

## A Hf-Nd isotopic correlation in ferromanganese nodules

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**Abstract.** The  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio was measured on 34 ferromanganese nodules, mostly from the Atlantic ocean. The different ocean basins are isotopically distinct with the extreme compositions being less radiogenic in the Atlantic ( $\epsilon_{\text{Hf}} \sim +1$ ) than in the Pacific ( $\epsilon_{\text{Hf}} \sim +9$ ). A good correlation of  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  is observed amongst most samples which supports that Hf isotopic compositions in nodules reflect those of ambient seawater. For a given  $\epsilon_{\text{Nd}}$ ,  $\epsilon_{\text{Hf}}$  is more radiogenic in ferromanganese nodules than in rocks from either the mantle or the crust. This correlation makes the coupled Hf-Nd systems a potential paleoceanographic tool. It is argued that a zircon-free clayish component of probable eolian origin may account for the radiogenic Hf in nodules.

### Introduction

As all rare-earth elements, which are well correlated with silica and enriched in deep Pacific relative to deep Atlantic waters [Klinkhammer *et al.*, 1983; Bertram and Elderfield, 1993; Jeandel, 1993], neodymium behaves as a nutrient. Its isotopic composition in the water column has been shown to be correlated with conservative tracers, such as salinity [Piepgras and Jacobsen, 1988]. Nd isotopic heterogeneities in both seawater [Piepgras and Wasserburg, 1980] and hydrogenous ferromanganese deposits [Goldstein and O'Nions, 1981] oppose ocean basins with Nd being more radiogenic in the Pacific than in the Atlantic Ocean. They are imposed by variably radiogenic Nd being injected at each end of the conveyor belt. The interest in this rather unique tracer of oceanic currents and seawater mixing has, however, remained limited because the analysis of other oceanographic markers, such as temperature, salinity, and nutrients, is far less painstaking than that of Nd isotopes. Nevertheless, the potential of Nd isotopes as a paleoceanographic tracer is strong, because, unlike salinity or nutrients, the record of isotopic properties in seawater can be preserved in authigenic material.

A single isotopic tracer does not provide enough degrees of freedom to describe the complexity of ocean water masses adequately. Lead isotopes have recently received renewed interest [Abouchami and Goldstein, 1995; Abouchami *et al.*, 1997; Christensen *et al.*, 1997; Ling, *et al.*, 1997], but will probably not find their maximum usefulness until more seawater data have become available. Hafnium isotopes represent another potential paleoceanographic tracer, which the advent of plasma source mass spectrometry is currently

bringing within reach for samples as small as 10-100 ng with a precision comparable to that of Nd isotope analyses [Blichert-Toft *et al.*, 1997]. The behavior of Hf in the water column is poorly known. Surprisingly, Hf shows no interbasin concentration variability, in contrast to geochemically similar Zr which clearly reacts as a nutrient [McKelvey and Orians, 1993; McKelvey, 1994]. Hf isotope compositions in the mantle and the crust span a range twice that of Nd [Patchett, 1983]. Although Hf isotopic heterogeneities have been identified amongst Mn nodules and encrustations, their range is limited to only *half* that of its Nd counterpart. This has been interpreted [White *et al.*, 1986] as indicating a more efficient mixing of Hf in seawater. The present work reports new Hf isotopic compositions for 34 Mn nodules from the Atlantic and the Pacific Oceans, whose Nd isotopic compositions are independently known, aimed at a better understanding of the coupled Nd-Hf isotope system in the ocean.

### Samples and Techniques

Atlantic nodule samples were obtained from the Lamont-Doherty Core Repository, and their geographic locations are shown in Figure 1. Sampling primarily covers the Atlantic basins, but, in order to get a reference for the Pacific, five nodules from this area previously analyzed by White *et al.* [1986] were reanalyzed.

