

Melt inclusions as indicators of the magmatic origin of carbonatite rare metal and rare earth minerals

Stanislav Sokolov*

Fedorovskii All-Russian Institute of Mineral Resources (VIMS), Staromonetnyi per. 31, Moscow 109017, Russia

Abstract

Carbonatite melts, originating in the course of crystallization or liquid differentiation of mantle-carbonatized alkaline magmas, could contain primary enhanced quantities of alkalis, phosphorous, and incompatible trace elements (Nb, Ta, Zr, REE, Sr, Ba). This statement, based upon experimental data relative to fractionation of carbonatite-forming systems and solubility of Nb and La in synthetic carbonate liquids, allows us to suggest magmatic nature of rare metal (RMM) and rare earth (REM) minerals in carbonatites. Crystallization of RMM and REM from carbonatite melts is supported by the results of the present melt inclusion study in minerals of carbonatites. We observe the: (i) presence of RMM and REM in the form of solid inclusions in magmatic host-minerals; (ii) microprobe analyses of daughter rare metal and rare earth phases, entering into composition of crystallized melt inclusions; and (iii) conservation by rare metal and rare earth minerals of melt inclusions with high temperatures of homogenization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbonatites; Trace elements; Rare metal/earth minerals; Melt inclusions

1. Introduction

Koster van Groos (1975) was the first to suggest that carbonatite melts could be formed as primary melting in the mantle and as products of crystallization or liquid differentiation of carbonatized, silica undersaturated magmas. This suggestion was later confirmed by numerous field and experimental studies (Bailey, 1990; Wyllie, 1989; Sokolov, 1993). The present paper is concerned with the latter two types of carbonatites.

Despite the fact that the magmatic origin of carbonatites is declared by almost all geologists, discussion continues about the magmatic or metasomatic nature of their rare metal and rare earth minerals (further

RMM and REM, respectively). Although some researchers of carbonatites, mainly in Russia, consider carbonatites to be magmatic rocks, formation of rare metal and rare earth mineralization is thought to be related to later superimposed metasomatism. At the same time, a distinct correspondence of the same RMM and REM to definite mineral types of the carbonatites is not consistent with an epigenetic formation as a result of metasomatic influence upon primary parageneses. Table 1 shows, in the example of complexes of ultrabasic-alkaline rocks and carbonatites, a regular change of the associations of the rock-forming minerals (carbonates, silicates and others) and RMM (REM) in polystage carbonatite process. It is clear that such regularity will be displayed only in the case if rare metal and rare earth elements are components of carbonatite-forming systems and evolve together with them.

* Fax: +7-95-951-5043.

E-mail address: vims@df.ru (S. Sokolov).

Table 1
Evolution of carbonatite mineral composition by stages of the carbonatite process

	Major minerals	REM–RMM
I stage	Calcite, clinopyroxene-I (aegirine–augite, augite–diopside), forsterite-I, melilite, monticellite-I, nepheline, wollastonite, biotite–phlogopite, hastingsite, K-feldspar, apatite-I, Ti-magnetite, pyrrhotite-I	Nb-perovskite (Nb), dysanallyte-I (Nb, TR _{Ce}), calzirtite (Zr, Nb), niocalite (Nb)
II stage	Mg-calcite ± dolomite, clinopyroxene-II (diopside, aegirine–diopside), forsterite-II, monticellite-II, cancrinite, phlogopite–tetraferriphlogopite, Mg-kataphorite, Mg-arfvedsonite-I, clinohumite-I, chondrodite-I, apatite-II, Mg-magnetite, pyrrhotite-II, chalcopyrite	Dysanallyte-II (Nb, Ta, TR _{Ce}), baddeleyite (Zr), pyrochlore-I (Nb), hatchettolite (Nb, Ta, U, Th), zirkelite (Zr, Nb)
III stage	Calcite, dolomite (Fe-dolomite), phlogopite–tetraferriphlogopite, tremolite, Mg-arfvedsonite-II, Mg-riebeckite, eckermannite, clinohumite-II, chondrodite-II, talc, serpentine, apatite-III, magnetite, ilmenite, sphene, pyrrhotite-III, pyrite	Pyrochlore-II (Nb), zircon-I (Zr), lueshite (Nb), eschynite (TR _{Ce} , Nb), burbankite-I (Sr, Ba, TR _{Ce})
IV stage	Dolomite (Fe-dolomite), ankerite, siderite, magnesite, rhodochrosite, richterite, aegirine, chlorite, K-feldspar, quartz	Pyrochlore-III (Nb), columbite (Nb), fersmite (Nb), zircon-II (Zr), monazite (TR _{Ce}), burbankite-II (Sr, Ba, TR _{Ce}), strontianite (Sr), celestine (Sr), carbocernaite (Sr, TR _{Ce}), bastnaesite (TR _{Ce}), parisite (TR _{Ce}), ancyllite (Sr, TR _{Ce})

