



FORAMS 2006

Foraminifera And Trace Metals

Chaired by Frans Jorissen and G. J. Reichart

Trace metals incorporated in the calcium carbonate of foraminiferal shells are becoming increasingly popular for the reconstruction of past environments. Past sea water temperature, carbonate chemistry, nutrient levels and possibly salinity are all reflected by differences in trace metals to calcium ratios. Although it is generally assumed that the incorporation of these trace metals follows thermodynamic relations known from inorganic calcium carbonate precipitation experiments, large offsets are commonly observed for foraminiferal biomineralisation. The mechanisms responsible for these offsets are, however, not or poorly known. Within this session we would like to invite contributions specifically addressing this lack in our current understanding. Particular questions to be addressed are the role of 1) biomineralisation and so-called vital effects, 2) ecological niches, 3) diagenetic overprinting in trace element partitioning. Furthermore we want to specifically invite contributions in which controlled foraminiferal culturing and/or new analytical techniques are applied for unraveling factors influencing foraminiferal biomineralisation and trace metal uptake.



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The use of benthic foraminifera as proxy for dissolved metals in Haifa Bay seawater, Israel

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The water of Haifa Bay (Israeli Mediterranean coast) are exposed to heavy metals introduced from point (Qishon and Na'aman Rivers) and diffusive sources. The dissolved heavy metals concentrations in the bay and along the coast are poorly known due to their extremely low concentrations and analytical complexity. Thus it is difficult to establish a routine long-term monitoring program and assess water quality in terms of ecological environmental criteria. The purpose of this study is to examine the use of metal concentrations in the tests of *Amphistegina lobifera* as proxy for variations of dissolved metal concentrations in seawater. The working hypothesis in this study is that benthic foraminifera precipitate their tests directly from sea water, reflecting a time integrated dissolved trace element concentration in ambient sea water. The tests precipitated by the benthic foraminifera establish an equilibrium state with the ambient seawater represented by a metal explicit distribution coefficient. The analysis of foraminiferal tests follows a cleaning procedure that removes detritus and mainly the inner cytoplasm. *Amphistegina lobifera*, symbiont-bearing larger foraminifera, lives in Haifa Bay in large numbers on rocky substrate. It reproduces 1-2 times a year with juveniles (~0.4 mg, on avg.) dominating during summer and adults (~1.5 mg, on avg.) during late fall to winter. Living specimens were sampled at two stations at ~10 m water depth and surface seawater were collected at the same time from 6 representative stations in Haifa Bay, in 8 bi-monthly cruises during 2003-04. Most of the dissolved heavy metals are enriched in Haifa Bay seawater by a factor of 3-10 compared with a control clean station located ~100 km offshore the Israeli Mediterranean coast. Mg concentrations in sea water vary seasonally while some heavy metal concentrations (Ni, Cd) are unrelated to seasonality and probably reflect short term influx of metals from land-base sources. All the heavy metals, determined by ICP-MS, were detected in the tests of *A. lobifera*. The variations of the minor (Mg, Sr, Li, B) elements ratios in *A. lobifera* seems

to be related to variations in its growth rates. The variations of some of the trace element ratios such as Ni, Cd and Pb in *Amphistegina* seems to be effected mainly by the ambient seawater fluctuation despite the differences in time-scale represented by each of these matrices, sporadic – sea water, vs. a prolonged growth period - foraminiferal test. A better understanding of the foraminiferal life cycle and the incorporation of HM in their tests will enable the use of foraminifera in assessing short and long-term trends of HM concentrations in coastal seawater.



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Influence of population dynamics of benthic foraminiferal Mg/Ca and Sr/Ca

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Interindividual and interspecies variability in foraminiferal shell-calcite Mg/Ca is well documented in field samples. Furthermore, foraminifera cultured under physicochemically-stable conditions had similarly large interindividual variability, which was an order of magnitude larger than the analytical precision. Sources of proxy signature variability in field samples are attributed to microhabitat and yet not fully understood vital effects. Microhabitat effects for conservative seawater constituents (Mg, Sr, and Ca), but may be significant for other environmental proxies associated with biomineralization (e.g., total alkalinity). Live Cell Tracker Green (CMFDA) labeled core-top benthic foraminifera are presented along with corresponding abundances and species diversities from cores collected in 2001 and 2005 from the shallow-slope environ of the Charleston Bump (31° 55.24'N, 79° 11.29'W; ~220m water depth; temp range: 9.4-11.2°C; calcite saturation state: 2.29-2.73). Species richness and diversity generally declined from 2001 to 2005 (2001, ~50 spp.; 2005, <25 spp.); however, overall total abundance increased in the most recent study year (2001, n=350, 6.1 individuals/cc; 2005, n>1500, ~30 individuals/cc). The species diversity of the 2005 core-top sample was dominated by *Chilostomella* sp., *Bulimina* sp., *Stainforthia* sp., *Cassidulina* sp., *Fursenkoina* sp., *Uvigerina* spp., *Bolivina* spp., *Nonionella* sp., *Triloculina* sp., and *Cibicides* spp., listed in descending abundance order. *U. peregrina* were present in both years; additionally, two species of *Uvigerina* were present in 2005 that were not present in 2001. In contrast, there was a single dominant species of *Nonionella* sp. in 2005 compared to multiple species from the 2001 study year. Two species were consistently found encased in sediment layer that could be easily removed,

