EXCESS HELIUM AND ARGON IN BERYL
AND OTHER MINERALS*

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Abstract

All beryl crystals appear to contain a quantity of helium and argon in great excess over that which can be accounted for from radioactive decay. Other magmatic minerals which have structural sites suitable for large non-essential atoms such as cordierite and tourmaline also show this excess in variable amount. It seems that this excess inert gas must represent a sample of the magmatic gases in the immediate environment of the forming crystal and as such can provide useful information on magmatic conditions. Although there are considerable differences in the helium and argon concentration even in the same beryl crystal, these are small compared to the one hundred-fold difference between crystals formed in the early Precambrian ($\sim$3.0 b.y.) and Paleozoic eras. This strong age effect is interpreted as suggesting more extensive outgassing of the mantle in the earlier phases of earth history.

Introduction

In 1908 Lord Rayleigh (Strutt, 1908) discovered that beryl contained helium in excess of the amount thought to be produced by the decay of the uranium and thorium in the mineral subsequent to its formation. This was in marked contrast to radioactive minerals, sulphides, selenides, arsenides, various native elements, igneous rocks, silica, silicates, phosphates, etc., which usually appeared to be more or less deficient in helium content. Various investigators have confirmed the existence of such an excess for beryl in all samples analyzed (Piutti (1913); Burkser et al. (1937); Hahn (1934); Fay et al. (1938); Khlopin (1941); Aldrich and Nier (1948).) On this point there is no disagreement. Rayleigh (Strutt, 1908) also reported an excess of helium in sylvite, halite and carnallite. Several German and Austrian workers (Hahn and Born (1935); Karlik and Knopf-Duschek (1950)) have also observed this phenomenon and have proposed that an excess of helium in these salts is a result of the decay of co-precipitated short-lived radioactive isotopes such as radium

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and its daughters. A significant excess of helium has also been reported, in a few cases, for magnetite and calcite (Keevil (1941); Hurley (1954)) and for tourmaline and possibly chrysoberyl (Khlopin and Abidov, 1941).

A new dimension was added to the excess helium problem by the isotopic study of He^3 and He^4 by Aldrich and Nier (1948) who obtained He^3/He^4 ratios of 12.0×10^{-7} for atmospheric helium; $0.5–3.0 \times 10^{-7}$ for twelve natural gas wells; 0.6 to 12.0×10^{-7} for seven beryl crystals; less than 0.3×10^{-7} for five radioactive minerals; and 24.0×10^{-7} and 120×10^{-7} for two spodumene crystals. The abnormal He^3 content of spodumene can be ascribed to the reaction $Li^6(n, He^4)H^3 \rightarrow He^3$ which is the most prolific lithospheric source of He^3 (Morrison and Pine, 1955). It should be noted, however, that equal quantities of He^3 and He^4 are produced in this reaction and so the very large excess of He^4 in beryl cannot be explained by this reaction.

All attempts to explain the origin of the excess helium as a result of nuclear reactions have failed (Morrison and Pine, 1955). This is not surprising in view of another observation by Aldrich and Nier (1948), who found an excess of argon as well as helium in several of the beryls that they studied. The fact that they did not find argon in all of their beryl measurements can probably be attributed to air leakage or the presence of hydrogen in their gas samples. In this work it was found that beryls from the Keystone area (in which Aldrich and Nier found no argon after making a large correction for contaminating atmospheric A^{40}) all have an excess of argon and in fact all beryls studied during this investigation clearly contained a great excess of argon as well as helium.

With the exception of beryl the actual magnitude of the excess gas reported in other minerals is not great. The technical difficulties in both the alpha ($<0.1\alpha$/mg. hr) and helium (volumetric) measurements on these minerals are sufficiently great by older methods that the results should be considered as only tentative.

In the present investigation in which isotope dilution techniques were used, it has been possible to confirm an excess of helium and argon in tourmaline although it is not as great as for beryl in the same pegmatite. In addition it was observed that cordierite also contains an excess of both helium and argon approximately equal in magnitude to that of beryl. A preliminary study of magnetite and calcite, from the localities for which the greatest helium excess was reported, has failed to confirm the actual existence of an excess of argon or helium in these minerals. On the other hand, definite evidence was found for excess inert gas in hornblende from several localities. It is quite possible that the reported excess helium in magnetite is actually due to amphibole contamination. For example, the anomalous samples reported by Hurley and Goodman

(1943) from the Sudbury region actually contained less than 50% magnetite. No evidence has been found for excess argon in mica (Damon and Kulp, 1957a).

This paper will be concerned almost entirely with the beryl-like minerals, in which the phenomenon of excess inert gas is most evident and unequivocal. Special attention will be given to the relative and absolute concentrations of these elements and their variation with time.

EXPERIMENTAL TECHNIQUES

The present study required the measurement of the helium content, argon content, potassium content and alpha activity of minerals of known geologic age. In addition the composition of the volatiles contained in several of these minerals was also determined by standard analytical mass spectrometric technique.

The vacuum fusion technique described by Carr and Kulp (1957) for argon and Damon and Kulp (1957b) for helium was used for gas liberation and purification. The mineral is fused by induction heating in a molybdenum crucible, mixed with He^3 and A^{38} tracers of known composition in the furnace, and quantitatively removed from the furnace system by the mercury diffusion pump to the purification system where it is purified, equilibrated and eventually sealed off into the sample break seal ampoule. The tracer preparation and calibration system and the mass spectrometric technique have been described in the above mentioned papers. In addition to the determination of He^4 and A^{40}; A^{36}, Ne^{20} and H_2^1 were also monitored during each mass spectrometric determination. In those cases where it was desired to determine the isotopic composition of the inert gases, no tracers were added.

The potassium content of the beryl, tourmaline, and cordierite samples was determined by a simple and inexpensive counting technique. This technique is a modification of the analytical method first described by Gaudin and Pannell (1948). It involves alpha and beta counting of a powdered sample. The beta count is taken with a 5 mil. aluminum absorber to eliminate Rb^{87} betas; this count is then reduced by an empirical correction for the betas resulting from the uranium and thorium series. The alpha count determines the magnitude of this correction. The resulting beta count rate is compared with a standard sample of potassium dichromate to determine the potassium content. Potassium dichromate was chosen as a standard because its density (2.69) is about the same as the silicates in question and also because it is not deliquescent. A Volchok-Kulp (1955) low-level beta counter was used for the work.

The results of a comparison of the α-β method with other methods are given in Table 1.

