Role of CO_2 on differentiation of ultramafic alkaline series: liquid immiscibility in carbonate-bearing phonolitic dykes (Polar Siberia)

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Abstract

The Maimecha-Kotui province in the North of Siberian platform is the largest province of ultramafic alkaline rocks in the world. The province comprises thirty-seven central-type complexes together with numerous dykes. The majority of dykes are radially disposed around the ultramafic alkaline massifs. Data are presented for dykes of the Dolbykha carbonatite complex, which comprises olivine and melilite nephelinites; nosean, calcite and cancrinite phonolites; calcite trachytes and calcite carbonatites.

Some peralkaline phonolitic dykes contain carbonate-bearing globules with sizes of 1–2 mm to 17–20 mm. Globules consist of polycrystalline calcitic aggregates together with albite, phlogopite, apatite, Sr-lueshite, zircon, ancylite, ilmenite and strontianite. The phonolites have phenocrysts of albite, phlogopite and ilmenite. Albite, phlogopite, calcite and nepheline are also present in the groundmass. Analysis of these materials in the light of experimental data on the liquid immiscibility in carbonate–silicate systems suggests that separation of carbonatite from phonolitic melts took place due to immiscibility in the liquid state. I propose that carbonate melts contained originally significantly higher alkali contents which were subsequently lost into the fluid phase due to the incongruent dissolution of calcium–sodium carbonates in aqueous fluid at low temperatures. The discovery of nyerereite in the carbonatite of Polar Siberia confirms this conclusion. I infer that one of the mechanisms for the genesis of carbonatite melt in Polar Siberia was liquid immiscibility in strongly differentiated phonolitic magmas.

The generation of the carbonatites was probably controlled by the depth (and P_{CO_2}) of the crustal magma chamber where differentiation took place and probably also by the alkalinity of melts, and the rapidity of magma ascent to the surface.

KEYWORDS: liquid immiscibility, carbonatites, phonolites, Polar Siberia.

Introduction

ALTHOUGH the majority of investigators consider carbonatites to be magmatic members of alkaline associations (Bell, 1989), the mechanisms for their genesis are still debated. Three groups of models are generally discussed:

1. carbonatites may be formed during the partial melting of carbonated mantle;
2. carbonatites are generated by liquid immiscibility in carbonate–silicate magmatic systems;
3. carbonatites extreme residua of prolonged fractional crystallisation.

Recent studies of the geochemistry of mantle nodules and primary mantle carbonates have led to the conclusion that carbonatite magmas may be generated in the mantle (Amundsen, 1987; Pyle and Haggerty, 1994; Kogarko *et al.*, 1995). The possibility that carbonatites may be formed during partial melting of carbonated peridotite receives support from experimental data (Wyllie, 1989; Wyllie *et al.*, 1990; Eggler, 1989). Mineralogical and geochemical investigations of some carbonatitic complexes are also in agreement with these ideas (Bailey, 1989; Kogarko, 1993).

Experimental investigations suggest that liquid immiscibility plays a leading role in the genesis of carbonatites (Freestone and Hamilton, 1980; Hamilton and Kjarsgaard, 1993; Kjarsgaard and Peterson, 1991). Experiments have demonstrated the presence of extensive fields of two immiscible liquids in the system $(SiO_2+Al_2O_3+TiO_2)$–$(MgO+FeO+CaO)$–(Na_2O+K_2O)–CO_2. The immiscibility gap expands with increasing pressure and alkali content and,

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according to Lee and Wyllie (in press), with decrease in magnesium concentration. From these data it was concluded that alkali-rich residual magmas may intersect the boundary of the silicate–carbonate liquid immiscibility gap under crustal conditions. However, Lee and Wyllie (1994, 1996) have pointed out a number of limitations on this hypothesis and maintain that there is no single process responsible for the formation of all carbonatites. According to Lee and Wyllie fractional crystallisation of carbonate-bearing alkaline magmas may be very important in the genesis of carbonatites, in agreement with ideas proposed by Twyman and Gittins (1987).

