Coupled molybdenum and niobium depletion in continental basalts

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Received 24 May 1995; revised 1 August 1995; accepted 5 August 1995

Abstract

Molybdenum concentrations have been determined for a suite of Late Cenozoic basalt lavas from the Basin and Range province of the western United States. Lavas older than about 5 Ma, which are thought to have had a lithospheric mantle source, are strongly depleted in Nb and Mo relative to La and Nd, respectively. Lavas younger than 5 Ma, which are chemically and isotopically similar to ocean island basalt, show no such depletion in either Nb or Mo. A close geochemical coherence between Nb and Mo is consistent with their similar ionic radii (Nb$^{5+}, 0.64; Mo^{4+}, 0.65$). Both elements are probably retained in residual rutile in a dehydrating subducted slab, while the overlying lithospheric mantle is enriched in large-ion lithophile elements (including light REE), contained in silica-rich hydrous fluids expelled from the slab.

1. Introduction

Depletion of Nb and Ta relative to similarly incompatible elements (e.g., La) is a characteristic feature of arc magmas [1], the continental crust [2] and many continental basalts [3]. Explanations for this depletion range from the retention of Nb and Ta during mantle melting (e.g., [4]) to relative deficiencies of Nb and Ta in the mantle source (e.g., [5]) but, whatever the cause, it is clear that the bulk partition coefficient ($D$) for Nb and Ta has been substantially higher than that for La at some stage [6]. Depletion in arc magmas is more likely to be a mantle source characteristic than a product of the mantle melting process, since La/Nb varies independently of the degree of melting in arc magmas [7]. The most likely explanation is that the mantle above a subducting slab is selectively enriched in large-ion lithophile elements (LILE) through the agency of fluids or magma expelled from the slab during dehydration and/or partial melting, while Nb and Ta are retained in a residual phase in the slab [1,5]. The most likely candidates for this phase are rutile, sphene and ilmenite [8], all of which have high $D_{Nb}$ in silicate melts [9]. If these phases are responsible for the depletion of Nb and Ta, then the agent through which LILE are transferred from the slab to the overlying mantle must be either a hydrous fluid or a silica-rich magma, and cannot be basaltic magma. Ti-bearing phases are soluble in basaltic silicate melt but relatively insoluble in silicic melt [10,11]. Nb and Ta are also extremely insoluble in aqueous fluids in equilibrium with rutile [12].

A useful test of the hypothesis that Nb and Ta depletions are caused by their retention in Ti-rich phases in a subducting slab would be to measure the concentrations of other elements similarly concentrated in these phases. Molybdenum is one such element. It is likely to occur as Mo$^{4+}$ at magmatic oxygen fugacity and in this state it would have a...
similar ionic radius (0.65 Å) to Nb$^{5+}$ (0.64 Å) [13]. MoO$_3$ has a distorted rutile structure [14] and mixed Mo–Ti oxides with a rutile structure have been synthesised [15]. Analytical data for Mo are scarce and determinations of Mo in rutile have not been reported. However, high concentrations of Mo have been reported from sphene in granite [16].

Newsom and Palme [17] have measured Mo concentrations in a large range of igneous rocks and find that it behaves as an incompatible element with a relatively constant Nd/Mo of 23.4 ± 30%. There is no indication from their data that arc rocks are depleted in Mo. In the present study, a suite of transitional to alkaline continental basalts from the Basin and Range province of the western US was chosen for analysis. These rocks show variable depletion in Nb, reflecting variable involvement of asthenospheric and subduction-enriched lithospheric mantle in their generation [18]. The basaltic magmas were generated by late Cenozoic extension and mantle decompression and their high contents of incompatible elements made them relatively immune to the effects of crustal contamination. Lavas older than 5 Ma have high and variable La/Nb, whereas those younger than 5 Ma have low La/Nb, consistent with a sublithospheric mantle source [18]. A suite of alkali basaltic lavas from the oceanic island of São Tomé and the continental Mt Cameroon were also analyzed for comparison. All the samples were analyzed for Nb, Mo, La, Ce and Nd, and the Basin and Range samples were also analyzed for Pb in order to assess the degree to which depletion in Nb is coupled with enrichment in Pb [6].

2. Analytical technique

All the analyses were carried out on pressed-powder samples by X-ray fluorescence (XRF) spectrometry using a Philips PW 1480 automatic spectrometer equipped with a Rh-anode X-ray tube. Analytical conditions are given in Table 1. Mo and Nb are ideally placed for high-precision XRF analysis with this instrument since their K lines have only slightly longer wavelengths than RhK$\alpha$. Corrections for matrix effects on the intensities of MoK$\alpha$, NbK$\alpha$, and PbL$_\beta$ were applied by using the count rate from the RhK$\alpha$ Compton scatter line as an internal standard. LaL$_\alpha$, CeL$_\beta$, and NdL$_\alpha$ were corrected using the Philips alphas procedure, based on major-element concentrations measured on the powder samples. Line-overlap corrections were applied using synthetic standards.

