

The control of weathering processes on riverine and seawater hafnium isotope ratios

- Germain Bayon Département des Géosciences Marines, Institut Français de Recherche pour l'Exploitation de la Mer, 29280 Plouzané, France
- Nathalie Vigier Centre de Recherches Pétrographiques et Géo-chimiques, 15 rue Notre-Dame des Pauvres, 54501 Vandoeuvre-lès-Nancy, France
- Kevin W. Burton Department of Earth Sciences, The Open University, Milton Keynes MK7 6AA, UK
- Agnès Brenot, } Centre de Recherches Pétrographiques et Géo-chimiques, 15 rue Notre-Dame des Pauvres, 54501
Jean Carignan } Vandoeuvre-lès-Nancy, France
- Joël Etoubleau Département des Géosciences Marines, Institut Français de Recherche pour l'Exploitation de la Mer, 29280 Plouzané, France
- Nan-Chin Chu Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK

ABSTRACT

Hafnium $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio variations in marine records are thought to reflect changes in continental weathering through time, but the behavior of Hf in rivers, and during weathering, is not well understood. Here, we present $^{176}\text{Hf}/^{177}\text{Hf}$ data for rivers, bedrock, soils, and leaching experiments for the Moselle basin, Vosges, France. These data strongly suggest that the $^{176}\text{Hf}/^{177}\text{Hf}$ composition of river waters is controlled by preferential dissolution of accessory phases (i.e., apatite, sphene) versus more resistant minerals (e.g., K-feldspar) and linked to the intensity of silicate weathering. Estimates for the global isotopic composition of riverine Hf suggest that the ocean Hf budget may be dominated by river input, and variations seen in marine records can be directly related to changes in silicate weathering intensity.

Keywords: hafnium isotopes, rivers, silicate weathering, ocean chemistry.

INTRODUCTION

Many attempts to reconstruct the link between climate change, crustal weathering, and ocean chemistry have focused upon measurements of radiogenic isotope ratios, such as Sr and Os, in ancient seawater records (e.g., Edmond, 1992; Ravizza and Peucker-Ehrenbrink, 2003). Deconvolving the silicate weathering signal from these isotopic records is not straightforward, however, mainly because the global riverine input of dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{186}\text{Os}/^{187}\text{Os}$ ratios is influenced to a great extent by weathering of nonsilicate rocks, carbonates, and organic-rich shales, respectively. In contrast to Sr and Os, Hf is primarily hosted in crustal rocks (granites, felsic volcanics, terrigenous sediments), exhibiting very low concentrations in carbonates (see the GERM Reservoir database; www.earthref.org/). Recent investigations of deep-sea ferromanganese crusts and nodules have suggested that the Hf isotopic composition of past oceans may serve as a sensitive tracer of silicate weathering (Albarède et al., 1998; Lee et al., 1999; Piotrowski et al., 2000; van de Fliedert et al., 2002, 2004a). On a plot representing Nd (ϵ_{Nd}) versus Hf (ϵ_{Hf}) isotopic compositions (Hf and Nd isotopic compositions are commonly expressed as ϵ_{Hf} and ϵ_{Nd} , respectively, which represent the deviation of $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for any sample from a reference value [CHUR, Chondritic Uniform

Reservoir: $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$; $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$), ferromanganese precipitates define a “seawater” array, characterized by radiogenic (high) Hf isotope values, which is distinct from the terrestrial array of oceanic basalts, continental crustal rocks, and sediments (Vervoort et al., 1999). Recent studies (Piotrowski et al., 2000; van de Fliedert et al., 2002, 2004a) have proposed that dissolution of the zircon-free component of continental rocks during crustal weathering releases a radiogenic fraction of dissolved Hf to rivers, thereby accounting for the high $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in seawater. Until now, however, it has not been possible to test this hypothesis directly because of analytical difficulties in measuring $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in low-level samples such as waters.

Here, we report direct measurements of $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for river waters draining silicate rocks, which bring new information on the global link between silicate weathering, climate, and ocean chemistry. Small monolithological watersheds are better suited than large rivers for studying processes and factors related solely to silicate weathering (e.g., Louvat and Allègre, 1997; Millot et al., 2002). The behavior of hafnium isotopes during silicate weathering was also investigated through laboratory experimental dissolution of granite samples, using nitric acid solutions, and analyses of natural rocks and soils.