Approximately 20 to 100 mg of sample taken from the nodule surface layer were spiked for Hf and dissolved in a mixture of HF-HNO<sub>3</sub>-HClO<sub>4</sub>. Chemical separation of Hf followed the procedure of Blichert-Toft *et al.* [1997]. In order to assess the contribution of diagenesis to the formation of the present samples, Fe, Mn, and other transition elements were analyzed by atomic absorption, but these results will be discussed elsewhere.

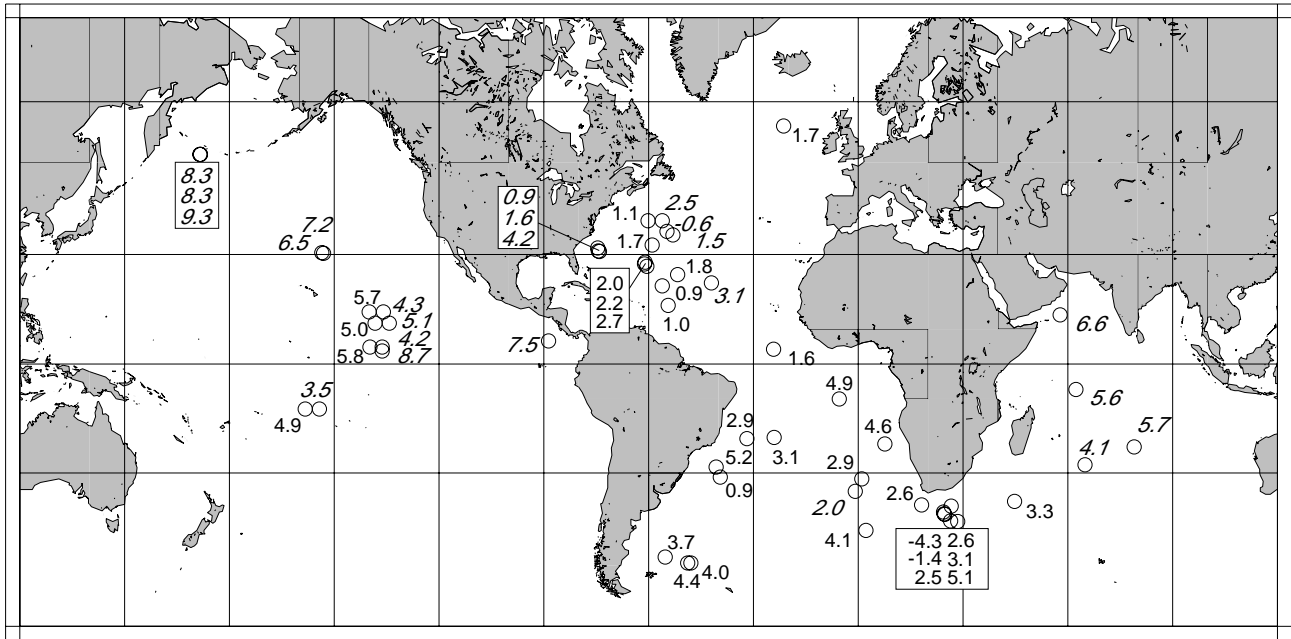
### Results and Discussion

The Pacific nodules seem to be overall poorer in Hf than Atlantic nodules. Nearly all  $\epsilon_{\text{Hf}}$  values are positive (Table 1). As shown on basaltic samples, the technique achieves an external reproducibility of Hf isotopic compositions very close to the standard error [Blichert-Toft *et al.*, 1997]. The isotopic variability is therefore significant and reflects natural heterogeneities. As noted previously [White *et al.*, 1986; Godfrey *et al.*, 1997], Hf is more radiogenic in Pacific than in Atlantic nodules. The northern Atlantic is characterized by the smaller  $\epsilon_{\text{Hf}}$  values, most of them in the range of +0.9 to +3.1, the southern Atlantic and the Indian Ocean by  $\epsilon_{\text{Hf}}$  values mostly between +2.5 and +6.6, and the Pacific by  $\epsilon_{\text{Hf}}$  values of +3.0 to +9.3. Slightly more radiogenic Hf in the Atlantic between 0 and 30°S may reflect the presence of Antarctic Bottom Water. Local variability may be important where mixing is strong, such as between the Atlantic and Indian Oceans. A few negative  $\epsilon_{\text{Hf}}$  values may reflect the

