

# Oxygen Isotopic Fractionation in a Silicate–Carbonate System during the Formation of Rocks of the Kovdor Pluton (Kola Peninsula)

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**Abstract**—The  $\delta^{18}\text{O}$  values of carbonates and silicates (Ol, Phl, Mt) of calcite carbonatites, phoscorites, ijolites, and turjaites of the Kovdor pluton have been studied for the first time to elucidate the role of processes of contamination, retrograde exchange, and high-temperature fractionation in a magmatic system. It is established that no processes of crustal contamination are registered in the isotopic characteristics of silicates and that the  $\delta^{18}\text{O}$  values of olivine, phlogopite, and magnetite are lower relative to the compositions typical of equilibrium with mantle peridotite. At the same time, the carbonates show a complementary enrichment in the  $^{18}\text{O}$  isotope relative to the composition of derivative mantle melts. The estimated closure temperature of the O isotopic composition of olivine and the cooling rates of rocks do not support a hypothesis on retrograde isotope exchange. A redistribution of O isotopes between silicate and carbonate constituents of melts in the magmatic system before the origination of the Kovdor pluton and its cooling is suggested. According to the O isotope data, the carbonate constituent at that moment could strongly be dominant (in 1.5–4.5 times) over the silicate one.

**Keywords:** O isotopes, fractionation, C isotopes, carbonatites, olivine, closure temperature, cooling rate of rocks, Kovdor pluton

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## INTRODUCTION

The geochemistry of stable isotopes of light elements is highly informative for the identification of the evolution of igneous complexes, including carbonatites. Most published data on the geochemistry of stable isotopes of carbonatites include the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of their carbonates, which are compared with the composition of primary igneous carbonate (PIC [1]) or primary mantle carbonatites (the derivatives of mantle melts) (PMC [2]) in  $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$  coordinates. The deviations of the measured carbonatite compositions from these compositions are interpreted within the known processes: mixing with crustal carbonates, partial decomposition of carbonates with  $\text{CO}_2$  separation, and the influence of a fluid or hydrothermal fluids. This approach is known from the end of the last century [3], and a great volume of O and C isotopic compositions of carbonates from carbonatites has accumulated over the last 30 years. Works dedicated to the study of the O isotopic composition of silicates from carbonatites are few in number. Except for limited data published in [4] and [5], in which the authors

estimated the closure temperatures of the O isotope system (Tc) of biotite (440–560°C) and magnetite (700–770°C) for some carbonatite complexes of the United States, Canada, and Brazil, data on the O isotopic composition of silicates from carbonatites are almost unknown. Based on the range of Tc values [5], the authors reached a conclusion on the retrograde isotope exchange at the cooling stage of carbonatite bodies, when the carbonate phase played the role of a diffuse environment.

Carbonatite complexes often exhibit a scenario when the  $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$  isotope data are shifted from the PIC field toward enrichment in heavy ( $^{18}\text{O}$  and  $^{13}\text{C}$ ) isotopes that can be considered either the involvement of sedimentary carbonate material or the result of isotope fractionation under mantle conditions [2, 6], during which the O and C isotopes are redistributed between silicate and carbonate melts. This shift is often characteristic of the carbonatite complexes, the geological setting of which excludes the contribution of crustal carbonate material as is typical of the Kovdor pluton [7]. If we accept the hypothesis on the formation of isotopic parameters of the Kovdor carbonates during the high-temperature fractionation of the carbonate–silicate system, it can be expected that this process should be reflected in the isotopic characteristics of silicates. Tracing this process requires, at least, its distinction from the retrograde isotope

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exchange, the possibility of which was indicated in [5]. To identify the relationships in the carbonate–silicate system during the formation of the Kovdor pluton, we studied the O isotopic composition of their silicates (olivine, phlogopite, pyroxenes, magnetite) and carbonates of rocks of this pluton.

