Single foraminiferal test chemistry records the marine environment

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ABSTRACT

We applied laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS) as a new and precise technique for measuring trace elements in benthic foraminifera (*Hoeglundina elegans*). With this technique, trace element concentrations were accurately measured without the elaborate cleaning required in standard methods. Contaminated coatings are easily excluded during spatially resolved analysis. Application of this new technique allowed us to calibrate the trace elements incorporated in single tests of living (when sampled) benthic foraminifera to ambient seawater temperature (Mg and Sr) and redox conditions (Mn) for the first time. Incorporation of Ba showed a more complex pattern that cannot be explained by a direct correlation to water column concentration.

Keywords: benthic foraminifera, trace metals, marine geochemistry.

INTRODUCTION

Trace element incorporation into foraminiferal tests is controlled by physical and chemical conditions in the marine environment and can thus be used to reconstruct past changes in these conditions over time (Lea and Boyle, 1989; Lear et al., 2000; Rosenthal et al., 1997). In addition to field collection, culturing studies have greatly improved the reliability of seawater temperature and nutrient reconstructions from the relative abundance of trace metals in foraminiferal tests (Lea et al., 1999; Lea and Spero, 1992; Nurnberg et al., 1996). However, extensive chemical and/or physical cleaning steps are required in established techniques to remove organic and inorganic coatings before bulk analysis, because only the lattice-bound trace metals in $CaCO_3$ can be related to seawater chemistry and temperature (Boyle, 1981). In this study we avoid this problem by performing depth-resolved laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS) multiple trace metal analyses from single foraminiferal tests. Living (when sampled) benthic foraminifera (Rose Bengal stained) were analyzed from two contrasting areas, the Bay of Biscay and the northern Arabian Sea. This approach allowed the calibration of foraminiferal trace metal contents to a large range of in situ living conditions.

METHODS

Box (Netherlands Indian Ocean Programme, Arabian Sea) and multicorer (Oxybent cruises, Bay of Biscay) sediment cores were subsampled vertically by cutting the sediment into 0.25–1.0 cm slices. Foraminifera were preserved in 95% ethanol, living specimens identified by using Rose Bengal staining and picked from the 150–600 μm fraction. Only well-stained specimens, with all chambers (except for the last one) bright red or rose were used. All foraminifera were collected from the topmost centimeter of the sediment. Temperatures were extrapolated from nearby conductivity-temperature-depth (CTD) stations in the Arabian Sea and were taken from Maillard (1986) for the Bay of Biscay, together covering a temperature range from 2.5 to almost 13 °C. Oxygen penetration was measured in the Bay of Biscay sediments using microelectrodes. Mn was measured in pore- and bottom-water samples, extracted in an oxygen-free atmosphere.

Foraminifera were ablated using a deep-ultraviolet-wavelength laser (193 nm), which is essential for the reproducible ablation of the fragile tests, because carbonates do not absorb laser radiation well at higher wavelengths (Jackson et al., 1992) (Fig. 1). The system employs a Lambda Physik excimer laser with GeoLas 200Q optics. Ablation was performed in a helium atmosphere at a pulse repetition rate of 5 Hz with an energy density at the sample surface of 10 J·cm^{-2}. Ablation craters were 25 μm in diameter, and between 200 and 300 nm depth of material was removed per pulse. A typical 40 s analysis resulted in a total sampling volume of <100 ng. Ablated particles were measured with respect to time (and hence depth) using a quadrupole ICP-MS instrument (Micromass Platform ICP). Calibration was performed against U.S. National Institute of Standards and Technology SRM 612 glass using the concentration data of Pearce et al. (1997) with Ca as an internal standard. Calcium is ideal, because (1) the concentration is constant at 40 wt% in all foraminiferal tests and (2) direct comparisons can be made with trace metal to Ca ratios from wet-chemical studies. Interelemental fractionation (Mank and Mason, 1999) was insignificant at the low depth/diameter ratio of the ablation craters produced in this study. A collision and reac-
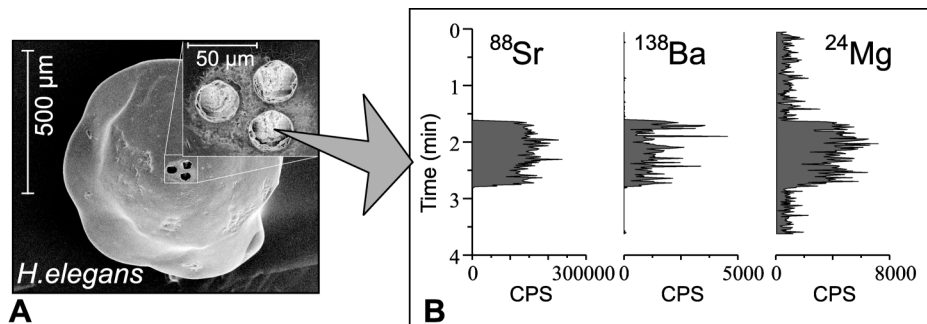

