



# Evidence from $^{10}\text{Be}$ and U series disequilibria on the possible contamination of mid-ocean ridge basalt glasses by sedimentary material

B. Bourdon, S. J. Goldstein, D. Bourlès, M. T. Murrell, C. H. Langmuir

## ► To cite this version:

B. Bourdon, S. J. Goldstein, D. Bourlès, M. T. Murrell, C. H. Langmuir. Evidence from  $^{10}\text{Be}$  and U series disequilibria on the possible contamination of mid-ocean ridge basalt glasses by sedimentary material. *Geochemistry, Geophysics, Geosystems*, 2000, 1, pp.1029-12. 10.1029/2000GC000047 . insu-03596934

**HAL Id: insu-03596934**

**<https://insu.hal.science/insu-03596934>**

Submitted on 4 Mar 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Copyright



# Evidence from $^{10}\text{Be}$ and U series disequilibria on the possible contamination of mid-ocean ridge basalt glasses by sedimentary material

**B. Bourdon**

Laboratoire de Géochimie et Cosmochimie, CNRS-IPGP, T14-24, 4 Place Jussieu, F-75252 Paris Cedex 05, France

**S. J. Goldstein**

Los Alamos National Laboratory, J514, Los Alamos, New Mexico 87545

**D. Bourlès**

Centre de Spectrometrie Nucleaire et de Spectrometrie de Masse, IN2P3-CNRS, Bât. 104-108, F-91405 Orsay, France, and Centre Européen de Recherche et d'Enseignement de Géosciences de l'Environnement, BP 80, F-13545 Aix-en-Provence Cedex 04, France

**M. T. Murrell**

Los Alamos National Laboratory, J514, Los Alamos, New Mexico 87545

**C. H. Langmuir**

Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York 10964

[1] **Abstract:** It has often been suggested that U series disequilibria measured in mid-ocean ridge basalts (MORB) can be perturbed by contamination with sedimentary or hydrothermal material found near the ridge axis where the basalts are erupted. Here we provide an independent way of estimating the maximum degree of contamination by sediment using constraints from  $^{10}\text{Be}$ . Since  $^{10}\text{Be}$  is mostly a cosmogenic nuclide and has a half life of  $1.5 \times 10^6$  years, any  $^{10}\text{Be}$  found in a MORB glass must result from contamination by sedimentary material where cosmogenic  $^{10}\text{Be}$  is enriched. Four MORB samples with a wide range in Th concentrations (87–550 ppb) were measured for U decay series and  $^{10}\text{Be}$ . No  $^{10}\text{Be}$  above the detection limit ( $6 \times 10^4$  to  $1 \times 10^5$  atoms) was measured in the glasses except for one sample that was not picked. Considering that the sedimentary contaminant contains  $10^9$  to  $10^{10}$  atoms/g, the maximum fraction of contaminant in the picked glasses is  $10^{-4}$  to  $10^{-5}$ . Mass balance calculations between a surficial contaminant and a hypothetical pristine glass with  $(^{231}\text{Pa}/^{235}\text{U}) = 1$  and  $(^{10}\text{Be}/^9\text{Be}) = 0$  show that only for the unpicked sample, nearly all the measured excess  $^{231}\text{Pa}$  can be accounted for by contamination. For the other samples, <15% to <1% of the excess  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  can be explained by incorporation of sedimentary material. This study reemphasizes the need for careful sample preparation for U series measurements in MORB, especially at low U levels (<50 ppb). It also confirms that the large U series excesses in carefully picked and cleaned MORB samples are magmatic in origin.

**Keywords:** U series;  $^{10}\text{Be}$ ; basalt; contamination; mid-ocean ridge.

**Index Terms:** Isotopic composition/chemistry; trace elements; mid-ocean ridge processes.

**Received** February 24, 2000; **Revised** June 13, 2000; **Accepted** June 30, 2000; **Published** August 11, 2000.



Bourdon, B., S. J. Goldstein, D. Bourlès, M. T. Murrell, and C. H. Langmuir, 2000. Evidence from  $^{10}\text{Be}$  and U series disequilibria on the possible contamination of mid-ocean ridge basalt glasses by sedimentary material, *Geochem. Geophys. Geosyst.*, vol. 1, Paper number 2000GC000047 [8266 words, 5 figures, 3 tables]. Published August 11, 2000.

## 1. Introduction

[2] The large parent-daughter fractionation in the U series decay chain first found by alpha spectrometry and then by mass spectrometric measurements of mid-ocean ridge basalt (MORB) glasses remains a paradoxical observation [Condomines *et al.*, 1981; Goldstein *et al.*, 1989]. All the U series nuclides used in mantle geochemistry (U-Th-Pa-Ra) are large-ion lithophile elements and are thus highly incompatible elements during melting processes. For the large degrees of melting found in mid-ocean ridge basalts, small fractionation in the parent-daughter ratio (e.g.,  $(^{238}\text{U}/^{230}\text{Th})$ ) is expected. These observations are generally difficult to explain with traditional melting models for the behavior of trace elements. This has led to the development of more sophisticated models that take into account both radioactive decay and transport of the nuclides [McKenzie, 1985; Williams and Gill, 1989; Spiegelman and Elliott, 1993]. These models still require rather extreme values of melt porosity ( $\approx 1\%$ ), which are usually taken as a free parameter in the modeling and are sometimes the subject of controversy [Chabaux and Allègre, 1994; Sims *et al.*, 1995; Elliott, 1997]. Thus establishing that the measured U series disequilibria do not result from seafloor contamination is a basic requirement before more inferences can be drawn about melting processes.

[3] Additionally, early measurements using gram quantities of MORB glasses had shown how sensitive the glasses are to surficial contamination. For example, Mn oxides that often

coat MORB glasses are enriched in  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  relative to their parent nuclides. Some indicators of contamination by seawater-derived material such as  $^{234}\text{U}/^{238}\text{U}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and B contents have been used in the literature [Condomines *et al.*, 1981; Goldstein *et al.*, 1989; MacDougall *et al.*, 1979]. None of these is particularly sensitive considering their respective analytical uncertainties and the difference in concentrations between contaminant and glass. In this study,  $^{10}\text{Be}$  has been used to estimate the maximum amount of sedimentary contaminant that could have been incorporated in the MORB glasses via assimilation, alteration, or surface contamination. There is virtually no  $^{10}\text{Be}$  in the mantle, so there should be no  $^{10}\text{Be}$  in an uncontaminated MORB glass. This makes  $^{10}\text{Be}$  a very sensitive tracer to contamination considering that it is particularly enriched in sedimentary material ( $10^8$ – $10^{10}$  atoms/g).