MATERIALS AND METHODS

Five rivers from the Moselle drainage basin (eastern France) were sampled in June 2003. Details on the sampling and analytical procedures are available in the GSA Data Repository.¹ All these rivers drain exclusively silicate rocks (granite, gneiss, sandstone) of Variscan age (ca. 330 Ma) from the Vosges Mountains, apart from one river (Avière), which also flows downstream on Triassic limestones and marl terranes. Major element concentrations were determined on aliquots of filtered waters by ICP-AES (Mg, Ca, Na, K, Si, Fe), ICP-MS (Al) and ion chromatography (SO_4^{2-} , Cl^- , NO_3^- , PO_4^{2-} , F^-).

A suite of four unaltered rocks from the Moselle basin was analyzed: two granites (GP3, BV-MOS1), one granito-gneiss (LPG1) and one sandstone (GV). Four soils were also studied: three granitic soils (GP1, GP2, and BV-MOS2), associated with the aforementioned granites, and one soil overlying limestones (GP7). A series of leaching experiments were conducted on GP3, LPG1, and GV, using diluted ultrapure nitric acid solutions of three different molarities (0.5 M, 2 M, and 6 M HNO_3). Major element chemistry for rocks and nonsoluble residues was determined by wavelength-dispersive X-ray fluorescence spectrometry. For Hf isotope analyses of rocks, soils, and nonsoluble residues, 100 mg of crushed samples were digested by alkaline fusion ($\text{NaOH-Na}_2\text{O}_2$), using a method described previously (Taicheng et al., 2002). This method ensures the total dissolution of resistant minerals (e.g., zircons) and allows the preconcentration of Hf and other trace elements by coprecipitation onto Fe-oxides.

Hf and Nd fractions were chemically purified using ion exchange separation techniques described elsewhere (Chu et al., 2002; Dosso

¹GSA Data Repository item 2006085, material and methods, Tables DR1–3, and details on calculations, is available online at www.geosociety.org/pubs/ft2006.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

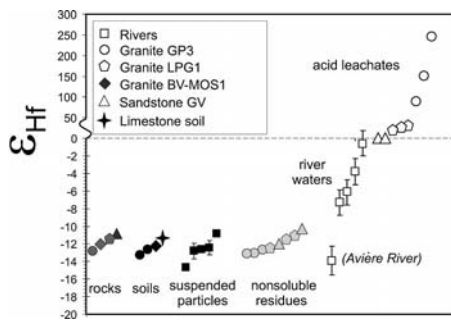


Figure 1. Hf isotope compositions for Moselle basin rivers (dissolved loads and suspended particles), bedrocks, soils, and acid leachates and nonsoluble residues. Errors reported for river waters are 2σ (external reproducibility; 1.56ϵ units). Errors for rocks, soils, suspended particles, nonsoluble residues, and acid leachates are within the size of symbols. Open symbols refer to rivers (square) and acid leachates (triangle, pentagon, circle); dark gray-colored symbols refer to whole rocks (circle, diamond, pentagon, triangle); light gray-colored symbols refer to nonsoluble residues; black symbols refer to river suspended particles (square) and soils (circle, diamond, star).

et al., 1991). The chemistry blank for Hf is ~ 10 – 15 pg, accounting for less than 0.5% of the sample total. Hf isotope analyses were performed at the Open University using a Nu Instruments multicollector ICP-MS. Nd isotope ratios were measured by TIMS (Triton, Finnigan) at the University of Brest (UBO, France).

