GEOCHEMISTRY

High-Temperature Carbonatite Melt and Its Interrelations with Alkaline Magmas of the Dunkel'dyk Complex, Southeastern Pamirs

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Convincing arguments in favor of immiscibility of magmatic melts (liquation) are still scarce. They are crucial for the interpretation of the formation of salt-rich magmatic bodies, in particular, carbonatites and associated apatite, fluorite, and other types of mineralization. The leading role of unmixing in the formation of relatively low-temperature (700–1000°C) postmagmatic carbonatite ore bodies was demonstrated in [1–3].

The high-temperature (>1050°C) silicate–salt immiscibility is insufficiently studied, and quantitative analyses of coexisting melts are available only for some assemblages [4–7].

The origin of magmatic carbonatites is commonly attributed to the generation from carbonated peridotites of the upper mantle or the crystallizational differentiation of mantle magmas enriched in Ca, CO_2, and incompatible elements. Both hypotheses have convincing geochemical and experimental support (see, for instance, [8, 9]). Most researchers argue against the third (unmixing) mechanism of the formation of carbonatite magmas. However, experiments with model systems under certain thermodynamic parameters [10–12] demonstrate the plausibility of exsolution of carbonatite melts from silicate ones. Intricate relations between silicate and carbonatite rocks define the significance of each argument in support of certain hypothesis in the study of natural objects.

This paper is aimed at studying the inclusions (microportions of mineral-forming media in minerals) in clinopyroxenes from a leucite fergusite sample taken from a diatreme of the Dunkel'dyk alkaline complex in

the southeastern Pamirs [13]. The Dunkel'dyk Complex is bounded in the north and the west by the Rushan–Pshart and Gunt-Alichur deep-seated faults, respectively, which were formed in the Paleozoic and partly rejuvenated in the Neogene. The complex includes subvolcanic massif, diatremes, and two dike belts. Rocks of the complex (fergusite, tinguaite, leucite and pyroxene syenites, syenite porphyry, borolanite, and granosyenite porphyry) are characterized by a potassic composition. The study region also comprises carbonatite dikes up to 20 m thick and a few hundred meters long [14].

The inclusions were analyzed on a Linkam TS 1500 and Linkam THMSG 600 heating/freezing stages. Inclusions (glasses and minerals) were analyzed on a Camebax Microbeam microprobe (N.N. Kononkova, analyst). Trace elements and REEs were determined on a Cameca IMS-4f ion microprobe.

Mineralogy of fergusite and inclusions in minerals is scrutinized in [5, 6, 13]. Phenocrysts are represented by clinopyroxene and leucite. The rock is crosscut by thin veinlets with dissemination of clinopyroxene, mica, and apatite in the carbonate matrix. This paper presents the results of the study of primary melt inclusions in clinopyroxenes. Despite a narrow range of compositional variations within $En_{34–38}Wo_{50}Fs_{13–17}$, the clinopyroxenes from the rock and veinlets show some differences. Euhedral clinopyroxene in the rock shows a distinct zoning emphasized by color variation from pale green (TiO_2 0.35 wt %) to dark green and occasional dark amber color (TiO_2 up to 0.99 wt %). The Na_2O content is as much as 0.98 wt %, while Mg/(Mg + Fe) = 0.69–0.60. Clinopyroxenes in the veinlets are anhedral and uniformly green. The Na_2O content in this variety is 0.65 wt %, while the Mg/(Mg + Fe) value increases to 0.79). In both clinopyroxenes, Na_2O shows a positive correlation with Mg#. The clinopyroxenes in the host rock contain silicate inclusions. However, some crystals include cores with irregular boundaries and compositions corresponding to clinopyroxene from

