

Editorial

Isotope geoscience has grown rapidly in the past decades as an increasing number of earth scientists have used isotopic data to understand more clearly the workings of the earth and her planetary neighbors. The ideas and the basic data that form the framework of isotope geoscience were contributed by a relatively small group of scientists many of whom are still alive. It is appropriate, therefore, that our Journal provide an opportunity to the founding fathers of our science to tell their story for the benefit of their young colleagues.

In this spirit I asked Professor E.K. Gerling of the Institute of Precambrian Geology and Geochronology in Leningrad to write an autobiographical account of his scientific work. He graciously agreed to do so and in due time prepared a manuscript in the Russian language. This manuscript was subsequently translated into English by Dr. Igor M. Gorokhov, who is a former student of Dr. Gerling.

I am very pleased indeed to present as a first article in this issue Dr. Gerling's account of his scientific career that spanned many decades and contributed greatly to the development of isotopic geochronometers for dating of rocks and minerals. Speaking for the isotope geoscientists of the world, I extend our congratulations and best wishes to Dr. Gerling on the occasion of his eightieth birthday on December 23, 1984.

I hope to present to our readers similar contributions from other pioneers of isotope geoscience in future issues of this Journal.

GUNTER FAURE (Editor-in-Chief)

Historical Review



E.K. GERLING

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REMINISCENCES ABOUT SOME WORKS CONNECTED WITH THE STUDY OF NOBLE GASES, THEIR ISOTOPIC COMPOSITION AND GEOCHRONOLOGY

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THE BEGINNING OF MY SCIENTIFIC ACTIVITY AND THE STUDY OF HELIUM GEOCHEMISTRY

In 1922 as a youth of seventeen I entered the Chemical Department of the Leningrad State University. Because of my pecuniary embarrassment I was employed as an analytical chemist in the Institute of Metals. At that time Professor N.M. Wittorff was the chief of the laboratory of analytical chemistry. In his laboratory I acquired the necessary skills and the ability for carrying out very precise quantitative determinations of micro-impurities in various metals and alloys. However, in two years I felt that pure analytical chemistry was not my calling and, in 1928, I took up other work on the technology of silicates at the Institute of Ceramics. By that time I

had passed all university examinations and proceeded to do graduate work on fluorine compounds of uranium under the supervision of V.G. Khlopin who was then an assistant professor. I completed the graduate work in the spring of 1929. In 1931 V.G. Khlopin hired me to come to the Central Scientific and Technical Laboratory of the "Strojgas" Trust in Leningrad for an elaboration of the procedure of helium and argon determination in natural gases. At that time the natural gases were studied insufficiently. The low level of information about the geochemistry of both helium and other inert gases was related to the lack of industrial interest in them. However, after the First World War when helium had been used for filling of dirigibles, the belligerents started to look for raw materials most suitable for the industrial production of this gas. The study of the helium content in natural gases in many countries resulted in the discovery of such gases with substantial helium concentrations.

V.G. Khlopin proposed to me a study of natural gases by means of his apparatus which was designed only for helium determinations. For such a study it was necessary to supplement his apparatus with a system containing metallic calcium for adsorption of all chemically active gases such as O_2 , N_2 , CO , CO_2 , H_2 , CH_4 , and other hydrocarbons. I decided to check the operation of the apparatus by means of a determination of argon in atmospheric air. To this end, a measured amount of air was reacted with metallic calcium heated to $650^\circ C$. The first results did show an increased content of argon in air which came up to 1% and more. A spectrographic study of this argon showed presence of hydrogen which was not adsorbed by calcium. I succeeded in getting rid of the hydrogen under the following curious circumstances. During one of my experiments the electric current was suddenly interrupted. I went to the switchboard to ascertain the cause of this accident. Having discovered the blown fuse, I changed it for a new one. While I was doing this, my furnace with metallic calcium cooled to $300^\circ C$. Subsequent spectrographic tests of the argon in the furnace showed an almost complete absence of hydrogen. I quickly pumped the gas out by the MacLeod manometer and measured its amount which corresponded exactly with its concentration in air (0.93%). I concluded that the temperature drop of calcium to $300^\circ C$ also decreased to very low values the pressure of hydrogen which originated as a result of dissociation of calcium hydride. These low amounts of hydrogen did not affect the accuracy of the determination of the amount of inert gases. Thus, after elucidation of the necessary operating conditions for adsorption of all the chemically active gases, including hydrogen, one could get down to large-scale determinations of the argon and helium contents of natural gases in the U.S.S.R.

My next work was carried out together with Mrs. E.M. Ioffe under the supervision of V.G. Khlopin who was my teacher. This work included the study of the influence of the composition of the gaseous phase on the extraction of helium from minerals and rocks. In particular, we were interested in the influence of hydrogen and hydrocarbons on the extrac-

tion of helium from uraninite. Theoretically, one would expect that all the gases which had higher adsorption power than helium or reacted chemically with minerals and rocks would affect the helium extraction. Such experiments were made on uraninite and khlopinite. Hydrogen, methane and other hydrocarbons were used as chemical reagents. In comparative experiments helium was extracted from the same minerals in a vacuum. These experiments showed that: (1) the amount of helium that escaped from minerals and the rate of its liberation depended on the composition of surrounding gaseous phase; and (2) the liberation of helium from minerals was facilitated in the presence both of the gases with higher adsorption power and those which reacted chemically with the minerals and thereby disturbed their structures. The liberation of helium from minerals was especially stimulated by unsaturated hydrocarbons and higher homologues of methane. After the completion of this work I came to the conviction that my future life would be fully devoted to the study of inert gases.