Because the problem of the genesis of carbonatites still remains unsolved, field evidence, geological and mineralogical observations on the interrelationships between carbonate and silicate material in magmatic rocks remains very important. I investigated a phonolitic dyke from the Maimecha-Kotui province (Polar Siberia) containing carbonate globules. The interrelationships between silicate and carbonate materials in these phonolites and the mineral compositions support the hypothesis that liquid immiscibility had occurred. Recently Peterson (1989) and Kjarsgaard and Peterson (1991) reported the possibility that alkali-poor carbonatites of Shombole Volcano (E Africa) were the result of silicate–carbonate immiscibility. Their study was based on the petrographic and experimental observations of nephelinites containing carbonate globules. In this paper I summarise data on the petrography and mineral composition of carbonate-bearing phonolites from Polar Siberia and conclude that the carbonate globules represent quench droplets of immiscible melt which separated in a crustal magma chamber during the differentiation of the phonolite magma. The liquid immiscibility was strongly controlled by CO_2 pressure and hence by the depth of magma chamber.

Geological setting

The Maimecha-Kotui ultramafic alkaline province is situated in the North of the Siberian platform in Polar Siberia and is one of the largest in the world, extending over an area 220 × 350 km (Fig. 1) between the Maimecha and Kotui rivers (Egorov, 1991; Kogarko *et al.*, 1995). The area of development of the alkaline-ultrabasic rocks comprises the western slope of the Anabar shield, from the margin of the middle Siberian platform in the north to the upper reaches of the Kotui river in the south. The alkaline rocks are concentrated close to the boundary of the platform with the Taimyr Depression in a zone which is intensely faulted. The structure of alkaline province is controlled by the Pyasinsko-Khatangsky rift system. There are in all thirty-seven ultramafic alkaline and carbonatitic intrusive complexes: this province is particularly noteworthy, not only for the abundance of carbonatites, but also for the association of many of them with ultramafic rocks. The rock types represented include dunite, pyroxenite, ijolite, melteigite, jacupirangite, phoscorite, melilitolites as well as carbonatite.

There are hundreds of dykes, including radial dykes which surround the ultramafic-alkaline massifs (for instance Bor-Juryakh, Romanicha, Odichincha, Dolbykha, Kugda) and so-called regional dykes, the majority of which have E–W and SE–NW strike. There are also ring-dykes, which are well exposed, for instance, in Dolbykha complex.

The Maimecha-Kotui radial dykes exhibit extreme differentiation and their trend covers the whole composition range from ultramafic alkaline dykes through picrites and meimechites to extreme residua represented by phonolites and carbonatites. The evolution of the Maimecha-Kotui dykes is very similar to that of the Western Greenland dyke swarm described by Nielsen (1993). Profound differentiation within the radial dykes of the Maimecha-Kotui province may be illustrated by SiO_2–MgO and SiO_2–CaO diagrams (Figs 2, 3). It may be noted that the SiO_2–CaO diagram permits efficient discrimination between larnite-normative and larnite-free compositions.

I investigated a series of radial dykes related to the Dolbykha massif which comprise alnoite, olivine-nephelinites, nephelinites, melilite nephelinites, cancrinite, nosean and calcite phonolites, calcite trachytes, calcite carbonatites and monchiquites. The Dolbykha massif is an intrusive complex *c.* 3 km^2 with a zonal structure. The central stock of the complex (0.3 × 0.5 km) is composed of melteigite having clinopyroxene as the principal mineral with subordinate nepheline, biotite, titanomagnetite, titanite and perovskite as well as minor olivine, aegirine-augite, apatite, phlogopite and K-feldspar. Ijolite forms a broad ring around the central stock and consists of nepheline and clinopyroxene with titanomagnetite, biotite, phlogopite, melanite, perovskite, titanite and apatite as minor constituents. Later nelsonite and phoscorite, containing apatite, magnetite, tetraferriphlogopite and pyrochlore were formed. The youngest rocks are coarse-grained biotite- and biotite-pyroxene-calcite-carbonatites which form an incomplete outer ring to the complex and which are themselves cut by fine-grained calcite carbonatites containing tetraferriphlogopite and richterite.

Petrography and mineralogy of carbonate-bearing phonolites

Some phonolite dykes contain carbonate-bearing globules with sizes from 1–2 mm to 17–20 mm.

