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Trace Element Partitioning Between Silicate Minerals and Carbonatite at 25 kbar and Application to Mantle Metasomatism

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With 1 Figure

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Summary

Experiments at 25 kbar and 1000 °C, on a model trace element-enriched carbonatite-peridotite mix, produced augite + pargasite ± garnet ± dolomite coexisting with a carbonatite melt. Proton microprobe analysis of the phases showed that key trace elements (Rb, Ba, Sr, Nb, Ta, Zr, Y and REE) all partitioned strongly into the melt (with the exception of Y, Ho and Lu in garnet), verifying that carbonatite is potentially a highly effective metasomatizing agent. The data also indicate that carbonatitic metasomatism will impart higher Ba/Rb, Ba/Nb, Nb/Ta, Sr/Ta, La/Ta, and lower Zr/Y, with little change to Sr/Nb, in affected mantle.

Zusammenfassung

Spurenelementverteilung zwischen Silikatmineralen und Karbonatit bei 25 kbar: Anwendung für die Mantel-Metasomatose

Experimente mit einer Modell-mischung von Karbonatit–Peridotit, angereichert mit Spurenelementen, produzierten bei 25 kbar und 1000 °C Augit + Pargasit ± Granat ± Dolomit coexistierend mit einer Karbonatitschmelze. Protonmikrosonden-Analyse der Phasen zeigte, dass alle Schlüsselspurenelemente (Rb, Ba, Sr, Nb, Ta, Zr, Y and REE) stark in der Schmelze angereichert werden (mit der Ausnahme von Y, Ho und Lu in Granat), was beweist, dass Karbonatit potentiell ein sehr effektives Agens für Metasomatose ist. Die Daten zeigen weiterhin, dass karbonatitische Metasomatose in betroffenen Mantel höhere Ba/Rb, Ba/Nb, Nb/Ta, Sr/Ta, La/Ta und niedrigere Zr/Y produziert, mit geringen Änderungen für Sr/Nb.

Introduction

Primary carbonatite magma has been produced in equilibrium with pargasite lherzolite at 21–30 kbar and 930–1080 °C (*Wallace* and *Green*, 1988). This evidence, combined with observations of mantle-derived spinel lherzolites enriched in jadeitic clinopyroxene, apatite and CO_2-rich fluid inclusions (*Yaxley* et al., 1991) supported suggestions that carbonatite melts might act as ephemeral metasomatic agents in the mantle (*Green* and *Wallace*, 1988). Compositional data from experiments (*Wallace* and *Green*, 1988) showed that Ti partitions strongly into pargasitic amphibole in preference to coexisting carbonatite melt ($D^{Ti}_{amph-carb} = 3.5$, where D is the partition coefficient i.e. weight ratio of element in mineral and coexisting melt). Geochemically, Ti is classed as a high-field-strength element (HFSE) and its behaviour may serve as a model for other HFSE. This led to the suggestion (*Green* and *Wallace*, 1988) that carbonatites might be effective in decoupling HFSE (in particular the trace elements Zr, Nb and Ta) from large-ion lithophile elements (LILE), since D's for the LILE were predicted to be much smaller than for HFSE (as modelled on Ti). The net result of this prediction is that carbonatites should have much higher LILE/HFSE than the mantle from which they were derived. Consequently, carbonatite melts trapped at higher levels in the mantle should impart a metasomatic fingerprint of increased LILE/HFSE. An important consequence is that carbonate metasomatism could be responsible for high LILE/HFSE in the mantle wedge overlying subduction zones, thereby explaining the high LILE/HFSE characteristic of magmas from this region. (*Green* and *Wallace*, 1988) Prior to this suggestion, geochemists usually attributed HFSE depletion in subduction zone magmas to retention of these elements in a residual titanate phase (*Foley* and *Wheller*, 1990) or to mantle-magma interaction (*Kelemen* et al., 1990).

Procedure

In the present study, a trace element-enriched carbonate-peridotite composition (Table 1) was prepared, using on a mixture of 70% dolomitic carbonatite (modelled on published experimental data; *Wallace* and *Green*, 1988) and 30% Hawaiian pyrolite. The trace elements (in ppm) Sr (1700), Y(1000), Zr(1000), Nb(3600) and La(6000) were added at levels broadly appropriate to the concentration range found for carbonatites (*Woolley* and *Kempe*, 1989; *Nelson* et al., 1988) but Rb(1000), Ta(2500), and Sm, Ho, Lu (each 7000), were greatly enriched to ensure concentrations well above detection limits. Augite and pargasite crystals (up to 150μ in size) were successfully grown from this composition but it was necessary to add 5wt.% SiO_2 and 3wt.% Al_2O_3 in a second experiment in order to obtain garnet.

