$^{234}U/^{238}U$ ratios in Quaternary planktonic foraminifera

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Introduction

The ($^{234}U/^{238}U$) activity ratio in seawater is thought to have remained constant at 1.144 for at least the last 260ka (Henderson *et al.*, 1993). If foraminifera are closed systems with respect to U, the decay of this ratio towards secular equilibrium therefore offers a potential chronometer. Demonstrating that this ratio can successfully be measured would also represent the first step towards U-Th dating of foraminifera.

In addition to the chronological potential, the $^{234}U/^{238}U$ ratio is also a sensitive indicator of the closure of foraminiferal calcite with respect to U. If closed, U concentrations in foraminifera may be a proxy for U concentrations in past seawater allowing investigation of changing fluxes of U into and out of the oceans (Russell *et al.*, 1994).

Measurement of the $^{234}U/^{238}U$ ratio in foraminiferal calcite is complicated by the very low concentration of U in the calcite (~30 ppb) and the considerably higher concentration in its MnO_2 coating (~10 ppm). It must therefore be demonstrated that the MnO_2 can be successfully removed and that the $^{234}U/^{238}U$ ratio can be accurately measured on small (< 1ng) U loads.

Analytical details

In this study, approximately 60mg each of *G. tumida* and *P. obliquiloculata* were picked from 5 depth horizons ranging from 5cm to 145cm (6ka to 162ka) in core ERDC-93P. This core is sited on the Ontong-Java Plateau at shallow depth (1619m) thus avoiding possible dissolution effects. Each sample was gently crushed, split into two replicates, and cleaned in a succession of reducing and oxidising solutions (modified from Boyle 1981). Cleaned samples were dissolved in 0.1M HNO_3 and centrifuged. An aliquot was removed and the Mn/Ca ratio measured by AA to assess the removal of the MnO_2 coating. U was separated from the remaining solution using standard anion exchange procedures. U concentrations and ratios were analysed on a VG354 mass spectrometer equipped with a low background ion counting system. To demonstrate the feasibility of measuring the $^{234}U/^{238}U$ ratio on small loads a series of 1ng loads of the U960 standard were run. ($^{234}U/^{238}U$) activity ratios from 12 beads averaged 0.965 ± 0.005 (2s.d.) in agreement with published values. Internal precision was typically 0.009 (2 s.d.).

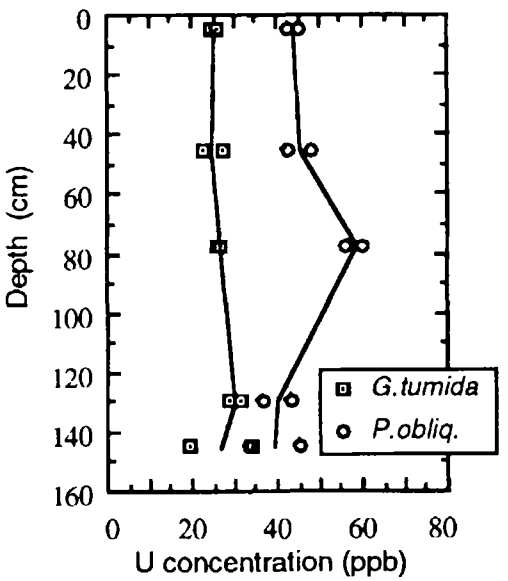

FIG. 1. U concentrations for replicate pairs of *G. tumida* and *P. obliquiloculata* samples. Analytical errors are similar to symbol size. The solid lines are drawn through the average of the two replicate analyses.

Results

Mn/Ca ratios of replicate pairs agree reasonably well. Mn/Ca increases from ~10 μM/M at 5cm to a maximum of 60 μM/M at 145cm. These values are comfortably lower than 100 μM/M and therefore within the bounds of acceptability adopted for Cd (Boyle 1983) and other trace element work. U concentrations in both species,

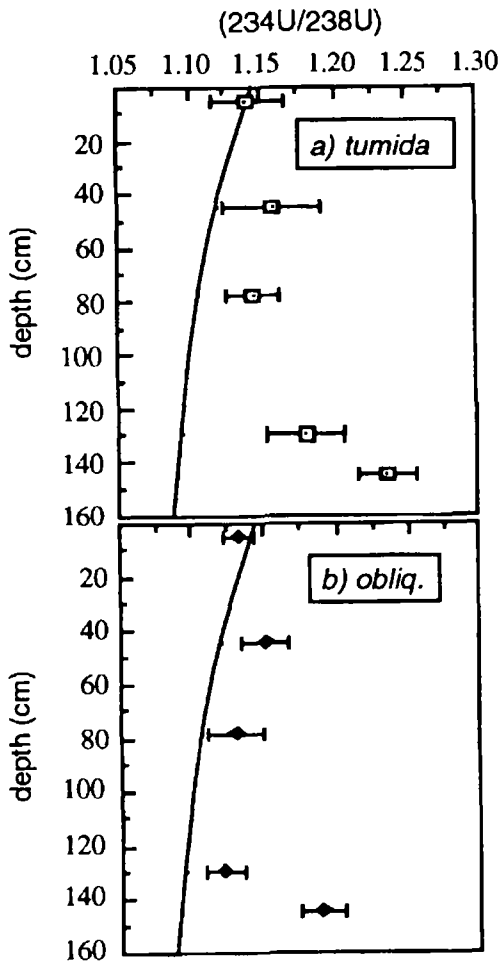

FIG. 2. Down core foraminifera ($^{234}U/^{238}U$) activity ratios. For each data point two replicate analyses were run: these were within error in every case. The curve represents the ratio expected if closed system decay of excess ^{234}U occurred, from an initial, modern seawater value.

particularly *tumida*, are broadly constant with depth and reproduce well (see Fig. 1). *Tumida* contains 25ppb U and *obliq.* 40ppb U.

$^{234}U/^{238}U$ ratios of replicate pairs were within error in every case. The 5cm depth samples yielded ($^{234}U/^{238}U$) activity ratios within error of the seawater value (see Fig. 2). However, samples do not exhibit decreasing $^{234}U/^{238}U$ ratios with depth in the core as would be expected from closed system radioactive decay. Instead, a smooth increase is seen to ($^{234}U/^{238}U$) activity ratios of ~1.250 at 162ka (see Fig. 2). This increase correlates with the increase in the Mn/Ca ratio.

Conclusions

Despite thorough cleaning of foraminifera to yield low Mn/Ca ratios the $^{234}U/^{238}U$ ratios suggest that the calcite has not remained closed with respect to U. This may reflect either limited addition of U in a resistant coating (e.g. manganese carbonate), or wholesale exchange of U between the calcite and 234U enriched pore waters. As U concentrations remain broadly constant down core, increasing the ratio by addition of U requires U with an unreasonably high $^{234}U/^{238}U$ ratio. It therefore appears likely that U exchange occurs. This implies that U is not bound in the lattice of calcite and is more susceptible to diagenesis than trace elements such as Cd which substitute for Ca.

References

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