Phosphorus partitioning in basalts: an experimental and ion probe study

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Introduction

Phosphorus behaves as an incompatible element during the early stages of crystallization of basaltic magmas, and due to its high solubility in depolymerized melt (Harrison and Watson, 1984) enrichments of up to 2–3 wt% P_2O_5 have been documented for a number of natural basic magmas before saturation of phosphate phases (Anderson and Greenland, 1969). Both of the features suggest that phosphorus can give valuable constraints on models of magma crystallization, such as the extent of crystallization along a liquid line of descent or the relative amount of trapped liquid in basic cumulate rocks (Henderson, 1968). In order to facilitate a quantitative interpretation of cristallisation processes of basalt, we present in this paper new crystal/liquid distribution coefficients for phosphorus. Since basaltic magmas enriched in phosphorus are also enriched in iron, a ferrobasaltic composition (Mg# = 0.37) was used as starting material in this experimental study. Phosphorus content of coexisting crystals and liquid was then analyzed with ion probe.

Experimental and analytical methods

In order to avoid that too many variables affect simultaneously phosphorus partition coefficients,
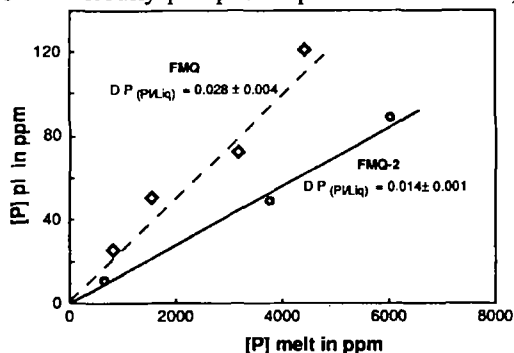

FIG. 1. P distribution between coexisting plagioclase and melt for two values of f_{O_2}

experiments were carried out in such a way that the only two variable parameters were the P_2O_5 concentration and the oxygen fugacity. This was achieved by i) using a single phosphorus-free 8 component ferrobasaltic starting composition to which various quantities of P_2O_5 were added, ii) fixing the temperature (1072°C) and the pressure (1bar), and iii) performing experiments over a range of oxygen fugacities between 2 log units below and 2 log units above the FMQ buffer. For each f_{O_2} studied, four or five P_2O_5-bearing compositions were run at the same time, so that the only variable is the P_2O_5 content of the starting material. All the glasses obtained in the run products at each f_{O_2} are multi-saturated with plagioclase, clinopyroxene, ilmenite, ± magnetite, ±olivine, ± pigeonite. In a previous study on the same experimental data set (Toplis et al., 1994), we have shown that, at fixed temperature, the progressive addition of P_2O_5 causes i) the disappearance of magnetite and olivine under oxidizing and reducing conditions respectively, and ii) the stabilization of pigeonite, leading to large changes in the composition of the coexisting melt, e.g. SiO_2 and FeO. Therefore, this data set, despite having been obtained at fixed temperature, allows us to test unambiguously the compositional dependence of P distribution coefficients. However, it is of interest to notice that, in the whole compositional range studied, plagioclase has a constant composition around An_{51}. In this paper, we report only partitioning data obtained isothermally at FMQ and FMQ-2.

The P contents of the coexisting phases were determined with the CRPG-modified Cameca IMS 3f ion microprobe. Samples were mounted in epoxy, polished and gold coated, then sputtered with a ≈ 1 nA intensity O^- primary beam, focused on a ≈ 5 μm diameter area. Positive secondary ions were analyzed at ≈ 800 mass resolution. The energy slit width was kept at 10 eV, the slit lined up for a nominal accelerating voltage of 4.5 kV and an energy filtering of 80 eV was achieved by decreasing the accelerating voltage applied to the sample. This

energy offset was adjusted every 4 minutes by measuring the ^{30}Si energy distribution. The major elements (Na, Mg, Al, Si, K, Ca and Fe) were measured together with P to control the chemical composition of the analyzed phase and to avoid any contamination problems. Counting times were 2 s on each peak, 6 s on P, with a waiting time of 1 s. Successive measurement cycles were accumulated for 20 minutes on each point. The P concentrations were determined in the glass by electron microprobe for each sample. The P/Si ratios determined by ion microprobe on the other phases were converted in concentrations by using the glass as reference, and assuming the same useful yield ratio for P and Si in the different phases, which seems acceptable with the use of energy filtering.