The precision decreases as the K content decreases due to background fluctuations, but there is no systematic difference. In most cases it was only necessary to set an upper limit on the K content of beryl and cordierite for the excess helium and argon study. Actually the precision of the α-β method does not compare unfavorably with the precision of potassium analyses for silicates in general (Fairbairn et al. 1951).

Alpha scintillation counters of the type described by Kulp, Holland and Volchok (1952) were used. One counter utilized a Dumont 6292 flat

TABLE 1. COMPARISON OF K ANALYSES BY COUNTING AND OTHER METHODS

Sample description	Counting method % K	Comparison method % K
Columbia River basalt (N.B.S. radium std. No. 788)	0.88	0.82
Chelmsford granite (N.B.S. radium std. No. 789)	4.47	3.81
Graniteville granite (N.B.S. radium std. No. 791)	4.30	4.60
Lake Kivu leucitite (GB8)	4.83	5.20 (i.d.)
Hawaiian olivine basalt (SD-2)	0.24	0.35 (i.d.)
Stillwater plagioclase	0.17	0.12 (i.d.)
McKinney feldspar	11.7	11.0 (G)
Wind River Canyon feldspar	9.65	9.39 (G)
Wilburforce antiperthite	3.39	3.73 (L)
Brown Derby feldspar	11.1	10.4 (L)
Black Hills feldspar	11.8	11.8 (L)
Beryl Mt., N.H. albite	0.35	0.39 (L), 0.42 (G)

i.d. = isotope dilution analysis by P. W. Gast.

G = analyzed in the University of Minnesota Rock Analysis Laboratory by the L. Lawrence Smith fusion method (Goldich and Oslund, 1956).

L = determined by Ledoux and Co. using a wet chemical method (Kallman, 1946).

faced 2-inch diameter tube with Dupont No. 1101 phosphor. The second counter utilized a 5-inch diameter Dumont 6364 photomultiplier.

The 2-inch counter was used only for determining the activity of samples for which insufficient material was available to take advantage of the improved geometry of the larger tube. The figure of merit for counting (square of sample count divided by background count) was 8-fold greater for the 6364 than the best obtainable with the 2-inch tube. This allowed low-level samples, which formerly required one week of counting, to be counted with adequate precision during one day.

The alpha counter was monitored by a traffic counter which recorded the accumulated count every 15 minutes. The counters were calibrated

with National Bureau of Standards rock samples. Where necessary corrections based upon Bragg's law (Nogami and Hurley, 1948) were made for the composition of the individual sample.

RESULTS AND OBSERVATIONS

The experimental data are recorded in Tables 2–6. The detailed sample description may be found in the appendix. Table 2 gives the total A^{40} and He^4 as well as the per cent excess for the samples used in the survey. The

TABLE 2. EXCESS HELIUM AND ARGON IN BERYL, CORDIERITE AND TOURMALINE

Sample No.	Locality	Mineral	Estimated geologic age, m.y.	A^{40} in microliters per gm.	He^4 in microliters per gm.	% excess argon	% excess helium
B1	Beartooth, Mont.	Beryl	2,750	32.0	96.2	>99.9	>99.7
B2	Huron Claim, Manitoba	Beryl	2,650	10.0	4.74	n.d.	n.d.
B3a, b	Greer Lake, Manitoba	Beryl	2,650	~1.5	57	>99.8	>99.8
B4	S. of Greer Lake, Manitoba	Beryl	2,650	~7	102	>99	>99.6
B5	Eräjärvi, Finland	Beryl	1,800	0.74	30.4	>97	>99.7
B6a, b, c	Peerless Mine, Keystone, S.D.	Beryl	1,630	2.2	10.6	>97	>99.7
B7	Keystone, S.D.	Beryl	1,630	1.16	12.9	98	>99.8
B8	Etta Mine, Keystone, S.D.	Beryl	1,630	n.d.	1.22	n.d.	n.d.
B9	Harding Mine, N.M.	Beryl	1,600	0.604	7.12	99	97
B10	Norrbotten, Sweden	Beryl	1,300	0.109	14.2	82	98
B11	Beryl Mt., N.H.	Beryl	320	0.045	0.718	>98	97
B12	Rumney, N.H.	Beryl	320	0.252	3.72	>99.4	87
B14	Haddam, Conn.	Beryl	280	0.152	5.14	99	99
C1	Ft. Victoria, So. Rhodesia metabasite (cordierite bearing)	foliated	2,700	0.613	21.4	>87	>95
C2	Orijärvi, Finland	Cordierite	1,800	0.136	10.6	>96	>99.4
C3	Geelkop, S.A.	Cord. schist	1,100	0.155	4.69	44	90
C4	Kragerö, Norway	Cordierite	1,300	~0.8	1.40	99	83
C5	Rakinankaratra, Madagascar	Cordierite	500	0.171	0.919	>99.3	>99.2
T1	Peerless Mine, Keystone, S.D.	Tourmaline	1,630	0.0182	0.283	60	63
T2	Hugo Mine, Keystone, S.D.	Tourmaline	1,630	0.117	n.d.	95	n.d.

Values preceded by approximation sign (~) were not determined by isotope dilution technique.
n.d. Value not determined.

geologic ages for most of these samples are well known from Rb/Sr, K/A and/or U/Pb dating in this and other laboratories, but in some cases it was necessary to rely on geological considerations such as the location of a particular sample in the Fennoscandian Shield area etc. (see appendix). Table 3 shows the repeat runs of various kinds. The experimental error in the determination of He^4 and A^{40} content should not exceed a few per cent.* Samples B3, B7, B11 and B13 indicate the

* Except in the few cases where only an approximate value was obtained without the aid of the isotope dilution technique.

