

INTERNATIONAL GEOLOGICAL CONGRESS

Report of
the Twenty-Third Session
Czechoslovakia
1968

PROCEEDINGS OF SECTION 6

Geochemistry

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**ACADEMIA
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Geochemistry

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Editorial

The Organizing Committee of the XXIII International Geological Congress has received a great number of papers for the different sections and symposia. Consequently, the selection of the papers to be printed was very difficult, as for technical and financial reasons not all the papers presented at the Congress could be published.

In the papers of this volume the Organizing Committee has made practically no editorial or linguistic alterations. Only in the case of evident formal or grammatical imperfections, there have been done minimal corrections by the editorial staff. It means that almost all the papers have been reprinted in the form in which they have been submitted.

The Organizing Committee
of the XXIII I.G.C.

On the Nature of the Excess Argon in Some Minerals

E. K. GERLING, I. M. MOROZOVA and V. D. SPRINTSSON

U. S. S. R.

Abstract: The paper deals with the examinations of excess content of Ar^{40} in some minerals of the Earth crust such as cordierites, beryls, chlorites and others. Considering the question on the nature of excess Ar^{40} the authors suggest the theory of impregnation of gases into crystalline lattice under high temperature and pressure conditions to be erroneous. The stated experimental dependence of the authors suppose another source of Ar^{40} formation (besides K^{40}). The source existed in remote past of our planet and up to now is completely (or almost completely) decayed.

In recent years at the Laboratory of Precambrian Geology the age determination of rocks by K-Ar method is carried out on minerals and rocks of most ancient parts of the Earth's crust. A number of data obtained within the interval from $7 \cdot 10^9$ to $15 \cdot 10^9$ y. obviously exceed the common value of the Earth's crust age and the age of the Earth as a planet. It seems expedient to us to divide the data into two groups to clear out the geochronological sense of all the data available.

The first group comprises the results obtained on xenoliths of basic and ultrabasic rocks, which according to geological and petrographical data probably were subtracted by magma in solid state (Moncha-Tundra, Kola Peninsula). The K/Ar ratio obtained in this case does not correspond to the age of intrusion, but reflects the distribution of these elements both in solid and magmatic melt. The determination of age values in this case can be of geochemical sense, since the age of the Earth matter can be estimated by the average content of Ar and K in a great number of similar samples. This age is considered to be about $6.800 \cdot 10^6$ y. [3]. The age is rather approximative because of lack of statistic data.

The second group of anomalously high figures of the age up to $15 \cdot 10^9$ y. was obtained on minerals and rocks that were formed in the Earth's crust, being crystallized in most cases *in situ*. Also referred here are high ages obtained on the rocks, having metamorphic texture. The second group comprises striated fine-grained and horny-like rocks of the mountain Nude of the Kola Peninsula (these rocks were called sudburites by V. A. Kotulskii) as well as all the examined cordierites, beryls, chlorites, uraninites and other minerals where the age is known in most cases, and the presence of excess Ar is doubtless (Table 1).

We shall discuss this group at length. The excess Ar content in some minerals, e. g.

Table 1.

Name and location	Absolute age 10 ⁶ y.	K g/g	Ar ⁴⁰ cc/g	Ar ⁴⁰ /K ⁴⁰	Apparent age 10 ⁶ y.
beryl, Siberia	330	0.0010	1.98 · 10 ⁻³	26	10,700
cordierite, Siberia	2000	0.00058	6.15 · 10 ⁻⁴	15.6	9,520
chlorite, Kola Peninsula	3500	1.7010 ⁻³	2.48 · 10 ⁻²	214	14,500
sudburite, Kola Peninsula					
Sample XIII					
cordierite fraction	3500	0.0103	2.19 · 10 ⁻²	21.2	10,500
chlorite fraction	3500	0.0102	1.95 · 10 ⁻²	27.6	10,650
eudialyte, Turji Mys	300	0.0060	1.65 · 10 ⁻⁴	0.404	3,020
talk, Norilsk	150	0.0011	5.10 ⁻⁶	0.669	3,800
tourmaline, Kola Peninsula	2300	—	2.37 · 10 ⁻⁴	—	—
diopside, Quebec, N. America	1650	8.6 · 10 ⁻⁵	9.64 · 10 ⁻⁶	1.74	5,500
uraninite, B. Lapot	1950	0.0022	6.8 · 10 ⁻⁵	0.445	3,150
pitchblende G-I	230	0.00023	3.7 · 10 ⁻⁵	0.235	2,240

in chlorite is difficult to explain, since it reaches anomalously high values of the order of $2 \cdot 10^{-2}$ cc STP/g. [4].

