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The Formation Conditions of Labuntsovite-Group Minerals in the Kovdor Massif, Kola Peninsula

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Abstract—In the Kovdor massif, labuntsovite-group minerals occur in dolomite carbonatite veins (labuntsovite-Mg), in a natrolite–calcite vein (lemmleinite-Ba and labuntsovite-Fe), and in calcite pockets and veinlets cutting fenites (late labuntsovite-Mg). They are closely intergrown with paragenetic carbonates, and this makes it possible to estimate their crystallization temperature from the fluid inclusions entrapped in dolomite (≥265°C) and calcite (175–225°C). The earlier labuntsovite-Mg was formed under relatively acidic conditions, whereas later labuntsovite–calcite mineralization was derived from alkaline solutions.

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The tempertature of carbonatite formation, in particular, in the Kovdor massif has been precisely estimated (Sokolov, 1993); however, not all minerals of carbonatites and accompanying rocks have been objects of thermometric study; this includes the labuntsovite-group minerals. In this paper, an attempt has been made to estimate the temperature characterizing formation of labuntsovite-bearing mineral assemblages in rocks from the Kovdor massif, where labuntsovite-group minerals with the general ideal formula $(Na\text{–}K\text{–}Ca\text{–}Sr\text{–}Ba)_{2-6}[(Mg\text{–}Mn\text{–}Fe\text{–}Zn)_{0-1}(Ti\text{–}Nb)_4(Si_4O_{12})_2] \cdot nH_2O]$ occur in various settings (*Mineraly* ..., 2003). Their identification based on IRS has been carried out by N.V. Chukanov of the Institute of Problems of Chemical Physics, Russian Academy of Sciences (Chernogolovka). Mineralogical study of the samples and determination of the chemical composition of carbonates was performed using optic microscopy, XRD, EPMA, spectrometry, and luminescent analysis.

Two samples characterize the veins of late dolomite carbonatite. One vein occurs in the carbonatite–phoscorite stock of the rare-metal–apatite–magnetite deposit (sample I) and another in pyroxenite (sample IV). Both veins are composed of ferroan dolomite-2, which has enriched levels of Fe and Mn (5.47 wt % FeO and 0.53 wt % MnO, as a mean of three analyses) as compared with rock-forming dolomite-1 (3.03 wt % FeO and 0.35 wt % MnO, as a mean of four analyses, data from R.P. Liferovich and the author). Crystals of labuntsovite-Mg, ancylite, and catapleite occur as ingrowths in the outer zones of ferroan dolomite-2 rhombohedra and form on them on along with dolomite-3, calcite, and strontianite, which are the most recent phases to form in geodes and caverns.

Sample II has been taken from the zonal natrolite–calcite vein hosted in ijolite. This sample corresponds to the central zone, enriched in calcite. Lemmleinite-Ba, occasionally found together with labuntsovite-Fe, is associated with major minerals and catapleite in cavernous cavities. The similar natrolite–calcite and almost monomineralic calcite veins crosscut ijolites, fenites, phoscorites, and carbonatites, including the latest dolomite varieties and relate to the derivatives of the postcarbonatite stage in the Kovdor massif (Epstein et al., 1972). Calcite of these veins is distinguished from calcite of all earlier rocks (calcite-bearing ijolites, phoscorites, carbonatites) by the low concentrations of typomorphic admixtures—Mg, Mn, Fe, Sr, Ba, and REE (Sokolov, 1984). Identical calcite occurs in pockets and veinlets cutting fenites (sample V). Labuntsovite-Mg is localized in the outer zones of large calcite rhombohedra (5–7 mm across) and also overgrows them.

The primary inclusions of the mineral-forming medium were studied in thin sections of all samples containing labuntsovite, dolomite, calcite, and natrolite. Sporadic and very small gas–liquid inclusions were revealed in the minerals of labuntsovite group and in natrolite. The inclusions suitable for homogenization temperature (T_{hom}) measurements have been found only in carbonates.

The rock-forming ferroan dolomite-1 from carbonatite veins (samples I and IV) contains primary melt and the accompanying fluid inclusions (Fig. 1), including sporadic vacuoles and their groups, which are spatially isolated from crosscutting microfractures, and related chains of secondary gas–fluid inclusions.