Background positions for all elements were placed as close as possible to the respective peaks. The choice of Mo background positions is especially critical because of the possibility of overlap with second-order CeK$_{\alpha1}$ on the peak, CeK$_{\alpha2}$ on the high-angle background and ZrK$_{\beta1}$ on the low-angle background. The second-order interference was removed by careful pulse-height filtering and by setting the high-angle background at a point on the shoulder of the second-order CeK$_{\alpha2}$ peak chosen to cancel the effect of second-order CeK$_{\alpha1}$ on the MoK$_\alpha$ peak. The effectiveness of this procedure was confirmed by analysing a sample of pure quartz spiked with a high concentration of Ce. The low-angle background position was placed between ZrK$_{\beta1}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>kV</th>
<th>mA</th>
<th>Collimator</th>
<th>Analyzing crystal</th>
<th>Background offset</th>
<th>Detector</th>
<th>Line overlap</th>
<th>Count time peak backdrop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>K$_{\alpha}$</td>
<td>80</td>
<td>30</td>
<td>fine</td>
<td>LiF200</td>
<td>±0.44°</td>
<td>scintillation</td>
<td>ZrK$_{\beta}$*</td>
<td>500 s</td>
</tr>
<tr>
<td>Nb</td>
<td>K$_{\alpha}$</td>
<td>80</td>
<td>30</td>
<td>fine</td>
<td>LiF200</td>
<td>±0.36°</td>
<td>scintillation</td>
<td>YK$_\beta$</td>
<td>500 s</td>
</tr>
<tr>
<td>Pb</td>
<td>L$_{\beta1}$</td>
<td>80</td>
<td>30</td>
<td>fine</td>
<td>LiF200</td>
<td>±0.26°</td>
<td>scintillation</td>
<td>-</td>
<td>500 s</td>
</tr>
<tr>
<td>La</td>
<td>L$_{\alpha1}$</td>
<td>50</td>
<td>50</td>
<td>fine</td>
<td>LiF200</td>
<td>±0.66°</td>
<td>flow</td>
<td>-</td>
<td>500 s</td>
</tr>
<tr>
<td>Ce</td>
<td>L$_{\beta1}$</td>
<td>50</td>
<td>50</td>
<td>fine</td>
<td>LiF200</td>
<td>+1.15°,-0.64°</td>
<td>flow</td>
<td>CrK$_\alpha*$</td>
<td>500 s</td>
</tr>
<tr>
<td>Nd</td>
<td>L$_{\alpha1}$</td>
<td>50</td>
<td>50</td>
<td>fine</td>
<td>LiF200</td>
<td>+0.64°,-1.15°</td>
<td>flow</td>
<td>CrK$<em>\alpha$,$\text{CeL}</em>{\beta1}$</td>
<td>500 s</td>
</tr>
</tbody>
</table>

* Overlap on background position.
and ZrK$_{\beta_2}$ and is subject to slight interference at high concentrations of Zr, the effect of which was removed by applying a small negative line-overlap correction. The only first-order interference on the MoK$_{\alpha}$ peak is from UL$_{\beta_3}$, but the effect of this will be negligible in basaltic rocks.

The spectrometer was calibrated with USGS and CRPG standards BIR-1, BCR-1, BHVO-1, SIM-1 (Mo only), QLO-1, BE-N, and AN-G (not Nb) using the values given by Jochum et al. [19] for Nb, and Govindaraju [20] for the other elements. Excellent calibration lines are obtained using these standards. In the case of Mo, repeated calibration gave RMS deviations of $< 0.5$ ppm from the calibration line. Precision estimates (2$\sigma$), based on at least ten analyses of standards and unknowns, are: Mo and Nb, 0.2 ppm; Pb, 0.8 ppm; La, Ce and Nd, 2 ppm.

3. Results

Analytical results are summarised in Table 2; the complete data set may be obtained from the author. The data from São Tomé and Mt Cameroon are indistinguishable and show a good positive correlation between Mo and Nd, with a mean Nd/Mo of 19 (Fig. 1). This value is within-error of the value (23.4 ± 30%) given by Newsom and Palme [17] for terrestrial samples. The apparent tendency for Nd/Mo to decrease slightly with increasing Nd (Fig. 1) suggests that Mo may be a little more incompatible than Nd, as proposed by Newsom et al. [21] (who compare Mo with Pr) and Sims et al. [22] (who compare it with Ce).