Up to the present time the most widespread treatment of the apparent anomalously high values of the age is the suggestion of the capture of Ar from the environment. It is common practice to refer to the works dealing with incorporation of Ar by mineral under high partial pressure and high temperature conditions [5, 7]. Yet the mentioned works state that for the incorporation of Ar of the order of $1 \cdot 10^{-2}$ cc/g found in beryls, cordierite and chlorite studied by us, the partial pressure of about 100 atm. is required. For natural conditions such a high pressure of Ar seems unreal. According to our calculation on melting of granite of $3.5 \cdot 10^9$ y. old with porosity of 1 per cent the partial pressure of Ar in magma should not exceed 0.1 atm. If we suppose the age of rocks which have undergone melting to be less than $3.5 \cdot 10^9$ y. and take Ar migration in the process of heating into consideration, the partial pressure of Ar in the magmatic hearth would equal 0.01–0.001 atm.

The mentioned considerations are confirmed by the results of investigations devoted to the content of magmatic gases in gaseous-liquid inclusions of various minerals [8].

As is seen from Table 2, the Ar-content in the inclusions is small, being equaled to $1 \cdot 10^{-5}$ – $1 \cdot 10^{-9}$ cc/g. Also in this table Ar partial pressures are given, which were calculated by us from the water content in gaseous-liquid inclusions. The Ar pressure is small and ranges from 0.024– $5 \cdot 10^{-6}$ atm. Consequently the Ar concentration in the magmatic hearth cannot be the main reason of the distortions of the Ar⁴⁰/K⁴⁰ ratio. It is only on the age of comparatively young minerals and rocks with low K-content and a large amount of gaseous inclusions, that the amount of the impregnated Ar can tell.

Table 2

Samples	Age of sample 10^6 y.	Water- content mg/g	Ar ⁴⁰ cc/g	Excess A ⁴⁰ cc/g	Partial pres. A ⁴⁰ atm.
Bethesda quartz	300—500	0.5	$1.2 \cdot 10^{-5}$	$1.2 \cdot 10^{-8}$	0.024
Brasil quartz	1,000—2,600	0.1	$7 \cdot 10^{-8}$	$6 \cdot 10^{-8}$	0.0007
Colorado quartz	10	1.4	$7 \cdot 10^{-9}$		$5 \cdot 10^{-6}$
Illinois fluorite	100—300	0.2	$2 \cdot 10^{-7}$	$3.5 \cdot 10^{-8}$	$1 \cdot 10^{-4}$
Illinois quartz	100—300	0.4	$5 \cdot 10^{-8}$	$3.5 \cdot 10^{-8}$	$1.5 \cdot 10^{-4}$

Some investigators [9] believe the excess Ar-content in beryls and cordierites to result from their crystalline structure of channel character. However, as it was mentioned above, the anomalously great amount of Ar is found in chlorite, having a lattice similar to that of layered mica.

All data stated above give evidence that the excess Ar-content in some minerals does not depend on their structure and on trapping of Ar from the environment. This statement is confirmed by some other data. In Figure 1 the theoretical curve of Ar/He

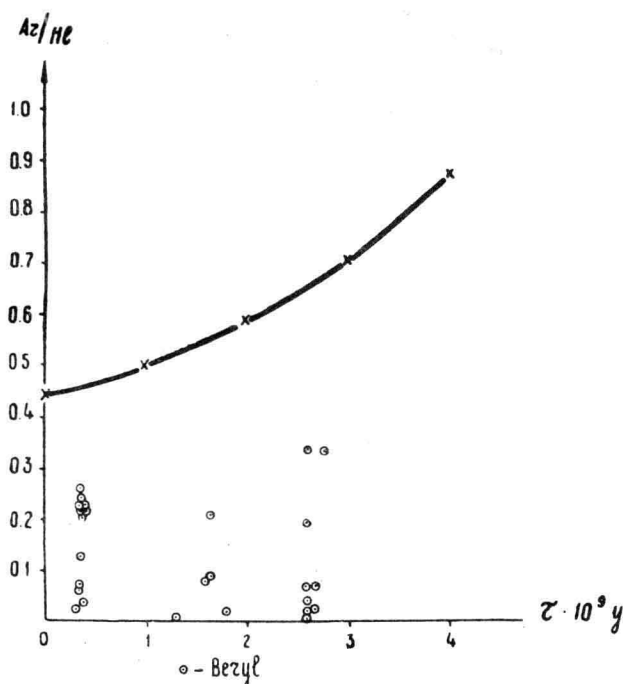


Fig. 1. Theoretical curve of the dependence on the age of magmatic hearth of Ar⁴⁰/He⁴ ratio
 × = experimental points obtained on beryls of varying age