Table 2
⁸⁷Sr/⁸⁶Sr ratios in rocks and minerals of the carbonatite complexes

Rock	Mineral	⁸⁷ Sr/ ⁸⁶ Sr	References
<i>Kovdor, Kola peninsula, Russia</i>			
Turjaite		0.7042	Landa et al., 1988
Ijolite		0.7046	
Calcite carbonatite		0.7035	Landa et al., 1984
Calcite carbonatite	Calcite	0.70335–0.70395	Zaitsev and Bell, 1995
Calcite carbonatite	Apatite	0.70341–0.70385	
Phoscorite	Calcite	0.70323	
Phoscorite	Apatite	0.70330–0.70359	
<i>Guli, Polar Siberia, Russia</i>			
Calcite carbonatite		0.7040	Landa et al., 1984
Dolomite carbonatite		0.7046	
<i>Vishnevogorskii, Urals, Russia</i>			
Calcite carbonatite		0.7010–0.7041	Sabachenko et al., 1994
<i>Khibina, Kola peninsula, Russia</i>			
Carbonatite		0.70392–0.70400	Kramm and Kogarko, 1994
<i>Oka, Quebec, Canada</i>			
Calcite carbonatite		0.70325–0.70332	Wen et al., 1987
Calcite carbonatite	Monticellite	0.70324	
<i>Gardiner, Greenland</i>			
Melteigite		0.7036	Nielsen and Buchardt, 1985
Melilitolite		0.7039	
Calcite carbonatite		0.7036	

2. Results of experimental investigations

The sub-crustal origin of carbonatites is undisputed, and is supported by their localization in zones of transstructural deep faults or rift systems and by data on Sr isotope abundances in rocks and minerals (Table 2). Model experiments with natural samples and artificial mixtures show that independent of origin (as a result of liquid immiscibility or crystallization differentiation), carbonatite melts might be enriched in Na, K, P, Sr, Ba, lanthanides, and also F and Cl (Hamilton et al., 1989; Kjarsgaard et al., 1995; Lee and Wyllie, 1996; Wendlandt and Harrison, 1979). In accordance with some authors (Kjarsgaard et al., 1995), isobaric lowering of temperature favours zirconium accumulation in carbonate liquids, while in accordance with data of other researchers (Veksler et al., 1998b), zirconium, niobium and tantalum are more readily concentrated in silicate liquids. At the same time, the presence of F in layered silicate–carbonate systems positively influences the distribution of niobium into the carbonate fraction (Jones et al., 1995). Due to chemical and crystallochemical similarity of niobium and tantalum, the same conclusion might be applied to tantalum. Relying upon the

results of their experiments, Hamilton et al. (1989) consider that the optimal combination of PTX-parameters might result in an increase in natural carbonate melts of not only sodium and phosphorous but also of the above-mentioned trace elements.

Transfer of incompatible trace elements by carbonatite melts and, consequently, possibility of precipitation from them of some RMM and REM are supported by experimental results on niobium and lanthanum solubility in synthetic carbonate liquids and crystallization of Nb- and La-containing phases at temperatures and pressures, of carbonatite formation. According to Watkinson (1970) and Jago and Gittins (1993), calciocarbonate liquids are able to dissolve 5–7.5 wt.% Nb₂O₅ at temperatures 950–600 °C and pressure 100 MPa. Crystallization of these liquids at first resulted in precipitation of a perovskite-type phase and then—during long temperature interval—of pyrochlore together with calcite. This corresponds to relations between perovskite and pyrochlore in natural carbonatites, particularly, in the carbonatites of the Oka complex.

