nent mixture. These amphiphilic molecules, through a combination of hydrophobic effects and π-stacking interactions, might intercalate into the organic shell of **3** and thereby expand its dimensions as similar effects have been observed in both natural and abiotic systems. For example, the morphology of lecithin vesicles can be modified by incorporating cholesterol molecules into the hydrophobic regions of the membrane interface (*17*). Amphiphilic molecules that were evaluated include the Na salts of benzenesulfonic acid, benzoic acid, and phenol. Success was not met in these cases, and this outcome was attributed to the interference of these compounds with the coordination of **2** to the lanthanide ions.

15. The tubular assembly crystallizes in the trigonal system, space group $P3_112$ (number 151), $a = b = 30.4533(11)$ Å and $c = 16.2800(8)$ Å, $V = 13075.4(9)$ Å^3, $Z = 3$, $\rho_{calc} = 1.733$ g cm^{-3}, $R_1 = 0.105$ [$I > 2\sigma(I)$], and λ(Mo Kα) = 0.70930 Å; standard errors in the last decimal place are given in parentheses. Details of the x-ray structure determination are available from the CCDC (deposition number CCDC 127798).
16. C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.* **112**, 5525 (1990).
17. M. N. Jones and C. Chapman, *Micelles, Monolayers, and Biomembranes* (Wiley-Liss, New York, 1995).
18. We thank C. Barnes for crystallographic assistance. This work was supported by the NSF.

16 April 1999; accepted 29 June 1999

Hafnium Isotope Stratigraphy of Ferromanganese Crusts

Der-Chuen Lee,[1] Alex N. Halliday,[2] James R. Hein,[3]
Kevin W. Burton,[4] John N. Christensen,[1] Detlef Günther[5]

A Cenozoic record of hafnium isotopic compositions of central Pacific deep water has been obtained from two ferromanganese crusts. The crusts are separated by more than 3000 kilometers but display similar secular variations. Significant fluctuations in hafnium isotopic composition occurred in the Eocene and Oligocene, possibly related to direct advection from the Indian and Atlantic oceans. Hafnium isotopic compositions have remained approximately uniform for the past 20 million years, probably reflecting increased isolation of the central Pacific. The mechanisms responsible for the increase in ^{87}Sr/^{86}Sr in seawater through the Cenozoic apparently had no effect on central Pacific deep-water hafnium.

Variations in the radiogenic isotope composition of seawater through time have the potential to provide information on changes in continental weathering, ocean floor hydrothermal activity, and ocean circulation (*1–3*) and their relation to tectonic and climatic events (*4–6*). Isotopic records of Sr, Nd, and Pb in ferromanganese crusts from all the major ocean basins have been used to study secular variations of seawater (*7–13*). Because of analytical difficulties, Hf isotopes have received little attention until recently (*14*). Here, we present the first high-resolution and precise Hf isotopic profiles for two ferromanganese crusts dredged from central Pacific seamounts in an attempt to constrain the evolution of Hf isotopes in central Pacific deep water.

The Hf isotopic composition of seawater has yet to be measured directly but might be expected to be far more variable than that of Nd for the following reasons. First, the magnitude of Hf isotopic variations that result from the time-integrated effects of mantle melting and igneous processes is about twice that of Nd (*15*). Second, during weathering, Lu/Hf and Hf isotopic compositions display extreme variability because of selective retention of unradiogenic Hf in the resistant mineral zircon, which tends to be concentrated in coarse coastal and fluvial sands (*16*). This contrasts with the lack of erosional and sedimentary fractionation in the Sm-Nd system (*2*). Third, radiogenic Hf appears to enter seawater through ocean hydrothermal systems (*14, 17*), in contrast to the efficient scavenging of rare earth elements around vents (*18*).

The outermost surfaces of ferromanganese nodules (*19*) and crusts (*14*) have geographically heterogeneous Hf isotopic compositions, suggesting a residence time in seawater that is shorter than the turnover time of the deep oceans. The Hf isotopic composition of crusts from the Pacific is relatively radiogenic compared to those from the Atlantic (*14, 19*), consistent with the ages of the surrounding continental areas (*14, 19*). However, these oceanic variations in Hf are no greater than those found for Nd, which (given the significant isotopic variations in input) implies that the residence time for Hf is probably longer than that of Nd. A major change in the relative importance of a particular flux should therefore produce a change in the regional Hf isotopic composition of seawater, but Hf may be fairly homogeneous within an area such as the Pacific Ocean.

