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Heavy metal uptake in foraminiferal calcite: results of multi-element culture experiments

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Abstract

The incorporation of heavy metals into the test of the shallow water benthic foraminifer *Ammonia tepida* was investigated under controlled laboratory conditions. Except for the concentrations of the trace elements, all other culture conditions such as pH, temperature and salinity were kept constant. In the experiments, the concentrations of Ni, Cu and Mn were 5, 10, and 20 times higher than those in natural North Sea water, whereas in a control experiment *foraminifera* were cultured in filtered natural North Sea water. Concentrations of Cu and Ni from newly grown chambers were determined by means of both μ-synchrotron XRF and laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS). Both independent analytical approaches agreed within the analytical uncertainty intervals. The calculated partition coefficients were 0.17±0.09 and 1.3±0.7 for Cu and Ni, respectively. Potential toxic and/or chemical competition effects might have lead to a decreasing incorporation rate of Cu and Ni into the calcite of the specimens of the tank with the highest chemical concentrations. Mn showed great scattering in the aquarium with the 20-fold higher element concentrations potentially due to antagonism effects with Cu. Nevertheless, the established partition coefficients now open the way for reconstructing past concentrations for these elements in sea water.

1 Introduction

Foraminifera are unicellular eukaryotic microorganisms (protozoa), found mainly in marine environments. They incorporate (trace) elements and thus isotope ratios from the sea water into their calcareous shells. For this reason geochemical data of foraminiferal tests are widely used as proxies in palaeo-climatology and oceanography (e.g. Boyle, 1981; Wefer et al., 1999; Lea, 2004).

According to Erez (2003) the actual process of calcification begins by sea water uptake into vacuoles by endocytosis. On their pathway through the cell various pumps

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and channels may operate to increase pH and possibly modify the elemental concentration in the vacuoles, which subsequently are exocytosed into a biomineralisation space. There, $CaCO_3$ is precipitated on an organic matrix that defines the outline of the new chamber. Trace elements present in sea water then co-precipitate with the cal-
cite and are thus incorporated into the shell. Physicochemical parameters such as pH, temperature, salinity or pressure may also influence on the incorporation of elements.

Geochemical proxies are routinely used to reconstruct palaeo environments. The use of oxygen isotopes for palaeothermometry was suggested by Urey (1947) and is still one of the most widely used proxies (e.g. Bemis et al., 1998; Lea, 2004). The
proxy toolbox has increased enormously ever since. Other approaches to reconstruct temperature are based on the Mg/Ca ratio (e.g. Nürnberg et al., 1996; Lea et al., 1999) or Ca isotope ratios (e.g. Nägler et al., 2000). Many other proxies have been developed. For instance B isotopes are used to determine pH changes in the ocean water (Sanyal et al., 2001; Yu et al., 2007) and Cd is a proxy for nutrient concentrations
(Boyle, 1988; Rickaby and Elderfield, 1999; Martin and Lea, 1998).

Most calibrations of foraminiferal proxies have been carried out using recent (i.e. core-top) sediment samples. However, in order to eliminate secondary contaminations and overgrowths, complex cleaning protocols have to be applied (e.g. Boyle and Keigwin, 1985/1986; Lea and Boyle, 1991; Martin and Lea, 2002). To eliminate these
difficulties, controlled laboratory cultures have been pioneered by Christoph Hemleben in Germany and Alan Bé in the US, focussing mostly on single elements and isotopes. The first experiments focussing on element partitioning (Li, Sr, Mg and Na) were carried out by Delaney et al. (1985). Later studies followed on the uptake of Cd (Boyle, 1988; Mashiotta et al., 1997; Maréchal-Abram et al., 2004), Ba (Lea and Spero, 1992,
1994), U (Russel et al., 1994) and V (Hastings et al., 1996). One of the latest studies published addressed Cu incorporation (de Nooijer et al., 2007).