As one will be able to see from the further presentation, for 50 years I dealt mainly with inert gases and only from time to time digressed from this direction by carrying out several studies on the isotope geochemistry of lead and strontium.

In 1933 I transferred to the Radium Institute in Leningrad and began to develop a technique of helium determination in rocks and minerals for their isotope dating. It was necessary for this study to install special equipment. I knew from the literature that Prof. F. Paneth and his disciples in Germany had constructed an apparatus which allowed them to measure very small amounts of helium. I took this apparatus as a base and modified it. First, I replaced almost all valves with mercury locks. Second, I heated the platinum crucible with the rock powder by a high-frequency current. Such a heating method allowed the rock powder to be melted either together with soda or to melt it directly at 1300°C and higher. The method permitted the complete liberation of helium without any losses. It was used for U-He age determination of granites, gneisses, gabbro-norites and other rocks of Karelia and the Kola Peninsula.

All the studied rocks of the Belomorian Series of Karelia gave lower age values relative to geological ideas. These low values were due to significant losses of helium (up to 90% and more) during the geological history of the rocks. However, the age data for loparite of the Khibiny Mountains and for knopite of the Africanda Tundra in the Kola Peninsula were in good agreement with the geological ideas about their age. These minerals contained several hundredth and even tenth of a cubic centimeter of helium per gram and nevertheless retained it. The loss of helium from minerals and rocks was expected to depend on its diffusion rate in crystalline structures. The diffusion of helium in certain minerals is so hampered that the probability of helium transportation in their intercrystalline spaces is very low and helium is maintained in them throughout all of their geological history. In contrast, helium diffuses very easily from some other

minerals. It was obvious that the differences in the abilities of the minerals to retain helium depended on their structural properties. According to this criterion, all minerals can be subdivided into three groups:

Group I. The minerals in which uranium and thorium participate in construction of the crystal lattice. They include uraninite, thorianite and others. The structure of these minerals is strongly damaged due to radioactive decay of uranium and thorium and favours loss of helium from them.

Group II. All metamict minerals, e.g. thorite, zircon, allanite and others, that were originally crystalline but were later converted into glassy masses. This damage of the structure results in helium losses up to 90%.

Group III. Minerals with resistant (close packing) crystalline structures that are the main factor responsible for helium retention as shown in Table I. The closer the ionic packing of the mineral, the less is the amount of helium lost. When the crystalline space of a mineral is occupied by over 60%, the helium loss is less than 10%.

TABLE I

Relationship between packing of ions in minerals and their corresponding losses of helium

Mineral and its location	Geological age	U-He age (Ma)	Loss of He (%)	Packing (%)
Albite, U.S.A.	Devonian	40	83	46
Labradorite, U.S.A.	Precambrian	101	80-90	46
Quartz, U.S.A.	Devonian	86	75	50
Limestones, U.S.S.R.	Permian	22-53	74-89	51
Sphene, U.S.S.R.	Precambrian	409	68	54
Ibid.	ibid.	600	60	54
Dolomite, Karelia, U.S.S.R.	early Proterozoic	577	40-50	57
Monazite, U.S.S.R.	early Precambrian	862	46	58
Samarskite, Urals, U.S.S.R.	late Carboniferous	248	10	63
Loparite, Kola Peninsula	late Devonian or early Carboniferous	280	10	66
Ibid.	ibid.	266	10	66
Knopite	Caledonian or Hercynian	358	10	66
Hematite	post-Eocene	26	—	68

*The loss of helium was calculated on the basis of the geochronological time scale of A. Holmes (1937), *The Age of the Earth*, Nelson, London, 263 pp.

Later it was proposed that the activation energy of helium transportation in the crystal lattice could be used as a criterion of helium retention in minerals. It was shown by experiments that, if the activation energy is equal to 36 kcal. mol⁻¹ (as for loparite), helium is maintained in the mineral throughout all of its geological history, provided that the mineral was not

TABLE II

Relationship between activation energy for He diffusion and the He retention by different minerals

Mineral or rock	Size fraction (mm)	U-He age (Ma)	Loss of He (%)	Activation energy (kcal. per g-at. He)			
				I	II	III	IV
Liparite	1-2	280	10	—	34.3	—	—
Poikilitic liparite	1-2	170	40	22.3	34.0	—	—
Monazite	0.2-0.5	852	47	6.3	27.8	41.4	50.3
Monazite	<0.1	852	47	—	28.7	40.5	—
Uraninite	0.2-0.5	48	97	9.6	15.0	—	—
Samarskite		248	10	—	59.0	71.0	81.0

heated to more than 100°C. It was well established that helium liberation from minerals corresponded to a spectrum of activation energy values (Table II). That phenomenon was interpreted as follows.

