

# Dolomite-calcite textures in early carbonatites of the Kovdor ore deposit, Kola peninsula, Russia: their genesis and application for calcite-dolomite geothermometry

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**Abstract.** In early calcite carbonatites of the Kovdor ore deposit four morphological types of dolomite are represented. In the first type, dolomite microcrystals occur as lamellae enclosed by optically continuous calcite. In the second, dolomite microcrystals occur as segmented rods, plates and xenomorphic grains, enclosed by optically discontinuous calcite, and in the third, dolomite is represented by grains of various morphologies, situated along calcite grain boundaries. The fourth type of dolomite occurs as a fine-grained aggregate, which develops along grain boundaries and cleavage cracks of calcite. From microscopic, scanning electron microscope and microprobe studies of these different types of dolomite microcrystals, as well as the calcite associated with them, it can be concluded that the first type of dolomite was exsolved from magnesian calcite during cooling. The second, and the third types of dolomite microcrystals were formed by recrystallization. The fourth type of dolomite was formed by metasomatic dolomitization. As the result of these two processes – recrystallization and metasomatic dolomitization – early dolomite microcrystals seldom occur. The composition of the early-formed primary magnesian calcite yielded temperatures of exsolution of dolomite from magnesian calcite between 665 and 700°C.

## Introduction

Calcite-dolomite intergrowths, while common in high-temperature marbles, are relatively rare in carbonatites. Dolomite crystals occur as rods, segmented rods, plates and xenomorphic grains enclosed in optically continuous and/or discontinuous calcite (van der Veen 1965; Carpenter 1967; Puustinen 1974; Puhon 1976, 1984; Kretz 1988).

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Phase relations in the system  $\text{CaCO}_3\text{-MgCO}_3$  have been summarised by Goldsmith (1983) and are the basis of a geothermometer based on the exsolution of dolomite from magnesian calcite. However, Kapustin (1983a, b, 1987) studied calcite carbonatites from a variety of Russian carbonatite complexes and concluded that dolomite microcrystals in calcite are due to metasomatic dolomitization and that the calcite-dolomite geothermometer is not applicable to carbonatites.

## Carbonatites of Kovdor ore deposit

The Kola peninsula of Russia contains many carbonatite and alkaline complexes that range in age from 360–380 Ma (Kramm et al. 1993). Included among these is the alkaline-ultrabasic Kovdor massif, which consists of a series of intrusions of silicate rocks and carbonatites. Rock types include olivinites, pyroxenites, melilite rocks, ijolite-melteigites, phoscorites, carbonatites and nepheline syenites. The complex is surrounded by a metasomatic aureole of fenite. The Kovdor ore deposit (Fe, P, Zr) is situated in the southwest part of the complex. The ore deposit is a stockwork of steeply dipping veins of phoscorites and carbonatites. The phoscorites were formed before the carbonatites and have variable amounts of apatite, forsterite, magnetite and calcite.

Several varieties of carbonatites have been recognised at Kovdor by Kapustin (1971) and Krasnova and Kopylova (1988). These carbonatites are subdivided as follow:

1. Early carbonatites – calcite with forsterite and phlogopite ( $C_I$ ); calcite with tetraferriphlogopite ( $C_{II}$ ), and
2. Late carbonatites – dolomite ( $C_{III}$ ); calcite-dolomite with ilmenite ( $C_{IV}$ ).

This paper present the results of a detailed study of dolomite and calcite from the  $C_I$  carbonatites.

## Methods of investigations

Dolomite and calcite are easily distinguished with the aid of the Alizarin Red S stain. Specimens were examined microscopically by a Fedorov universal stage to ascertain the angular relationship between the optic axes of calcite and dolomite, and by SEM (scanning electron microscope; Hitachi S-430) to determine crystal morphology, size of dolomite microcrystals, dolomite orientation within cal-

cite crystals, and to estimate the amount of dolomite microcrystals within the calcite hosts. For SEM investigations specimens of carbonatite  $10 \times 10 \times 5$  mm and cleaved calcite crystals 0.5 to 10.0 mm across were used. These were etched in 1% HCl for 1, 7 and 15 s at room temperature before being vacuum-coated with Au.