Many trace metals are important for the biological productivity in the ocean and follow a nutrient-type depth profile within the water column. Especially some first row transition metals are known to be essential in low concentrations. On the other hand,

some local processes such as hydrothermal activity may enrich the trace element composition of sea water dramatically (German and von Damm, 2004). Also changes in redox conditions (e.g. Morford and Emerson, 1999) or anthropogenic pollution sources may influence heavy metal distribution in sea water. Such changes will also potentially
5 be recorded by *foraminifera*. Frequently, pollution studies focus on bulk sediment analyses and/or foraminiferal distribution patterns though (e.g. Vilela et al., 2004; Buzas-Stephens and Buzas, 2005; Carnahan et al., 2008). As polluted sediments are usually suboxic or anoxic due to enrichment in organic matter with high levels of sulphate reduction, heavy metals often are accumulated and bound to highly insoluable minerals
10 such as sulfides. Thus toxins are not bio available and the real level of pollution remains unknown. Only with increasing oxygen level heavy metals may be remobilised in the sediment and exposed to the water. Thus, analyses of foraminiferal calcite trace metal incorporation potentially allows a more realistic monitoring of marine pollution. However, except for Cu (de Nooijer et al., 2007), there are no calibrations available
15 for first row transition metals such as Mn and Ni. To fill this gap and to provide a basis for a more complete understanding of the partitioning of heavy metals between foraminiferal calcite and sea water, we conducted multi-element culture experiments under controlled laboratory conditions for oxidising environments of sediment surfaces.

2 Methods

20 ### 2.1 Sampling and culturing procedures

Sediment containing the shallow water benthic foraminifer *Ammonia tepida* was collected at low tide in an intertidal mudflat of the national park Wadden Sea of Lower Saxony at Dorum-Neufeld (Germany). In the laboratory the sediment was sieved over a 125 μm sieve and the residue was washed with filtered (0.2 μm) sea water. Then liv-
25 ing *foraminifera* were hand picked under a microscope using a very fine brush and 100 individuals were transferred into the sediment-free aquaria – each containing 1.25 L

of culture solution. The aquaria were thoroughly cleaned with 10 vol.-% HNO_3 and subsequently rinsed with reverse osmosis water (ROW, conductivity <0.067 µS) before use. A stock solution with defined concentrations of Mn, Co, Ni and Cu was prepared using ICP-standard solutions (1000 µg/mL in 5 vol.-% HNO_3 each) (Specpure from Alfa Aesar, Germany) and ROW water. The concentrations used in the experiments are listed in Table 1. Before use, the pH of the stock solution was raised to about 8.0 with 1 M NaOH (p.a.) in order to match the pH of the sea water used in the culture experiments. Subsequently appropriate volumes of the stock solution were added to the sea water (filtered with a 0.2 µm filter) until approximately the five-, ten-, and 20-fold concentrations of natural North Sea water were reached. As a last step, the culture solutions were filtered again using a 0.2 µm filter to eliminate possible precipitation in the aquaria. In addition, a reference batch without the "element-cocktail" was prepared. Before the stock solution was mixed with the sea water, the fluorescent label calcein (bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-fluorescein) (Sigma-Aldrich) was added at a concentration of 5 mg/L to mark newly grown chambers (Fig. 1).

The aquaria were covered with a lid to minimise evaporation and placed in a temperature controlled cabinet at 14.5±0.2 °C. Salinity 24 psu, pH (8.0±0.1) and temperature were stable for the duration of the experiments. The culture solution was changed every 4 weeks to avoid bacterial build-up. Weekly measurements of the culture solution's elemental composition by high resolution inductively coupled plasma mass spectroscopy (HR-ICP-MS type Axiom from VG Elemental) confirmed that the target concentrations remained within an acceptable range (Table 1). The accuracy of the analyses was accomplished by measuring the certified water reference sample CRM-TMWD (High Purity Standards, USA) in every analytical batch. A mixture of dried algae (*Phaeo-dactylum triconortum*, *Dunaliella salina* and *Isochrisis galbana*) was added for food. Feeding took place at the beginning of the experiment and every time the food was depleted: 6 and 8 weeks after the start of the experiment. The total duration of the experiments was 82 days.