Phase relations on the section calcite–portlandite–lanthanum hydroxide at pressure 100 MPa (Jones and Wyllie, 1983) show that with temperature increase

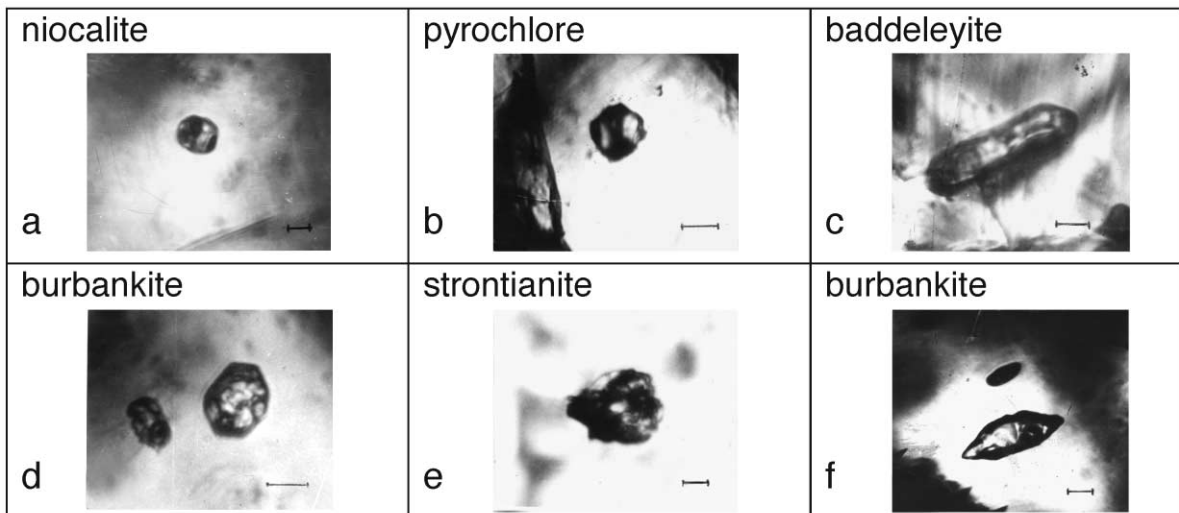


Fig. 1. Microphotographs of melt inclusions in rare metal and rare earth minerals: (a) niocalite, calcite carbonatite, Oka complex; (b) pyrochlore, calcite carbonatite, Ozernyi complex; (c) baddeleyite, phoscorite, Kovdor complex; (d) burbankite, dolomite–calcite carbonatite, Vuori-Yarvi complex; (e) strontianite, dolomite–calcite carbonatite, Vuori-Yarvi complex; (f) burbankite, calcite carbonatite, Khibina complex. In all cases, the scale bars are equal to 10 μm .

Table 3
Melt inclusions in rare metal and rare earth minerals from rocks of carbonatite series

Complex	Rock (stage)	Mineral	T_{gom} (°C)	References
Guli, Polar Siberia, Russia	Calcite–forsterite–magnetite phoscorite (I)	Dysanalyte	–	Present work
Gardiner, Greenland	Apatite–phlogopite–magnetite phoscorite (?)	Perovskite	–	Present work
Oka, Quebec, Canada	Monticellite–calcite carbonatite (I)	Niocalite	850–890	Sokolov, 1994
Ozernyi, Yakutia, Russia	Forsterite–calcite carbonatite (II)	Pyrochlore	670–720	Sokolov, 1978
Kovdor, Kola peninsula, Russia	Dolomite–forsterite–magnetite phoscorite (II)	Baddeleyite	>770	Present work
	Forsterite–calcite carbonatite (II)	Baddeleyite	–	Present work
	Fe-dolomite carbonatite (IV)	Zircon	625–720	Sokolov, 1981
Vuori-Yarvi, Kola peninsula, Russia	Dolomite–calcite carbonatite (III)	Burbankite	≥ 550–580	Present work
		Strontianite	–	Present work
Chernigovskii, Ukraine	Calcite carbonatite (?)	Baddeleyite	≥ 860	Voznjak et al., 1981
Khibina, Kola peninsula, Russia	Albite–calcite carbonatite (II)	Burbankite	–	Present work
Vishnevogorskii, Urals, Russia	Calcite carbonatite (?)	Zircon	>400	Petrova and Talantsev, 1992

