# Origin and evolution of carbonatite magmas

## L.I.Panina

*Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences,*

*Novosibirsk, Russia*

**Inroduction**

Nowadays, genetic discussions focus mainly on the sources and mechanisms of formation of carbonatite melts, their initial composition, and character of transformation during crystallization. There are three most popular concepts on the *sources* and *mechanisms of carbonatite melt formation*: (a) carbonatite melts are formed in the mantle as primary segregations of interstitial liquid, (b) carbonatite melts appear owing to liquid immiscibility in a parental deeply derived nephelinite or melilitite magma during its high-temperature evolution, and (c) carbonatite melts are residual low-temperature products of the crustal differentiation and fractionation of alkaline magmas.

*The initial composition of carbonatite melts* is a topic of considerable debate. It varies widely in nature with respect to both carbonate and silicate components and the degree of enrichment in alkalis and trace components. The enrichment of alkalis in some extrusive carbonatites was considered by some researchers as a characteristic of primary carbonatite magmas, and the paucity of alkaline carbonatites in nature was explained by the loss of alkalis from the melts during their crystallization. In contrast, other authors argued that calc-alkaline carbonatite melts are primary, and the enrichment of alkalis is related to late stages of their evolution.

The analysis of melt inclusions in the minerals of carbonatites and spatially associated ultrabasic, basic, and alkaline rocks from various regions of the world has provided answers to many of questions.

**Review of melt inclusions**

The results of studies of melt inclusions in minerals of different alkaline-ultrabasic and alkaline-basic carbonatite complexes, kamafugites, lamproites and kimberlites are discussed. The review showed that minerals in all above-mentioned rocks contain melt inclusions of silicate, silicate-salt and carbonate-salt composition. The earliest olivines contain mainly primary silicate melt inclusions. Later formed clinopyroxene, perovskite and melilite were found to additionally contain primary silicate-salt and, less often, carbonate-salt melt inclusions. The latter are more typical of late crystallization stage minerals - apatite, foids and carbonates. Salt inclusions were also present as secondary inclusions in earlier minerals (for example, in olivine from the Udachnaya-East kimberlites, Yakutia). All melt inclusions are enriched with $CO_2$, Na, K, F, Cl, P, whose content gradually increases from silicate and silicate-salt to salt melts (Table 1.). *It is beyond doubt that these volatile salt components are of mantle origin.*

Most likely, they accumulated in deep faults which resulted from mantle activity and development of plumes. Volatile components there, probably, interacted with mantle source, realizing its metasomatic processing and promoting origin of mantle-derived magmas. The concentration of volatiles, without doubt, affected the degree of melting of mantle source and the composition of Si-undersaturated primitive magmas. The latter is inferred from the composition of primary silicate inclusions in olivine.

Crystallization of mantle-derived magma begins at high temperature ($>>$1320-1350$^o$C) with separation of mafic minerals, manly olivine. Gradual accumulation of volatile and salt components in generated primitive melts caused their fluidization, which is implied by the occurrence of primary silicate-salt inclusions in clinopyroxene, perovskite, melilite. Fluidization led to pulsating separation and movement of melt from mantle sources to upper horizons.

The most fluidized magma often formed diatremes and explosion pipes (for example, kimberlites). When the content of salt components reached critical values, magmas became inhomogeneous. At about 1300$^o$C it exhibited silicate-carbonate liquid immiscibility. Evidence for this comes from the observations of immiscibility in silicate-carbonate inclusions during heating experiments. Immiscibility was accompanied by redistribution of elements: most part of fluids together with Ca passed from magma to carbonate-salt fraction (*initial carbonatite melt*), while silicate melt, respectively, became depleted in these components and was gradually Si-saturated. Immiscible silicate and carbonate fractions were either spatially separated or were in equilibrium with each other. In the latter case, when the equilibrium was disturbed, immiscibility disappeared and melts became homogeneous again.

