Experimental constraints on the evolution of iron and phosphorus-rich melts: experiments in the system $\text{CaO-MgO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2\text{-H}_2\text{O-CO}_2$

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Carbonatites occur on most continents and are often associated with economic ore deposits. In rare cases, carbonatites are associated with particular Fe and P-rich rocks, the latter of which can also be of economic importance and can form ores for copper, zirconium, or platinum group elements. Here I present some novel experimental constraints in Fe and P-rich carbonate and silicate-rich systems as a starting point to better understand the origin of these rock types. Phase relations in the system $\text{CaO-MgO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ were studied at elevated temperatures (1000–1400 °C) and at high pressures (1 GPa). The liquidus of the systems studied varies between 1300 and 1400 °C. Liquidus phases are, depending on bulk composition, olivine or magnetite. Apatite, pyroxenes and calcite were found to generally crystallize at much lower temperatures. Using experimentally determined mineral and melt compositions, melt compositions were calculated for fractional crystallization of Fe- and P-rich carbonate-rich silicate magma.

Keywords: Carbonatite, Fractionation, Phoscorite, System $\text{CaO-MgO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2\text{-H}_2\text{O-CO}_2$

INTRODUCTION

Carbonatites are magmatic rocks, which occur on most continents. In rare cases, carbonatites may be associated with particular Fe and P-rich silicate and carbonate-rich rocks which consist primarily of magnetite, apatite, forsterite-rich olivine, and calcite (Verwoerd, 1967). These rocks were named Phoscorites after the ‘Phosphate Development Corporation’ and were first described at Phalaborwa, South Africa (Russell et al., 1954). Many phoscorites are of economic importance and are often mined for copper, iron, phosphorus, zirconium, and platinum group elements (Fontana, 2006; Rudashevsky et al., 2004).

Phoscorite deposits are primarily found in alkali complexes on the Kola Peninsula in Russia e.g., (Lee et al., 2006), in the Maymecha-Kotuy Province in Siberia (Kogarko et al., 1997), in northern Finland (Vartiainen, 1980; Lee et al., 2003; Lee et al., 2005), in Southern Africa (Johnson, 1966; Verwoerd, 1967; von Backström and Jacob, 1979; Eriksson, 1984), as well as in Brazil (Issa Filho et al., 1984; Ribeiro et al., 2005; Fontana, 2006).

In the field, phoscorites are almost always associated

with carbonatites which seemed to imply genetic relations between carbonatite and phoscorite (Verwoerd, 1967; Sokolov, 1983; Eriksson, 1984). Genetic models for the origin of phoscorite vary between metasomatic (von Backström and Jacob, 1979), fractional crystallization (von Backström and Jacob, 1979), and liquid immiscibility (Verwoerd, 1967; Lapin and Vartiainen, 1983).

One of the best-studied phoscorite bodies occurs on the Kola Peninsula at Kovdor, Russia. The Kovdor phoscorite ore body is part of a large alkaline ultrabasic intrusion, which was emplaced some 400 Ma ago. The main body of the intrusion consists of turjaite, clinopyroxenites, peridotites, and ijolites. The phoscorite-carbonatite complex forms only a small part of the entire intrusion (Krasnova, 2001; Krasnova et al., 2004). Based on detailed mapping and geochemical analysis, multiple intrusions of phoscorite and carbonatite have been identified (Krasnova and Kopylova, 1988; Krasnova et al., 2004;). The evolution of magmatic phoscorite rocks at Kovdor may be summarized as follows (Krasnova et al., 2004): First intruded phoscorites which were rich in olivine and apatite and contained only small amounts of magnetite. These rocks were followed in succession by magnetite-olivine apatite rocks with only small amounts of calcite. All carbonatite-phoscorites (i.e., >50% calcite) were in-

terpreted to be younger than the main phoscorites and form cross-cutting veins with sharp contacts (Krasnova et al., 2004).

Despite the increasing interest in phoscorite, especially from an economic point of view e.g., (Ribeiro et al., 2005; Rudashevsky et al., 2004), there is no experimental information on the genetic relationships between phoscorites and carbonatites.

In this paper we will not be able to comprehensively unravel the origin of phoscorites, the experiments presented here must be understood as an exploratory study into the phase relations in complex Fe- and P-rich systems. This brings us to the choice of bulk compositions, pressures and temperatures of the experiments. As naturally occurring mineral assemblages of phoscorites vary substantially, it is hard, if not impossible, to precisely estimate bulk composition of naturally occurring phoscorite bodies. Furthermore, it is unclear if phoscorites evolve from carbonatites by fractional crystallisation or if indeed some independent phoscorite parental magma existed (Krasnova et al. 2004).

