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THE APPLICATION OF ISOTOPIC DATING METHODS FOR PROSPECTION AND EXPLORATION OF NUCLEAR RAW MATERIAL

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Abstract

Among the geological methods of forecasting and exploring radioactive raw material deposits isotopic dating methods determine an important prospect criterion - the time of ore deposition. For a number of studied Paleozoic hydrothermal uranium deposits a long duration (100-160 m.y.) and a complex polychronal character of multistage ore process are established with the age intervals from 15-30 to 100 m.y. between successive stages.

During two last decades, isotopic dating methods improving precision of genetic conceptions and efficiency of geological prospection have played an important part among geological, methods of forecasting and evaluating industrial uranium stock of some territories.

A combined application of different methods of nuclear geochronology - lead isotope method for ores, argon and strontium method for rocks developed in the regions of uranium deposits - permits to perform a paragenetic synchronization of ore processes with specific stages in the development of tectonics, magmatic activity, metasomatism and hydrothermal activity. All this gives new important information promoting further development of modern metallogeny /1, 2/.

For effective and correct use of the isotopic dating information it is necessary to appreciate the real possibilities of the methods connected both with characteristics of the material studied and the degree of their conformity with closed geochemical systems and with resolution of methods which is assumed to be $\pm$3-5% of the age determined using modern mass-spectrometric and analytical techniques. Thus, for ancient pre-Cambrian deposits with mineralization age about 2 milliard years only on account of analytical errors (mainly when determining uranium and lead concentration) the scatter for mineral formations of the same age can be obtained within $\pm$60-100 million years when using for calculations isotopic ratios of $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$. Only employing the radiogenic lead isotopic ratio $^{207}Pb/^{206}Pb$ less subject to the influence of ordinary geochemical processes and determined to within $\pm$1%, the scatter of age values can be reduced up to $\pm$20 million years. Even in the case of considerable discordance of age values for different isotopic ratios for pre-Cambrian ores the most reliable value is that, determined by $^{207}Pb/^{206}Pb$.

According to the published data /3/, the interval duration between separate phases of tectonic process is estimated to be within 15-20 million years. Therefore, it is difficult to devide pre-Cambrian ore processes to consecutive stages of minerogenesis connected with tectonic fracturing according to isotopic dating values. As a result of detailed comprehensive study of ores we can only distinguish large epochs of ore deposition.

For Phanerozoic ore processes (< 500 million years) the possibility of using $^{207}Pb/^{206}Pb$ isotopic ratio is greatly limited by requirements of high-precision mass-spectrometric analysis, by small correction for impurity of ordinary lead and by significant uncertainty of calculated age data caused by physical reasons. So, the main isotopic ratios for age calculations of Phanerozoic uranium ores are $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$. At the same time these ratios can be affected by substantial disfortion from superimposed geochemical processes.

To overcome the difficulties involved, at present different versious of graphical isochronous methods are used in which for series of minerals of the same age affected by later metamorphism processes the mathematical evaluation of the most probable averaged age value can be done /4/. At the same time the reliability of geochronological data greatly increases with the use of special mineralogo-geochemical methods determining the degree of conservation of dated materials.

The use of sufficiently well conserved and mineralogically studied ore materials for accumulation of necessary sta-

tistics has allowed to devide the ore formation process into successive stages for a series of Phanerozoic ore deposits. As an example of such division of Paleozoic ore formation process based on detailed overall study we can cite isotopic age data obtained for one uranium deposit with a complex, polychronous ore mineralization (see Table I.).

T a b l e I.

Isotopic dating values for a Paleozoic uranium deposit

Mineral association	Age values (million years) $206_{Pb}/238_{U}$	Age values (million years) $207_{Pb}/235_{U}$	Isochronous age	Ore deposition stages
Apatite-arshinovite brannerite	429,418,450	435,415,419	415 ± 11	Silurian
Molibdenit-coffinit-nasturan	384,364,355 350	362,357,354 341	370 ± 10	Devonian
Nasturan-carbonate	273,267,243 236,240,279 256,277,218 209,218,208	274,276,248 241,270,301 288,309,266 245,270,277	254 ± 8	Permian

Note. Isochronous age was calculated by isochrone in coordinate system: $207_{Pb}/204_{Pb}$: $235_{U}/204_{Pb}$.