In case of spatial separation, silicate and silicate-carbonate melts further evolved in different ways (Fig. 1). Silicate melts on slow cooling differentiate, fractionate and form rocks at upper lithosphere. Carbonatite melts reached higher horizons and on rapid uplifting and rapid quenching preserved their initial composition (for example, carbonatite lavas from Oldoinio Lengai volcano in Tanzania). Study of salt inclusions in minerals show that, when uplifting and cooling was slower, initial carbonatite melts in the 0range from 1200 to 800-600$^o$C separated into immiscible fractions of alkali-sulfate, alkali-phosphate,

# Table 1. Homogenization temperatures and chemical compositions (wt.%) of inclusions of alkaline carbonatite melts and their immissible fractions in minerals.

| Rock | Host mineral | Inclusion type | Thom°C | CaO | Na$_2$O | K$_2$O | SO$_3$ | P$_2$O$_5$ | Cl | F | MgO | FeO | SrO | BaO | SiO$_2$ | Al$_2$O$_3$ | Referenes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Alkaline ultrabasic rocks, Krestovskii intrusion** | | | | | | | | | | | | | | | | | |
| Olivine- | Prv, core | Si-carb | 1250* | 22.81 | 4.08 | 12.11 | 4.31 | 0.48 | - | - | 1.64 | 3.02 | 0.20 | 0.86 | 9.87 | 1.55 | Panina et al., |
| monticel- | Ap | alk-carb | 800* | 22.07 | 26.65 | 1.55 | 4.51 | 1.41 | 6.03 | - | 0.84 | 0.35 | 1.26 | 0,00 | 1.82 | 0.11 | 2001; |
| lite-melili- | Mtc | alk-sulf | 890 | 9.95 | 26.10 | 9.90 | 13.10 | 3.94 | 1.51 | - | 1.40 | 1.08 | 0.94 | 0.55 | 1.88 | 0.00 | Panina, |
| te | Mtc | alk-phosph | 890 | 24.98 | 22.84 | 3.30 | 3.05 | 28.29 | 0.05 | - | 1.67 | 0.49 | 1.70 | 0.35 | 1.96 | 0.00 | 2005. |
| " | Cpx | alk-chlor | 840 | 2.79 | 26.33 | 11.64 | 0.10 | 0.10 | 31.01 | - | 0,00 | 1.34 | 0,00 | 0,00 | 4.18 | 0.69 | " |
| " | Cpx | Ca-carb | 810 | 53.79 | 1.10 | 0.84 | 0.00 | 0.16 | - | - | 0.27 | 0.22 | 0.93 | 0,00 | 0.82 | 0.05 | " |
| **Alkaline ultrabasic rocks, Guli pluton** | | | | | | | | | | | | | | | | | |
| Ca-carbo- | Prv, core | alk-carb | - | 27.75 | 24.23 | 1.01 | 0.00 | - | 0.07 | - | 0.00 | 0.00 | 0.34 | - | - | - | Kogarko et al., |
| natite | Prv, core | Ca-carb | - | 54.60 | 0.00 | 0.00 | 0.27 | - | 0.00 | - | 0.00 | 0.00 | 0.94 | 0.00 | - | - | 1991 |
| **Alkaline ultrabasic rocks, Gardiner complex** | | | | | | | | | | | | | | | | | |
| Melili- | Mel | alk-carb | 1060 | 19.19 | 28.83 | 0.48 | - | 0.84 | - | - | 0.68 | 0.95 | 1.46 | 12.04 | 0.73 | 0.1 | Nielsen et al., |
| tolite | | | | | | | | | | | | | | | | | 1997 |
| **Alkaline ultrabasic rocks Pian di Celle Volcano, Italia** | | | | | | | | | | | | | | | | | |
| Venanzite | Ol | Si-carb | >1180 | 22.04 | 0.61 | 1.61 | 0.38 | 0.42 | 0.12 | - | 6.08 | 4.02 | 0.46 | 0.08 | 21.54 | 3.29 | Panina et al., |
| (kamafugite) | Ol | Ca-carb | 700 | 54.17 | 0.08 | 0.05 | 0.01 | 0.17 | 0.01 | - | 0.34 | 0.37 | 0.47 | 0.11 | 1.51 | 0.00 | 2003 |
| **Alkaline basalts, Eastern Pamirs** | | | | | | | | | | | | | | | | | |
| Fergusite | Cpx | Si-carb | ≥1000 | 37.24 | 2.85 | 1.97 | - | - | - | - | 0.19 | 5.54 | 0.34 | 0.92 | 16.12 | 3.41 | Solovova |