![Fig. 1. Variation of Mo and Nd in alkali basalt samples from an ocean island (São Tomé, grey symbols) and a continental intraplate volcano (Mt Cameroon, black symbols). The two suites of basalt have Nd/Mo = 19, comparable with the ratio for terrestrial basaltic rocks (23.4±30%) determined by Newsom and Palme [17].](image_url)

Plots of La against Nb, and Mo against Nd for Basin and Range basalt samples are given in Fig. 2 and it is clear that Mo and Nb are closely coherent in these samples. Nb and Mo behave as incompatible elements (comparable with La and Nd respectively) in basalts younger than 5 Ma. These rocks show good correlations between the respective pairs of elements, although La/Nb and Nd/Mo are both lower than in the São Tomé and Mt Cameroon samples (Table 2). Nd/Mo is significantly lower

<table>
<thead>
<tr>
<th></th>
<th>São Tomé mean</th>
<th>Mt Cameroon mean</th>
<th>B&amp;R (&lt;5 Ma) mean</th>
<th>B&amp;R (&gt;5 Ma) mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n=72 1σ</td>
<td>n=69 1σ</td>
<td>n=100 1σ</td>
<td>n=90 1σ</td>
</tr>
<tr>
<td>Mo</td>
<td>3.4 1.5</td>
<td>3.4 1.0</td>
<td>3.4 1.2</td>
<td>1.4 0.6</td>
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<tr>
<td>Nb</td>
<td>86.9 21.2</td>
<td>88.0 23.9</td>
<td>59.2 19.5</td>
<td>18.6 11.7</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>2.5 0.8</td>
<td>6.9 3.9</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>63.1 15.8</td>
<td>60.5 17.8</td>
<td>33.2 9.3</td>
<td>31.6 16.9</td>
</tr>
<tr>
<td>Ce</td>
<td>122.4 30.6</td>
<td>125.7 32.3</td>
<td>70.1 18.5</td>
<td>69.2 36.6</td>
</tr>
<tr>
<td>Nd</td>
<td>58.0 12.9</td>
<td>61.8 13.9</td>
<td>33.8 7.1</td>
<td>35.9 16.2</td>
</tr>
<tr>
<td>Nd/Mo</td>
<td>18.9 5.3</td>
<td>18.8 3.1</td>
<td>10.9 3.2</td>
<td>28.0 13.9</td>
</tr>
<tr>
<td>La/Nb</td>
<td>0.73 0.08</td>
<td>0.69 0.06</td>
<td>0.58 0.06</td>
<td>1.94 0.87</td>
</tr>
<tr>
<td>Ce/Pb</td>
<td>30.3 10.1</td>
<td>11.7 7.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2. Variation of (a) Nb and La and (b) Mo and Nd in basaltic lavas from the Basin and Range province of the western US. The younger basalts (< 5 Ma) are chemically and isotopically similar to ocean island basalt and probably have a source in the sub-lithospheric mantle, whereas the older basalts (> 5 Ma) have chemical and isotopic characteristics which suggest a lithospheric mantle source [18,23].

Fig. 3. Correlation of Mo and Nb in basaltic lavas from the Basin and Range province. The good correlation between Mo and Nb in the Basin and Range basalts and the lack of variation in Nb/Mo with Nb concentration suggests that Nb and Mo have similar bulk $D$ both during slab dehydration/melting and during mantle melting.

than the ratio determined by Newsom and Palme [17]. The older Basin and Range basalts, by contrast, are strongly depleted in Nb and Mo with respect to La and Nd and show very poor La–Nb and Nd–Mo correlations. The relative depletion in the two elements, however, is similar (by a factor of 3.3 for Nb and 2.6 for Mo), so that Mo correlates well with Nb for the Basin and Range samples as a whole (Fig. 3).

The samples used in this study are transitional to alkali basalts and, consequently, the concentrations of Nd and Mo fall at the upper end of the range determined by Newsom and Palme [17]. The two samples of alkali basalt analyzed by these authors show as wide a range of Nd/Mo (10.7 and 147, respectively) as that reported here.

4. Discussion

The younger Basin and Range basalts are compositionally and isotopically similar to ocean island basalt and probably have a source within the sub-lithospheric mantle, whereas the older basalts have chemical and isotopic characteristics which suggest a lithospheric mantle source [18,23]. Many of the older basalts have sufficiently high concentrations of incompatible elements (Fig. 2) that they are relatively immune from the chemical and isotopic effects of crustal contamination, so their compositions must reflect that of the mantle source. Variation in La/Nb independent of La content in the older basalts (Fig. 2) suggests that variable La/Nb is a feature of the source and not a product of the partial melting process (cf. [7]). The mantle source for the older basalts was therefore depleted in Nb relative to La. The most likely explanation for this is that the lithospheric mantle beneath the western US was enriched in LILE (including light REE) through subduction processes accompanying Proterozoic crustal accretion [23]. The subsequent melting of this lithospheric mantle during late Cenozoic extension has generated basaltic magmas, which have inherited this ancient subduction signature.