Helium escaping from the first position having a low activation energy is due to diffusion caused by disturbances of the crystal lattice. The amount of this helium in minerals is very small. The major amount of helium is present in the second position and is removed by diffusion through the crystal lattice. For some minerals, e.g. monazite and samarskite, there are two additional positions from which helium escapes with even greater activation energies. This helium resides in individual crystal-lattice cells.

At the same time up to 1941 we dealt with the problem of making quantitative separations of helium from neon together with G.M. Yermolin. We found that neon was completely adsorbed on charcoal at -215°C. Such a cooling was achieved by means of two consecutive methods: (1) by pumping-out of the liquid air; and (2) by desorption of hydrogen from the coal.

THE ESTIMATE OF THE AGE OF THE EARTH'S CRUST

In July of 1941, after the beginning of the war, the Radium Institute was evacuated to the city of Kazan where we stayed until January 1945. During the evacuation my collaborators and I were unable to continue our studies of helium geochemistry and were occupied mainly with the reading of the scientific literature. At this time I read the paper by A.O. Nier which was devoted to the determination of the isotope composition of ore lead samples of various ages and origins. Among the samples analysed by A.O. Nier was a galena specimen from Greenland which contained very small additions of radiogenic lead with mass numbers of 206, 207 and 208. This lead had the most primitive isotopic composition relative to that of modern

lead. Therefore it could be used for the calculation of the minimum age of the earth's crust.

The calculation showed that the accumulation of radiogenic isotopes in modern ore lead could have occurred in 3.5–4.0 Ga. Hence it followed that the age both of the earth's crust and the earth as a whole cannot be less than this estimated value. Somewhat later the same calculation based on A.O. Nier's isotopic data was made by F.G. Houtermans in Germany.

THE POTASSIUM-ARGON METHOD AND ITS APPLICATION TO GEOLOGICAL AGE DETERMINATION

Looking through the foreign scientific journals, I came across a paper by G.J. Sisoo that appeared in 1937 which attracted my attention. There was an indication of the possibility of the decay of ^{40}K by the capture of an electron from the surrounding electron shell with the production of ^{40}Ar . This possibility followed from the rule which stated that, if the middle of three isobars is radioactive and disintegrates by giving off an electron, it must always disintegrate by *K*-capture as well. The exceptionally high content of ^{40}Ar in the earth's atmosphere relative to the other inert gases was another argument in favour of the possibility of ^{40}Ar generation from the ^{40}K nucleus. The occurrence of such a *K*-capture in nature had to be proved by experiment. However, I was not able to begin this study until 1947, because first, according to the wish of V.G. Khlopin, I carried out an urgent study concerning the search for fission xenon in uranium materials together with Mrs. N.V. Baranovskaya.

With that latter end in view, a special apparatus was constructed based on the dissolution of uraninite in hydrochloric acid (with specific gravity of 1.12) from which atmospheric xenon was removed beforehand. Xenon and argon escaping during the dissolution of the mineral were adsorbed by charcoal cooled by liquid air and helium was transferred to a special gas container. The separation of the argon-xenon mixture was made on the charcoal cooled to -120°C . At this temperature argon was pumped out. The procedure of the argon-xenon mixture separation was repeated twice. The purity of xenon was verified by optical spectroscopy. The average content of xenon (for two experiments) in the sample of an old uraninite was of 0.77 mm^3 per kg of mineral. The uranium-xenon age of this uraninite was equal to 1.68 Ga. This value was in satisfactory agreement with the uranium-lead age of 1.85 Ga for this uraninite. The subsequent development of the uranium-xenon method of age determination was undertaken some years later by Yu.A. Shukoljukov who was then a post-graduate student at the Laboratory of Precambrian Geology. He showed that most of the studied minerals lost significant fractions of xenon (and krypton) during their geological history.

After completion of the work on the extraction of xenon from uraninite I returned to the idea of providing experimental proof of *K*-radioactivity

of the ^{40}K nucleus. In order to achieve this objective it was necessary to determine the isotopic composition of argon extracted from a potassium-bearing mineral. I carried out this study together with N.E. Titov. Professor M.G. Meshcheryakov made available to us the Nier-type mass spectrometer that had been constructed at the workshop of the Radium Institute. We met with great difficulties in putting this instrument into operation. In particular the measurement of the ion currents of the argon isotopes presented a rather serious problem. The amplifier constructed by us was unstable and we had to abandon its use. The measurement of ion currents was carried out by means of a Lutz—Edelman electrometer using the charging technique. First the isotopic composition of atmospheric argon was studied. The content of ^{36}Ar in atmospheric argon was equal to 0.3% and agreed fairly well with Nier's value. Afterwards we studied the isotopic composition of argon extracted from sylvite of the Solikamsk deposit. The mass spectrometric analysis showed that ^{36}Ar was absent in this gas and that it contained only ^{40}Ar . Argon extracted from this sylvite was studied five times and each time we were convinced of the absence of ^{36}Ar in it. To make sure that ^{36}Ar was lacking in the gas extracted from the sylvite, before each experiment with this mineral we analysed atmospheric argon in which ^{36}Ar was always present. The measurements of ion currents by means of the Lutz—Edelman electrometer using the charging technique were very labour-consuming and took up a lot of time. Our measurements started at 8 p.m. and lasted until the next morning. After termination of these experiments N.E. Titov and I had satisfied ourselves that ^{40}Ar in sylvite was in fact generated as a result of K -capture by the nucleus of ^{40}K . The same results were obtained by L.T. Aldrich and A.O. Nier in 1948.