## 2. Sample Selection and Analytical Methods

[4] The samples selected for this study are a series of MORB glasses with variable Th-U concentrations, which should be variably sensitive to sediment contamination. All these samples are taken from the ridge axis, which presumably means that they must be young: VE32 is from the East Pacific Rise, north of the Orozco transform; sample DO3-1B is from the Lucky Strike seamount, Mid-Atlantic Ridge; and D15 is from the Mid-Atlantic Ridge near the Azores at  $37^\circ 17'\text{N}$ , south of the Lucky Strike area. These samples were selected because large amounts of fresh glass



were available for both  $^{10}\text{Be}$  and U series analysis. As 5–10 g of picked glass were necessary for  $^{10}\text{Be}$  analysis, this limited the set of samples that could be used for this study.

[5] Glass chips were carefully selected under a microscope by removing all chips showing signs of alteration or Mn crust coatings, except for sample DO3-1B-unpicked (u), which was not picked. This sample (same as DO3-1B-picked (p) except for its selection procedure) is used throughout this study as a reference for the maximum contamination. Clearly, all the glasses but DO3-1B-u were clean and did not show any signs of alteration or coatings. The surface of DO3-1B-u was tarnished but did not show any palagonite or typical alteration phase. The samples were then ground in an agate mortar that had been previously cleaned with quartz.

[6] The leaching methods used for removing contamination in U series and  $^{10}\text{Be}$  studies are generally distinct. For the purpose of this study, only one method, originally designed for effi-

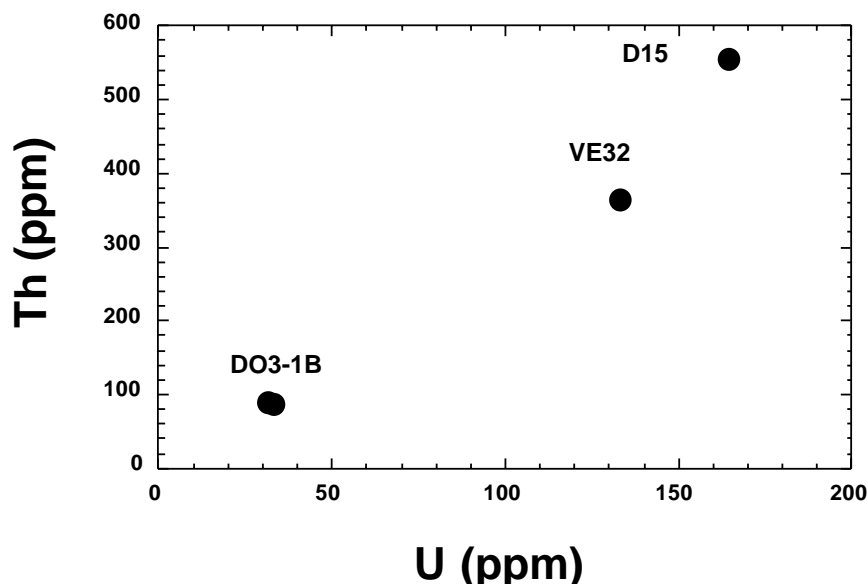
cient leaching of authigenic  $^{10}\text{Be}$  through dissolution of hydrous phases such as Mn oxides [Bourlès, 1988], was selected because the estimate of the fraction of sediment present in the sample is based on  $^{10}\text{Be}$ . It was then checked that this leaching method efficiently dissolves Pa. This was done by leaching a  $\text{MnO}_2$  precipitate doped with  $^{233}\text{Pa}$  with the same solution as the one used for leaching the glass. Since  $\approx 100\%$  of the  $^{233}\text{Pa}$  within the precipitate is released during this procedure, any Pa contained within the natural  $\text{MnO}_2$  matrix will be dissolved during the leaching procedure. This means that we can assume that the dissolution of  $\text{MnO}_2$  does not lead to Pa-Be fractionation during experimental processing of the samples.

[7] The glass chips were leached with a 20 mL mixture of 0.04 M  $\text{NH}_2\text{OH}$ , HCl (hydroxylammoniumchloride, Merck<sup>TM</sup>) in 25% volume acetic acid at 90°C for 6 hours [Bourlès, 1988]. Subsequently, the samples were rinsed four times with distilled water and we saved the leachates for Be analysis. After drying, the glass samples were ground in an agate mortar

**Table 1.** U Series Data for Leached MORB Glasses<sup>a</sup>

	Sample				
	DO3-1B-u	DO3-1B-p	VE32	D15	TML-Standard
U, ppb	33.1	31.6	133	164.	10860
Th, ppb	87.2	89.1	365	554	30750
Pa, fg/g	37.8	25.8	101	109	3535
( $^{230}\text{Th}/^{232}\text{Th}$ )	1.426	1.268	1.270	1.161	1.072
$\pm 2\sigma$	0.038	0.019	0.012	0.005	0.007
( $^{230}\text{Th}/^{238}\text{U}$ )	1.231	1.170	1.139	1.279	1.001
Th/U	2.639	2.822	2.742	3.367	2.832
( $^{231}\text{Pa}/^{235}\text{U}$ )	3.438	2.455	2.285	1.989	0.999
$\pm 2\sigma$	0.033	0.023	0.018	0.023	0.006
( $^{234}\text{U}/^{238}\text{U}$ )	1.0146	1.0028	1.0006	1.0016	0.9984
$\pm 2\sigma$	0.0038	0.0066	0.0015	0.002	0.002
( $^{226}\text{Ra}/^{230}\text{Th}$ )			2.34	2.96	-
$\pm 2\sigma$			0.07	0.06	-

<sup>a</sup>Errors for U and Th concentrations are <0.3% and <0.4%, respectively, at the 2 $\sigma$  level. Errors for Pa concentrations are <1.1% at the 2 $\sigma$  level. Blanks for U, Th, and Pa are 17 pg, 63 pg, and <0.1 fg, respectively. Blanks for U and Th isotope compositions are 150 pg and 330 pg, respectively.



