

# NUCLEAR-ANALYTICAL AND MINERALOGICAL PRINCIPLES AND TECHNIQUES FOR PREDICTION AND INVESTIGATION OF THE NATIVE-PURE RARE ISOTOPE OCCURRENCE

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Combining nuclear microanalytical, mineralogical, crystallochemical and geochemical approaches, the authors analyze a possibility of natural occurrence of enriched or even pure and superpure rare isotopes that can be extracted from ores. Methods of and results from the investigations of these isotope anomalies are presented.

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## INTRODUCTION

By the middle of the XXth century the importance of the isotope enrichment and pure and superpure isotope production to the further development of civilization has been generally recognized. At present isotope starting materials are employed in atomic industry; from stable isotopes a wide spectrum of tracer atoms are obtained, e.g. to produce various radioactive isotopes for therapeutic and diagnostic purposes in medicine. Isotope shifts exhibited by different properties of materials can be used for providing security of bank notes, documentation, all sorts of information, for controlling laser systems, etc. Pure isotopes have use in nuclear and other fields of research, suggesting that in the XXIst century, most of them if not all stable and long-lived isotopes now numbering 288 [1], will find applications.

Isotope separation is an expensive process, so pure isotopes, especially rare ones cost from ten to hundred thousand times more than a corresponding mixture of natural isotopes of similar purity. Thus, a search for and utilization of anomalously enriched natural isotopes might be very promising.

The ratio of radioactive isotopes and derived thereof radiogenic isotopes conserved in hard minerals and natural glasses is extensively applied to dating geologic formations.

## SPECIFYING THE RANGE OF SEARCH FOR NATIVE PURE RARE RADIOGENIC ISOTOPE

Pure stable radiogenic isotopes can be formed in the course of natural radioactive transformations in which radiogenic nuclides produce atoms with chemical properties differing from those of atoms whose nuclei undergo the transformations. If the event takes place in minerals, the newly formed atoms may be "conserved" in the mineral structure. The newly formed atoms may belong to an abundant or trace element present in the crystal or to an element that cannot be detected with most sensitive detection techniques. In the latter case to be discussed here, a new element formed in the crystal as a result of a radioactive decay is accumulated as a pure iso-

tope. In this situation the crystal structure and geochemical history of the mineral formation should be favorable for accumulation of a radioactive element, but unfavorable for occurrence of an element to which a radiogenic isotope belongs.

For example, three-layer packets in the mica structure (Fig. 1) are joined by large univalent cations,  $K^{+1}$ . If a mineral-forming medium includes rare alkalis whose atoms also constitute large cations ( $Rb^{+1}$ ,  $Cs^{+1}$ ), they can substitute potassium isomorphically. At the same time, in the mica structure there is no position to be occupied by a large divalent ion of strontium whose original content in mica is very low.  $^{87}Sr$  produced via a beta-decay of  $^{87}Rb$  is probably held in the structure due to the defect formation with the local substitution of  $(OH)^{-}$  for  $O^{2-}$ .

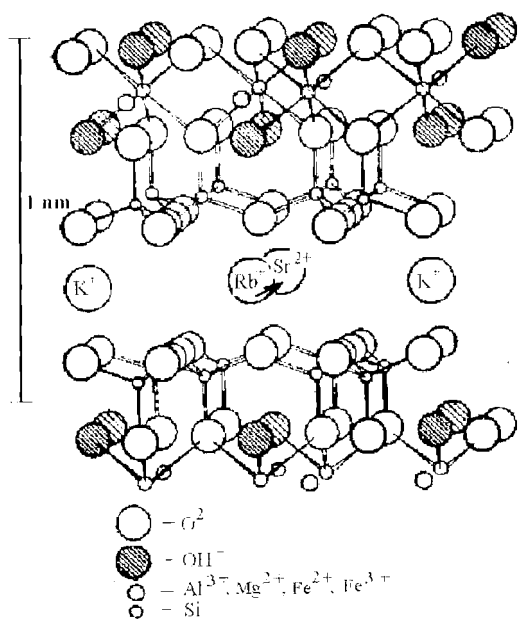
Radioactive decays favoring the accumulation of rare stable isotopes depend on the concentration of the original radioactive nuclide ( $C_{pa}$ ) and the ratio of its half period ( $T_{1/2}$ ) and the host mineral age ( $t$ ):  $C_{pr} = C_{pa} \cdot [\exp(t_n \cdot 2 \cdot t / T_{1/2}) - 1]$ , where  $C_{pr}$  is the radiogenic isotope content in the mineral matrix.