TABLE 3. VARIATIONS OF HELIUM AND ARGON IN BERYL

Sample No.	Source of beryl	He^4 in micro- liters per gram	A^{40} in micro liters per gram	Remarks
B5	Eräjärvi, Finland		0.735	identical samples
B5	Eräjärvi, Finland		0.748	
B13a	Stoneham, Maine		0.220	opposite ends of 6 cm. crys-
B13b	Stoneham, Maine		0.165	tal
B7	Keystone, S.D.	12.9		solid piece of crystal
B7	Keystone, S.D.	10.4		adjacent piece crushed un- til all material passed through 200 mesh screen
B11a	Beryl Mt., N.H.	0.718		aquamarine, $0.22\,\alpha$/mg./hr.
B11b	Beryl Mt., N.H.	0.915		golden beryl, $4.92\,\alpha$/mg./hr.
B3a	Greer Lake, Manitoba	68.0	~2	south pit
B3b	Greer Lake, Manitoba	47.0	~1	north pit

location variations which may occur. Sample B11 shows clearly that the excess helium content is definitely not related to the alpha activity. Table 4 shows the results of a search for atmospheric contamination and magmatic neon and A^{38}. Table 5 records the more detailed study of a single large beryl crystal and closely associated tourmaline. Table 6 gives the analysis of the total gases (corrected for blank) derived from three samples of beryl during fusion. The results are reported on a water-free basis as obtained by mass spectrometric technique. Keewatin beryl (Beartooth, Wyoming) and Paleozoic beryl (Beryl Mt., N.H.) contained very nearly the same amount of water (about 0.2%). This was deter- mined by freezing the water into a 300 cc. bulb as evolved during fusion

TABLE 4. He/Ne, A^{40}/A^{36} AND A^{40}/A^{38} RATIOS IN BERYL AND CORDERITE*

Sample No.	Sample location	Mineral	He/Ne	A^{40}/A^{36}	A^{40}/A^{38}
B1	Beartooth, Montana	Beryl	$>4 \times 10^4$	$>100,000$	$\geq 110,000$
B2	Huron Claim, Manitoba	Beryl	$>2 \times 10^5$	$>30,000$	
B4	S. of Greer Lake, Manitoba	Beryl	$>1.5 \times 10^6$	$>48,000$	$\geq 65,000$
B6	Peerless Mine, S.D.	Beryl	$>4 \times 10^5$	$>15,000$	
B9	Harding Mine, N.M.	Beryl	$>2 \times 10^4$	$>30,000$	
C1	Fort Victoria, So. Rhod.	Cordierite bearing foliated metabasite	$>2 \times 10^5$	$>18,000$	
B5	Eräjärvi, Finland	Beryl	$>6 \times 10^4$	$>65,000$	$\geq 170,000$

* The He/Ne and A^{40}/A^{36} ratios are minimum figures because no correction was made for air leakage. The 38 peak was corrected assuming all of the 36 peak was due to air leakage and so represents the excess over atmospheric. The gas was purified over hot calcium and CuO but there is still the possibility of an impurity and so the A^{40}/A^{38} value is considered to be a minimum value.

TABLE 5. He, A, K CONTENT AND ALPHA ACTIVITY OF A LARGE BERYL CRYSTAL AND
TOURMALINE FROM PEERLESS MINE PEGMATITE, KEYSTONE, S.D.

Sample No.	He^4 microliters per gram	A^{40} microliters per gram	K %	Alpha Activity α/mg./hr.	He^4/A^{40}
B6a	4.75 (4.63) 4.99	3.97 (3.97)	0.028	0.375	1.2
B6b	15.9 (15.9)	3.15 (3.15)	0.011	0.049	5.0
B6c	11.1 (10.9)	2.17 (2.11)	0.537*	0.336	5.2
T1	0.283 (0.178)	0.0182 (0.0108)	0.07	0.168	16.5

Numbers in parentheses are the excess Helium and Argon Content.
He^4/A^{40} ratio is for the excess gas.
* Contaminated with sericite.

and then heating the bulb in a warm water bath until the liquid phase
disappeared.

These results make possible the following observations:

(1) All beryl, cordierite and tourmaline studied in this work contained

TABLE 6. CHEMICAL COMPOSITION OF THE WATER FREE GASES
EVOLVED FROM BERYL DURING FUSION

Constituent	Beryl Mt. beryl B11a %	Keystone beryl B7 %	Beartooth beryl B1 %
CO_2	75.0	62.0	75.5
CO	2.5	1.8	2.7
N_2	8.8*	9.7	6.1*
H_2	13.0	20.5	2.0
O_2	0.4	0.1	0.4
H_2	0.07	1.6	9.6
A	0.004	0.2	3.3
CH_4	0.2	3.4	0.3
H_2S	0.02	0.07	0.02
$\dfrac{N_2+A+He}{CO_2}$	0.12	0.19	0.25
$\dfrac{A+He}{N_2}$	0.008	0.19	2.1

* Determined by Dr. T. Hoering and Mr. R. Scanlan (Chemistry Department, University of Arkansas).

All other analyses were made by Mr. W. Ault and the authors using a C.E.D. No. 401 mass spectrometer. CO was distinguished from N_2 in the B7 analysis by the relative proportions of $m/e=12$ and $m/e=14$.

a large excess of both helium and argon over that required from radio-
active decay. In many cases the amount of helium and argon produced
within the mineral by radioactive decay was only a fraction of one per
cent of the total (Table 2).

  (2) The content of helium, argon and potassium and the alpha activity
varied in crystals of beryl from the same pegmatite and even within a
single crystal (Tables 3 and 5). The content of helium and argon in
crystals from different localities is extremely variable. The potassium
content of beryl is usually very low ($<0.2\%$). The high value for sample
B6C (0.537% K, Table 5) was due to sericite impurity which had not
been completely removed. The alpha activity is quite variable ($<.05$ to
5 α/mg. hr.) but it is usually less than 1 α/mg. hr.
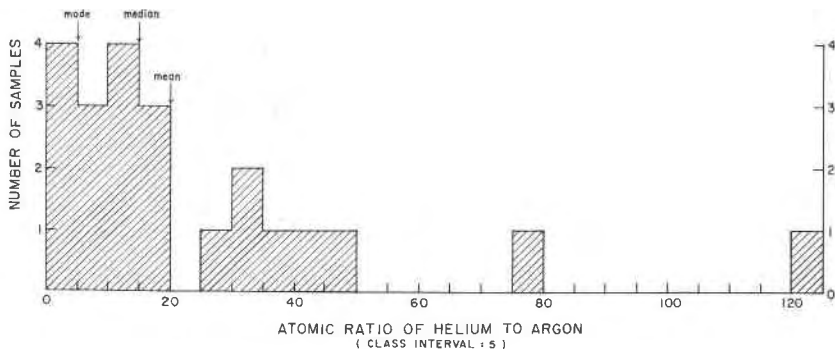
FIG. 1. Ratio of helium to argon in beryl and cordierite.

  (3) The ratio of helium to argon in crystals from different pegmatites
varied from 0.5 to 130 and even varied from 1 to 5 in a single crystal
(Table 5). Qualitatively, it may be stated that the He^4/A^{40} ratio histo-
gram (Fig. 1) is a skewed distribution, with a mode equal approximately
to 8, a median value equal to 15 and a mean value of 20. The mode is
approximately equal to the relative production rate of helium to argon
by radioactive decay in average shale, granite or basalt. The variation
of the He^4/A^{40} ratio is much as might be expected from a fortuitous
sampling process.

