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Ilya V. Veksler · Hans Keppler

Partitioning of Mg, Ca, and Na between carbonatite melt and hydrous fluid at 0.1–0.2 GPa

Abstract Experimental studies of the element distribution between carbonatite melts and hydrous fluids are hampered by the fact that neither the fluid nor the melt can be isochemically quenched in conventional high-pressure vessels. In order to overcome this problem, we used a double-capsule technique to separate immiscible fluid and melt phases during and after the runs. The inner platinum capsules were charged with carbonate mixtures ($CaCO_3$, $MgCO_3$ and Na_2CO_3) and placed inside the outer capsules charged with distilled water and diamond powder. The latter was used as an inert trap for solids precipitating from the fluid on quenching. Carbonate melt and hydrous fluid equilibrated through a small hole left in the upper end of the inner capsule. The runs were performed in rapid-quench cold-seal pressure vessels at 0.1–0.2 GPa and 700–900 °C in the two-phase (fluid + melt) stability region. Both quenched melt and quenched fluid were dissolved in dilute HCl and analysed by inductively coupled plasma atomic emission spectroscopy. The results show that under all conditions investigated, fluid/melt partition coefficients for Ca and Mg are similar and several times smaller than those for Na. At 0.1 GPa and a water/carbonatite ratio of 1 (by weight), the partition coefficients are $D_{Na} = 0.35 \pm 0.02$, $D_{Ca} = 0.09 \pm 0.02$, and $D_{Mg} = 0.13 \pm 0.01$. Between 700 and 900 °C, the effect of temperature on partitioning is negligible. However, D_{Na} increases significantly with decreasing water/carbonatite ratio in the system. Our data show that the release of a hydrous fluid enriched in sodium and simultaneous crystallisation of calcite can transform an alkaline, vapour-saturated carbonatite melt into a body of pure calcite surrounded by zones of sodium metasomatism. Thus, it is quite possible that carbonate magmas with substantial amounts of alkalies were common parental liquids of plutonic carbonatites.

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Introduction

The chemical composition of carbonatite magmas is the subject of much controversy since several decades. There is still no general consensus whether the parental melts are essentially calcitic (similar to the composition of most plutonic carbonatites and some effusive flows), dolomitic, like magnesiocarbonatite intrusions of Rufunsa valley, Zambia (Bailey 1990), or sodium rich, similar to the natrocarbonatite lavas of Oldoinyo Lengai, Tanzania (Dawson 1989). The main arguments *pro et contra* each of the three possibilities were summarised in a number of comprehensive reviews (e.g. Gittins 1989; Bailey 1993; Lee and Wyllie 1994). At the present time none of the hypotheses can be ruled out and there are good reasons to believe that carbonatite magmas are chemically and genetically diverse.

In case of carbonatites the reconstruction of parental liquid from bulk analyses of solidified rocks is extremely difficult. Carbonatite melts, composed mainly of alkali and alkaline earth carbonates, are the most volatile-rich terrestrial magmas with exceptionally low viscosity, down to 1–5 Pa s, as measured for the Oldoinyo Lengai natrocarbonatite lava by Dawson et al. (1990). These features result in high crystallisation and reaction rates and make fractional crystallisation, metasomatism and wall-rock reactions very effective in changing the composition of carbonatite liquid and its crystallisation products.

Water is believed to be an important component of carbonatite liquids. It plays a crucial role in many currently accepted models of carbonatite magmatism since it dramatically decreases liquidus temperatures down to the values consistent with geological observations (Wyllie and Tuttle 1960; Wyllie 1989). In models that

regard calcitic and dolomitic rocks as cumulates of sodium-rich parental melts, aqueous fluids often account for removal of excess alkalies and fenitization of country rocks (McKie 1966). These models are likely to be valid for complex intrusions where carbonatites are found in association with and genetically linked to a diverse group of ultramafic and alkaline silicate rocks. Metasomatic alteration of country rocks around carbonatite bodies (von Eckermann 1966; McKie 1966) and studies of fluid and melt inclusions trapped in rock-forming minerals (Rankin 1977; Rankin and LeBas 1974; Nielsen et al. 1997; Veksler et al. 1998) support the view that aqueous fluids are effective agents for the transport of highly soluble components such as alkali carbonates.