We analyzed two ferromanganese crusts, CD29-2 and D11-1, dredged from central Pacific seamounts at water depths of 2.3 and 1.8 km, respectively (*20*). Both crusts grew throughout most of the Cenozoic and have been studied intensively (*10–12, 20, 21*), and their growth history and state of preservation are well understood. We sliced ~0.5 mm samples through the crusts, each equivalent to a growth interval of about 0.3 million years (My), based on ^{10}Be chronology and extrapolation (*11*). A series of samples with average age differences of ≤1 My were analyzed (*22*).

Both crusts exhibit variations in Hf isotopic composition of about $4\varepsilon_{Hf}$ (*22*) (Fig. 1) and have present-day Hf isotopic compositions that are comparable to those of other hydrogenous crusts from the Pacific (*14, 19*). The two crusts display similar systematic fluctuations in their Hf records from the earliest Eocene until about 20 million years ago (Ma). The ε_{Hf} is especially high in both crusts at 25 to 24 Ma and at 33 to 32 Ma and is low at ~28 Ma. The slight offset in these changes between the crusts can be accounted for by the uncertainty of the extrapolated Co and ^{10}Be ages (Fig. 1) (*21*). The more extensive record for D11-1 shows a major dip and rise in the Eocene, and low values at about 44 and 40 Ma. Both crusts display a slight rise in ε_{Hf} between 20 and 6 Ma, but the effect is small (Fig. 1).

Phosphatization is a common feature among thick ferromanganese crusts from the Pacific (*23*), and both CD29-2 and D11-1 show evidence of phosphatization before 26 Ma and before 20 Ma, respectively (*11, 23*). However, P concentrations vary by an order of magnitude through the phosphatized interval of each crust (*11, 23*). There is no sign in either crust that the Hf isotopic composition or the Lu/Hf ratio varies with P (Fig. 1). Furthermore, despite very different phosphatization records, the major fluctuations in Hf isotopic composition for the two crusts are well correlated. As a consequence, phosphatization has clearly been of negligible importance to the Hf isotope compositions. Diagenesis is also unlikely to alter the long-term Hf isotope records in ferromanganese crusts (*24*).

Instead, we consider that the Hf isotopic variations reflect gradual modification of central Pacific deep water by changes in sources and circulation through time. That these two crusts, separated by more than 3000 km, yield comparable isotopic compositions indicates that the ambient seawater, central Pacific deep water, has always remained

---

[1]Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA. [2]Institut für Isotopengeologie und Mineralische Rohstoffe, Department für Erdwissenschaften, ETH-Zentrum, NO C61, Sonneggstrasse 5, CH-8092 Zürich, Switzerland. [3]U.S. Geological Survey, MS 999, 345 Middlefield Road, Menlo Park, CA 94025, USA. [4]Department des Sciences de la Terre, Universite Blaise-Pascal, 63038 Clermont-Ferrand, France. [5]Institut für Analytische Chemie und Spurenanalytik, ETH Zürich, Laboratorium für Anorganische Chemie, Universitätsstrasse 6, CH-8092 Zürich, Switzerland.

well-mixed in terms of Hf isotopes. This confirms the view that the residence time of Hf is reasonably long and has remained so throughout most of the Cenozoic. There is no correlation between the Hf isotope records and independent estimates of spreading rate or volcanic activity in circum-Pacific arcs (Fig. 1) (*25*). Similarly, the enhanced hydrothermal activity on the East Pacific Rise during the past 20 My (*26*) is not mirrored in the Hf record (Fig. 1). Thus, Hf does not seem to be a sensitive tracer for ocean floor hydrothermal activity (*14, 17*).

The records imply that the Hf isotopic composition ($\varepsilon_{Hf} = +6 \pm 1$) of central Pacific deep water was constant over the past 20 My. In addition to the major changes in Pacific volcanism and hydrothermal activity over this period, Earth experienced acute coeval changes in tectonics and climate. Yet even before 20 Ma the average composition ($\varepsilon_{Hf} = +6 \pm 2$) was very similar to what it is today. Consequently, any satisfactory theory to account for the Hf isotopic composition of seawater must predict why a region the size of the central Pacific that admixes Hf from such a large area sustains a reproducible Hf isotopic composition for so long.