RESULTS

Results for river dissolved loads, suspended particles, and leaching experiments are presented in Figure 1 and in the GSA Data Repository (see footnote 1). Dissolved loads of rivers in eastern France span a wide range of ϵ_{Hf} , from -13.9 to -0.6 , which is more than five times that of ϵ_{Nd} for the same suite of samples (from -11.1 to -8.7 ; Fig. 1; Table DR2 [see footnote 1]). Suspended particles from the same rivers exhibit much lower ϵ_{Hf} values, from -14.7 to -10.8 . Similar findings were obtained from our dissolution experiments of Vosgian granites. Acid leachates are characterized by very radiogenic signatures (up to $\epsilon_{\text{Hf}} \sim +250$). In contrast, nonsoluble residues exhibit lower ϵ_{Hf} values, from -13.1 to -10.4 , that are almost identical to those of bulk rocks (-12.8 to -11.0), soils (-11.3 to -13.2), and river suspended particles (Fig. 1). The observation that both soils and whole rocks exhibit similar Hf isotopic composition shows that only a very small fraction of dissolved Hf is remobilized from whole rocks during silicate weathering. The Hf isotopic homogeneity for all rocks, soils, residues, and particles analyzed in this study is best explained by the ubiquitous presence of minerals resistant to weathering, notably zircon, a min-

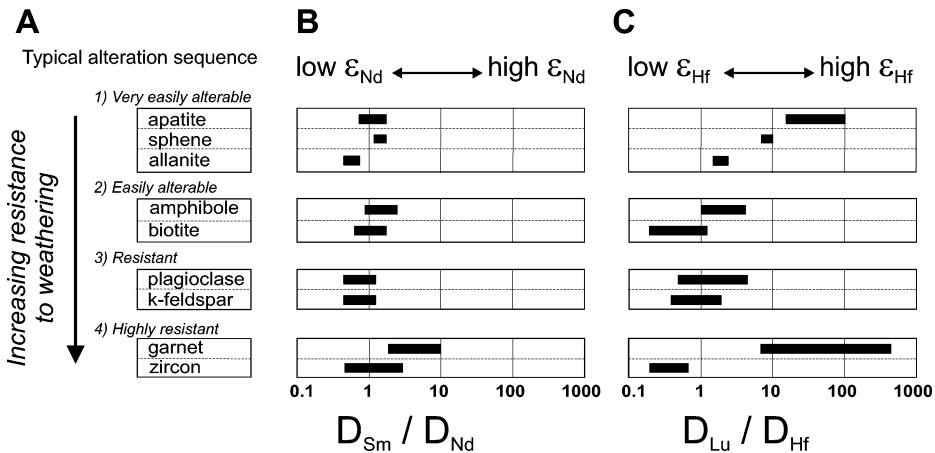


Figure 2. The link between Hf isotopes and silicate weathering intensity. **A:** Typical sequence of alteration during weathering of granitic rocks. This sequence is based on early studies (Goldich, 1938; Ollier, 1984) and more recent experimental work (Harlavan and Erel, 2002; Erel et al., 2004). **B and C:** Lu-Hf and Sm-Nd mineral-liquid partition coefficient ratios (D) for most common granite-forming minerals (compiled from <http://earthref.org/GERM>). Alteration of biotite occurs typically at early stages of granitoid dissolution, but biotite is often loaded with inclusions of accessory minerals (e.g., apatite, sphene, allanite, zircons).

eral that dominates the Hf budget in granitic rocks and is highly resistant to weathering. Note that the Avière River represents an exception in this study because it flows over marl and carbonate-rich terranes, which dissolve congruently during chemical weathering. Hence, suspended and dissolved loads in the Avière River both exhibit very similar Hf isotopic compositions.

LINKING Hf ISOTOPES TO SILICATE WEATHERING PROCESSES

The river data from eastern France represent the first direct evidence that granite weathering can lead to the preferential release of radiogenic Hf in the river dissolved load. The wide range of ϵ_{Hf} values in Moselle river waters cannot be explained by changes in bulk rock compositions because all Vosgian rocks and soils analyzed in this study exhibit a similar Hf isotopic signature. The presence of Al- and Fe-rich mineral colloids in the dissolved river loads, too fine to be retained by $0.2 \mu\text{m}$ membrane filters, also cannot account for ϵ_{Hf} variations because no correlation is observed between ϵ_{Hf} and $\text{Al}/\text{TZ}+$ or $\text{Fe}/\text{TZ}+$ ratios (with $\text{TZ}+$ being related to the total cationic charge; Table DR1). Therefore, it seems most likely that the Hf isotopic variations in Moselle rivers reflect the preferential dissolution of specific mineral phases during weathering.