Synthesis experiments were carried out at 25 kbar and 1000 °C for 26 hours using a 12.7 mm piston-cylinder apparatus, KCl/pyrex pressure cells, CERAMIT internal components and standard techniques (*Green* and *Pearson*, 1985). Pressure and temperature were chosen to be within the range of conditions where carbonatite melts may exist in equilibrium with peridotite (*Wallace* and *Green*, 1988). Samples were initially moistened ($< 1\%$ H_2O) and then sealed in $Ag_{70}Pd_{30}$ tubing. Apart from Lu in garnet, crystals appeared homogenous with respect to trace element distribution (variation < 2 standard deviations of the mean). In the case of Lu in garnet, anomalously Lu-rich garnet cores were obtained, and only rim values

Table 1. *Mineral-melt partition coefficients* (D = weight ratio of element in mineral and in coexisting carbonatitic matrix) *at 25 kb, 1000 °C*. Bracketed values denote standard deviations where multiple mineral and matrix analyses were obtained, from two different experiments. In the case of garnet only one rim determination was obtained from one experiment

	1	2	3	4
Rb	0.28 (.06)	0.004 (.003)	—	0.02 (.002)
Sr	0.04 (.01)	0.03 (.01)	0.003	0.37 (.03)
Ba	0.01 (.02)	0.006 (.002)	0.003	0.02 (.003)
Y	0.19 (.03)	0.22 (.02)	1.4	0.28 (.02)
Zr	0.23 (.03)	0.29 (.03)	0.54	0.05 (.006)
Nb	0.06 (.01)	0.01 (.001)	0.003	0.02 (.002)
Ta	0.13 (.03)	0.03 (.001)	—	—
La	0.02 (.03)	0.02	0.009	0.12 (.01)
Sm	0.09 (.02)	0.08 (.01)	0.05	0.12 (.02)
Ho	0.26 (.04)	0.28 (.01)	1.94	0.31 (.001)
Lu	0.15 (.01)	0.23 (.01)	11.6* (.6)	—

1 = pargasite; 2 = augite; 3 = garnet; 4 = dolomite.
* Denotes electron microprobe determination.

were used for partition coefficient determination (cf. *Green* et al., 1989). At the conclusion of experiments, the capsules were observed to have split. However, this does not appear to have affected crystal growth in the carbonate melt, or, apart from observed addition of 2–3% BaO, 8–12% SiO_2 and 3–4% Al_2O_3 from the CERAMIT components, the overall integrity of the silicate-carbonate composition. In fact, the barium appeared to be homogeneously distributed in both minerals and matrix and can be treated usefully as an additional minor component in the experimental system. Although the experiments were unbuffered, the absence of graphite suggests that fO_2 was not low and probably $> {}^{\sim}$ EMOG (enstatite + magnesite + olivine + graphite) buffer (*Green* and *Wallace*, 1988).

Results

Partition coefficients for the trace elements are presented in Table 1. Both pargasite and augite show moderate to strong incompatibility for all trace elements with D values varying from 0.004 to 0.3. Garnet shows the well documented (*Henderson*, 1982) compatibility for Y and heavy rare earth elements (HREE) such as Ho and Lu.

The data given in Table 1 indicate that the HFSE Zr, Nb and Ta are not significantly more compatible in pargasite and augite crystallized from carbonatite melts than are typical LILE (Rb, Ba and Sr). Thus the trace element evidence does not support the suggestion that carbonatites might decouple HFSE from LILE, based on the compatibility of Ti in pargasite crystallizing in equilibrium with carbonatite (*Green* and *Wallace*, 1988).

The relative effect of carbonatite and silicate liquids as metasomatizing agents is illustrated in Fig. 1. This diagram is interpreted as a plot of 2-liquid partition coefficients between silicate (basanite *Adam* et al., 1992) and carbonatite liquids at ~25 kbar and 1000 °C. These 2-liquid partition coefficients were independently determined for liquids in equilibrium with both pargasite and augite, and show good agreement, apart from values for Rb and Ba in augite, which could not be measured directly (*Adam* et al., 1992). Overall, Fig. 1 shows that the alkaline earth elements (Ba, Sr), REE, Y and Rb are favoured by carbonatite, but the HFSE partition evenly between the two liquids except for a slight preference of Ta and Ti for the silicate liquid. Comparison with 2-liquid partition coefficient data obtained at 1050 °C and 3 kbar (*Hamilton* et al., 1989), shows that with decreasing pressure from 25 to 3 kbar there is an apparent increase in $D^{\text{silicate liquid}}_{\text{carbonatite liquid}}$ for all elements. However, there are some compositional differences between the 2 sets of liquid pairs (e.g. the *Hamilton* et al. 1989 pair had very low MgO and high alkalies compared with the pair from the present work), so that close comparison is not possible. Nevertheless, where *Hamilton* et al. (1989) observed a systematic decrease in 2-liquid D (for the REE and Ta) for the pressure range 1 to 6 kbar, the present data suggest this trend must flatten out as the pressure increases to 25 kbar. The most noteworthy result is that the REE favour the silicate liquid at low pressure and the carbonatitic liquid at high pressure.

