https://doi.org/10.31241/FNS.2018.15.097

CHEMICAL COMPOSITION OF Ca-Mg-Sr CARBONATES AND THE STABLE ISOTOPE $\delta^{13}C$ STUDY: THE KOVDOR MASSIF SHOWCASE (KOLA REGION, NW RUSSIA)

Huber M.[1]*, Hałas S[2], Mokrushin A.V.[3], Neradovsky Yu.N.[3], Lata L.[4], Sikorska-Jaworowska M.[5], Skupiński S.[1]

[1] *Maria Curie-Skłodowska University, Earth Science and Spatial Management Faculty, Geology and Lithosphere Protection Department, 2 cd Kraśnicka St., 20-718 Lublin, Poland;*

[2] *Maria Curie-Skłodowska University, Mass Spectrometry Laboratory, Institute of Physics, Lublin, 1 M. Curie-Skłodowska Sq., 20-031 Lublin, Poland.*

[3] *Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, 14 Fersman Str., 184209 Apatity, Russia;*

[4] *Maria Curie-Skłodowska University, Earth Science and Spatial Management Faculty, Soil Science and soil Protection Department, 2 cd Kraśnicka St., 20-718 Lublin, Poland;*

[5] *Polish Geological Institute, 4 Rakowiecka St., 00-975 Warszawa, Poland.*

**Corresponding author e-mail: mhuber@poczta.umcs.lublin.pl*

Abstract

The current study provides new data on $\delta^{13}C$ of carbonates from the REE-rich Paleozoic Kovdor massif. It is an ultramafic, alkaline and carbonatite intrusion in the north-eastern part of the Baltic Shield (Kola region, Russia). The carbonates have been sampled from the main outcrop of the phoscorite-carbonatite Kovdor massif. According to Rb-Sr and U-Pb data, its age is 420-360 Ma [3, 10]. The massif was formed in the active zone of a continental type as a result of hot spot plutonism on the Kola Peninsula. The selected ore minerals have been analyzed with optical and electron microscopy (Hitachi SU6600 with EDS attachment), whereas $\delta^{13}C$ has been determined in the Mass Spectrometry Laboratory, Maria Curie-Skłodowska University. The works aim at studying the stable isotope in representative Ca-Mg-Sr carbonatites sampled by V.V. Balagansky in 2003. They have been analyzed using ICP-OAS and XRF in the Department of Soil Science in order to estimate metal concentrations.

Keywords: geochemistry, stable isotope analysis, Ca-Mg-Sr carbonatites, REE Kovdor massif, Baltic Shield.

Introduction

The Baltic Shield is a segment of the East European Craton (EEC). In its northern part there are numerous alkaline (agpaitic) rock intrusions of the early Proterozoic age, such as the Elt'ozero and Gremyakha-Vyrmes [8, 11, 13, 14]. The Baltic Shield is marked by volcanic activity of the continental type that produced numerous Paleozoic intrusions, carbonatite and alkaline ones mainly. These intrusions are rich in REE [9, 10, 12] and occur on the Kola Peninsula (the Khibiny and Lovozero massifs, Kovdor, Afrikanda, Turiy Mys, etc.), in Karelia and Finland (e.g. Sokli). They are also found under cover of sedimentary rocks, e.g. in Poland (Tajno intrusion, etc.).

On the Kola Peninsula this magmatism was associated with hot spots and produced a series of intrusions [1, 2, 6, 9, 10]. Earlier Zaitsev and Bell had studied some carbonatites from Kovdor [15]. We collected hydrothermally treated samples rich in Ca-Mg-Sr and REE from the main outcrop of the Kovdor massif and compared them with carbonate veins from Pechenga and the Lapland Granulite Belt on the Kola Peninsula.

Methods

The sampled carbonatites have been analyzed using an optical polarizing microscope Leica DM2500P and a scanning electron microscope Hitachi SU6600 with EDS in the Department of Geology and Lithosphere Protection at the Maria Curie-Skłodowska University (UMCS) in Lublin, Poland. The stable isotope analysis ($\delta^{13}C$ and $\delta^{18}O$) has been made in the Institute of Physics (UMCS), Lublin, using a dual inlet and a triple collector mass-spectrometer. The selected samples have been studied using the LA-ICP-OAS (laser ablation inductively coupled plasma mass spectrometry) analysis (model ELAN DRC II, Perkin

Elmer with the (LA) LSX-500 laser ablation system of CETAC) at the Soil Science and Soil Protection Department (UMCS). The XRF analysis has been performed on the Epsilon 4 at the Department of Geology and Lithosphere Protection. Cathodoluminescence (CL) observations have been carried out in the Polish Geological Institute in Warsaw using the CCL 8200 mk3 (cold-cathode) device linked with an Optiphot 2 polarizing microscope. For these studies the voltage of 14-16 kV and the electron beam intensity of 400-600 μA have been applied. Micrographs have been taken on 1600 ISO Fujifilm.