Evidence from Partition Coefficient Ratios

The decoupling between Sm-Nd and Lu-Hf isotopic systems during weathering is illustrated clearly by comparing partition coefficient ratios $D_{\text{Lu}}/D_{\text{Hf}}$ and $D_{\text{Sm}}/D_{\text{Nd}}$ for most common granite-forming minerals (Fig. 2) with a typical weathering sequence (Fig. 2A). The Hf isotopic composition of any mineral

depends on the mineral age, its initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, and its parent/daughter ratio ($^{176}\text{Lu}/^{176}\text{Hf}$). Due to the radioactive decay (half-life = 3.6×10^{10} yr) of ^{176}Lu to ^{176}Hf , minerals characterized by a high $^{176}\text{Lu}/^{176}\text{Hf}$ ratio (i.e., high $D_{\text{Lu}}/D_{\text{Hf}}$) acquire a radiogenic Hf isotopic signature (high ϵ_{Hf}) with time. Previous studies have shown that Sm and Nd are not fractionated significantly during weathering processes (e.g., Öhlander et al., 2000; Andersson et al., 2001), explaining why dissolved and suspended loads of rivers generally exhibit similar Nd isotopic compositions (e.g., Goldstein and Jacobsen, 1987). This is because Sm and Nd have similar partition coefficients (e.g., $D_{\text{Sm}}/D_{\text{Nd}} \sim 1$) in most common granite-forming minerals (Fig. 2A). In contrast, $D_{\text{Lu}}/D_{\text{Hf}}$ ratios (and hence ϵ_{Hf} values) decrease systematically from the least resistant to the most resistant minerals (Fig. 2C), except for garnet, which is highly resistant to weathering processes. These observations demonstrate the link between the Hf isotopic composition of river waters and silicate weathering intensity.

Evidence from Granite Leaching Experiments

Experimental dissolution studies have shown that calcium-rich accessory phases (apatite, allanite, sphene) are dissolved during the initial stage of granite weathering (Fig. 2A) (Harlavan and Erel, 2002; Erel et al., 2004; Aubert et al., 2004). Alteration of ferromagnesian minerals (amphiboles, biotite) occurs typically in early stages of granitoid dissolution. For other major granite-forming minerals (plagioclase, K-feldspar), weathering generally occurs later. The same sequence of alteration has been observed during our leaching

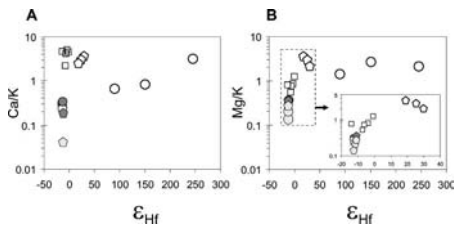


Figure 3. Ca/K and Mg/K ratios versus ϵ_{Hf} values of rocks, rock leachates and residues, and river waters from the Vosges Mountains. Symbols are in Figure 1.

experiments. Granite leaching with the weakest acid solution (0.5 M HNO₃) leads to a significant loss of Ca and P (Table DR3), indicating that apatite and possibly other Ca-rich phases are dissolved preferentially. Considering that all P leached from granite samples with 0.5 M HNO₃ solutions is derived from the dissolution of stoichiometric apatite [Ca₅(PO₄)₃(F,Cl,OH)], mass balance calculations suggest that dissolution of apatite with 0.5 M HNO₃ solutions accounts here for ~90% of total leached calcium. This is confirmed by the highly radiogenic Hf signature for acid leachates ($\epsilon_{\text{Hf}} \sim +30$ for LPG1; $\epsilon_{\text{Hf}} \sim +250$ for GP3), in accord with our estimates for the Hf isotopic composition of Vosgian apatites ($\epsilon_{\text{Hf}} \sim +200$ –1000; see the Data Repository [see footnote 1]). For each granite, the overall correlation between Ca/K ratios and ϵ_{Hf} in bedrocks, acid leachates, and residues (Fig. 3A) demonstrates that the Hf isotopic composition of acid-soluble fractions is controlled by the preferential dissolution of very radiogenic accessory minerals (e.g., apatite, sphene) versus more resistant unradiogenic minerals such as plagioclase and K-feldspar. A graph plotting ϵ_{Hf} versus P/K for whole rocks, acid leachates, and nonsoluble residues (not shown here) would also demonstrate that radiogenic apatite has been dissolved preferentially over feldspars during leaching experiments.