Published Nd isotopic records for CD29-2 and D11-1 were not very comprehensive (*11*); we therefore obtained Nd isotopic compositions of selective samples from D11-1 corresponding to times of major systematic shifts in Hf (48 to 28 Ma; Fig. 2). In general, Nd isotopic compositions of both crusts became more radiogenic up until ~4 Ma when ε_{Nd} decreased (Fig. 2), indicating very different behavior from Hf. Nd and Hf isotopic compositions of the outermost surfaces of most ferromanganese nodules are correlated from all the major ocean basins (*19*). However, our data imply that changes in Hf and Nd isotopes in seawater in the central Pacific were decoupled throughout much of the Cenozoic and that the transport of Nd and Hf must be different.

No general relation is found between Hf and Pb isotope records in either crust (Fig. 2). However, some parallel features are seen, such as low points in the $^{207}Pb/^{206}Pb$ ratios and ε_{Hf} at around 15 Ma in CD29-2. The much stronger maximum in Pb isotopes at ~10 Ma is, however, not found in Hf. In D11-1, a sharp decline in ε_{Hf} and $^{207}Pb/^{206}Pb$ ratios occurs between 24 and 21 Ma, but the major decrease in Hf around 28 Ma is not reflected in Pb. Overall, the well-defined variations in Pb and Nd isotopic compositions in central Pacific seawater during the past 20 Ma are not paralleled by variations in Hf isotopes (Fig. 2). This is consistent with Hf having a longer residence time and therefore recording mixing of a larger region of ocean water than Nd and Pb. Therefore, Hf isotopes should preserve a better correlation with larger scale changes, and a more appropriate comparison might be with the timing of global changes in erosion and ocean circulation.

The best monitors of global changes in erosion come from the position of the carbonate compensation depth, ocean sediment volume, and the marine $^{87}Sr/^{86}Sr$ record (*27*).

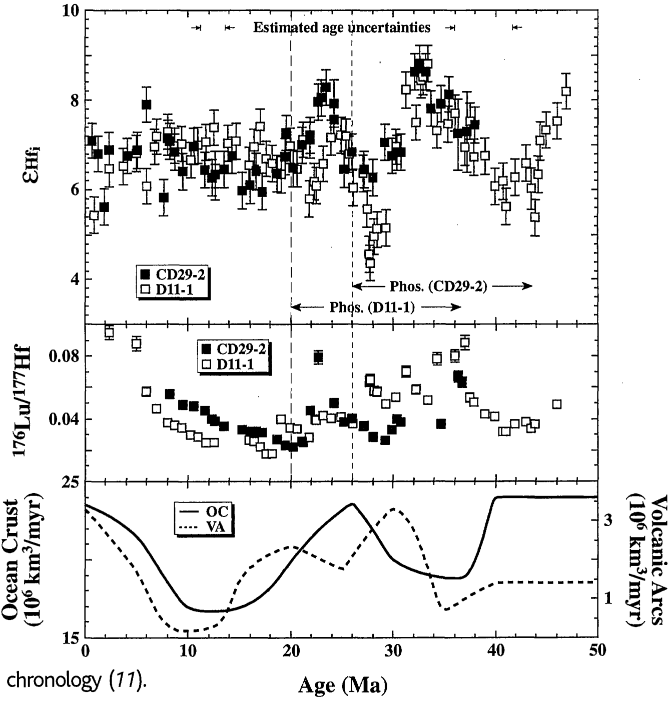

Fig. 1. Initial ε_{Hf} (ε_{Hf_i}) versus age for CD29-2 and D11-1 combined, and Lu/Hf ratios versus age for selected samples from CD29-2 and D11-1 (*22*). The estimated productions of oceanic crusts and volcanic arcs over the same period of time (*25*) are also plotted for comparison. The timing of phosphatization (*11*) for CD29-2 (26 Ma) and D11-1 (20 Ma) are shown by vertical dashed lines. The uncertainty of ^{10}Be chronology increases with age, and is estimated to be ≥2 My at ~10 Ma (*11*). No age uncertainty is given for Co-based chronology (*21*), and the minimum age uncertainty at ≥30 Ma was estimated assuming a linear increase of the uncertainty based on the ^{10}Be chronology (*11*).

