

Short-term metasomatic control of Nb/Th ratios in the mantle sources of intraplate basalts

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ABSTRACT

Variations in the niobium/thorium ratio in basaltic rocks are thought to be related to the long-term extraction of continental crust from the mantle and the extent of sediment recycling and mixing in the mantle. However, basalts erupted between 13 and 3 Ma from a single volcanic center in the Cantal alkali massif (France) have Nb/Th of 10.5–18.7, a range encompassing nearly the entire basalt record. Cantal basalts are isotopically homogeneous, ruling out variable sediment contamination of their mantle sources. Instead, the new data indicate a mineralogical control on Nb/Th in a veined mantle source. We postulate that the large Nb/Th variations are the result of a metasomatic process, called percolative fractional crystallization, that produced veins containing pyroxene and Nb-rich oxide within the upper mantle. Short-term metasomatic-induced variations in mantle Nb/Th may have occurred throughout the geologic record, and provide an alternative explanation to sediment recycling for Nb/Th heterogeneity in the upper mantle.

Keywords: oceanic-island basalt, metasomatism, heterogeneity, upper mantle, recycling, geochemistry, Cantal massif.

INTRODUCTION

Certain incompatible trace element ratios in basalts such as Nb/Th have been used to trace the timing of extraction of continental crust from the mantle (Hofmann et al., 1986) and the extent of sediment recycling and mixing in the mantle (Weaver, 1991; Rehkämper and Hofmann, 1997). A progressive increase in Nb/Th is observed from a mean of ~8, the primitive (undifferentiated) mantle ratio, in ancient basalts to values as high as 20 in some modern basalts formed at mid-ocean ridges (MORBs) and oceanic islands (OIBs). This suggests long-term evolution of mantle Nb/Th by gradual extraction of the continents (Nb/Th <5) over at least 3.5 b.y. of Earth history (Collerson and Kamber, 1999), rather than more rapid, early continent extraction (Armstrong, 1981). Variability in Nb/Th of basalts of particular ages may reflect the presence of unhomogenized recycled crust-derived sediment in mantle (e.g., Kerrich et al., 1999), generally associated with Sr, Nd, and Pb isotopic variations (Weaver, 1991). However, we have discovered that basalts erupted between 13 and 3 Ma in the Cantal alkali massif (France) show an increase in Nb/Th from 10.5 in the oldest basalt to 18.7 in the youngest. This range in Nb/Th (10.5–18.7) is almost as large as that found in picrites and tholeiites from all major oceanic islands (from 8 to 20; Jochum et al., 2001). The Cantal basalts are homogeneous with respect to their Sr, Nd, Pb

isotopic compositions, ruling out variable sediment contamination of their mantle sources. The Nb/Th variations observed in Cantal basalt define a previously unknown short-term metasomatic process in their mantle source.

RESULTS AND DISCUSSION

The Miocene alkali massif of the Cantal (Central Massif, France) was eroded deeply during the ice age and thus provides a good opportunity to study the compositional evolution of lavas erupted during its complete volcanic history. There were two main periods of basalt emission, the so-called Infracantalian period (13–9.5 Ma) and the Supracantalian period (younger than 9.5 Ma, but mainly between 6 and 3 Ma). The basalts show a substantial composition range from alkali basalts to basanites, explained by variations in the degree of partial melting of a common mantle source (Wilson et al., 1995; Pilet et al., 2002). The compositions are similar to those of OIBs with large enrichments in Th, U, Nb, Ta, and light rare earth elements (LREEs), and smaller enrichments for heavy REE, Sr, Y, and K, relative to MORB. The two periods of basalt volcanism have similar major element and Sr, Nd, and Pb isotopic compositions, but subtle trace element differences (Table 1). In particular, at a given Th content, LREE concentrations overlap in the two groups (Fig. 1A), whereas Nb is enriched in Supracantalian basalts (Fig. 1B). The Nb enrichment is associated with an

apparent change in incompatibility of Nb relative to Th during partial melting (Fig. 1C). The Infracantalian basalts have more or less constant Nb/Th (10–12), independent of the level of Th enrichment and thus the degree of partial melting. Similar partition coefficient values for Nb and Th are suggested for this mantle melting event. In contrast, the Supracantalian basalts have Nb/Th varying from 12.5 for Th-rich basanites to 18.7 for comparatively Th-poor alkali basalts. These variations suggest that Nb is less incompatible than Th during mantle melting. Ta shows behavior similar to that of Nb in both groups, so that Infracantalian basalts have more restricted Ta/Th than Supracantalian basalts. The coherence of these trace element variations within each basalt group and the similarity of their isotopic compositions exclude fractional crystallization, crustal contamination, or magma mixing at crustal or mantle levels as the reason for the trace element differences between the Infracantalian and Supracantalian basalts. Only mineralogical modification of the mantle source seems able to explain, simultaneously, the enrichment of Nb and Ta contents and the change in the relative degrees of incompatibility during partial melting between Nb and Ta, and Th.