The table shows that the total duration of ore complex forming process is 160 million years and covers a range of time from Silurian to Permian period with age intervals of 45 and 116 million years between successive stages.

For another deposit in the same way the possibility was considered for isolation of 5 successive stages of minerogo-

nesis connected with the origin of new systems of mineralized fractures traversing the earlier ore bodies. Using veined uraninite-coffinite-nasturan ores we have obtained age values with a good agreement for both isotopic ratios. Average values for successively developed mineral associations form the following series:

I	II	III	IV	V
430	400	385	360	330 m.y.

The duration of ore complex formation is 100 million years and covers a geological epoch from Silurian to Medium Carbonic period. It is evident, that such a fractional division into age groups with differences of 15-30 million years could not be sufficiently well established if it were not confirmed both by mutual intersections of mineralized fractures and by mineralogo-geochemical parameters of the specimen studied.

Thus, for Paleozoic uranium ore deposits a long duration (100-160 million years) and a complicated polychronous character of multistage process of ore complex formation are established. When the earliest ore mineral associations (420-430 million years) are of Silurian period, an extensive development of ore process is noticed in Devonian period (350-370 million years), and final stages in Carbonic and Permian periods including the latest hydrogenic processes of ore redeposition during Upper Paleozoic activity period (330-250 million years).

It should be noted that according to argon method data for magmatic and metamorphic rocks of the same ore province very closed age reference points are established, which allow

to reveal the correlation links for tectono-magmatic, metasomatic and ore-forming hydrothermal processes. Uranium deposits are fine indicators fixing postore phases of tectonic movements and connected with them intensification of hydrothermal processes.

From generalized results of isotopic-geochronological studies of some uranium deposits one can see their fundamental importance both for genetic conception development and hence for prediction and rational direction of geological prospecting, and for evaluation of promise of flanks and depth of worked deposits.

The problem of extensive use of lead isotope method is complicated by the fact of widely met discordance of calculated age values according to different isotopic ratios which involves considerable difficulties in correct choice of values of the true age of ores and minerals. First of all, this is connected with deterioration of closure of geochemical mineral systems conditioned by different superimposed processes, producing partial losses of mother and daughter elements. Accordingly, isotopic ratios used for dating can be significantly distorted. The experience of geochronological investigations performed for many years has allowed to evaluate the importance of series of spontaneous processes resulting in a modification of mineral structure. The significance of radiogenic lead partial loss has been establised impirically long ago; this causes underestimation of age values according to the main isotopic ratios $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$. The mechanism and geochemical factors of preferential loss of lead

compared to uranium, which is more apt to migration, are not well understood.

For evaluation of degree of closure of uranium-lead system in radioactive minerals and suitability of uranium minerals for use as geological chrometers special mineralogo-geochemical and radiochemical methods are developed. The principal object of such investigations consists in determination of internal structure state of minerals by means of ore and electron microscopy, track radiography, X-ray structure analysis, determination of the valent state of uranium ("oxygen coefficient"), character of radioactive equilibrium of uranium with intermediate fission products, coefficients of Rn emanation and U, Ra, Pb leaching.

We have obtained important results using, together with the cited methods, local X-ray microprobe analysis for investigation on the state of uranium-lead system in the main types of uranium ore minerals. Basic results of these investigations can be formulated as follows.

1. For the most widespread ore-forming uranium minerals (oxide group - uraninite and nasturan, titanate group of brannerite type, silicate group of coffinite type) different bonding strength is established between radiogenic lead in mineral structure which decreases in the mentioned sequence.

2. Stabilization of atoms of radiogenic lead is possible only in the case when they occupy vacant lattice points. As lead is foreign element in crystal lattice of uranium mineral structures, it can form chemical bonds with lattice components only by way of "forced isomorphism" /5/ to uranium.