## BRIEF CHARACTERISTICS OF THE KOVDOR PLUTON

The Kovdor pluton ( $378.6 \pm 0.4$  Ma) [8], which is located in the Kola Peninsula among Late Archean–Early Proterozoic gneisses, has been studied well, and its structure has been described in numerous publications [7, 9]. The pluton of alkali-ultramafic rocks has a typical ring structure: its central part is occupied by olivinites, which are surrounded by consecutively intruding nepheline pyroxenites, melilite-bearing rocks, melteigites, and ijolites. All of them are intruded by carbonatites, and their intrusion was preceded and accompanied by fluids, which metasomatically alter the previously formed rocks. In the northern inner part of the pluton, the calcite carbonatites form large veins (the so-called phlogopite complex) [10] with phlogopitized and pyroxenitized olivinites and carbonatized pyroxene–phlogopite rocks. In the southwestern part of the Kovdor pluton, the carbonatite complex, closely associated with phoscorites<sup>1</sup> [11], occurs in a zone of longitudinal faults and consists of conjugated steeply dipping vein bodies, which are pinched out at a depth of 2.5 km [9, 12].

## MATERIALS AND METHODS

For this study, we used representative samples of igneous rocks of the phoscorite–carbonatite complex (calcite carbonatite, phoscorite, ijolite), the phlogopite complex (calcite carbonatite), and turjaite (Mt. Vysokaya). In addition to the isotopic parameters of carbonates measured in bulk samples, the O isotopic composition was studied in olivine, magnetite, phlogopite, pyroxene, and nepheline of the same samples. The representative rock fragments (~100 g) were crushed and sieved through sieves of different sizes. A fine-grained part of the sample was used for the O and C isotopic composition of carbonates. The larger fractions were treated by HCl to remove carbonates, washed by distilled water, and dried. After that, the silicates and oxides were picked up on monomineral fractions under a binocular microscope. The correctness of mineral sampling was controlled by the analysis of the composition of selected grains on a JSM-5610LV scanning electron microscope at the Institute of the Geology of Ore Deposits, Petrography, Miner-

<sup>1</sup> Phoscorites are igneous rocks that consist of the same minerals (carbonate, apatite, magnetite, olivine, and (or) phlogopite) as carbonatites with a much lower (30–5%) amount of carbonates.

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The isotope analysis of carbonates of some bulk samples and some calcite grains was conducted on a DeltaV+ mass spectrometer equipped with a GasBenchII complex in a constant He flow regime (CF IRMS). The carbonates were decomposed by orthophosphoric acid at 70°C. All samples were measured 2–3 times, and the measurement accuracy of the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values was  $\pm 0.1\text{‰}$ . The O isotopic composition of silicates and oxides was analyzed by fluoridation using laser heating on a Delta<sup>plus</sup> (ThermoQuest, Finnigan) mass spectrometer in the double inflow regime. The analytical accuracy of the measurement of the  $\delta^{18}\text{O}$  values was  $\pm 0.1\text{‰}$  or better.

## RESULTS

### Carbonates

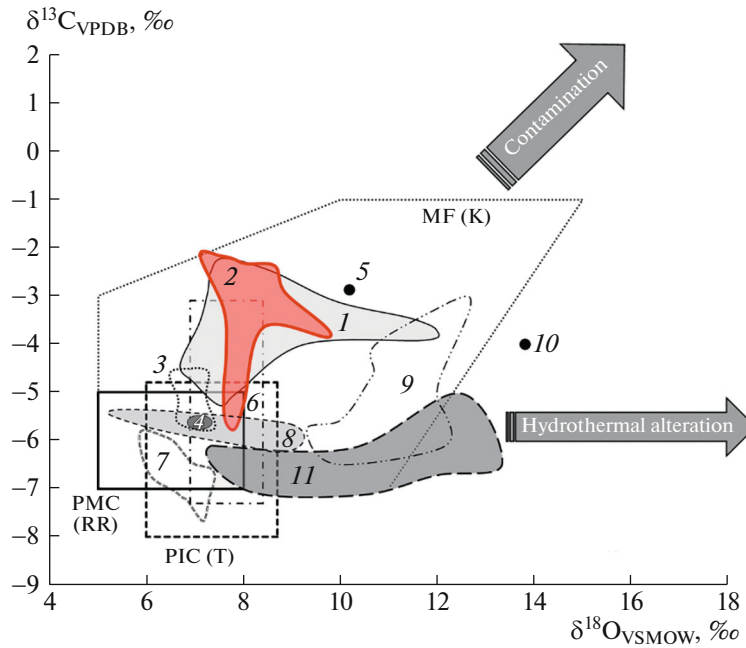
The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of bulk carbonate samples vary from 7.8 to 9.6‰ and from –5.8 to –2.7‰, respectively. A narrower range of these values was identified for single calcite crystals sampled manually from hand specimens:  $\delta^{18}\text{O} = 7.2$  to 8.2‰ and  $\delta^{13}\text{C} =$  from –3.6 to –2.4‰. Relative to the PIC and PMC, these values occur close to the upper boundaries of the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values and are beyond these fields on the isotope “carbonate” plot (Fig. 1).

