Benthic foraminiferal Zn/Ca, a new tracer of deep water palaeocirculation

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Deep water formation has been implicated as an important driving force of major climatic changes in the geologic record. Our knowledge of the past distribution and circulation of deep water masses has primarily been derived from $\delta^{13}C$ and Cd/Ca measurements of fossil benthic foraminifera. For example, North Atlantic Deep Water (NADW) today carries signatures of high $\delta^{13}C$ and low Cd; benthic foraminiferal data suggest that during the last glacial maximum (LGM), NADW shoaled to become Glacial North Atlantic Intermediate Water (GNAIW), allowing low-$\delta^{13}C$, high-Cd Antarctic Bottom Water (AABW) to penetrate farther into the North Atlantic (e.g. Boyle and Keigwin, 1982; Duplessy et al., 1988). Unfortunately, these two tracers often give conflicting or ambiguous results (Boyle, 1992), indicating the need for additional proxies.

Zn holds the promise of being another useful palaeotracer. Its dissolved profile in the modern ocean is nutrient-like, with near-zero concentrations in surface waters and maximum concentrations below 1000 m depth (Bruland et al., 1978). Dissolved Zn covaries strongly with dissolved Si, probably because the two elements have similar rates and sites of uptake and regeneration, in analogy to the relationship between Cd and P. Deep water formation and circulation create large gradients of Zn and Si in today's deep ocean. Dissolved Zn concentrations range from ~1 nmol kg^{-1} in the deep North Atlantic to ~9 nmol kg^{-1} in the deep North Pacific. There is a particularly large (five to seven-fold) increase in Zn between the deep North Atlantic and the deep Southern Ocean. This is much larger than the corresponding Cd gradient, and suggests that Zn may be a very sensitive palaeotracer of AABW and its interactions with NADW.

Several criteria must be met before Zn can be used as a palaeoceanographic proxy. First, modern benthic foraminifera must accurately record the Zn concentrations of overlying bottom waters. We test this hypothesis by performing a coretop calibration, in which we compare Zn/Ca ratios of Holocene foraminifera to modern seawater Zn concentrations predicted from seawater Si measurements. Secondly, glacial-age foraminifera must also be accurate Zn recorders, with no serious diagenetic influences on Zn/Ca ratios. We make a preliminary examination of this issue by measuring Zn/Ca in several LGM samples. Finally, the oceanic inventory of Zn should ideally be constant with time. The oceanic residence time of dissolved Zn is poorly constrained, with estimates ranging from 3 to 30 kyr. We will assess any potential change in the Zn inventory by measuring Zn/Ca in the deep glacial equatorial Pacific, where Zn fluctuations due to circulation changes are expected to be small. If significant changes are evident, a glacial global inventory could eventually be made and a whole-ocean correction could be applied to glacial data, such as that used for $\delta^{13}C$ (Duplessy et al., 1988).