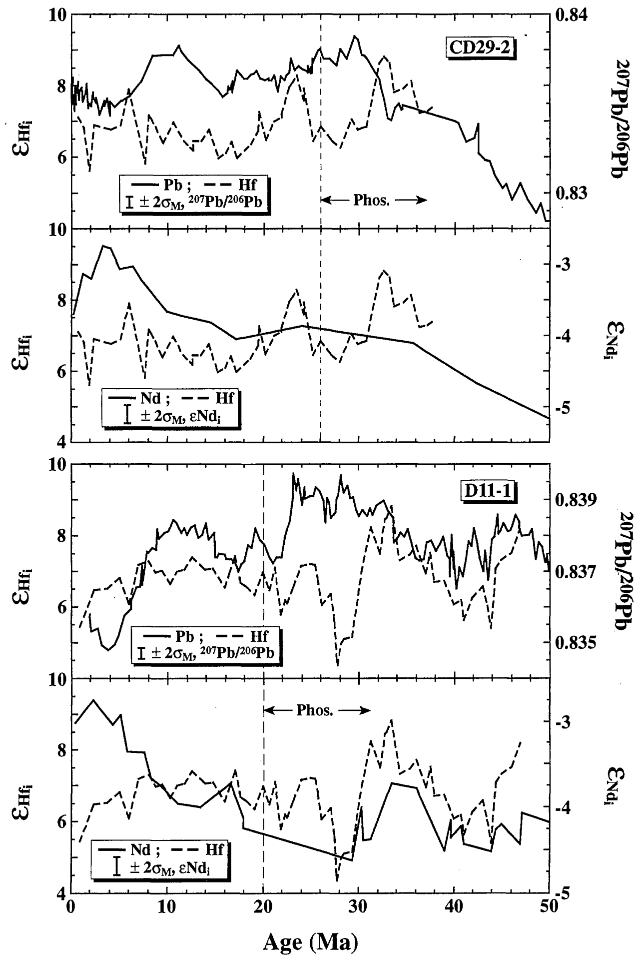

Fig. 2. Patterns of Hf, Pb, and Nd isotopic records versus age for CD29-2 and D11-1. The Pb data are taken from (*12*), and Nd data are from (*11*) and this study.

The Sr isotope record shows that seawater became more radiogenic rapidly through the Oligocene (from $\sim$34 Ma), then more gradually in the early to mid-Miocene ($\sim$18 Ma). This pattern is commonly thought to reflect increased weathering accompanying the uplift of the Himalayas and the onset of southern and northern hemisphere glaciations (*27*). The time interval from 34 to 18 Ma encompasses the major changes in Hf isotopic composition. If weathering was more intense from 34 to 18 Ma, this may have also affected the Hf record. However, such an explanation does not account for the observation that ^{87}Sr/^{86}Sr has continued to increase since 18 Ma, whereas $\varepsilon_{\mathrm{Hf}}$ stabilized after 20 Ma. Furthermore, the early (Eocene) Hf records of the crusts show large fluctuations, yet this was a time of extremely low weathering accompanied by steady and less radiogenic ^{87}Sr/^{86}Sr. Therefore, changes in the weathering style appear to have had no predictable effect on Hf isotopic composition. Given their even shorter residence times, a Nd or Pb record in ferromanganese nodules and crusts that accurately depicts large-scale changes in continental weathering is considered unlikely (*9, 13*).