from 610 to 700 °C and increasing CO₂/H₂O ratio, solubility of lanthanum hydroxide in simplified carbonatite systems increases from 20 to 40 wt.%. Jones and Wyllie came to a conclusion that bastnaesite might crystallize together with calcite from magmatic carbonate liquids in the process of temperature falling from liquidus (650–625 °C) to eutectic (543 °C) and under definite relations of carbon dioxide, water and fluorine.

3. Results of melt inclusions study

A study of the minerals in carbonatites and other rocks and inclusions entrapped by them provides more reliable evidence of RMM–REM magmatic crystallization. Firstly, such minerals as columbite and monazite are identified by means of microprobe analysis as solid inclusions in topaz from pegmatites and ongonites, which contained inclusions of silicate melts with homogenization temperatures of 650–700 °C (Kovalenko et al., 1996; Naumov et al., 1991). Secondly, some RMM and REM are found among daughter phases of non-heating crystallized melt inclusions: (i) strontium–barium and rare earth carbonates in carbonatite forsterite from Kovdor complex, Russia (Veksler et al., 1998a); (ii) REE-rich zirkelite in titanite and celestine in apatite from various alkaline rocks and phoscorites of the Mushugai-Khuduk carbonatite complex in Mongolia (Andreeva et al., 1995, 1998).

Further evidence of RMM and REM magmatic origin is an entrapment by syngenetic melt inclusions (Fig. 1). At the present time, they are established in

different minerals of many carbonatite complexes. Table 3 contains results of our research and literature data. The melt inclusions are present in carbonatites and phoscorites of various mineral compositions both in early and late carbonatites. The above carbonatites are related to different formational types and are connected with ijolites and melilitolites (Oka, Kovdor, Vuori-Yarvi and other complexes), with miaskitic and agpaite nepheline syenites (carbonatites of the Urals and the Khibina massif, respectively).

It should be noted that seeking and study of inclusions in rare metal and rare earth minerals are difficult due to their intense color and opacity. But as far as these minerals in carbonatites are in equilibrium relations with silicates, carbonates and apatite, which contain melt inclusions, one might suggest that they were also crystallized from a melt.

4. Conclusions

In accordance with the data of the model experiments (Hamilton et al., 1989; Kjarsgaard et al., 1995; Lee and Wyllie, 1996; Wendlandt and Harrison, 1979), carbonatite melts—derivatives of processes of crystallization or liquid differentiation of mantle magmas—might accumulate alkalis, phosphorous and incompatible trace elements. This is very possible due to the fact that the carbonatite melts comprise (along with Na, K, P; Sokolov, 1999; Sokolov et al., 1999) carbon dioxide, water and fluorine, with which the high-field strength elements (Nb, Ta, Zr) and lan-

thanides readily form complex compounds. This suggestion is supported by high solubility of niobium and lanthanum in the synthetic carbonate liquids (Watkinson, 1970; Jago and Gittins, 1993; Jones and Wyllie, 1983).

Capability of natural carbonatitic melts to transport trace elements and precipitate corresponding rare metal and rare earth minerals—concentrators is substantiated by the presence of zirkelite, celestine and carbonates of Sr, Ba, REE as daughter phases of melt inclusions in the minerals of the carbonatite complexes (Andreeva et al., 1995, 1998; Veksler et al., 1998a). Indisputable support of magmatic crystallization of RMM and REM of carbonatites and phoscorites consists in an entrapment by melt inclusions, characterized by high homogenization temperatures (see Fig. 1 and Table 3).

Magmatic rare metal and rare earth mineralization, established in many carbonatite massifs, is characterized by a considerable variety of mineral species, which concentrate practically all typomorphic for carbonatite process incompatible trace elements. However, this does not mean that all rare metal and rare earth mineralization in carbonatites have a magmatic origin, because in many cases, the mineral associations composing carbonatites display heterogeneous nature (Sokolov, 1995).