At the end of the experiment all tests were cleaned of organics (6–8 vol.-% NaOCl, Merck) twice for two to three hours (Mashiotta et al., 1999; Pak et al., 2004). Finally, the tests were rinsed four times with ROW water.

2.2 Analytics

2.2.1 μ-synchrotron XRF

Using a liquid glue (Tesa, Beiersdorfer, Germany), two rows (each consisting of five individuals) of *foraminifera* shells were stuck up-side down on a 3 µm mylar film that was attached to plastic slide mounts. The glue as well as the mylar film were tested for their trace element contents before use. The contents of all elements of interest were clearly below the detection limits for μ-synchrotron XRF determinations. Newly grown chambers as well as some old chambers were analysed by μ-synchrotron XRF. These measurements were performed at the FLUO-beamline of ANKA synchrotron facility (Karlsruhe). Using an excitation energy of 12.5 keV and focussing by refractive lenses to a point size of 2×5 µm the chambers were analysed by line scans, averaging five points per line in newly grown chambers and three points in old chambers. Due to the fact that foraminiferal tests consist of calcite, in unfiltered sample spectra the Ni-K lines are overlain by an intense Ca sum-peak. To eliminate this interference, a 20 µm secondary beam aluminium filter was mounted in front of the fluorescence detector. Due to low trace element concentrations in the sub µg/g and lower µg/g range, long measuring times (500 s) were necessary at each point. Trace element contents in the tests were quantified by fundamental parameters. Geometry effects caused by the uneven shape of the tests were corrected by calculating the absorption of the incoming beam from the count rate of the primary monitor (in front of the sample) and the secondary monitor (behind the sample). Since the calcium concentration (40 wt.%) is constant in calcite, the average path length of the outgoing beam could be calculated using Ca as internal standard (Kramar et al., 2010).

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The fundamental parameter calculations were adjusted for trace element calibration purposes by using a pressed calcite pellet (containing 756 µg/g Cr and 727 µg/g As) and the MPI-DING reference glass StHS6/80-G standard (Max-Planck-Institut für Chemie, Germany) (Jochum et al., 2000) as primary standards.

2.2.2 LA-ICP-MS

Since µ-synchrotron XRF is a non-destructive technique, Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) measurements on the same chambers could be carried out later on. For these measurements specimens were fixed on a double-sided adhesive tape and mounted on plastic stubs.

The analyses were conducted at Utrecht (Department of Earth Sciences) by means of an Excimer laser (Lambda Physik, Germany) equipped with GeoLas 200Q optics at a wavelength of 193 nm. The ablation was conducted in a helium atmosphere. Pulse rate was adjusted to six pulses per second with an energy density of 1 J/cm^2 at the surface of the sample. The laser beam was set to a diameter of 80 µm. The ablated material was analysed with a Micromass Platform quadrupole ICP-MS facility. To minimise spectral interferences on the minor isotopes of Ca a collision and reaction cell was used (Mason and Kraan, 2002). Calcium was used as an internal standard, via the ^{44}Ca isotope, at the same time monitoring ^{42}Ca and ^{43}Ca. For calibration of trace element contents NIST SRM 610 glass standard (National Institute of Science and Technology, USA) (Pearce et al., 1997) and the in-house GJR matrix-matched calcite standard was applied. Concentrations of Cu and Ni were calculated using ^{63}Cu and ^{60}Ni. The internal precision of Cu and Ni was better than 4.8% and 4.7%, respectively.

The resulting trace element (TE) and calcium concentrations were used to calculate partition coefficients according to the following expression:

$$D_{TE} = (TE/Ca)_{calcite}/(TE/Ca)_{sea\,water}. \tag{1}$$

3 Results

3.1 Culture media

Continuous monitoring of the culture solution reveals that the trace element concentrations of the water corresponded to the targeted concentrations. The elements of the stock solution therefore did not precipitate or get used to an appreciable degree when mixed with the marine water with the duration of the experiment (Fig. 2 and Table 1).