Matters are further complicated by often very large grain size of naturally occurring phoscorite minerals, i.e. meter-sized apatite crystals and fist sized magnetite single crystals, which further complicates estimation of bulk rock chemistry. However, Krasnova et al. (2004) have developed a rigorous approach to estimate bulk rock chemical composition of Kovdor phoscorites based on careful mapping and bulk rock chemical analysis of a large number of samples.

As a starting point to explore phase relations in Fe- and P-rich silicate-carbonate system, three different bulk compositions in the system CaO-MgO-Fe₂O₃-P₂O₅-SiO₂-H₂O-CO₂ were chosen. It is quite obvious that these three compositions cannot be exhaustive but they are to be seen as a starting point to unravel the magmatic evolution of Fe- and P-rich silicate carbonate magma.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Crystallization experiments were performed at high pressures and high temperatures to simulate fractional crystallization of Fe- and P-rich carbonate-silicate liquids. Three different synthetic bulk compositions (SKHDPH1, SKHDPH2, SKHDPH3) were chosen to investigate phase relations (Table 1). Starting materials consisted of mixtures of oxides (Fe₃O₄, SiO₂), carbonates (CaCO₃), phosphates [Ca₅(PO₄)₃OH] and hydroxides [Mg(OH)₂; see Table 1 for details]. The starting material mixtures were ground under acetone in an agate mortar to produce homogeneous mixtures. Starting materials were placed into

Table 1. Starting materials

	SKHDPH1	SKHDPH2	SKHDPH3
CaO	33.1	12.7	22.3
MgO	3.4	24.4	8.9
Fe ₃ O ₄	29.6	14.0	34.9
P ₂ O ₅	12.5	1.1	6.3
SiO ₂	6.4	28.0	16.6
H ₂ O	2.0	10.9	0.1
CO ₂	13.0	8.9	10.9

Bulk compositions used in the experiments. Note that SKHDPH1 is modelled after the proposed bulk composition of the Kovdor phoscorite intrusion (Krasnova et al. 2004), whereas SKHDPH2 and SKHDPH3 are estimated bulk compositions to cover a wide range of possible phoscorite bulk compositions.

Fe-saturated platinum metal capsules and welded shut using a conventional arc welder. No attempt was undertaken to control redox states during the runs. However, experimental run products only contained magnetite, no other Fe-oxides or even metallic Fe was observed.

All experiments were conducted at 1.0 GPa in a conventional end-loaded piston cylinder apparatus (Prowatke and Klemme, 2006). The pressure assembly consisted of a graphite heater surrounded by a thin layer of Duran® glass (Schott AG, Germany) and a layer of natural talc. This assembly has been pressure calibrated using the fayalite = quartz + ferrosilite (Bohlen et al., 1980) and picrochromite + quartz = enstatite + eskolaite reactions (Klemme and O'Neill, 1997; Klemme and O'Neill, 2000). Experiments were conducted using the piston-in routine: First, a pressure of about 0.25 GPa was applied. Then the sample was heated up to about 550 °C to soften the glass. During the final compression, pressure and temperature were raised simultaneously. Pressure was kept constant (± 0.05 GPa) automatically during the experiments using a screw driven hydraulic system. Temperatures were measured with calibrated W₉₅Re₅-W₇₅Re₂₅ thermocouples inserted axially into the assembly using four-bore high-purity Al₂O₃ tubing. No correction was made for the dependence of thermocouple emf on pressure. The sample was placed in the hotspot of the assembly, and temperature uncertainties were calibrated to be less than 15 °C.

Experiments were conducted at temperatures between 1000 °C and 1400 °C final run temperatures. Initially, however, all experiments were heated to 1400 °C for 30 min and were subsequently cooled to the desired final run temperature at a rate of 1°/min. Details of the experimental run conditions (pressures, temperatures, bulk compositions, run durations) are given in Table 2. The experimental runs were terminated by shutting off electrical power. Typical initial quench rates are in the order of 100 °C/second. Experimental run products were sectioned longitudinally with a miniature diamond saw, and one half