Analyses of the carbonatite samples were made by Polezhaeva in the laboratory of the Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Apatity. Electron-microprobe analyses were obtained using a CAMECA MS-46 instrument with wavelength-dispersion spectrometers. The following analytical standards were used: diopside (for Ca), pyrope (Mg), ilmenite (Fe), rhodochrosite (Mn), celestine (Sr). Instrumental conditions were: 20 kV accelerating voltage (25 kV for Sr), 20 nA beam current. A 10  $\mu\text{m}$  (Table 1) and a 5  $\mu\text{m}$  (Table 2) diameter defocussed beam was used during analyses. Mineral compositions in Table 1 are averages of five spots within a single calcite grain. Standard deviations (1-sigma) were estimated as 0.21–0.56% for CaO, 0.04–0.08 for MgO, 0.01–0.05% for FeO, MnO, 0.03% for Sr – calcite; 0.29–0.74% for CaO, MgO, 0.06–0.07% for FeO, 0.02–0.05% for MnO, 0.03% for SrO – dolomite. The  $\text{CO}_2$  was calculated by stoichiometry based on 1 C for calcite and 2 C for dolomite per formula unit.

### Dolomite and calcite from early carbonatites $C_1$

Dolomites are found in all stages of carbonatite activity at Kovdor. Four morphological types of dolomite were recognised in the early  $C_1$  carbonatites. Type 1 dolomite occurs within calcite grains. Figure 1 shows that the type 1 dolomite microcrystals form parallel lamellae whose lengths range from 50 to 300 microns with diameters from 5 to 45 microns. These lamellae are in optical continuity. Dolomite microcrystals are homogeneous and have constant diameter along their length. Dolomite and enclosing calcite have essentially parallel optic axes. In two samples the optic axis of dolomite was perpendicular to that of the enclosing calcite, a feature also reported by Kretz (1988) in marbles.

The amount of dolomite contained within a discrete calcite grain is between 9.0 to 12.0 vol.%. This was determined in sections normal to the length of the lamellae, this being the most suitable orientation (Puhan 1976).

Type 1 dolomite is always found in the centre of discrete calcite grains.

Type 2 dolomite occurs within calcite grains along with type 1 dolomites. Type 2 dolomite microcrystals are more abundant than type 1 and have a variable morphology of rods and plates consisting of several segments (Fig. 2a, b); sometimes a xenomorphic grain of dolomite is present within calcite (Fig. 2c). Rods and plates do not all extinguish simultaneously nor are their optic axes parallel to the host calcite. Variation among 14 measurements was 15–45°. They range in length from 50 to 500 microns and have diameters from 25 to 100 microns. The content of dolomite within individual calcite grains was 4.0 to 6.5 vol.%. Xenomorphic dolomite grains have different sizes (0.3–1.2 mm) and morphology (Fig. 2c) and with optic axes varying from that of the enclosing calcite of 20 to 85° (on 21 measurements). It is concluded that type 2 dolomite is not regularly distributed within the calcite.

Type 3 dolomite occurs as discrete grains distributed along the grain boundaries of the calcite (Fig. 3). This type of dolomite shows variable morphology, commonly with “small crystal faces”, and is associated with grains of forsterite, phlogopite, apatite and magnetite.

Type 4 dolomite occurs as fine-grained aggregates along calcite grain boundaries and cleavage cracks within calcite crystals (Fig. 4). An association with tetraferriphlogopite, clinohumite and tremolite is typical.

