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Sr-Nd-Pb isotope systematics of U-bearing albitites of the Central Ukrainian Uranium Province: implication for the source of metasomatizing fluids

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INTRODUCTION

Sodium metasomatites are relatively widely distributed in the world and often contain uranium mineralization that occasionally may reach industrial scale [4]. Uranium concentrations in deposits of this type are rather low but resources can be quite large especially in the areas where sodium metasomatites achieve wide distribution. As was pointed out by [4], deposits of this type are significantly underexplored and may represent a promising target for further exploration. This is especially true as sodium metasomatites often contain complex mineralization that, besides U, includes Th, Sc, V, Nb, HREE, and Ag.

The Central Ukrainian Uranium Province (CUUP) hosts several large deposits and numerous subeconomic deposits and occurrences. The production started in 1951 and since that time two deposits were completely exhausted. The remaining U resources of the CUUP exceed 300 000 t U with grade varying between 0.05 to 0.20 wt. % U [4].

In spite of the long history of exploration and exploitation of Na-metasomatite type of U deposits in Ukraine, many questions regarding their origin still remain unanswered. The main questions that were debated during decades are related to the source of the metasomatic fluids and the source of ore components. A lot of studies were focused on the geological structure of U deposits in the CUUP, on their mineralogical and chemical compositions, and on stable isotope systematics. Results of these studies were summarized in [1, 4, 13]. However, high-quality geochemical data regarding these deposits were absent until recently [4, 5], whereas radiogenic isotope data is still absent that hampers a reasonable discussion about origin and evolution of the Na metasomatites and about the source of ore components.

The present ideas regarding the origin of metasomatic fluids and their ore load are controversial. The main problems are: (1) a source of huge volumes of high-temperature hydrothermal solutions (with meteoritic waters, basin waters and magmatic fluids being the main alternatives; complex sources evolving in time were also invoked [4]); (2) a source of U and Na, as large volumes of these elements cannot be derived from low-crustal and mantle lithologies, and middle- to upper-crustal sources were considered. However, simple calculations indicate that hydrothermal leaching of the host upper-crustal rocks cannot produce such enrichment as these rocks are relatively poor in both U and Na, and huge volumes of leached rocks are unknown in the area; (3) the association of elements typical for this type of deposits includes elements that are more typical for mafic alkaline igneous complexes rather than for felsic crustal rocks.

In our contribution, we present new Sr-Nd-Pb isotope data obtained for Na-metasomatites of the CUUP and for a large variety of host rocks and discuss possible contribution of different sources to the origin of this type of U deposits.

GEOLOGICAL SETTING

The CUUP is located in the central part of the Ukrainian Shield, within the predominantly Palaeoproterozoic Inhul mobile belt, and partly within the Mesoarchaean Middle Dnieper domain. Most of the deposits and occurrences are located near the southern contact of the Korsun-Novomyrhorod anorthosite-mangerite-charnockite-granite (AMCG) complex (1757-1744 Ma, [7]) where they are hosted by the Novoukrainka gabbro-monzonite-granite massif (2038-2028 Ma, [3, 10]) and granites and migmatites of the Inhul Complex (2022-2062 Ma, [8, 11, 12]). Several deposits are located within in the Kryvyi Rih synform structure which is filled mainly with siliciclastic sediments and banded iron formation. The age of this structure remains poorly constrained and commonly regarded as Palaeoproterozoic to Neoarchaean.

Na-metasomatites being confined to the major fault zones closely associate with numerous mafic dykes widely distributed in the same area. Some of the mafic dykes are older than metasomatites and can be affected by sodium metasomatism whereas other dykes clearly cut metasomatic bodies. Available geochronological data [6] indicate the formation of the mafic dykes at ca. 1800 Ma.

Depending on the lithology of the host rocks, Na-metasomatites are represented by two main mineralogical types. The first type develops after felsic igneous rocks and represented by albitite. The second type includes aegerine-riebeckite metasomatites that develop after iron-rich rocks of the banded iron formation. In all cases, metasomatic bodies are confined to the major fault zones and occur as irregular elongated zoned bodies that were traced along strike for several km whereas the widths of metasomatic bodies may reach several hundred meters and over. The largest bodies were traced by drillings down to 1200 meters and over.

In the further description, we shall focus on the first type of the Na-metasomatites, i.e. on U-bearing albitites. In a generalized form, zoning in these rocks can be described as a gradual transition from unaltered host rock (granite, migmatites, gneiss etc.) to quartz-free (desilicified) microcline-albite metasomatite ("syenite") and then to albitite. This rock succession formed during the progressive (albititic) stage of the alkaline sodic metasomatic process. The late mineral assemblage that includes phlogopite (or late chlorite), carbonate and hematite are often superimposed on the internal parts of albitites. Besides this, secondary quartz, epidote, and microcline are often superimposed on intermediate and external parts of the metasomatic bodies. These minerals are regarded as developed during removal of silica, calcium, and potassium from central (albititic) parts of metasomatic bodies [1, 4, 13].