Methods

The following benthic foraminiferal species were picked from washed sediment samples (>250 μm fraction): *Cibicidoides wuellerstorfi*, *C. kullenbergi*, *Nuttallides umbonifera*, *Hoeglundina elegans*, and *Uvigerina* spp. Each monospecific sample was crushed and split into subsamples consisting of the equivalent of ~4 to 14 individual shells. These were then subjected to the same cleaning process that is used for Cd/Ca analysis, namely a four-step process of clay removal, metal oxide reduction, organic matter oxidation, and weak acid leach (Boyle and Keigwin, 1985/6; Boyle et al., 1995). Cleaned samples were dissolved with trace-metal clean 0.075 N HNO_3. Ca was measured by flame atomic absorption spectrophotometry (AAS) and Zn, Cd, and Mn were measured by graphite furnace AAS. All elements were measured in succession on the same dissolved aliquots. Extra precautions were taken against contamination by airborne particles throughout the process.
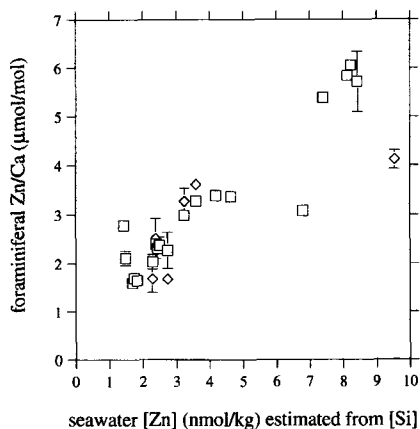
FIG. 1. Zn/Ca of Holocene (>1500 m) *C. wuellerstorfi* (squares) and *Uvigerina* spp. (diamonds) *vs* bottom water Zn concentrations estimated from nearest GEO-SECS Si measurements. The Zn:Si equation used was $Zn=0.050Si+0.79$. Each symbol is a mean of one to three measurements, and error bars are standard errors $(1\sigma/n^{\frac{1}{2}})$.
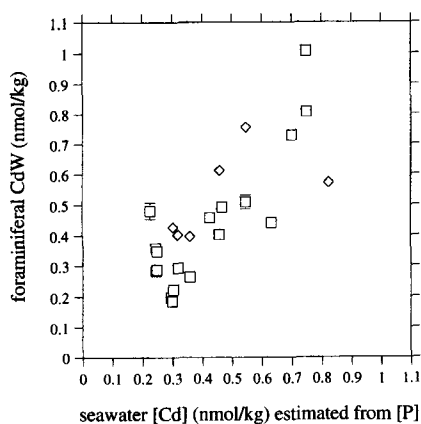
FIG. 2. CdW $(=[(Cd/Ca)_{foram}/D_{p,Cd}][Ca]_{water})$ of the same coretop samples presented in Fig. 1 *vs* bottom water Cd concentrations estimated from nearest GEO-SECS P measurements. The Cd:P equations used were $Cd=0.208P$ (for P <1.34 μmol kg^{-1}) and $Cd=0.398P-0.254$ (for P >1.34 μmol kg^{-1}) (Boyle *et al.*, 1995). Symbols are as in Fig. 1.

Results and discussion

Zn/Ca and Cd/Ca were measured in various Holocene coretops from throughout the world's oceans. The Zn/Ca results from *C. wuellerstorfi* and *Uvigerina* spp. from the first 20 cores (>1500 m depth) are shown in Fig. 1, plotted *vs.* seawater Zn estimated from nearest GEOSECS Si measurements. The Zn/Ca data correlate generally well with predicted Zn concentrations, indicating that these two taxa record bottom water Zn concentrations. Lowest Zn/Ca values are found in the North Atlantic (mean of 2.0 $\pm$ 0.5 μmol mol^{-1}), intermediate values in the South Atlantic (2.8 ±0.6 μmol mol^{-1}), and highest values in the tropical Pacific (5.9 $\pm$ 0.2 μmol mol^{-1}), following the expected pattern. Outliers occur at the Detroit Seamount (51°N Pacific), a region where coretop Cd/Ca is also much lower than expected (Boyle, 1992), and at 4148 m in the Vema Channel (31°S Atlantic), a sample for which severe partial dissolution may be an issue. Excluding these two cores, the mean Zn distribution coefficient $(D_{p,Zn} = [(Zn/Ca)_{foram}/[Zn]_{water}][Ca]_{water})$ for *C. wuellerstorfi* and *Uvigerina* spp. is 9.3 ±2.8. We have not identified any depth dependence for this $D_{p,Zn}$. For comparison, Fig. 2 shows CdW $(=[(Cd/Ca)_{foram}/D_{p,Cd}][Ca]_{water})$ from the same coretops, plotted *vs* seawater Cd estimated from nearest GEOSECS P measurements.

Data are too sparse at this time to determine whether or not *C. kullenbergi, N. umbonifera,* and *H. elegans* record bottom water Zn concentrations, but preliminary results suggest that if they do, these three species may have different $D_{p,Zn}$ values than *C. wuellerstorfi* and *Uvigerina* spp. Zn/Ca of LGM *C. wuellerstorfi* and *Uvigerina* spp. from the Rio Grande Rise (31°S Atlantic) are generally consistent with Cd/Ca and a shoaling of NADW to form GNAIW. This suggests, in a preliminary sense, that Zn/Ca will be a useful deep water tracer on glacial/interglacial timescales. Glacial data from other regions, including the tropical Pacific, will shed further light on this subject.

References

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