Such a state is characteristic for natural uranium oxides - uraninite and nasturan having oxygen coefficient $O/U \leqslant 2{,}60\text{-}2{,}63$, lattice parameter $a_o \geqslant 5{,}41\text{-}5{,}42$ Å and equilibrium ratios of uranium with intermediate fission products. According to X-ray microprobe data they are characterized by uniformly dispersed lead distribution in mineral structure and by strictly constant value of lead - uranium ratio in different locations in mineral which corresponds to real age (Fig. 1). Uranium oxides which meet these requirements are reliable geochronometers.

3. Secondary processes of nasturan (uraninite) modification - oxidation ($O/U > 2{,}63$), hydration and others are accompanied by essential structural change with isotope redistribution and their partial carrying away from minerals. In this case, isotopic ratios Pb/U can be greatly distorted to one or another direction (Fig. 2). For the paths of lead migration electrochemical processes are of great importance as they result in lead fixation on surface films or on colomorphous sulphide minerals (pyrite, molibdenite, femolite).

In this case radiogenic isotope ratio $^{207}Pb/^{206}Pb$ can retain its geochronometrical value of modification of minerals is connected with modern hypergenesis.

4. Uranium titanate groupe of brannerite type ($U/Ti_2O_6/\cdot nH_2O$) is widly spread in metasomatic uranium mineralization and is ordinarily characterized by metamict state (weakening of structure under radiation). Chemical bonds of radiogenic lead in brannerite structure are considerably weakened. The position of its most part does not correspond to

the state of "forced isomorphism" to uranium. As a rule, lead is nonuniformly dissipated (in atomic form?) in crystals and is concentrated in their microdistortions; it is present in the form of metallic, oxide or sulphide lead filling the pores and cracks (Fig. 3).

Unstable state of radiogenic lead in the uranium titanate structure determines the possibility of its migration outside the mineral. This fact often makes unefficient the use of monomineral brannerite fractures for dating, specially in the case of fine-dispersed ore type. At the same time for pegmatoid coarse crystals of brannerite sufficiently reliable age values can be obtained even at nonuniform distribution of radiogenic lead. Such a case is shown in Fig. 3 where horisontal dotted line marks the quantity of lead corresponding to real age of given brannerite (300 million years).

The study of cogenetic pairs of uranium oxides and titanates has shown that irrespective of age, geochemical conditions of medium and degree of metamictity the conservation of radiogenic lead is distinctly less in brannerites (Fig. 4). All this considerably restricts the use of uranium titanates for radiologic dating.

5. Uranium silicates of coffinite type $U/SiO_4/\cdot nH_2O$ have turned out to be quite unacceptable for radiologic dating. According to modern mineralogical data /6/, the coffinite structure is energetically unstable, undergoing spontaneous fission with formation of pseudomorphs of more stable oxide components. Our investigations on uranium-lead system state in a series of coffinite speciemens of different age (from

pre-Cambrian to Mesozoic) have shown a very low concentration background of radiogenic lead at the level of 0,0n-0,n%, irrespective of the speciemen age. Practically all radiogenic lead is removed from coffinite structure. It concentrates in structure distortions from which it migrates under action of porous solutions or by diffusion. Thus, the presence of coffinite often observed in nasturan ores is responsible for intensive processes of radiogenic lead redistribution which reduces the geochronometric value of such ores. Uranium-silicate ores can be used for dating only in the form of bulk samples.

6. The use of X-ray microprobe analysis for study of the dated radioactive minerals /7/ provides, in principle, new information on uranium-lead system state and on processes of uranium mineral modification. The data obtained with this expressive method showing the character of distribution of basic structural components allow to develop new criteria for suitability evaluation of different types of uranium minerals for ore process dating and to suggest more substantiated methods of sampling for radiologic dating.

As a result of the studies performed we can give some practical recommendations on dating technique. So, for macroscopically detectable vein-type and coarse-embedded minerals it is necessary to use monomineral fractions of uranium ores corresponding to the particular paragenetic associations. For fine-dispersed submicroscopic metasomatic mineralization it is wise to use only bulk samples. A more detailed specification of mineral fractions results in acquisition of incorrect

age values.