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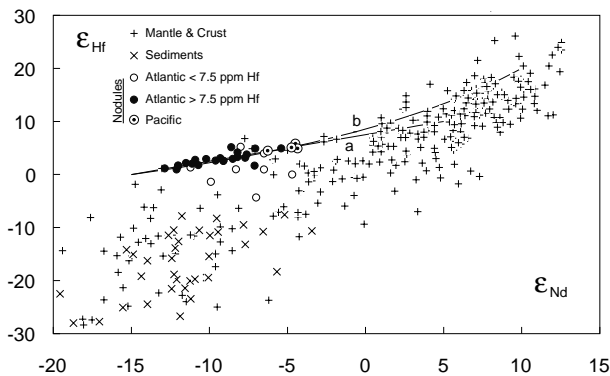
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**Figure 1.** World map of  $\epsilon_{\text{Hf}}$  data from Mn-nodules and encrustations. Figures in roman characters refer to the present work, those in italic to the work of Godfrey *et al.* [1997].

presence of a diagenetic or detrital component (e.g., sample RC14-D1 with Mn/Fe > 8).



**Figure 2.** Correlation between  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  for the nodules analyzed in this study. Also represented are Hf and Nd isotope data available at this stage on basalts, continental crustal rocks, and sediments, some compiled from literature, but most from our own recent unpublished sets of data. Two mixing lines have been drawn: (a) The Hf/Nd ratios of the two end-members are identical, and the radiogenic end-member has  $\epsilon_{\text{Nd}} \sim +5$  and  $\epsilon_{\text{Hf}} \sim +10$  as ocean island and orogenic magmas (b) The radiogenic end-member is twice as concentrated in Nd but has the same Hf concentration as the non-radiogenic end-member, in agreement with available analytical data Bertram and Elderfield [1993]; Jeandel [1993]; McKelvey [1994]; the radiogenic end-member has  $\epsilon_{\text{Nd}} \sim +10$  and  $\epsilon_{\text{Hf}} \sim +20$  as MORB. In both cases, we chose the unradiogenic end-member to have  $\epsilon_{\text{Nd}} = -15$  and  $\epsilon_{\text{Hf}} = 0$ . The present observations cannot resolve the two models.

The overall pattern of inter-ocean basin Hf isotope variability described by previous authors [White *et al.*, 1986; Godfrey *et al.*, 1997] holds with a substantially enlarged set of data (Figure 1). The argument made elsewhere [Albarède *et al.*, 1997] that regional isotopic extrema correspond to sites of input suggests that the northwestern tropical Atlantic acts as the source of unradiogenic Hf ( $\epsilon_{\text{Hf}} \sim +1$ ), while the most radiogenic Hf ( $\epsilon_{\text{Hf}} \sim +9$ ) is incorporated into the Pacific at the other end of the conveyor belt. As previously argued for Nd [Albarède and Goldstein, 1992; Albarède *et al.*, 1997], the intermediate values of the Indian Ocean do not indicate a significant source associated with the sedimentary and riverine input from the Himalayas. Good correlations exist between  $\epsilon_{\text{Hf}}$  values and Hf contents on a local scale, e.g., positive for the northwestern Atlantic and negative for the southwestern Atlantic, but their interpretation must await water-column data.