In order to use this new radioactivity for geological age determinations, it was necessary to determine the decay constant of K -capture of ^{40}K . With this aim in mind, I together with N.E. Titov and G.M. Yermolin carried out new research using a geochemical approach. We studied potassium-bearing minerals (nepheline, microcline, sylvite and carnallite) from rocks whose ages had been determined by the U—Pb and U—He methods by analysis of uranium-bearing minerals. Four determinations gave a value of $(6.1 \pm 1.2) \cdot 10^{-11} \text{ a}^{-1}$ for the K -capture constant. The first experiments using the potassium radioactivity for geological age determination were carried out in 1951 at the Radium Institute. At the same time the graduate student T.G. Pavlova determined under my supervision the ages of two stone meteorites. Her results showed for the first time the possibility of using the potassium radioactivity for dating not only terrestrial rocks and minerals but also meteorites.

In 1951 I moved to the Laboratory of Precambrian Geology of the U.S.S.R. Academy of Sciences. This laboratory was organized by Academician A.A. Polkanov. I dealt here with the further development of the K —Ar method and its application to geological problems. In the first place

it was necessary to refine the value of the K -capture constant of ^{40}K which was formerly determined on potassium feldspars. I used muscovite and other micas which keep argon better than microclines and nephelines do. These minerals were extracted from pegmatites of the White Sea (Belomorian) region. The age of coexisting uraninites from the pegmatites was previously determined by the U—Pb method. The new value of the K -capture constant of ^{40}K proved to be $5.50 \cdot 10^{-11} \text{ a}^{-1}$ and agreed well with the value obtained by G.W. Wetherill in the U.S.A., based also on a geochemical approach. This value was employed for dating of potassium minerals in many geochronological laboratories of the U.S.S.R. over a long period of time. Subsequently, it was replaced by values obtained by physical methods and now we use the value recommended by the International Subcommittee on Geochronology in 1977.

When working with micas it was observed that in some cases argon was lost in the cold trap cooled with liquid air used for freezing of water vapour. The post-graduate student T.V. Koltzova noted that this effect was observed if the mica contained a great amount of fluorine. While heating fluorine-bearing micas a reaction occurs that generates silane (SiH_4). If this gas is frozen with water vapour, the crystalhydrate of silane forms. Argon is cocrystallized with the crystalhydrate-forming solid solutions such as $x\text{Ar} \cdot y\text{SiH}_4 \cdot 6\text{H}_2\text{O}$. The amount of argon cocrystallizing with silane in some experiments exceeded the amount of the latter by more than ten times. In order to decompose this compound it is necessary to pass the gas over metallic calcium heated to 650°C .

The first K—Ar results obtained at the Laboratory of Precambrian Geology for micas from rapakivi and other Karelian granites were entirely inconsistent with the geological estimates of the age of these rocks at that time. The discrepancy between geological and geochronological estimates amounted to ~ 1 Ga. The Karelian geologists assumed that rapakivi granites, being the youngest rocks in this region, cannot be older than 0.6 Ga. The Karelian granites, in turn, were compared by all geologists with the Gothian granites with an age of 0.8—1.0 Ga. However, our K—Ar dates for the rapakivi granites were 1.6 Ga and for the Karelian granites 1.8 Ga. The reliability of our age determinations was borne out by the good agreement between K—Ar dates of micas and U—Pb dates of uranium minerals in the Belomorian granites. A similar agreement of age values obtained by the two methods was also observed in some other regions. This implied that the geological estimates of the ages of the granite were not correct. However, the geologists at the Laboratory of Precambrian Geology did not agree with my conclusions and believed that I overestimated the reliability of my age data. Since I got no support from the geologists who worked in Karelia, I decided to appeal to the Ukrainian geologists with the offer to determine the age of the Korosten rapakivi granite by the K—Ar method. After receiving the mica samples from this granite my colleagues and I made a start. However, the age of 1.7 Ga which we obtained

did not suit the Ukrainian geologists either. They thought that these micas contained excess argon which resulted in an overstatement of the age in excess of 1 Ga.

The outcome of this discussion was unexpected. In the fall of 1954 the young scientist G.W. Wetherill from the U.S.A. visited my laboratory while passing through Finland. He informed me about the age values obtained in the U.S.A. by the Finnish geochronologist O. Kouvo for minerals from the Vyborg rapakivi granite by the U—Pb and Rb—Sr methods. These values agreed remarkably well with our K—Ar data.