**Figure 1.** Th versus U concentrations in the leached MORB glasses. The samples selected in this study span much of the range found for MORBs in the literature [Bourdon *et al.*, 1996a, 1996b].

washed with water and acetone. The reagents that we used are analytical grade reagents and did not leave any residue on the glass surfaces.

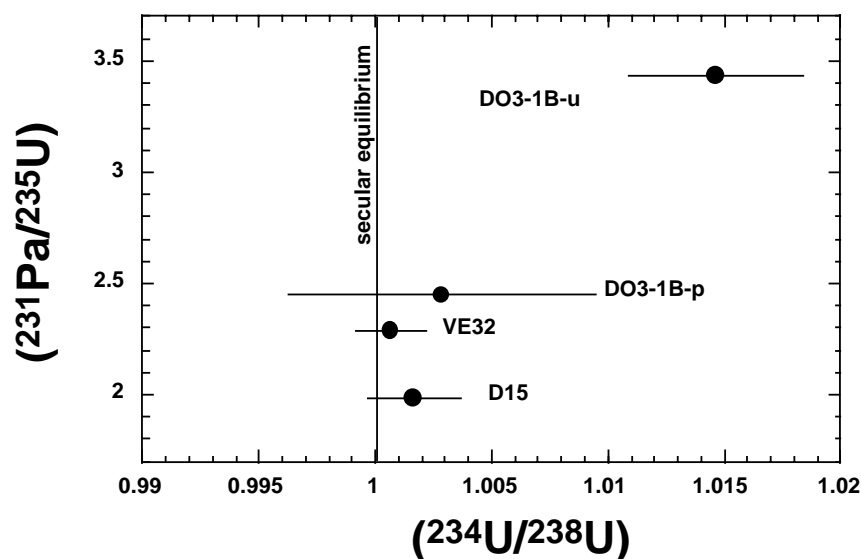
[8] The leachates and residues were analyzed for  $^{10}\text{Be}$  and  $^9\text{Be}$  following the analytical procedure described by *Bourlès* [1988]. Uncertainties on  $^{10}\text{Be}$  were estimated by propagating a 5% instrumental uncertainty ( $1\sigma$ ) based on counting statistics of  $^{10}\text{Be}$  events and a uncertainty in blank correction ( $1\sigma$ ). The  $^9\text{Be}$  measurements were made by standard additions using graphite furnace atomic absorption spectrometry (Perkin Elmer model Zeeman/3030 spectrometer, model HGA furnace, model AS-60 autosampler). A constant conservative uncertainty of 5% ( $1\sigma$ ) for  $^9\text{Be}$  determinations was adopted on the basis of reproducibility tests and on best fit lines obtained by standard addition methods. The leached MORB glasses were analyzed for U and Th, Ra and Pa by isotope dilution following the procedure described by *Goldstein et al.* [1989], *Pickett et al.* [1994], and

*Claude-Ivanaj et al.* [1998]. Uncertainties and procedural blanks related to these methods are given in the Table 1 footnotes.

### 3. Results

#### 3.1. U Series Disequilibria

[9] The Th and U concentrations for the MORB samples range from 87 to 554 ppb and from 33 to 165 ppb, respectively (Table 1 and Figure 1). This is a rather large range for normal MORB (NMORB) and enriched MORB (EMORB). Blanks are negligible relative to the amount of Th and U that are measured here and cannot account for the differences in concentrations. Rather, we believe that the difference between the DO3-1B-u and DO3-1B-p samples can be attributed to contamination since sediment is an obvious component of the “unpicked” sample. It could also be due to sample heterogeneity because this sample contains small plagioclase phenocrysts.



**Figure 2.** The  $^{231}\text{Pa}/^{235}\text{U}$  versus  $^{234}\text{U}/^{238}\text{U}$  activity ratios for the leached MORB glasses. All the samples display equilibrium values for  $^{234}\text{U}/^{238}\text{U}$  except for the unpicked MORB glass DO3-1B-u. In addition, the  $^{231}\text{Pa}/^{235}\text{U}$  ratios of DO3-1B-u and DO3-1B-p samples are significantly different.

[10] Both ( $^{230}\text{Th}/^{238}\text{U}$ ) and ( $^{231}\text{Pa}/^{235}\text{U}$ ) data for the leached MORB are well within the range found for MORBs in the literature [Goldstein *et al.*, 1989, 1991; Lundstrom *et al.*, 1995; Bourdon *et al.*, 1996a, 1996b; Pickett and Murrell, 1997; Goldstein *et al.*, 1993] (Table 1 and Figure 2). There is a marked difference in ( $^{230}\text{Th}/^{238}\text{U}$ ) in samples DO3-1B-p (1.17) and DO3-1B-u (1.23). This difference can be attributed to contamination by Mn crusts, which are  $^{230}\text{Th}$  rich and may have not been completely leached from DO3-1B-u. Similarly, the highest ( $^{231}\text{Pa}/^{235}\text{U}$ ) value (3.44) was found for the unpicked sample DO3-1B-u and is significantly higher than for the picked sample DO3-1B-p (2.45). It is not surprising that  $^{231}\text{Pa}$ - $^{235}\text{U}$  disequilibrium should be sensitive to contamination, but this had not been previously reported in the literature.

[11] The ( $^{234}\text{U}/^{238}\text{U}$ ) ratios were also measured in the MORB glasses. All the samples except for sample DO3-1B-u show equilibrium values within error (Figure 2). Sample DO3-1B-u

shows contamination by seawater-derived material with a ( $^{234}\text{U}/^{238}\text{U}$ ) ratio of 1.15.

[12] Two of the MORB glass residues (D15 and VE32) are all characterized by excess  $^{226}\text{Ra}$  relative to  $^{230}\text{Th}$ . This indicates that the MORBs must all be young (less than  $\sim 10$  kyr old) unless all the  $^{226}\text{Ra}$  excess is due to contamination by a Ra-rich phase.