Out of the 34 samples for which both the Nd and Hf isotopic compositions are known, 27 define a reasonably good correlation (Figure 2). When the Atlantic samples with less than 7.5 ppm Hf are disregarded, the correlation becomes excellent. We surmise that the outliers have incorporated a diagenetic or a detrital component. Differences in Hf isotopic composition between the top and the bottom of the same nodule were previously reported, although they hardly exceed the associated analytical uncertainty [Godfrey *et al.*, 1997] and are significantly smaller than inter-ocean heterogeneities. This, and evidence that samples with a lower Hf concentration tend to deviate more from the correlation than those with higher Hf contents, indicate that either diagenesis affected some of the nodules to a certain extent or that a red-clay fraction could not be separated from the oxihydroxide matrix. Nevertheless, considering that the Nd isotopic composition of nodules reflects that of ambient seawater very closely [Albarède and Goldstein, 1992], the good correlation between the isotopic compositions of Hf and Nd in most fer-

**Table 1.** Hf isotope composition results

| Sample                    | Long.  | Lat.    | Depth, m  | Mn/Fe | Hf, ppm | $^{176}\text{Hf}/^{177}\text{Hf}$ (2s) | $\epsilon_{\text{Hf}}^a$ | $\epsilon_{\text{Nd}}^b$ |
|---------------------------|--------|---------|-----------|-------|---------|--|--------------------------|--------------------------|
| <i>Northwestern basin</i> |        |         |           |       |         |  |                          |                          |
| V27-D5                    | 56°16N | 21°24W  | 1509-1641 | 1.6   | 8.68    | 0.282820 (12)                          | 1.70                     | -12.0                    |
| V26-D1                    | 32°26N | 58°58W  | 3453      | 0.9   | 10.23   | 0.282819 (4)                           | 1.66                     | -7.1                     |
| RC15-D21                  | 28°02N | 61°00W  | 5028-5161 | 1.1   | 11.29   | 0.282833 (5)                           | 2.16                     | -11.5                    |
| RC15-D19                  | 27°36N | 61°08W  | 5706-5877 | 1.6   | 12.91   | 0.282849 (10)                          | 2.72                     | -10.9                    |
|                           |        |         |           |       | 14.09   | 0.282852 (6)                           | 2.83                     | -10.8                    |
|                           |        |         |           |       | 12.76   | 0.282862 (20)                          | 3.18                     | "                        |
| RC15-D23                  | 27°04N | 60°28W  | 5725-5891 | 1.2   | 12.11   | 0.282829 (8)                           | 2.02                     | -11.1                    |
| V25-D14                   | 24°57N | 51°45W  | 3140      | 1.1   | 11.10   | 0.282822 (8)                           | 1.77                     | -10.7                    |
| RC5-D1                    | 21°51N | 56°09W  | 4049      | 1.0   | 8.87    | 0.282798 (11)                          | 0.92                     | -12.1                    |
| RC11-6PC                  | 16°38N | 54°21W  | 5707      | 1.0   | 7.03    | 0.282799 (19)                          | 0.95                     | -8.3                     |
| <i>Northeastern basin</i> |        |         |           |       |         |  |                          |                          |
| V30-D2                    | 4°15N  | 24°19W  | 4399      | 1.1   | 12.11   | 0.282817 (6)                           | 1.59                     | -12.0                    |
| V27-133                   |        |         |           | 2.4   | 4.75    | 0.282720 (12)                          | -1.84                    |                          |
| <i>Southwestern basin</i> |        |         |           |       |         |  |                          |                          |
| V26-57                    | 20°46S | 24°08W  | 5297      | 3.0   | 7.88    | 0.282859 (6)                           | 3.08                     | -9.3                     |
| RC15-D13                  | 20°58S | 31°48W  | 4141-4150 | 1.2   | 13.00   | 0.282855 (9)                           | 2.94                     | -8.5                     |
| V17-T85                   | 47°35S | 43°21W  | 5492-5497 | 0.4   | 0.97    | 0.282772 (26)                          | 0.00                     | -4.7                     |
| RC15-D5                   | 48°28S | 55°14W  | 2394-2915 | 1.1   | 8.75    | 0.282878 (13)                          | 3.75                     | -7.6                     |
|                           |        |         |           |       | 9.60    | 0.282905 (19)                          | 4.70                     | "                        |