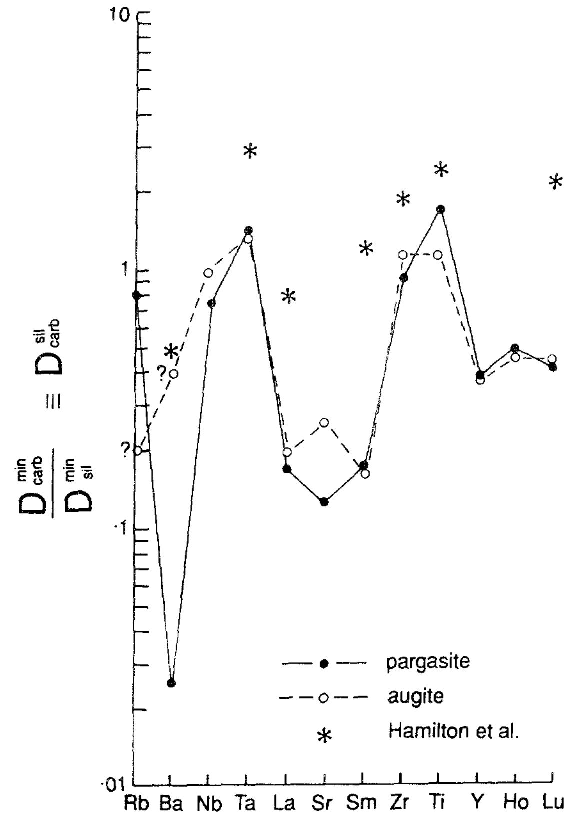

Fig. 1. Ratio of partition coefficients (D's) between amphibole, clinopyroxene and carbonatite or silicate (basanitic) liquids (ie effectively 2-liquid (silicate-carbonatite) partition coefficients). For comparison 2-liquid partition coefficients for silicate (nephelinite)-carbonatite pairs determined at 3 kbar, 1050 °C are plotted (*Hamilton* et al., 1989). (∗). *min* mineral; *sil* silicate liquid; *carb* carbonatite liquid.

These contrasting partition relationships for key trace elements between pargasite/augite and silicate and carbonatitic melts allow identification of geochemical ratios which *may* indicate whether a silicate (*Green* and *Liebermann*, 1976) or a carbonatite (*Green* and *Wallace*, 1988) melt was responsible for metasomatism of a particular mantle region. Thus relative to primitive mantle (*Sun* and *McDonough*, 1989) Ba/Rb, Sr/Ta, Ba/Nb, Nb/Ta, La/Ta should increase, Sr/Nb remain unchanged and Zr/Y decrease for carbonatite metasomatism, while Sr/Nb, Sr/Ta, La/Ta should decrease, Zr/Y increase and Ba/Rb, Ba/Nb, Nb/Ta remain unchanged (or Nb/Ta increase slightly) for silicate liquid (e.g. nephelinitic magma) metasomatism. Changes in element ratios, different from these two predictions, may indicate either alternative metasomatizing agents (e.g. fluids), or the presence of additional residual phases (e.g. titanates), or a more complex history of geochemical recycling (e.g. involving sediments). For example, an average island arc basalt (*McCulloch* and *Gamble*, 1991), has very high Ba/Nb (133) and Sr/Nb (247), high Sr/Zr (7.1) and only slightly increased Zr/Y (2.7) when compared with primitive mantle (*Sun* and *McDonough*, 1989), (9.8, 30, 1.9 and 2.4, respectively). It therefore cannot come from a mantle source which was simply modified by carbonatite or silicate liquid metasomatism. The contribution of some additional factor appears to be required as well (e.g. a fluid cf. *McCulloch* and *Gamble*, 1991).

Finally, the partition coefficient data may be applied to testing the proposal that carbonatite metasomatism may be responsible for observed trace element enrichment in lherzolite samples from the mantle. This is done by calculating the trace element content of hypothetical carbonatite liquids which may have been in equilibrium with metasomatized lherzolites, where the trace element content of pargasite and augite in these lherzolites has been determined (*O'Reilly* et al., 1991). The predicted concentrations of Rb, Sr, Ba, Y, Zr and Nb fall within or close to the concentration range published for carbonatites (*Woolley* and *Kempe*, 1989; *Nelson* et al., 1988). This indicates that these cases are consistent with carbonatite metasomatism, but does not prove such a process took place.

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