The Nb and Ta contents in mantle peridotites may be controlled by the presence of amphibole (Eggins et al., 1998) or Ti-rich oxide phases (rutile), which concentrate Nb and Ta (Bodinier et al., 1996; Kalfoun et al., 2002). The higher levels of Nb and Ta in Supracantalian basalts can be explained by the addition of ~4% of amphibole or a very small amount of rutile (~0.01%) to the mantle source prior to partial melting (Figs. 1B, 1C). As much as 10% melting of this source would produce Nb/Th vs. Th trends in the derived melts that mimic those of the Supracantalian basalts. Between 3% and 6% partial melting of an unmetasomatized mantle source produces constant Nb/Th with decreasing Th, as in the Infracantalian basalts. The presence of amphibole in the mantle source is thought to have controlled the K content of the Cantal basalts during partial melting (Wilson and Downes, 1991). Because the K content of Infracantalian and Supracantalian basalts is similar (Table 1),

TABLE 1. REPRESENTATIVE ANALYSES FOR CANTAL BASALTS

Type of rocks: Sample:	Supracantalian basalts 9.5–3 Ma				Infracantalian basalts (13–9.5 Ma)			
	Basanite 31	Basanite 9	Alk. bas. 37	Alk. bas. 39	Basanite M6	Basanite M12	Basanite M3	Alk. bas. M5
Th*	9.0	7.7	5.5	3.4	10.0	8.9	8.4	5.2
U*	2.7	2.5	1.6	0.9	2.7	2.5	2.7	1.4
Nb†	114.3	113.8	83.2	62.2	106.0	90.0	100.4	58.0
Ta*	8.3	7.6	5.6	4.1	7.3	5.5	6.5	3.9
K†	1.69	2.13	1.30	1.10	1.26	0.96	2.06	1.52
La*	76.6	59.4	45.9	32.8	81.4	69.6	68.8	46.3
Nb/Th	12.65	14.84	15.01	18.04	10.65	10.08	11.95	11.23
Nb/U	42.3	46.1	52.0	69.1	40.0	36.5	36.8	42.9
Ta/Th	0.91	0.99	1.01	1.20	0.73	0.62	0.78	0.76
Nb/La	1.49	1.92	1.81	1.90	1.30	1.29	1.46	1.25
Ta/La	0.108	0.128	0.122	0.126	0.089	0.08	0.095	0.085
La/Th	8.48	7.74	8.28	9.51	8.18	7.79	8.19	8.96
Th/U	3.35	3.11	3.46	3.83	3.75	3.63	3.08	3.82
⁸⁷ Sr/ ⁸⁶ Sr [‡]	2 × 10 ⁻⁵ **	0.70337	0.70345	0.70352	0.70347	0.70343	0.70360	0.70362
¹⁴³ Nd/ ¹⁴⁴ Nd [‡]	6 × 10 ⁻⁶ **	0.51286	0.51285	0.51286	0.51287	0.51281	0.51283	0.51281
²⁰⁶ Pb/ ²⁰⁴ Pb [§]	0.003**	19.76	19.68	19.57	19.56	19.62	19.73	19.47
²⁰⁷ Pb/ ²⁰⁴ Pb [§]	0.003**	15.63	15.63	15.62	15.64	15.64	15.63	15.65
²⁰⁸ Pb/ ²⁰⁴ Pb [§]	0.006**	39.47	39.40	39.34	39.35	39.45	39.20	39.45

*Th, U, Ta, and La analyzed by instrumental neutron activation analysis (INAA) (P. Sue Laboratory, Saclay, France).

†Nb and K by X-ray fluorescence (Centre d'Analyse Minérale, University of Lausanne, Switzerland).

‡Sr and Nd isotopic ratios by thermal-ionization mass spectrometer (TIMS) (Department of Mineralogy, University of Geneva, Switzerland; Department of Earth Science, Memorial University of Newfoundland, Canada).

§Pb isotope ratios by multicollection inductively coupled plasma–source mass spectrometry (Institute of Geological Sciences, University of Bern, Switzerland) and by TIMS (Department of Earth Science, Memorial University of Newfoundland, Canada).