A similar agreement was obtained for the Karelian granites. This fact convinced me definitely that in the dispute between the geologists and geochronologists the latter were right. Shortly afterwards, I informed the Scientific Council of the Laboratory about our recent data and about the information I had obtained from G.W. Wetherill. I concluded my speech with the words:

“It is not realistic that three methods based on the radioactive decay of three different parent elements, such as uranium, rubidium and potassium could give consistent age values which would be overstated in comparison with the geological age of the rock. The only possible conclusion which follows from this comparison is that the geological estimate of the age value is erroneous.”

In three days the director of the Laboratory, Academician A.A. Polkanov, invited me into his office and explained the essence of the mistake of the geologists. He said that according to earlier geological ideas, Soviet Karelia contained all geological formations with the age from the late Cambrian to the Archean. This was indeed not the case and rocks younger than 1.6 Ga should be looked for, probably, in the territories of Finland, Sweden and Norway.

A.A. Polkanov got in touch with Norwegian, Swedish and Finnish geologists and shortly after that many mica samples were received from Scandinavia by my laboratory. Indeed, it was in this territory that the missing age values in the range 0.4—1.6 Ga were found. At that time I worked with great enthusiasm. A.A. Polkanov and I plotted the measured age values on geological maps which were sent to us by Scandinavian geologists. We discussed the results with great exhilaration. It was for me the most interesting and happy period. We decided that in order to obtain a more complete age pattern for Karelia, the Kola Peninsula and other regions of the U.S.S.R., it was also necessary to use the Rb—Sr and the U—Pb methods. The Rb—Sr method was established in my laboratory when A.A. Polkanov was still alive. M.L. Yashchenko and I.M. Gorokhov made a valuable contribution to the development of this method. The U—Pb method was established by us later.

The geochronological results we obtained were published in several papers by A.A. Polkanov and me. We made the following conclusions. Four major cycles of sedimentation and metamorphism occurred over

the range of 3.5–1.6 Ga in the eastern part of the Baltic Shield, including the Kola Peninsula, Karelia and Finland. Two Precambrian cycles were recognized in Sweden and Norway, the first (Svecofennian) with the age of 1.6–1.2 Ga and the second (Gothian–Karelian) with the age of ~0.9–1.0 Ga. In addition, the age values of 0.23–0.52 Ga related to the Hercynian and Caledonian orogenies were found in the Kola Peninsula, in Karelia and in Norway. Thus, the whole time range of 3.5–0.2 Ga from the Katarchean to the Paleozoic was filled by isotopic age values. Similar studies were completed together with A.M. Pap on micas from the Precambrian rocks of Byelorussia. In this region we obtained many K–Ar age values in the range 1.2–1.6 Ga as was the case for Norwegian and Swedish rocks. These age values were obtained not only on micas but also on amphiboles which were shown to retain radiogenic argon better than micas. So the Svecofennian cycle of sedimentation and metamorphism was found in the territory of the U.S.S.R. but not in the region where geologists had presumed its existence.

Numerous K–Ar age values for micas from the White Sea (Belomorian) region were in the interval of 1.6–1.9 Ga. However, in the same area some biotites gave K–Ar ages of ~2.0 Ga and even 2.4 Ga. One could reasonably suggest that the Belomorian rocks, which underwent repeated metamorphism and granitization, are older than 1.6–1.9 Ga. That agreed with the opinion of many geologists working in this region. The supposed old age was borne out later by U–Pb dates of 2.8 Ga on zircons from the granite situated to the north of the Kandalaksha Bay. These age determinations were made at the V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry in Moscow. The final corroboration of the Archean age of the Belomorian rocks was given in the 1970's at my institute by I.M. Gorokhov and his collaborators who used the Rb–Sr whole-rock method and also obtained the value of 2.8 Ga. Thus, the second metamorphic event in this region with an age of ~1.8 Ga resulted both in a loss of radiogenic argon from the old micas and in the production of new micas. Such a "rejuvenation" of micas was shown by K.O. Kratz, S.B. Lobach-Zhuchenko and me to be widespread both in Karelia and in the Kola Peninsula.

That fact caused me to search for other natural objects that are more resistant to "rejuvenation" than biotite. Our choice eventually fell upon amphiboles and basic rocks containing small amounts of potassium. Determinations of the activation energy of argon released from different minerals gave us the possibility to judge the argon retention in them during reheating. These results are given in the Table III.

It is seen that amphiboles have far greater activation energies than micas and therefore they ought to retain radiogenic argon better than micas. This conclusion was subsequently substantiated by numerous experimental data obtained by me and my colleagues: T.V. Koltzova, I.M. Morozova, I.I. Matveeva, S.Z. Yakovleva, V.D. Sprintson, Yu.D. Pushkarev and B.V. Petrov.

The basic rock samples under investigation included some drill cores from the Kola Peninsula (Montshe–Tundra Hill and neighbouring areas).