  (4) The three minerals for which a gross excess of inert gas has been
found have in common an atomic structure based upon a 6-membered
silica tetrahedron ring (Bragg (1937); Hambuerger and Buerger (1948)).
Beryl and cordierite are isostructural but in cordierite magnesium-
aluminum replaces beryllium-aluminum and on the average one alumi-
num atom replaces one silicon atom in the ring. Fe^{+2} can substitute

partially or wholly for Mg in cordierite. According to Schaller and Stevens (1955), variations in the composition, specific gravity and indexes of refraction of beryl are due to progressive substitution of Li^+ for Al^{3+} along with Al^{3+} for Be^{2+} in the beryl structure; the charge unbalance being satisfied by concomitant substitution of alkali ions, principally Na^+ and Cs^+ into the tubular channels defined by the tetrahedral rings. The structure of tourmaline is much more complex, being composed of alternate layers of 6-membered silica tetrahedra rings with magnesium octahedra and boron triangles, Na^{+1} occupying the central position in the ring.

It can be seen (from Tables 2 and 5) that in the same pegmatite, the magnitude of the excess gas is much less for tourmaline than for beryl. On the other hand, cordierite and beryl appear to accept the inert gases with equal facility.

(5) There appears to be no direct relationship between the helium and argon content and the immediate environment. The beryl crystals occurred in a rather uniform environment of quartz, muscovite and feldspar. The existence of radioactive minerals in a pegmatite (e.g. B2) or the nonexistence of such minerals (e.g. B4) cannot be correlated with the helium content. Cordierite from a metamorphosed terrain such as Orijärvi (C2) or in a metamorphosed basalt (C1) has accepted as much inert gas as beryl of equivalent age (compare C2 with B10) keeping in mind that cordierite composes only a third part of the metabasite (C1 with B3). On the other hand (Fig. 2 and Table 5), the extension of the beryl crystal from the wall zone into the intermediate zone in the Peerless pegmatite was accompanied by a remarkable change in the helium to argon ratio. However, this may be merely a fortuitous correlation.

(6) The elemental and isotopic abundances of the inert gases are not at all similar to their abundances in the atmosphere (Table 4). Neon has not yet been observed in beryl (a more sensitive mass spectrometer is being constructed for this purpose at the Lamont Geological Observatory), but a lower limit can be set on the ratio of helium to neon of at least 10^6 compared with 0.3 in the atmosphere. The ratio of A^{40} to A^{36} is greater than 100,000 to 1 in the Beartooth beryl compared with 295 to 1 in the atmosphere. (The A^{40}/A^{36} ratios given in Table 4 are quite conservative because no effort was made to correct for the small amount of A^{36} which is always present due to air leakage.) The A^{40}/A^{38} ratio is much higher than would be expected from the work of Gerling et al. (1956). These workers found one part of A^{38} per 50,000 parts of A^{40} in mica of Keewatin age after atmospheric correction, and the content decreased in younger micas in such a way as to indicate a potassium parent with a 10^9 year half life. An attempt by J. W. Winchester (1957—private com-
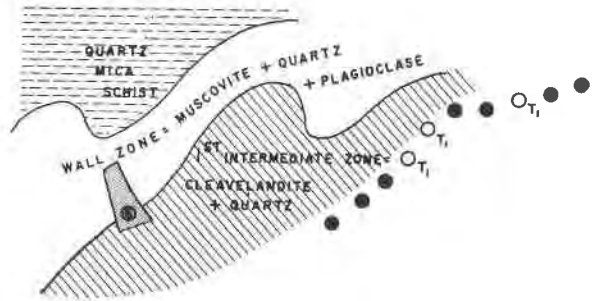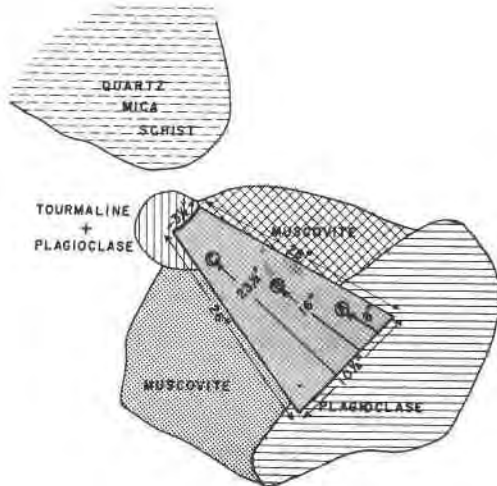
FIG. 2. Peerless Mine pegmatite, Keystone, South Dakota.

munication) to produce long-lived K^{38} by the Ca^{40} (d, α) K^{38} reaction did not succeed.

(7) Lord Rayleigh (1933) analyzed a large number of beryls of different age and came to the conclusion that there was a marked tendency for the oldest beryls to contain the largest quantity of helium. This work has been almost completely overlooked (except for a recent remark by A. Holmes, 1955) in the literature on this subject, despite the ususual quantity of helium ($\sim$.08 std. cc.) observed, for example, in a beryl from a pegmatite south of Yaduir near Bangalore, Mysore, India. The Pb^{207}/Pb^{206} age of monazite from this pegmatite was 2,300 m.y. Khlopin and Abidov (1941), on the other hand, state that there was no connection between helium and mineral age in beryls which they studied.
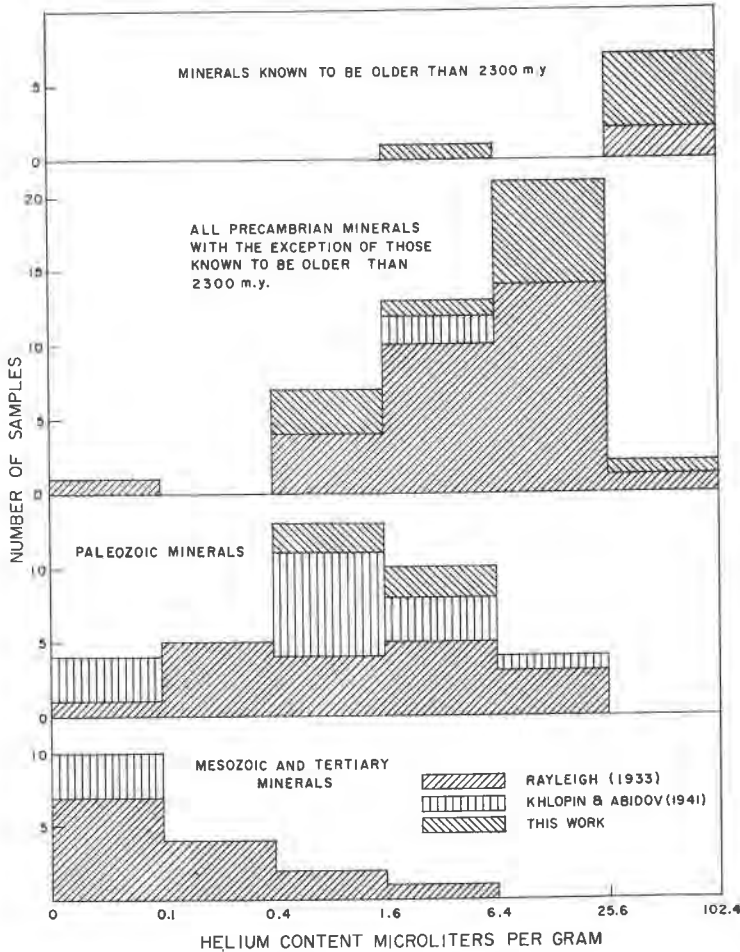
Fɪɢ. 3. Helium content of beryl and cordierite of various ages for class intervals arranged
according to a geometric progression.