As an illustration showing the existance of considerable shifts in isotopic ratios of mineral fractions, we can cite the results of analysis of two fractions taken from pre-Cambrian nasturan-coffinite metasomatic ore mineralization. The ore concentrate (fraction with specific weight $d > 3,3$) with high uranium content has shown a significant loss of radiogenic isotopes ^{206}Pb and ^{207}Pb. At the same time in a more light fraction (with specific weight $d < 3,3$) consisting mostly of ore-bearing rock, an excess of radiogenic lead is revealed. The calculated age values illustrate convincingly this process of partial lead removal from uranium minerals:

	$\frac{206}{238}$	$\frac{207}{235}$	$\frac{207}{206}$
Ore concentrate ($d > 3,3$)	1456	1561	1810 m.y.
Ore-bearing rock ($d < 3,3$)	3282	2456	1850 m.y.

It should be noted that the age values calculated by lead radiogenic isotope ratio for both fractions are close and provide the most reliable dating of ore process.

Another example refers to Paleozoic uranium-phosphatic ores of Devonian period with bulk sample age of 370-350 million years. The mineral fractions separated from these ores have shown a considerable scatter in age values. The ore concentrate with uranium content hundreds times as much as that of initial ore has shown the deficit of radiogenic lead up to 60-80%. The concentration curves of uranium and lead obtained

with X-ray microprobe on polished ore sections have shown distinct uranium peaks corresponding to finest precipitations of uranium ore and considerably wider aureoles of radiogenic lead.

As can be seen from the foregoing, the acquisition of reliable isotopic age data must be based on the results of careful overall mineralogo-geochemical and radiochemical study of uranium mineral ores. Isotopic dating values are quite necessary for modern understanding of ore-forming processes and minerogenesis problems, for determination, forecasting and evaluation of promissing areas. This is particularly important in those cases when isotopic dating values require the introduction of significant corrections in geological and metallogenic conceptions developed earlier.

The investigations on isotopic dating of uranium deposits and ore provinces must be considered as an indispensable part of the whole combination of works at the study and development of ore-raw material base for atomic energy.

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Figures

Fig. 1. Uranium and lead concentration curves according to unmodified nasturan.

Fig. 2. Uranium and lead concentration curves according to hydrated nasturan.

Fig. 3. Uranium and lead concentration curves according to brannerite.

Fig. 4. Titanium, uranium and lead concentration curves according to cogenetic nasturan and brannerite crystals.