TABLE III

Activation energies for argon release from silicate minerals

Mineral	Biotite	Phlogopite	Muscovite	Amphiboles			Pargasite
				north Ladoga region	Karelia		
					south	north	
Activation energy (kcal. mol ⁻¹)	57	67	92	140	135	172	200

Their study was made with the assistance of Yu.A. Shukoljukov, V.A. Maslenikov, T.V. Koltzova, I.I. Matveeva and S.Z. Yakovleva in the beginning of the 1960's. The bulk of the K—Ar age values for these basic rocks fell in the 2.5—3.6 Ga range. Even higher values were obtained for pyroxenites and lenticular bodies of peridotites and olivinites (xenoliths?) included in them. At first I assumed that they corresponded to the age of the mantle material transferred into upper levels of the earth. However, the increasing body of evidence proved that most of the K—Ar age values for such xenoliths were in the range of 3.8—10.0 Ga, i.e. well above the age of the earth (4.5 Ga). The rocks were sure to include an excess of radiogenic argon. It is noteworthy that in the 1950's excess argon had not been found in whole-rock samples of stone meteorites which also contained minerals similar to those of basic and ultrabasic rocks. The K—Ar whole-rock ages of these meteorites were found by Mrs. K.G. Rik and me to be ~4 Ga and did not exceed the accepted age of the earth. At the same time, I together with L.K. Levsky found in the Staroye Pesyanoye meteorite the primary noble gases (helium, neon and argon) which were adsorbed during the formation of the meteorite.

The occurrence of excess ⁴⁰Ar in ancient basic rocks was not a great surprise because excess ⁴⁰Ar had been found previously in beryls by L.T. Aldrich and A.O. Nier in 1948*¹ and in cordierites by P.E. Damon and J.L. Kulp in 1958*². Subsequently, we found excess ⁴⁰Ar in chlorite (1967) and sulphides (1972). In 1972, K.K. Zhirov at the Geological Institute in Apatity (the Kola branch of the U.S.S.R. Academy of Sciences) also discovered excess ⁴⁰Ar in sulphides of the Kola Peninsula. All these minerals included excess helium as well. Both helium and argon could be expected to be absorbed by these minerals from the environment in the course of magma crystallization. In order to check this hypothesis, N.V. Kotov and Yu.D. Pushkarev at Leningrad State University studied the sorption of argon by

*¹L.T. Aldrich and A.O. Nier (1948), Argon⁴⁰ in potassium minerals. *Phys. Rev.*, 74: 876—877.

*²P.E. Damon and J.L. Kulp (1958), Excess helium and argon in beryl and other minerals. *Am. Mineral.*, 43: 433—457.

TABLE IV

Partial pressure of argon in minerals containing excess radiogenic ^{40}Ar

Sample and sampling location	Age (Ga)	Water content (mg g ⁻¹)	$^{40}\text{Ar}^*$ (10 ⁻⁶ cm ³ g ⁻¹)	Excessive $^{40}\text{Ar}^*$ (10 ⁻⁶ cm ³ g ⁻¹)	Partial pressure of $^{40}\text{Ar}^*$ (atm.)
Quartz, Bethesda, Md., U.S.A.	0.3–0.5	0.5	12	12	0.024
Quartz, Volta Bala, Minas Gerais, Brazil	1–2.6	0.1	0.07	0.006	0.0007
Quartz, Creede, Colo., U.S.A.	0.01	1.4	<0.007	—	0.000005
Fluorite, Hill Mine, Ill., U.S.A.	0.1–0.3	0.2	0.2	0.02	0.0001
Quartz, Hill Mine, Ill., U.S.A.	0.1–0.3	0.4	0.05	≥0.035	0.00015

Data from S.N.I. Rama, S.R. Hart and E. Roedder (1965), Excess radiogenic argon in fluid inclusions. *J. Geophys. Res.*, 70: 509–511.

*Radiogenic ^{40}Ar .

micas. The micas were heated in an autoclave under a pressure of argon of more than one hundred standard atmospheres. Only when such high pressure was used did the micas absorb argon amounts (10^{-3} – 10^{-2} cm³ g⁻¹) equal to that found in ancient beryls. However, such a pressure appears to be unreal in nature. J.V. Smith and W. Schreyer in 1962 and also S.N.I. Rama, S.R. Hart and E. Roedder in 1965 determined the content of radiogenic argon in the gaseous–liquid inclusions of some minerals. Based on the amounts of liquid water and argon in the inclusions, I have estimated the partial pressure of argon in them. As is seen from Table IV, this pressure is not high and does not exceed a few hundredth of a standard atmosphere. Similar data for quartz in pegmatite were obtained by E.M. Prasolov at the All-Union Oil Research Institute in Leningrad. It follows from the above data that the partial pressure of argon in magma is not great and the minerals crystallizing from this magma can absorb only a negligible amount of argon. This hypothesis was also not able to explain the dependence of the amounts of excess argon and helium on the age of the minerals which, for the first time, was noted for beryls by R.J. Strutt in 1933 and later was observed for cordierites, feldspars and sulphides.