| RC16-D10                  | 28°25S | 40°45W  | 4388      | 1.7   | 5.40    | 0.282919 (18)                          | 5.20                     | -8.0                     |
| V16-188                   | 30°56S | 39°27W  | 4665      | 1.3   | 6.81    | 0.282798 (6)                           | 0.92                     | -6.5                     |
| V31-D12                   | 49°34S | 48°24W  | 3000-3929 | 1.8   | 7.38    | 0.282897 (6)                           | 4.42                     | -6.3                     |
| V15-138PC                 | 49°35S | 48°46W  | 2725      | 1.5   | 6.39    | 0.282884 (6)                           | 3.96                     | -6.5                     |
| <i>Southeastern basin</i> |        |         |           |       |         |  |                          |                          |
| RC13-D5                   | 9°58S  | 5°23W   | 1227-1561 | 2.1   | 8.26    | 0.282911 (6)                           | 4.92                     | -5.4                     |
| V22-151                   | 31°29S | 1°02E   | 3043      | 1.0   | 8.97    | 0.282854 (8)                           | 2.90                     | -10.2                    |
| V22-126                   | 41°10S | 26°30E  | 2791      | 2.8   | 7.09    | 0.282845 (10)                          | 2.58                     | -9.1                     |
| RC14-D1                   | 37°52S | 26°41E  | 2531-2942 | 8.3   | 3.21    | 0.282649 (12)                          | -4.35                    | -7.0                     |
| V29-D3                    | 43°07S | 2°07E   | 3967      | 2.0   | 10.04   | 0.282889 (11)                          | 4.14                     | -8.2                     |
|                           |        |         |           |       | 10.19   | 0.282875 (9)                           | 3.64                     | "                        |
| V29-D12                   | 22°27S | 7°33E   | 3265      | 1.2   | 4.59    | 0.283137 (49)                          | 1.29                     | -11.2                    |
|                           |        |         |           |       | 4.44    | 0.282902 (34)                          | 2.97                     | "                        |
| V34-D26                   | 41°16S | 28°24E  | 3895-4314 | 1.1   | 11.27   | 0.282861 (10)                          | 3.15                     | -7.7                     |
| V34-D25                   | 39°07S | 24°22E  | 4546-4775 | 2.2   | 11.69   | 0.282917 (36)                          | 5.13                     | -8.6                     |
| V22-D7                    | 37°33S | 18°06E  | 3147      | 1.1   | 7.44    | 0.282846 (12)                          | 2.62                     | -9.6                     |
| V22-121PC                 | 39°38S | 24°35E  | 3592      | 1.0   | 6.87    | 0.282733 (17)                          | -1.38                    | -9.9                     |
| V34-D28                   | 39°46S | 24°46E  | 2853-2963 | 1.2   | 9.34    | 0.282844 (14)                          | 2.55                     | -9.1                     |
| RC14-D3                   | 36°45S | 44°46E  | 2050-2479 | 2.4   | 7.90    | 0.282864 (8)                           | 3.25                     | -8.2                     |
| V19-D11                   | 38°04N | 60°13W  |           |       | 7.60    | 0.282804 (16)                          | 1.13                     | -12.9                    |
| <i>Pacific</i>            |        |         |           |       |         |  |                          |                          |
| MW74-2-SBT4               | 4°32N  | 140°21W |           |       | 3.84    | 0.282937 (14)                          | 5.84                     | -4.5                     |
| RC11-D19                  | 14°52N | 140°02W |           |       | 4.99    | 0.282934 (5)                           | 5.73                     | -4.4                     |
| RPOC-76 (SBT-5)           | 11°44N | 138°21W |           |       | 3.76    | 0.282913 (7)                           | 4.99                     | -4.4                     |
| V18-SBT120                | 12°52S | 158°19W |           |       | 8.61    | 0.282910 (5)                           | 4.88                     | -7.1                     |

<sup>a</sup> $^{176}\text{Hf}/^{177}\text{Hf} = 0.28216 \pm 1$  for JMC-475. Chondrite  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$  [Blichert-Toft and Albarède, 1997]

<sup>b</sup>[Simonetti, Abouchami, Goldstein, and Vervoort, unpublished]

romanganese nodules supports that these elements are not incorporated independently. The Hf isotopic composition of ferromanganese nodules therefore more likely reflects the composition of ambient seawater than a diagenetic component.