In this paper we examine the effects of fluid separation at low, crustal pressures and present experimental data on element partitioning between melt and hydrous fluid in the $CaO-MgO-Na_2O-CO_2-H_2O$ synthetic system. The system represents the main cations and major volatile components of carbonatite magmas. Concentrations of FeO, K_2O, F, Cl and SO_2 may be significant in some natural compositions, but in order to avoid additional complications we decided to minimise the number of components and limit the study to the five-component system. When choosing starting compositions and water contents of experimental charges we did not try to reproduce any particular natural liquid, but were mostly concerned with limitations of experimental techniques and analytical instruments. Our main objective was to obtain good quality, quantitative data on the element partitioning.

Studies in carbonatite-fluid systems are hampered by the fact that neither phase can be quenched isochemically in conventional high-pressure vessels. The re-equilibration rates during cooling are very high and compositions of quench products often do not represent those of the phases at high pressures and temperatures. In this paper we present an attempt to overcome the quenching problems using double capsules and rapid-quench cold-seal pressure vessels. This technique allowed effective separation of fluid and melt phases during and after the runs and resulted in quantitative estimates of the fluid-melt partition coefficients.

Previous work

Experimental data on the fluid-melt phase equilibria in carbonatite systems are scarce. Wyllie and Tuttle (1960) inferred a wide miscibility gap between carbonatite liquid and coexisting fluid in the system $CaO-CO_2-H_2O$. The compositions were not determined, but it was assumed that the solubility of CaO in the H_2O-CO_2 fluid was low. Wyllie and Boettcher (1969) extended this work to higher pressures. Distinct liquid and fluid phases were shown to coexist up to 4 GPa, but their mutual solubility apparently increased with pressure. Koster van Groos (1990) studied the $Na_2CO_3-H_2O$ system by high-pressure differential thermal analysis. The second critical end-

point on the Na_2CO_3 + melt + fluid curve was located at 500 ± 10 °C and 0.15 GPa with an estimated H_2O content of 88 ± 2 wt%. At pressures above the critical point, solid Na_2CO_3 presumably coexists with a supercritical fluid of variable composition. Liquidus phase equilibria revealed the ternary ($Na_2O-CO_2-H_2O$) nature of the system. The results imply a broad vapour-melt miscibility gap below the critical point. Finally, Dernov-Pegarov and Malinin (1976) studied the solubility of calcite in K_2CO_3 and K_2CO_3 + Na_2CO_3 solutions with molality from 1 to 15 at 400 and 500 °C. Maximum solubilities were in the order of few wt%
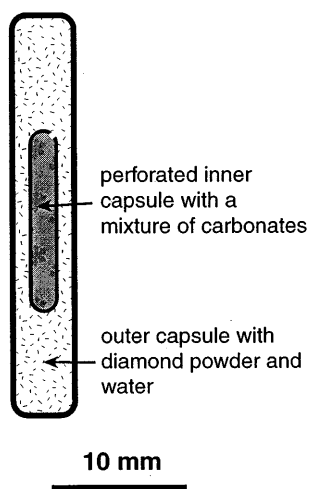
Experimental and analytical methods

Starting materials were mechanical mixtures of reagent grade carbonates ($CaCO_3$, $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5 H_2O$ and Na_2CO_3). The mixtures were dehydrated at 150°C and subsequently kept in a desiccator. Between 40 and 110 mg of the mixtures (Table 1) were sealed in platinum capsules with a diameter of 3.5 mm, 25 mm length and 0.2 mm wall thickness. The charged capsules were then annealed in conventional cold seal bombs at 700–900 °C and 0.1 GPa. The purpose of this step was to convert the charge into a massive, solid piece of carbonate without any pore space. After this heat treatment, a small pinhole was drilled into the upper end of the capsules. They were then inserted into larger platinum capsules (5 mm diameter, 3.5 mm length, 0.2 mm wall thickness) together with 45 to 170 mg of distilled water. The remaining space of these outer capsules was filled with diamond powder of 40–60 microns grain size. After that, the outer capsule was sealed. Figure 1 illustrates the resulting double capsule.