### Silicates and Oxides

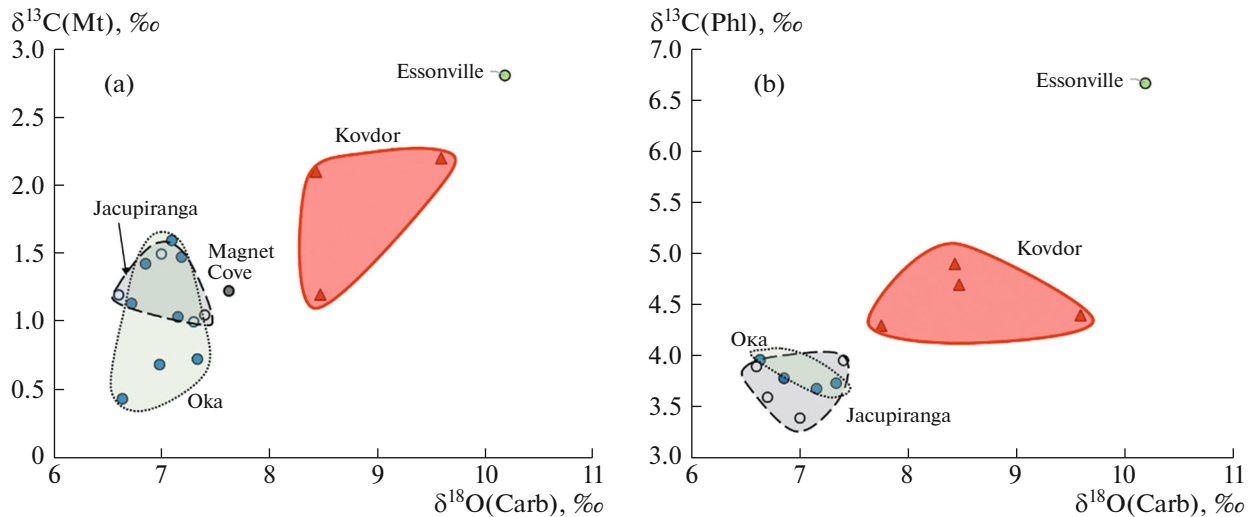
The O isotopic composition of silicates and magnetite from the ijolite samples of the phoscorite–carbonatite complex shows a regular depletion in the  $^{18}\text{O}$  isotope relative to the values typical of olivine of mantle peridotites ( $5.18 \pm 0.28\text{‰}$ ) [17] and equilibrium minerals. The  $\delta^{18}\text{O}$  values of magnetite, olivine, phlogopite, pyroxene, and nepheline are 1.2–2.2, 3.9–4.8, 4.3–5.4, 4.9–5.1, and 4.6–5.3‰, respectively. Figures 2a and 2b show the O isotopic composition of magnetite and phlogopite relative to that of carbonates of these rocks and the available data for carbonatites of the United States, Canada, and Brazil [4, 5]. Our results are generally consistent with a common positive correlation between  $\delta^{18}\text{O}$  values of carbonates and silicates, which indicates both their common O source and the active interaction of their isotopic systems.