In this work an effort was made to obtain beryl from very old pegma-
tites in order to decide between the conflicting evidence. The results of
the previous investigators have been included with the present work and
a histogram has been plotted for the helium content of beryl with the
class intervals arranged according to a geometric progression (Fig. 3).
A histogram based on exponential (base = 10) class intervals also brings
out the relationship but does not distinguish as well between the two
Precambrian groups. (Class intervals based on a natural log base would
bring out the relationship as well as the geometric progression.) A glance
at this histogram confirms Lord Rayleigh's observation and also demon-

strates the reason that Khlopin and Abidov did not observe this relation-
ship, i.e., their analyses include only two Precambrian samples.

The relationship is peculiar; qualitatively the helium content increases
with age very much as might be expected if beryl were a radioactive
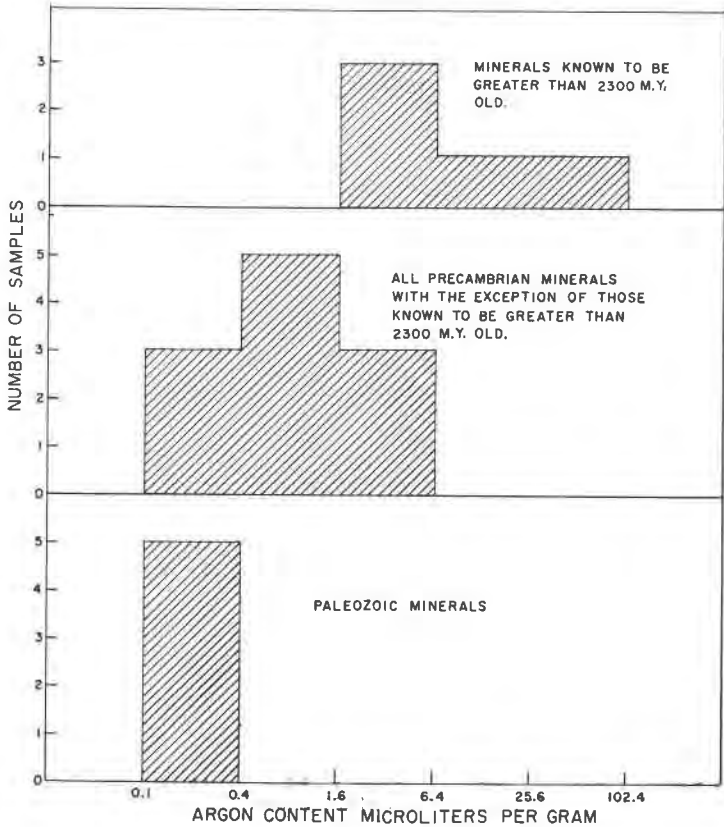mineral containing varying amounts of pure U^{235}, which of course it does

Fig. 4. Argon content of beryl and cordierite of different ages for class intervals arranged
according to a geometric progression.

not. There is no correlation between alpha emission and helium content.
Furthermore, the same age relationship holds for the argon content
(Fig. 4). Incidental to this, note that the one beryl from Manitoba which
does not fall in the 25.6 to 102.4 microliter per gram class interval con-
tains a quantity of argon second only to the Beartooth beryl from Wyo-
ming. Lord Rayleigh (1933), not knowing about the argon content of
beryl, made a fruitless search for an unknown alpha emitter.

It may be stated that the helium and argon content of beryl and cordierite increases with the age of the mineral and there is no relationship between this phenomenon and the alpha emission, potassium content, chemical composition or mineralogical environment of the mineral.

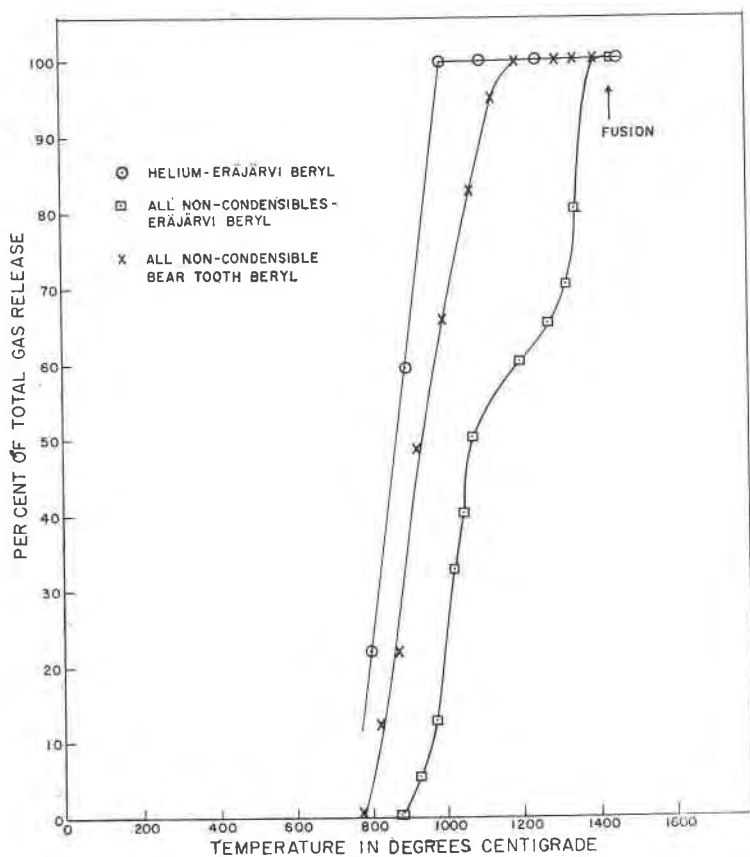(8) The chemical composition of gases released from beryl upon fusion

