High precision Pb isotopes in Fe-Mn crusts from the NE Atlantic: a proxy for palaeosources and palaeocean circulation

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Mixing in the oceans is traced using conservative properties (salinity, temperature....) of water masses where mixing is reflected as linear arrays (Broecker and Peng, 1982). The potential of Pb isotopes as tracers of ocean circulation was first demonstrated by the consistency of Pb isotopic variations in Circum-Antarctic Fe-Mn deposits with the present-day ocean bottom water circulation in this region (Abouchami and Goldstein, 1995). Although Pb itself is a non-conservative element, binary mixing between water masses or sources will still result in straight linear arrays when plotted in Pb isotope space. However, resolution of such mixing lines depends on the accuracy with which Pb isotope ratios can be measured.

In recent studies, palaeoseawater records of Pb and Nd isotopes were obtained using dated depth-profiles from hydrogenous Fe-Mn crusts, and have shown that long-term Pb and Nd isotopic changes in the Pacific and Atlantic appear to be related to deep water circulation changes (Abouchami *et al.*, 1997; Burton *et al.*, 1997; Christensen *et al.*, 1997). So far, because of limitations in analytical precision, only variations in $^{206}Pb/^{204}Pb$ ratios have been resolvable.

We report high precision Pb isotopic data ($2\sigma_{ext.} \leqslant 100$ ppm, a factor of 10 better than conventional analyses) obtained using a Pb triple spike (Galer and Abouchami, This volume), together with Nd isotopic composition on depth profiles from two Fe-Mn crusts from the eastern Atlantic basin. Crust 121DK was dredged from Tropic Seamount which lies off West Africa (24°53'N, 21°42'W, 2000 m), while crust 65GTV comes from the Lion Seamount, west of the Straits of Gibraltar (35°20'N, 15°20'W, 1500 m). These crusts grew in the cores of NADW and MOW at rates of 3 mm/Ma and 4.5 mm/Ma, respectively, as inferred from ^{10}Be data (Koschinsky *et al.*, 1996). The profiles provide a 12 Ma record of changes in eastern North Atlantic Deep Water (ENADW), and over the past 8 Ma for Mediterranean Outflow Water (MOW).

Results

The Pb isotopic record from crust 121DK lying in ENADW off the west African coast, spans the last 12 Ma and displays $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of 18.83 to 18.98, 15.69 to 15.73 and 38.95 to 39.08, respectively. The 8 Ma isotopic record from crust 65GTV provides the first pre-anthropogenic Pb isotopic characterization of MOW. MOW proves to be quite distinctive and has systematically lower Pb isotope ratios ($^{206}Pb/^{204}Pb$ = 18.70–18.78; $^{207}Pb/^{204}Pb$ = 15.66–15.68 and $^{208}Pb/^{204}Pb$ = 38.78–38.86) than the Tropic seamount crust. The pattern of variation in $^{206}Pb/^{204}Pb$ ratio has a quasi-cyclic character, which we subdivide into 3 time slices: 12 to 8 Ma, 8 to 4 Ma and 4 to 0 Ma. Within each 'cycle', the changes in $^{206}Pb/^{204}Pb$ ratios occur gradually but quite systematically with time, a pattern not documented from Fe-Mn crust records before. The $^{206}Pb/^{204}Pb$ variations with time in crust 65GTV appear to mirror those of crust 121DK.

The high precision Pb isotopic data also allow us to resolve highly detailed variations in all three Pb isotope ratios for the first time. In Pb-Pb isotope space, the Pb isotopic variations over time in the two Fe-Mn crusts display well-defined mixing lines. Three different mixing lines can be distinguished in crust 121DK, indicating that changes in Pb sources in the NE Atlantic occurred at about 8 and 4 Ma. Similarly, Pb isotope ratios in samples from the last 4 Ma in crust 65GTV display a well-defined mixing line in both $^{206}Pb/^{204}Pb$ *vs* $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ *vs* $^{208}Pb/^{204}Pb$ space. Perhaps more striking, though, is that there is a gradual change in Pb isotopic compositions along the mixing lines with time. Thus, during distinct time slices, the end-members components had fixed isotopic compositions and the Pb mixing proportions at the locations of the crusts changed systematically and gradually with age.

Despite some fluctuations, ε_{Nd} values overall exhibit less variation than those of the three Pb isotope ratios. Nd isotopic compositions in crust 121DK (ε_{Nd} = −10.8 to −11.8) are less radiogenic compared to crust 65GTV (ε_{Nd} = −8.9 to −11). There is a general decrease in ε_{Nd} toward the present-day in both crusts, starting around 3 to 4 Ma ago.

Discussion

We interpret the Pb isotopic variations throughout the last 12 Ma in crust 121DK as reflecting binary mixing between two components: NADW and Southern Component Water (SCW). The quasi-cyclic character of $^{206}Pb/^{204}Pb$ fluctuations, as well as variations in the mixing proportions of SCW and NADW end-members along the mixing lines, appear to be correlated with changes in deep water circulation. These results further imply that the process of NADW advection into the eastern Atlantic and its mixing with SCW have been in operation throughout the last 12 Ma, entirely consistent with early Miocene production of NADW, as inferred from palaeoceanographic studies and GCM sensitivity tests.

The 8 Ma record of MOW (crust 65GTV) demonstrates that Pb and Nd sources switched from predominantly internal, Mediterranean sources prior to 4 Ma to mainly external sources after 4 Ma. We relate the gradual increase of Pb isotope ratios seen following the end of the Messinian to enhanced input of Saharan dust into the water column in the eastern Atlantic. The strengthening of the 'Saharan' isotopic signal since about 4 Ma reflects the increased aridity and dustiness in the Saharan and sub-Saharan regions documented during this time. Although Pb and, to a less extent, Nd isotope ratios are distinct during the Messinian (~6.5−5 Ma), there is no clear evidence for either a shut-down of MOW or a stronger North Atlantic signal during this period. The fact that a similar isotopic signal is observed, with an even higher amplitude in the ENADW record, shows that this signal is a feature of the whole eastern Atlantic.

From 3 to 4 Ma ago, a source of radiogenic Pb and unradiogenic Nd appears to have dominated not only the eastern Atlantic but the world oceans, since it is seen ubiquitously in other Fe-Mn crusts at this time. Thus, there is a global change in Pb and Nd inputs to the world oceans and this isotopic signal must be conveyed around the globe via the ocean circulation or in the atmosphere. While the closure of the Panama gateway may have played an important role in the global change in the source(s) and/or fluxes of Pb and Nd to the oceans 3−4 Ma ago, other events may have, in conjunction, lead to those recorded over the past ~12 Ma.

In conclusion, the two highly precise Pb isotopic records from the eastern Atlantic effectively fingerprint the ocean and atmosphere circulation changes in this region over the past 12 Ma, demonstrating the overwhelming sensitivity of Pb isotopes for global change provenance studies.

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