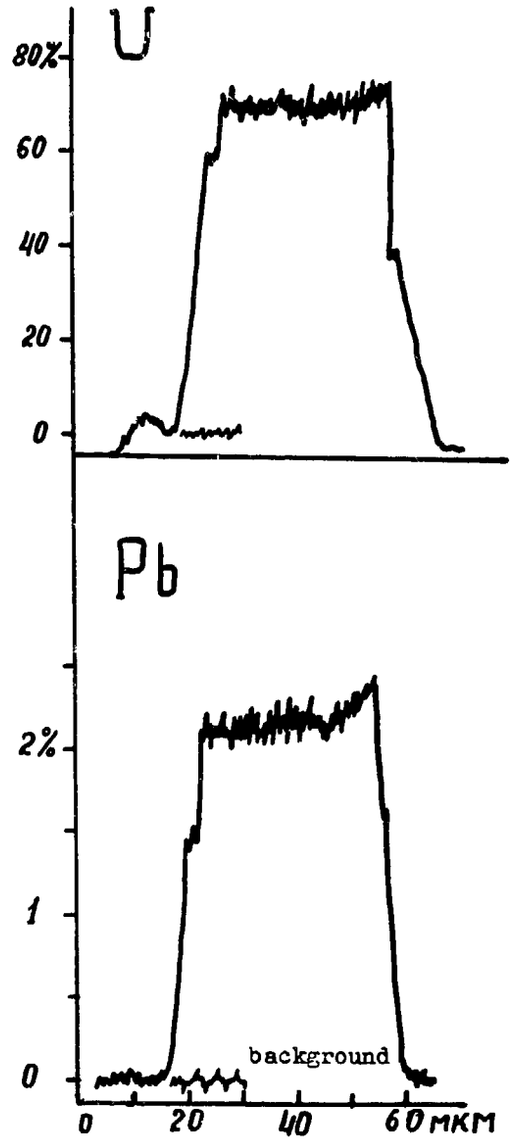

FIG. 1

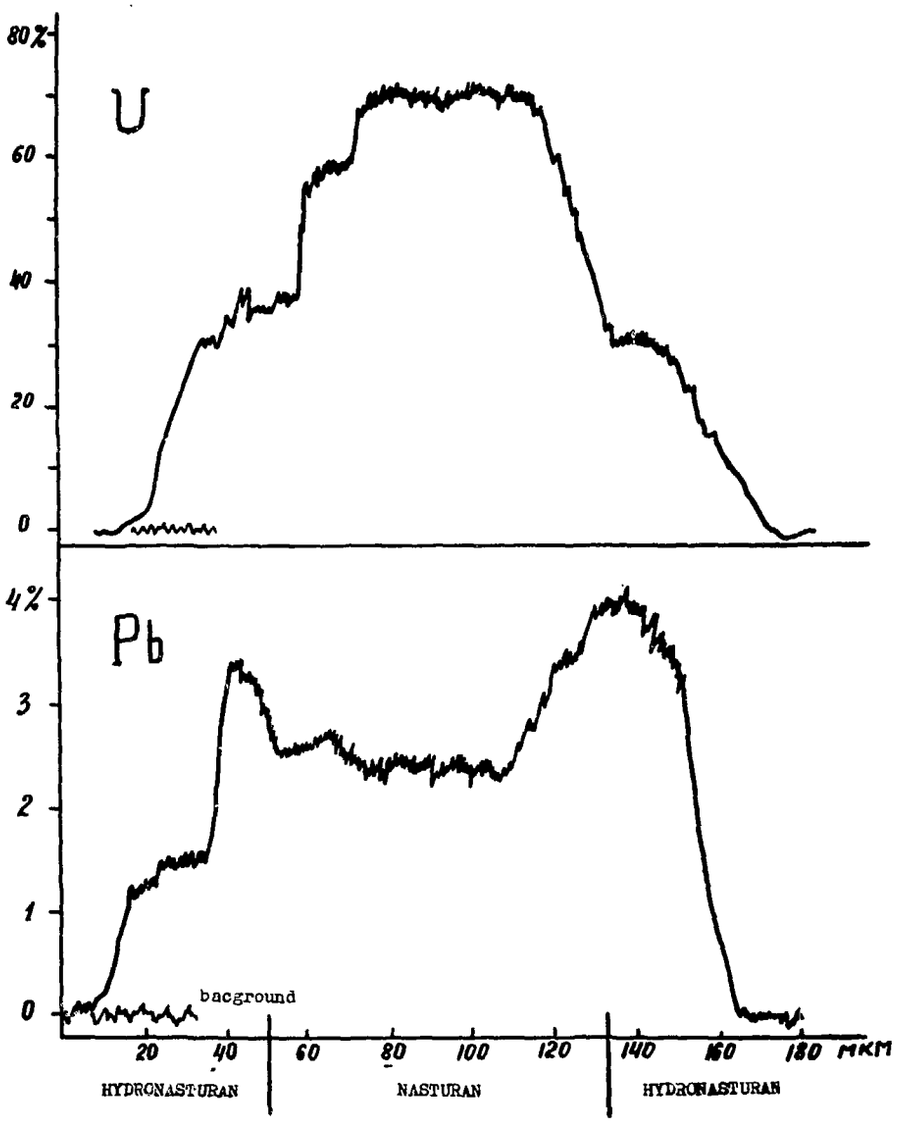
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FIG. 2