### Relationships between various dolomite types

The carbonatite  $C_1$  veins can be divided into four distinct groups on the basis of morphology, size, and orientation of the enclosed dolomite grains. The first group, rarely observed, contains both type 1 and type 2 dolomite crystals. The type 1 dolomite typically occurs in the central part of calcite grains, while type 2 dolomite is restricted to the outer parts. Type 3 dolomite is rare. The second

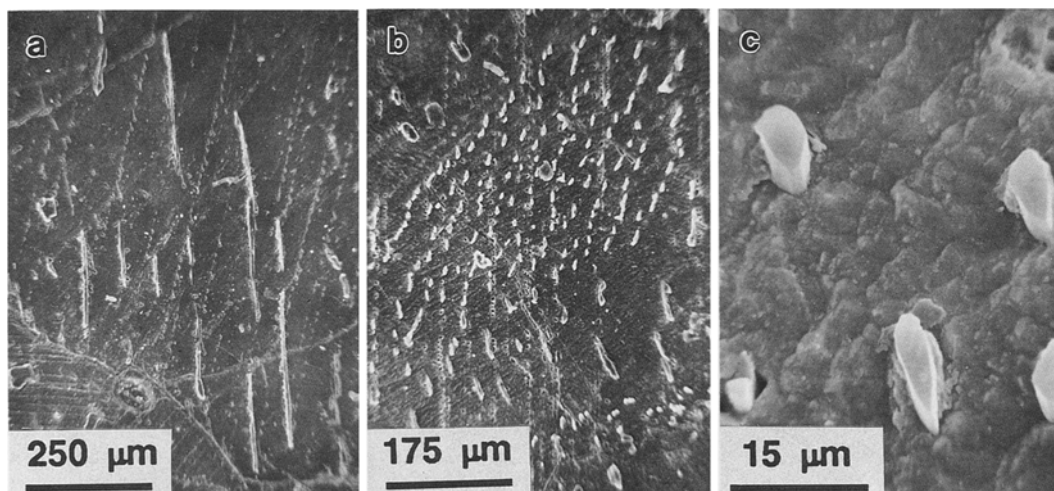


Fig. 1a–c. SEM images of type 1 dolomite microcrystals: a section parallel to lamellae; b–c section perpendicular to lamellae; c detail of b. Sample 7/454.5

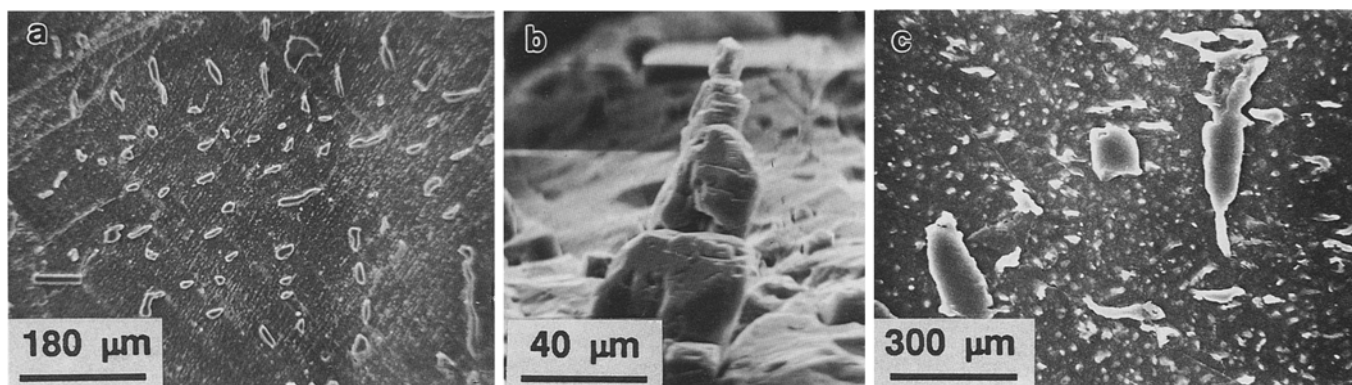


Fig. 2a–c. SEM images of type 2 dolomite microcrystals: a general view; b segmented rod; c discrete grains. a Sample 7/454.5; b–c sample 70/85