References

- Andreeva, I.A., Naumov, V.B., Kovalenko, V.I., Listratova, Ye.N., Kononkova, N.N., 1995. Magmatic celestite in melt inclusions in apatite from the Mushugai-Khuduk alkali volcanoplutonic complex in South Mongolia. *Trans. Russ. Acad. Sci. Earth Sci. Sect.* 339A (9), 154–159.
- Andreeva, I.A., Naumov, V.B., Kovalenko, V.I., Kononkova, N.N., 1998. The chemical composition of melt inclusions in sphene from theralites of the Mushugai-Khuduk carbonatite complex, Southern Mongolia. *Trans. Russ. Acad. Sci. Earth Sci. Sect.* 361 (5), 708–712.
- Bailey, D.K., 1990. Mantle carbonatite eruptions: crustal context and implications. *Lithos* 26, 37–42.
- Hamilton, D.L., Bedson, P., Esson, J., 1989. The behaviour of trace elements in the evolution of carbonatites. In: Bell, K. (Ed.), *Carbonatites: Genesis and Evolution*. Unwin Hyman, London, pp. 405–427.
- Jago, B.C., Gittins, J., 1993. Pyrochlore crystallization in carbonatites: the role of fluorine. *S. Afr. J. Geol.* 96, 149–159.
- Jones, A.P., Wyllie, P.J., 1983. Low-temperature glass quenched from a synthetic, rare earth carbonatite: implication for the origin of the Mountain Pass deposit, California. *Econ. Geol.* 78, 1721–1723.
- Jones, J.H., Walker, D., Pickett, D.A., Murrell, M.T., Beattie, P., 1995. Experimental investigations of the partitioning of Nb, Mo, Ba, Ce, Pb, Ra, Th, Pa, and U between immiscible carbonate and silicate liquids. *Geochim. Cosmochim. Acta* 59, 1307–1320.
- Kjarsgaard, B.A., Hamilton, D.L., Peterson, T.D., 1995. Peralkaline nephelinite/carbonatite liquid immiscibility: comparison of phase composition in experiments and natural lavas from Oldoinyo Lengai. In: Bell, K., Keller, J. (Eds.), *Carbonatite Volcanism: Oldoinyo Lengai and the Petrogenesis of Natrocarbonatites*. Springer, Berlin, pp. 163–190.
- Koster van Groos, A.F., 1975. The effect of high CO₂ pressure on alkalic rocks and its bearing on the formation of alkalic ultrabasic rocks and the associated carbonatites. *Am. J. Sci.* 275, 163–185.
- Kovalenko, V.I., Tsareva, G.M., Naumov, V.B., Hervig, R.L., Newman, S., 1996. Pegmatite magma from volhynia: composition and crystallization parameters determined by magmatic inclusion studies. *Petrology* 4 (3), 277–290.
- Kramm, U., Kogarko, L.N., 1994. Nd and Sr isotope signatures of the Khibina and Lovozero agpaetic centres, Kola Alkaline Province, Russia. *Lithos* 32, 225–242.
- Landa, E.A., Shergina, Yu.P., Larin, A.M., Krasnova, N.I., Murina, G.A., 1984. Interaction of mantle and crust matter and metasomatic processes. In: Korzhinskii, D.S. (Ed.), *Metasomatism and Ore Formation*. Nauka, Moscow, pp. 19–29 (in Russian).
- Landa, E.A., Shergina, Yu.P., Fefilova, L.V., 1988. On the isotopic composition of strontium in ultramafic, alkaline-ultramafic, and some other rocks of the Maimecha-Kotui and Karelia-Kola regions. *Dokl. USSR Acad. Sci.* 298, 960–963 (in Russian).
- Lee, W.-J., Wyllie, P.J., 1996. Liquid immiscibility in the join NaAl-Si₃O₈-CaCO₃ to 2.5 GPa and the origin of calcicarbonatite magmas. *J. Petrol.* 37, 1125–1152.
- Naumov, V.B., Solovova, I.P., Kovalenko, V.I., Guzhova, A.V., 1991. The crystallization of topaz, albite, potassium feldspar, mica and columbite from ongonite magmas. *Geochem. Int.* 28 (3), 120–125.
- Nielsen, T.F.D., Buchardt, B., 1985. Sr-C-O isotopes in nephelinitic rocks and carbonatites, Gardiner complex, tertiary of East Greenland. *Chem. Geol.* 53, 207–217.
- Petrova, G.A., Talantsev, A.S., 1992. Melt inclusions in the Urals carbonatites (abstract). *Thermobarogeochemistry of Geological Processes*. Geoinformmark, Moscow, p. 52 (in Russian).
- Sabachenko, V.N., Gundobin, A.G., Sandimirova, G.P., Almkhamedov, E.A., Kalmychkova, T.N., 1994. Sr-isotopes in the rocks of formational type of near-fault alkaline carbonate-silicate metasomatites and related carbonatites. *Geol. Geofiz.* 3, 60–69 (in Russian).
- Sokolov, S.V., 1978. Study of inclusions of mineral-forming environments in carbonatite pyrochlore (abstract). *Thermobarogeochemistry in Geology*. Far East Scientific Centre, Vladivostok, pp. 62–63 (in Russian).
- Sokolov, S.V., 1981. New data on conditions of origin of Kovdor apatite-magnetite deposit. *Proc. USSR Mineral. Soc.* 5, 581–588 (in Russian).