A similar relationship is also observed between Mg/K ratios and ϵ_{Hf} (Fig. 3B). High Mg/K ratios in our granite leaching experiments most likely reflect dissolution of both amphibole (actinolite) and biotite. It is unclear how dissolution of ferromagnesian minerals may affect the Hf isotopic composition of acid leachates. Although biotite is most likely characterized by low ¹⁷⁶Hf/¹⁷⁷Hf (Fig. 2), it is often loaded with inclusions of accessory minerals (e.g., apatite, sphene, allanite, zircon), whose dissolution (for apatite and sphene) may release a radiogenic fraction of Hf. Overall, the positive correlation between Mg/K ratios and ϵ_{Hf} for whole rocks, acid leachates, and nonsoluble residues is in accord with our hypothesis that the Hf isotopic composition of acid leachates is controlled primarily by the preferential dissolution of very radiogenic ac-

cessory minerals (e.g., apatite, sphene) versus more resistant feldspars.

Evidence from River Chemistry

The major element chemistry of rivers draining silicate rocks is controlled primarily by silicate weathering reactions (e.g., White and Blum, 1995; Millot et al., 2002), although dissolution of nonsilicate Ca-rich minerals (e.g., trace calcite, apatite) and biological processes may also influence to a great extent fluxes of some dissolved elements such as Ca and Si (e.g., White et al., 1999; Blum et al., 2002; Derry et al., 2005). In Figure 3B, Mg/K ratios for silicate rivers correlate positively with ϵ_{Hf} values, plotting between acid leachates and residual fractions. Certainly, our leaching experiments were designed to achieve far from equilibrium conditions (i.e., very low pH, high solution/sample weight ratios) in order to avoid any secondary mineral precipitation, and this may not be representative of field conditions. However, the relationship between Mg/K and ϵ_{Hf} observed both in silicate rivers and during laboratory experiments does support our hypothesis that the Hf isotopic signature of rivers draining silicate rocks is directly linked to the preferential dissolution of selective minerals (apatite, sphene, ferromagnesian minerals) versus more resistant feldspars.

Other processes such as isotopic exchange between particles and the dissolved load (Porcelli et al., 2001), and/or the presence of mineral colloids in the dissolved fractions, most probably play an additional role in the transport of dissolved Hf into rivers. However, there is evidence here for a strong weathering control on riverine ϵ_{Hf} . On geological time scales, it is expected that the Hf isotopic composition of rivers varies in response to major changes in the style of chemical weathering related to climate change, and this has fundamental implications for the Hf isotopic composition of seawater and its evolution through time.

IMPLICATIONS FOR THE OCEAN Hf BUDGET AND THE EVOLUTION OF SEAWATER ϵ_{Hf} THROUGH TIME

To date, the ϵ_{Hf} value for seawater has been inferred from the analysis of deep-sea ferromanganese crusts and nodules, but the sources of hafnium to the ocean remain poorly constrained. Recent studies have suggested that dissolved Hf contributions from hydrothermal vents and dissolution of aeolian dust are probably negligible for the ocean, indicating that rivers may represent a major source of dissolved Hf for the ocean (van de Flierdt et al., 2004a, 2004b). In the Atlantic Ocean, the source of Hf is thought to be derived primarily from the erosion of Proterozoic and Archean cratons in Canada, Greenland, and Scandina-