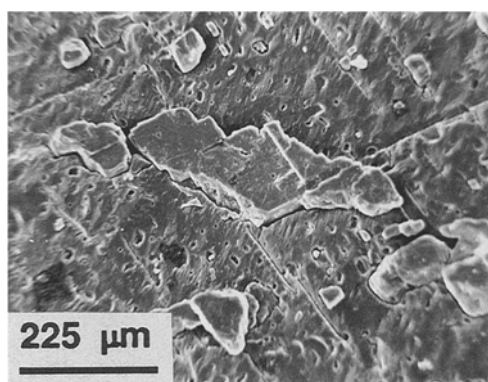


Fig. 3. SEM image of type 3 dolomite microcrystals. Discrete grain. Sample 70/85

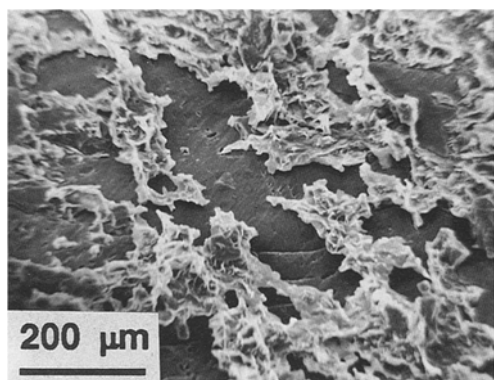


Fig. 4. SEM image of type 4 dolomite microcrystals. Fine-grained aggregate. Sample 7/143.3

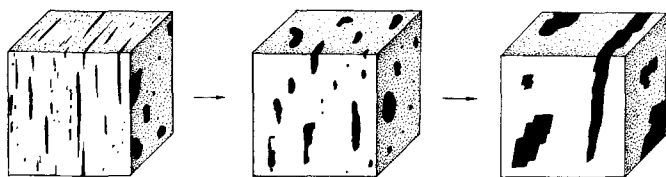


Fig. 5. Changes in dolomite morphology and sizes in carbonatites  $C_1$ . From left to right one can see progressive changes from the first morphological type to the second and third types. Black represents dolomite

group contains only type 2 and 3 dolomite and type 1 is absent. The third group contains mainly type 3 dolomite and type 2 dolomite is rare. The fourth group contains type 4 dolomite; type 2 and 3 dolomite rarely occur in this latter group and type 1 dolomite is absent.

Petrographic observations of the relations of dolomite types 1, 2 and 3 in various groups of carbonatites  $C_1$  shows the following changes in dolomite morphology and sizes (Fig. 5). The suggested changes of dolomite microcrystals may be attributed to recrystallization, widely developed in the early carbonatites (Zhabin 1971). The process of recrystallization is the result of mineral growth by diffusion (redistribution) in response to change in temperature. If there are any mineral microcrystals enclosed by other host minerals, the microcrystals may be displaced in intergranular spaces by recrystallization (Grigorev 1961).

Thus, types 2 and 3 dolomites may be considered as transformed type 1 dolomite. Evidence for this includes an increase in size of the microcrystals, change in morphology, and optical discontinuity. The decrease in dolomite content from 9.0–12.0 vol.% (type 1) to 4.0–6.5 vol.% (type 2) is also consistent with this model, as well as the dolomite observed along calcite grain boundaries (type 3).

#### Composition of dolomite and calcite

Table 1 summarizes the microprobe analyses from calcite-dolomite pairs from six samples for all types of dolomite.

Type 1 dolomite microcrystals are characterized by high contents of Fe and low abundances of Sr and Mn, typical for most dolomites. The dolomite contains more Fe + Mn and less Sr than the enclosing calcite. Similar Fe + Mn relations were detected for the types 2, 3 and 4 dolomites and enclosing calcite, but type 4 dolomite is characterized by relatively high contents of Fe. Calcite, associated with dolomites 3 and 4, contains just a little less Mg than present in the calcite enclosing dolomites 1 and 2; contents of Fe and Mn are similar. Thus, the carbonatites  $C_1$  with types 1, 2 and 3 dolomite are considered chemically closed systems during recrystallization.