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C. oolina and *N. turgida*. Mg/Ca and Sr/Ca signatures were investigated to test if patchy population densities alter these element/calcium ratios, potentially confounding paleoproxy interpretations. Controlled cultures inoculated with benthic foraminifera collected from Charleston Bump are presented for comparisons to field values.

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Using intermediate or deep-dwelling foraminifera in paleoceanography

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Understanding climate changes requires developing an improved understanding in past as well as present temperature-driven variations in ocean circulation. Hydrographic properties of surface and bottom ocean have been the focus of many paleoceanography studies, yet few of these have focused on the water column's vertical structure. Yet this structure is important to the climate system because most of the ocean's heat content is stored in the top few 100's of meters. Past changes in oceanic circulation must have been accompanied by changes in this vertical structure of the water and had a corresponding impact on climate. Deep-dwelling planktonic foraminifera from various water depths provide a proxy for such changes in the deep ocean. Here we study subsurface waters in the North Atlantic Ocean, which are strongly influenced by heat transport.

We measured oxygen isotopic composition and trace elements on five selected species: *Globigerina bulloides*, *Globigerinoides ruber*, *Pulleniatina obliquiloculata*, *Globorotalia inflata* and *Globorotalia truncatulinoides* (separatively dextral and sinistral forms). This species prosper in different seasons and live at different depths. For example *G. ruber* lives during summer close to the surface, whereas *G. truncatulinoides* typically is found in winter up to 500 m. By analysing these different species we attempt to reconstruct the thermal and salinity structure of the water above and in the thermocline.

To use these proxies correctly, we made a calibration for each species by analysing modern North Atlantic core-tops. Considering the sparse number of studies available, we have assumed the isotopic equilibrium, calculating isotopic temperature according to the paleotemperature equation. Measuring trace elements in foraminiferal calcite permits us to calculate the Mg/Ca ratio. According to thermodynamics, Temperature controls Mg incorporation into inorganic calcite crystals. There is increasing evidence suggesting that foraminiferal tests follows this law and then Mg/Ca ratio can be used as a paleothermometry tool for foraminiferal habitats. Thus our calibration associates trace elements ratios from core tops to isotopic temperatures.

These new Mg/Ca calibrations for surface-dwelling species are close to previously published studies. Our Mg/Ca ratio calibrations for *G. inflata*, *G. truncatulinoides* and *P. obliquiloculata* yield results that are similar to those predicted by the thermodynamic relationship with different coefficients for each species. Although imperfect, our calibrations for deep-dwelling species are the first to extend over such a large temperature range.

Currently, we are refining this calibration by sediment analysis that should yield a better understanding of the diagenetic processes that affect the Mg/Ca ratio during fossilisation in the sediment.

We have applied our strategy to two cores:

- CHO288-54 located south of Cuba;
- and MD99-2203 located just offshore of Cape Hatteras.

These two cores are influenced by warm water transport coming from the tropical warm pool. Comparison between records for *G. ruber* and *P. obliquiloculata* in the CHO288-54 core suggest a strong modification of the water column structure that may be related to shifts in the position of the Inter-tropical Convergence Zone (ITCZ). The MD99-2203 core is just below the separation point of the Gulf Stream from the east coast of the United States. Changes in water column structure deduced from comparison of this records from *G. ruber*, *G. truncatulinoides* dextral, and *P. obliquiloculata* in this core are linked to latitudinal shifts in the Gulf Stream. In the two cores, deep-dwelling foraminifera reveal a major change around 8000 years BP.



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Trace elements distribution in foraminiferal shells from a biomineralization perspective

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Trace elements in foraminiferal shells (e.g. Mg, Cd, Ba) are widely used in paleoceanographic reconstructions. Yet, the biomineralization processes strongly modify the concentration of these metals, within and between species and hence the reliability of these paleoceanographic proxies is reduced. Recent advances in understanding foraminiferal calcification provide a framework for mechanistic understanding of trace element variability that is associated with the biomineralization process. In parallel micro-analytical techniques (i.e. SIMS, LA-ICP-MS, nano-SIMS, EPMA and others), reveal large intra-shell variability associated with the biomineralization process. This information, together with *in situ* and laboratory proxy calibration experiments, help to formulate a conceptual model for trace elements incorporation into foraminiferal shells.