To identify possible rare isotopes that can be preserved in pure form in mineral matrices certain boundary conditions for their accumulation were considered.

## MINIMAL RADIOACTIVE ATOM HALF-PERIOD REQUIRED FOR RADIOGENIC ISOTOPE ACCUMULATION

Even the age of oldest earth minerals is far smaller than that of their constituent atoms. The Solar System age and the minimum age of its matter is approximately 4.8 billion years. Planets including our Earth are 4.5 billion years old. The first half-billion years of Earth's life have recently been termed the "Hades era" from the old-Greek word "Hades" which in ancient mythology was the name of a place where souls went after death, i.e. hell of a kind.

This term reflects a modern idea of the conditions on Earth at that time: heavy meteorite "bombing", with catastrophes of planetary scale following one after another and the whole Earth mass to the depth of tens of kilometers from the surface being many times shifted, mixed and melted.



**Fig. 1.** A diagram of radiogenic strontium location in the Rb bearing biotite structure  $(K,Rb)(Mg,Fe)_3[Al-Si_3O_{10}](OH,F)_2$

Thus, on early Earth long-lived radioactive nuclei could not be found in more or less long-lived crystals and their decay products could not be accumulated in a hard matrix. The onset of a more quiet period in Earth's history is displayed in the age of the oldest rocks that by modern estimates approaches 3.7...4.0 billion years. Relatively abundant are rocks  $(3.7...3.4) \cdot 10^9$  years old. Somewhat younger are the oldest ores, i.e. natural formations of contrasting chemical composition enriched by certain chemical and mineral components and thus suitable for extractions. The oldest ores are  $(3.0...3.4) \cdot 10^9$  years of age. This is precisely the age of the oldest rocks and ores of the Ukrainian Shield [2] that occupies an area of about 200 thousand km<sup>2</sup>, i.e. one-third of the Ukrainian territory (Fig. 2).



**Fig. 2.** Location of the Ukrainian Shield (shaded)

Thus, the age of nuclides, including radioactive one, exceeds the age of the oldest minerals by at least  $(0.8...1.1) \cdot 10^9$  years for rocks and  $(1.4...1.8) \cdot 10^9$  years for ores.

To specify boundary conditions for the search for radiogenic isotopes "conserved" in the ancient mineral structure we assumed the minimum time interval between the production of a nucleus and its fixation in a certain solid (crystalline) phase to be  $10^9$  years in a first approximation. The fraction of the initial radioactive

atom preserved after the time,  $t$ , is determined by the equation  $C=1/2^{(t/T)}$  where  $C$  is the radioactive atom concentration in terms of the initial concentration after the time,  $t$ , for the half-period,  $T_{1/2}$ . So in the exponent we have the number of half-periods within the time elapsed since the nuclide production. In our case it is  $10^9$  years. Hence, even with a 100% initial concentration after a billion years the ppm or higher contents would be preserved only by radioactive nuclei with half-periods longer than 10 million years.

Since the initial concentration of radioactive atoms in minerals is invariably much lower than unity (most frequently by as much as a factor of 10) this figure can be taken to be the lower limit of the half-period value in the investigation of possible cases of rare radiogenic isotope accumulation in mineral matrices.

### PREDICTIONS FOR ACTIVE NATURAL ENRICHMENT OF RARE ISOTOPES INCLUDING POSSIBLE FORMATION OF PURE AND SUPERPURE ISOTOPE

We have performed a search for natural nuclides that via a radioactive decay can generate nuclides of new elements, which in turn can produce in minerals sufficiently high concentrations of radiogenic isotopes to be reliably detected. The lower limit of the half-period is assumed to be equal to  $10^8$  years as pointed out above.

The typical life time of the oldest minerals was assumed to be  $3 \cdot 10^9$  years.