The double-capsule runs were carried out in rapid-quench cold-seal pressure vessels at 0.1–0.2 GPa and 700–900 °C in two-phase (fluid + melt) stability region (Table 1). Data on phase equilibria in the systems $Na_2CO_3-H_2O$ (Koster van Groos 1990), Na_2CO_3-$CaCO_3$ (Cooper et al. 1975) and $CaO-MgO-CO_2-H_2O$ (Wyllie 1989) suggest that at these temperatures the reactant mixtures were well above the liquidus. During the runs the double capsule was kept in a vertical position with the pinhole of the inner capsule at the top. In this geometry the carbonatite melt could not mechanically flow out of the inner capsule, but chemical exchange was possible through the pinhole. A similar experimental design was originally described by Ryabchikov et al. (1989). It proved to be essential in these experiments that the charge of the inner capsules was already a massive block of carbonate at the start of a double-capsule experiment. If loose powders were used, they tended to be squeezed out of the inner capsule during the initial compression and heating of the capsule. We carefully controlled the weight of the double-capsule assemblages at every step prior to and after the runs. If unexpected weight losses or gains suggested leakage the runs were discarded.

After run durations of a few days, the double capsules were isobarically quenched to room temperature within 1–2 seconds. The recovered capsules were cooled in liquid nitrogen and perforated with a needle. The cooling prevented explosive release of carbon dioxide and uncontrolled losses of solution from the capsules. Total amounts of gaseous CO_2 released upon opening of the capsules were in the order of a few mg only. The perforated assemblages were dried in an oven for several hours at 150 °C until all water had evaporated. The capsules were then carefully opened and material was separately recovered from the outer and inner capsules. Dried material recovered from outer capsules was a loose diamond powder with small amounts of tiny carbonate particles attached to the surface of diamond grains (Fig. 2). These carbonates were interpreted to be a dry residue from an aqueous fluid. The inner capsules contained a solid fine-grained aggregate of carbonate crystals apparently quenched from a melt. Fragments of the material from the inner capsules were examined under a micro-

Table 1 Run conditions

Run #	P, GPa	T, °C	Duration, h	Composition of carbonate reactant mixture, wt%			Initial charge, mg		H_2O-carbonate ratio
				$(MgCO_3)_4$ *MgO	$CaCO_3$	Na_2CO_3	Carbonates	H_2O	
1	0.1	700	120	20	40	40	65.7	45.34	0.690
2	0.1	800	94	20	40	40	68.98	45.10	0.654
6	0.1	700	115	20	40	40	50.31	60.05	1.19
9	0.1	750	44	20	40	40	70.3	63.10	0.897
10	0.1	850	44	20	40	40	66.59	61.25	0.871
12	0.1	800	138	30	20	50	59.08	84.27	1.43
14	0.1	900	120	20	40	40	67.29	79.04	1.17
15	0.2	850	93	20	40	40	72.43	141.0	1.95
17	0.1	850	67	–	50	50	102.8	61.05	0.594
18	0.1	850	67	30	20	50	58.81	80.52	1.37
21	0.2	850	96	50	–	50	39.72	166.3	4.19
22	0.2	850	96	30	20	50	67.94	136.8	2.01
25	0.1	900	46	–	50	50	109.2	79.47	0.728
26	0.1	900	46	50	–	50	52.2	80.44	1.54
29	0.2	850	66	30	20	50	76.75	159.4	2.08
33	0.1	900	45	30	20	50	60.57	80.41	1.33

perforated inner capsule with a mixture of carbonates

outer capsule with diamond powder and water

10 mm

Fig. 1 Schematic diagram of the double-capsule assemblage

scope in immersion oil and revealed no signs of sub-liquidus crystallisation and crystal setting. Run products from inner and outer capsules were separately dissolved in dilute HCl. The solutions were analysed by ICP-AES (inductively coupled plasma atomic emission spectroscopy).

