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Isotopic geochemistry of carbonatites of Ukraine

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ABSTRACT. — In Ukraine there are carbonatites and carbonatite-like rocks of Precambrian (1.8-3.0 Ma) and Palaeozoic (0.4 Ma) age. Overall, these carbonatites have isotopic and geochemical characteristics similar to carbonatites in other world localities, but sometimes they are peculiar. Infact the oldest (2.09 Ma) carbonatites of Chernigovka complex show some peculiarities of isotope composition. In this rocks the $\delta^{18}O$ varies from 5.9 to 17.5‰ accordingly with the reduction of FeO contents in carbonatites. Unusual low ratio of $^{87}Sr/^{86}Sr$ (0.7005) has been measured in carbonates of «calciphyre» inclusions in Archean granites (3.0 Ma – granites and 2.9 Ma – «calciphyres»)
Isotope composition of Palaeozoic carbonatites testifies about exchange between these rocks and surface material.

RIASSUNTO. — In Ucraina ci sono carbonatiti e rocce simili alle carbonatiti del Precambrico (1,8-3,0 Ma) e del Palaeozoico (0,4 Ma). Nel complesso queste carbonatiti hanno caratteristiche isotopiche e geochimiche simili alle carbonatiti di altre parti del mondo, ma in alcuni casi mostrano delle peculiarità. Le carbonatiti più vecchie (2,09 Ma) del complesso di Chernigovka hanno composizioni isotopiche particolari. In queste rocce $\delta^{18}O$ varia da 5,9 a 17,5‰ in accordo con la diminuzione del FeO nelle carbonatiti. Inusuali bassi valori del rapporto $^{87}Sr/^{86}Sr$ (0,7005) sono stati misurati nei carbonati costituenti inclusioni «calciphyre» nei graniti Archeani (3,0 Ma – graniti e 2,9 Ma – «calciphyres»).

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La composizione isotopica delle carbonatiti Paleozoiche testimonia lo scambio tra queste rocce ed i materiali di superficie.

KEY WORDS: *carbonatites, isotope composition, Ukraine, Chernigovka complex.*

INTRODUCTION

On European continent there are carbonatite complexes of different age (from Archean to Quarternary), chemical composition and metallogeny. Most of these different aged carbonatite massifs are located within the Fennoscandian and Ukrainian Precambrian shields (Fig. 1). Often it is difficult to explain their origin and their geological meaning without isotopic data assistance, because it is difficult to distinguish igneous carbonatites rocks from similar crystalline carbonate rocks formed by metamorphism or metasomatism.

In Ukraine crop out carbonatites of different ages, from Precambrian (Chernigovka massif, 2090 Ma) to Devonian (Pokrovo-Kyreyevo massif, 350 Ma), and three main stages of carbonatite formation may be distinguished: I – 2100 Ma, II – 1800-2000 Ma and III – 350-400 Ma (Table 1).

PRECAMBRIAN CARBONATITES

The Chernigovka carbonatite complex is the most completely studied. It is a deeply eroded carbonatite complex, down to at least 20 km, as suggested by mineral paragenesis (Kryvdik, Tkachuk, 1990). The carbonatites are associated to alkaline rocks (Kogarko *et al.*, 1995; Kryvdik, Tkachuk, 1990). The U-Pb zircon age of Chernigovka carbonatites is 2090±20 Ma (Sherbak *et al.*, 1995). According to Sr, Nd, O, C isotope ratios it is most likely that these carbonatites are from a mantle source. In particular, form this locality came the carbonatite samples with the lowest $^{87}Sr/^{86}Sr$ ratio (0.7013) ever found in worldwide carbonatites (Bell, Blenkinsop, 1989).

The carbonatite rocks from Chernigovka are characterised by $\delta^{13}C$ and $\delta^{18}O$ values that do not exceed the limits of the primary carbonatite field (Fig. 2). In our opinion, most of these rocks have not been affected by any noticeable contamination by crust material, or exchange with surface components.