FIG. 5. Release of gas as a function of temperature for beryl.

is presented in Table 6. The solid pieces of beryl (not powdered) were fused in vacuum without flux and collected without chemical treatment in a 300 cc. bulb. The fusion took place in a molybdenum crucible placed within the quartz-tube furnace. Before melting the beryl the system was carried through a mock fusion without placing a sample in the system. The gases obtained from this "blank run" were, except for the inert gases, very similar in composition to the gases obtained from the

Paleozoic beryl (B11a). Enough beryl was fused to minimize the error due to the blank ($<10\%$ of total volume).

Except for the inert gases and nitrogen the concentrations may not be directly related to primary volatile components trapped in the lattice. Atmospheric gases adsorbed on the surfaces of the beryl undoubtedly contribute to the gases evolved. Furthermore, as pointed out by Wahler (1956), CO, H_2, CH_4, O_2, H_2S can result from decomposition of water, CO_2 and adsorbed organic compounds followed by recombination to produce the observed distribution of the chemical elements among the chemical compounds. As a case in point, through optical prisms it was observed that transport of molybdenum from the crucible to the beryl occurred in the presence of water vapor, presumably by way of an oxide of molybdenum. When beryl was first desiccated by heating to 1200° C. in a graphite crucible, this phenomenon was no longer observed.

Undoubtedly much of the CO_2 and H_2O are more than superficially located within the beryl (the non-essential water content of beryl is well known) and the nitrogen is also most certainly retained within the beryl by more than superficial adsorption. The content of nitrogen and the nitrogen isotope abundances of many of the beryls investigated in this work are being determined by Dr. T. Hoering and associates at the University of Arkansas. Their preliminary results (T. Hoering, personal communication) on a number of beryl and cordierite samples definitely show that the nitrogen content of beryl and cordierite is higher than that of igneous rocks by a factor of 10 to 100.

Thus H_2O, CO_2, N_2 and the inert gases are the most abundant primary constituents evolved upon fusing beryl. For a Paleozoic beryl the proportions are approximately $H_2O = 80\%$, $CO_2 = 16\%$, $N_2 = 2\%$, inert gases = trace and for the most ancient beryl $H_2O = 77\%$, $CO_2 = 16\%$, $N_2 = 2\%$ and inert gases $= 3\%$. *Thus, the proportion of the inert gases increases but there is essentially no change in H_2O, CO_2 and N_2 with increasing age.* This can most clearly be seen by the ratio of (A+He) to N_2 in the last row of Table 6.

Wahler (1956) heated beryl until decrepitation and maintained this temperature for only 5 minutes to avoid chemical reactions. The composition of gases evolved by this method was very similar to that observed in the present study but less in volume by a factor of 3 to 4. However, heating for a short period of time at the temperature at which decrepitation first takes place will not completely degas beryl.

The following experiment was performed: A small sample (1 g.) of beryl was heated to 700° C.; this temperature was maintained while chemically active gases were cleaned up on hot calcium, and argon was adsorbed on charcoal at liquid nitrogen temperature until the pressure, as determined by a McLeod gauge, no longer increased appreciably.

Undoubtedly, if this temperature had been maintained for a sufficient period of time, more helium would have been evolved by diffusion, but the value plotted in Fig. 5 represents all the helium that could be readily evolved at this temperature. The temperature was then raised and the process continued until fusion. No change in pressure was observed from 1100° C. to fusion at 1450° C. or thereafter. Thus all of the helium was evolved long before fusion. However, in other experiments (Fig. 5) by observing the manometer reading as the gases came off before clean-up, it was ascertained that the non-condensable gases are most rapidly evolved upon decrepitation but the temperature had to be raised to 1200° C. or higher to completely outgas the beryl. Böse (1936), upon heating powdered beryl, observed that gas was so suddenly and rapidly released upon decrepitation that the powder was blown about in the furnace. This was not observed with the solid pieces of beryl during this investigation. In the case of fine-grained mica, however, flakes may actually be violently ejected from the crucible at about 800° C. if the temperature is raised too rapidly. Böse found that upon decrepitation (zerfalls), which took place between 700–1200° C. for different beryls, there is a decrease in density amounting to from 0.1% to 0.8%. He also states that inclusion free and alkali free beryls decrepitate at higher temperatures. Böse observed the formation of sublimate rings on cooled quartz tubes upon heating beryl powders to 1200° C. The successive sublimate zones contained different metals such as Fe, Ni, Mn, Na, etc. This observation was checked by heating a 5 g. sample of beryl from Harding Mine, N. M. to 1200° C. in a quartz tube which was plugged with glass wool at the cooled end. The glass wool was then placed in 1/1 nitric acid to dissolve metal ions, evaporated to near dryness; distilled water was added and the solution evaporated down to several milliliters. In this case also the Fe, Mn, Na, Be, Li, etc. spectrographic lines* were observed, but there was little or no change in the emission spectrum of the beryl itself before and after heating. In particular the Na lines before and after were identical. It must be concluded, in this case, that the mass transfer was quite small.

ORIGIN OF THE INERT GASES IN BERYL, CORDIERITE AND TOURMALINE

There are three basic hypotheses which may be proposed to explain the excess inert gases in beryl, cordierite and tourmaline:

(1) Helium and argon are created within the crystal lattice by (*a*) an unknown source of radioactivity or (*b*) nuclear reactions.

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* Emission spectrography was done by Dr. K. K. Turekian, Department of Geology, Yale University.

(2) The concentration of the inert gases in these mineral lattices increases with time by diffusion into the lattices from the surroundings.

(3) The "excess" helium and argon were occluded by the mineral at the time of its formation.

It is concluded that the last hypothesis is the only reasonable one.

Hypothesis (1), the internal creation hypothesis, can be dispensed with immediately. A search for the products of necessary nuclear reactions demonstrates that they can only be on the order of 1 part per 10^5 inert gas atoms present. Furthermore, the possibility of the existence of an unknown radioactive source of both argon and helium cannot be taken seriously in view of the extensive nuclear studies which do not indicate either experimental or theoretical possibilities for any radioactive source of A^{40} other than K^{40}. One of the major results of this work was the demonstration that excess argon invariably accompanies excess helium in these minerals which precludes nuclear generation as indicated.