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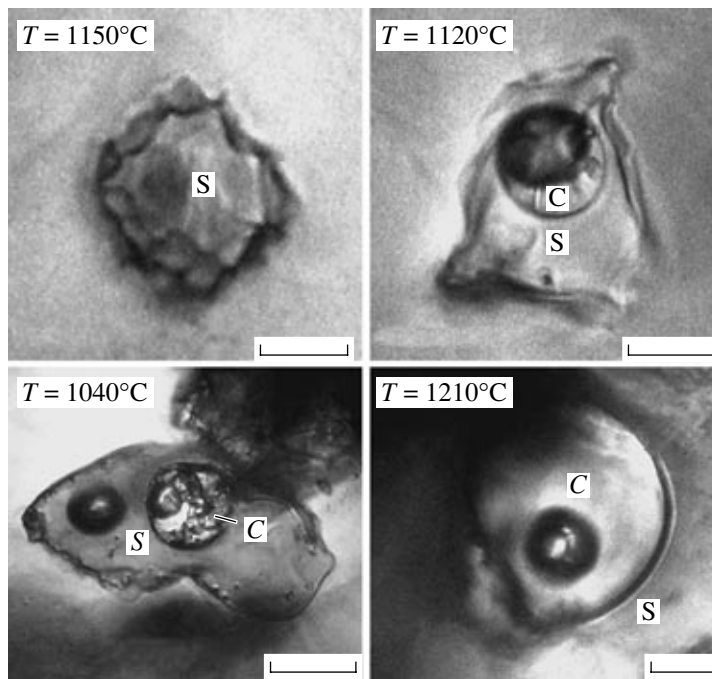
Fig. 1. Transmitted light microphotographs of melt inclusions in the clinopyroxene from veinlets. The variable proportions of silicate and carbonate material in the inclusions are shown. Indicated temperatures correspond to experimental conditions. Carbonatite melt is universally crystallized after a sharp temperature decrease (quenching). (S) Silicate glass, (M) mixture of carbonates and silicate minerals (at run temperature). (S) and (C) are melts. Scale bar 10 μm.

veinlets. Such cores have a rim of zoned clinopyroxene that is typical of fergusite. They contain silicate and carbonate inclusions. Clinopyroxenes in the veinlets contain melt inclusions of syngenetic silicate, carbonate, and mixed silicate–carbonate types with variable proportions of silicate and carbonate melts. This fact indicates heterogeneity of mineral-forming melt, which is one of the most important signatures of unmixing. The crystallized inclusions and veinlet groundmass contain the same minerals: aegirine, kalsilite, perovskite, Ba–Sr-bearing phases (carbonates), feldspars, apatite, scapolite, complex phosphate, fresnoite (Ba–Ti silicate), microsommite, K–Cl-bearing sulfide (djerfisherite), and various zeolites [5, 6]. The dissolution of daughter minerals in the carbonate and carbonate–silicate inclusions begins at 450–500°C. After their complete dissolution at 1120–1150°C, the silicate matrix of the combined inclusions contains carbonatite melt globules that move randomly within the vacuoles (Fig. 1). Each globule contains a gas bubble (fluid phase), which disappears simultaneously in both portions of the inclusions at 1150–1180°C. Carbonatite melt crystallizes at a sharp temperature decrease (quenching). The homogenization temperature of silicate inclusions in the rock clinopyroxene is slightly lower (no more than 1150°C).

The phase boundary between the silicate matrix and carbonatite melt globules does not disappear up to 1210°C; i.e., the initial melt already passed the stage of higher-temperature unmixing at the moment of liquidus mineral crystallization.

Chemical compositions of daughter phases and silicate glasses from heated inclusions indicate the high contents of volatiles (F, Cl, and S) in the magma. The

Table 1. Representative chemical analyses of quench glasses of melt inclusions in clinopyroxenes from the rock and carbonatite veinlet, wt %
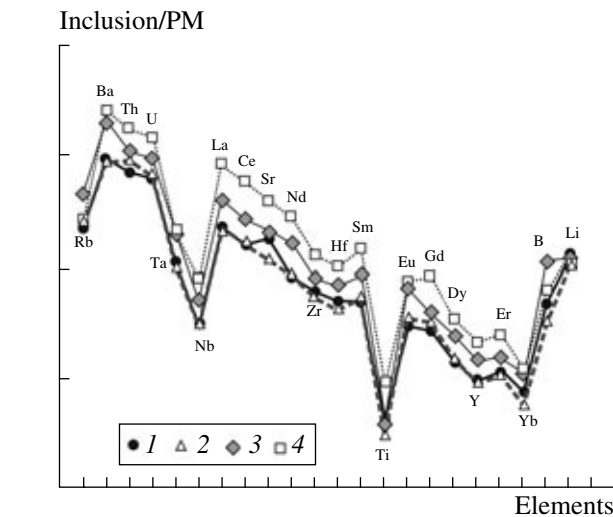
Component	1	2	3	4	5	6
SiO_2	49.75	54.25	52.94	46.19	50.64	51.35
TiO_2	0.96	0.89	0.54	1.62	0.59	0.64
Al_2O_3	12.86	15.71	18.02	13.32	14.99	16.16
FeO	5.82	4.70	5.92	7.76	5.23	4.78
MgO	2.12	0.95	1.22	2.84	2.23	1.49
CaO	9.22	5.06	4.27	9.63	7.08	4.68
Na_2O	6.12	5.39	5.30	4.11	3.74	3.92
K_2O	8.00	9.39	8.59	9.31	11.53	12.56
Cl	0.70	0.52	0.30	0.31	0.24	0.37
S	0.12	0.05	0.29	0.20	0.10	0.10
Total	95.67	96.91	97.39	95.29	96.37	96.05