### 3.2. Be Isotopes

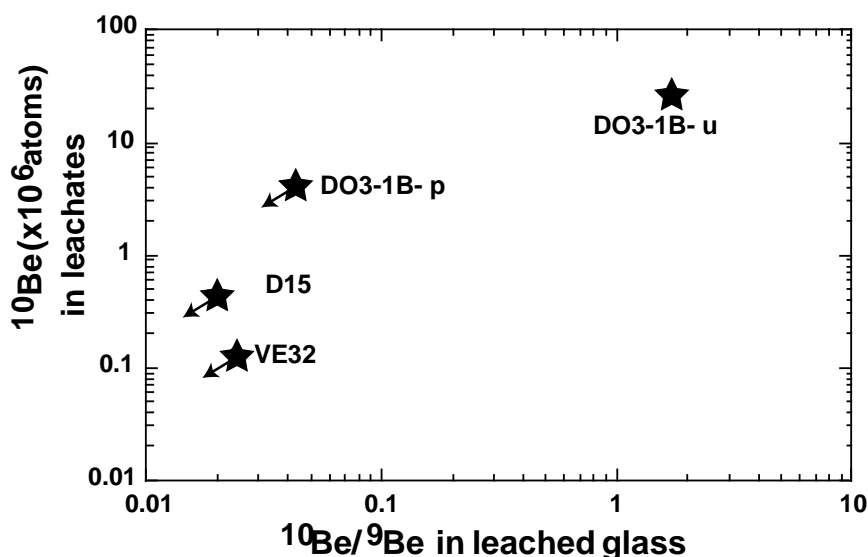
[13] Beryllium isotopes ( $^9\text{Be}$  and  $^{10}\text{Be}$ ) were measured in the leachate solutions as well as within the leached glasses. In both cases, their abundance were normalized to the mass of glass leached to allow comparison (Table 2).

[14] The  $^9\text{Be}$  concentrations of the leachates are relatively constant and range from 9.3 to 13.3 ppb. The highest  $^{10}\text{Be}$  concentration measured in the leachate solutions was measured for the unpicked glass DO3-1B-u ( $9.3 \times 10^6$  atoms/g of leached glass). For the other samples the

**Table 2.** The  $^{10}\text{Be}$ ,  $^9\text{Be}$ , and ( $^{10}\text{Be}/^9\text{Be}$ ) Data for Leachates and Leached MORB Glasses<sup>a</sup>

	Sample							
	D03-1B-u	D03-1B-u	D03-1B-p	D03-1B-p	D15	D15	VE32	VE32
	leachate	glass	leachate	glass	leachate	glass	leachate	glass
$^{10}\text{Be}$ , $10^6$ atoms	$26.9 \pm 1.6$		$4.26 \pm 0.49$		$<0.127$		$0.43 \pm 0.13$	
$^{10}\text{Be}$ , $10^6$ atoms/g		$2.69 \pm 0.30$		$<0.0626$		$<0.0730$		$<0.101$
$^9\text{Be}$ , $10^{16}$ atoms	$0.259 \pm 0.013$		$0.232 \pm 0.012$		$0.127 \pm 0.006$		$0.086 \pm 0.004$	
$^9\text{Be}$ , ng/g glass	13.3		13.8		8.51		9.33	
$^9\text{Be}$ , $10^{16}$ atoms/g		$1.58 \pm 0.08$		$1.45 \pm 0.07$		$3.08 \pm 0.15$		$5.03 \pm 0.25$
$^{10}\text{Be}/^9\text{Be}$ , $10^{-10}$	$103.7 \pm 8.1$	$1.71 \pm 0.21$	$18.4 \pm 2.3$	$<0.043$	$<1.00$	$<0.024$	$5.04 \pm 1.56$	$<0.020$

<sup>a</sup>All the glasses are leached. Errors are given at the  $1\sigma$  level.



**Figure 3.** The amount of  $^{10}\text{Be}$  in the leachates versus ( $^{10}\text{Be}/^9\text{Be}$ ) in the leached MORB glasses. Significant levels of  $^{10}\text{Be}$  are found in the leachates, while the leached glasses have very low ( $^{10}\text{Be}/^9\text{Be}$ ) ratios. This diagram shows that some contamination may be left in the glasses even after leaching since DO3-1B-u has  $^{10}\text{Be}$  level well above the detection limit, although it was leached like the other samples.

leachate  $^{10}\text{Be}$  concentration normalized to glass weight is at least 6 times lower. The ( $^{10}\text{Be}/^9\text{Be}$ ) ratios in the leachates range from  $<1 \times 10^{-10}$  for D15 to  $1 \times 10^{-8}$  for the unpicked sample (Figure 3). This variability induced by variations of  $^{10}\text{Be}$  concentration in the leachate solutions most likely reflects disparities in the amount of contaminant present on the glass chips prior to leaching. Since the glasses were slightly etched after leaching, some  $^9\text{Be}$  might be coming from the leached glass itself.

[15] The  $^9\text{Be}$  concentrations in the leached glasses range from 0.22 to 0.75 ppm. The fraction of  $^9\text{Be}$  contained in the leachates relative to the leached glasses represents 5–6% of the total. For all the samples but DO3-1B-u,  $^{10}\text{Be}$  concentrations within the leached glasses are below the detection limit ( $0.6\text{--}1 \times 10^5$  atoms of  $^{10}\text{Be}$ ) and are lower than the values given by Valette-Silver *et al.* [1987] for MORB glasses.