The apparently linear character of the correlation observed in Figure 2 may be misleading and the isotopic composition of the radiogenic ‘mantle’ end-member could fall anywhere between that of mid-ocean ridge ( $\epsilon_{\text{Nd}} \sim +10$ ,  $\epsilon_{\text{Hf}} \sim +20$ ) and that of ocean island or orogenic basalts ( $\epsilon_{\text{Nd}} \sim +5$ ,  $\epsilon_{\text{Hf}} \sim +10$ ) depending on the Hf/Nd ratio assumed for each end-member (see caption of Figure 2).

The correlation of Figure 2 is at an angle with the mantle-crust array. For a given  $\epsilon_{\text{Nd}}$  value, Mn nodules have more radiogenic Hf than crustal or mantle rocks. Although different Nd and Hf residence times in the ocean could account for isotopic compositions departing from the mixing

hyperbolae drawn through end-members [Elderfield, 1992], the mean composition of ferromanganese nodules plots well outside the field of crust and mantle-derived rocks. The unradiogenic ‘crustal’ component is therefore more radiogenic than expected from its Nd isotopic composition, regardless of the Hf/Nd ratio assigned to the end-member. It has been observed by White *et al.* [1986] that the Hf isotopic composition of Mn-nodules plots on the radiogenic side of deep-sea clays. These authors interpreted the Hf and Nd isotopic data on deep-sea clays and nodules as signaling the strong resistance of the low Lu/Hf zircon to weathering. They argued that detrital zircon is concentrated in shelf sediments and turbidites, while weathering forms clays and liberate ions in runoff at the expense of more fragile minerals. Exchange with suspended clay transported across ocean basins appears less plausible. The largest source of detrital continental material is in the Indian Ocean [Milliman and Meade,

1983] and yet, just as for Nd, the nodule Hf looks neither particularly unradiogenic nor variable. On the contrary, a geographic minimum of Hf and Nd isotopic compositions, which *must* signal an input of these elements, is associated with the tropical gyre in the western Atlantic, where lateral transport is minimum. Alternatively, input of radiogenic Hf and unradiogenic Nd can be eolian since the heavy zircons are not easily transported by winds. Just as for Pb [Schaule and Patterson, 1981] and Nd [Jeandel, 1995; Albarède et al., 1997], the eolian contribution should be taken into account in the balance of dissolved oceanic Hf.

We finally suggest that the coupled Nd-Hf isotope system can be used for paleoceanographic studies. As long as the bulk of the samples derived from the mantle and the crust define an array distinct from that delineated by ferromanganese nodules, and provided water-column studies confirm that Nd and Hf in nodules and their ambient seawater are similar, the identification of a marine signal in authigenic material should become much more reliable than that obtained from the analysis of Nd isotope compositions alone.

**Acknowledgments.** This work was initiated thanks to the encouragement of Steve Goldstein and Al Hofmann. We are grateful to Philippe Télouk for decisive help with the mass spectrometer. Paul Capiez carried out the transition element analyses. Ross K. Stevenson reviewed an early draft. Stephanie Schmidberger helped with chemical separation. A. Simonetti is grateful for financial support in the form of a NSERC postdoctoral fellowship. Continuing support by the Institut des Sciences de l'Univers and Ministère de l'Éducation Nationale was essential to the maintenance of the P54.

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(Received May 8, 1998; revised August 25, 1998; accepted August 27, 1998.)