Figure 1. A: Scanning electron microscope image of *H. elegans* from Bay of Biscay (station OB I, 2755 m below sea surface) with ablation craters. Inset shows craters in detail. B: Time resolved laser-ablation inductively coupled plasma–mass spectrometry data; middle part (1.6–2.75 min) represents measurements during ablation. Varying response (counts per second, CPS) during ablation is caused by variable quantity of material removed by each laser pulse but is accounted for by normalization to Ca.

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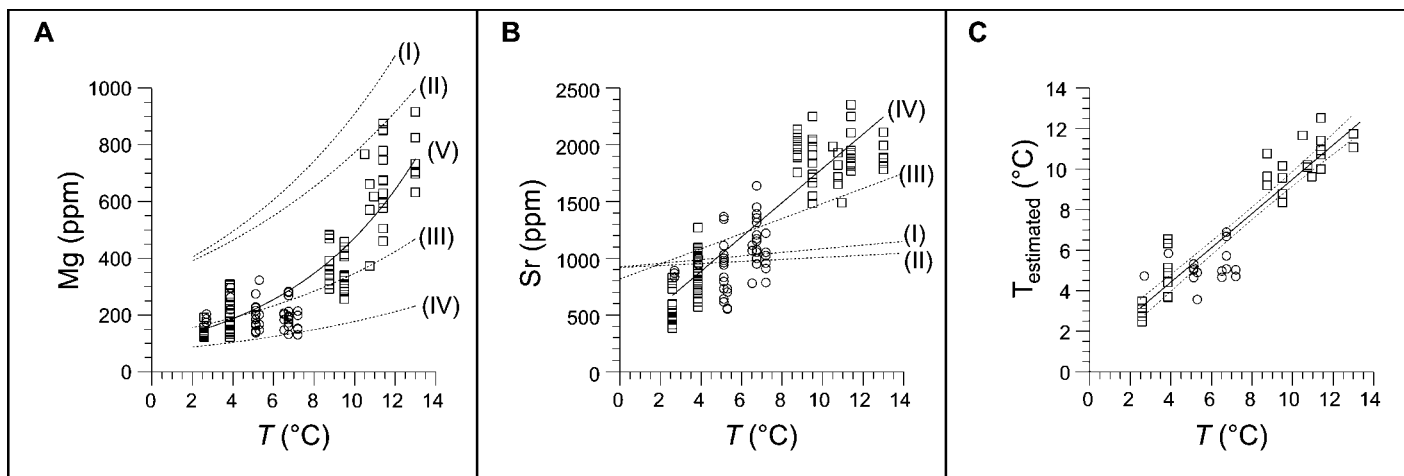
Figure 2. A: Foraminiferal Mg concentration for individual ablation craters vs. bottom-water temperature (*T*) for *H. elegans*. Circles—Arabian Sea; squares—Bay of Biscay. Dashed lines indicate earlier regressions for benthic foraminifer *C. floridanus* (I) by Rosenthal et al. (1997) and for planktonic foraminiferal species *O. universa* (II) and *G. bulloides* (III) by Lea et al. (1999) and *G. ruber* (IV) by Lea et al. (2000). Solid line represents best fit for *H. elegans* (V) (this study). B: Foraminiferal Sr concentration vs. bottom-water temperature for *H. elegans*. Symbols as in A. Dashed lines indicate earlier regressions for planktonic foraminiferal species *O. universa* (I) and *G. bulloides* (II) by Lea et al. (1999) and for two benthic foraminiferal species *C. wuellerstorfi* and *C. refulgens* (III) by Rathburn and DeDeckker (1997). Solid line represents best fit for *H. elegans* (IV) (this study). C: Estimated temperatures based on single foraminiferal tests on nonlinear multivariate regression of Sr and Mg vs. actual bottom-water temperature: $T = 2.54 \ln(0.0123\,[Mg]) + 0.003[Sr]$, where concentrations are in ppm. Dashed lines indicate 95% confidence limits for regression.

tion cell (discussed further in Mason and Kraan, 2002) was used to give improved results by reducing spectral interferences on the minor isotopes of Ca (^{42}Ca, ^{43}Ca, and ^{44}Ca). Multiple isotopes were used where possible to confirm accurate concentration determination (^{24}Mg, ^{26}Mg, ^{27}Al, ^{55}Mn, ^{88}Sr, ^{137}Ba, ^{138}Ba). Relative analytical errors, based on repeated analyses of pressed carbonate powders, were ±4% for Mg, ±2% for Sr, ±9% for Ba, and ±5% for Mn.