SOME HYPOTHESES ON THE ORIGIN OF EXCESS RADIOGENIC ARGON IN MINERALS AND ROCKS

The difficulties encountered when one tries to explain the above observations by the impregnation hypothesis caused me to advance another

one which considered the excess ^{40}Ar and ^4He to be products of the triple fission and alpha-decay of superheavy nuclei. These nuclei were predicted by theoretical physics to have atomic numbers from 110 to 126 and atomic masses in excess of 300. The elements with atomic numbers 110 (EcPt), 114 (EcPb), and 120 (EcRa) should be the most suitable. That is why I had to consider in detail the chemical peculiarity of minerals containing excess argon and helium in order to examine the possibility of the production of these gases in the course of fission of the three mentioned superheavy nuclei. With this goal in mind, the minerals with excess helium and argon were subdivided by me into three chemical groups:

The first group. This group included such minerals as calcite, cancrinite, sphene and plagioclase in which calcium is one of the major elements, and minerals in which calcium enters as an isomorphic admixture (1% and more), e.g. beryl, cordierite, tourmaline and chlorite. The superheavy element with atomic number 120 having alkali-earth properties has to be included into calcium-bearing minerals crystallizing from magma.

The second group. The excess helium and argon in sulphides could be due to decay of the superheavy nucleus with atomic number 110 having the properties of platinum-group metals. According to the Bulgarian authors I. Bonchev and S. Peneva, and the Vlasov rule, the 110th element with the atomic weight of 294 and a magic number of neutrons should cocrystallize with Fe^{2+} , Cu^{2+} and Ni^{2+} in sulphides.

The third group. This group contains galena and native bismuth. The excess helium in these minerals may be due to the decay of EcPb and EcBi with atomic numbers of 114 and 115.

The main argument in favour of the radiogenic origin of excessive ^{40}Ar in the mentioned groups of minerals is, in my opinion, the dependence of the excess ^{40}Ar content on the ages of the samples. If it is representative of the accumulation of radiogenic argon due to the decay (the triple fission) of the hypothetical superheavy elements, one can try to estimate their half-lives. Individual data for cordierites, plagioclases and sulphides result in values on the order of 0.3–0.4 Ga.

If excess ^{40}Ar in a number of minerals is supposed to be a product of triple fission, the accumulation of ^3He in the same minerals can be expected. I think that such a conclusion can be drawn from the data obtained in my laboratory for beryl and amphibole by T.V. Koltzova, A.N. Komarov, S.Z. Yakovleva and I.N. Tolstikhin, the content or excess ^3He apparently being qualitatively correlated with that of excess ^{40}Ar .

The data for meteorites by some American researchers support the hypothesis of the occurrence of the superheavy elements which decay by the triple-fission process.

E. Anders and his collaborators showed that the primordial inert gases in carbonaceous meteorites are involved in the mineral referred to as mineral Q whose abundance in meteorites amounts to several tens of ppm. This mineral contains, besides primordial inert gases, also marked amounts

both of ^{40}Ar of obscure genesis and of xenon with an isotopic composition different from that of xenon that originated by the fission of uranium, plutonium, californium and curium. I observed that the concentrations of xenon and excess ^{40}Ar are correlated with one another. Because mineral *Q* contains several per cent of sulphides, one can explain this correlation by the decay of the superheavy element with atomic number of 110 (EcPt?). In addition, the quantity of ^{136}Xe varies with the age according to the equation of radioactive decay. I calculated ages of the samples on the basis of the concentrations of radiogenic ^{129}Xe in them and then the half-life of the hypothetical element which proved to be of the order of 10 Ma. Clearly, this element could not be preserved until the present and has essentially decayed.

The triple fission of superheavy elements may account for the isotope heterogeneity of such light elements as calcium, titanium and strontium, which was found in E-1-4-1 white inclusions of the Allende meteorite by G.J. Wasserburg and his colleagues. These anomalies are typical only for isotopes that are not screened by stable isobars and also for very abundant isotopes. According to E.K. Jessberger, the same inclusions contain a great deal of the excess ^{40}Ar .

Further theoretical and experimental investigations are required to check the hypothesis of the natural occurrence of the triple-fission fragments of superheavy elements.

In some cases, most commonly for minerals of basic and ultrabasic rocks, the K—Ar method gave very high age values which could not be explained by the hypothesis of the superheavy element fission. In particular, in my laboratory I.M. Morozova obtained for pyroxenites and peridotites of the Moncha Pluton (the Kola Peninsula) a positive correlation in a K— ^{40}Ar plot which corresponds to an age of ~ 10 Ga. A similar relationship for samples from the same pluton was obtained at the Max Planck Institute in the Federal Republic of Germany. These data led me to some doubts concerning the constancy of the decay constant of ^{40}K . The possibility of change of radioactive decay constants results from Dirac's theory of the change of world constants, including the gravity constant, in the course of the evolution of the universe. The time-dependent change of the gravity constant should entail changes of the radioactive decay rates of elements, these changes having to depend strongly on the mode of radioactive decay. In order to recognize these changes, I and G.V. Ovchinnikova at the end of the 1960's considered the age values for terrestrial and lunar rocks and meteorites obtained by the K—Ar (*K*-capture), U—Pb (alpha-decay), and Rb—Sr (beta-decay) methods. The detected discrepancies were explained by the time changes of the radioactive decay rate.