Note: (1–3) Melt inclusions in the clinopyroxene from the rock; (4–6) melt inclusions in the clinopyroxene from carbonatite veinlet.
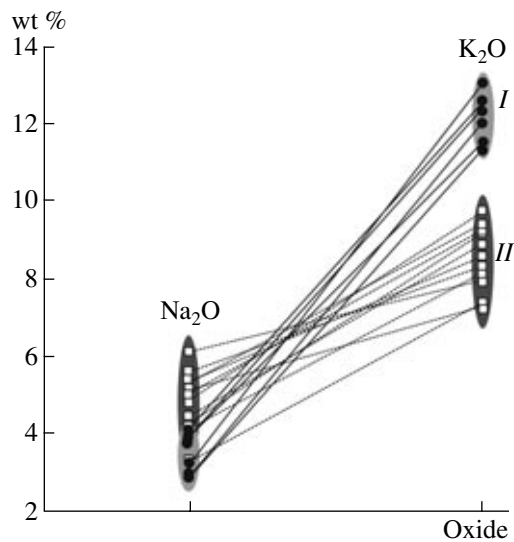
Fig. 2. Concentrations of K_2O and Na_2O in the melts of inclusions in clinopyroxenes from (*I*) carbonatite veinlet (light gray field) and (*II*) rock (dark gray field).

Fig. 3. Primitive mantle (PM)-normalized spidergram of concentrations of REE and trace elements in silicate melts (glasses) of inclusions in the clinopyroxene from (*1*) rock and (*2*) veinlet (carbonate-free inclusions); (*3*) inclusions with carbonate occupying no more than 10 vol % of vacuole; (*4*) inclusions with carbonate occupying up to 50 vol % of vacuole.

presence of CO_2 and H_2O is reflected in the crystallization of carbonates and zeolites at later stages. In addition, the presence of rare CO_2-bearing fluid inclusions indicate CO_2-saturation of the melts. Water is present in fluids in significantly crystallized carbonate-bearing and silicate melt inclusions. Based on ion microprobe data, the water content is within 1.75–1.60 wt % in the clinopyroxene-hosted silicate inclusions from both the rock and veinlets. According to experimental data, the H_2O solubility in carbonate melts at equal *T–P* parameters could be at least two times higher [15].

The silicate melts in the clinopyroxene-hosted inclusions from the veinlet and the rocks have nearly similar chemical compositions (Table 1). However, the earlier melts in the veinlet are characterized by higher K_2O contents (Fig. 2). The K_2O/Na_2O ratio is as high as 3 (average of 8 analyses). In contrast, melts in the rock have a lower K_2O/Na_2O ratio (1.6, average of 14 analyses). In addition, the total alkali content in silicate inclusions from the veinlets is higher (maximum up to 16.5%) than that in the rock (14.8 wt %).

Table 2. Concentrations of REE and trace elements in quench silicate glasses of melt inclusions in clinopyroxenes from the rock and carbonatite veinlet, ppm

Element	1	2	3	Element	1	2	3
V	171.178	188.669	168.439	Dy	11.181	16.393	11.676
Cr	131.871	145.159	104.771	Zr	691.423	786.468	624.205
Rb	144.619	139.864	164.338	Sm	22.388	32.425	24.910
Ba	6732	10868	6320	Ti	5629	5476	4162
Th	61.167	117.403	81.668	Y	44.435	63.736	43.786
U	13.488	22.975	14.768	Gd	16.318	28.393	20.298
Ta	4.694	6.821	4.234	Yb	3.863	5.534	2.997
Nb	21.919	32.528	23.535	Eu	5.162	10.218	6.204
La	156.589	224.916	148.214	Er	5.732	7.707	5.428
Ce	290.170	446.591	311.366	B	33.448	31.360	23.526
Sr	3907.3	5600.4	2550.2	Li	212.837	622.413	175.348
Nd	116.503	172.591	125.947	H_2O	1.75	n.d.	1.60
Hf	15.854	16.960	13.220	F	0.74	0.85	0.58