3.2 Newly grown foraminiferal calcite

All *foraminifera* survived the culture period of 82 days. In one of the aquaria reproduction occurred, but only one juvenile foraminifer was found after termination of the experiments. 7 individuals of the 5-fold concentrated tank got lost during water changes. New chambers were formed in all aquaria – for the reference batch 47% of the specimens formed at least one new chamber. In the 5-, 10- and 20-fold concentration tanks this was 53%, 41% and 29% of the individuals, respectively (Table 2).

3.3 Comparison of the applied analytical techniques

Due to analytical problems with Co (below detection limits) and to the high variability in the Mn concentration, the results of these elements are not considered any further.

The precision of LA-ICP-MS measurements for some element analyses is low, as the measured concentrations were too close to the detection limit. Although the LA-ICP-MS measurements for Cu and Ni display a similar range to that measured by μ-synchrotron XRF, some data are not conclusive. This is mainly due to the fact that some chambers of the analysed *foraminifera* had very thin chamber walls. The short ablation time resulted in poor signal statistics. Another problem is the very long synchrotron beam times needed to achieve proper results.

Despite all of this clear trends are observed for Cu and Ni. Irrespective of the analytical technique (LA-ICP-MS or μ-synchrotron XRF), the concentration of Ni as well as of

Cu reveal clear trends in the calcite corresponding to the concentrations in the culture medium (Table 1, Figs. 2 and 3).

3.4 Partition coefficients of Ni and Cu

Figure 3 shows the partition coefficients for Ni and Cu. The solid lines are equivalent to the calculated partitioning values (median values). The dotted lines connect quartile values, which display the area of uncertainty.

The calculated partition coefficient for Cu and Ni range between 0.1 and 0.25 and between 0.6 and 2.0, respectively. The scattering (Fig. 4) for the Mn data only allow a very uncertain estimate of D of at least 2.4. Co was not detectable. It should be noted that a wide scattering of some data is not unusual in biological experiments (Reichart et al., 2003; Dueñas-Bohórquez et al., 2009; Dissard et al., 2010a,b).

A systematic decline in the concentration of Ni and Cu incorporated in newly grown chambers was observed in the *foraminifera* from the 20-fold trace element experiment in comparison to those grown at the 10-fold concentration of natural sea water (Fig. 3). This decline was determined by both analytical techniques.

4 Discussion

4.1 Partition coefficients

The partition coefficients for Cu (D_{Cu}) and Ni (D_{Ni}) were calculated based on data measured with two different analytical methods. According to both methods the D_{Cu} lies between 0.1 and 0.25. On the bases of the μ-synchrotron XRF measurements D_{Cu} was found to be 0.18±0.08, whereas with the LA-ICP-MS a range of 0.08 and 0.15 was measured (D_{Cu}=0.12±0.04), giving an average D_{Cu} of 0.17±0.09. This is slightly lower than, but in the same range as the previous measured partition coefficient for Cu by de Nooijer et al. (2007: 0.25±0.15 using the LA-ICP-MS). Although de Nooijer

et al. (2007) used the same LA-ICP-MS set-up as the current study, the μ-synchrotron measurements by themselves compare better with their findings.

For Ni a broader range was observed. The D_{Ni} varied between 0.6 and 2.0 (D_{Ni}=1.3±0.7) as well as 0.7 and 1.7 (D_{Ni}=1.2±0.5) using μ-synchrotron XRF and LA-ICP-MS, respectively. Again both techniques lie within proper agreement. As there is no published D_{Ni} data for *foraminifera*, we suggest using the value of 1.3±0.7 for further applications.

4.2 Experimental uncertainties

The element concentrations in the culture solutions do scatter generally within an acceptable range. For some elements, notably Mn, a larger variance was observed because Mn reacts very sensible already to slight changes in redox conditions.