Experimental results

Composition of run products

The ICP-AES chemical analyses of the material extracted from inner and outer capsules are presented in Table 2. Anhydrous compositions are listed as equivalent carbonates. All the successful runs revealed two distinct compositions in the inner and outer capsules which implied that conjugate fluid and melt coexisted at the P-T conditions of our runs. Aside from some minor Ca/Mg variations, the main difference between melt and fluid is in the Na contents. This is illustrated in Fig. 3 by

Fig. 2 Run products from an outer capsule: diamond powder (grain size 40–60 microns) and carbonate particles attached to the surface of diamond grains

projections of fluid-melt tie-lines in the Na_2CO_3-$CaCO_3$-$MgCO_3$ ternary. The majority of tie-lines are directed towards the Na_2CO_3 corner. The compositions of

Table 2 Compositions of dried run products from outer and inner capsules (ICP-AES data in wt% of carbonates) and fluid-melt partition coefficients (D, by weight)

Run #	P, GPa	T, °C	Dry fluid residue (outer capsules)				Quenched and dehydrated melt (inner capsules)				D fluid/melt		
			Composition, wt%			Weight fraction[a]	Composition, wt%			Weight fraction[a]	Mg	Ca	Na
			$MgCO_3$	$CaCO_3$	Na_2CO_3		$MgCO_3$	$CaCO_3$	Na_2CO_3				
1	0.1	700	13.29	24.79	61.92	0.259	24.56	44.29	31.15	0.741	0.144	0.149	0.530
2	0.1	800	7.60	10.88	81.52	0.211	24.57	47.46	27.97	0.789	0.075	0.055	0.705
6	0.1	700	16.26	20.76	62.98	0.251	22.17	46.23	31.60	0.749	0.121	0.074	0.329
9	0.1	750	18.39	22.96	58.65	0.224	23.54	43.25	33.21	0.776	0.151	0.102	0.340
10	0.1	850	15.20	24.20	60.60	0.227	23.28	43.73	32.99	0.773	0.125	0.106	0.351
12	0.1	800	31.16	11.57	57.27	0.345	32.35	23.77	43.87	0.655	0.175	0.089	0.238
14	0.1	900	17.45	19.61	62.94	0.277	23.21	46.75	30.04	0.723	0.136	0.076	0.379
15	0.2	850	13.96	17.71	68.33	0.030	22.07	39.74	38.20	0.970	0.009	0.006	0.025
17	0.1	850	–	11.34	88.66	0.099	–	54.27	45.73	0.901	–	0.031	0.288
18	0.1	850	18.27	9.91	71.82	0.307	39.34	22.58	38.08	0.693	0.080	0.076	0.325
21	0.2	850	27.78	–	72.22	0.184	62.14	–	37.86	0.816	0.017	–	0.073
22	0.2	850	9.42	5.41	85.17	0.111	35.90	20.17	43.93	0.889	0.013	0.013	0.095
25	0.1	900	–	36.14	63.86	0.068	–	51.07	48.99	0.932	–	0.062	0.113
26	0.1	900	27.98	–	72.02	0.082	52.19	–	47.81	0.918	0.026	–	0.073
29	0.2	850	31.34	14.15	54.52	0.249	32.58	20.79	46.63	0.751	0.096	0.068	0.116
33	0.1	900	20.00	10.54	69.46	0.225	34.89	22.69	42.41	0.725	0.079	0.064	0.225

[a] Weight fractions of initial carbonate charge calculated by means of mass-balance equations (see text for the details)

starting carbonate mixtures are also plotted and provide a check for the mass balance between measured fluid and melt compositions. It should be noted that despite the fluid being strongly enriched in Na, it also contains appreciable amounts of Mg and Ca.