Melt inclusions consist of crystalline aggregate of solid phases (partly isotropic) and two-phase fluid segregation in which the homogenization (gas → liquid) occurred at 190–220°C. The occurrence of primary

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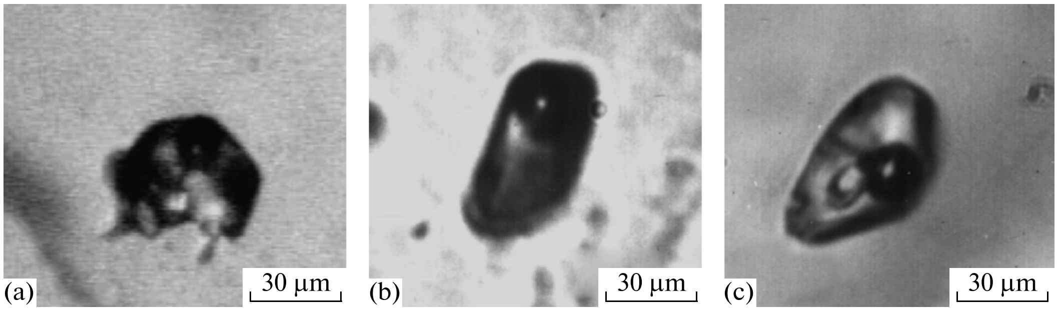

Fig. 1. Inclusions in ferroan dolomite-1: (a) melt, (b) two-phase fluid (gas + liquid), (c) multiphase fluid (gas + liquid + isotropic and anisotropic crystalline phases).

fluid inclusions in the host mineral indicates that the carbonatite melts parental for the veins were saturated with aqueous fluid.

The first signs of crystallite dissolution in melt inclusions appeared beginning from 250°C and notable melting was observed at temperatures reaching 380–400°C. We failed to achieve a homogenization of the inclusions, because of the intense decrepitation of secondary fluid inclusions with T_{hom} no higher than 240°C, which damaged both melt inclusions and the host mineral at 320–430°C. The retained smaller melt inclusions underwent depressurization at 460–515°C, most likely due to the high pressure of the fluid phase containing therein. Similar phenomena were induced by heating of inclusions in ferroan dolomite-2.

It should be noted that when rock-forming ferroan dolomite occurs in similar carbonatite veins devoid of minerals from labuntsovite group, it contains few fluid inclusions, so that we were able to homogenize melt inclusions at 530–610°C.

The primary gas–liquid and multiphase fluid inclusions (gas + liquid + 1-2-3 solid phases) are recognized in ferroan dolomite-1 (Fig. 1b, 1c). The daughter solid phases, which are mostly isotropic, have nearly cubic, rounded, or short-prismatic habit (5–7 vol % of all inclusions). The relatively high temperature of dissolution onset (120–130°C) as compared with KCl and slow dissolution kinetics show that the isotropic phase is halite. The hermetic multiphase fluid inclusions are homogenized into liquid at 290–360°C.

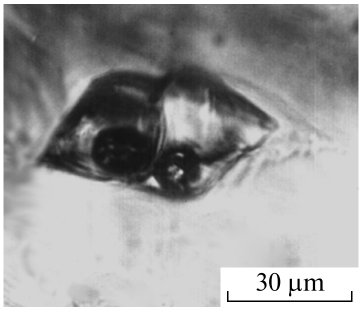

Fig. 2. Crystal–fluid inclusion in ferroan dolomite-2.

The rhombohedral ferroan dolomite-2 from geodes and caverns contains primary inclusions of the following types: (1) rare melt inclusions in central parts of crystals; (2) crystal–fluid inclusions with 35–45% of total volume occupied by gas and liquid; and (3) fluid inclusions (gas + liquid ± isotropic crystalline phase). It is noteworthy that only fluid inclusions were established in the outer zones of rhombohedra containing labuntsovite-Mg inclusions.

The melt inclusions retained their integrity up to 380–450°C, and the host mineral cracked into small fragments above this temperature range. When crystal–fluid inclusions are being heated, a gas bubble disappears at 150–190°C, then isotropic solid phases dissolve at 180–230°C, and later on, these inclusions decrepitate at 340–410°C.

Primary fluid inclusions in dolomite-2 are similar to those in dolomite-1. A few of them opened at 185–270°C; a majority remained closed and homogenized into liquid from 335°C (inner parts of crystals) to 265°C (in outer zones). The homogenization temperature of the secondary gas–liquid inclusions was 190–215°C. Primary inclusions in the late dolomite-3 correspond to these inclusions in phase composition and homogenization temperature.

In calcites from samples II and V, the primary gas–liquid inclusions sharply prevail over the fluid inclusions with solid daughter phases (Fig. 3). In both samples, the inclusions are similar in morphology and dimensions. They are elongated (10–20 μm in length) or equant (5–25, occasionally up to 40 μm across). When being heated, almost all inclusions remained hermetic and homogenized in liquid at 180–210°C (sample II) and 175–225°C in sample V.

According to our data, the primary gas–liquid inclusions in calcite from other postcarbonatite calcite and natrolite–calcite veins free of labuntsovite mineralization homogenized at 170–195°C.