Sometimes, however, the carbonate has higher $\delta^{18}O$ values (up to 17.5‰), than measured in carbonate from carbonatites. $\delta^{18}O$ values correlate positively with an increment of the magnetite modal amount in the rocks and a decrement of FeO contents in carbonates (Fig. 3). The initial FeO contents in calcites from carbonatites approaches 2.5 wt% and $\delta^{18}O$ value are about 5‰. The FeO contents in dolomites reach 5.9 wt % (Kryvdik *et al.*, 1997). The $\delta^{18}O$ value increases up to 13-14 or even 17.5‰ with the drop of iron contents in carbonates (Fig. 3). This is considered as a result of thermal dissociation of their primary siderite component. This dissociation may occur as following: $6FeCO_3 \rightarrow 2Fe_3O_4 + 5CO_2 + C$. This reaction may also explain the formation of graphite associated with magnetite in carbonatites. Enrichment of carbonates with the ^{18}O isotope is observed from the north to the south of the linear-stretched carbonatite massif with the change of its erosion depth. The temperature of crystallization (510-1050°C) calculated by the calcite-graphite and carbonate-magnetite isotopic geothermometers shows an early magmatic and a postmagmatic recrystallization of carbonate (Kryvdik *et al.*, 1997).

Dyke and veins of carbonatite composition were found in Octyabrskiy and Mala Tersa massifs. The width of dykes and veins is of 1 m. They crosscut syenites, mariupolites and pyroxenites. The carbonate in the dykes and veins are enriched in Sr, and REE. Metasomatic alteration zones are most often present along the contact between dykes and country rocks. Carbonatite dykes and veins have a K-Ar age of 1600-1800 Ma and the U-Pb age of the country rocks is 1800±10 Ma. In the carbonatites of Octyabrskiy and Mala-Tersa massifs the $\delta^{13}C$ = -7±1‰, $\delta^{18}O$ = 10±1‰ isotopic values are very consistent. Nd and Sr isotopic ratios and the REE distribution indicate that carbonatites formed in the crust before their remelting during the emplacement of the alkaline rocks.

Chlebodarovka carbonatite dyke is situated near the Octyabrskiy massif in charnokites and rarely in metamorphic basic rocks. The width of the Chlebodarovka dyke is up to 0.5 m. This carbonate forming the dyke is enriched in Sr (up to 2 wt%) and REEs (up to 0.5 wt%). The carbonatites contain apatite, alkali amphiboles, biotite, pyrochlore, monazite, fluorite, sulfides. Fenite metasomatism developed only along the contact carbonatite-charnokites forming a metasomatic zone 2-3 times wider than the carbonatite dyke. The fenite zone is absent along the contact carbonatite dyke-metamorphic country rocks.

In Taromske quarry there are xenoliths of carbonate-bearing rocks (earlier called calciphyres). Their dimensions amount to 0.6m. The rocks consist of calcite, olivine, diopside, tremolite, phlogopite, apatite and allanite. They are enriched in Sr (up to 2 wt%) and REE (up to 500 ppm). The country granites are Archean (age near 3 Ga). The K-Ar age of mica from carbonate rocks is 2950 Ma. Taking into consideration the low $^{87}Sr/^{86}Sr$ ratio (0.7005) we suppose these carbonatite rocks could have been dragged from the mantle to the