## DISCUSSION

The narrower variations in  $\delta^{18}\text{O}$  values ( $7.4 \pm 0.1\text{‰}$ ) and wider variations in  $\delta^{13}\text{C}$  values (from –5.2 to –2.6‰) were previously determined for carbonates of the Kovdor pluton [13]. Our results exhibit more significant variations in the O isotopic composition at similar variations in the C isotopic composition. All values of carbonates occur at the upper limit of the PIC and PMC boxes but are mostly beyond them (Fig. 1).



**Fig. 1.**  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of carbonates of the Kovdor rocks in comparison with data on some world carbonatites: 1, carbonatites of the Kola Peninsula: Turii Cape, Vuorijarvi, Sokli (D-04) [13]; 2, Kovdor (present work); 3, Canada (Oka, H-03) [5]; 4, United States (Magnet Cove, H-03) [5]; 5, Canada (Essonville, H-03) [5]; 6, Sweden (Alnö, T-67) [1]; 7, Tanzania (Ol Doinyo Lengai, KZ-06) [14]; 8, Transbaikalia (Khalyuta, D-10) [16]; 9, China (Miaoya, C-18) [15]; 10, India (Chkhota Udaipur, PR-06) [2]; 11, Brazil (Araxá, Catalão, Tapira, SC-95 [4]; Jacupiranga, H-03 [5]); PIC, primary igneous carbonate (T-67) [1]; PMC, primary mantle carbonatite (RR-06) [2]; MF field, compositions of carbonates formed at the expense of isotope fractionation in mantle conditions (Kyser, 1990).



**Fig. 2.** O isotopic composition of (a) magnetite and (b) phlogopite relative to  $\delta^{18}\text{O}$  values of carbonates of carbonatite samples. The data on carbonatites of Canada, the United States, and Brazil are given according to [4, 5].

Nonetheless, as for many classical carbonatites, the isotopic compositions of the Kovdor pluton are located in a field of mantle high-temperature fractionation [6], which also can enclose the composition of carbonatites without involvement of isotopically heavy sedimentary carbonates. In fact, the geological setting of the Kovdor pluton suggests no contamination of

sedimentary material. This is indicated by the lower  $\delta^{18}\text{O}$  values of silicates and oxides, which in case of contamination by isotopically heavy sedimentary carbonates should be higher.

The interaction of  $\delta^{18}\text{O}$  values between silicates and carbonates of the Kovdor carbonatites is complemen-

tary: if carbonates are characterized by higher  $\delta^{18}\text{O}$  values relative to the PMC (Fig. 1), silicates have lower  $\delta^{18}\text{O}$  values relative to those typical of mantle equilibria. For example, the range of  $\delta^{18}\text{O}$  values from  $3.9 \pm 0.1$  to  $4.8 \pm 0.2\%$  for olivine is much lower than that for olivine from mantle peridotites ( $5.18 \pm 0.28\%$ ) [17]. It was previously suggested [5] that the lower  $\delta^{18}\text{O}$  values of silicates from carbonatites are a result of ret-

rograde exchange during cooling of plutons. Olivine, which has low diffusion rates [18] and reliably registers the closure temperature of its O isotopic system ( $T_c$ ), however, was not studied in this work. Using the  $\delta^{18}\text{O}$  values of olivine and other minerals of the studied rocks, we estimated  $T_c$  of olivine from the equation, which takes into account the amount of minerals in the cooling rock [19]:

$$T_{\text{Ol}} (\text{°C}) = \sqrt{\frac{A_{\text{Ol-Cc}} \times 10^6 (X_{\text{Cc}} + X_{\text{Mt}} (1 + A_{\text{Cc-Mt}}/A_{\text{Ol-Cc}}))}{(\delta_{\text{Ol}} - \delta_{\text{R}})}} - 273,$$

where  $T_{\text{Ol}}$  (°C) is the  $T_c$  of olivine;  $A_{\text{Ol-Cc}}$  and  $A_{\text{Cc-Mt}}$  are the coefficients of thermometric equations for olivine–calcite and calcite–magnetite mineral pairs, respectively [20];  $X_{\text{Cc}}$  and  $X_{\text{Mt}}$  are the oxygen amount of calcite and magnetite in the rock, respectively;  $\delta_{\text{Ol}}$  is the value corresponding to the measured  $\delta^{18}\text{O}$  value (Ol); and  $\delta_{\text{R}} = X_{\text{Ol}}\delta_{\text{Ol}} + X_{\text{Mt}}\delta_{\text{Mt}} + X_{\text{Cc}}\delta_{\text{Cc}}$  is the mass balance for the rock.