The homogenization temperatures of inclusions in dolomite and calcite are summarized in the table. The

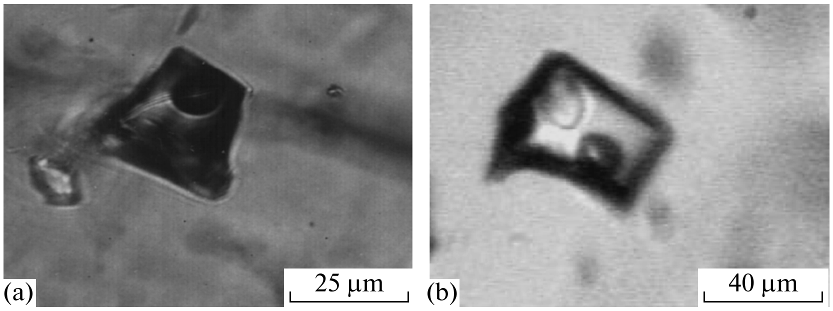

Fig. 3. Inclusions in calcite: (a) two-phase fluid (gas + liquid) and (b) multiphase fluid (gas + liquid + isotropic crystalline phase).

close spatiogenetic links of these carbonates to the in- and overgrown minerals from the labuntsovite group give us grounds to suppose that both are characterized by a nearly identical formation temperature.

The study of primary inclusions in the consecutively arising minerals allows us to trace the evolution of the aggregative state of mineral-forming medium from the phase composition of the inclusion fills at the moment of their homogenization. Available data show that the phase composition of inclusions in dolomite gradually changes with transition of fluidized carbonatite melt to hydrothermal solution. The ferroan dolomite-1 crystallized during magmatic stage, whereas dolomite-2 was formed in geodes from a heterogeneous system containing residual portions of melt–brine and a separate fluid phase. The former was entrapped into sporadic melt and predominant crystal–fluid inclusions, while the latter was captured by fluid inclusions. The later labuntsovite-Mg, ancylite, catapleite, dolomite-3, calcite, and strontianite crystallized from solution under conditions of dropping *PT* parameters.

The amount of those primary fluid inclusions, the damage of which in the process of heating was induced by internal pressure rather than by decrepitation of secondary inclusions, was substantially diminished. This indicates that the fluid pressure was released by the time when hydrothermal mineral assemblages began to crystallize in geodes. Such a variation in pressure facilitated an increase in the solution acidity (Shcherbina, 1967), which, in turn, led to enrichment of dolomite-2 in Fe and Mn as more acid elements than Ca and Mn. The further replacement of dolomite-3 (Ca, Mg) with calcite (Ca) and joint crystallization of strontianite (Sr) are evidence for increase in alkalinity, i.e., for acidity wave propagation in carbonatite-forming systems (Samoilov, 1977).

Inasmuch as the primary fluid inclusions in calcite from samples II and V avoided decrepetation, which requires a high internal pressure of aqueous solution, we assume that fluid pressure during the formation of natrolite–calcite veins in ijolite and calcite veinlets and pockets in fenite did not exceed 400 atm (Naumov et al., 1966). Therefore it is quite reasonable to suggest that the crystallization temperature of this calcite and the paragenetic lemmleinite-Ba, labuntsovite-Fe, and labuntsovite-Mg, even if exceeded, and then not by much, measured $T_{\text{hom}} = 175–225$°C. In addition, the experimental results on the synthesis and breakdown of natrolite determine the upper boundary of its stability as no higher than 250°C (Senderov and Khitarov, 1966). The formation of dolomite rather than calcite together with natrolite at such a temperature indicates an alkaline reaction of the mineral-forming medium.

Based on the aforementioned data, the following conclusions can be drawn:

(1) The appearance of hydrothermal association from geodes and caverns in dolomite carbonatites of the Kovdor massif is genetically related to the carbonatite process.

(2) In the course of Fe-dolomite carbonatite formation, the mineral-forming medium evolved from fluid-saturated melt to a hydrothermal solution against the background of temperature and fluid pressure drop.

(3) Mineral assemblages including hydrous labuntsovite-Mg, ancylite, and catapleite were formed from a residual fluid at the postmagmatic stage completing carbonatite formation.

(4) The crystallization of minerals pertaining to the labuntsovite group and associated with calcite in ijolites and fenites postdated carbonatite formation and developed at somewhat lower temperature than formation of labuntsovite-Mg in dolomite carbonatite and at a lower concentration of solution.

Homogenization temperature (°C) of inclusions in carbonates associated with minerals of the labuntsovite group

Host mineral	Inclusion type	
	melt (crystal–fluid)	fluid
Dolomite-1	>460–515, 530–610	290–360
Dolomite-2	>380–450 (340–410)	265–335
Dolomite-3	Do not occur	190–215
Calcite	″	175–225

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