The transport of LILE-rich fluids from subducting slabs into the continental lithosphere (mantle and crust) is an irreversible process of considerable geodynamic significance. The elements transported in this way are mostly those with very low $D_{\text{mantle-melt}}$. 


but with two principal exceptions [6]. Firstly, Nb (and Ta), which are incompatible during silicate melting, are apparently compatible during this process and must be retained in the residue, possibly in rutile or sphene [8]. This explains the deficiency of Nb (and Ta) in arc magmas, the continental crust and some continental basalts. Secondly, Pb is about as incompatible as Ce during silicate melting, but appears to be much more incompatible in subduction processes [6]. Thus, arc magmas, continental crust and some continental basalts have anomalously high concentrations of Pb. Enrichment in Pb, correlated with depletion in Nb, in the older Basin and Range basalts is shown in Fig. 4. The younger basalts have a mean Ce/Pb of about 30 (Table 2), similar to the value of 25 for oceanic basalts [24], whereas the older basalts have a much lower mean Ce/Pb (12).

A consequence of the subduction process is that the sub-lithospheric mantle becomes relatively enriched in Nb (and Ta) and depleted in Pb, compared with other incompatible elements, as a result of residual subducted slab material being stirred back into the convecting mantle [6,8]. Variation in La/Nb among oceanic basalts may, therefore, reflect different amounts of subducted ocean crust in their mantle source [8]. It may be significant that the younger Basin and Range basalts have both lower La/Nb and lower Nd/Mo than typical ocean island basalt (e.g., São Tomé; Table 2). This implies an enrichment in both Nb and Mo, possibly due to a relatively large proportion of residual subducted slab material, in the sub-lithospheric mantle beneath the western US.

The data presented here suggest that Mo, as well as Nb and Ta, is retained in a subducting slab during dehydration and/or partial melting. The good correlation between Mo and Nb in the Basin and Range basalts (Fig. 3) and the lack of obvious variation in Nb/Mo with Nb concentration suggests that Nb and Mo have similar bulk D both during slab dehydration/melting and during mantle melting. Since Mo ought to be concentrated in Ti-bearing phases, this coherence strengthens the case for such phases being responsible for retention of Nb and Ta.

Both rutile and sphene are common accessory minerals in eclogites [25], but only rutile is capable of fractionating Nb and, by implication, Mo from La and Nd, respectively. For silicic melts, $D_{\text{Rutile}}^{\text{exh}} = 6$ [9] and $D_{\text{La}}^{\text{Nb}} = 5 - 10$ [26]. Thus, residual sphene will not fractionate La/Nb and, since $D_{\text{Nd}}^{\text{Nb}} > D_{\text{La}}^{\text{Nb}} (\sim 20, [26])$, it is more likely to retain Nd than either Nb or Mo. $D_{\text{Rutile}}^{\text{Nb}} = 30$ [9] and $D_{\text{Mo}}^{\text{Ce}}$ are probably very low. $D_{\text{Rutile}}^{\text{Mo}}$ is much lower than $D_{\text{Rutile}}^{\text{Nb}}$ so rutile is the most likely residual phase.

Values of $D_{\text{Rutile}}^{\text{Mo}}$ have not yet been measured experimentally, and Mo is rarely determined in igneous rocks and mineral phases. There are insufficient data from arc basalt to demonstrate a coherence between Mo and Nb but there is some evidence that the continental crust is depleted in Mo. Data compiled by Wedepohl [27] gives a value of 18.5 for Nd/Mo in the upper continental crust, comparable with the terrestrial basalt value [17], but a much higher value (46.8) in the lower crust. These estimates, however, are based on old data [16] and may not be very reliable. A better estimate of Mo abundances in the continental crust is that of Sims et al. [22], who analyzed pre-Archaean Australian shale and continental loess and found an average Mo/Ce of $0.018 \pm 0.012$. This value is significantly lower than that determined, by the same authors, in oceanic basalt (0.032 \pm 0.009). For comparison, Nb/La in average continental crust is 0.63 [27], and in ocean island basalt is 1.30 [28] (1.37 in São Tomé basalt, Table 2). Thus, both Mo and Nb are depleted in the continental crust by about a factor of 2 compared with oceanic basalt. This, coupled with the data
presented here, provides good evidence that a Ti-bearing phase, probably rutile, with $D_{M\text{Go}} \approx D_{Nb}$, is responsible for the retention of Nb, Ta and Mo during dehydration and/or partial melting of subducted oceanic crust.

Acknowledgements

Field work in the western US and West Africa was funded through research grants from NATO and the UK NERC, respectively. The Mt Cameroon samples were collected by members of the 1989 Operation Raleigh expedition to Cameroon. Mike Norry and three anonymous referees are thanked for their constructive comments on the manuscript, and Bernie Wood for discussion on the geochemical behaviour of molybdenum. [FA]

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