- Sokolov, S.V., 1993. Geological Formational Types, Origin and Formation Conditions of Carbonatites. Geoinformmark, Moscow, 73 pp. (in Russian).
- Sokolov, S.V., 1994. Formation Conditions of the Oka Carbonatites (abstract). GAC–MAC Joint Annual Meeting, 16–18 May 1994. Waterloo, Ontario, Abstracts.
- Sokolov, S.V., 1995. Heterogeneity of Carbonatites and Related Rocks. Geoinformmark, Moscow, 47 pp. (in Russian).
- Sokolov, S.V., 1999. Melt inclusion phase composition in monticellite from carbonatites of the Oka complex, Quebec, Canada (abstract). *Terra Nostra* 6, 286–287.
- Sokolov, S.V., Veksler, I.V., Senin, V.G., 1999. Alkalis in carbonatite magmas: new evidence from melt inclusions. *Petrology* 7 (6), 602–609.
- Veksler, I.V., Nielsen, T.F.D., Sokolov, S.V., 1998a. Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implications for carbonatite genesis. *J. Petrol.* 39, 2015–2031.
- Veksler, I.V., Petibon, C., Jenner, G.A., Dorfman, A.M., Dingwell, D.B., 1998b. Trace element partitioning in immiscible silicate–carbonate liquid systems: an initial experimental study using a centrifuge autoclave. *J. Petrol.* 39, 2095–2104.
- Voznjak, D.K., Kvasnitsa, V.K., Krochuk, V.M., 1981. Hardened melt inclusions in the baddeleyite from the carbonatites of Sea-of-Azov area. *Dokl. USSR Acad. Sci.* 259, 952–955 (in Russian).
- Watkinson, D.H., 1970. Experimental studies bearing on the origin of the alkalic rock–carbonatite complex and niobium mineralization at Oka, Quebec. *Can. Mineral.* 10 (3), 350–361.
- Wen, J., Bell, K., Blenkinsop, J., 1987. Nd and Sr isotope systematics of the Oka complex, Quebec, and their bearing on the evolution of the sub-continental upper mantle. *Contrib. Mineral. Petrol.* 97, 433–437.
- Wendlandt, R.F., Harrison, W.J., 1979. Rare earth partitioning between immiscible carbonate and silicate liquids and CO₂ vapor: results and implications for the formation light rare earth-enriched rocks. *Contrib. Mineral. Petrol.* 69, 409–419.
- Wyllie, P.J., 1989. Origin of carbonatites: evidence from phase equilibrium studies. In: Bell, K. (Ed.), *Carbonatites: Genesis and Evolution*. Unwin Hyman, London, pp. 500–545.
- Zaitsev, A., Bell, K., 1995. Sr and Nd isotope data of apatite, calcite and dolomite as indicators of source, and the relationships of phosphorites and carbonatites from the Kovdor massif, Kola peninsula, Russia. *Contrib. Mineral. Petrol.* 121, 324–335.