**Table 1.** Microprobe analyses of calcite (C) and dolomite (D) from early carbonatites C<sub>1</sub>, wt%

Sample	7/515.5		7/454.5		70/85	
	C	D	C	D	C	D
Mineral Dolomite type	1		1		1	
CaO	54.59	29.63	54.62	29.74	54.45	29.87
MgO	0.86	21.50	1.09	21.61	1.00	21.80
MnO	0.10	0.23	0.11	0.14	0.12	0.19
FeO*	0.09	0.72	0.13	0.66	0.04	0.69
SrO	ND	ND	ND	ND	0.45	0.19
CO <sub>2</sub>	43.92	47.32	44.21	47.43	44.11	47.87
Total	99.56	99.40	100.16	99.58	100.17	100.61
Ca	0.98	0.98	0.97	0.98	0.97	0.98
Mg	0.02	0.99	0.03	0.99	0.02	0.99
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.01	0.02	<0.01	0.02	<0.01	0.02
Sr	ND	ND	ND	ND	0.01	<0.01
C	1.00	2.00	1.00	2.00	1.00	2.00
Dolomite microcrystals vol.%		11.9		9.2		9.0
Calcite host vol.%	88.1		90.8		91.0	
Sample	70/85		25/85		7/143.3	
Mineral Dolomite type	C	D	C	D	C	D
	2		3		4	
CaO	54.40	29.59	54.61	29.84	54.93	29.87
MgO	0.91	21.68	0.54	21.42	0.48	21.01
MnO	0.09	0.20	0.09	0.13	0.10	0.30
FeO*	0.11	0.79	0.05	0.50	0.15	1.33
SrO	ND	ND	ND	ND	ND	ND
CO <sub>2</sub>	43.82	47.50	43.55	47.20	43.78	47.40
Total	99.33	99.76	98.84	99.09	99.79	99.91
Ca	0.97	0.97	0.98	0.99	0.98	0.90
Mg	0.02	0.99	0.01	0.99	0.01	0.97
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.01	0.02	<0.01	0.01	<0.01	0.03
Sr	ND	ND	ND	ND	ND	ND
C	1.00	2.00	1.00	2.00	1.00	2.00
Dolomite microcrystals vol.%		5.3		ND		ND
Calcite host vol.%	94.7		ND		ND	

FeO\*, total Fe as FeO; ND, not determined

The distribution of Mg, Fe and Mn were studied in calcite enclosing the types 1, 3 and 4 dolomite. Preliminary microprobe traverses were made across dolomite and calcite from three morphological types to see if any changes in the content of Mg, Fe, and Mn could be observed. There were none in dolomites 3 and 4, but changes were observed for the calcite-dolomite boundary in dolomite 1, and quantitative analyses were made (Table 2). The Mg content decreases in calcite close to the dolomite lamellae.

## Discussion and conclusions

Similar morphological types of dolomite were described by Kapustin (1983a, b, 1987) and all dolomites in early carbonatites were regarded by Kapustin as metasomatic. In our opinion, only the dolomite of the fourth type was probably formed by metasomatic processes. The character of dolomite grain morphology (Fig. 4) and the character of mineral associations (together with dolomite one can observe secondary tremolite, tetraferriphlogopite and clinohumite) afford striking evidence of this. Kapustin's supposition that the dolomite microcrystals of the first, the second and the third types are also metaso-

**Table 2.** Variations in chemical composition of calcite near dolomite lamellae of the first morphological type, wt%

Sample	7/515.5					
Analysis	1	2	3	4	5	6
CaO	54.53	55.16	54.26	55.19	54.88	55.01
MgO	0.56	0.63	0.65	0.71	0.87	1.00
MnO	0.12	0.12	0.12	0.13	0.17	0.15
FeO*	0.07	0.06	0.06	0.05	0.08	0.08
CO <sub>2</sub>	44.53	44.10	43.41	44.21	44.18	44.41
Total	98.81	100.07	98.50	100.29	100.18	100.65
Mg*	1.41	1.56	1.64	1.76	2.16	2.47