ratio dependence on age in the magmatic hearth is given. All the experimental points obtained on beryls of varying age are below the curve. In the following Figure 2 the theoretical curve of Ar/He dependence on the time of cordierite formation is represented. As is seen from this figure, in this case no direct connection between the Ar/He ratio and the age is observed either, which is no evidence in favour of the impregnation theory.

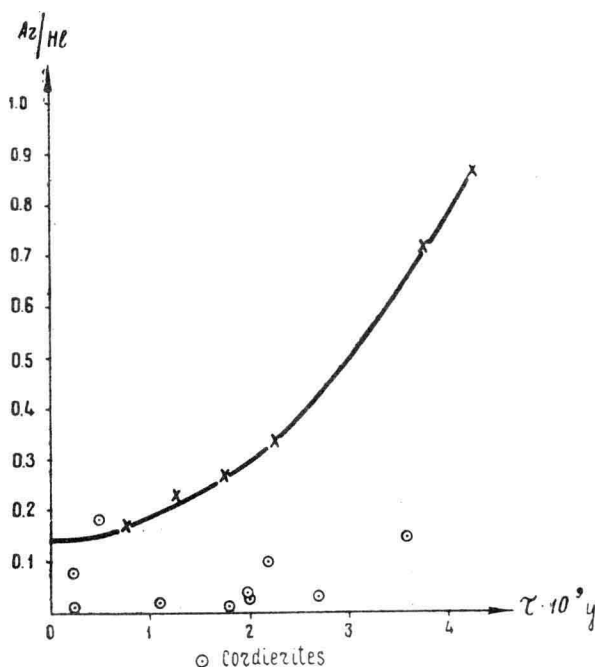


Fig. 2. Calculated curve of the dependence on the cordierites age of $\text{Ar}^{40}/\text{He}^4$ ratio
 \times = experimental points

Experimental determination of the activation energy Ar and He isolating from minerals is of special significance. This made it possible to calculate the gas losses at various temperatures. We found that He completely escaped from cordierite at 400 °C within several hours, and for Ar it is necessary some hundred years to be isolated. Thus only if high partial pressure of these gases kept unchanged during the time of cooling of cordierites up to temperature at 20 °C, both He and Ar could be preserved in them. Yet, in this case excess He and Ar would be characteristic of absolutely all the minerals associated with cordierite and beryl; but it is not observed. Besides it must be taken into consideration that isolation of water-steam and other gases takes place under metamorphic conditions of cordierite formation, and constant (unchanged) concentration of He and Ar can be hardly supposed.

The only suggestion is that both He and Ar were formed in minerals (after their complete cooling) as a result of an unknown nuclear process. The same conclusion was

drawn by the authors [6] in studying excess Ar in uranium minerals. As is seen from Figure 3, the amount of Ar^{40} in uranium minerals and its position in the crystalline lattice agree with the excess of Ar^{38} isotope which is believed to be undoubtedly of nuclear origin. Correlation is strictly preserved in spite of the change of uranium, Ar^{40} and Ar^{38}