RESULTS AND DISCUSSION

Contamination from clay minerals, iron and manganese (hydr)oxide coatings, barite crystals, calcareous nannofossils, and organic material is often a major problem in foraminiferal trace element analysis. Most contamination is adhered (after the death of the organism) onto the outer surface of the tests, accumulates in pores, or forms distinct particles inside individual chambers (e.g., barite, pyrite). Rigorous purification procedures have been developed to remove such extraneous phases (Boyle, 1981; Lea and Boyle, 1993), which although effective are also extremely laborious. Analysis by LA-ICP-MS avoids contaminating phases during the analysis of single tests as coatings and material adhered to outside of the tests are rapidly removed. This component can be monitored and excluded by the simultaneous analyses of elements associated with such contamination (e.g., Al, Mn). Furthermore, pore-containing test sections could be avoided during laser ablation. *Hoeglundina elegans* is particularly suited for LA-ICP-MS because of its thick aragonitic test. Because elemental counting statistics improve with ab-

lation time (i.e., number of scans), the thick umbilical side was found to give better data than the thinner spiral side. After thorough investigation of depth profiles from every ablation crater, a broad interval was selected for concentration calculation for only the actual test carbonate. Aluminum was used to monitor surface contamination with clay particles, and Mn was used to avoid inclusion of secondary carbonate and manganese (hydr)oxides overgrowth in the concentration calculations.

Laser ablation samples successively deeper (and older) carbonate from the test wall with increasing analysis time. Because *H. elegans* constructs its test in such a way that newly added chambers embrace already existing chambers, progressively ablated carbonate belongs to sequentially older parts of the specimen. Changes in chemical composition during ablation may therefore relate to changes in trace elements built in during the organism's life. However, the ablation profiles for *H. elegans* are remarkably constant with depth. This result suggests that *H. elegans* prefers a stable environment throughout its life, but is difficult to confirm because precise data about the longevity of deep ocean benthic foraminiferal taxa do not exist. However, in view of the existing data on shallow-water taxa, which have a life span of one month to two years (Murray, 1991), and the rapid reproductive response of deep-sea taxa to phytodetritus deposition (Gooday, 1988), we speculate that *H. elegans* builds most of its test in a short time. For planktonic foraminifera, it has been shown that differences in calcification rates during different life stages influence the minor element and isotopic composition (Lohmann,

1995; Nurnberg et al., 1996). For *H. elegans* such changes in calcification rate, if present, did not appear to influence trace metal incorporation. However, an increase in Mg concentrations associated with gametogenesis cannot be excluded because we only analyzed living (when sampled) specimens.

Foraminiferal tests from the same superficial sediment samples show significant compositional differences (Figs. 2A and 2B). Because the specimens were alive during sample retrieval, these differences cannot be attributed to admixing of older specimens by bioturbation, or by the introduction of redistributed dead tests from upslope. Therefore, the observed interspecimen differences have to be explained either by (1) a response to short-term (i.e., within the life span and calcification period of the foraminifer) changes in bottom-water properties, (2) differences in microhabitat occupied during calcification, or (3) unknown biological factors. Large interspecimen differences in Ba and Mn (Fig. 3) suggest that the trace metal composition is influenced by the microhabitat.