Table 2. Experimental run conditions and experimental results

Run#	T / °C	P/ GPa	d/ h	Start mat	Phases present
#34	1000	1.0	69	SKHDPH1	Cc (13), Spi (44), Apt (36), Cpx (7)
#26	1100	1.0	36	SKHDPH1	Quench (40), Spi (40), Apt (20)
#27	1300	1.0	32	SKHDPH1	Quench (51), Spi (29), Apt (20)
#33	1400	1.0	4.7	SKHDPH1	Quench (84), Spi (16)
#41	1000	1.0	101	SKHDPH2	Spi(29), Cpx(23), Ol(37), Apt(10), Fl
#39	1100	1.0	68	SKHDPH2	Spi(29), Cpx(23), Ol(37), Apt(10), Fl
#40	1200	1.0	44	SKHDPH2	Quench (28), Ol (33), Cpx (20), Spi (19)
#50	1300	1.0	21	SKHDPH2	Quench (81), Ol (19)
#38	1400	1.0	1.2	SKHDPH2	Quench (100)
#82	1000	1.0	72	SKHDPH3	Spi(43), Apt(39), Cc(14), Cpx(4)
#81	1100	1.0	65	SKHDPH3	Spi(43), Apt(39), Cc(14), Cpx(4)
#76	1250	1.0	22	SKHDPH3	Quench(18), Spi(39), Apt(34)
#80	1400	1.0	4.5	SKHDPH3	Quench(76), Spi(24)

Temp, temperature in °C; P, pressure in GPa; d, run duration in hours; Start mat, starting material; Quench, quenched melt; Fl, fluid; Ol, olivine; Spi, magnetite spinel; Apt, apatite; Cc, calcite; Cpx, clinopyroxene.

Phases present: Numbers in brackets refer to modal percent based on mass balance considerations.

Run # refers to the internal run number.

Table 3. Major element compositions of experimental run products

Run No	Phase	CaO	MgO	FeO*	Fe ₂ O ₃ *	SiO ₂	P ₂ O ₅	Total
80	Spi		12.7	16.3	69.0	0.5	0.1	98.6
	Quench	38.8	10.0	14.5		25.4	11.3	100
76	Spi		14.5	20.1	65.0	0.1		99.7
	quench	25.2	14.4	9.5		50.9		100
	Apt	56.8	0.1			0.9	41.1	98.9
40	Ol	0.3	53.0	5.6		41.1		100
	Cpx	26.8	15.9	3.0		54.0	0.1	99.8
	Spi		15.0	18.0	66.0	0.4		99.4
50	Ol		51.1	8.9		40.1	0.1	100.2
	Quench	17.4	20.1	20.1		40.3	2.0	100
33	Spi		2.1	29.9	67.6			99.6
	Quench	53.6	3.5	14.0		10.8	18.1	100
27	Spi		1.3	32.0	65.2			98.5
	Apt	56.1				0.8	40.9	97.8
	Quench	57.3	7.0	7.0		26.5	2.1	100

Representative major element compositions of experimental run products as analysed with electron microprobe.

Quenched liquids were analysed using raster beam scanning techniques.

Phases in other experiments (runs 82, 81, 41, 39, and 34) were too small to be analysed. Quench, quenched melt; Ol, olivine; Apt, apatite; Cpx, clinopyroxene; Spi, spinel (magnetite). Quenched melt analyses were normalized to 100%.

* Note that Fe was measured as total iron and FeO and Fe₂O₃ in spinel analyses was calculated assuming ideal crystal chemistry of spinel

mounted in epoxy and carefully polished with non-hydrous diamond-based polishing pastes. The experimental run products were inspected using optical microscopy and scanning electron microscopy.

Minerals and quench products were analysed for major elements with the electron microprobe (EMP). Polished sections were carbon coated for electron microprobe analysis, using a Cameca SX51 electron microprobe operated using an accelerating voltage of 15 kV and a beam current of 6 nA. To minimize element volatility and a “damage” to quench materials under the electron beam an area of several tens of µm was scanned with a 1 µm beam. Counting times were 10 s on peak and 5 s on background

for all elements. The standards used were corundum (Al), periclase (Mg), magnetite (Fe) wollastonite (Ca, Si), olivine (Fe, Mg, Si) and synthetic apatite (P). The raw data were corrected with the 'PAP' software (Pouchou and Pichoir, 1985). In this context, it should be noted that H₂O and CO₂ cannot be analysed with electron microprobe techniques. This has consequences for the analysis of quenched melts as we can only estimate total H₂O+CO₂ concentration based on totals of microprobe analyses but the ratio H₂O/CO₂ cannot be determined with EMP techniques. Additionally, some experimental run products were powdered and analysed with conventional XRD techniques using a Siemens D500 diffractometer.

Figure 1. Shown are modal percentages of minerals and melts at different temperatures estimated from back-scattered electron images of experimental run products and mass balance calculations. L, melt; Apt, apatite; Mgt, magnetite spinel; Ol, olivine; Cpx, clinopyroxene; Cc, calcite. See text for discussion.