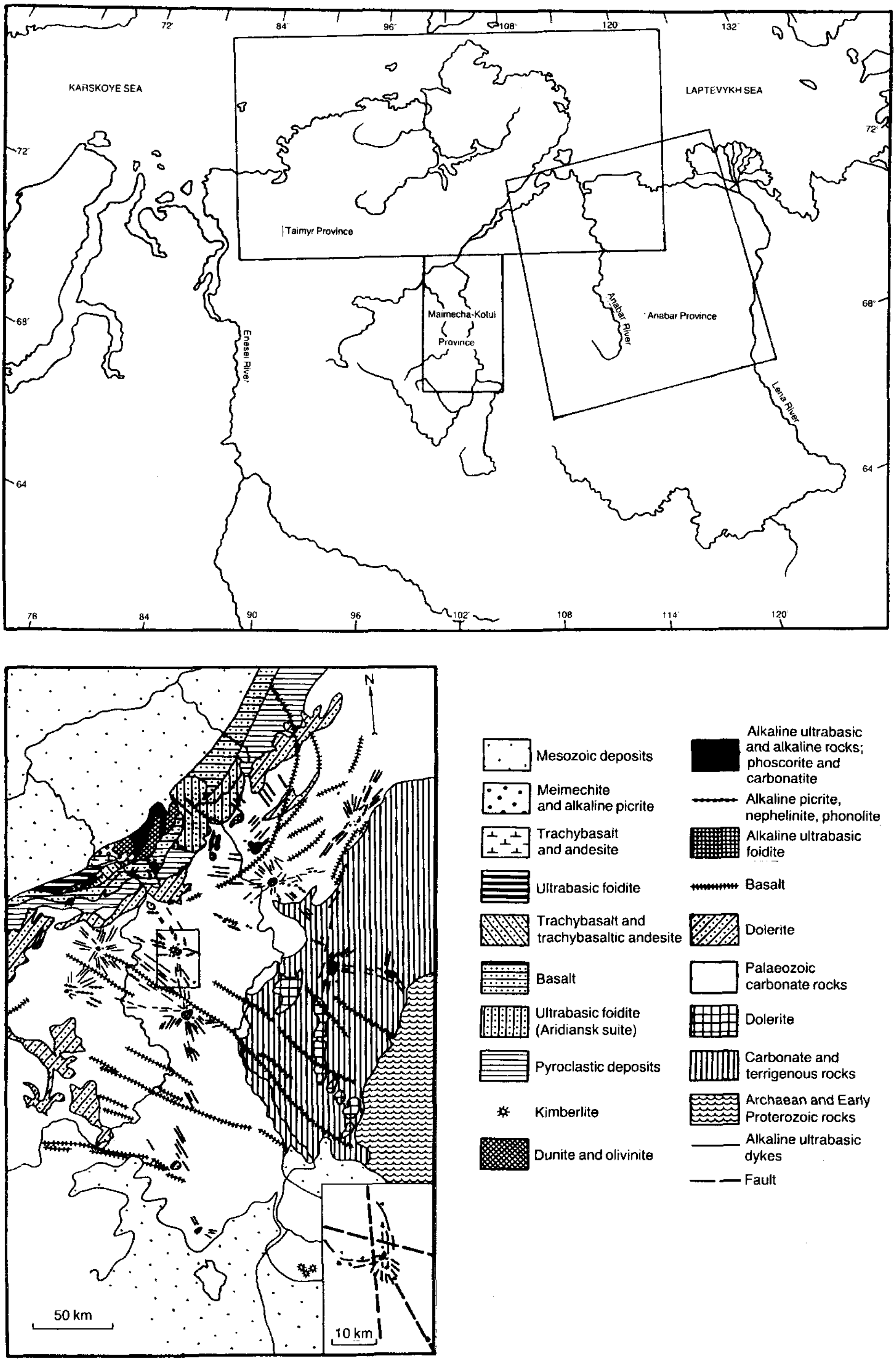

FIG. 1(*a*). Map showing the location of the Maimecha-Kotui province and the adjacent Taimyr and Anabar provinces (after Kogarko *et al.*, 1995). (*b*). General geology of the Maimecha-Kotui province (after Egorov, 1991) The inset diagram shows the Dolbykha group of intrusions, which are located in the centre of the province.