via. Moselle rivers have water chemistry very similar to that of other major rivers draining old silicate basins (Gaillardet et al., 1999; Millot et al., 2002). Our Hf isotopic data can be used, therefore, as a first approximation, for estimating the global riverine ϵ_{Hf} input to the Atlantic Ocean. Using (1) the general equation of radioactive decay for the Lu-Hf system [$(^{176}\text{Hf}/^{177}\text{Hf})_{\text{sample}} = (^{176}\text{Hf}/^{177}\text{Hf})_{\text{initial}} + (^{176}\text{Lu}/^{177}\text{Hf}) \times (e^{\lambda t} - 1)$], where $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{sample}}$ is the present-day Hf isotopic composition of a given rock or mineral, $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{initial}}$ is the Hf isotopic composition of the rock or mineral when it was formed, t yr ago, and λ is the radioactive decay constant, $1.867 \times 10^{-11} \text{ yr}^{-1}$, (2) estimated initial ¹⁷⁶Hf/¹⁷⁷Hf ratios for Moselle granites, and (3) our measured ϵ_{Hf} values for Moselle silicate rivers, we can calculate the global range of dissolved ¹⁷⁶Lu/¹⁷⁷Hf released during granite weathering (see the Data Repository [see footnote 1] for details). Then, considering a mean age of 1800 Ma for the North Atlantic silicate province, we can estimate the isotopic composition of the dissolved Hf fraction released during silicate weathering in the North Atlantic area. The range of ϵ_{Hf} calculated here (from ~-3 to +6.5) is very similar to that reported previously for Atlantic seawater values, from ~-2 to +4. This lends support to the hypothesis that the oceanic Hf budget is dominated by riverine input and, hence, can be controlled through time by changes in silicate weathering rates.

The Hf isotopic composition of seawater has varied significantly over the last 50 m.y., and this has been attributed to major changes in ocean circulation and/or continental weathering (Lee et al., 1999; Piotrowski et al., 2000; van de Flierdt et al., 2002, 2004a). In the North Atlantic and South Pacific Oceans, deep-sea ferromanganese crusts have recorded marked Hf isotopic variations, toward low ϵ_{Hf} values, which have been linked to enhanced mechanical erosion following the onset of Northern Hemisphere and Antarctic glaciations, respectively (Piotrowski et al., 2000; van de Flierdt et al., 2002, 2004a). It has been suggested that those ϵ_{Hf} excursions toward unradiogenic values reflect enhanced breakdown of unradiogenic zircon during glacial weathering. Our new Hf isotope data show, however, that changes in the style of silicate weathering (i.e., alteration of apatite and other radiogenic accessory minerals versus more resistant unradiogenic feldspars) have probably driven changes in the Hf isotopic composition of seawater through time.

Another noticeable feature in the Hf isotope record from North Atlantic ferromanganese crusts is the gradual increase of ϵ_{Hf} from ca. 15 to 3 Ma (from $\epsilon_{\text{Hf}} \sim +1$ to +4), which preceded the decrease toward modern Atlantic

seawater ϵ_{Hf} values ($\epsilon_{\text{Hf}} \sim -1$; Piotrowski et al., 2000; van de Fliedert et al., 2002). The change toward higher ϵ_{Hf} values at ca. 15 Ma coincides with the initiation of global cooling, which is known to have intensified throughout the Miocene until the establishment of permanent ice caps in the Northern Hemisphere, ca. 3 Ma (e.g., Shackleton et al., 1984). It is likely that global cooling and appearance of the first ice sheets from ca. 15 Ma (Thiede et al., 1998) have favored mechanical disaggregation of rocks, through freeze-thaw and grinding, thereby increasing the surface area of fresh material exposed to chemical erosion. Such a change in the weathering style of North Atlantic cratons would likely lead, at first, to the alteration of radiogenic accessory minerals (e.g., sphene, apatite), thereby explaining the trend toward higher ϵ_{Hf} values from ca. 15 to 3 Ma. Then, at ca. 3 Ma, intensified physical erosion associated with the establishment of permanent ice caps would result in the weathering of more resistant minerals (e.g., biotite, feldspars), with lower $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. The evolution of ϵ_{Hf} in Atlantic late Cenozoic deep waters is therefore in accord with the observations documented here. Our study shows that Hf isotopes in rivers and seawater can be very sensitive to changes in the style and intensity of silicate weathering. Future studies using Hf isotopes in marine and sedimentary records should enable us to refine our understanding on the global link between climate change, continental weathering, and ocean chemistry.

