

FLUID COMPONENT OF CARBONATITE MELTS

SOKOLOV, S. V.¹

¹ All-Russian Scientific-Research Institute of Mineral Resources; Staromonetnyi per. 31, Moscow 119017, Russia.
E-mail: vims@df.ru

Fluids play diverse and often major role in many magmatic processes. Their significance is especially great in carbonatite petrogenesis, as far as formation of carbonate melts under real values of T-parameter proved to be possible only in the presence of carbon dioxide - water fluid phase (Paterson, 1958; Wyllie, Tuttle, 1960). Later it was established that H₂O, CO₂ and F could be dissolved in considerable quantities in carbonatite melts, in which phase transformations occur in the presence of fluid which has substantially carbon dioxide-water composition.

Apart from indirect evidences being results of experimental petrology concerning model melts, participation of volatile components (H₂O, CO₂, F, Cl, S) in natural carbonatite forming systems is displayed by: 1) mineral parageneses of carbonatites composed by carbonates, micas, amphiboles, apatite, humite, serpentine, chlorites, sulfides; 2) fenitization halos around carbonatite stocks; 3) exocontact reaction zones, bordering carbonatites, which are enriched in ones or others of the above mentioned minerals; 4) joint occurrence in carbonatite minerals of primary melt inclusions (MI), containing fluid (gas + liquid) isolations, and syngenetic fluid inclusions (FI). The latter confirms saturation of carbonatite melts by fluids, which in the course of crystallization or during sharp decrease of outer pressure (influence of tectonic movements) separated volatile components as independent phase.

Results of inclusion studies from carbonatite minerals of Russia, Scandinavia, India, Canada and Eastern Africa using the methods of thermometry and cryometry, water leaches, Raman spectroscopy and gas chromatography allowed us to estimate quantitatively thermodynamic (PTVX) properties of fluid component of carbonatite-forming systems (Andersen, 1986; Jaireth et al., 1991; Morogan, Lindblom, 1995; Rankin, 1975, 1977; Samson et al., 1995,a,b; Sokolov, 1993; Ting et al., 1994 and our new data – see table).

Homogenization temperatures of MI in apatites and carbonates from carbonatites of the consecutive stages decrease from 950-900 to 500°C (Sokolov, 1996). Synchronous with them FI homogenize, as a rule, into liquid phase. Therefore in this temperature range of carbonatite formation, fluids were in liquid-like states that were characterized by increased density caused by outer pressure and/or rather high salinity. The last assertion is confirmed by presence in gas-liquid inclusions of daughter crystals – in the first place halite, nahcolite and sylvine and also calcite, dolomite, shortite and kalicinite.

These data completely coincide with results of bulk and individual analyses of FI, which characterize not only composition and salinity of liquid phase but also density of solutions trapped by inclusions. In many cases as regarding their composition, the cations are exclusively represented by alkalis; Na content being constantly higher than that of K, sometimes for 1-2 orders, and in the Oka massif (Canada) potassium is completely absent. At the same time alkaline-earth elements (Ca>Mg) are found in inclusions of minerals of the Kola Peninsula carbonatites, but these elements being in subordinate quantities relative to alkalis. Anionic composition of solution is rather constant, carbonate-chloride, with various relations between chlorine ion and carbonate or bicarbonate ions; however almost exclusively haloid solutions are known (Gulinskii, Russia; Fen, Norway; Oka complexes). Sulphate ion and fluorine are secondary components of FI carbonatites of the Kola Peninsula and Oka. Concentrations of soluble salts display significant ranges (from first to almost 50 wt. %). Density of water solutions in inclusions ranges from 0.58 to 1.26 g/cm³.

Composition of many inclusions corresponds or is very close to the system NaCl+H₂O±CO₂, whose phase diagram is well studied in geological important area of PTVX-parameters. If we know solution concentration, homogenization temperature of FI and formation temperature of the host mineral (which may be accepted as T_{hom} of syngenetic MI), a possibility emerges to estimate a value of fluid pressure. Our and literature data testify to the fact that carbonatitic magmatic systems are characterized by high values of fluid pressure, attaining 4.6-5.1 kbar (Kovdor and Gulinskii complexes, Russia; Oka, Canada – our data) and even 6.2 kbar (Sukulu complex, Uganda – Ting et al., 1994). Baric regime was characterized by instability both during all process of carbonatite formation and during its separate stages. By the end of carbonatite process, a decrease of pressure to 3.4-2.25 kbar is observed.

Pressure fluctuations resulted in stratification of fluid phase, which is testified by coexistence in one mineral of FI of different composition – aqueous, often of high salinity, and carbon dioxide ones or hydrocarbon ones which occur very seldom. Carbon dioxide inclusions as a rule are distributed in carbonatites locally. Gas-chromatographic analysis displays in general low to moderate CO₂ contents in carbonatite volatile phase (1.6-5.3 mol/kg H₂O), which very seldom exceed 20 mol/kg H₂O (Vuori-Yarvi complex, Russia). Increased concentrations of CO₂ by the end of process are established in the carbonatites of the Kola Peninsula (Sokolov, 2001).

Among hydrocarbons methane occupies a dominant position, its fraction in volatile phase is in average 1-2 orders inferior relative to carbon dioxide. Independent hydrocarbon and aqueous-hydrocarbon (methane) FI found in carbonates and apatites from the Kovdor and Sukulu carbonatites (Sokolov, 1993; Ting et al., 1994) are characterized by low salinity.

Chlorine and fluorine belong to characteristic volatile components of the carbonatite-forming systems. Chlorine is easily redistributed into fluid phase, whereas fluorine is retained by carbonate melts and is bound in mineral lattices. Therefore, low fluorine contents are fixed in liquid phase of FI (0.7-1.3 mg/l).

The above data allow us to make a conclusion about sufficient similarity of composition and other properties of carbonatite fluids related to alkaline-ultrabasic complexes of various regions. In the course of development of the carbonatite process general fluid saturation increases, but fluid pressure decreases, role of CO₂ and K increases relative to Cl and Na correspondingly, hydrocarbon FI obtain wider development. Therefore, conditions of generation and evolution of the fluids themselves, as well as parent for them carbonatite melts are rather similar in general features.

Properties of carbonatite fluids

Massifs	Composition	Na/K	C, wt. %	d, g/cm ³	P _{fl} , kbar
Russia: Kovdor, Vuori-Yarvi, Turii Mys, Gulinskii	Na, K, Mg, Ca, Cl, CO ₂ ± (SO ₃ , F, CH ₄)	1.8-14	6-50	0.75-0.83	2.75-5.15
Scandinavia: Fen, Alnö	Na, K, Cl, CO ₂ , Mg(?), Fe(?)	>1	2-35	0.76-1.10	4.5
India: Sung Valley	Na, K, Cl, CO ₂	–	9-38	–	3.5-4.7
Canada: Oka	Na, K, Cl, CO ₂ , SO ₃ , Ca(?)	3.5->275	4.2-4.9	0.77-1.26	3.8-4.9
Eastern Africa: Wasaki, Sukulu, Tororo	Na, K, Cl, CO ₂ ± CH ₄	2.4-16	12.1-42.4	0.58-1.17	2.25-6.2

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