Major changes in Pacific Ocean circulation are a more reasonable explanation for the change from a variable to a constant Hf isotopic composition at about 20 Ma. Circulation changes relevant to Hf isotopes are those caused by the closing of gateways and those that increase the efficiency of ocean water mixing. Two major gateways may be important in this respect. During the early Cenozoic a major gateway existed north of Australia, which was at that time still located close to Antarctica (*3*). This deep Indonesian seaway would have allowed rapid egress of equatorial waters directly from the Indian Ocean into the Pacific. During the Eocene and Oligocene this gateway closed as Australia migrated northward. Today, Indian Ocean water mixes with circum-Antarctic water south of Australia before northward migration into the Pacific (*3*). Since 20 Ma, Hf from the Indian Ocean has possibly been removed before northward-advected Antarctic deep water reached the central Pacific. During the Eocene there would have been easy direct access, so that any major changes in erosion and plate reorganization in the Indian Ocean would have had a direct effect on Pacific Ocean Hf. Also, the Panama gateway separated North and South America and would have allowed communication between the Atlantic and Pacific oceans until the mid-Miocene, when it started to shallow and close. The present-day Hf isotopic composition of Atlantic seawater is significantly less radiogenic than those of the Pacific and Indian oceans, which are about the same (*14*). The similarity in Hf isotopic compositions between the Indian and Pacific oceans is difficult to reconcile with the view that the closure of the Indonesian gateway had a significant influence on central Pacific Hf (*14, 19*). Whether this similarity extends back through the Cenozoic is a matter for further study. The differences between the Hf isotopic compositions of the Atlantic and Pacific extend back through the Cenozoic (*28*). It therefore seems plausible that, in the early Cenozoic, Atlantic water was able to flow westward into the Pacific Ocean and mix with central Pacific deep water. This would be consistent with Pb isotopic data (*12*). The second kind of change in circulation that may have developed as a consequence of climate change is an increase in the vigor of mixing within the Pacific itself, such that the admixing of heterogeneities from the north and south Pacific became more thorough. It has been suggested on the basis of Pb isotopic data that the mixing efficiency of the central Pacific increased through the Cenozoic (*12*). However, further data for other Pacific crusts are needed to confirm or refute this theory. What is clear is that with the present relative isolation of central Pacific deep water, Hf isotopic compositions largely reflect the average of net inputs from around the Pacific basin. It is striking that the composition of these inputs has not changed through the past 20 My. Therefore, the changes in ^{87}Sr/^{86}Sr in the global seawater record must reflect changing inputs outside the vicinity of the Pacific Ocean or processes that do not affect Hf.

