The Nd isotope composition of ancient seawater from foraminifera: systematics and a case-study from the Pleistocene of the Labrador Sea

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The isotopic compositions of Nd and Pb have been shown to exhibit considerable spatial variability in the world's oceans (e.g. Albarede and Goldstein, 1992; von Blanckenburg *et al.*, 1996 and references therein). This feature is due to the short residence times of these elements in seawater and the variability of local continental input. For the same reason, these elements are expected to show secular variations in the oceans on timescales of thousands to millions of years. Studies of hydrogenous Fe-Mn crusts have demonstrated the existence of long-term trends that have been linked to variable rates of continental input and tectonically-driven changes in ocean circulation (e.g. Christensen *et al.*, 1997 and references therein). Data on shorter timescales are much more difficult to obtain because of the paucity of high-resolution records of the isotopic composition of these elements in seawater. However, it is these shorter timescales that are relevant to the changes in ocean circulation and continental weathering rates that accompany climate changes such as glacial-interglacial cycles. Here we present Sm-Nd isotopic data on modern and Pleistocene foraminifera with a dual objective. Firstly, we demonstrate that the isotope systematics of foraminifera strongly suggest that they provide a faithful record of past changes in the Nd isotope composition of the oceans. Secondly, we present data for planktonic Pleistocene foraminifera from the Labrador Sea that point to major shifts in the isotope composition of this important component of North Atlantic Deep Water (NADW) over the past 2.2 Ma. These secular shifts are most readily explained in terms of changes in the source of terrigenous inputs during global glaciation.

Results

The principal datset derives from ODP site 647 in the Labrador Sea where a 102 m thick sequence of carbonate-rich sediments, containing abundant foraminifera of species N. pachyderma, have been deposited since 2.2 Ma. We have also analysed two different species (*P. obliquiloculata* and *G. menardii*) of foram from ODP site 758 in the Indian Ocean along with samples of modern foraminifera derived from plankton tows. It is well-established that diagenetic Mn coatings dominate the trace element inventories of foraminifera and must be removed to obtain seawater signatures. This has been done using established techniques (Boyle and Keigwin, 1985/86) for all the core samples studied here. In addition, we have analysed bulk sediments and uncleaned foram samples in order to investigate the mass balance relationships between coating and foraminferal calcite.

There are several observations that strongly suggest that the Nd inventories of the foraminfera reflect contemporaneous seawater signatures. Most important is our finding that the range of Nd concentrations in the core samples (0.7–3 ppm) is indistinguishable from that found for plankton tow samples. Secondly, there is a concentration difference between the two species from the Indian Ocean (0.7 ppm in *G. Menardii* and 1.6 ppm in *P. obliquiloculata*) that is maintained down-core. Thirdly, the Nd concentration in the Labrador Sea samples is 2–3 times higher than those from the Indian Ocean, reflecting the same relationship between Nd concentrations in present-day local seawater. In terms of isotope systematics, the core-top sample from the Labrador Sea yields a Nd isotope composition ($\varepsilon Nd = -17.9 \pm 0.16$; where εNd is the measured $^{143}Nd/^{144}Nd$ ratio relative to the chondrite reservoir) that is indistinguishable from local surface water (-17.9 ± 0.5; Piepgras and Wasserburg, 1987) but distinct from local deep water (-13.4 ± 0.5; Piepgras and Wasserburg, 1987). In addition, the cleaned samples are up to 3 epsilon units different

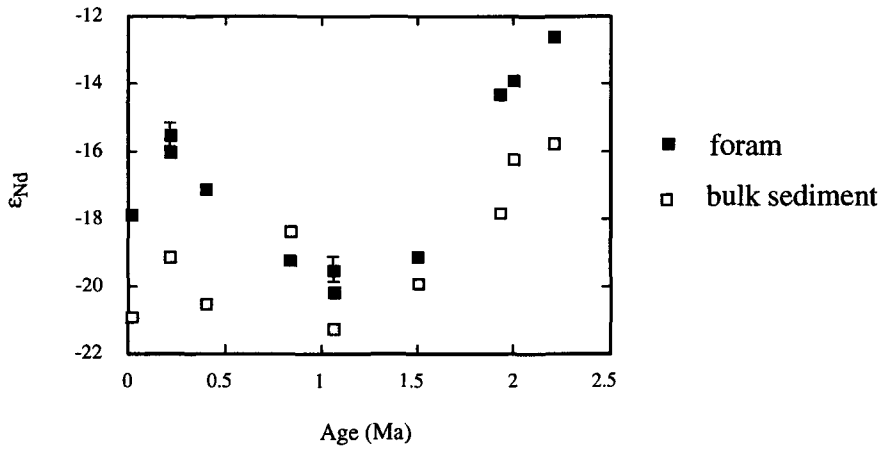

FIG. 1. Nd isotopic data for *N. pachyderma* and host sediment for ODP site 647 in the Labrador Sea over the past 2.2 Ma.

from the host bulk sediment. Finally, separately picked and cleaned duplicates of cleaned foram samples yield identical results as do the two species from the Indian Ocean core. The Labrador Sea samples exhibit a well-defined, coherent shift in eNd from −13 to −20 between 2.2 and 1.2 Ma, before rising again to around −18 at the present-day.

Discussion

The above criteria strongly suggest that cleaned foraminifera faithfully preserve the Nd isotopic composition of seawater. If this is so, the Labrador Sea data preserve a record of the secular shifts in the isotopic composition of seawater Nd over the past 2.2 Ma. The long-term shift is towards more unradiogenic Nd during the Pleistocene as compared to more radiogenic Nd both before the onset of major glaciation and at the present-day. This conclusion is consistent with previous findings that the majority of ice-rafted detritus is primarily derived from old continental crust on the North American continent (e.g. Gwiazda *et al.*, 1996 and references therein) - a source that is known to be characterised by very unradiogenic Nd. Labrador Sea Water at present froms about 30% of mature NADW. The change towards unradiogenic Nd in Labrador Sea surface waters over the past 2.2 Ma is sufficient of itself to explain the shift of NADW towards more unradiogenic values in that time interval. Similarly, the advection of this Nd into the Pacific can explain the recent shift towards more unradiogenic Nd in deep Pacific waters without any requirement for the intensification of NADW flow.

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