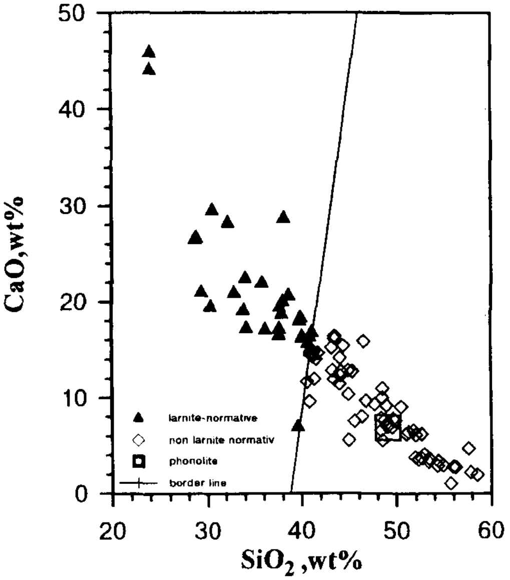

FIG. 2. CaO–SiO$_2$ plot for radial dykes of Polar Siberia.

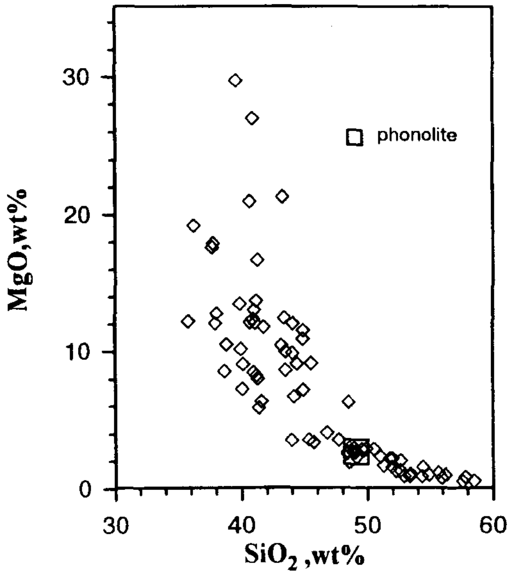

FIG. 3. MgO–SiO$_2$ plot for radial dykes of Polar Siberia.

One globule-bearing phonolite (N 873) was chosen for detailed investigation. The phonolite consists of phenocrysts (~10 %) of albite, phlogopite, and ilmenite, globules (~20 %) and groundmass (~70 %). The globules consist of polycrystalline calcite aggregates and contain albite, mica, apatite, cancrinite, Sr-lueshite, zircon, ancylite, ilmenite, strontianite (Figs. 4 and 5). Occasionally albite is seem rimming the phlogopite suggesting a reaction relationship. The globules are characterised by sharp contacts with the groundmass, and groundmass crystals, mainly albite, showing a flow structure around them. The groundmass is fine-grained and includes albite and phlogopite with subordinate K-feldspar and nepheline. Apatite, ilmenite, ancylite, and Sr-lueshite are present as accessories. Representative microprobe analyses of mineral phases are given in Table 1. There is substantial substitution of Ca by Sr in the apatites and calcites. Similar features was described by Kjarsgaard and Peterson (1991) in a globular nephelinite from Shombole.

Discussion

These observations, in the light of experimental data on liquid immiscibility in carbonate-silicate systems,

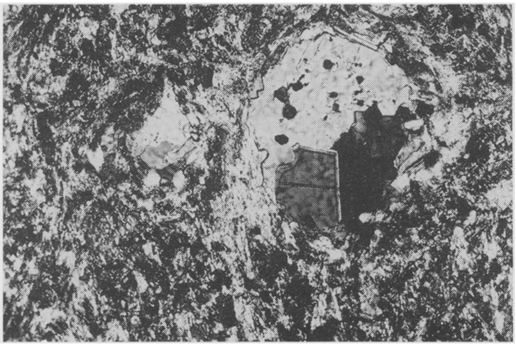

FIG. 4. Carbonate globule in phonolite N 873 under cross nicols. Magnification × 250.

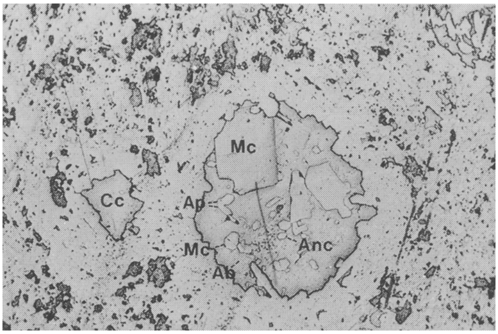

FIG. 5. The same carbonate globule in phonolite N 873, in reflected light. Key: mc – mica, Anc – ancylite, Ab – albite, cc – calcite, Ap – apatite.