RESULTS AND DISCUSSION

Experimental results

Experimental results are presented in Tables 2 and 3. The solidus for the three selected bulk compositions was found between 900 °C and 1000 °C at 1.0 GPa and the liquidus was found around 1400 °C or slightly above. The

experiments indicate the following crystallization sequence for the selected bulk compositions (Table 2 and Figure 1).

Figure 1 illustrates the crystallization sequence for the three selected bulk compositions. With falling temperatures, SKHDPH1, which is a Fe-rich bulk composition, crystallizes first magnetite, followed by apatite, calcite, and clinopyroxene at lower temperatures. SKHDPH2, which is a bulk composition high in Mg and Si with relatively little P and Ca, first crystallizes olivine, followed by clinopyroxene, magnetite and apatite. SKHDPH2 does not crystallise any significant amounts of calcite even in the lower temperature runs. Large round holes in the experiments at 1000 °C and 1100 °C indicate the presence of a free C-H-O fluid phase (Table 1). SKHDPH3, a bulk composition high in Ca, Fe and Si, first crystallises magnetite upon cooling, followed by apatite, calcite and clinopyroxene at lower temperatures (Fig. 1). In none of our experiments we observe liquid immiscibility.

Using the experimental results, we can examine the observed sequence of crystallization on Fe- and P-rich magmatic rocks. Depending on bulk composition, magnetite or olivine may be a liquidus phase, followed by crystallization of apatite and calcite at lower temperatures (Fig. 2). Our experiments clearly show that calcite (virtually iron-free) crystallises late from strongly fractionated Fe- and P-rich carbonate-silicate melts. It may, at first sight, seem paradoxical to see more or less pure calcite crystallising from melts in very iron-rich bulk compositions but this is due to the fact that most iron is trivalent and has partitioned into early liquidus spinels, whereas all remaining divalent iron partitions readily into olivine or clinopyroxene rather than into carbonates.

Mineral chemistry

Table 3 lists mineral and melt compositions. Note that, due to too very small melt pockets, the quenched melt could not be analysed in experiments at lower temperatures. Mineral compositions generally agree rather well with natural spinel, olivine and apatite compositions (e.g., Krasnova et al. 2004). Olivines are Mg-rich with FeO concentrations of about 5–7 wt%.

There is no obvious effect of temperature on olivine composition. Apatites and magnetite compositions are also not strongly affected by falling temperature or changing bulk composition. Calcite could only be identified using SEM, but ‘clean’ analyses with EMP were not possible as the crystals were smaller than 5 µm. However, semi-quantitative energy dispersive (EDS) scans using a scanning electron microscope (SEM) indicate almost pure calcite with very low Mg and Fe concentrations (<1 wt%).

Figure 2. Back-scattered electron images of selected experimental run products. Scale bars as indicated. (A) Run 33: phases present are spinel (grey crystals) and quenched melt. (B) Run 34: subsolidus: phases present are apatite (dark grey), magnetite (white), clinopyroxene, calcite. (C) Run 27: phases present are spinel (very light grey), apatite (darker grey and acicular crystals), and quenched melt. (D) Run 39: phases present are spinel (white), apatite (grey), olivine (dark grey), clinopyroxene (light grey).

Implications for the origin of phoscorites by fractional crystallization?

The origin of phoscorites remains uncertain. As most phoscorites are associated with carbonatites, fractionation of a carbonatitic parental magma ranges among the most likely hypotheses. The experiments presented here are certainly not sufficient to conclusively argue against liquid immiscibility as mechanism to form phoscorite. However, the experiments may be useful as a starting point to unravel phase relations in a complicated system. The results show clearly that there is no liquid immiscibility in parts of the system $\text{CaO-MgO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2\text{-H}_2\text{O-CO}_2$. This is surprising as phosphorus is known to affect melt structure substantially and liquid immiscibility in phosphorus-rich systems is a well known phenomenon (Rabinovich et al., 1980; Ryerson and Hess, 1980; Mysen, 1998; Suk, 2001) and we can only speculate that this also holds for the parental magmas which crystallized the minerals which make up phoscorites. Clearly, further experi-

ments in more carbonate-rich systems are needed to further evaluate the behaviour of iron and phosphorus in fractionating carbonatitic systems.