Thus the hypotheses are reduced to occlusion at the time of mineral formation or subsequent diffusion of these constituents into the lattices.

The "excess" helium and argon content might conceivably be accounted for by the diffusion of the inert gases into the crystal lattice progressively with time (hypothesis 2) but this does not appear probable for several reasons. First, the partial pressure of helium and argon into the intergranular spaces must be so much lower than inside the mineral that a sufficient concentration of the correct sign would not be present. The general loss of argon from perthitic feldspars may be cited in this instance. Second, the average 2.7 billion year old beryl has about a 500 fold greater inert gas content than a 0.1 b.y. old beryl, wherever the ages differ by only a factor of 27. Third, diffusion within the crystal carried on for a sufficiently long period of time to explain the age effect would tend to homogenize the inert gases in the mineral rather than support large observed differences in the inert gas content within a single crystal. The large single beryl crystal from the Peerless mine shows a concentration gradient of helium from the center B towards both ends of the crystal in Fig. 2 (see Table 5), whereas the gradient for argon is from the intermediate zone to the wall zone instead of the uniform distribution which would be expected from diffusion. Further, it would appear in this case from the mineralogical environment, the source of the argon would be by way of the mineral plagioclase and thus diffusion would have to defy a 100-fold difference in argon concentration across the mineral interface. It seems most likely that, if anything, both argon and helium should diffuse out of the minerals. Actually, if Schaller and Stevens (1955) are correct, the channels in beryl are not open, being occupied in part by Na^+ and Cs^+ which would block the channels and impede diffusion in either direction.

Occlusion at the time of mineral formation appears to be the correct explanation (Hypothesis 3). The fact that minerals with the six membered ring structure and large open spaces in their lattices are the most prolific source of excess gas must be more than coincidental. *It seems inescapable that occlusion takes place primarily within the channels defined by the six membered rings.* No doubt some occlusion takes place in liquid-gas inclusions. For example, Wahler (1956) observed the spectral lines of helium and argon from the gases obtained from Madagascar quartz by decrepitation. The quartz in this case contained many inclusions. Thus any mineral containing "holes" of any kind which are enclosed in the mineral structure and large enough to contain helium and argon should be considered as a possible source of excess inert gas. Even the amphiboles may contain "excess" inert gas. The position occupied by (Na, K) in hornblende for example is seldom completely filled by the alkali cations and in the ideal tremolite structure it is completely vacant.

Not only the inert gases are enriched in beryl-like minerals. The enrichment of cesium in specimens like the Eräjärvi beryl which contain very little potassium can be explained by the greater ionic radius of cesium. Cesium is not accepted by the feldspars as readily as rubidium. It is concentrated in the residual liquids and gases and can be enriched relative to both rubidium and potassium (Goldschmidt, 1954, p. 166). Thus it is enriched in beryl where it can aid in the $(Na^+, Cs^+) - (Li^+, Be^{+2})$ substitution. Also, as mentioned before, the nitrogen content of beryl and cordierite is 10 to 100 times that of igneous rocks and furthermore, it is present in the molecular form (N_2) primarily rather than as the ammonium ion (NH_4^+) as in igneous rocks (T. Hoering and R. Scanlan, personal communication, 1957).

Since the channels in the beryl-like structure appear to provide a suitable location for the excess inert gases and other "fugitive" constituents, it is unreasonable to imagine that the mineral can form in a pegmatitic environment replete with gases and volatiles, without occluding at least some of these constituents. However, it is necessary to supply a mechanism to keep the gases in the ring. If the gases are relatively loosely bound by Van der Waal's forces, then it is difficult to see why they are not pumped out in vacuum as was observed for a sample of zeolite. Zeolites are very much like charcoal in their behavior towards gases with the exception that the pores in the structure are of constant diameter and cannot accept gas with molecular weights above 50 (Eitel, 1954). Below molecular weight 50, charcoal and the zeolites are analogous. For example, CO_2 is adsorbed more readily than helium. If beryl were behaving in the same way, then more argon would be adsorbed than helium. But this is not the relationship that is observed for beryl; the helium to argon ratio is much as would be expected from the production rates in a peg-

matitic environment, making allowance for the greater variability of the trace element uranium and thorium compared with a major element such as potassium (Fig. 2). Water is held much more tightly in beryl than in the zeolites. Upon heating beryl, little water is given off below 800° C., after which water is released rapidly. Furthermore, it is necessary to heat beryl to much higher temperatures before all water is released. No exchange of lithospheric with atmospheric inert gas appears to take place during the weathering process. The Manitoba beryls, which have been exposed to extensive weathering, did not contain a measurable quantity of neon. Thus the occlusion of gases in beryl-like minerals does not appear to be at all similar to the presorption phenomenon and the gases appear to be held in by some such mechanism as a cationic block (suggested by F. E. Wickman, personal communication, 1955). The fact that helium is completely released before other non-condensable gases during degassing can be explained by the more rapid diffusion of the smaller helium atom past the cationic block.

Diffusion is exponentially dependent upon temperature. The self diffusion coefficient increases with temperature according to the following relationship:

$$D_T = D_o e^{-E/RT}$$

where E is the energy of activation per mole, R is the gas constant and T is the temperature. The helium degassing curve for beryl behaves as if not all locations for helium were identical (Fig. 5). At 800° C. not all of the helium comes out at the same rate. In the laboratory experiment, it was necessary to raise the temperature step-wise until at 1100° C. helium was completely released. This could be explained by the cationic block hypothesis. Imagine one of the channels defined by a $[Si_6O_{18}]$ ring containing cations and helium atoms. A particular helium atom in the process of diffusion encounters a Na^{+1} (radius = 0.97 Å) cation and because its Van der Waal's diameter (2.90 Å) is much greater than the space usually available between the cation and oxygen atoms in the tetrahedra ($\sim$1Å), it must wait until a fortuitous combination of thermal vibrations allows it to pass. But not all of the cations have the same ionic radius; it next encounters a Cs^{+1} cation (radius = 1.67Å) presenting a more formidable barrier, etc. In this way the cationic block explains the different locations, each location having a different activation energy E due to statistical fluctuations and variations in the alkali content of beryl which have previously been observed (R. H. Jahns, 1955, p. 1094).