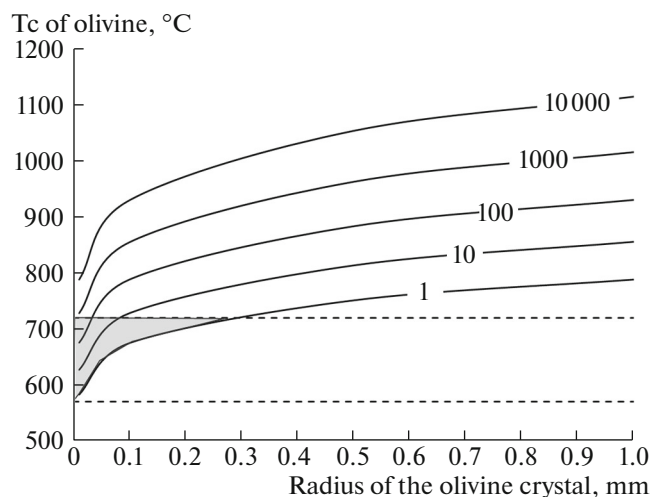
It was suggested in calculations that the O isotopic composition of olivine was mainly affected by magnetite and calcite, because the amount of phlogopite is extremely low in our samples. The  $T_c$  values for carbonatites and phoscorites from the phoscorite–carbonatite complex are 720 and 570°C, respectively, whereas the carbonatites from the phlogopite complex showed a temperature of 700°C. These values are close to the published ones [5] for the carbonatite plutons of Brazil, Canada, and the United States, which were calculated by the simple ratios of the  $\delta^{18}\text{O}$  values in the Cc–Mt and Cc–Bt mineral pairs without the mutual influence of minerals. For the Cc–Bt equilibrium

temperature, however, the authors yielded real estimations of the cooling rate of rocks ( $10^3$ – $10^4$ °C/Ma), whereas the calculated cooling rates for the Cc–Mt pair are unreal. In our opinion, this can indicate an inconsistent scenario of retrograde isotope exchange during the origination of the carbonatite complexes.

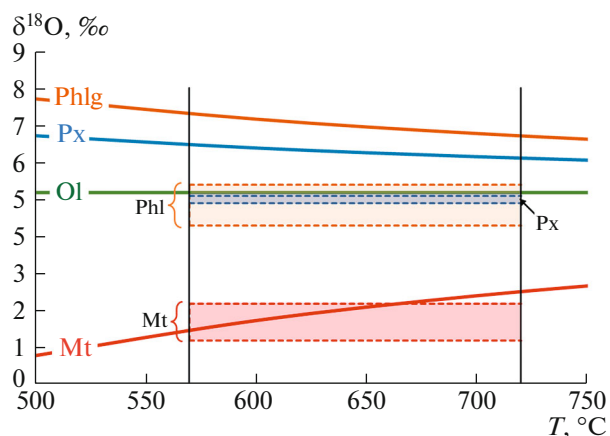
Our  $T_c$  values of olivine contradict the retrograde exchange, because they lead to unreal estimations of the cooling rates of the pluton. Figure 3 shows the calculated lines of the change of  $T_c$  of olivine depending on the crystal size at different cooling rates of the rock based on the diffusion characteristics of forsterite [18]. It is evident that, for reliable cooling rates of the crystalline rock at real crystal sizes (a few millimeters), the  $T_c$  of olivine should be significantly higher than that for the Kovdor rocks. The available low  $T_c$  estimations of olivine are thus incompatible with retrograde exchange, although the isotope interaction between silicates and carbonates of carbonatites is evident (Fig. 2).