TABLE 1. The compositions of phonolite and minerals from carbonate globules and groundmass

Elem.	Phono-	Albite			Mica			Calcite		Ilmenite		Sr-lueshite	Ancylite	Apatite	Strontianite
Wt.%	lite N873	Phen.	G.m.	Globule	Phen.	G.m.	Globule	G.m.	Globule	Phen.	Globule	Globule	Globule	Globule	Globule
SiO_2	49.07	67.98	68.08	68.89	37.09	37.23	36.65	0.41	0.23	0.63					
TiO_2	0.60				3.12	2.36	2.26	0.13		52.28	53.79	3.45	0.10		0.30
Al_2O_3	16.31	19.65	19.33	19.52	13.27	11.77	12.85	0.23	0.10	0.35				0.23	
FeO	3.50	0.19	0.10		20.17	21.50	22.18	3.14	2.42	45.43	45.14	1.29			
MnO	0.16		0.09					0.01	1.26	1.15	1.39	0.26			
MgO	2.71				13.28	11.86	12.61	0.83	0.73	0.17				0.22	
CaO	6.83	0.39		0.18	0.09	0.26	0.02	52.87	54.96	0.19		12.09	2.83	52.90	8.18
Na_2O	8.03	10.52	11.22	11.73	1.17	0.60	0.63	0.17	0.22	0.28	0.28	7.85			
K_2O	4.17	1.01	0.20	0.09	8.59	9.36	9.69	0.23							
P_2O_5	1.33													40.84	
CO_2	6.95														
F														3.87	
Total	99.66	99.74	99.02	100.41	96.78	94.94	96.89	59.37	61.03	100.48	100.60	93.85	75.35	95.38	68.89
SrO								1.16	0.91			5.03	27.23	1.19	58.56
BaO								0.19	0.20			0.08	0.28		1.85
Nb_2O_5												63.39			
La_2O_5												0.17	17.04		
CeO_2												0.24	22.47		
Nd_2O_3													5.40		

suggests that separation of carbonatite from phonolitic melts took place as a result of liquid immiscibility. Petrographic data support this hypothesis of the flow-fabric in the groundmass which clearly indicates that the globule was in existence while the phonolite was still above its solidus. The great similarity in the mineral composition of groundmass and globules, demonstrates that both were in equilibrium (Table 1). As has been already noted, the increasing alkalinity of carbonate-bearing magmatic systems favours the appearance of immiscible liquids. The boundary of the liquid immiscibility field in the system Na_2O–K_2O–Al_2O_3–SiO_2–CaO–CO_2 corresponds to an agpaicity index [$(Na_2O+K_2O)/Al_2O_3$] close to 1 (see Fig. 15-1; Bell, 1989). This implies that in agpaitic melts with $(Na_2O+K_2O)/Al_2O_3 >1$, liquid immiscibility is more likely to occur. The phonolite investigated has an agpaicity index of 1.1, and therefore formation of immiscible liquids in it is unsurprising. The crystallisation of phlogopite phenocrysts enriched in Al also results in the increase in peralkalinity of the residual melt.

The presence of Sr-lueshite in the globules also supports the alkaline character of the carbonate melt because lueshite can only crystallise from peralkaline compositions (Kogarko *et al.*, 1982). I propose that the conjugate carbonate melts initially contained significantly higher amounts of alkali which were subsequently lost. This is in agreement with experimental data on the Na_2O–K_2O–SiO_2–Al_2O_3–CaO–CO_2 system in which the direction of the tie-line corresponds to more alkaline compositions being in equilibrium with carbonate immiscible liquids.