Because Mg incorporation is essentially independent of salinity, it is becoming an increasingly important tool for reconstructing seawater temperatures (Lear et al., 2000; Nurnberg et al., 1996; Rosenthal et al., 1997). Both Mg and Sr show a strong correlation with bottom-water temperature (Fig. 2). The concentration of Mg increases exponentially, whereas Sr shows a linear relationship to temperature. Variability within tests, between individual ablation craters (average standard deviation 44 ppm for Mg, 90 ppm for Sr), is on the same order as the variability between tests
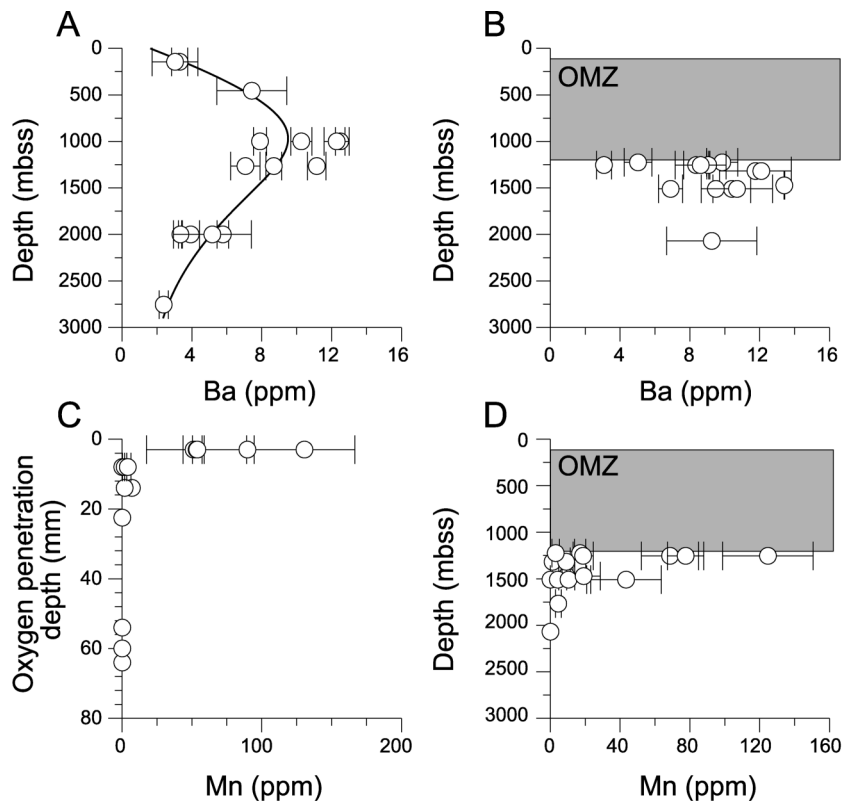
Figure 3. A and B: Profiles through water column (mbss—meters below sea surface) for *H. elegans* Ba from Bay of Biscay (A) and Arabian Sea (B) core tops. For Bay of Biscay, trend line has been plotted; in Arabian Sea diagram, position of local oxygen minimum zone (OMZ) is indicated. C and D: Mn concentrations in test carbonate, plotted against oxygen penetration depth (Bay of Biscay [C]) and water depth (Arabian Sea [D]). Position of local OMZ is indicated for Arabian Sea.

(average standard variability 60 ppm for Mg, 140 for Sr). The observed variability, however, is higher than can be explained by analytical error, suggesting that heterogeneity both within and between tests may set a limit to the accuracy of foraminiferal trace metal–based environmental reconstructions. Influence of growth rate on Sr and possibly Mg incorporation (Lorens, 1981) could explain differences between tests from the same location and between different parts of the test. Changes in growth rate over geological time reflecting environmental variability could therefore affect the accuracy of paleotemperature reconstructions.

Although *H. elegans* makes its test out of aragonite, this fact has no major influence on the Mg versus temperature relationship, which tightly fits between earlier calibrations of cultured calcitic planktonic foraminifera (Fig. 2A). Core-top calibrations of the calcitic benthic foraminifera *C. refulgens* and *C. wuellerstorfi* predict slightly higher Mg concentrations (Rathburn and DeDeckker, 1997). However, large variability in benthic foraminiferal Mg incorporation has been shown (Lear et al., 2000). Sr concentrations are also similar to those of cultured planktonic foraminifera, although Sr increases more rapidly with temperature (Fig. 2B). Core-top calibra-

tion of Sr for *C. refulgens* and *C. wuellerstorfi* (Rathburn and DeDeckker, 1997) shows a more moderate increase with temperature. Although Sr concentrations are similar to those found for calcitic tests, the relation to temperature may be fundamentally different. It has been suggested that variables other than temperature, such as pressure and growth rate (Lea et al., 1999), are factors for controlling Sr incorporation into calcite. The good correlation with temperature ($r^2 = 0.77$) in our results, better than that with depth ($r^2 = 0.65$), suggests that for *H. elegans* temperature has major control on the amount of Sr incorporated into the test.

The Mg and Sr concentrations were combined for a nonlinear regression (Fig. 2C). Estimated temperatures give a 95% confidence interval of 1.7 °C for a single foraminifer using the combined Arabian Sea and Bay of Biscay data set, and a 1.2 °C confidence interval if only the Bay of Biscay data set is used. The confidence range must be attributed mainly to natural variability, which is much larger than the analytical error. The reliability of the temperature estimates can be greatly improved by averaging analyses from multiple specimens.