ACKNOWLEDGMENTS

We gratefully acknowledge C. Hémond, M. Benoit, and C. Bassoulet from the Institut Universitaire Européen de la Mer (Brest, France) for the access to the Triton mass spectrometer and technical assistance. We are grateful to A. Cohen for assistance on the Nu Plasma at the Open University. L. Reisberg and C. France-Lanord are thanked for advice and discussion. R. Hannigan, J.D. Blum, and J.D. Vervoort are also thanked for providing insightful comments on this manuscript.

REFERENCES CITED

Albarède, F., Simonetti, A., Vervoort, J.D., Blitcher-Toft, J., and Abouchami, W., 1998, A Hf-Nd isotopic correlation in ferromanganese nodules: *Geophysical Research Letters*, v. 25, p. 3895–3898.

Andersson, P.S., Dahlqvist, R., Ingri, J., and Gustafsson, Ö., 2001, The isotopic composition of Nd in a boreal river: A reflection of selective weathering and colloidal transport: *Geochimica et Cosmochimica Acta*, v. 65, p. 521–527.

Aubert, D., Probst, A., and Stille, P., 2004, Distribution and origin of major and trace elements (particularly REE, U and Th) into labile and residual phases in an acid soil profile (Vosges Mountains, France): *Applied Geochemistry*, v. 19, p. 899–916.

Blum, J.D., Klaue, A., Nezat, C.A., Driscoll, C.T., Johnson, C.E., Siccama, T.G., Eagar, C., Fa-

hey, T.J., and Likens, G.E., 2002, Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems: *Nature*, v. 417, p. 729–731.

Chu, N.-C., Taylor, R.N., Chavagnac, V., Nesbitt, R.W., Boella, R.M., Milton, J.A., German, C.R., Bayon, G., and Burton, K.W., 2002, Hafnium isotope ratio analysis using multi-collector inductively coupled plasma mass spectrometry: An evaluation of isobaric interference corrections: *Journal of Analytical Atomic Spectrometry*, v. 17, p. 1567–1574.

Derry, L.A., Kurtz, A.C., Ziegler, K., and Chadwick, O.A., 2005, Biological control of terrestrial silica cycling and export fluxes to watersheds: *Nature*, v. 433, p. 728–731.

Dosso, L., Hanan, B.B., Bougault, H., Schilling, J.-G., and Joron, J.-L., 1991, Sr-Nd-Pb geochemical morphology between 10° and 17°N on the Mid-Atlantic Ridge: A new MORB isotope signature: *Earth and Planetary Science Letters*, v. 106, p. 29–47.

Edmond, J.M., 1992, Himalayan tectonics, weathering processes and the strontium isotope record in marine limestones: *Science*, v. 258, p. 1594–1597.

Erel, Y., Blum, J.D., Roueff, E., and Ganor, J., 2004, Lead and strontium isotopes as monitors of experimental granitoid mineral dissolution: *Geochimica et Cosmochimica Acta*, v. 68, p. 4649–4663.

Gaillardet, J., Dupré, B., Louvat, P., and Allègre, C.J., 1999, Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers: *Chemical Geology*, v. 159, p. 3–30.

Goldich, S.S., 1938, A study of rock weathering: *Journal of Geology*, v. 46, p. 17–58.

Goldstein, S.J., and Jacobsen, S.B., 1987, The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in seawater: *Chemical Geology*, v. 66, p. 245–272.

Harlavan, Y., and Erel, Y., 2002, The release of Pb and REE from granitoids by the dissolution of accessory phases: *Geochimica et Cosmochimica Acta*, v. 66, p. 837–848.

Lee, D.-C., Halliday, A.N., Hein, J.R., Burton, K.W., Christensen, J.N., and Gunther, D., 1999, Hafnium isotope stratigraphy of ferromanganese crusts: *Science*, v. 285, p. 1052–1054.

Louvat, P., and Allègre, C.J., 1997, Present denudation rates at Réunion island determined by river geochemistry: Basalt weathering and mass budget between chemical and mechanical erosions: *Geochimica et Cosmochimica Acta*, v. 61, p. 3645–3669.

Millot, J., Gaillardet, R., Dupré, B., and Allègre, C.J., 2002, The global control of silicate weathering rates and the coupling with physical erosion: New insights from rivers of the Canadian Shield: *Earth and Planetary Science Letters*, v. 196, p. 83–98.