Results

The rocks have been sampled from the Kovdor intrusion of the Paleozoic age in the western part of the Kola Peninsula. The intrusion consists of ultrabasic rocks, i.e. olivinites and pyroxenites, that comprise a magnetite-apatite-phlogopite ore body [6, 9, 10]. The intrusion was formed in one out of many faults in crystalline basement rocks of the Kola Peninsula. The mineralization of the Kovdor massif is complex and multiphase. The rocks are rich in zircon, baddeleyite, francolite (non-typical forms of apatite), apatite, phlogopite, vermiculite, diopside, calcite, dolomite, etc. There are also numerous phlogopite-magnetite phoscorites and products hydrothermal processes. The mineralization is rich in trace and rare elements [9, 10].

Results of the isotope analysis

The $\delta^{13}C$ isotope analyses of the Kovdor carbonates testify to the coal origin from the Earth's mantle (cf. Fritz and Fontes, 1986). These isotopes are found in almost all samples and have similar values. The highest ones refer mainly to dolomite from the phoscorite samples (3 and 6). Analyses of carbonatites (sample 5) provide similar results. They are much close to the works by Zaitsev and Bell (1995). The lowest carbon content $\delta^{13}C$ was recorded in samples 1, 2 and 4. It might be linked to the contamination of dioxide during the water migration in secondary processes. Similarly, respondents ranked values of oxygen isotopes ^{18}O from carbonates in all samples. Very low values of oxygen isotopes (lower than in measurements by Zaitsev and Bell [15]) may be obtained from meteoric fluids that are incorporated by an isotope exchange reaction in CO_2 solution–HCO^{-}-CO_3^{2-}.

Geochemical characteristics of rocks

According to ICP-OAS and AAS analyses, the carbonates include calcium (dominating), magnesium and strontium accompanied by potassium, sodium, zinc and iron and lanthanum. Analyses of carbonates and their surrounding rocks (diopside-apatite nephelinites, samples nos. 07Kv, 08Kv, 09Kv) with the XRF method provided results much similar to those obtained with the ICP method. These rocks are rich in magnesium, calcite and contain up to 2 % admixture of strontium. They also have cerium, lanthanum and barium. Among the main elements there are Na, Al, Si, K, P, Cl. The rocks are accompanied by large amounts of Zr, Fe, Mn, Ti, V, Cr and such trace metals, as Co, Ni, Cu, Zn and As. In the discussed rocks there are also Sm, Nd admixtures with minor amount of the Y group.

Disscussion

The Kovdor intrusion mainly consists of ultrabasic rocks and carbonatites. Analyses of these rocks indicate their close relationship with deep zones of the Earth (mantle). It is witnessed by both isotopic and microprobe analyses of minerals with rare earths sampled by many researchers in this region [1, 12]. This intrusion is closely related to numerous carbonatite intrusions of the same age on the Kola Peninsula (e.g. Afrikanda), in Finland (eg. Sokli) and many other places of the Baltic Shield. These rocks originate from a hot spot that occurred in the Early Palaeozoic and contributed to the continental magmatism in this region. It also contributed to many changes in surrounding rocks. Carbonatite veins associated with these processes were also found in the archaic structure of the Lapland Granulite Belt [4] and in Pechenga. Carbon isotope $\delta^{13}C$ [‰] was found at the level of -4.83 to -19.62 and oxygen isotopes $\delta^{18}O$ [‰ VPDB] were discovered at the level -9.43 to -20.79. Leaving aside issues of minor contamination resulting from the migration of solutions in the environment, they indicate the impact of hot spots that produced a number of changes as a secondary environment among older rocks. These results outline multistadial processes of carbonatite cry-

https://doi.org/10.31241/FNS.2018.15.097

stallization with the mixing of fluids and rocks. It is confirmed by previous geochemical studies indicating REE mineralization (the cerium group) [4]. The presence of light elements of the cerium group is characteristic for most alkaline massifs in the Kola region [6]. The presence of such major elements, as Na, Al, Si, is also related to small amounts of silicates (phlogopite, diopside) and accessory nepheline (K, Na), apatite (P, Cl) and baddeleyite (Zr, Bayanova et al. 1997). The occurrence of iron, titanium, vanadium and chromium can be explained by the presence of numerous ore minerals, i.e. magnetite, titanomagnetite and spinels. The presence of sulphides is related to trace metals (V, Cr, Co, Ni, Cu, Zn, As). While the magnetite-spinel association may correspond to basic primary alloys, a trace metal admixture shows that hydrothermal processes were associated with the after-magmatic ones. It explains the results of the carbonate isotope analyses. Sm, Nd, and minor Y may testify to the contamination of supracrustal rocks (old metamorphic rocks) in the vicinity of the intrusion [5].