Partition coefficients

The total amount of solids extracted from the outer capsules constituted a small fraction of the initial mass of carbonate. The weight fractions of total carbonate dissolved in the fluid and remaining in the melt were calculated from mass balance considerations based on the chemical analyses of the anhydrous residues given in Table 2. For each component i, the following mass balance equation has to be fulfilled:
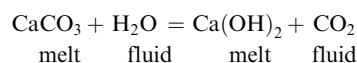
$$x_i^{fluid} c_i^{fluid} + (1 - x_i^{fluid}) c_i^{melt} = c_i^{bulk}$$

with x_i^{fluid} – fraction of the total amount of component i originally loaded into the capsule that dissolved in the fluid, $c_i^{fluid}, c_i^{melt}, c_i^{bulk}$ – concentration of i in the anhydrous fluid residue, the anhydrous melt, and the bulk carbonate mixture, respectively.

By solving such equations for all the components, the weight fraction of total solute present in the fluid was calculated. The data in Table 2 indicate that usually between 10 and 25 wt% of the carbonates originally loaded into the double capsule entered the fluid. From these data, the fluid/melt partition coefficients of Na, Ca, and Mg were calculated (Table 2). In these calculations, it was assumed that the water solubility in the carbonate melt was in the order of 10 wt%, in accordance with our own measurements of water solubility at 0.1 GPa (publication in preparation).

Figure 4 shows fluid/melt partition coefficients of Na, Mg, and Ca at 0.1 GPa and a bulk ratio of water/carbonate of 1. Between 700 and 900 °C, the temperature dependence of partitioning appears to be negligible. The slight increase seen for Na may very well be within analytical error. Average partition coefficients are $D_{Na} = 0.35 \pm 0.02$, $D_{Ca} = 0.09 \pm 0.02$, and $D_{Mg} = 0.13 \pm 0.01$. A plot of partition coefficients versus the bulk water/carbonate ratio at 0.1 GPa and 700–900 °C is given in Fig. 5. While D_{Ca} and D_{Mg} are almost constant, D_{Na} clearly decreases with increasing water/carbonate ratio.

The dependence of partition coefficients on the bulk water/carbonate ratio can easily be understood by considering the following equilibrium:

$$CaCO_3 + H_2O = Ca(OH)_2 + CO_2$$
$$\text{melt} \quad \text{fluid} \quad \text{melt} \quad \text{fluid}$$

with the equilibrium constant

$$K = (f_{CO_2}/f_{H_2O})_{fluid}/(a_{Ca(OH)_2}/a_{CaCO_3})_{melt}$$

Similar equilibria can be written for the Mg and Na components in the system. These equilibria imply that H_2O does not only physically dissolve in the melt, but it partially reacts with the carbonates to form hydroxides. This is in agreement with the small, but measurable amount of CO_2 released upon piercing the capsules after experiments. Obviously, a higher bulk concentration of H_2O in the system will shift these equilibria to the right hand side and therefore change the bulk composition of the melt. Accordingly, it is not surprising that some partition coefficients depend on the water/carbonate ratio in the system.

The experiments at 0.1 and 0.2 GPa in the binary carbonate systems Na_2CO_3-$CaCO_3$ and Na_2CO_3-

★ reactant mixtures
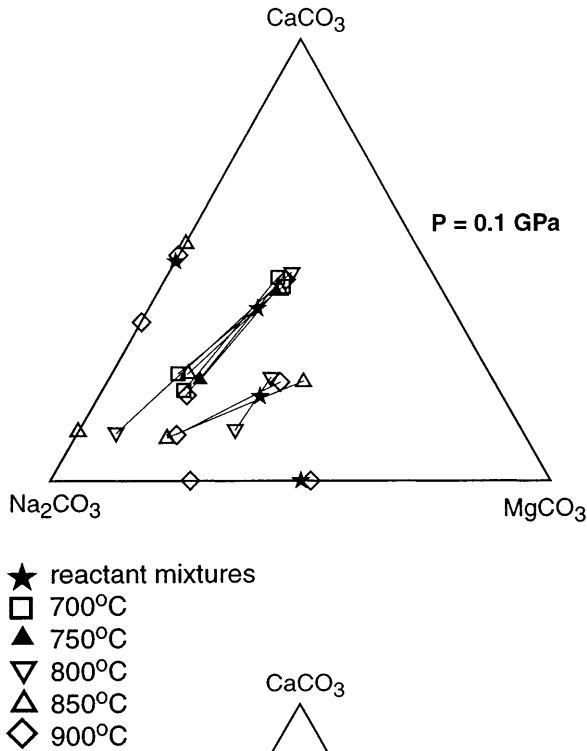□ 700°C
▲ 750°C
▽ 800°C
△ 850°C
◇ 900°C