The alkalis are inferred to have subsequently been lost into the fluid phase due to incongruent dissolution of calcium-sodium carbonate in aqueous fluid at lower temperatures (Dernov-Pegarev and Malinin, 1976). Our discovery of nyerereite as micro-inclusions in perovskite in the Guli carbonatite of Polar Siberia (Kogarko *et al.*, 1991) confirms this assumption. From the experimental data of Lee and Wyllie (1996) I can conclude that, under the higher pressure (2.5 GPa), liquid immiscibility does exist even in miaskitic melts (Fig. 6) while under lower pressure (1 GPa) in the same system immiscibility

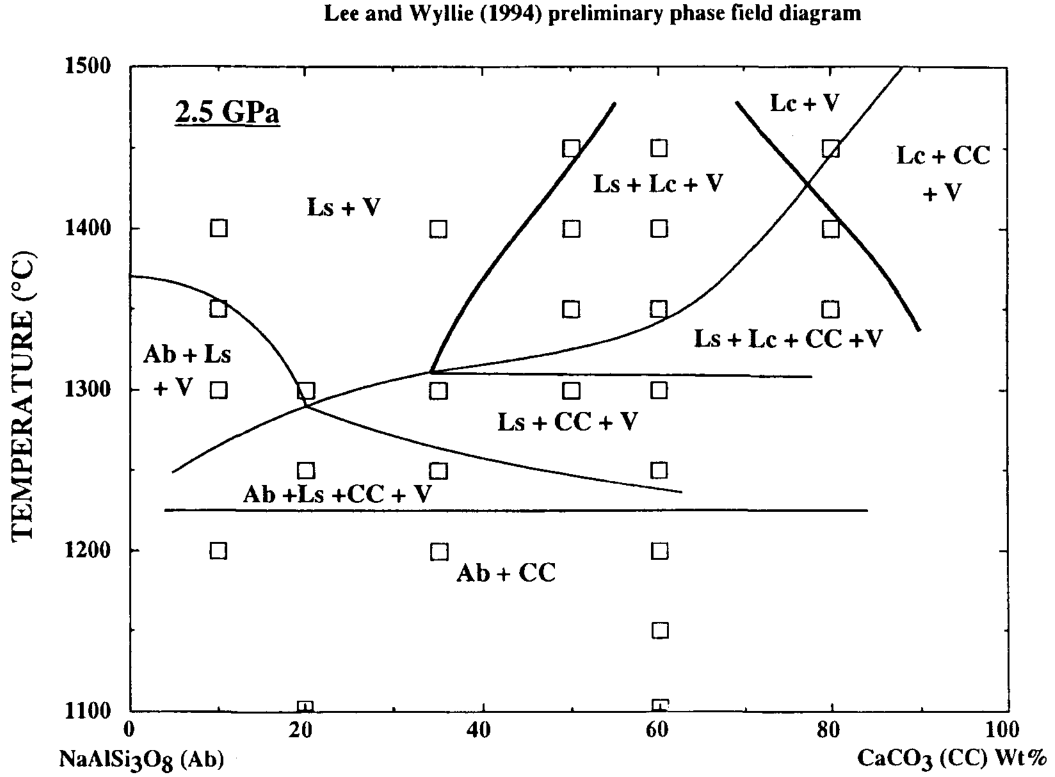

FIG. 6. Isobaric phase fields intersected by the join Albite (Ab) – Calcite (CC) at 2.5 GPa (Lee and Wyllie, 1994, 1996).