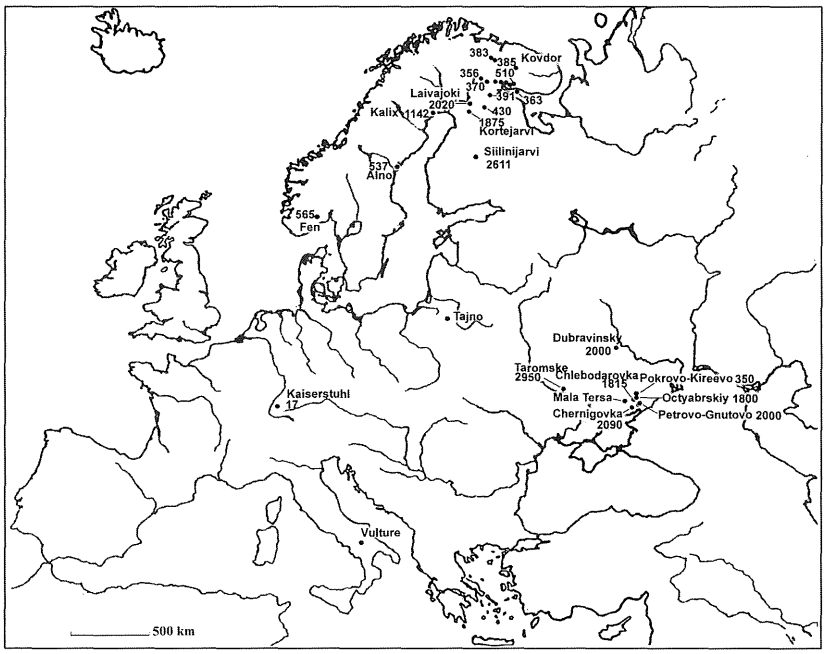

Fig. 1 – Distribution and dates of carbonatites in Europe.

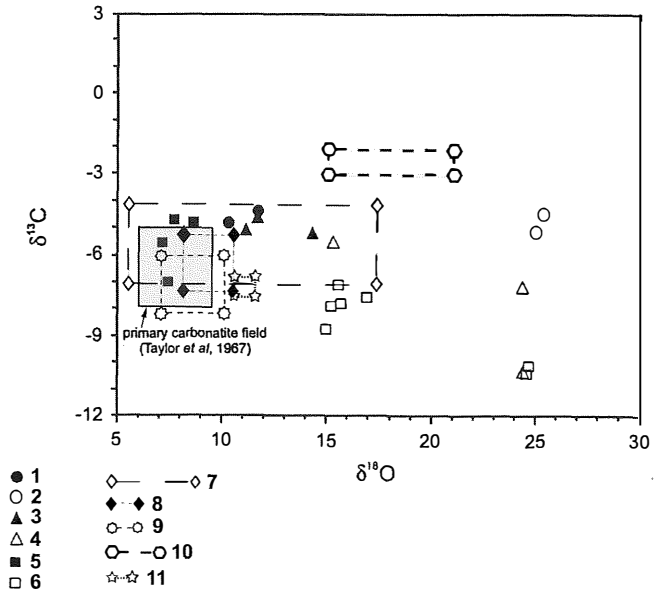

Fig. 2 – Carbon and oxygen isotope composition in carbonatites of Ukrainian shield, West Eifel, Kaiserstuhl, Vulture.
1 – Vulture sovite; 2 – Vulture carbonatite ash; 3 – West Eifel carbonatite; 4 - West Eifel carbonatite ash; 5 – Kaiserstuh soviet; 6 – Kaiserstuh extrusive carbonatites; 7 – Chernigovka car,onatite field; 8 – Octyabrsky massif carbonatite field; 9 – Chlebodarovka carbonatite field; 10 – Pokrovo-Kireevo carbonatite field; 11 – Taromske carbonatite field.

TABLE 1

Isotope geochemistry of carbonatites and some carbonate rocks of Ukraine

Deposit	Geological situation	Method, age (Ma) K-Ar	U-Pb	$^{87}Sr/^{86}Sr$	Isotope composition $^{143}Nd/^{144}Nd$	E_{Nd}	$\delta^{13}C_{carb}$, ‰ PDB	$\delta^{18}O_{carb}$, ‰ SMOW
Chernigovka	Thick bodies (to 100 m) in gneisses and granitoids	1750-1900 (mica) 1950-2100 (amp)	2090	0.70131	0.511585	+0.64	-5.6±1.5	5.6-17.1
Octyabrsky	Small veins (to 0.5 m) in mariupolites, syenites and piroxenites	1600-1800 (mica)	1800*	0.70242	-	-	-6.3±1	9.5±1
Chlebo-darovka	Small dikes in charnokites	1815 (amp)	2030*	0.70258	0.512323	+1.7	-7.1±1.1	9.1±2
Petrovo-Gnutovo	Dikes with parisite in granitoids		2000*	0.70671			-6.8±1.1	10.1-16.6
Pokrovo-Kireyevo	Extrusive carbonatites	350		0.70533	-	-	-5.1±3	15-21
Taromske	Xenoliths in granites	2950 (mica)	3050*	0.70052	0.512193	+1.92	-7.2±0.4	11.1±0.5
Mala Tersa	veines in syenites	1700-1900*	1800-2000*	0.70232	-	-	-6.4±1	10.7-16.2