Fig 3 Compositions of reactant mixtures and run products projected onto the $CaCO_3$-Na_2CO_3-$MgCO_3$ ternary (wt%). Conjugate melts and anhydrous fluid residues from inner and outer capsules are connected by *tie-lines*. Fluid compositions are always enriched in Na_2CO_3

$MgCO_3$ give results that are generally similar to those already discussed. As one can see from Fig. 3, the fluid is always enriched in Na relative to Ca and Mg. Because of the limited data available, however, we cannot yet fully quantify the effect of pressure and Na:Ca:Mg ratio on partition coefficients.

Discussion

Evidence for the fluid transport around carbonatite bodies

In view of the difficulty to preserve carbonatite fluids at well-controlled experimental conditions it is no surprise
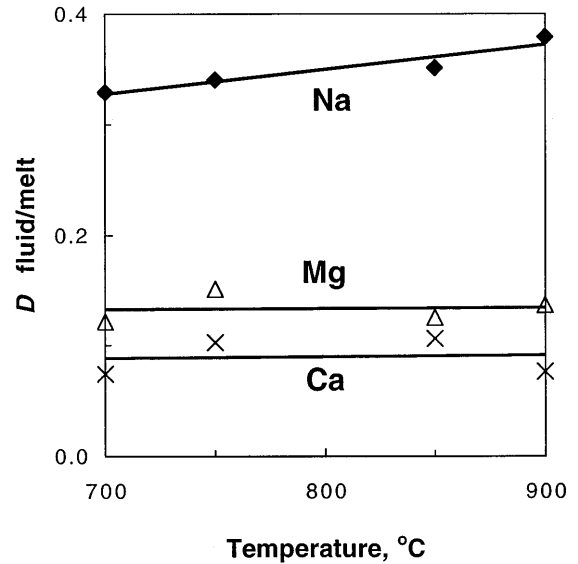

Fig. 4 Temperature dependence of fluid/melt partition coefficients of Na, Ca, and Mg at 0.1 GPa and a bulk water/carbonate ratio of 1 ± 0.2. *Lines* are linear regression fits
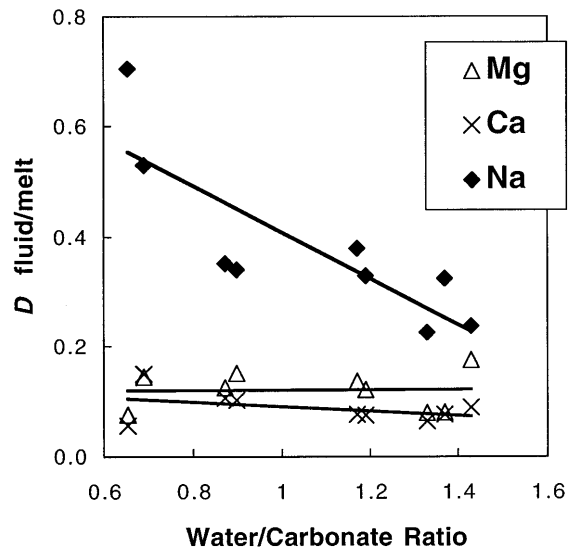

Fig. 5 Effect of the bulk water/carbonate ratio of the fluid/melt partitioning of Na, Ca, and Mg at 0.1 GPa and 700–900 °C. *Lines* are linear regression fits

that the search for their traces in natural systems is even more difficult. In the field, important evidence is provided by extensive metasomatic alteration of country rocks around many carbonatite intrusions (McKie 1966). Both mineralogy and bulk rock chemistry of the metasomatic zones suggest a significant influx of alkalies and their redeposition by fluid-rock reactions.