**Maximum uncertainties for Sr, Nd, and Pb isotope ratios.

it is unlikely that addition of amphibole to the source of Supracantalian basalt produced the observed enrichment of Nb and Ta. It appears that Nb and Ta enrichments in the Supracantalian basalts are related to the deposition of Nb(Ta)-rich oxides such as rutile in the mantle source of the basalts just prior to their genesis.

Studies of spinel peridotite xenoliths from the East African rift (Bodinier et al., 1996; Bedini et al., 1997) have demonstrated that deposition of Nb- and Ta-rich oxides within the mantle results from the percolation and differentiation of basaltic melts derived from mantle plumes. This differentiation mechanism, called percolative fractional crystallization (PFC) by Harte et al. (1993), can explain the crystallization of different minerals (amphibole, mica, clinopyroxene, apatite, ilmenite, and rutile) in dikes, veins, or metasomites by flow of melt in channelways or by pervasive melt migration within the enclosing mantle peridotite. This mechanism is interpreted as a modal metasomatic process.

A result of the PFC mechanism is the appearance of green-core aegirine-augite pyroxene xenocrysts (hereafter GCPX) in Cantal basalts erupted after 9.5 Ma (Fig. 2A). The GCPX are associated with apatite, ilmenite, and amphibole, all phases predicted by the PFC model. Various studies have demonstrated that GCPX crystallize in alkali-differentiated liquids at high pressure (Duda and Schmincke, 1985; Pilet et al., 2002). GCPX crystallization could take place in the lower crust (Duda and Schmincke, 1985), but a fluid-inclusion study performed on GCPX from Hungarian basalts

(Szabo and Bodnar, 1999) points to an upper-mantle origin for GCPX. The similarity between compositions of GCPX and those of augite in amphibole veins of spinel peridotite xenoliths from La Palma (Canary Islands) (Pilet et al., 2002) strongly suggests crystallization of GCPX within upper mantle veins. Furthermore, Sr, Nd, Pb, and O isotopic compositions of GCPX in continental flood basalts from Yemen (Baker et al., 2000) indicate the absence of crustal contamination during GCPX crystallization and a direct relationship with an asthenosphere-derived mantle plume.

GCPX from Cantal basalts exhibit large variations in Nb/Th, Ta/Th, and Nb/Ta (Fig. 2B). Large variations in Nb/Ta are generally not observed in basaltic liquids (Green, 1995), but may be observed in differentiated liquids that are formed by fractionation of amphibole and Ti oxides. Cantal GCPX can be modeled (Fig. 2B) as the products of differentiated liquids from which 1%–2% rutile had been fractionated, based on Nb/Ta and Ta/Th systematics ($K_{\text{Nb}}^{\text{rutile/L}}$ is ~10–160 and $K_{\text{Ta}}^{\text{rutile/L}}$ is twice as large; Green, 1995; Bodinier et al., 1996). Amphibole and ilmenite do not have sufficiently large and contrasting partition coefficients for Nb and Ta (Green, 1995; Tiepolo et al., 2000) to explain the GCPX data by fractional crystallization. The results are further evidence for a relationship between the crystallization of GCPX and Nb-rich rutile, previously described in Australian mantle xenoliths (Wass, 1979) and in syenitic xenoliths of probable mantle origin present in Scottish basalt (Upton et al., 1999). The implication here

