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Element partitioning between immiscible melts and geochemical anomalies in igneous rocks

I.V. Veksler[1], A.M. Dorfman[2, 3], P. Dulski[1] and D.B. Dingwell[3]

[1] GFZ Potsdam, Germany (veksler@gfz-potsdam.de)
[2] Vernadsky Institute, Moscow, Russia (mandorf@mega.ru)
[3] Geo&Umwelt, LMU, Munich, Germany (Dingwell@lmu.de)

Although fractional crystallisation is the main process by which magmas evolve, several types of liquid immiscibility may occur in magmatic melts and provide an effective means of element enrichment and fractionation. Some carbonatites likely form by immiscibility and other types of salt melts (chloride, fluoride, borate) may form in granitic magma chambers. We present experimental constraints on element partition coefficiemnts (*D*'s) between granitic melts and conjugate fluoride, chloride and carbonate melts. Experiments were carried out at 750-950 °C, 100 MPa in a centrifuge autoclave and cold-seal pressure vessels using dry and water-bearing mixtures of synthetic glasses and reagent-grade salts (fluorides, chlorides and carbonates) doped with trace elements (REE, HFSE, LILE, Sn, Be, W). Run products were analysed by EMP and ICP-MS. As for mineral-melt partitioning, two-liquid *D*\s depend primarily on ionic properties: formal charges (*Z*) and ionic radii (*r*). In all the studied salt-silicate pairs of immiscible liquids, at a given *P*, *T* and bulk composition, Ca Mg and light REE show the greatest affinity to salt melts and the highest two-melt *D* values. Among alkalis and alkaline earths, *D* values gradually decrease in the order $\mathrm{Mg} \leq \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} \leq \mathrm{Cs}$, consistent with the decrease of *Z/r* values of the mono- and divalent cations. In contrast, elements that form cations with *Z*=3(+) and higher (Al, Si, REE, HFSE, W and P), show strong deviations from the simple *D-Z/r* relations. REE and HFSE with almost identical *Z/r* (e.g., Y-Ho, Nb-Ta and Zr-Hf) are often strongly fractionated between the liquids, so that D_{Nb} and D_{Zr} are systematically higher than D_{Ta} and D_{Hf}. Fractionation of Y and Ho depends on the type of the salt melt: for carbonate melt $D_{\mathrm{Y}} \sim D_{\mathrm{Ho}}$; for fluoride melt $D_{\mathrm{Y}} > D_{\mathrm{Ho}}$ ($D_{\mathrm{Y}}/D_{\mathrm{Ho}} \sim 1.2$); and for chloride melt $D_{\mathrm{Y}} < D_{\mathrm{Ho}}$ ($D_{\mathrm{Y}}/D_{\mathrm{Ho}} \sim$ 0.76-0.8). In case of the fluoride-silicate partitioning, D_{REE} show also subtle periodicity, consistent with the lanthanide tetrad effect, related to the gradual filling of the inner 4f electron sub-shell. Experimental constraints on the two-melt *D* values provide insights into speciation and stability of chemical bonds in multicomponent silicate melts containing non-silicate anions. Our results are applicable to fluid-melt partitioning, may help to explain some anomalous variations in mineral-melt *D*'s, not constrained by *Z* and *r*, and also non-chondritic Y/Ho, Zr/Hf, and Nb/Ta, as well as the REE tetrad patterns observed in some types of igneous rocks.

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La, Ce, Nd and Sr partition between apatite and minette magma

J. Plá Cid[1], P. Enrique[2], H. Conceição[1] and L.V. Nardi[3]

[1] Federal University of Bahia, Brazil (jorge.pla@bol.com.br; herbet@cpgg.ufba.br).
[2] Barcelona University, Spain (pedro@natura.geo.ub.es)
[3] Federal University of Rio Grande do Sul, Brazil (lauro.nardi@ufrgs.br).

Introduction

Apatite is largely found in mafic microgranular enclaves formed by co-mingling of minette lamprophyres and potassic syenite magma in southern Brazil. This mingling started at mantle-pressures [1] and most enclaves preserved its chemical composition by similarity with syenitic magma. Apatite euhedral crystals (ap-1) crystallize together diopside-phlogopite-(pyrope) paragenesis at near-liquidus conditions, and also as acicular (ap-2) crystals during undercooling. Light Rare Earth Elements (LREE) and Sr concentrations were determined by electron microprobe at Barcelona (Spain) and Rio Grande do Sul (Brazil) Universities for calculating the partition of these elements with minette magma and to verify their variation during magmatic evolution.

Results

Only the ap-1 crystals were used to determine the partition values. Sr contents are extremely high, normally above 1300ppm, and reaching up to 2100 ppm. The partition values are between 5.1 and 8.2. La+Ce+Nd amounts are around 1500ppm, and are very similar in both ap-1 and ap-2. However, the LREE concentrations are less homogeneous than Sr. The partition data estimated for these elements are: La (11.8 to 30.6), Ce (16.1 to 33), and Nd (12 to 31). The low Sr-partition values found in clinopyroxene and mica[2], which are below 0.2, suggest that fractionation of these phases attenuates the decrease of Sr in the magma caused by apatite crystallization. Similar behaviour is assumed for LREE, which have parttition data below 1[2]. Then, during crystallization of ap-mica-cpx paragenesis in minette liquids the geochemical controll of such elements is due to apatite fractionation.

References

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