Calcein binds to Ca as calcium carbonate is precipitated and therefore is incorporated into the mineralised structure (Bernhard et al., 2004). Although Lu and Allen (2002) report that Cu incorporation competes with Mg and Ca (its incorporation is reduced by increasing Ca or Mg concentrations), Hintz et al. (2004) suggest that the (trace) element incorporation is not affected by the use of calcein. They argue that measured Mg/Ca ratios in calcein labelled chambers were of the same magnitude as the ratios in unlabelled chambers. Our measured Mg/Ca ratios (not shown here) confirm this assumption. One can expect a similar behaviour for Ni. Similarly, Dissard et al. (2009) state that calcein does not affect the incorporation of the elements Mg and Sr into foraminiferal calcite.

As shown in Table 2, our experiments were successful. Overall about 42% of the *foraminifera* in culture grew at least one chamber. Only in the experiment with the highest trace metal concentration a slightly lower percentage of new chambers was produced. No malformed chambers were seen and all individuals survived. Considering all this, the overall conditions for the experiment must be valued as reasonably good.

4.3 Biological effects and influences

The elements Mn, Ni and Cu usually are present only at very low levels in sea water (e.g. Table 1). Of these, Mn occurs at lowest concentration in the North Sea water we used (see Table 1). All of these metals seem to be essential for the growth of organisms and exhibit a nutrient-type distribution or a hybrid distribution (a combination of nutrient-type and scanvenged-type distributions) in the open seas (Jones and Murray, 1984; Bruland and Lohan, 2004; Morel et al., 2004).

Nevertheless, the severe drop of trace element concentration in the shells grown in the 20-fold concentration tank, shown in Fig. 3, might have a biological reason. All the trace metals used in this study are bioactive; they are involved in enzymatic activities (Nelson and Donkin, 1985). A deficiency may lead to a limited production whereas an excess may inhibit growth (Sunda, 1988–1989; Bruland et al., 1991). The lower chamber growth rate (see Table 2 for details) circumstantiates that. In consequence of the usage of a multi-element mixture in the culture medium, it is possible that one (or more) of the applied elements reached its (their) toxic level to *Ammonia tepida* even though not being lethal.

Ni is known to be a highly toxic element, even tough it is a cofactor in the urease enzyme that hydrolyses urea, which is an important source of nitrogen in the oceans (Oliveira and Anita, 1986). Ni also serves as a cofactor in various other enzymes. Due to this, Ni must be accounted as an important constituent in the growth of diatoms and should be present in low concentrations (Syrett and Peplinska, 1988). Dyhrman and Anderson (2003) observed the same for some dinoflagellates. We do not know if Ni is an essential element for *foraminifera* or an essential micronutrient necessary in the life cycle of marine microorganisms in general. Apart from this, urease activity, and thus Ni, is essential for microbiologically-induced calcite precipitation. Culture experiments with *Escherichia coli* reveal that up to a certain Ni concentration the calcite precipitation is enhanced, whereas above that concentration Ni will inhibit calcite precipitation (Bachmeier et al., 2002). Thus Ni seems to be a limiting factor for various processes.

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Results of Mann et al. (2002) indicate that Cu may be toxic or nearly toxic to various phytoplankton species. It is rather unlikely, however that Cu is the cause for possible inhibition or expulsion mechanisms as de Nooijer et al. (2007) used higher concentrations in their experiments than we did. Furthermore le Cadre and Debenay (2006) showed that *Ammonia tepida* is not only resistant to higher Cu concentrations than we applied in our experiments, but also grew new chambers and even reproduced. However, trace metal interactions are possible. For instance, processes in which one element becomes toxic due to the limitation of another, have been observed before (Bruland et al., 1991; Egleston and Morel, 2008). Egleston and Morel (2008) also found that several trace metals may simultaneously be limiting and toxic to oceanic biota.