MINERAL COMPOSITION

Albite occurs as the main (up to 90 %) rock-forming mineral, whereas the amount of mafic minerals usually does not exceed 10 %. The typical mafic minerals are alkaline amphibole, alkaline pyroxene, epidote, chlorite, diopside, actinolite, and garnet. The proportion of albite and mafic minerals is generally defined by the composition of the initial rock. The amount of pyroxene varies from almost 0 to 10 %. Pyroxenes belong to aegirine (amount of the Ca component varies from 0 to 45 mol. %) and diopside-sahlite (amount of the Na component varies from 0 to 20 mol. %). Pyroxenes that contain over 10 % Sc2O3 occur as well-defined inclusions within the aegirine-pyroxene matrix. Amphibole usually associates with pyroxene and varies in composition from riebeckite to slightly alkaline actinolite. Garnets belong to the andradite-grossular series and occur mainly in deposits located in the Novoukrainka granite massif where the amount of garnet may reach 50 %. Garnets occur in association with diopside, actinolite, and epidote; sometimes it may be found in association with aegirine. Epidote is a rock-forming mineral in so-called "syenites"and certain types of albitites. It often replaces garnet in the garnet-diopside metasomatites. Epidote in albitites of the Partizanske ore field contains a large amount of Sr. Accessory minerals in albitites are apatite, zircon, titanite, monazite, uranothorite, allanite, which present in all types of U-bearing sodic metasomatites. Phenakite, thortveitite, and schorlomite are rare minerals. The origin of accessory minerals is not clear as they may represent relict phases left from the initial (pre-metasomatic) rocks.

Albitites contain also various opaque minerals, including hematite, magnetite, titanomagnetite, rutile, ilmenite, galena, pyrite, chalcopyrite, sphalerite etc. Native silver in concentration reaching up to 1 % in Na-metasomatites of the Kryvyi Rih –Kremenchuk zone was known for a long time. In the northern part of the Vatutinske deposit concentration of silver reaches 300 ppm. The accompanying minerals are galena, pyrite, marcasite, chalcopyrite, sphalerite, minerals of U, Ti, and Ba.

Main U minerals are uraninite (U4+, U6+ Pb, Ca, REE, Zr)O2-x and brannerite (U4+, Ca, Th, Y)[(Ti, Fe)2O6]· nH2O. Uraninite is unevenly distributed and absent in some deposits. Electron microprobe analyses have revealed the presence of up to 20.51 % PbO, 6.20 % CaO, 0.78 % Y2O3, 3.90 % Ce2O3, and 1.72 % ZrO2. Brannerite occurs as the main ore mineral in many of the deposits of the CUUP. It often develops after Ti and Ti-bearing minerals; there is a persistent association of brannerite with rutile, anatase, carbonate minerals, quartz, and sericite.

GEOCHEMISTRY

Our data demonstrate regular variations of the chemical composition in the vertical profile across the albitite bodies. Being compared to the host granite, albitites demonstrate a sharp decrease in the abundances of SiO2 and K2O. Al2O3 slightly increases near contacts against host granites and then decreases in the central part of the metasomatic body. Most other major oxides show significant enrichment in albitites. Fe2O3, CaO, TiO2, and MgO demonstrate pronounced enrichment in the U-rich central (axial) parts of the albitite body. Na2O is sharply increased in metasomatites, but demonstrate a moderate decrease in the axial part of the body.

According to [4], distribution of REE in barren albitites is very close to that in the host granite. In general, barren albitites are slightly enriched with respect to LREE, and depleted in HREE, being compared to the host granite, but these differences are not significant. Our new data indicate that albitite samples rich in U are highly enriched in HREE. We suppose that metasomatic fluids responsible for U enrichment were also rich in HREE. This feature is not typical for felsic rocks that may be considered as the main source of U (and Na).

SR-ND-PB ISOTOPE SYSTEMATICS

A set of whole-rock samples was collected at the Novokostyantynivka and Novooleksiivka deposits. These rocks were analyzed for Sr, Nd, and Pb isotopes. As can be seen from Sr isotope data, metasomatic rocks have isotope signature typical for the crustal rocks. Specifically, rocks of the Novokostyantynivka deposit have 87Sr/86Sr(1800) in the range 0.7087 to 0.7105, whereas in the rocks of the Novooleksiivka deposit 87Sr/86Sr(1800) varies from 0.7172 to 0.7207. There is no strict correlation between 87Rb/86Sr and 87Sr/86Sr ratios that makes impossible the construction of isochrons and production of reasonable Rb-Sr isotope ages. This indicates inhomogeneity of the Sr isotope composition that could result from the variable host rock/metasomatic rock ratio in our samples.

In the Novooleksiivka deposits samples were collected systematically across the vertical section of the metasomatic body. As follows from our results, there is a tendency for albitite samples in the axial part of the body to have less evolved initial Sr isotope composition. This tendency may indicate that the metasomatic fluids were derived from a source that had a lower Rb/Sr ratio than the upper crustal granites. However, this question requires further confirmation on other deposits.