| porphyry | | | | | | | | | | | | | | | | | et al, 1996 |
| **Alkaline-basic rocks, Mushugai Khuduk complex, Mongolia** | | | | | | | | | | | | | | | | | |
| Mt-Ap | Ap | phosph-sulf | 1290* | 46.5 | 0.25 | - | 29.85 | 16.85 | - | 1.35 | - | - | 0.95 | - | 1.35 | - | Andreeva, |
| Theralite | Ap | phosph-carb | 1200* | 54.09 | 0.10 | - | 0.50 | 17.64 | - | 1.78 | - | 2.59 | - | - | 1.20 | - | 2000 |
| Celestite- | Fl | phosph-sulf | 670 | 35.00 | 2.70 | 3.90 | 33.10 | - | 0.10 | 5.50 | - | - | 9.90 | 1.20 | - | - | Naumov |
| fluorite rock | Fl | chlor-sulf | 670 | 26.00 | 11.10 | 3.70 | 29.00 | - | 10.90 | 2.10 | - | - | 5.70 | 1.90 | - | - | et al, 1988 |
| **Synnyr ultrapotassic massif** | | | | | | | | | | | | | | | | | |
| K-felds- | Ap | sulf-carb | 1050* | 30.90 | 7.90 | 4.50 | 24.80 | 0.80 | - | 0.20 | - | - | 1.50 | - | - | - | Panina, |
| pathized | Ap | alk-sulf | 1020 | 13.72 | 14.66 | 0.87 | 46.14 | 8.83 | 0.02 | - | 0.03 | 0.01 | 8.83 | 0.14 | 0.01 | 0.00 | Usoltseva, |
| ditroite | Ap | Ca-carb | 700 | 53.80 | 0.03 | 0.00 | 0.00 | 0.46 | 0.01 | - | 0.2 | 0.27 | 2.50 | 0.01 | 0.17 | 0.08 | 2003 |
| **Khani alkaline-basic massif** | | | | | | | | | | | | | | | | | |
| Pyroxenite | Cpx | Ca-carb | - | 56.61 | 0.03 | 0.01 | 0.03 | 0.08 | - | 0.02 | 0.14 | 0.93 | - | 0.02 | 2.63 | 0.10 | Panina et al., |
| | | | | | | | | | | | | | | | | | 1987 |
| **Malyi Murun ultrapotassic massif, Central Aldan** | | | | | | | | | | | | | | | | | |
| Mtc-Me-Ol | Mtc | Si-carb | 1280* | 27.18 | 5.75 | 2.39 | 10.81 | 0.33 | 0.34 | 0.45 | 5.83 | 0.85 | 0.21 | 0.11 | 12.90 | 0.36 | Panina, |
| Lamproite | Ap | sulf-carb | 1170* | 25.20 | 16.31 | 0.96 | 16.90 | 9.36 | 0.09 | - | 0.01 | 0.02 | 1.11 | 0.06 | 0.03 | 0.00 | Usoltseva, |
| Mtc-Me-Ol | Ol | alk-sulf | >1000 | 17.86 | 20.77 | 0.37 | 37.27 | 0.13 | 0.66 | 0.38 | 5.09 | 0.57 | - | 0.09 | 7.73 | 0.00 | 1999, 2000 |
| Lamproite | Ap | Ca-carb | 890 | 53.01 | 0.28 | 0.04 | 0.08 | - | - | - | 0.01 | 0.00 | 2.00 | 1.73 | 0.02 | 0.00 | " |
| **Lamproites, Molbo R., Central Aldan** | | | | | | | | | | | | | | | | | |
| Lamproite | Ap | alk-sulf | - | 0.25 | 8.17 | 39.00 | 36.43 | 0.51 | 0.01 | - | 0.00 | 0.08 | - | - | 0.00 | 0.18 | Panina, |
| | | | | | | | | | | | | | | | | | Konev, 1995 |
| **Cocites, Vietnam** | | | | | | | | | | | | | | | | | |
| Cocite | Cpx | Si-carb | - | 24.58 | 14.52 | 0.20 | - | 0.19 | - | - | 0.04 | 0.24 | 2.32 | 0.05 | 0.91 | 0.00 | Panina et al., |
| | | | | | | | | | | | | | | | | | 1998 |
| " | Phl | sulf-carb | - | 28.72 | 0.26 | 0.05 | 15.36 | - | - | - | 0.41 | 0.48 | 3.79 | 29.96 | 0.78 | 0.46 | New datas |
| " | Ap | Ca-carb | - | 36.72 | 0.10 | 0.81 | - | 1.24 | - | - | 0.73 | 0.80 | 1.79 | 0.08 | 3.60 | 1.27 | " |
| **Kimberlites, Udachnaya-East pipe, Yakutia** | | | | | | | | | | | | | | | | | |
| Kimberlite | Ol | alk-chlor | - | | 33,9 | 5,6 | | | 60,5 | | | | | | | | Golovin |
| Kimberlite | Ol | alk-carb | - | 43,41 | 11,08 | 4,87 | 1,61 | | - | | 0,54 | 0,63 | 1,01 | 0,00 | | | et al, 2007 |