Analyzing the data and bearing in mind that there may be more than one decay channel, we found 30 preservations in minerals of 28 radiogenic stable isotopes in concentrations that in cases of favourable mineral compositions can be determined using modern techniques. The examination of the present-day mineralogy data permits us to predict certain abundant mineral formations most advantageous for the radiogenic isotopes to accumulate (Table).

From these, for 10 nuclides, with considerable isotope enrichment, the pure isotope formation is not possible for crystallochemical and geochemical reasons. Thus, due to the presence of invariably two uranium isotopes in minerals, two radiogenic lead isotopes (<sup>206</sup>Pb, <sup>207</sup>Pb) cannot be present there in the pure form.

The accumulation of pure radiogenic isotopes of rare earth produced via a decay of radiogenic nuclides of this group, is impossible because of the chemical proximity and permanent coexistence of elements belonging to this group in the mineral crystals.

8 isotopes can be contained in mineral matrices in the pure form in concentrations above the ppm range, suggesting a possibility of their extraction as monoisotope products by means of modern technologies. 6 isotopes can be present in mineral matrices in the pure form in concentrations ranging from ppm to ppb. 4 isotopes can be found in concentrations from  $10^{-9}$  to  $10^{-11}$ .

The table highlights occurrences of pure isotopes that are easy to identify with modern analytical techniques and amenable to extraction from ores by conventional physicochemical and chemical enrichment proce-

dures. Presented separately are isotopes that can be extracted from the Ukrainian ores.

Predicted radiogenic isotope enrichment of minerals (for ore age of 3 billion years)