The fact that high concentrations of Ni and Cu may harm marine life, possibly implies that some expulsion or inhibiting cellular mechanism has been triggered and that the *foraminifera* stopped incorporating these metals. It is also known that (at low Mn concentrations) toxic metals like Cu, Cd, Ni or Zn inhibit the Mn uptake. In terms of chemical competition Mn binding is blocked by (toxic) trace metals, which bind to the receptor sites on transport specialised membrane proteins designed for the acquisition of nutrients (Sunda and Huntsman, 1983, 1996, 1998a). Once the toxins are bound, the membrane nutrient-metal uptake system cannot distinguish between nutrient and toxicant.

The sort of antagonism between Mn and Cu, described by Sunda and Huntsman (1998b) for the green alga *Chlamydomonas*, also can be observed in our culture experiment. Figures 3 and 4 demonstrate that the concentrations of Cu and Mn seem to result from this antagonistic effect – at least in the 5- and 10-fold normal sea water concentration tanks. In the tests from these experiments the Mn concentration is very low relative to the Cu concentration. Only the tests from the 20-fold concentration tank show the opposite behaviour. In contrast to Ni and Cu, which are depleted, Mn, although displaying a wide scattering, is dominantly incorporated. This could mean that due to the high level of Mn in the water, Mn is able to out compete Cu from the uptake

positions and "win" the metal competition for the membrane binding sites. The situation for Ni could be similar – the toxicant is blocked by the nutrient. Another possibility might be that Cu and Ni potentiate their toxicity in alliance such that the *foraminifera* omit these metals and rather selectively take up Mn.

5 Conclusions

The present study was conducted to determine the partition coefficients of trace elements typical for changing redox conditions, hydrothermal activity and environmental pollution in benthic *foraminifera*. The partition coefficients for Cu and Ni are 0.17±0.09 and 1.3±0.7, respectively. This will allow using fossil *foraminifera* to determine the Cu/Ca and Ni/Ca ratios of sea water in environmental studies.

The environmental conditions in multi-element culture experiments are more similar to natural growing conditions than in commonly used single element experiments. The drop of the Ni and Cu incorporation into foraminiferal calcite implies quenching effects that have to be considered, if results from single element experiments are transferred to the natural environment. High toxic concentrations of certain elements might not be reconstructed in the correct way.

In addition to LA-ICP-MS, μ-synchrotron XRF turned out to be a very useful method to assess the concentration of trace elements in calcareous foraminiferal tests with the advantage that the sample material is not destroyed and optimisation of analytical conditions is possible at the same measuring point.

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Table 1. Mean concentrations of the elements Mn, Ni and Cu in the culture solutions. Reference=North Sea water without added trace elements, 5-, 10- and 20-fold indicate 5-, 10-, and 20-fold concentrations of the used North Sea water.

	Manganese [µg/L]	Nickel [µg/L]	Copper [µg/L]
Mean reference	2.93±2.02	4.83±2.57	13.82±2.25
(µmol/L)	(0.053±0.037)	(0.082±0.044)	(0.217±0.035)
Mean 5-fold	4.73±1.84	13.58±4.13	64.28±14.79
(µmol/L)	(0.086±0.033)	(0.231±0.070)	(1.012±0.233)
Mean 10-fold	6.21±2.45	21.75±3.07	107.82±9.87
(µmol/L)	(0.113±0.045)	(0.371±0.052)	(1.697±0.155)
Mean 20-fold	11.49±3.07	38.10±6.14	209.04±16.72
(µmol/L)	(0.209±0.056)	(0.649±0.105)	(3.290±0.263)

Table 2. Chamber growth of the cultured *foraminifera*.