References and Notes

1. W. H. Burke *et al.*, *Geology* **10**, 516 (1982).
2. S. L. Goldstein and R. K. O'Nions, *Nature* **292**, 324 (1981).
3. W. W. Hay, *Geol. Rundsch.* **85**, 409 (1996).
4. E. Maier-Reimer, U. Mikolajewicz, T. J. Crowley, *Paleoceanography* **5**, 349 (1990).
5. W. S. Broecker and G. H. Denton, *Geochim. Cosmochim. Acta* **53**, 2465 (1989); A. M. Macdonald and C. Wunsch, *Nature* **382**, 436 (1996).
6. U. Mikolajewicz, E. Maier-Reimer, T. J. Crowley, K.-Y. Kim, *Paleoceanography* **8**, 409 (1993).
7. A. Aplin, A. Michard, F. Albarède, *Earth Planet. Sci. Lett.* **81**, 7 (1986).
8. B. L. Ingram, J. R. Hein, G. L. Farmer, *Geochim. Cosmochim. Acta* **54**, 1709 (1990).
9. F. Albarède and S. L. Goldstein, *Geology* **20**, 761 (1992); ———, D. Dautel, *Geochim. Cosmochim. Acta* **61**, 1277 (1997).
10. W. Abouchami, S. L. Goldstein, S. J. G. Galer, A. Eisenhauer, A. Mangini, *Geochim. Cosmochim. Acta* **61**, 3957 (1997); R. K. O'Nions, M. Frank, F. von Blanckenburg, H.-F. Ling, *Earth Planet. Sci. Lett.* **155**, 15 (1998); K. W. Burton, H.-F. Ling, R. K. O'Nions, *Nature* **386**, 382 (1997); F. von Blanckenburg, R. K. O'Nions, N. S. Belshaw, A. Gibb, J. R. Hein, *Earth Planet. Sci. Lett.* **141**, 213 (1996); F. von Blanckenburg, R. K. O'Nions, J. R. Hein, *Geochim. Cosmochim. Acta* **60**, 4957 (1996).
11. H.-F. Ling *et al.*, *Earth Planet. Sci. Lett.* **146**, 1 (1997).
12. J. N. Christensen, A. N. Halliday, L. V. Godfrey, J. R. Hein, D. K. Rea, *Science* **277**, 913 (1997).
13. M. Frank and R. K. O'Nions, *Earth Planet. Sci. Lett.* **158**, 121 (1998).
14. L. V. Godfrey *et al.*, *ibid.* **151**, 91 (1997).
15. J. Patchett, *Geochim. Cosmochim. Acta* **47**, 81 (1983).
16. J. Patchett, W. M. White, H. Feldmann, S. Kielinczuk, A. W. Hofmann, *Earth Planet. Sci. Lett.* **69**, 365 (1984).
17. W. M. White, J. Patchett, D. BenOthman, *ibid.* **79**, 46 (1986).
18. A. N. Halliday, J. P. Davidson, P. Holder, R. M. Owen, A. M. Olivarez, *Geophys. Res. Lett.* **19**, 761 (1992).
19. F. Albarède, A. Simonetti, J. D. Vervoort, J. Blichert-Toft, W. Abouchami, *ibid.* **25**, 3895 (1998).
20. J. R. Hein *et al.*, *U.S. Geol. Surv. Open File Rep. 87-663* (1987); J. R. Hein *et al.*, *U.S. Geol. Surv. Open File Rep. 90-407* (1990).
21. M. Frank, R. K. O'Nions, J. R. Hein, V. K. Banakar, *Geochim. Cosmochim. Acta*, in press.
22. All samples were dissolved in 6 N HCl and dilute HF. The chemical separation of Hf was achieved using two sets of columns. The first set was adapted from the first column of the Hf chemistry developed by Salters and Hart (*29*), but on a much reduced scale of $\sim$1 ml of Bio-Rad AG1 ×8 (200 to 400 mesh) anion resin. 4 N HF was used in sample loading and elution of the matrix, and 6 N HCl + 1 N HF was used to extract Hf. The bulk of Ti and Zr were extracted using a second column consisting of $\sim$0.7 ml of Eichrom Ln resin (50 to 100 μm); sample loading, elution, and extraction of Hf were all achieved using 2 N HCl + 0.1 N HF. The Nd fractions were extracted from the insoluble residues (predominantly fluorides) of the first-column chemistry following the chemical separation outlined in Lee *et al.* (*30*). Multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) isotopic measurement was as described (*31*). Replicate measurements of JMC 475 Hf and JMC Nd standards give a mean ^{176}Hf/^{177}Hf = 0.282161 ± 9 and a mean ^{143}Nd/^{144}Nd = 0.51183 ± 2. The Lu/Hf ratios of selected fractions were determined at ETH Zürich using a Perkin Elmer ELAN 6000 ICP-MS with a Cetac MCN6000 desolvating nebulizer, and the data are consistent with the isotope dilution measurements. See *Science* Online (www.sciencemag.org/feature/data/1040614.shl) for both data sets. All the Hf isotopic data, including those of Godfrey *et al.* (*14*), have been corrected for radioactive ingrowth of ^{176}Lu and are expressed as $\varepsilon_{\mathrm{Hf}}$, deviations from the chondritic (bulk Earth) Hf isotopic composition (*32*) in parts per 10^4. The 2σ analytical uncertainty was typically 40 ppm or better for Hf, $\leq$30 ppm for Nd, and $\leq$5% for Lu/Hf ratios. Total procedure blank was $\leq$20 pg for Hf, which was negligible.
23. J. R. Hein *et al.*, *Paleoceanography* **8**, 293 (1993); A. Koschinsky, A. Stascheit, M. Bau, P. Halbach, *Geochim. Cosmochim. Acta* **61**, 4079 (1997).
24. G. M. Henderson and K. W. Burton, *Earth Planet. Sci. Lett.*, in press.
25. K. Kaiho and S. Saito, *Terra Nova* **6**, 376 (1994).
26. M. Lyle, M. Leinen, R. M. Owen, D. K. Rea, *Geophys. Res. Lett.* **14**, 595 (1987).
27. F. M. Richter and D. J. DePaolo, *Earth Planet. Sci. Lett.* **90**, 382 (1988).
28. D.-C. Lee *et al.*, *Eos* **79**, F443 (1998); A. Piotrowski *et al.*, *ibid.* **80**, S184 (1999).
29. V. J. M. Salters and S. R. Hart, *Earth Planet. Sci. Lett.* **104**, 364 (1991).
30. D.-C. Lee, A. N. Halliday, J. G. Fitton, G. Poli, *ibid.* **123**, 119 (1994).
31. D.-C. Lee and A. N. Halliday, *Int. J. Mass Spec. Ion Proc.* **146–147**, 35 (1995).
32. J. Blichert-Toft and F. Albarède, *Earth Planet. Sci. Lett.* **148**, 243 (1997).

33. We thank F. Albarède and M. Frank for comments, C. H. Stirling and D. A. H. Teagle for discussion, and M. W. Johnson for technical assistance. Supported by the U.S. Department of Energy and NSF.

5 April 1999; accepted 2 July 1999