Original isotope	Atom percent abundance	Decay type*	Half-period, years	Newly formed isotope	Predicted content in mineral, mass %	Possible mineral matrix (Simplified Formula)
<sup>40</sup> K	<b>0,0117</b>	<b>B (89,28%)</b>	<b>1,27·10<sup>9</sup></b>	<sup>40</sup> Ca	<b>0,0n</b>	<b>Halides, Potassium Silicates</b>
<sup>40</sup> K	<b>0,0117</b>	<b>EC(10,72%)</b>	<b>1,27·10<sup>9</sup></b>	<b>40Ar</b>	<b>0,0n</b>	<b>As above</b>
<sup>48</sup> Ca	0,187	2B	5·10 <sup>19</sup>	<sup>48</sup> Ti	2·10 <sup>-11</sup>	Calcite (CaCO <sub>3</sub> ) and other carbonates
<sup>50</sup> V	0,25	B (17%)	1,4·10 <sup>17</sup>	<sup>50</sup> Cr	5·10 <sup>-11</sup>	Vanadium-oxides, Vanadium-bearing acmite (Na(Fe, V) Si <sub>2</sub> O <sub>6</sub> )
<sup>50</sup> V	0,25	EC (83%)	1,4·10 <sup>17</sup>	<sup>50</sup> Ti	2,4·10 <sup>-10</sup>	As above
<sup>50</sup> Cr	0,25	2EC	1,8·10 <sup>17</sup>	<sup>50</sup> Ti	3,5·10 <sup>-8</sup>	Chromite (Fe Cr <sub>2</sub> O <sub>4</sub> )
<sup>87</sup> Rb	<b>27,835</b>	<b>B</b>	<b>4,88·10<sup>10</sup></b>	<sup>87</sup> Sr	<b>0,0n</b>	<b>Micas (see text), Pollucite (Cs,Na,Rb)<sub>2</sub> Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub></b>
<sup>96</sup> Zr	2,8	2B	3,9·10 <sup>19</sup>	<sup>96</sup> Mo	1,5·10 <sup>-10</sup>	Zircon (ZrSiO <sub>4</sub> )
<sup>100</sup> Mo	9,63	2B	2·10 <sup>19</sup>	<sup>100</sup> Ru	10 <sup>-9</sup>	Molybdenite (MoS <sub>2</sub> )
<sup>113</sup> Cd	12,22	B	9,3·10 <sup>15</sup>	<sup>113</sup> In	n·10 <sup>-8</sup>	Sphalerite (ZnS)
<sup>115</sup> In	95,71	B	4,41·10 <sup>14</sup>	<sup>115</sup> Sn	4,5·10 <sup>-6</sup>	Rare minerals of In, cassiterite (SnO <sub>2</sub> )
<sup>123</sup> Te	0,908	EC	>10 <sup>13</sup>	<sup>123</sup> Sb	<8·10 <sup>-5</sup>	Tellurides
<sup>138</sup> La	<b>0,0902</b>	<b>EC (66,4%)</b>	<b>1,05·10<sup>11</sup></b>	<sup>138</sup> Ba	<b>7,5·10<sup>-4</sup></b>	<b>Monazite<sup>1</sup>, Britholite<sup>2</sup></b>
<sup>138</sup> La	0,0902	B(33,6%)	1,05·10 <sup>11</sup>	<sup>138</sup> Ce	5·10 <sup>-4</sup>	As above
<sup>142</sup> Ce	11,08	2B	>5·10 <sup>16</sup>	<sup>142</sup> Nd	10 <sup>-9</sup>	As above
<sup>144</sup> Nd	23,8	A	2,29·10 <sup>15</sup>	<sup>140</sup> Ce	10 <sup>-6</sup>	As above
<sup>147</sup> Sm	15	A	1,06·10 <sup>11</sup>	<sup>143</sup> Nd	10 <sup>-3</sup>	As above
<sup>148</sup> Sm	11,3	A	7·10 <sup>15</sup>	<sup>144</sup> Nd	10 <sup>-6</sup>	As above
<sup>149</sup> Sm	13,8	A	>2·10 <sup>15</sup>	<sup>145</sup> Nd	10 <sup>-6</sup>	As above
<sup>152</sup> Gd	0,2	A	1,08·10 <sup>14</sup>	<sup>148</sup> Sm	10 <sup>-7</sup>	As above
<sup>174</sup> Hf	0,162	A	2·10 <sup>15</sup>	<sup>170</sup> Yb	10 <sup>-7</sup>	Zircon (ZrSiO <sub>4</sub> )
<sup>176</sup> Lu	<b>2,59</b>	<b>B</b>	<b>3,7·10<sup>10</sup></b>	<sup>176</sup> Hf	<b>10<sup>-3</sup></b>	<b>Monazite<sup>1</sup>, Britholite<sup>2</sup></b>
<sup>184</sup> W	30,642	A	>3·10 <sup>17</sup>	<sup>180</sup> Hf	10 <sup>-7</sup>	Wolframite (Fe,Mn)WO <sub>4</sub>
<sup>186</sup> Os	1,58	A	2·10 <sup>15</sup>	<sup>182</sup> W	10 <sup>-7</sup>	Osmiridium (Ir,Os)
<sup>187</sup> Re	<b>62,6</b>	<b>B</b>	<b>4,12 10<sup>10</sup></b>	<sup>187</sup> Os	<b>10<sup>-4</sup></b>	<b>Molybdenite (MoS<sub>2</sub>)</b>
<sup>187</sup> Re	62,6(<1·10 <sup>-4</sup> %)	A	3·10 <sup>10</sup>	<sup>183</sup> W	10 <sup>-9</sup>	As above
<sup>190</sup> Pt	<b>0,01</b>	<b>A</b>	<b>6,5·10<sup>11</sup></b>	<sup>186</sup> Os	<b>10<sup>-4</sup></b>	<b>Platinum (Pt)</b>
<sup>232</sup> Th	~100	Decay chain	1,40·10 <sup>10</sup>	<sup>208</sup> Pb	<b>0,01</b>	<b>Thorianite (ThO<sub>2</sub>), Monazite<sup>1</sup></b>
<sup>235</sup> U	0,72	As above	7,04·10 <sup>8</sup>	<sup>207</sup> Pb	1,7·10 <sup>-3</sup>	Utaninite (UO <sub>2</sub> )
<sup>238</sup> U	99,275	As above	4,47·10 <sup>9</sup>	<sup>206</sup> Pb	0,037	As above

\* Type of decay: (A) α-decay, (B) β-decay, (2B) double β-decay, (EC) electron capture, and (2EC) double electron capture.

- Bold Roman type: pure rare isotope occurrences easily identifiable with modern analytical techniques;  
Bold italics: pure isotope occurrences in Ukrainian ores already found and those to be identified.
- Normal type: isotope enrichment with possible formation of pure isotopes in concentrations below the detection limit of conventional modern techniques.
- Crossed type: active isotope enrichment, but without pure isotope production.