Conclusions

The studied samples are representative carbonatites from the Kovdor massif. These rocks refer to the igneous continental type supported by the stain of heat that produced numerous intrusions and changes in the East European Craton rocks (the Baltic Shield). Most of the studied samples are various kinds of phoscorites rich in calcite, dolomite, pyroxene and phosphates. There are also rocks with diopside, vermiculite and feldspar. Isotopic and geochemistry analyses of these rocks indicate their origin to be related to deep structures of the Earth (mantle). It also makes the mineralization rich in REE, those of the cerium group mainly [6, 9, 7, 10], with contamination of surrounding supracrustal rocks in hydrothermal processes. Examined rock samples of vein occurring in the further environment of the intrusion (Pechenga and Lapland Granulite Belt rocks) show clearly the wide range of influence of the spots also through a system of old divisions in this part of the Baltic Shield.

References

1. ARZAMASTSEV, A.A., 1995. Paleozoic plutonic complexes. In: Mitrofanov, F.P. Geology of the Kola Peninsula. Apatity. P. 85-103.
2. AGAPHONOV, L.V., CHEPUROV, A.I., LAVRENT'EV, YU.G., POKACHALOVA, O.S. (1974): Regularly oriented inclusions in olivine from ultrabasites of Koriakiya. Geol. Geophys.6, 49-60 (in Russ.).
3. BAYANOVA T.B., KIRNARSKIY Yu.M., LEVKOVICH N.V. (1997): U-Pb study of the baddeleyite from rocks of Kovdor massif, Izv. Akad. Nauk, 356, 4, 509-511.
4. HUBER M., HAŁAS S., SIKORSKA M. Evolution of prehnite albite-calcite veins in Metamorphic rocks from the Lapland Granulite Belt (Kandalaksha region of Kola Peninsula). Geologija 2007; 57: 1-7.
5. HUBER M.A., 2014, Geology of the Lapland Granulite Belt of the Kandalaksha region, Kola Peninsula, Russia, TMKarpinski Publisher, pp 135 (in Polish)
6. HUBER M.A., LATA L., 2015: Mineralogy and petrographic characteristic of carbonate samples from Kovdor (Kola Peninsula, N Russia). JBES 5(1): 34-89
7. HOMENKO, V.M., PLATONOV, A.N. & KRASNOVA, N.I. (1991): Optical properties of phlogopite of the Kovdor massif. Izv. Akad. Nauk SSR, Ser. Geologicheskaya 12, 94-105 (In Russ.).
8. KOGARKO L.N. (1987): Alkaline rocks of the eastern part of the Baltic Shield (Kola Peninsula), Geological Society, London, Special Publications, 30, 531-544.
9. KOGARKO, L.N. & RYABCHIKOV, I.D. (1969): Differentiation of alkaline magmas rich in volatiles. Geochem. Int. 6, 2011-2021.
10. KRAMM, U., KOGARKO, L.N., KONONOVA, V.A. & VARTIAINEN, H. (1993): The Kola Alkaline Province of the CIS and Finland: precise Rb-Sr ages define 380-360 Ma age range for all magmatism. Lithos 30, 33-44.
11. MITROFANOV, F.P., BALASHOV Yu.A., Geochronology and genesis of layered basic intrusions, volcanites and granite-gneisses of the Kola Peninsula. RAS, Apatity. 1990.
12. POZHILIENKO V. I., GAVRILENKO B.V., ZHIROV D.V., ZHABIN S.V. Geology of mineral areas of the Murmansk Region. Apatity, RAS. 2002: 360.
13. SULIMOV, B.I., KOLCOVA, T.P, NECHAYEV, S.A., AFANASEVA, N.V., DOMBROVSKAYA, T.P. (1999): Schematic geological map of the Kovdor massif, Murmansk Region, Kovdor Mine Press.
14. VASILIEVA, V.V., MATVEEV, I.V., TURCHENKO, S.I., KRASNOVA N.I. (2000): The second life for phlogopite from the Kovdor deposit. Proc. Russ. Mineral. Soc. (Annual Meeting, St. Petersburg), 48-50 (in Russ.).
15. ZAITSEV A.N. and BELL K. (1995): Sr and Nd isotope data of apatite, calcite and dolomite as indicators of the source and relationships of phoscorites and carbonatites from the Kovdor massif, Kola Peninsula, Russia. Contrib. Mineral. Petrol. 121, 324-335.