This contradiction can be solved if we suggest that silicates and carbonates of carbonatites interacted before the beginning of crystallization and cooling of the pluton. This suggestion is consistent with the O isotopic composition of all other silicates in the Kovdor rocks. They exhibit a general depletion in the heavy O isotope relative to the compositions, which should be equilibrated with mantle olivine (Fig. 4). The solid lines in Fig. 4 show the correlation between the temperature and the  $\delta^{18}\text{O}$  values of phlogopite, pyroxene, and magnetite, which are in equilibrium with olivine of the mantle peridotite (we used a value of 5.18‰ [17]). The calculations were conducted using the equation of O isotopic fractionation at higher (>600°C) temperatures [20]. The dotted line in Fig. 4 shows the intervals of the measured compositions of phlogopite, pyroxene, and magnetite in the Kovdor rocks. The vertical lines limit the range of  $T_c$  estimations of olivine in our work. It is evident that almost all  $\delta^{18}\text{O}$  values of silicates of the Kovdor rocks in a wide temperature range are significantly lower than is required for equilibrium with olivine from the mantle peridotites.

This means that both olivine and all silicates of the Kovdor rocks probably underwent depletion in the  $^{18}\text{O}$



**Fig. 3.** Closure temperature ( $T_c$ ) of olivine depending on the crystal radius at different cooling rates of the rock (numbers on lines are cooling rate, °C/Ma). The gray field corresponds to the range of  $T_c$  values of olivine in the present work.



**Fig. 4.** Calculated lines of the Phl, Px, and Mt compositions (solid lines) in equilibrium with olivine of mantle peridotites. Colored fields contoured by a dotted line, and the Phl, Px, and Mt compositions from this work. The vertical lines are the extreme Tc values of olivine calculated in this work.

isotope at high temperatures, which was accompanied by complimentary enrichment in this isotope by carbonates. This redistribution of O isotopes could have occurred after the separation of the carbonate–silicate melt prior to the origination and crystallization of rocks of the pluton. If we accept that the observed isotope shifts in carbonates and silicates of the Kovdor rocks are a result of complimentary redistribution of O isotopes between the immiscible melts, then we can estimate the approximate mass balance between equilibrated silicates and carbonates. A negative isotope shift of olivine by 0.4–1.2‰, which is accompanied by a positive shift in carbonate by 1.5‰, corresponds to a mass balance of carbonate and the silicate melt of 1.5–4.5 indicating the strong predominance of the carbonate part of the melt over the silicate part in the primary magmatic system.

If our suggestion is correct, similar  $\delta^{18}\text{O}$  ratios of carbonates and silicates could be a feature of other carbonatite complexes. It is likely that the enrichment in the light O isotope of silicates will be striking for objects without any contamination or a significant impact of external fluids, which are able to distort the primary redistribution of O isotopes between silicate and carbonate melts. Unfortunately, the limited data available now hinder reliable substantiation of this hypothesis, whereas the available data are in agreement with it.

## CONCLUSIONS

The first O isotopic composition of silicates and oxides from rocks of the Kovdor pluton are presented and compared with that of carbonates of the same rocks. The  $\delta^{18}\text{O}$  values of silicates, first of all, olivine, indicate the absence of any contribution of the heavy

O isotope to the formation of carbonatite melts. Our estimations of Tc values of olivine contradict the hypothesis of retrograde isotope exchange, because it requires unreal low cooling rates of rocks. It is established that the carbonates and silicates of rocks of the pluton are connected by complementary ratios of the  $\delta^{18}\text{O}$  values. This indicates their common O source and the presence of a stage of redistribution of O isotopes in the evolution of the pluton, which could occur after the liquation of the carbonatite melt but prior to the beginning of crystallization of rocks of the pluton and their cooling. The balance calculation indicates the strong predominance of carbonates over silicates in the magmatic system that was the source of melts that formed the Kovdor carbonatite complex.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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