In a study of Alnö alkaline and carbonatite complex in Sweden von Eckermann (1948) proposed to extend the meaning of fenite to include all products of contact metasomatism induced by alkaline and carbonatite intrusions regardless of original country rock type. Since

that time numerous fenites have been studied and the examples include fenitization of a broad spectrum of mafic (Verwoerd 1966; Morbidelli et al. 1986) to felsic (von Eckermann 1966; McKie 1966) igneous rocks. Although the course of fenitization differs in detail at different localities, the general pattern is an enrichment in alkalies, Ca, ferric iron, H_2O and CO_2 accompanied with an extensive removal of SiO_2. Elementary gains and losses are indicated through the zones of progressive fenitization where components of fenitizing fluids are fixed in a number of characteristic mineral assemblages (e.g. McKie 1966; Morbidelli et al. 1986). Typical fenite minerals include alkali-rich and silica-undersaturated alumosilicates (e.g orthoclase, albite, nepheline, and cancrinite) aegirine, hydrous silicates (amphiboles and phlogopite) and carbonates (calcite). The mineralogy and bulk rock chemistry suggest that fenitization is caused by fluids rich in alkalies, H_2O and CO_2. Another important field observation, first made by von Eckermann (1948, 1966) at Alnö and then confirmed at other localities (Dawson 1964; Morbidelli et al. 1986) was that carbonatites rather than associated ultra-alkaline ijolitic silicate rocks were the source of the fenitizing fluids.

On a microscopic level traces of fluid separation from carbonatite melts are represented by fluid inclusions especially abundant in apatite from different carbonatite localities worldwide (e.g. Rankin 1977; Rankin and LeBas 1974; Samson et al. 1995). The inclusions provide evidence for high-temperature, alkali-rich CO_2-H_2O fluids which are related to carbonatites and contain also significant amounts of Cl and SO_2. It appears that cations in the inclusions are dominated by Na with subsidiary K and low concentrations of Mg, Fe and Ca (Samson et al. 1995).

Fluid separation and fluid transport of water-soluble components may have important consequences for carbonatite evolution. Not only country rocks, but common carbonatites such as sövite appear to be affected by fluid activity.

Sövite and parental melts of plutonic carbonatites

Sövite – a monomineralic calcite rock – is the most common type of plutonic carbonatite. The genesis of sövite and its relationship to parental carbonatite melts is a subject of long-standing controversy. Models for generation of carbonatite melts essentially consider two options (e.g. Gittins 1989): (1) that carbonatites are products of a primary carbonatite magma generated by partial melting of a carbonated mantle peridotite; or (2) that the melts are secondary and produced by differentiation of a mantle-derived silicate magma. In neither case is a pure calcitic liquid likely to be parental and significant chemical fractionation is required for sövite formation.

Compositions of primary carbonatite liquids are constrained by experimental data on near-solidus melts in equilibrium with CO_2 and H_2O bearing peridotites at mantle pressures (e.g. Wallace and Green 1988; Thibault et al. 1992; Dalton and Wood 1993), by compositions of carbonatite bodies that show no connection to alkaline silicate magmatism (Bailey 1990; Harmer and Gittins 1998) and by studies of mantle xenoliths (Yaxley et al. 1998). At depth ($P > 2.5$ GPa) the melts appear to be dolomitic (Bailey 1993; Gittins 1989; Wyllie 1989). On ascent they evolve by wall-rock reaction to higher Ca/Mg values (Dalton and Wood 1993), but the content of $CaCO_3$ component does not exceed a maximum of ~85 wt% (Lee and Wyllie 1994). Other major components of the liquid (apart from $CaCO_3$ and $MgCO_3$) are: SiO_2, FeO, Na_2O, K_2O and H_2O. The content of SiO_2 strongly depends on temperature and rapidly increases within the first percent of partial melting from 5 to > 25 wt% SiO_2 (Dalton and Presnall 1998). The concentrations of alkalies and water in liquids produced in the experiments depend upon a choice of the source peridotite composition and can be high in equilibrium with fertile, amphibole- and phlogopite-bearing mineral assemblages, e.g. 5.51 wt% Na_2O and 2.03 wt% H_2O in experiments by Wallace and Green (1988). Water and alkalies are effective fluxing components. At shallow depths they can be responsible for decreasing liquidus and solidus of the primary carbonatite and eventually they can be lost by fluid separation and metasomatism. For example, intense K metasomatism caused by primary carbonatite magmas is indicated by abundant phlogopite and feldspar in pyroclastics around bodies of primary dolomitic and calcitic carbonatites (Bailey 1990).