alkali-fluoride, alkali-chloride, and Fe-Mg-Ca-carbonate compositions . Under favorable conditions, milti-phase immiscibility could result in different types of carbonatites: from common calcite compositions to S-P-Cl-enriched compositions (like Western Transbaikalia, Mushugai-Khuduk in Mongolia, Mountain Pass in California and Tomtor in Eastern Siberia).

## Conclusions

1. The available data on melt inclusions in minerals suggest primarily that carbon dioxide, alkalis, halides, sulfur, and phosphorus are intrinsic components of all deeply derived alkaline magmas and have obviously a mantle origin.

2. During the ascent, crystallization, and fractionation of early high-magnesium minerals, silicate–carbonate liquid immiscibility phenomena occur at high temperatures (about 1300°C) in deep magmas owing to rapid changes in temperature and pressure.

3. The carbonate–salt melts enriched in Ca, alkalis, S, F, Cl, and P spatially separated from their parental silicate magmas are *primary carbonatite melts*.

4. In spite of potassic or sodic type of alkalinity of

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spatially associated rocks, the processes of carbonatite melt segregation, the enrichment of particular volatile components, and evolutionary transformations occurring in the melts are uniform, even through carbonatites relate to different rock associations.
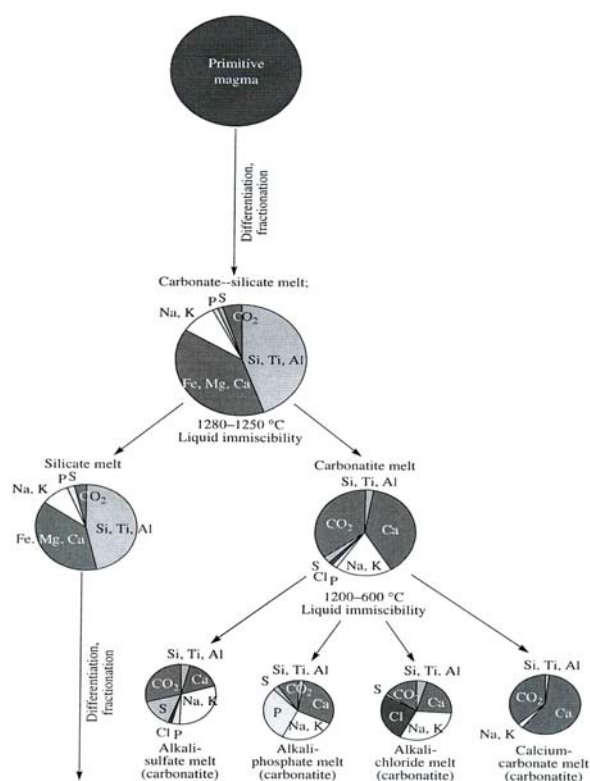


**Fig. 1.** Flow chart illustrating the mechanism of two-phase carbonate-silicate liquid immiscibility and polyphase carbonate-salt liquid immiscibility in deep-seated magmas.

5. In response to a considerable decrease in temperature and pressure, carbonatite melts become unstable and unmix into immiscible fractions: alkali-sulfate, alkali-phosphate, alkali-chloride, alkali-fluoride, and essentially calcium-carbonate melts. The phenomena of multistage carbonate–salt liquid immiscibility proceeds within a considerable temperature range, from 1200°C and higher to 800–600°C. The essentially calcium-carbonate melts are final exhausted products of the evolution of primary carbonatite melts, which complete their unmixing after the removal of other immiscible salt fraction.

6. In natural basic–ultrabasic macroscopic systems, polyphase carbonate–salt liquid immiscibility usually occurs during slow cooling and prolonged evolution of deep alkaline melts in the Earth's crust. Under favorable conditions, it may result in the formation of various types of intrusive carbonatites, including widespread calcite carbonatites and rare rocks enriched in sulfur, phosphorus, and halides.

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