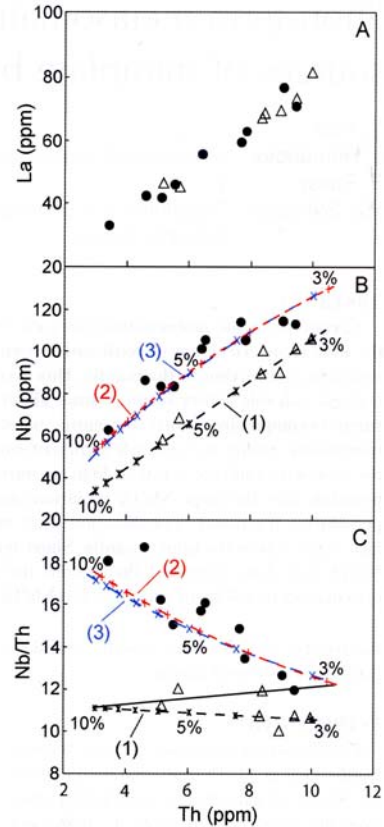


Figure 1. A: La vs. Th for Infracantalian (13–9.5 Ma, open triangles) and Supracantalian basalts (9.5–3 Ma, filled circles). At similar concentrations of both major and moderate incompatible trace elements (Sr to Lu), Infracantalian basalts tend to be enriched in Th, U, La, and Ce compared to Supracantalian basalts. B: Nb vs. Th. C: Nb/Th vs. Th. In B and C, partial melting curve (1, black dashed lines) for Infracantalian basalts is calculated for source composed of 55% olivine, 25% orthopyroxene, 18% clinopyroxene, and 2% garnet; $K_{\text{D}}^{\text{min/L}}$ values are from Halliday et al. (1995). Chemical composition of source is calculated by assuming that it formed Infracantalian basalt M6 after 3% partial melting. Partial melting curve (2, red dashed lines) is calculated for mantle source assumed for Infracantalian basalt in presence of 4% amphibole. $K_{\text{D}}^{\text{mp/L}} = 0.5$ for Nb (Tiepolo et al., 2000) and 0.001 for Th (Halliday et al., 1995). Amphibole composition is taken from amphibole + clinopyroxene xenoliths in Cantal Basalt (Th: 0.85 ppm; Nb: 85 ppm). Partial melting curve (3, blue dashed lines) is calculated from source mantle derived for Infracantalian basalt with addition of 0.01% of rutile. $K_{\text{D}}^{\text{rutile/L}} = 160$ for Nb; Nb concentration in rutile is 26,500 ppm (Bodinier et al., 1996). $X\%$ = degree of partial melting.

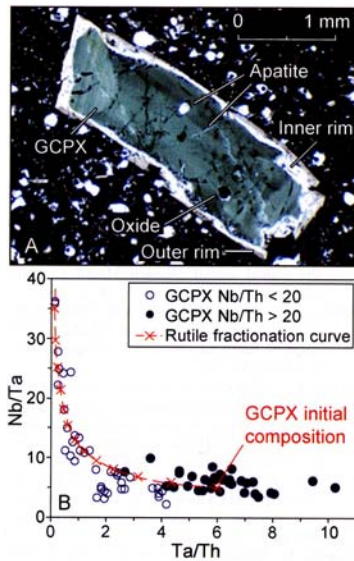


Figure 2. A: Typical green-core pyroxene (GCPX) of aegirine-augite composition with apatite, oxide, and glass inclusions. Light chromian augite inner rim and brownish titanian augite outer rim in equilibrium with enclosing basaltic liquid surround GCPX. B: Ta/Th vs. Nb/Ta variations in different GCPX grains. GCPX analyses obtained by laser-ablation inductively coupled plasma-mass spectrometry at Memorial University of Newfoundland (Canada). Rutile fractionation curve (red dashed line) was calculated by assuming that GCPX crystallized in equilibrium with differentiated liquid that evolved by fractionation of rutile. $K_{\text{rutile}}^{\text{Nb/Ta}} = 0.01$ for Th, 160 for Ta, and 80 for Nb (Green, 1995; Bodinier et al., 1996). X% = percent of rutile fractionation.

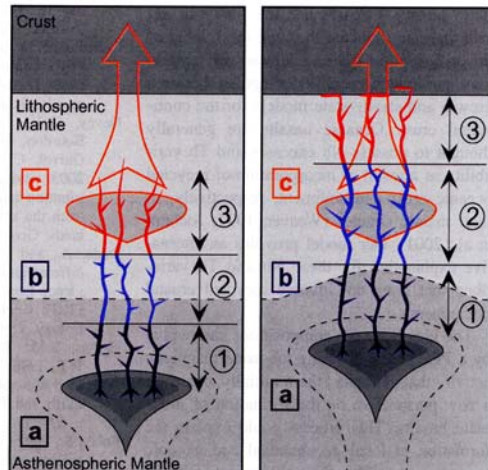
is that GCPX formed from residual liquids generated during the last stages of a PFC process that crystallized rutile.

MODEL FOR THE GENERATION OF BASALTS WITH VARIABLE Nb/Th

A schematic diagram of a physical model for the generation of the Cantal basalts by the PFC process is presented in Figure 3. There are three steps: (1) decompression melting of asthenospheric mantle in a rising hot mantle diapir or "hot finger" related to a plume (Granet et al., 1995); (2) rise and pervasive migration of asthenospheric melts into the overlying lithospheric mantle, forming veins by a PFC process; and (3) variable degrees of partial melting of the heterogeneous lithospheric source to form basaltic to basaltic liquids parental to Cantal lavas.

