularity stems from the fact that the phylum has a long and diverse geological history and because the majority of brachiopod species have shells composed of low-magnesium calcite, which is stable over geological timescales. A major assumption underlying such an application is that brachiopod biominerals are invariably deposited in isotopic equilibrium with the surrounding seawater, and that the isotopic measurements from fossils are therefore useful environmental indicators. However, certain parts of the brachiopod shell show pronounced vital effects in stable oxygen and carbon isotope composition (Carpenter & Lohmann, 1995). This phenomenon is particularly noticeable in the thin outermost primary layer of the shell, and in specialised parts of the secondary shell layer that make up muscle attachment areas and various internal processes that continue to grow throughout the life of the organism. Recent investigations at Glasgow have also revealed that there are also pronounced inter-specimen and well as intra-specimen variations in the oxygen isotopic composition of brachiopod shells from the same locality.

This study aims to investigate the stable oxygen and carbon isotope signals from a range of modern and fossil brachiopod shells from a variety of environments to assess how accurate they are as recorders of the isotopic composition of seawater. Brachiopods with different types of skeletal ultrastructure are being investigated to determine whether different biomineralisation regimes have any effect on isotopic composition. In the first instance, the variation in isotopic signals from different parts of the shell of *Neothyris lenticularis* has been investigated. The means of sample preparation was investigated to identify how sample preparation influences isotopic ratios measured. Samples from specimens of *N. lenticularis*, collected in New Zealand, were prepared for isotopic measurements using a low speed drill with a dental burr and scraping using dental tools. The isotopic composition of samples extracted by these two methods, from various regions of the shell, was determined. In each case samples were divided with half the material plasma ashed to destroy organic material. Preliminary results indicate that the methods of extraction used had no significant effect. However, significant differences were recorded between the plasma ashed and non-plasma ashed samples with significantly lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values recorded for plasma ashed samples. Variations in the isotope composition in different regions of the shell occurs with lower values of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in calcite from the primary layer, muscle attachment areas and cardinal process in comparison to non-specialised secondary layer calcite, tooth and pedicle opening areas.

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CC04 : WEpo06 : PO

Tree Ring Indicators of Climate in Northern Eurasia

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The stable carbon isotope ratios over a period of 100 years from 10 oak trees from two sites with different hydrological conditions (one 'wet', one 'dry') in Southwest Finland and in East Anglia, U.K., were compared to local climatic parameters.

We have measured stable carbon isotope ratios in the late wood of 100 consecutive annual rings in oak trees growing under two different hydrological conditions (one 'wet', one 'dry') in both Southwest Finland and in East Anglia, U.K. At each of the four locations, five oak trees were used to construct a stable isotope time series, which was then compared with local climatic parameters.

Significant correlations were found between $\delta^{13}\text{C}$ and relative humidity, temperature and precipitation for both wet and dry sites at both geographical locations. This indicates that oak trees from wet and dry sites in Southwest Finland and East Anglia can be used for palaeoclimatic reconstruction. No significant statistical difference was found between isotope/climate correlations for the wet and dry sites. This indicates that trees from sites with different hydrological conditions respond in the same way to climate. We also found no statistical difference in the isotope/climate relationship between the two geographical locations. Thus, trees from two distinct geographical locations are shown to respond in the same way to climatic parameters.

These findings have important implications for palaeoclimatic reconstruction as site hydrology and geographical location may have little impact on the relationship between isotope ratios and climate. Site specific considerations may therefore be of limited concern in site selection for stable isotope dendroclimatic studies. This is important for the reconstruction of longer isotope time series, where the exact provenance of the timber may be unknown.

