High resolution $^{230}Th/^{232}Th$ and $^{234}U/^{238}U$ chronology of a hydrogenous Fe-Mn crust from the NE Atlantic

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Hydrogenous ferromanganese crusts form as a result of direct precipitation of Fe and Mn oxy-hydroxides from seawater. Simultaneously, these oxy-hydroxides scavenge some trace elements, including Th and U, making Fe-Mn crusts very suitable for U-series dating and growth rates determination (1). High resolution Th-U chronology in hydrogenous Fe-Mn crust Va13-2 from the Central Pacific has provided a means of relating the variations of long-lived radiogenic isotopes of Pb and Nd to climate changes in successive Fe-Mn oxides layers over the last ~400 kyr (2).

Dating Fe-Mn crusts with U-series relies on the assumptions of a constant initial composition and closure of the system after deposition. Previous studies have shown that these assumptions are not always valid (3). Since the U isotopic composition of seawater has remained constant during the late Quaternary, the uncertainties associated with $^{234}U_{excess}-^{238}U$ dating are mostly related to secondary remobilization processes. In contrast, Th isotopes are relatively insensitive to alteration and should, therefore, be more reliable for dating purposes. Although ^{230}Th and ^{232}Th have the same chemical properties, these nuclides come from distinct sources and follow different oceanic cycles. While ^{230}Th is directly produced by radioactive decay of ^{234}U in the water column, ^{232}Th is essentially derived from the dissolution, or *in situ* incorporation, of detritus supplied by rivers and aeolian dusts. However, because of the short residence time of Th in seawater (~30 yrs), the $^{230}Th_{excess}$ may have varied, invalidating its use for dating. In order to circumvent this, it has been suggested that the $^{230}Th_{excess}/^{232}Th$ ratio may be more reliable, as ^{232}Th acts as a monitor of the initial ^{230}Th present in the crust (3). Recently, Chabaux *et al.* (3) attempted to provide an assessment of the closed-system assumption by comparing the $^{230}Th_{excess}/^{232}Th$ and $^{234}U_{excess}/^{238}U$ chronometers. However, even if the two chronometers do agree, the origin of variations in the $^{230}Th/^{232}Th$ ratio remain to be explained, undermining the reliability of the $^{230}Th_{excess}/^{232}Th$ technique.

Here, we present depth profiles of $^{230}Th/^{232}Th$ and $^{234}U/^{238}U$ isotopic ratios together with U and Th concentrations measured by ID-TIMS in a Fe-Mn crust from the NE Atlantic – crust 121DK – located on Tropic seamount (24°53'N/21°42'W, 2000 m water depth), approximately 470 km off Cape Blanc, West Africa.

Sampling and analytical procedure

Crust 121DK (~5 cm thick) was drilled at high resolution and sampled continuously every 50 μm to 1.5 mm depth. The analysed fractions represent depth intervals between 100 and 200 μm, yielding sample weights of approximately 3 to 6 mg. After addition of ^{229}Th and ^{236}U spikes, and dissolution, Th and U were separated using techniques described previously (4). Approximately 50 ng of U and Th were loaded onto separate Re filaments coated with colloidal graphite, and measured by ion counting on a Finnigan MAT-261 mass spectrometer. Typical uncertainties are ~ 0.5% for concentrations and between 1–2% for U and Th isotopic ratios.

Results and discussion

Variations in $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ with depth yield growth rates of 2.95 ± 0.15 and 3.62 ± 0.17 mm/Ma (2σ respectively. These values are consistent with the ^{10}Be growth rate (3 ± 0.3 mm/Ma) reported by Koschinsky *et al.* (5). In contrast to Th, the U isotopic record appears to be more perturbed, and $^{234}U/^{238}U$ ratios yield a growth rate of ~4 mm/Ma. The U, Th and Th/U ratios vary significantly, from 10.06 to 13, 43.3 to 67.5 ppm and 4.2 to 6.7, respectively.

The broadly similar growth rates inferred from $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ chronometers suggest that the initial ^{230}Th remained relatively constant over time, and that the crust behaved as a closed system to Th exchange. The slightly larger growth rate derived from $^{230}Th_{excess}/^{232}Th$ may, in part, be related to the huge terrigeneous input into the Eastern Atlantic (5,6). Interestingly, the data indicate that the growth rate and the $^{230}Th/^{232}Th$ sea water composition remained constant locally.

The variations in Th/U ratios may partly reflect variable dust inputs from the nearby Saharan regions, but variations in the scavenging rates of Th and U, which could also generate the observed variations, cannot be excluded. Therefore, unambiguous identification of a dust signal is not currently possible.

The inferred $^{230}Th/^{232}Th$ initial isotopic composition (2.5×10^{-4}) is relatively low compared to those previously measured in Fe-Mn crusts from the Pacific and Indian oceans (3), in complete agreement with direct seawater measurements of $^{230}Th_{excess}$ (6). This low value may either reflect a high ^{232}Th flux arising from the large detrital input and/or increased scavenging of ^{230}Th as a result of the high biological productivity in this region of the eastern Atlantic.

The two principal conclusions of this study are: (i) growth rates can be successfully derived from the $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ chronometry, even for Fe-Mn crusts sampled in the area of continental margins. In contrast, the $^{234}U/^{238}U$ chronometer appears to be less reliable in the case of crust 121DK, due to the high sensitivity of U to secondary remobilization; (ii) by combining information from different dating techniques, a reliable chronology for Fe-Mn crusts can be established.

References

1. Ku, T. L. and Broecker, W.S. (1967) *Earth Planet. Sci. Lett.*, **2**, 317–20.
2. Eisenhauer, A., Wasserburg, G.J., Chen, J.H., Papanastassiou, D., Frank, N., Mangini, A. and Bollhöffer, A. (1992) *Euro. J. Mineral*, **6**, 330
3. Chabaux, F., Cohen, A.S., O'Nions, R.K., Hein, J.R. (1995) *Geochim. Cosmochim. Acta*, **59**, 633–8.
4. Claude-Ivanaj, C., Bourdon, B., Allègre, C.J. (1997) *Earth Planet. Sci. Lett.*, in press.
5. Koschinsky, A., Halbach, P., Hein, J.R., Mangini, A. (1996) *Geol. Rundsch*, **85**, 567–76.
6. Mangini, A. and Key, R.M. (1983) *Earth Planet. Sci. Lett.*, **62**, 377–84.