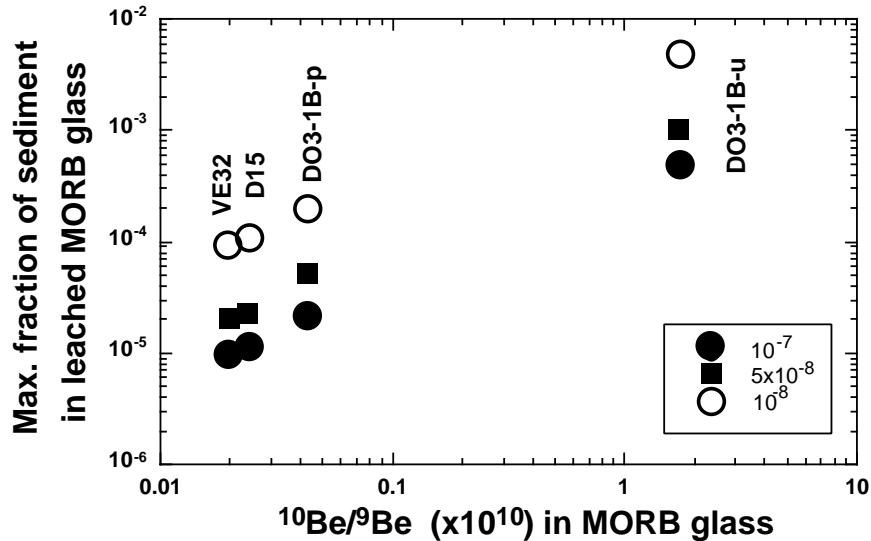
[16] These data indicate that little, if any,  $^{10}\text{Be}$  is contained within the glass. Most of the measured  $^{10}\text{Be}$  in sample DO3-1B-u is most likely associated with surface contamination. This also demonstrates that chemical cleaning of MORB samples through a leaching procedure is not always sufficient for removing all traces of contamination and that sample selection is critically required. Tests in previous studies [e.g., Reinitz and Turekian, 1989] had not proven that all the contamination had been entirely removed. Using  $^{10}\text{Be}$  as a monitor, we show that even after leaching, some contamination can remain.

## 4. Mass Balance Calculations for Glasses and Leachates

### 4.1. U Series

[17] In order to determine the contribution of U series excess nuclides that is linked to sedimentary contamination, we developed simple mass





**Figure 4.** Estimated mass fraction of sedimentary contaminant versus ( $^{10}\text{Be}/^9\text{Be}$ ) ratios in leached MORB glasses. See text for details of the calculation. The estimates strongly depend on the ( $^{10}\text{Be}/^9\text{Be}$ ) assumed for the sedimentary contaminant. For all the samples but DO3-1B-u the estimates correspond to upper limits.

balance calculations. To do so, some assumptions are required. First, we assumed that there is no  $^{10}\text{Be}$  in the glass prior to contamination because the mantle beneath the ridge cannot contain a nuclide that is only produced at significant rates in the atmosphere. Second, we assumed that the measured U series nuclides as well as the measured  $^{10}\text{Be}$  were part of the same sedimentary phase and that there is a single contamination process. This last assumption relies on the fact that  $^{10}\text{Be}$  is only cosmogenically produced. Finally, we also assumed that the analyzed glass is characterized by no disequilibrium in the U series chain prior to contamination. We make this last hypothesis to test whether all the observed disequilibrium can be explained by contamination. The maximum contribution of sedimentary phase is thus calculated using the maximum amount of  $^{10}\text{Be}$  present in the glass after leaching.

[18] The ( $^{234}\text{U}/^{238}\text{U}$ ) activity ratio  $>1$  (Table 1) measured for DO3-1B-u unambiguously indicates contamination of the U-series nu-

clides in this MORB glass sample. The U series characteristics of the contaminant may thus be determined using the differences between DO3-1B-u and DO3-1B-p samples by determining the fraction of U in the glass derived from sediment. For this, we assume that the ( $^{234}\text{U}/^{238}\text{U}$ )<sub>sed</sub> ratio is equal to the seawater value (1.15) since sediments at the ridge axis must be very recent. Then, the best way to proceed is to estimate the fraction of sediment  $X_{\text{sed}}$  based on Be systematics, as shown below.

[19] Assuming that the ( $^{10}\text{Be}/^9\text{Be}$ ) of the contaminant end-member is in the range of Atlantic Ocean surface manganese crusts (i.e.,  $1 \times 10^{-7}$  to  $1 \times 10^{-8}$  [Bourlès *et al.*, 1991; Bourlès, 1992; von Blanckenburg *et al.*, 1996]), the fraction of sedimentary contaminant can be estimated:

$$X_{\text{sed}} = \frac{[^9\text{Be}_{\text{basalt}}(^{10}\text{Be}/^9\text{Be}_{\text{mix}} - ^{10}\text{Be}/^9\text{Be}_{\text{basalt}})]}{[^9\text{Be}_{\text{sed}}(^{10}\text{Be}/^9\text{Be}_{\text{sed}} - ^{10}\text{Be}/^9\text{Be}_{\text{basalt}}) + ^9\text{Be}_{\text{basalt}}(^{10}\text{Be}/^9\text{Be}_{\text{mix}} - ^{10}\text{Be}/^9\text{Be}_{\text{basalt}})]}$$



**Table 3.** Compositions of Sedimentary Contaminant in MORB Glasses

	Value Used in Calculation	Total Range <sup>a</sup>
U, ppm	1	0.3–3 <sup>a</sup>
( <sup>234</sup> U/ <sup>238</sup> U)	1.15 ± 0.01 <sup>a</sup>	-
( <sup>230</sup> Th/ <sup>238</sup> U)	6.25	2.5–6.8
( <sup>231</sup> Pa/ <sup>235</sup> U)	30	10–33
<sup>9</sup> Be, atoms/g	3 × 10 <sup>16</sup>	1–3 × 10 <sup>16a</sup>
<sup>10</sup> Be/ <sup>9</sup> Be	5 × 10 <sup>-8</sup> –1 × 10 <sup>-7</sup>	5 × 10 <sup>-8</sup> –1 × 10 <sup>-7a</sup>

<sup>a</sup>Estimates based on literature data [Shimmield and Price, 1988; Anderson *et al.*, 1990; German *et al.*, 1993; Bourlès *et al.*, 1991; Bourlès, 1992; von Blanckenburg *et al.*, 1996]. Other estimates are based on mass balance calculations explained in the text.

The results of the calculations, taking  $3 \times 10^{16}$  atoms/g as the <sup>9</sup>Be concentration in the sediment, are plotted in Figure 4. A larger (<sup>10</sup>Be/<sup>9</sup>Be) value of the contaminant end-member (e.g.,  $1 \times 10^{-7}$ , as in the Pacific Ocean) would lower the estimated amount of contamination, which, in turn, would mean a smaller effect on the U series nuclides. For samples DO3-1B-p, VE32, and D15 the maximum amount of sedimentary contaminant ranges from  $2.9 \times 10^{-5}$  to  $5.2 \times 10^{-5}$ , which implies that the U concentrations in the contaminant range from 0.3 to 3 ppm (Table 3). A further step is to determine the U series characteristics of the sedimentary contaminant. This can be done through evaluation of the (<sup>231</sup>Pa/<sup>235</sup>U) and (<sup>230</sup>Th/<sup>238</sup>U) ratios (Table 3) based on the estimated fraction of U in the glass derived from sediment. Both estimates compare well with (<sup>231</sup>Pa/<sup>235</sup>U) and (<sup>230</sup>Th/<sup>238</sup>U) ratios of metalliferous sediments found near ridges [Shimmield and Price, 1988; Anderson *et al.*, 1990; German *et al.*, 1993]. The range for estimates reported in Table 3 takes into account uncertainties in the various parameters.