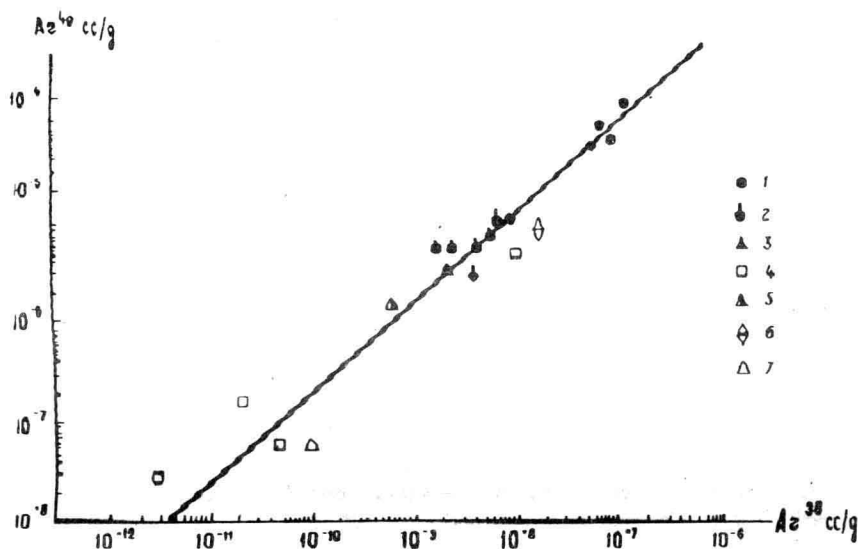


Fig. 3. Relation between the Ar^{40} and Ar^{38} -content in uranium minerals

1 - uraninites, $2 \cdot 10^9$ y. [6]; 2 - nasturans, $0.2 \cdot 10^9$ y. [6]; 3 - mendelejewite, $0.4 \cdot 10^9$ y. [6]; 4 - thucholites, $0.6 \cdot 10^9$ y. [1]; 5 - monazite, $0.5 \cdot 10^9$ y. [10]; 6 - pitchblende, $0.6 \cdot 10^9$ y. [10]; 7 - euxenite, $0.6 \cdot 10^9$ y. [10]

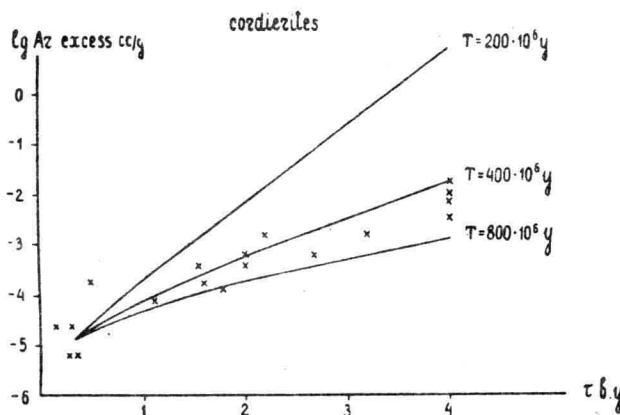


Fig. 4. Curves of the dependence on the cordierites age of excess Ar^{40} -content

— = theoretical curves calculated for definite periods of half-decay; x = experimental points

concentration by 3-4 orders and also in spite of variations of chemical composition in such various minerals as uraninite, monazite, pitchblende, and others. It made us suppose that a different (besides K^{40}) nuclear source of the formation of Ar^{40} occurred in nature, being concentrated in uranium minerals.

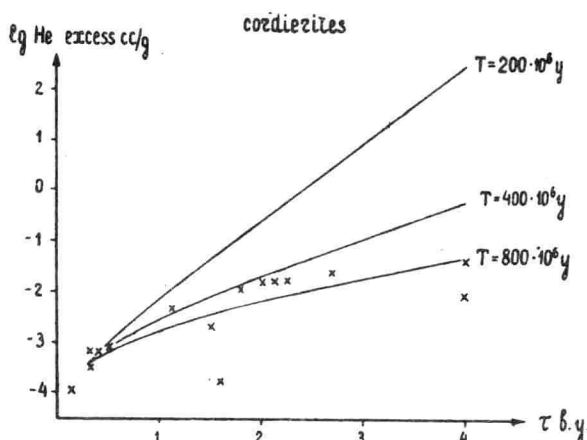


Fig. 5. Curves of the dependence on the cordierites age of excess He^4 -content
 — = theoretical curves calculated for definite periods of half-decay; x = experimental points

If we assume that the formation of Ar^{40} is due to an intermediate isotope possessing sufficiently long decay period, the excess of Ar^{40} in cordierites, beryls and other minerals would be explained then. Besides, the fact would become clear that in chloritisation of some cordierites excess Ar seems to be inherited by chlorite anew formed, and in chloritisation of micas and in metamorphism of other K_2 -bearing minerals the complete loss of radiogenic gas takes place.

If the different source besides K^{40} existed in nature, the excess content of Ar in cordierites and beryls should depend upon the age of these minerals. Such a dependence for beryls was already stated in literature [2]. We studied analogous dependence for cordierite of varying age (see Fig. 4). As one can see from Figure 4, rather distinct relation between the excess Ar-content and age of minerals exists. Besides, all the experimental points are concentrated around the theoretical curve with half decay-period T equalling to $400 \cdot 10^6$ years.

Similar curve is also received for He-content in cordierites (Fig. 5).

All considerations stated above give us the possibility to guess the existence of a different source of Ar^{40} (besides K^{40}) in remote past period of the Earth that had disintegrated completely or almost completely.

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