Neodymium isotope composition, in contrast to Sr, is much more consistent in both studied deposits and allows construction of a rather good isochron. The age yielded by the isochron (1728 ± 110 Ma) corresponds within error to the U-Pb age previously obtained for the U deposits of the CUUP. εNd value according to the isochron is -4.8 and indicates the crustal source of albitites, in accordance with Sr isotope data.

There is, however, a small systematic difference between the Novokostyantynivka and the Novooleksiivka deposits: the average εNd(1800) value for the Novokostyantynivka albitites is -3.7, and for the Novooleksiivka albitites is -4.5. These results are consistent with Sr isotope data, according to which the Novooleksiivka deposit reveal more “evolved”crustal source.

Lead isotope compositions indicate the great prevalence of radiogenic Pb, whereas “common”Pb is virtually absent. This allows calculation of the Pb-Pb age of the deposits formation. There is no sufficient difference in the age of the Novokostyantynivka and Novooleksiivka deposits, both deposits were formed at 1810 ± 17 Ma. This age is in good agreement with the previously obtained U-Pb ages and with Sm-Nd isochron age (sees above).

The obtained isotope results can be compared with data available for the main lithologies present in the area. Albitites of the Novokostyantynivka deposit plot between fields of the Novoukrainka massif and Korsun-Novomyrhorod AMCG Complex, closer to the Novoukrainka field. In contrast, albitites of the Novooleksiivka deposit plot entirely within the field defined by the Inhul granitoid Complex. It has Nd isotope characteristics similar to the Novoukrainka massif but differs by their much higher Sr isotope values.

DISCUSSION AND CONCLUSIONS

Many features of the U-bearing Na-metasomatites of the Central Ukrainian Uranium Province have received a due attention of the researchers. These features include the geological structure of the deposits, their mineral composition and some aspects of the isotope geochemistry (O, C, and H isotopes, see [4] for an overview). However, some features, very important for the understanding of the origin of Na-metasomatites and related mineralization still remain underexplored. For instance, high-quality geochemical data regarding metasomatic rocks are still very limited in number. This is especially true with respect to U ores geochemistry of which is still poorly studied. The same can be said about isotope geochemistry of Sr, Nd, and Pb.

In the author‘s opinion, following features are very important for the understanding of the origin of Na-metasomatites and related mineralization: (1) close spatial relation of the Na-metasomatites with the Korsun-Novomyrhorod AMCG plutonic complex. Most of the deposits and occurrences are located within 30 km away from the contact of the complex. In addition, Na-metasomatites closely associate with numerous mafic and ultramafic dykes of tholeiitic affinity; (2) close temporal relationships with mafic dykes which according to the available geochronological and geological data intruded simultaneously with the formation of Na-metasomatites at c. 1815-1800 Ma. The Korsun-Novomyrhorod AMCG Complex is 50-60 M.y. younger, but its formation may have started at c. 1800 Ma, as evident from findings of older xenolith of anorthositic rocks; (3) “Mixed”geochemical characteristics of the Na-metasomatites: these rocks are rich in Na, U, Th, Sc, V, Nb, HREE, and Ag. This combination of elements is not typical for felsic rocks and can be rather related to mafic alkaline sources; (4) newly obtained Sr and Nd isotope data indicate crustal sources of the main volume of Na-metasomatites.

Formation of the mafic dykes and Korsun-Novomyrhorod AMCG Complex was linked to a long-lived mantle plume [6, 7], although relation of the mafic magmatism to the rotation-caused crustal extension and mantle melting was also proposed [2, 9]. In any case, emplacement of numerous mafic dykes and formation of the huge Korsun-Novomyrhorod AMCG Complex implies the presence of the large-scale thermal anomaly in the mantle and low crust. Metasomatizing fluids were probably generated in the upper mantle and on the way through the crust they have achieved crustal isotope signature. However, their useful load was probably derived from the mantle as crustal felsic rocks can hardly be considered as a source of such elements as Sc, V, Nb, HREE. We assume that metasomatizing fluids may be related to mafic alkaline melts which were responsible for the formation of various alkaline (syenites, aegerine-riebeckite syenites) and subalkaline (monzonites) rocks that are present in the Korsun-Novomyrhorod plutonic complex.

It is interesting that available isotope geochemical data indicate the significant dependence of the isotope composition of the Na-metasomatites on low-crustal (?) rocks. Both studied deposits occur within the Novoukrainka gabbro-monzonite-granite massif and there is no reason to assume that host rocks for these two deposits are very different in terms of their isotope composition. However, one of the deposits (Novokostyantynivka deposit) has Sr-Nd isotope composition more typical for the Novoukrainka rocks, whereas another deposit (Novooleksiivka deposit) reveals Sr-Nd isotope composition more typical for the Inhul granites. Some differences in their mineralogy and geochemistry may also occur, but this question requires further detailed investigation. According to our model, metasomatizing fluids were derived from the hot upper mantle melts from which they have inherited their useful load. On the way through the low crust they achieved their crustal isotope signature which apparently was not significantly modified during the interaction with the upper-crustal rocks.

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