<sup>1</sup>Monazite (Ce,La, Nd...Lu, Th)PO<sub>4</sub>, <sup>2</sup>Britholite (Ca, Ce, La, ...Lu)<sub>5</sub>(SiO<sub>4</sub>, PO<sub>4</sub>)<sub>3</sub>(OH,F)

## IDENTIFIED PURE RADIOGENIC ISOTOPES

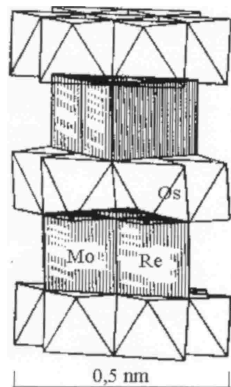
- Ancient rocks and ores are the most suitable objects for investigations of the pure rare isotope production from initial radioactive isotopes present in sufficient concentrations. As mentioned above, a convenient testing ground for these studies is the Ukrainian Shield where we work with minerals (2...3)·10<sup>9</sup> years old. Since in most cases, especially in those of practical interest, pure isotopes are produced via a β-decay or electron capture, direct mass-spectrometry techniques are not applicable to the search and identification of pure isotopes produced. Simple, (in this application) fast and non-destructive analytical methods are activation techniques. Mostly the gamma-activation analysis was employed performed with high-current linacs at the KFTI NSC [3-5] and complemented by neutron-activation techniques with chemically prepared samples and also by using experimental neutron activation methods at the research reactor WWR –M of the INR. This combination permitted the concentrations of the radiogenic and one of nonradiogenic isotopes to be determined whereof the radiogenic isotope purity was calculated.

in that the recoil atom occupies a vacant octahedron in the crystal structure (Fig. 3) slightly modifying it to produce a defect.

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A high degree of purity (above 96%, with natural abundance of 7%) was also determined for radiogenic strontium-87 in rubidium-bearing biotites.

It is intended to use minerals of the Ukrainian Shield to identify other naturally-pure isotopes formed in mineral matrices of foreign composition.



**Fig. 3.** Diagram of the impurity Re and Os atom location in the molybdenite structure

### CONCLUSIONS

- 1) The range of search for native pure rare radiogenic isotopes which can be extracted as monoisotope products by means of modern technologies has been specified.
- 2) The methods for investigation of such isotopic anomalies were proposed.
- 3) The existence of pure  $^{187}\text{Os}$  and  $^{87}\text{Sr}$  isotopes in the Ukrainian ores was found.

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## ЯДЕРНО-ФИЗИЧЕСКИЕ И МИНЕРАЛОГИЧЕСКИЕ ПРИНЦИПЫ И МЕТОДЫ ПРОГНОЗИРОВАНИЯ И ИССЛЕДОВАНИЯ СЛУЧАЕВ СУЩЕСТВОВАНИЯ РЕДКИХ ИЗОТОПОВ В ПРИРОДНО-ЧИСТОМ СОСТОЯНИИ

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Путём сочетания ядерно-физических, минералогических, кристаллохимических и геохимических подходов проанализирована возможность накопления в природе в существенно обогащённом или даже в чистом и сверхчистом виде некоторых обычно редких изотопов, которые могут быть выделены из руд. Рассмотрены методы и результаты исследования подобных изотопных аномалий.

## ЯДЕРНО-ФІЗИЧНІ І МІНЕРАЛОГІЧНІ ПРИНЦИПИ І МЕТОДИ ПРОГНОЗУВАННЯ І ВИВЧЕННЯ ВИПАДКІВ ІСНУВАННЯ РІДКІСНИХ ІЗОТОПІВ У ПРИРОДНО-ЧИСТОМУ СТАНІ

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На основі поєднання ядерно-фізичних, мінералогічних, кристалохімічних і геохімічних підходів проаналізовано можливість накопичення в природі в суттєво збагаченому і навіть в чистому та надчистому стані деяких звичайно рідкісних ізотопів, що можуть бути відокремлені з руд. Розглянуто методи і результати вивчення таких ізотопних аномалій.