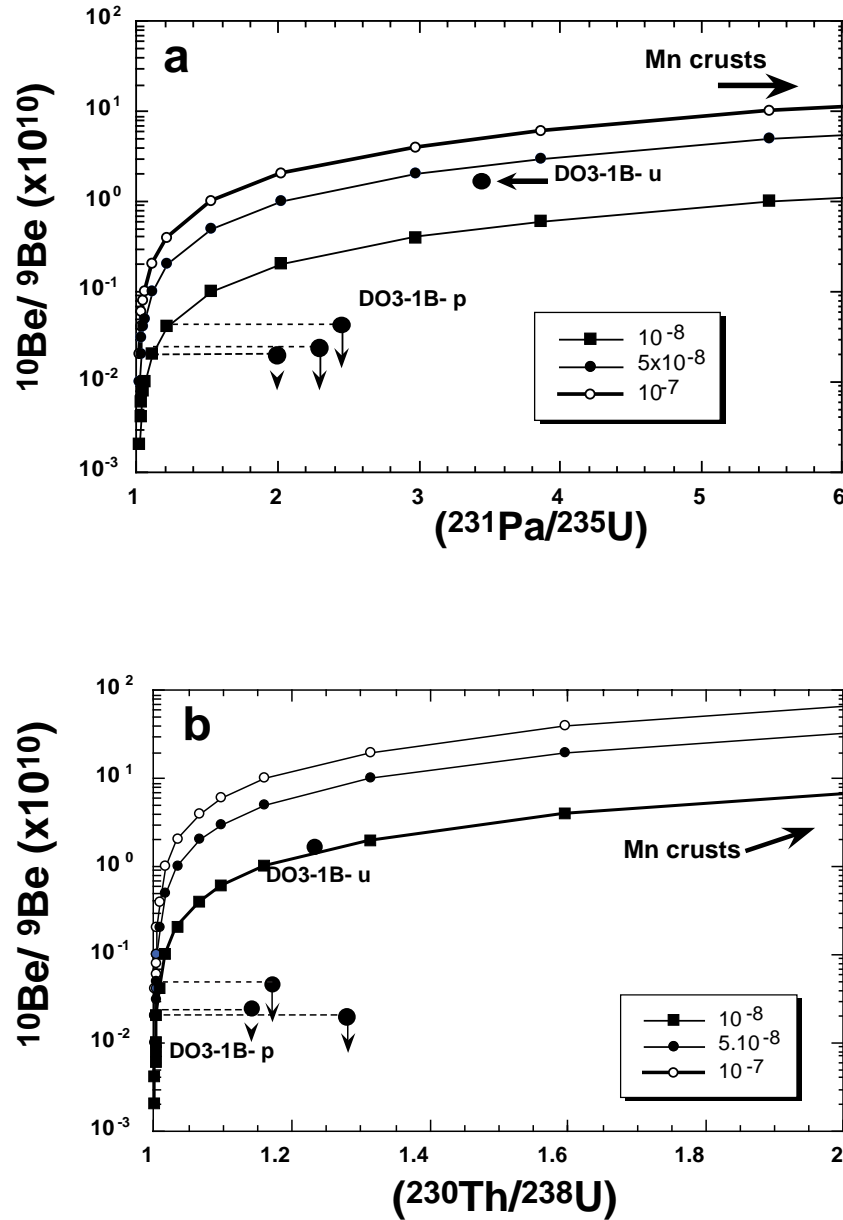
[20] On the basis of these estimates the effect of contamination on the (<sup>231</sup>Pa/<sup>235</sup>U) and (<sup>230</sup>Th/<sup>238</sup>U) ratios can be calculated assuming no excess daughter prior to contamination ((<sup>231</sup>Pa/<sup>235</sup>U) = 1 and (<sup>230</sup>Th/<sup>238</sup>U) = 1) (Figure 5). The mixing lines shown in Figure 5 thus represent the maximum effect of contamination on (<sup>231</sup>Pa/<sup>235</sup>U) and (<sup>230</sup>Th/<sup>238</sup>U). For sample

DO3-1B-p, using the maximum (<sup>10</sup>Be/<sup>9</sup>Be), contamination results in a <5% excess of <sup>231</sup>Pa over <sup>235</sup>U, while for the two other samples, VE32 and D15, the induced excess is <1%. The same methodology can be applied to (<sup>230</sup>Th/<sup>238</sup>U) disequilibrium. Once again, the effect of sedimentary contamination is <1%, using conservative estimates for the (<sup>10</sup>Be/<sup>9</sup>Be) ratios in the sedimentary contaminant (Table 3).

[21] If one considers that the sedimentary contaminant is characterized by a (<sup>10</sup>Be/<sup>9</sup>Be) ratio of  $1 \times 10^{-8}$ , the value measured in the DO3-1B-u leachates, the (<sup>231</sup>Pa/<sup>235</sup>U) resulting from contamination in DO3-1B-u is 1.20. This should, however, be considered a maximum value since the leaching procedure may leach some <sup>9</sup>Be from the glass and thus lower the (<sup>10</sup>Be/<sup>9</sup>Be) ratio in the contaminant. For the other glasses the effect of such a contamination is <1% for both (<sup>231</sup>Pa/<sup>235</sup>U) and (<sup>230</sup>Th/<sup>238</sup>U) ratios.