Perforate (calclitic radial) foraminifera precipitate two types of CaCO_3 that are completely different in their mode of formation and in their chemical composition. Primary calcite is precipitated in close association with the organic matrix, and is enriched in Mg, S, Na and possibly other trace elements. Secondary calcite is precipitated on both sides of the primary calcite, mainly by a process of seawater vacuolization. The secondary calcite, (roughly 95 % of the calcite in the shell), which displays the typical calclitic-radial texture, is composed of low-Mg calcite with low concentrations of S, Na, and other trace elements. The proportion between the two calcite types may change with environmental parameters (e.g. temperature). Ca and other trace elements may reach the calcification site in one of two pathways or their combinations:

- 1) Via seawater vacuolization which represent the main pathway in the perforate foraminifera.
- 2) By various membrane transport mechanisms that involve ion specific channels and pumps (probably the main mechanism in imperforate foraminifera).

The vacuolization pathway involves the formation of large seawater vacuoles that become alkaline ($\text{pH} > 9$) and have higher then seawater inorganic carbon concentration. The vacuolated seawater which may be further modified

(possibly to increase Ca and lower Mg), are the main supply of ions to the privileged calcification space. Other vacuoles may exocytose the depleted (in Ca^{2+} and CO_3^{2-}) solutions in another region of the cell membrane. At the crystal formation site, other phenomena which are associated with precipitation from a closed reservoir, the presence of various organic molecules and the precipitation of unstable (amorphous) phases may further modify the concentrations of the trace elements. In the privileged calcification space, the influence of the organism on the crystals chemistry may be controlled by various other mechanisms including channels, pumps and complexing agents. In the case of Mg^{2+} it seems that the organism removes this ion from the calcification site. This causes large variability in the Mg content of different species in addition to the effect of temperature. The removal of Mg in planktonic foraminifera and in deep benthic foraminifera (both are most important for paleoceanographic reconstructions), may turn out to be the most energy demanding process during their calcification process.



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Assessing the influence of diagenesis and salinity on a Pliocene Mg/Ca and $\delta^{18}\text{O}$ record from the Caribbean

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We present Mg/Ca and $\delta^{18}\text{O}$ data from Caribbean ODP Site 1000 for the Pliocene time interval 4.5-3.8 Ma. Analyses were performed on the planktonic foraminifer *Globigerinoides sacculifer* in order to reconstruct changes in sea surface temperature (SST) and sea surface salinity (SSS) due to the progressive closure of the Panamanian Gateway. Mg/Ca ratios at central Caribbean Site 1000 increase toward maximum values of ~ 7 mmol/mol, translating into $\text{SST}_{\text{Mg/Ca}}$ of $\sim 35^\circ\text{C}$ with amplitudes of $\sim 5^\circ\text{C}$. $\delta^{18}\text{O}$ values also show an increasing trend with amplitudes increasing to $\sim 1.4\text{‰}$. Mg/Ca and $\delta^{18}\text{O}$ are positively correlated with each other following precessional cyclicity, suggesting that $\delta^{18}\text{O}$ is dominated by changes in salinity.

Since SSTs up to 35°C are not realistic for open-ocean conditions, the Mg/Ca ratios are probably not just representing a primary paleoceanographical signal but are influenced by other factors as well. The positive correlation with $\delta^{18}\text{O}$, the large amplitudes in $\delta^{18}\text{O}$, and cultivating experiments on the influence of salinity on Mg/Ca imply that the extreme Mg/Ca ratios of Site 1000 might have been altered by large salinity variations.

However, the studied time interval is also characterized by precessional cycles in the occurrence of the coccolithophorid *Florisphaera profunda*, which is a proxy for productivity, and in aragonite content. Minima in aragonite correlate with maxima in Mg/Ca and $\delta^{18}\text{O}$. This indicates that during periods with high productivity, aragonite dissolved within the sediment and might have reprecipitated

as diagenetic calcite. SEM analyses, indeed, show a crystalline overgrowth on the cleaned foraminiferal tests of those samples with extreme Mg/Ca ratios. Therefore, another possible solution for the unrealistic Mg/Ca ratios is a high-Mg diagenetic overprint. LA-ICP-MS was used to determine if the crystalline overgrowth can be held responsible for the high Mg/Ca ratios. The profiles, however, show that the Mg content of the crystalline overgrowth is not significantly higher than in the foraminiferal tests and, hence, did not contribute to the high Mg/Ca ratios. However, we do not exclude the possibility of other diagenetic processes, like diffusion or total recrystallization, to have altered the foraminiferal tests.