Aquarium	Individuals	Number of chambers grown					Individuals [%] that grew chambers
		1	2	3	4	5	
Reference	100	10	14	12	9	2	47
5-fold NSW	93[*]	22	19	8	0	0	53
10-fold NSW	100	22	16	3	0	0	41
20-fold NSW	100	20	9	0	0	0	29

[*] Seven individuals got lost during water changes; NSW = North Sea water.
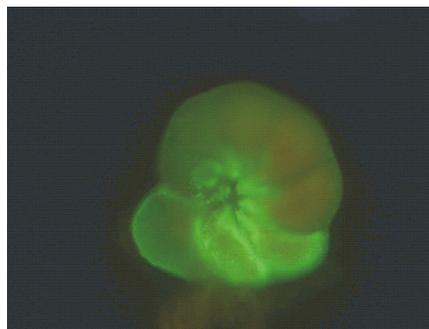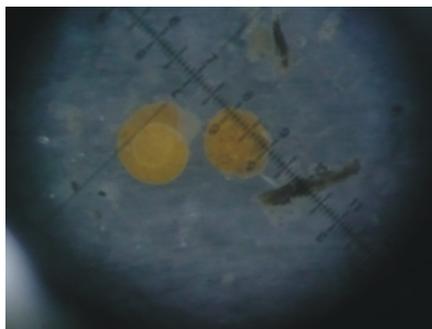
Fig. 1. *Ammonia tepida* under the light microscope (left), *Ammonia tepida* under UV light showing newly grown chambers marked with calcein (right).
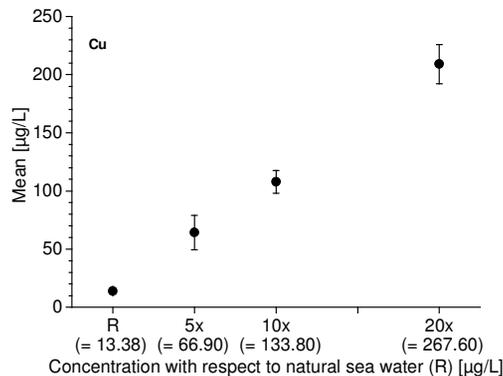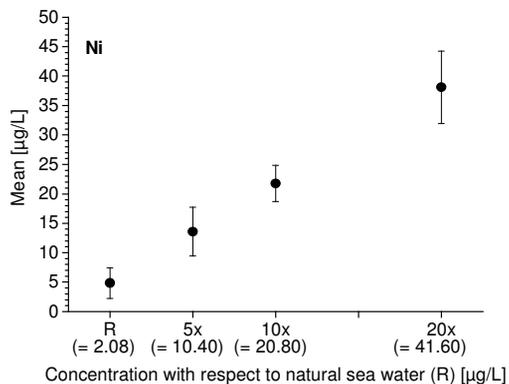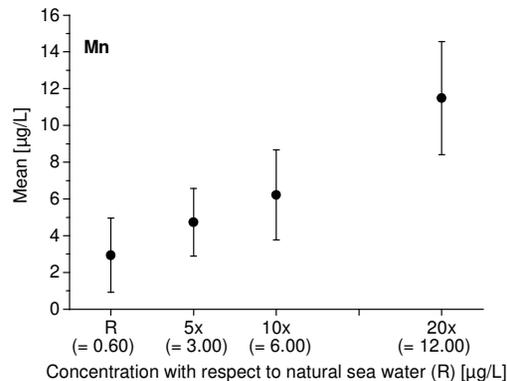
Fig. 2. Variation in the concentration of Mn (top), Ni (lower left) and Cu (lower right) in the culture solutions during the experiment; R=reference (natural sea water).