For two reasons, trace element compositions of basalts produced by this mechanism are mainly controlled by the composition of

Figure 3. Schematic model for (A) Infracantalian and (B) Supracantalian basalt genesis. a: During plume upwelling (Granet et al., 1995), oceanic-island basalt melts are produced by partial melting of asthenospheric mantle. b: Rising melts percolate along channelways or pervasively through asthenospheric and then lithospheric peridotite; they undergo percolative fractional crystallization (PFC) process, precipitating amphibole, clinopyroxene, oxide, and apatite in veins. Three main zones with different compositions are distinguished in veins: (1) mafic pyroxenite veins; (2) differentiated veins with clinopyroxene, amphibole, Nb- and Ta-rich oxide (such as rutile), ilmenite, and apatite; and (3) veins extremely enriched in Th, U, and light rare earth elements relative to Ta and Nb, which are depleted as result of rutile fractionation. These latter veins are composed of GCPX, apatite, amphibole, ilmenite, and residual melts. Geochemical evolution of differentiated GCPX-bearing veins is similar to model proposed by Bedini et al. (1997) to explain evolution of PFC process. c: Melt percolation and vein deposition are associated with migration of thermal front across lithospheric mantle (Lenoir et al., 2001). Partial melting of veins and enclosing depleted lithospheric mantle forms Cantal basaltic liquids. Because Infracantalian and Supracantalian basalts have similar major element compositions, their depths of mantle melting must have been similar (Albarède, 1992). As PFC proceeded, vein compositions at depth of melting evolved from type 3 during Infracantalian basalt activity to type 2 during Supracantalian basalt activity.



A. Infracantalian basalts B. Supracantalian basalts

the veins. First, because the solidus temperature of the veins is lower than that of the enclosing lithospheric mantle, the presence of 5% of veins in the mantle can enhance melt productivity of the source by 20%–40% (Hirschmann and Stolper, 1996). Second, concentrations of incompatible trace elements are 40–80 times higher in vein minerals than in lithospheric spinel peridotite minerals (e.g., GCPX have 12–40 ppm La, whereas clinopyroxene from depleted peridotite xenoliths from Massif Central contain only 0.3–0.6 ppm La; Zangana et al., 1999).

The hypothesis that the source of basaltic rocks is composed of a metasomatically enriched component dispersed in ambient depleted mantle has been suggested for many years (Hanson, 1977). In particular, vein-plus-wall-rock-melting mechanisms have been proposed in order to explain the origin of potassic alkaline magmas (Foley, 1992) and the garnet signature observed in MORB (Hirschmann and Stolper, 1996). Our short-term metasomatic model differs from previous models in that (1) vein formation is an early product of the hotspot melting activity that leads to basalt genesis and (2) the mineral assemblage and chemistry of the vein evolve so that compositions of derived intraplate basalts change with time. GCPX have been described

in many alkaline volcanic massifs, including both oceanic (Canary Islands, Isla da Trinidad) and continental settings (Germany, Italy, Scotland, Hungary, Wyoming, Uganda, Yemen, Morocco, China, Australia). Xenocrysts from Scottish basalts (Upton et al., 1999) demonstrate that GCPX have formed since at least the Carboniferous-Permian. Thus, the formation of GCPX and therefore the PFC process probably correspond to a general petrologic mechanism of hotspot activity. Our model, for example, can explain recent data for small seamounts associated with Tahiti and Pitcairn Islands (Devey et al., 2003). Phonolites and trachytes erupted from these small volcanoes demonstrate that differentiated magmas are derived from the initial melting products of a new fertile batch of mantle. Extensive crystal fractionation of the initial basic magma has been postulated to explain the evolution to the phonolitic compositions (Devey et al., 2003). As an alternative, we propose that the PFC process could produce this phonolitic composition, as demonstrated by the similarity of the composition of GCPX and phonolitic pyroxene (Pilet et al., 2002).

The observed short-term variation in mantle Nb/Th complicates use of the ratio as a tracer of long-term rates of continent extraction over

Earth history. In particular, the Nb/Th of basalts may not indicate the long-term value of this ratio within the mantle reservoir and so may not unequivocally distinguish between growth and steady-state models for the continental crust. Oceanic basalts are generally thought to possess Nb excesses and Th variability as a result of incorporation of recycled oceanic crust and sediment, respectively, in their mantle sources (Weaver, 1991; Jochum et al., 2001). Our model provides an alternative explanation for these Nb and Th variations that does not involve recycled crustal components.

The idea that vein compositions can evolve by a PFC process, during the same magmatic activity that generated them initially, opens up a new perspective on the formation of intraplate basalts. This process could explain the formation of local geochemical and isotopic heterogeneity within the upper mantle without involving a complex mantle history. The mineralogy, degree of trace element enrichment, and proportion of veins within enclosing mantle all contribute critically to the final composition of basaltic melt extracted from the heterogeneous source.

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