The distribution of Ba in the ocean is similar to properties such as alkalinity and silica content (Lea and Boyle, 1989; Lea, 1993). Ba

is removed from surface waters through barite precipitation. Subsequently this barite is partially released again at the seafloor. Northwestern Atlantic seawater Ba profiles show a steady increase with depth (Chan et al., 1977). However, when plotting Ba concentrations for *H. elegans* recovered from the top sediment layer versus water depth, maximum Ba values are observed at intermediate depths in the Bay of Biscay. This offset indicates that factors other than water-column Ba are influencing Ba incorporation. Because the foraminifera were living when sampled, this change cannot be attributed to loss of Ba owing to preferential dissolution, as suggested for fossil *C. wuellerstorfi* (McCorkle et al., 1995). The strong decrease with depth suggests a pressure dependency for Ba incorporation into aragonite, although increased alkalinity with depth might be an influence. To separate such a depth effect, specimens from contrasting areas should be compared. Unfortunately, the foraminiferal Ba values from the Arabian Sea do not allow for such a comparison, owing to the relatively small depth transect, below the oxygen minimum zone.

We observed different Ba concentrations as a function of the living depth (in the sediment) of *H. elegans*. Foraminifera from the interval sampled closest to the sediment-water interface have average Ba values of 4.5 ppm (n = 12); at 0.25–0.5 cm foraminiferal Ba concentrations are 11.3 ppm (n = 12). This increase in Ba concentrations with depth in the sediment suggests higher pore-water Ba deeper in the sediment, probably owing to ongoing barite dissolution.

H. elegans is generally considered an oligotrophic taxon (e.g., Lutze and Coulbourn, 1984; Mackensen et al., 1995), living close to the sediment-water interface. Although often considered strictly epifaunal, a closer inspection of the data (e.g., Corliss, 1985; Jorissen et al., 1998) shows that some stained specimens also occur in slightly deeper (top 2 cm) sediment layers, a phenomenon that can be observed in all taxa considered epifaunal (Jorissen et al., 1998). This fact implies that only the lower Ba values can be considered as representative for the bottom-water chemistry, whereas higher values may be influenced by pore water. Consequently, analyses obtained using conventional bulk techniques may overestimate Ba concentrations with respect to seawater. Single-specimen LA-ICP-MS analyses circumvent problems of Ba concentrations being influenced by pore-water chemistry and reveal both the average and the range of Ba concentrations.

Under suboxic conditions in sediments, solid-phase manganese is reduced, and Mn^{2+} is released into the pore waters. This process can result in the precipitation of $MnCO_3$ coatings,

which contain generally high concentrations of Cd and Ba, on foraminiferal tests (Boyle, 1983). It is essential to exclude these coatings from the measurements. As long as the foraminifera are alive, precipitation of either $MnCO_3$ or manganese (hydr)oxides is prevented, because the test is protected by a protoplasm envelope. Our results show, however, that elevated pore-water Mn concentrations also cause direct Mn incorporation into the carbonate of the foraminiferal test.

In most foraminiferal tests from the Bay of Biscay the Mn concentration was below the analytical detection limit. All Bay of Biscay stations have well-aerated bottom waters. However, oxygen penetration depth varies as a function of different oxygen consumption rates. In three stations from the Bay of Biscay, where oxygen penetration depths fell below 15 mm (Fig. 3C), foraminifera incorporated Mn in detectable concentrations. The station with the highest carbonate Mn shows high pore-water Mn concentrations already in the top centimeter and even sometimes in the benthic boundary layer above the sediment-water interface. Arabian Sea samples from low bottom-water oxygen stations show increased Mn concentrations in their test carbonate (Fig. 3D) that are not related to outer Mn coatings. Oxygen penetration depth has not been measured in the Arabian Sea sediments, but Mn cycling is known to be high in the sediments deposited below the local oxygen minimum zone (van der Weijden et al., 1999). *H. elegans* is absent in the oxygen minimum zone sediments, but Figure 3D shows increased test Mn in specimens that lived close to the lower boundary of the oxygen minimum zone. High pore-water Mn apparently also increases Mn incorporation (Middelburg et al., 1987) in foraminiferal test calcite. Large variability in Mn concentrations between specimens can be attributed to slightly different microhabitats, resulting in large differences in pore-water Mn because of steep and shallow pore-water Mn gradients. Differences within single specimens may be due to vertical migration in the sediment during its life cycle.

Profiles of redox sensitive elements, which are often used for the reconstruction of redox conditions, are subject to later changes owing to ongoing diagenesis. This is not the case for the concentrations recorded in the carbonate. Therefore, LA-ICP-MS measurements of redox-sensitive elements in the test carbonate of foraminifera have a great potential for reconstructing past pore-water redox gradients.

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