## 4.2. Osmium

[22] This study also enables us to address the question of the impact of sedimentary contamination on Os isotope systematics. On the basis of the <sup>10</sup>Be measurements the fraction of contaminant does not exceed  $5 \times 10^{-5}$  to  $10^{-4}$  in leached MORB glasses. This value will perhaps depend on the leaching procedure being used, but it nevertheless permits us to give a first-order assessment of contamination in the case of the Re-Os system. Os concentrations



**Figure 5.** (a) The  $(^{10}\text{Be}/^9\text{Be})$  versus  $(^{231}\text{Pa}/^{235}\text{U})$  in the leached MORB glasses. The model curves computed using three different  $(^{10}\text{Be}/^9\text{Be})$  ratios for the sedimentary contaminant represent mixing lines between a hypothetical MORB glass with a  $(^{231}\text{Pa}/^{235}\text{U})$  ratio equal to 1 and a Mn crust with the characteristics given in Table 3. None of the samples except DO3-1B-u can be explained by such a mixing process. The dashed lines join the measured value to the model value of  $(^{231}\text{Pa}/^{235}\text{U})$  for a given  $(^{10}\text{Be}/^9\text{Be})$  ratio. Measured  $(^{231}\text{Pa}/^{235}\text{U})$  ratios are greater than model values, which shows that mixing with Mn-crusts cannot explain  $(^{231}\text{Pa}/^{235}\text{U})$  in basalts. (b) The  $(^{10}\text{Be}/^9\text{Be})$  versus  $(^{230}\text{Th}/^{238}\text{U})$  ratios in the leached MORB glasses. The model curves calculated using three different  $(^{10}\text{Be}/^9\text{Be})$  ratios for the sedimentary contaminant represent mixing lines between a hypothetical MORB glass with  $(^{230}\text{Th}/^{238}\text{U}) = 1$  and a Mn crust whose characteristics are given in Table 3. As in Figure 5a, the measured  $(^{230}\text{Th}/^{238}\text{U})$  are too large to be explained entirely by contamination with Mn crusts.



measured in MORB range from 1 to 30 ppt [Schiano *et al.*, 1997], which is considerably smaller than Os concentrations found in Mn crusts (1000–3000 parts per trillion (ppt)). If one assumes a fraction of assimilated sediment of 1 to  $5 \times 10^{-5}$ , the calculated  $^{187}\text{Os}/^{186}\text{Os}$  ratio of the mixture is 1.49 for an initial Os concentration of 1 ppt ( $X_s = 1 \times 10^{-5}$ ) and 1.086 for an initial concentration of 30 ppt ( $X_s = 5 \times 10^{-5}$ ). Thus, given the maximum sediment fractions deduced from  $^{10}\text{Be}$ , there is leverage for covering the whole range in ( $^{187}\text{Os}/^{186}\text{Os}$ ) ratios isotopes found in MORB glasses by sediment contamination. This simple model calculation does not necessarily mean that all the Os isotope data in MORB glasses are explained by contamination by Mn crusts. It indicates that when considering the maximum amount of sediment included in MORB glasses, caution is in order especially when dealing with low-level samples.

## 5. Discussion and Perspective

[23] This study using combined U-series nuclides and cosmonuclide  $^{10}\text{Be}$  measurements in MORB glasses shows that the amount of contamination by sedimentary material is lower than  $10^{-4}$  for most samples. This implies that sedimentary contamination accounts for <1% of the excess nuclides ( $^{230}\text{Th}$  and  $^{231}\text{Pa}$ ) measured in these leached MORB glasses. As expected, this effect is slightly more pronounced for depleted samples (<50 ppb U), which are intrinsically more sensitive to contamination. The consequences of sedimentary contamination on  $^{226}\text{Ra}$  are more difficult to assess since the carrier of this nuclide is likely to be barite instead of manganese oxides. Early work by Krishnaswami and Cochran [1978] has shown that the surfaces of Mn nodules are depleted in  $^{226}\text{Ra}$  relative to  $^{230}\text{Th}$ . Thus contamination by Mn oxides should not lead to  $^{226}\text{Ra}$  in the lavas. To confirm this proposition, more data combining  $^{10}\text{Be}$  and  $^{226}\text{Ra}$  in sediments, including sediments that are Ra-rich, are needed.

[24] Overall, this study demonstrates that even with the low fraction of contaminant found here, some geochemical tracers in MORB glasses (e.g., Os isotopes) can be very sensitive to near-ridge sediment contamination and that cosmogenic  $^{10}\text{Be}$  may be a very powerful tool for distinguishing pristine magmatic signature from secondary contamination. A combined study using both  $^{10}\text{Be}$  and Os isotopes would help in assessing the origin of radiogenic  $^{187}\text{Os}$  signatures in MORB. Finally, the main result of this study is to confirm that the large U series daughter excesses in carefully picked and cleaned MORB samples are magmatic in origin and not due to contamination by Mn crusts.

## Acknowledgments

[25] Careful reviews by two anonymous reviewers have greatly helped in improving this paper. We would also like to thank Claude Allègre for a careful reading of the manuscript. B.B. thanks CNRS for support. S. J. G. and M. T. M. wish to acknowledge the Geosciences Research Program, Office of Basic Energy Sciences, U.S. Department of Energy, for support.

## References

- Anderson, R. F., Y. Lao, W. S. Broecker, S. E. Trumbore, H. J. Hofmann, and W. Wolfli, Boundary scavenging in the Pacific Ocean: A comparison of  $^{10}\text{Be}$  and  $^{231}\text{Pa}$ , *Earth Planet. Sci. Lett.*, **96**, 287–304, 1990.
- Bourdon, B., A. Zindler, C. H. Langmuir, and T. Elliott, Constraints on mantle melting at mid-ocean ridges from global  $^{238}\text{U}$ - $^{230}\text{Th}$  disequilibrium data, *Nature*, **384**, 231–235, 1996a.
- Bourdon, B., C. H. Langmuir, and A. Zindler, Ridge-hotspot interaction along the Mid-Atlantic Ridge between  $37^{\circ}30'$  and  $40^{\circ}30'\text{N}$ : The U-Th disequilibrium evidence, *Earth Planet. Sci. Lett.*, **142**, 175–189, 1996b.
- Bourlès, D., Etude de la géochimie de l'isotope  $^{10}\text{Be}$  et de son isotope stable  $^9\text{Be}$  en milieu océanique: Application à la datation des sédiments marins, Ph.D. thesis, Univ. Paris-Sud, Orsay, France, 1988.
- Bourlès, D., Beryllium isotope geochemistry of hydrothermally altered sediments, *Earth Planet. Sci. Lett.*, **109**, 47–56, 1992.
- Bourlès, D. L., G. M. Raisbeck, E. T. Brown, F. Yiou, and J. M. Edmond, Beryllium isotope systematics of sub-