The role of hydrous fluids appears to be even more important when sövite is generated from a secondary carbonatite melt in association with alkaline silicate rocks. Fractional crystallisation and silicate-carbonate liquid immiscibility are two plausible mechanisms for the evolution of secondary carbonatite (Kjarsgaard and Hamilton 1989; Wyllie 1989). However, without fluid separation these two processes alone can hardly account for the formation of monomineralic sövite. Experimental constraints on mineral-liquid and liquid-liquid element partitioning (e.g. Kjarsgaard and Hamilton 1989; Lee and Wyllie 1994) suggest that secondary carbonatite liquids in equilibrium with alkaline mineral assemblages should have alkali contents well above those observed in sövite. For example, Lee and Wyllie (1998) conclude from the results of experimental studies that in many magmatic systems compositions of the least evolved calcite-precipitating liquids tend to cluster near the composition range 70–80 wt% $CaCO_3$, 10–20 wt% Na_2CO_3 and 5–10 wt% silicates. Alkali-rich secondary carbonatite liquids are strongly supported by abundant Na-K-Ca and Na-Mg carbonate daughter minerals in crystallised melt inclusions from the Gardiner and Kovdor complexes (Nielsen et al. 1997; Veksler et al. 1998). Alkalies, water and other fluxing components concentrate in residual portions of carbonatite and cannot be removed either by fractional

crystallisation, or liquid immiscibility. Low-pressure separation of magmatic hydrous fluids and/or subsolidus hydrothermal leaching may account for the loss of alkalies.

Our data show that a hydrous fluid in equilibrium with a carbonatite melt is indeed enriched in Na relative to Mg and Ca. The enrichment factors (fractionation of Na from Ca and Mg by a factor of 3–5), however, are not sufficient to explain the conversion of an alkali-rich carbonatite melt into a body of sövite by the action of fluid/melt interaction alone. However, this situation changes, if fluid saturation is reached in the melt simultaneously with the precipitation of calcite. Massive fractionation of calcite could strongly enrich the residual melt with sodium. If sodium is then at the same time preferentially enriched in the evolving fluid, it is indeed conceivable that at the end of this process virtually all sodium has been removed by the fluid. In this context, it is interesting to note that according to Fig. 5, the fluid/melt partition coefficient of sodium is particularly high if the ratio of fluid/melt is low, which corresponds to the point when water saturation is reached in the melt. The data in Fig. 5 suggest that at a very low water/carbonate ratio (about 0.1–0.2) D_{Na} may even reach unity. This is perfectly consistent with the observation of supercritical behaviour in the Na_2CO_3-H_2O system by Koster van Groos (1990) above 0.15 GPa.

Thus, the fractionation of an immiscible fluid enriched in alkali carbonates accompanied by calcite crystallisation may eventually transform an alkaline, vapour-saturated carbonatite melt into a body of monomineralic calcitic carbonatite surrounded by zones of fenitization. Water-soluble alkali carbonates may further be removed by low-temperature post-magmatic circulation of meteoric waters. It is quite possible (as evidenced by the study of melt inclusions by Nielsen et al., 1997, and Veksler et al., 1998) that carbonatite magmas with substantial amounts of alkalies are not restricted to the unique natrocarbonatite lavas of Oldoinyo Lengai, but may also include common, calcite-precipitating parental liquids of many plutonic carbonatites.

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