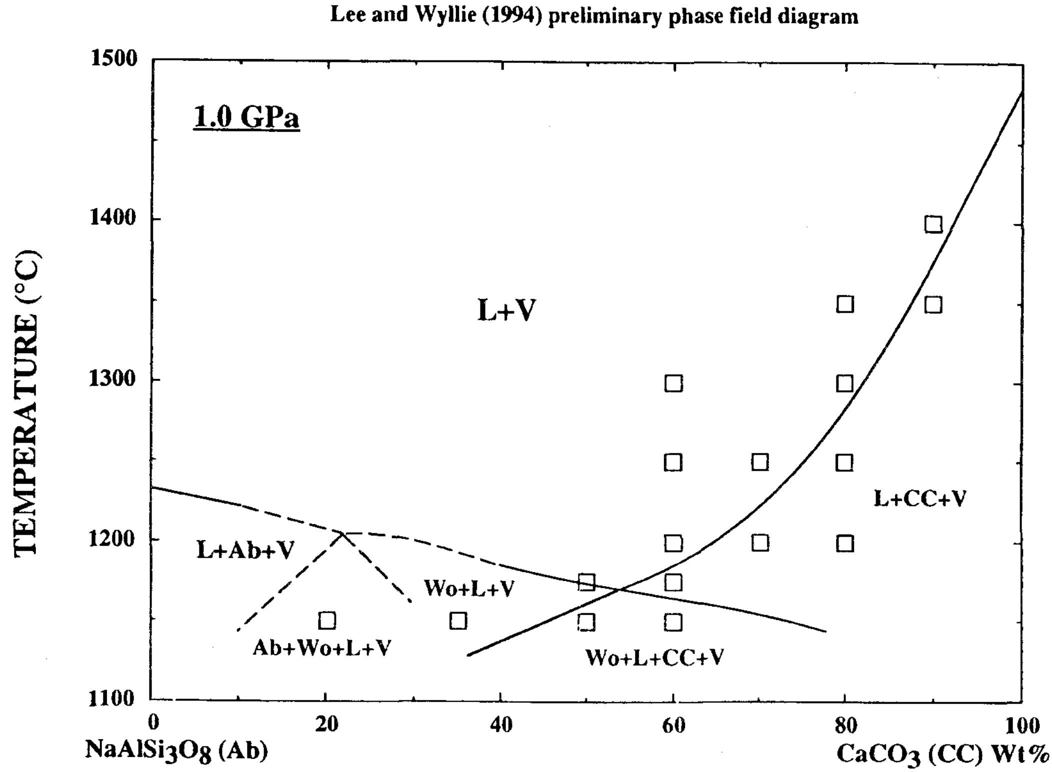

FIG. 7. Isobaric phase fields intersected by the join Albite (Ab) – Calcite (CC) at 1 GPa (Lee and Wyllie, 1994, 1996).

phenomena are absent, primarily as a result of degassing (Fig. 7). Calcite, melilite and wollastonite may crystallise as liquidus phases because the melt becomes very Ca-rich. In one phonolitic dyke (N 2003) of the Dolbykha complex, calcite does occur as phenocrysts (Fig. 8) and there is no sign of immiscible behaviour. CO_2 plays a major role in determining the differentiation of phonolitic magmas. Under high P_{CO_2}, the separation of an immiscible carbonate liquid occurs. At lower P_{CO_2} liquid immiscibility does not occur and calcite may crystallise either as a phenocryst or in groundmass. At still lower pressures carbonates are not formed as a consequence of loss of carbon dioxide and mineral assemblages including either melilite or wollastonite result. Thus one of the important mechanisms for the genesis of carbonatite melts in Polar Siberia was liquid immiscibility in strongly differentiated phonolitic magmas. The generation of the carbonatites is probably controlled by (i) the depth (and P_{CO_2}) of a crustal magma chamber, (ii) the alkalinity of melts, and (iii) the rapidity of magma ascent to the surface.

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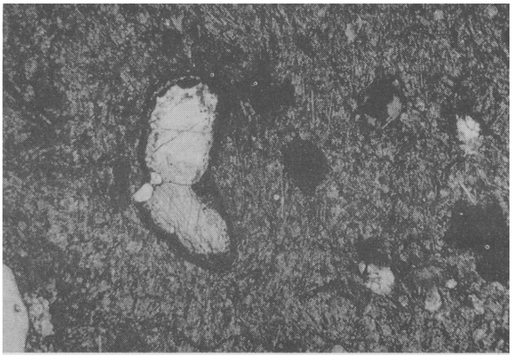

FIG. 8. Phenocrysts of calcite in phonolite N 2003, under crossed nicols. Magnification × 100.

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References

Amundsen, H.E.F. (1987) Evidence for Liquid Immiscibility in the Upper Mantle. *Nature* **327**, 692–5

Bailey, D.K. (1993) Carbonate magmas. *J. Geol. Soc. London*, **150**, 637–51.

Baker, M.B. and Wyllie, P.J. (1990) Liquid Immiscibility in a Nepheline-Carbonate System at 25 kbar and Implications for Carbonatite Origin. *Nature*, **346**, 168–70.

Bell, K. (1989) (Editor) *Carbonatites: Genesis and Evolution*. Unwin Hyman, London, 618 pp.

Dernov-Pegarev, V.F. and Malinin, S.D. (1976) Solubility of Calcite in High Temperature Aqueous Solutions of Alkali Carbonate and the Problem of the Formation of Carbonatites. *Geochimia*, **5**, 643–57 (in Russian), translated as: *Geochem. Internat.*, **13**, 1–13.