Results

The partition coefficients, $D_{mineral-melt} = [P]_{mineral}$ / $[P]_{melt}$, determined from the experimental charges are summarized in Table 1. Each partition coefficient corresponds to an average of 3 to 6 analyses performed on different phases in each sample, except those noted in italics that correspond to a single measurement. Our results confirm the general incompatibility of phosphorus in the major basic rock-forming minerals (Koritnig, 1965). In detail, phosphorus mineral-melt partition coefficients decrease in the following order: olivine > clinopyroxene ⩾ plagioclase ≫ ilmenite ⩾ magnetite from 0.093 and 0.076 for olivine and clinopyroxene respectively to 0.0016 for magnetite. Our data point out that $D^{pl-melt}$ is dependent on f_{O_2}, but constant at a fixed f_{O_2} with mean values of 0.0142 ± 0.0012 at FMQ-2 and 0.0282 ± 0.0043 at FMQ (Fig. 1). On the other hand, $D^{cpx-melt}$ is significantly dependent

on the composition both in terms of P_2O_5 and SiO_2 contents (Table 1) and to a lesser extent on the oxygen fugacity. While the data presented for $D^{pl/melt}$ are in fair agreement with those obtained by Anderson and Greenland (1969) between basaltic groundmass and phenocryst mineral separates, a significant discrepancy is observable for $D^{ol/melt}$ (0.019–0.055, their data), $D^{cpx/melt}$ (0.009–0.0017) and $D^{ilm/melt}$ (0.05). Nevertheless, one can note that our lower $D^{cpx/melt}$ values include those obtained by these authors.

Discussion

Given the similarity of the radii of Si^{4+} and P^{5+}, the larger incompatibility of phosphorus in oxide phases (ilm and mt) in comparison to silicate phases (ol, pl and cpx) suggests that the solubility of phosphorus in minerals is linked mainly to replacement of Si by P in SiO_4-tetrahedra. Moreover, it is clear that, for this ferrobasaltic composition, the incompatibility of phosphorus in silicate minerals decreases from olivine to clinopyroxene to plagioclase. This supports the view that the more polymerized a mineral, the less silicon is replaced by phosphorus (Koritnig, 1965), which is most likely to be due to the stronger covalent bond character of P^{5+} compared to Si^{4+}. A similar behaviour is also documented in liquid/liquid partition coefficients where phosphorus is strongly partitioned into the most depolymerized melt. $D^{pl/melt}$ increases with the oxygen fugacity suggesting a strong affinity between P and Fe^{3+} both in the melt and plagioclase. All of this shows the complex solubility of phosphorus in both minerals and melt, and demonstrates that phosphorus can be a powerful tool to decipher both basaltic cristallization processes and the structure of silicate melt.

TABLE 1. Phosphorus contents and partition coefficients in ferrobasalts

Run[*]	f_{O_2}	[P] melt in ppm	Wt% SiO$_2$ melt	D P pl/melt	D P cpx/melt	D P ol/melt	D P ilm/melt	D P mt/melt
	FMQ-2							
Fe115		211 ± 13	51.78	-	0.0643 ± 0.0080			
Fe116		1379 ± 46	51.60	0.0152 ± 0.0037	0.0546 ± 0.0089			
Fe118		7580 ± 46	48.51	0.0128 ± 0.0012	*0.0262*			
Fe 119		9588 ± 168	48.50	-	0.0108 ± 0.0011	*0.0930*		
Fe120		12125 ± 196	47.82	0.0145 ± 0.0025	0.0091 ± 0.0006		0.0023 ± 0.0005	
	FMQ							
Fe131		123 ± 6	56.09	-	*0.0562*		*0.0036*	
Fe132		1674 ± 22	54.61	0.0305 ± 0.0123	0.0761 ± 0.0017			*0.0016*
Fe133		3100 ± 75	52.02	0.0324 ± 0.0062	0.0460 ± 0.0067			0.0022 ± 0.0006
Fe134		6359 ± 121	49.71	0.0227 ± 0.0113	0.0505 ± 0.0100			
Fe135		8877 ± 85	48.75	0.0273 ± 0.0108	0.0229 ± 0.0009			

*See Toplis *et al.*, 1994 for detailed discussions of the experimental conditions