CC04 : WEpo07 : PO

The Study of Trace Metals in Modern Marine Sediments to Refine their use as Proxies in Palaeoceanography

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In order to understand the relationship between authigenic precipitation of U, Mo, Zn, and Cd and the properties of marine environment, we have studied the vertical distribution of these metals and the major redox species (oxygen, nitrate, manganese, reactive iron, sulfate, carbon and sulfur) in modern sediments. We have sampled four sites from 150 to 2800 m depth in the Bay of Biscay. In the shallowest stations, where sediments are highly bioturbated, organic carbon levels are higher than 2% and sulfide minerals are abundant. In the deepest stations, sediments are much less bioturbated, and organic carbon levels are lower. In all sites, early diagenesis reactions follow the well established depth sequence of redox reactions, based on the bacterially mediated oxidation of organic matter. Authigenic U and Mo were successfully extracted by an ascorbate solution. Mo is associated with Mn-oxides in the oxic part of the cores. In the anoxic layer of the sediment, Mo precipitates as a detectable authigenic phase only when sulfide minerals are present, i.e., when the sulfatoreduction process becomes important. In anoxic sediment, Cd and Zn enrichment is a good tracer of sulfide production. Uranium precipitates at the depth of reactive iron (III)

reduction. The concentrations we measured agree with values calculated using estimated accumulation rates and a model of diffusive flux of dissolved U between bottom water and the depth where iron-oxides are reduced. Authigenic U concentrations appears to give informations about this depth. Bioturbation induces a vertical (temporal) shifting between the sedimentary recording of trace metals and the time of the formation.

CC04 : WEpo08 : PO

Time-Lags Inferred by Early Diagenesis: Tests with a Numerical Model of U, C_{org} and Al Burial to Simulate the Paleooceanographic Time Series

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Different signals, as trace and major elements, isotopes, and microfossils, are commonly considered as synchronous at a given level of a sedimentary record. However, in modern sediment, it is obvious that the uptake of compounds sensitive to redox conditions like Mo, U and Re takes place a few centimeters below the sediment-water interface. Therefore, it is likely that the dating scales of these signals might be different of signals derived from sedimentation of conservative particles (Al, microfossils). In order to improve our understanding of this phenomenon, we have constructed a numerical model of organic carbon, aluminium and uranium burial at non-steady state based on the widely used advection-diffusion-reaction equation. The three species are defined by distinct behaviours in the sedimentary system. The aluminium is a conservative species, the organic carbon is a non-conservative species degraded in superficial sediment and the uranium is a species affected by redox conditions. Numerical results clearly demonstrate the importance of a dynamic description of sediment. By introducing a simultaneous variation of incoming fluxes of C_{org} and Al, geochemical profiles of Al, C_{org} and U clearly show separate distributions after burial. Each species record the synchronous variation of the incoming fluxes, but the position in the sedimentary pile of the recording differs from a species to another. We also show that bioturbation smoothes the variation with different amplitudes depending on the considered element. The model presented in this study provides a useful tool to better understand the distributions of paleoceanographic signals.

CC04 : WEpo09 : PO

Temporal Evolution and Origin of Recent Atmospheric Lead Fall-Out over French Alps: Constraints from Lead Concentration and Isotopic Ratio from two Lake Sediment Records

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The concentrations and isotopic ratios of lead were analysed in two ²¹⁰Pb-dated sediment cores from two different environments : lakes Le Bourget and Anterne (French Alps), in order to build a reliable record of the atmospheric lead pollution, at least on a regional scale, over the last two centuries. The temporal evolution of lead concentration in the two remote records reveals excellent agreement, with notably two peaks in concentration at 1905 and 1970 AD. In both records, the decrease in concentrations after the 70's must be attributed to petroleum crisis. The abrupt decrease recorded in both lakes during the 90's is probably due to growing use of unleaded gasoline. Isotopic ratios validate this hypothesis : Pb concentration evolves clearly in an opposite way with ²⁰⁶Pb/²⁰⁷Pb ratio, marking thus the anthropogenic influence on lead atmospheric fluxes. The good timing agreement of both lead concentration curves is an additional argument to validate the age-depth models used and thus the contamination chronology proposed. Further, if identified in other sedimentary records, the peaks in lead concentration of 1905 and 1970 AD could be used as chronostratigraphic marks. The comparison of the lead concentration chronology with industrial data situates the maximum of contamination five years before the maximum use of lead in gasoline in Europe, but is contemporaneous with the maximum use in the USA (Nriagu, 1989). So, the global use of lead in gasoline seems to drive lead contamination of the environment over French Alps and probably thus over the western European border.

Nriagu JO, *Nature*, **338**, 47-49, (1989).