- marine hydrothermal systems, *Earth Planet. Sci. Lett.*, **105**, 534–542, 1991.
- Chabaux, F., and C. J. Allègre,  $^{238}\text{U}$ - $^{230}\text{Th}$ - $^{226}\text{Ra}$  disequilibria in volcanics—A new insight into melting conditions, *Earth Planet. Sci. Lett.*, **126**, 61–74, 1994.
- Claude-Ivanaj, C., B. Bourdon, and C. J. Allègre, Ra-Th-Sr isotope systematics in Grande Comore Island: A case study of plume-lithosphere interaction, *Earth Planet. Sci. Lett.*, **164**, 99–117, 1998.
- Condomines, M., P. Morand, and C. J. Allègre,  $^{230}\text{Th}$ - $^{238}\text{U}$  radioactive disequilibria in tholeiites from the FAMOUS zone (Mid-Atlantic Ridge,  $36^{\circ}50'\text{N}$ ): Th and Sr isotopic geochemistry, *Earth Planet. Sci. Lett.*, **55**, 247–256, 1981.
- Elliott, T., Fractionation of U and Th during mantle melting: A reprise, *Chem. Geol.*, **139**, 165–183, 1997.
- German, C. R., N. C. Higgs, J. Thomson, R. Mills, H. Elderfield, and J. Blusztajn, A geochemical study of metalliferous sediments from the TAG hydrothermal mound,  $26^{\circ}08'\text{N}$ , Mid-Atlantic Ridge, *J. Geophys. Res.*, **98**, 9683–9692, 1993.
- Goldstein, S. J., M. T. Murrell, and D. R. Janecky, Th and U isotopic systematics of basalts from the Juan de Fuca and Gorda Ridges by mass spectrometry, *Earth Planet. Sci. Lett.*, **96**, 134–146, 1989.
- Goldstein, S. J., M. T. Murrell, D. R. Janecky, J. R. Delaney, and D. A. Clague, Geochronology and petrogenesis of MORB from the Juan de Fuca and Gorda Ridges by  $^{238}\text{U}$ - $^{230}\text{Th}$  disequilibrium, *Earth Planet. Sci. Lett.*, **107**, 25–41, 1991.
- Goldstein, S. J., M. T. Murrell, and R. W. Williams,  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  chronology of mid-ocean ridge basalts, *Earth Planet. Sci. Lett.*, **115**, 151–159, 1993.
- Krishnaswami, S., and J. K. Cochran, Uranium and thorium series nuclides in oriented ferromanganese nodules: Growth rates, turnover time and nuclide behavior, *Earth Planet. Sci. Lett.*, **40**, 45–62, 1978.
- Lundstrom, C. C., J. Gill, Q. Williams, and M. R. Perfit, Mantle melting and basalt extraction by equilibrium porous flow, *Science*, **270**, 1958–1961, 1995.
- MacDougall, J. D., R. C. Finkel, J. Carlson, and S. Krishnaswami, Isotopic evidence for uranium exchange during low-temperature alteration of oceanic basalt, *Earth Planet. Sci. Lett.*, **42**, 27–34, 1979.
- McKenzie, D.,  $^{230}\text{Th}$ - $^{238}\text{U}$  disequilibrium and the melting processes beneath ridge, *Earth Planet. Sci. Lett.*, **72**, 149–157, 1985.
- Pickett, D. A., and M. T. Murrell, Observations of  $^{231}\text{Pa}$ / $^{235}\text{U}$  disequilibrium in volcanic rocks, *Earth Planet. Sci. Lett.*, **148**, 259–271, 1997.
- Pickett, D. A., M. T. Murrell, and R. W. Williams, Determination of femtogram quantities of protactinium in geologic samples by thermal ionization mass spectrometry, *Anal. Chem.*, **66**, 1044–1049, 1994.
- Reinitz, I., and K. K. Turekian,  $^{230}\text{Th}$ / $^{238}\text{U}$  and  $^{226}\text{Ra}$ / $^{230}\text{Th}$  fractionation in young basaltic glasses from the East Pacific Rise, *Earth Planet. Sci. Lett.*, **94**, 199–207, 1989.
- Schiano, P., J.-L. Birck, and C. J. Allègre, Osmium-strontium-neodymium-lead isotopic covariations in mid-ocean ridge basalt glasses and the heterogeneity of the upper mantle, *Earth Planet. Sci. Lett.*, **150**, 363–379, 1997.
- Shimmield, G. B., and N. B. Price, The scavenging of U,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  during pulsed hydrothermal activity at  $20^{\circ}\text{S}$ , East Pacific Rise, *Geochim. Cosmochim. Acta*, **52**, 669–677, 1988.
- Sims, K. W. W., D. J. DePaolo, M. T. Murrell, W. S. Baldrige, S. J. Goldstein, and D. A. Clague, Mechanisms of magma generation beneath Hawaii and mid-ocean ridges: Uranium/thorium and samarium/neodymium isotopic evidence, *Science*, **267**, 508–512, 1995.
- Spiegelman, M., and T. Elliott, Consequences of melt transport for uranium series disequilibrium in young lavas, *Earth Planet. Sci. Lett.*, **118**, 1–20, 1993.
- Valette-Silver, J. N., F. Tera, J. Klein, and R. Middleton, Beryllium 10 in hydrothermal vent deposits from the east Pacific ridges: Role of sediments in the hydrothermal processes, *J. Geophys. Res.*, **92**, 11,364–11,372, 1987.
- von Blanckenburg, F., R. K. O’Nions, N. S. Belshaw, A. Gibb, and J. R. Hein, Global distribution of beryllium isotopes in deep ocean water as derived from Fe-Mn crusts, *Earth Planet. Sci. Lett.*, **141**, 213–226, 1996.
- Williams, R. W., and J. B. Gill, Effects of partial melting on the uranium decay series, *Geochim. Cosmochim. Acta*, **53**, 1607–1619, 1989.