Eggler, D.H. (1989) Carbonatites, Primary Melts and Mantle Dynamics. In *Carbonatites: Genesis and Evolution* (K. Bell, ed.). Unwin Hyman, London, pp. 561–79.

Egorov, L.S. (1991) *Ijolite Carbonatite Plutonism (Case History of the Maimecha-Kotui Complexes, Northern Siberia)*. Nedra, Leningrad, 260 pp. (in Russian).

Freestone, I.C. and Hamilton, D.L. (1980) The Role of Liquid Immiscibility in the Genesis of Carbonatites. *Contrib. Mineral. Petrol.*, **73**, 105–17.

Hamilton, D.L., Kjarsgaard, B.A. (1993) The Immiscibility of Silicate and Carbonate Liquids. *South African J. Geol.*, **96**, 139–42.

Kjarsgaard, B.A. and Peterson, T.D. (1991) Nepheline-Carbonatite Liquid Immiscibility at Shombole Volcano, East Africa. *Mineral. Petrol.*, **43**, 293–314.

Kogarko L.N. (1993) Geochemical Characteristics of Oceanic Carbonatites from the Cape Verde Islands. *South African J. Geol..*, **96**, 119–125.

Kogarko, L.N., Tugarinov A.A. and Krigman L.D. (1982) Phase Equilibria in the System Nepheline-Lueshite. *Dokl. Acad. Nauk*, **263**, 985–7 (in Russian), translated as *Dokl. Acad. Sci. USSR: Earth Sci. Sect.*, **263**, 170–2.

Kogarko, L.N., Plant, D.A., Henderson, C.M.B., and Kjarsgaard, B.A. (1991) Na-rich Carbonate Inclusion in perovskite and Calzirtite from the Guli Intrusive Ca-carbonatite, Polar Siberia. *Contrib. Mineral. Petrol..*, **109**, 124–9.

Kogarko, L.N., Kononova, V.A., Orlova, M.P. and Woolley, A.R. (1995) *Alkaline Rocks and Carbonatites of the World. Part two: Former USSR*. Chapman and Hall, London UK, 224 pp.

Lee, W-J. and Wyllie, P.J. (1994) Experimental Data Bearing on Liquid Immiscibility, Crystal Fractionation and the Origin of Calciocarbonatites and Natrocarbonatites. *Internat. Geol. Rev..*, **36**, 797–819.

Lee, W-J. and Wyllie, P.J. (1996) Liquid Immiscibility in the Join $NaAlSi_3O_8$–$CaCO_3$ to 2.5 GPa and the Origin of Calciocarbonatite Magmas. *J. Petrol..*, **37**, 1125–52.

Lee, W-J. and Wyllie, P.J. (in press) Liquid Immiscibility between Nephelinite and Carbonate from 1.0 to 2.5 GPa compared with Mantle Melt Compositions. *Contrib. Mineral. Petrol.*

Nielsen, T. (1993) Alkaline Dyke Swarms of the Gardiner Complex and the Origin of Ultramafic Alkaline Complexes. *Geochimia*, **8**, 112–4 (in Russian), translated as *Geochem. Internat.*, **31**, 112–4.

Peterson, T.D. (1989) Peralkaline Nephelinites. 1. Comparative Petrology of Shombole and Oldoinyo. *Contrib. Mineral. Petrol.*, **101**, 458–78.

Pyle, J.M. and Haggerty, S.E. (1994) Silicate-carbonate Liquid Immiscibility in Upper Mantle Eclogites: Implications for Natrosilicic and Carbonatitic Conjugate Melts. *Geochim. Cosmochim. Acta*, **58**, 2997–3011.

Twyman, J.D. and Gittins, J. (1987) Alkalic Carbonatite Magmas: Parental or Derivative? In *Alkaline Igneous Rocks* (J.G. Fitton and B.G.J. Upton, eds.). Geological Society Special Publication No.30, 85–94, Blackwell Scientific Publishers, Oxford and London.

Wyllie, P.J. (1989) Origin of Carbonatites: Evidence from Phase Equilibrium Studies. In *Carbonatites: Genesis and Evolution* (K. Bell, ed.). Unwin Hyman, London, 500–45.

Wyllie, P.J., Baker, M.B. and White, B.S. (1990) Experimental Boundaries for the Origin and Evolution of Carbonatites. *Lithos*, **26**, 3–19.

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