Öhlander, B., Ingri, J., Land, M., and Schöberg, H., 2000, Change of Sm-Nd composition during weathering of till: *Geochimica et Cosmochimica Acta*, v. 64, p. 813–820.

Ollier, C.D., 1984, *Weathering* (2nd edition): London, Longman, 280 p.

Piotrowski, A.M., Lee, D.C., Christensen, J.N., Burton, K.W., Halliday, A.N., Hein, J.R., and Gunther, D., 2000, Changes in erosion and ocean circulation recorded in the Hf isotopic compositions of North Atlantic and Indian Ocean ferromanganese crusts: *Earth and Planetary Science Letters*, v. 181, p. 315–325.

Porcelli, D., Andersson, P.S., Baskaran, M., and Wasserburg, G.J., 2001, Transport of U- and Th-series nuclides in a Baltic shield watershed and the Baltic sea: *Geochimica et Cosmochimica Acta*, v. 65, p. 2439–2459.

Ravizza, G., and Peucker-Ehrenbrink, B., 2003, Chemostratigraphic evidence of Deccan volcanism from the marine osmium isotope record: *Science*, v. 302, p. 1392–1395.

Shackleton, N.J., Backman, J., Zimmerman, H., Kent, D.V., Hall, M.A., Roberts, D.G., Schitker, D., Baldauf, J.G., Desprairies, A., Homrighausen, R., Huddleston, P., Keene, J.B., Kaltenback, A.J., Krumsiek, K.A.O., Morton, A.C., Murray, J.W., and Westberg-Smith, J., 1984, Oxygen isotope calibration of the onset of ice-rafting and history of glaciation in the North Atlantic region: *Nature*, v. 307, p. 620–623.

Taicheng, D., Hangtin, C., and Xianjin, Z., 2002, Determination of rare and rare earth elements in soils and sediments by ICP-MS using $\text{Ti}(\text{OH})_4\text{-Fe}(\text{OH})_3$ co-precipitation preconcentration: *Journal of Analytical Atomic Spectrometry*, v. 17, p. 410–413.

Thiede, J., Winkler, A., Wolf-Welling, T., Eldholm, O., Myhre, A.M., Baumann, K.-H., Henrich, R., and Stein, R., 1998, Late Cenozoic history of the polar North Atlantic: Results from ocean drilling: *Quaternary Science Reviews*, v. 17, p. 185–208.

van de Fliedert, T., Frank, M., Lee, D.-C., and Halliday, A.N., 2002, Glacial weathering and the hafnium isotope composition of seawater: *Earth and Planetary Science Letters*, v. 201, p. 639–647.

van de Fliedert, T., Frank, M., Lee, D.C., Halliday, A.N., Reynolds, B.R., and Hein, J.R., 2004a, New constraints on the sources and behavior of neodymium and hafnium in seawater from Pacific Ocean ferromanganese crusts: *Geochimica et Cosmochimica Acta*, v. 68, p. 3827–3843.

van de Fliedert, T., Frank, M., Halliday, A.N., Hein, J.R., Hattendorf, B., Günther, D., and Kubik, P.W., 2004b, Tracing the history of submarine hydrothermal inputs and the significance of hydrothermal hafnium for the seawater budget—A combined Pb-Hf-Nd isotope approach: *Earth and Planetary Science Letters*, v. 222, p. 259–273.

Vervoort, J.D., Patchett, P.J., Blichert-Toft, J., and Albarède, F., 1999, Relationships between Lu-Hf and Sm-Nd isotopic systems in the global sedimentary system: *Earth and Planetary Science Letters*, v. 168, p. 79–99.

White, A.F., and Blum, A.E., 1995, Effects of climate on chemical weathering in watersheds: *Geochimica et Cosmochimica Acta*, v. 59, p. 1729–1747.

White, A.F., Bullen, T.D., Davison, V.V., Schulz, M., and Clow, D.W., 1999, The role of disseminated calcite in the chemical weathering of granitoid rocks: *Geochimica et Cosmochimica Acta*, v. 63, p. 1939–1953.

Manuscript received 16 August 2005

Revised manuscript received 13 January 2006

Manuscript accepted 17 January 2006

Printed in USA