Note: (1, 2) Silicate inclusions in clinopyroxene from the rock; (3) carbonate-free silicate inclusions in clinopyroxene from carbonate–silicate veinlets (average of 3 analyses). H_2O and F are given in wt %; (n.d.) not determined.

The silicate melts are characterized by high LREE/HREE values ($La_N/Yb_N = 30$–35); high contents of Ba, Th, and U; and low contents of Nb. The contents of trace and REEs in silicate melt equilibrated with carbonate material (clinopyroxene-hosted inclusions from the veinlet) are identical to those in the melt from primary inclusions in fergusite clinopyroxenes (Table 2, Fig. 3).

The diagram of the PM-normalized distribution of incompatible elements reveals an important geochemical feature of the studied melts: sharp negative anomalies of Nb, Ta, and Ti. This fact indicates that their relation with calc-alkaline magmatism played the key role in the generation of new continental crust.

Silicate melts in the clinopyroxene-hosted inclusions from veinlets and the rock have similar geochemical signatures, indicating their derivation from a common source.

Thus, one can see a distinct geochemical relation between carbonatite and alkaline basaltic melts that produced the rocks of the massif. Silicate melts in the clinopyroxene-hosted inclusions from the veinlet correspond to the earliest melt entrapped by fergusite phenocrysts, indicating unmixing of the melt into silicate and carbonate liquids at the early stage of the primary magma evolution. Thermometric studies confirmed the conclusion on the existence of two melts at temperatures higher than 1150°C. The melts are saturated in volatiles (especially in H_2O and CO_2). They are characterized by high alkalinity, predominance of K_2O over Na_2O, and similar enrichment in trace elements and REEs. The carbonate-rich melt produced carbonatites within the complex.

REFERENCES

1. A. H. Rankin and M. L. Le Bas, Nature **250**, 206 (1974).
2. R. T. Aldous and A. H. Rankin, *Proceedings of the 4th Meeting of Geological Society of British Isles, Sheffield, England, 1979* (Sheffield Univ., Sheffield, 1979).
3. I. P. Solovova, I. D. Ryabchikov, L. N. Kogarko, and N. N. Kononkova, Geochem. Int. **36**, 377 (1998) [Geokhimiya, No. 5, 435 (1998)].
4. B. A. Kjarsgaard and T. Peterson, Mineral. Petrol. **43**, 293 (1991).
5. I. P. Solovova, A. V. Girnis, and A. V. Guzhova, Geokhimiya, No. 3, 383 (1993).
6. I. P. Solovova, A. B. Girnis, and I. D. Ryabchikov, Petrology **4**, 319 (1996) [Petrologiya **4**, 339 (1996)].
7. I. A. Andreeva, V. B. Naumov, V. I. Kovalenko, and N. N. Kononkova, Dokl. Akad. Nauk **343**, 273 (1995).
8. R. E. Harmer and J. Gittins, J. Petrol. **39**, 1895 (1998).
9. J. A. Dalton and B. J. Wood, Earth Planet. Sci. Lett. **119**, 511 (1993).
10. B. A. Kjarsgaard and D. L. Hamilton, Miner. Mag. **52**, 43 (1988).
11. B. A. Kjarsgaard and T. Peterson, Mineral. Petrol. **43**, 293 (1991).
12. I. C. Freestone and D. L. Hamilton, Contrib. Mineral. Petrol. **73**, 105 (1980).
13. E. A. Dmitriev, in *Cenozoic Potassic Alkaline Rocks of the Eastern Pamirs* (Dushanbe, 1976) [in Russian].
14. A. R. Faiziev, F. Sh. Iskandarov, and F. G. Gafurov, in *Mineralogy, Thermobarogeochemical Conditions, and Genesis of the Dunkel'dyk REE–Fluorite Deposit, Eastern Pamirs* (Dushanbe, 2000) [in Russian].
15. H. Keppler, Am. Miner. **88**, 1822 (2003).