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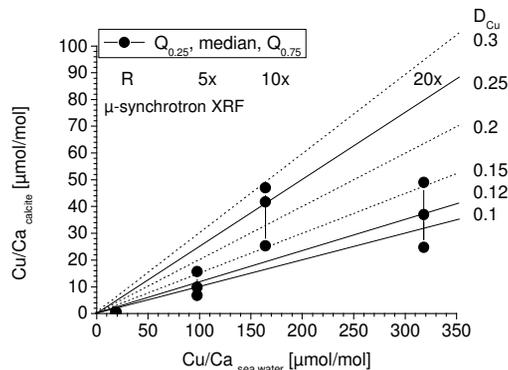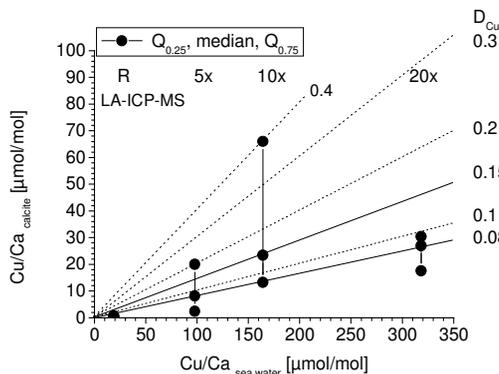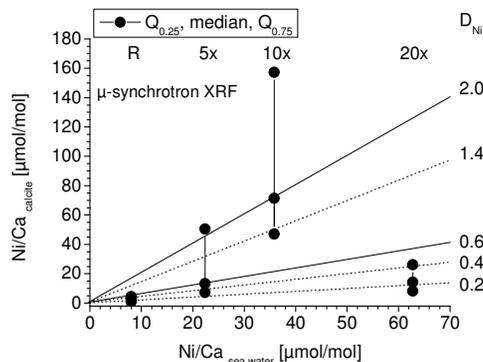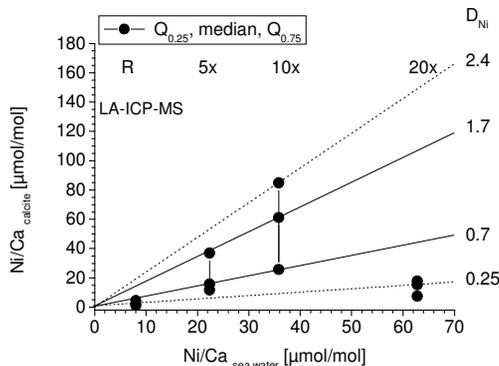
Fig. 3. Partition coefficients of Ni (upper two graphs) and Cu (lower two graphs) – measured with LA-ICP-MS (left side) and μ-synchrotron XRF (right side). The upper dots in each graph show the 25% quartile, the middle dots display the median value and the lower dots are equivalent to the 75% quartile of the observed concentration ratios. Solid lines are fitted to connect the median values. Dotted lines display a connection of the upper and/or lower quartiles and are afflicted with the area of uncertainty.
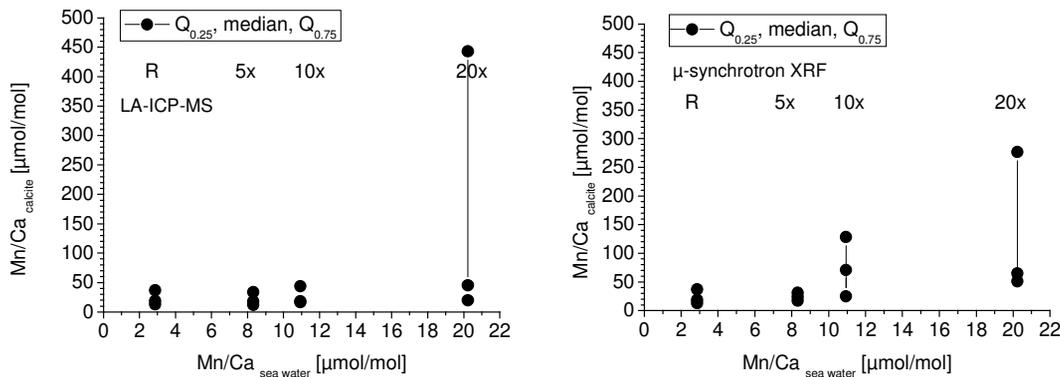
Fig. 4. Measurements of incorporated Mn. Explanation of the dots as in Fig. 3.