With the experiments one will not be able to conclusively elucidate the origin of phoscorite. However, the experiments show that fractional crystallization of Fe- and P-rich magma will result in strikingly different melt compositions, mainly driven by the partitioning behaviour of the chemical elements during fractionation. To illustrate this better, melt compositions were calculated from experimentally derived mineral and melt compositions and estimated modal proportions of minerals and melts at different temperatures using mass balance considerations (Fig. 3). Consider, for example, a fractionating melt of SKHDPH1 composition. Upon cooling, SKHDPH1 melts will crystallize magnetite, closely followed by apatite. Crystallisation of magnetite (and apatite) from the system depletes the melt in Fe, P, and initially also Ca. Consequently, melts will be substantially enriched in silica and CO_2 . Melts at temperatures below about 1250 °C contain

Figure 3. Calculated melt compositions assuming perfect fractional crystallization of phoscorite liquids using mineral and melt compositions (Table 3) and estimated modal abundances of minerals and melt at different temperatures (Figure 1).

more than 30% carbonate component and are very similar to carbonatite melts. This leads to crystallization of calcite and clinopyroxene just before the solidus is reached at temperatures between 1000 °C and 1100 °C.

Matters are slightly different in SKHDPH2 bulk compositions. Here the initial liquids at 1400 °C, which is above the liquidus of this system, are characterized by

high Mg, Si, and water but relatively low contents of Ca and Fe. Isobaric cooling of melts in this system results in crystallization of olivine, followed by clinopyroxene, magnetite and apatite with decreasing temperatures. The solidus for this system lies between 1100 °C and 1200 °C. As forsterite olivine crystallizes between 1400 °C and 1300 °C, melts are initially depleted in Mg and Si and enriched in Ca, P and volatiles. Upon further cooling in a fractionating melt, clinopyroxene and magnetite crystallize at temperatures between 1300 °C and 1200 °C. This leads to a dramatically different melt composition at 1200 °C, with low silica, Mg and very high H₂O and CO₂ concentrations. Melts between 1200 °C and 1100 °C are in essence carbonatite melts with normative carbonate contents of more than 50%. Crystallization of apatite at temperatures below 1200 °C will further deplete the melt in phosphorus and water. However, no carbonates were found in the experiments which were run at subsolidus temperatures at 1100 °C. This does not necessarily exclude the presence of tiny carbonate crystals, which cannot be detected in a complex, extremely fine-grained sample. However, the presence of large holes in the capsules seems to suggest the presence of a fluid phase in the experiments.

Phase relations in SKHDPH3 compositions are slightly different again. At temperatures between 1300 °C and 1400 °C, magnetite and apatite crystallise. Fractionation of apatite and magnetite depletes the remaining liquid in Fe, P, and Ca. Consequently, melts under these conditions will be enriched in silica, CO₂, and Mg. The enrichment of CO₂ in these silicate melts leads to the crystallization of calcite and clinopyroxene before the solidus of this system is approached at temperatures between 1100 °C and 1200 °C.

It is interesting to note that the solidus in the systems studied here increases systematically as a function of bulk CO₂ content between from 1050 °C at 8.9% CO₂ to 1175 °C at 13% CO₂, in much the same fashion as described by Dasgupta and Hirschmann (2007). The system here, however, is ever so more complicated as our experiments contain much more Na, K, H₂O, and P than the system studied by Dasgupta and Hirschmann (2007) so that it is very difficult to disentangle the different effects of cations on the solidus.

Liquid immiscibility between silicate and carbonate melts

Previous experimental information on liquid immiscibility in magmatic systems is limited. Efforts have focussed on systems with immiscibility between carbonate and silicate liquids (Hamilton et al., 1979; Wendlandt and Harrison,

1979; Kjarsgaard and Hamilton, 1988; Kjarsgaard and Peterson, 1991; Lee and Wyllie, 1996; Lee and Wyllie, 1997; Suk, 2001; Suk, 2003;). However, there is little data in Fe- and P-rich chemical compositions. Moreover, the role of phosphorus on the physical properties of iron-rich silicate liquids and on the silicate-carbonate immiscibility region is uncertain and more data is clearly needed (Suk, 2001). It is well known that phosphorus affects physical properties of silicate melts substantially (Dingwell et al., 1993; Toplis et al., 1994; Toplis and Dingwell, 1996; Mysen, 1998; Mysen and Cody, 2001). Dingwell et al. (1993), for example, report that addition of phosphorus to silicate melts decreases viscosity and the degree of polymerisation of silicate melts. On the other hand, addition of phosphorus to carbonate melts does not seem to affect the immiscibility gap between silicate and carbonate melts (Suk, 2001). However, there is no experimental data on the effect of Fe on phase relations in phosphate-rich systems and more experimental data in simple systems (e.g., CaO-Na₂O-FeO-Fe₂O₃-SiO₂-P₂O₅-CO₂ or similar simple systems) are needed to further our understanding of the possible role of liquid immiscibility between silicate liquids and carbonate liquids.

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