* - country rocks (granites and alkaline rocks)

crust about 3 Ga ago. Such carbonate fragments were possibly to be primary carbonatite-forming material.

Paleozoic carbonatites

The Pokrovo-Kyreevo alkaline massif is located within junction zone between Donbass and Azov block of the Ukrainian shield. Carbonatite body is interbedded with basalts. The carbonatite body looks like a lava flows. The rock is mainly composed by calcite, some titanomagnetite and apatite. Some analyses of the rock (Shramenko *et al.*, 1992) indicate fairly high values of Sr (0.47 wt%) and Ce and La (either is 0.5 wt%). The K-Ar age is 350 Ma. As the carbonatites of Pokrovo-Kyreyevo alkaline massif are represented by effusive facies, and their isotopic data essentially differ from the above-mentioned rocks ($\delta^{13}C$ from –2.2 to – 8.5‰; $\delta^{18}O$ up to 21.0‰). The stable isotope values of Pokrovo-Kyreevo carbonatites can not be explained applying Rayleigh distillation effect since in this case the rocks represent an open system. Besides, as is generally known, (Bell, 1989) effusive carbonatites are usually enriched with heavy

isotopes of carbon and oxygen because isotope exchange with heavy atmospheric and metamorphogene components may occur during their emplacement.

Discussion

The carbonatites of the Ukrainian Shield and other complexes of Europe have C, O, Sr, Nd isotopic ratios (Fig. 3, 4) indicating that they are mantle-derived. We consider a Sr-Nd isotope system evolution diagram (Fig. 4), for the evaluation of the crustal contamination on the carbonatite compositions. In this model we consider different mixture of low crust material (I), upper crust (IV) and mantle (III) (Faure, 1989). From Fig. 4 is evident that the carbonatites of Chernigovka, Chlebodarovka and Taromske carbonate body as well as some inclusions in kimberlites and lamproites of Australia have been not contaminated by Earth crust material.

Some similarities can be seen also comparing the ages of the Ukrainian and the Fenoscandian shield carbonatites. The time span of formation of the carbonatites in the Fennoscandian shield is wide: from 2615 Ma (eg. Siilinjarvi; Bayanova *et al.*, 2002) to 350 Ma (eg. Kovdor, Khibiny), as it wide for the Ukrainian carbonatites: For example Chernigovka complex, Lavajoki (2020 Ma) and Tikshozero (near 2000 Ma) can be compared with Fennoscandian shield complexes.

The Chernigovka, Tikshozero and Yeletozero carbonatites have got also other similarity with carbonatites occurring within the Fenoscandian shield such as: country rocks composition, ages, carbonatite composition, C and O isotope composition. The Ukrainian and Fennoscandian shield carbonatites compositional comparison are reported in detail in Zagnitko *et al.*, (2000).