Alternatively, $\delta^{18}\text{O}$ records from several species from Site 1000 were compared with those from southern Caribbean Site 999, which is not affected by diagenesis. Comparison of $\delta^{18}\text{O}_{G. \text{sacculifer}}$ of Site 1000 with $\delta^{18}\text{O}_{G. \text{sacculifer}}$ from Site 999 shows that the large amplitudes and precessional cyclicality of Site 1000, concordant with the aragonite variability, are absent at Site 999, pointing to a diagenetic overprint. Nevertheless, these differences can also be explained by paleoceanographical variations. Arguments against diagenesis come from the comparison of the $\delta^{18}\text{O}$ records of the benthic foraminifer *Cibicidoides wuellerstorfi* and the deep dwelling planktonic foraminifer *Globorotalia crassaformis*. The *C. wuellerstorfi* records are similar to each other, showing obliquity variability, while the diagenetic signal would have introduced a precessional variability. The $\delta^{18}\text{O}$ records of *G. crassaformis* do show precessional variability at both sites, but the amplitudes are very weak in comparison with the $\delta^{18}\text{O}$ record of *G. sacculifer* at Site 1000.

In conclusion we state that at least part of the record of Site 1000 is altered by either salinity or diagenesis, but that although multiple approaches have been used, neither can give a conclusive explanation to the observed anomalous data. Hence, we argue that these data should be handled with care when interpreted paleoceanographically.



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Calibrating trace element incorporation in cultured benthic foraminifera using laser ablation ICP-MS

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Foraminiferal trace element based proxies rely on empirically determined relationships between partition coefficients and environmental variables. Calibration of foraminiferal trace element incorporation using controlled growth experiments makes it possible to vary a single parameter, keeping all others constant. A disadvantage of such experiments, however, is that analyses are restricted to either offspring generated during the experiments, or when using juveniles, by ignoring carbonate formed prior to the experiment. Benthic foraminifera are generally growing relatively slow, adding a single chamber to their test every few weeks. Here we present first results on single chamber calibration of Mg/Ca and Cu /Ca ratios. Specimens were kept at a various copper-concentrations and at different temperatures and salinities for two months. To monitor calcification, fluorexon was added to the culture-medium. This chemical is incorporated in the test of foraminifera during growth and under UV light shows which chambers were formed from the moment the fluorexon was added. After the incubation, craters of 80 micron were ablated in the newly formed calcite using an Excimer 193nm deep ultra violet laser (Lambda Physik) with Geolas optics. Laser ablation of calcite, especially the fragile tests of foraminifera, requires ablation at ultra violet wave lengths since higher wave lengths result in uncontrolled cleavage. A collision and reaction cell was used to give improved results by reducing spectral interferences on the minor isotopes of Ca. Single chambers were analyzed for their test carbonate Cu, Mg, and Sr concentrations. First results show the potential of this approach for calibrating benthic foraminiferal trace metal incorporation under controlled, experimental conditions.



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**Intra-shell variability of trace element distributions
in benthic foraminifera obtained by LA-ICP-MS**

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The trace and minor elemental compositions in foraminifera are established tools for reconstructing past water temperatures and water mass properties. Usually measurements represent averages of several (10-30) whole shells. Little attention has been paid to variations in the elemental composition within single shells. However, this can be important in cases where the elemental composition is partially a function of the ontogenetic stage, or where certain shell parts are preferentially lost in less than perfectly preserved material. Here we investigate the intra-shell variability of Mg/Ca, Sr/Ca, and Ba/Ca in the benthic foraminifer species *Cibicides wuellerstorfi* and *C. kullenbergi* from sediment core tops by using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Both species are frequently used for reconstructions of past bottom water conditions. For this study, elemental compositions were determined on single shells along a dense grid (spacing 80 μm by 80 μm) resulting in at least 60 measuring points per shell. The observed heterogeneity within single tests is significant with standard deviations of about 30% for Mg/Ca, 13% for Sr/Ca, and up to 100% for Ba/Ca. It is surprising that Mg/Ca which is thought to be mainly affected by water temperature revealed high ranges of up to 320% between lowest and highest values. Between neighbouring chambers and even within single chambers, the variability of trace element/Ca ratios is high as well. Although the trend is not continuous, mean trace element/Ca ratios tend to increase from juvenile chambers towards the final chamber. Highest values are observed in the vicinity of the shell edges, whereas the inner part is more homogeneous and is often characterized by lower values. Since patch-like chamber formation has been documented in cultured species, the observed variations of trace element/Ca ratios within single shells may be related to microenvironmental changes (e.g. pH, carbonate ion concentration) during calcification or changes in the rate of calcification. Nevertheless, values of Mg/Ca averaged from multiple spot measurements confirm that water temperature is the major factor controlling Mg uptake into foraminiferal shells.