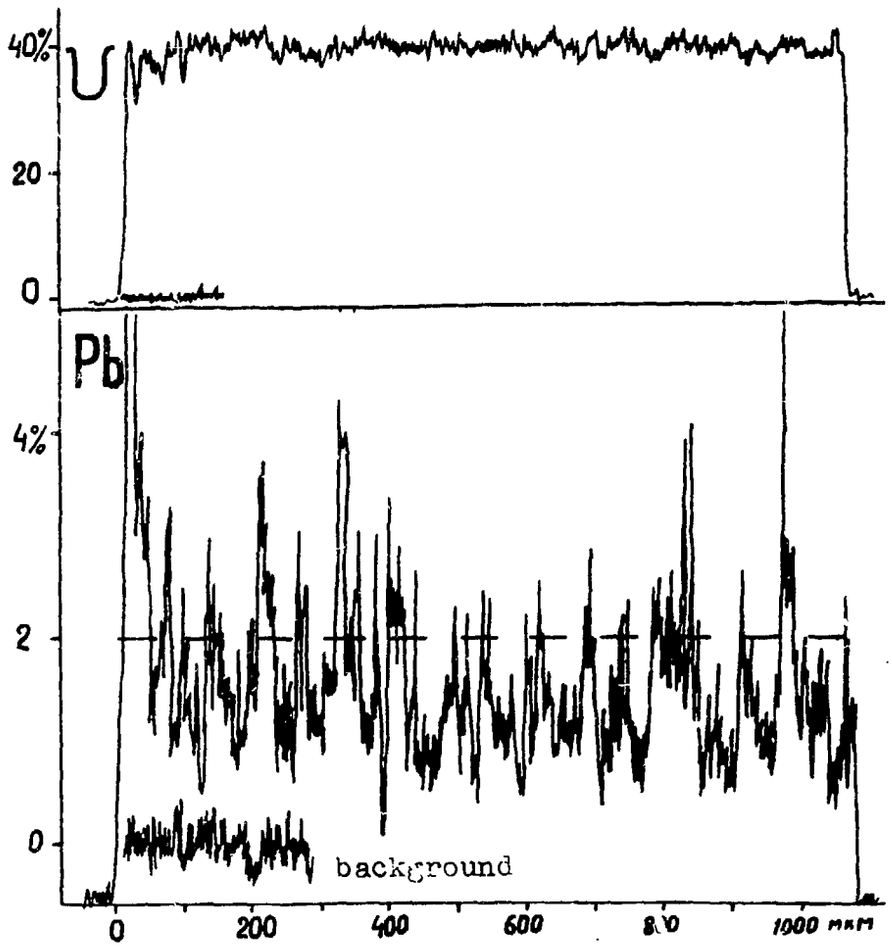

FIG. 3

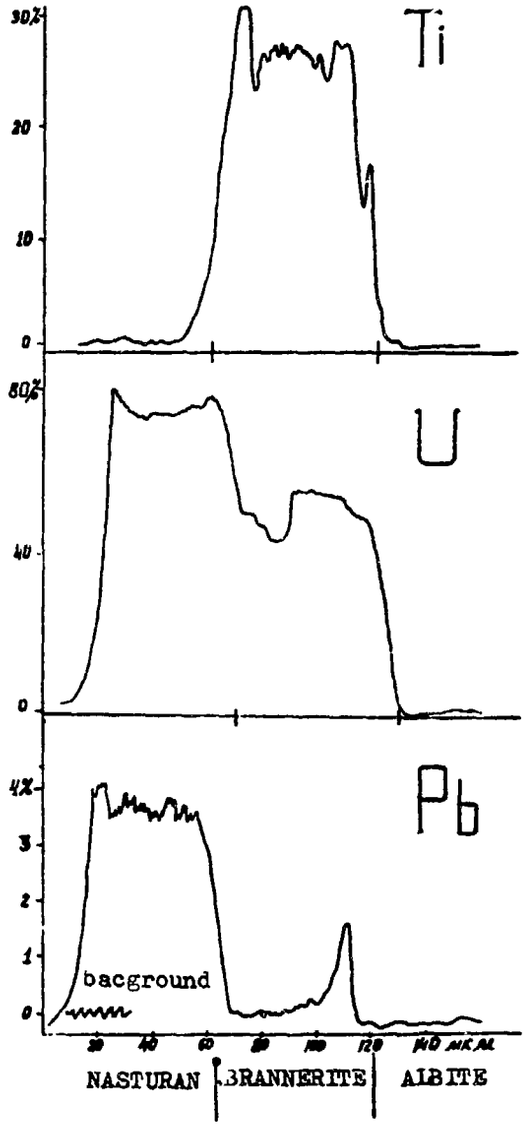
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FIG. 4