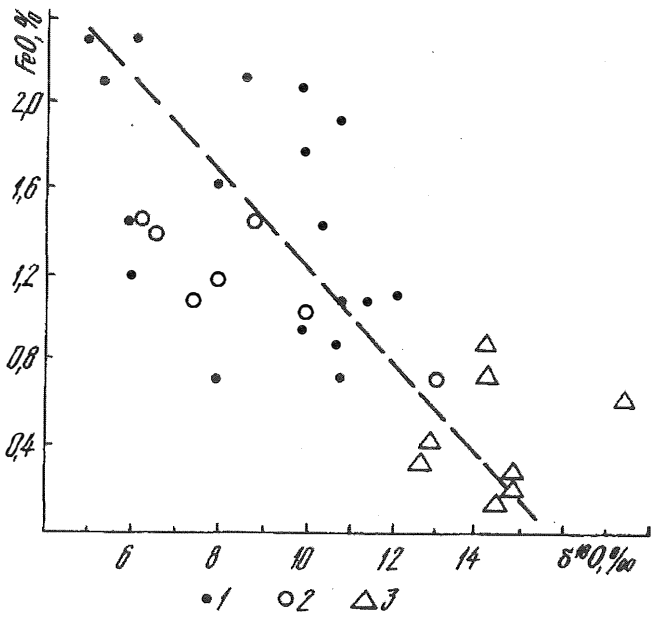

Fig. 3 – Correlation between $\delta^{18}C$ and $\delta^{13}C$ in calcite and degree of iron oxidation in carbonatites.
1 - soviets and alvikites;
2 - beforsites (calcite + dolomite);

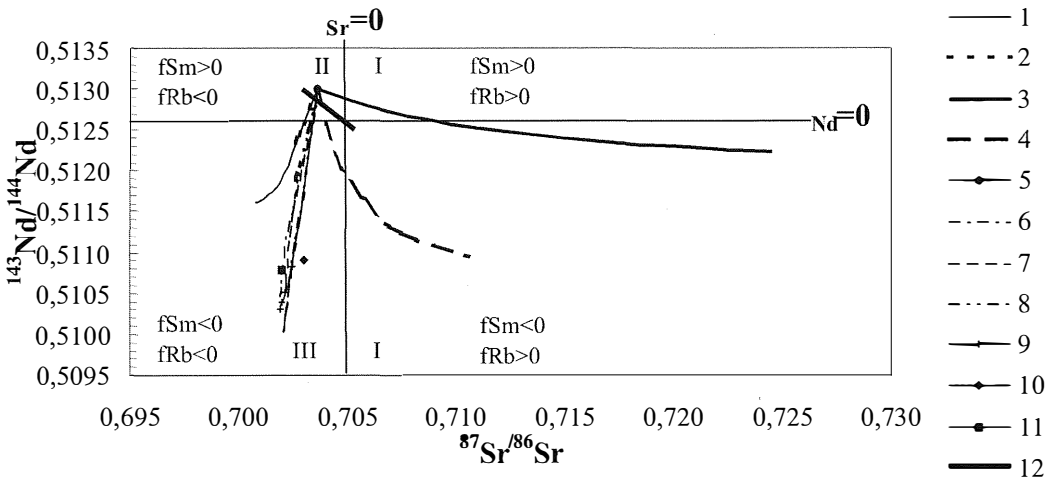

Fig. 4 – Hyperbola of mixing for rocks of continental crust, continental tholeitic basalts and carbonatites [For] Carbonatites of massifs and occurrences: 1 – Chernigovka, 2 – Chlebodarovka (vein), 6 - Mt. Weld (Australia), 7 - Spanish River (N. America), 8 - Borden (ibid.), 9 - Cargill (ibid.). 3 – upper crust; 4 – low crust; 5 - continental tholeites. 10, 11 - subcalcian garnets from inclusions in diamond of Baltfouteen (Kimberli) and Finish. 12 - mantle sequence.

CONCLUSIONS

Thus we consider the carbonatite source of Chernigovka massif (first stage) was the mantle and these magmas have been intruded into crust 2090 Ma ago. Carbonatite intrusions in other alkali-syenite massifs like Octyabrskiy, Mala Tersa and Chlebodarovka can have accompained the final alkali rock emplacement (about 1800 Ma). These small volume, carbonatites differ slightly from carbonatites of first stage in isotopic ratios and mineral compositions. In some cases a remobilization of first stage carbonatites and their re-intrusion as second stage dykes and veins maybe even occurred. The study of the isotope systems (Sm-Nd, Rb-Sr, Pb-Pb) changes occurred in these rocks during their evolution from their formation as primary carbonatites to their possible remobilitization and intrusion as second veins and dikes, can be done. Infact, Pokrovo-Kyreevo carbonatites present hybrid isotopic characteristics likely produced by this kind of evolution.

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