Sample	7/454.5					
Analysis	1	2	3	4	5	6
CaO	54.17	54.30	54.87	54.26	54.91	54.43
MgO	0.65	0.83	0.89	1.01	1.04	1.23
MnO	0.08	0.07	0.10	0.08	0.12	0.08
FeO*	0.13	0.10	0.10	0.13	0.10	0.08
CO <sub>2</sub>	43.36	43.63	44.16	43.82	44.37	44.17
Total	98.39	98.93	100.12	99.30	100.54	99.99
Mg*	1.64	2.08	2.21	2.52	2.57	3.05

1, 5 microns from dolomite lamellae; 6, 80 microns from dolomite lamellae, analysis "step" is 15 microns. FeO\*, total Fe as FeO; Mg\*, 100Mg/(Ca + Mg) – atomic percent

matic seems to be improbable from our point of view. We conclude that type 1 dolomite microcrystals were exsolved from magnesian calcite solid solution. The main evidence is: (1) the special features of type 1 dolomite, including the morphology, sizes, optical orientation, quantitative correlations and the character of dolomite distribution within the enclosing calcite; (2) the chemical composition of type 1 dolomite and associated calcite. The distribution of Mg, Fe, Mn and Sr between dolomite and calcite, and the existence of Mg profiles in calcite near dolomite lamellae are supporting evidence for exsolution. As reported by Sidorov and Rudashevskii (1979) and Kretz (1988) the existence of such Mg profiles suggests that the dolomite lamellae are the result of Mg segregation from calcite solid solution.

If the type 1 dolomite is formed by exsolution, a temperature can be estimated for this process. The possible composition of primary magnesian calcite was calculated (Table 3) based on the percentages of dolomite and calcite in several grains and the result of microprobe analyses. This approach to calculating primary Mg contents was discussed in detail by Puhan (1976). The temperature of exsolution of dolomite from magnesian calcite was estimated on the basis of the calcite-dolomite solvus (Goldsmith 1983) using the calculated composition of primary calcite. Correction for Fe to the calcite-dolomite geothermometer was based on the data of Powell et al. (1984). Temperatures that were calculated, after applying the correction for Fe, are 665–700°C (Table 3). If the calcite-dolomite geothermometer were used with data from the type 2 and type 3 dolomites, the formation of which are the result of recrystallization processes, then the estimat-

**Table 3.** Calculated composition of primary magnesian calcite, wt%

Sample	7/515.5	7/454.5	70/85
CaO	51.62	52.33	52.24
MgO	3.32	2.98	2.87
MnO	0.12	0.11	0.13
FeO*	0.16	0.18	0.10
SrO	ND	ND	0.43
CO <sub>2</sub>	44.31	44.51	44.46
Total	99.53	100.11	100.23
Ca	0.91	0.92	0.92
Mg	0.08	0.07	0.07
Mn	<0.01	<0.01	<0.01
Fe	<0.01	<0.01	<0.01
Sr	ND	ND	<0.01
C	1.00	1.00	1.00
T°C (solvus)	670 (25)	645 (20)	635 (20)
T°C (corrected for Fe)	700 (25)	675 (20)	665 (20)

FeO\*, total Fe as FeO

ed temperature would be incorrect, and would probably yield values considerably less than the true exsolution temperature for the calcite-dolomite pair.

This result is in good agreement with the temperatures estimated for phoscorite formation of the Kovdor ore deposit (Harlamov 1978). In contrast, our result differs with the temperature estimation made for early carbonate formation available in the literature (on the basis of Mg content in calcite): 455–465°C by Talantsev (1980),

540–600°C by Kopylova et al. (1980) and 430–490°C by Chernyshova (1981). These different values can be attributed to the different methods of determining calcite composition and the samples selected for investigations.

We have shown in the Kovdor carbonatites ( $C_1$ ) four distinct types of dolomite. The first is formed by exsolution, the second and third are formed during recrystallization and the fourth is produced by metasomatism. We consider that only the type 1 dolomites are primary. Our findings suggest that care must be taken when temperature estimates are made using the calcite-dolomite geothermometer.

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