In my opinion, the inconstancy of the radioactive decay rates could account for K—Ar biotite ages up to 4—5 Ga obtained by K.K. Zhironov of the Geological Institute of the Kola Branch of the U.S.S.R. Academy of Sciences in Apatity. These values were obtained for ancient granites of

the Kola Peninsula near the Great Rapids of the Voronja River. The rocks had a complicated geological history and the U—Pb age for their zircons is 2.7—2.8 Ga. By incremental heating of these biotites after neutron irradiation B.M. Gorokhovskiy in my laboratory obtained $^{39}\text{Ar}/^{40}\text{Ar}$ plateaux for a wide temperature range and the estimated age values did not differ from the data of the conventional K—Ar method. Plotting of the incremental heating data in $^{36}\text{Ar}/^{40}\text{Ar}$ — $^{39}\text{Ar}/^{40}\text{Ar}$ coordinates, proposed by G.J. Wasserburg in 1981, led to the same result. As a rule, plateau-like patterns are not observed for minerals containing excess argon, such as plagioclase, chlorite, epidote and others, and one may conclude that the biotites of the Great Rapids of the Voronja River contain only two argon species: air argon and radiogenic argon.

The resolution of the question about the constancy of the radioactive decay rate is of great importance not only for geochronology but for geology as a whole.

OTHER GEOCHRONOLOGICAL STUDIES COMPLETED UNDER MY SUPERVISION AT THE INSTITUTE OF PRECAMBRIAN GEOLOGY AND GEOCHRONOLOGY DURING THE LAST 30 YEARS

It can be seen from the above that for about fifty years I mainly dealt with the investigation of noble gases. Now there are two mass spectrometers at my institute used for isotopic analyses of gases in geological materials and four solid-source mass spectrometers.

One of the gas mass spectrometers was utilized for the Xe—Xe method of age determination which was suggested in the 1970's by Yu.A. Shukoljukov who worked at that time in my laboratory. He worked together with G.Sh. Ashkinadze, a fine experimenter with a lucid and creative mind who unfortunately died untimely. Now both of the gas mass spectrometers are equipped with computers and are employed chiefly for argon isotopic analyses.

A number of geochronological studies by the U—Pb, Rb—Sr and K—Ca methods have been accomplished in my laboratory with solid-source mass spectrometers.

U—Pb method. At the beginning of the 1960's we, together with Yu.A. Shukoljukov, published a paper devoted to the age calculation of uraniferous minerals with substantial amounts of common lead. Later the U—Pb work was carried out by my graduate students. In the first place I should like to note the work of the late G.I. Shestakov who first determined the activation energy of lead diffusion in uranium minerals at the beginning of the 1970's. At the same time, A.D. Iskanderova at the All-Union Geological Institute in Leningrad studied under my supervision the evolution of the isotopic composition of lead in ancient marine carbonates and showed that it changed in time just like the lead in the earth's crust. At the end of the 1970's A.F. Lobikov studied the U—Pb systems in some Karelian

granites. He showed that the age of granite emplacement may be established after the removal of mobile forms of uranium and lead from whole-rock samples by means of laboratory acid leaching. At the present time, U—Pb studies in my institute are carried out under the supervision of O.A. Levchenkov.

Rb—Sr method. The early Rb—Sr age determinations on micas were performed at my laboratory in the middle of the 1950's under the supervision of M.L. Yashchenko and later we proceeded to use the whole-rock isochron method. The survey of results for the Precambrian rocks of the Baltic Shield was published by I.M. Gorokhov and me in 1974.

In 1961 M.L. Yashchenko and E.S. Varshavskaya found that some minerals from pegmatite veins, specifically the secondary albite, show anomalously high Rb—Sr ages. They proposed a method for calculating the age of formation of secondary minerals based on the values of their initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. At the end of the 1970's we, together with E.S. Varshavskaya and M.E. Salier, resumed this work and obtained some new data for pegmatitic tourmalines from the Kola Peninsula and the Urals. I think that these data allow estimates of the duration of pegmatite formation in these regions of 40—100 Ma. We are going to carry on the study of Rb—Sr systems in pegmatitic minerals on the basis of careful selection of different mineral generations.

K—Ca method. Age determinations by this method entail great difficulties due to the necessity of measuring the isotopic composition of calcium. O.A. Levchenkov and G.V. Ovchinnikova in the middle of the 1970's studied, under my supervision, a number of micas from the rocks of the Baltic Shield with an age of ~ 2.7 Ga. These micas contained appreciable amounts of radiogenic ^{40}Ca . Its abundance in biotites was $\sim 5\%$ and 7% of the total calcium; in lepidolite, 11% ; and in muscovite, 14% . Later, with the assistance of A.N. Kostoyanov, an attempt was made to determine the K—Ca age of the biotites from the Kola Peninsula whose K—Ar ages are anomalously high (~ 5 Ga). The K—Ca age values of these micas proved to be considerably lower than their K—Ar ages.

At present I am making a search for the xenon formed in natural objects by the ^{244}Pu fission. Such xenon has been discovered in lunar rocks, meteorites and in the earth's atmosphere. Signs of this gas were also discovered in some terrestrial materials. The data are insufficient for any reliable conclusion. An attempt is necessary to find the decay products of ^{244}Pu in the ancient rocks of the earth. It is not ruled out that the xenon formed by ^{244}Pu fission may be used for age determination both of ancient terrestrial rocks and meteorites.

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