If the deduction is correct, that helium and argon are occluded at the time of mineral formation, then the source of these gases must be in the volatiles present in the immediate environment at the time of mineral formation. The isotopic constitution of the inert gases is what would be

expected by derivation from the mantle or crustal rock (originally sedimentary) already degassed of its juvenile or atmospheric inert gases and enriched in He^4 and A^{40} by radioactive decay.

Consider a pegmatite being formed during the process of regional metamorphism; according to Jahns (1955), pegmatites are essentially restricted to terrains of igneous and metamorphic rocks. The first step is the accumulation of molten material along with a gas phase in a relatively (or momentarily) closed volume. The initial partial pressure of the inert gases in the pegmatite before crystallization begins will, of course, be the same as their partial pressure in the immediate environment. This in turn will have been set by (1) the size of the local crustal volume from which the inert gases have been released (2) the degree of completeness of the release in this volume (3) the quantity introduced from the deeper crust and/or mantle (4) the length of time during which temperatures within the source volume are sufficiently high to allow the escape of inert gases from crystal lattices in which they are produced and (5) the production rate of helium and argon throughout the period of time in which they are accumulated preceding and during their mobilization. It is expected that the higher heat production in the mantle and crust in earlier times would produce higher initial partial pressures of the inert gases in the pegmatites due to all five factors mentioned above and, therefore, account for the age effect.

Local variations in the concentration of the inert gases in individual beryl minerals or even within a single crystal are probably a result of continual variation in the partial pressure of these gases during the crystallization of a pegmatite. Several processes are involved here: the rate of crystallization, the relative "tightness" of the pegmatite volume, the hydrostatic pressure.

In most pegmatites crystallization proceeds from the walls inward, concentrating the volatiles in the remaining space. If the enclosing volume is tightly sealed, the vapor pressure will change continually during crystallization. If the volume can lose gas fairly easily, the pressure of the gas phase will be maintained at the hydrostatic pressure for that volume. The actual pressure probably fluctuates considerably from the hydrostatic as the base level. Thus a beryl or portion thereof would contain more or less helium and argon depending on the total pressure at the time of mineral formation.

The concentration of helium and argon being produced by radioactive decay within the pegmatite volume during crystallization is trivial compared to the quantity acquired by mobilization from a much larger volume of rock in which the inert gases have accumulated for a much longer period of time.

It is evident that the age effect cannot solely be due to the *increased rate of production of helium and argon in the past*. This can be shown as follows:

The helium production, 2.7×10^9 years ago, was approximately two-fold greater for the uranium series and 1.15 fold greater for the thorium series. The A^{40} production was higher than at present by a factor of about 4.4. This only provides a factor of two to four, whereas a factor of 100 to 1000 is needed. But the increased rate of heat production by radio-activity during the early period must be taken into consideration. U^{235} and K^{40} produce about 15% of the present radiogenic heat (Rankama, 1954) but 2.7×10^9 years ago they produced about 50% of the total radiogenic heat. The total heat production would also be higher by a factor of two.

The effect of radioactive heat production would be to increase the geothermal gradient in the crust raising the "normal" temperature at any depth. This in turn would allow for greater leakage of argon and helium out of radioactive minerals by diffusion. The other fugitive constituents being chemically active would lag behind, thus raising the partial pressure of helium and argon in the "free" or mobile volatiles. The locus of the incipient pegmatite can be idealized as a small volume of total mobilization surrounded by zones of lesser mobility until in the outermost zone only the inert constituents are significantly mobile. The mobile fugitive constituents are free to mix at this point before recrystallization has begun, the tendency being to occupy any free volume which is accessible and suitable.

Recently Jacobs and Allen (1956) have considered various models for the thermal history of the earth. Concerning a model for a radioactive earth with an initial central temperature of 4500° C., they state (p. 157), "Near the surface, conditions appear to have been greatly different in the far past from those existing at present—in fact, there may even have been remelting of material near the surface (down to about 100 km.) during this first thousand million years or so. If so, this could explain the now fairly well-established fact that the Earth as a whole is about $4\frac{1}{2}$ thousand million years old, whereas no rocks have been found much older than about three thousand million years. (A similar suggestion was made by W. D. Urry, some years ago.) However, this brief temperature rise at the beginning soon ceased and cooling commenced. The rate of cooling was greater in the past than it is now, and this suggests that orogenic activity may have decreased with time, and perhaps have been caused by different processes in the far past."

It is the rate of heat production due to radioactive decay which could produce an exponential effect in the quantity of helium and argon re-

leased. Derivation of larger quantities of the inert gases from the mantle in the past than at present may contribute significantly toward the age effect. An early extensive degassing of the mantle would release large quantities of nitrogen, inert gases, water and other volatiles to the atmosphere and ocean. Evidence for such an early deep seated degassing has been given in another paper (Damon and Kulp, 1957). Recently Poldervaart (1955, p. 138) has summarized evidence for the chemical evolution of the earth and has concluded that "Initially degassing may have been more rapid in the primitive earth." About 1.8 billion years of earth history took place before the formation of the 2.7 billion year old beryls and cordierite which are listed in Table 2. During this early expanse of time the ratio of inert gas to nitrogen in the mantle would increase because whereas nitrogen (and the inert gases) would be released to the crust and atmosphere, the inert gases would be continually produced in the mantle by radiogenic decay. Recycling of nitrogen in the crust by sedimentation and granitization would maintain a certain proportion of nitrogen in the crust relative to the atmosphere. Thus 2.7 billion years ago as well as at present there would be two sources of inert gases with different composition of volatiles. The mantle would have a relatively high inert gas to nitrogen ratio, whereas the crust would have a relatively low ratio of inert gases to nitrogen. Thus an early extensive degassing prior to 2.7 billion years ago decreasing exponentially towards the present could supply the necessary mixture of crustal and mantle volatiles needed to explain the age effect. In this case the size of the local crust area involved is not as important as the relative contribution in time due to volatiles from a more deep seated source which rise into the crust and permeate the site of regional metamorphism.

It may therefore be concluded that the age effect showing greater helium and argon content in older beryls can be explained by the greater mobilization of the inert gases in earlier times as a result of the increased heat production both in the mantle and the crust. The local variation in concentration of the inert gases in minerals of the same pegmatite can be related to fluctuation in the partial pressure of these gases during crystallization history.

THE EFFECT OF TEMPERATURE AND PRESSURE

According to Cherdyntsev and Kozak (1949) the amount of helium in beryls increases with increasing temperature of formation. Yoder and Eugster (1955) in their study of muscovite have shown that the relative amounts of Na and K can be used as a geologic thermometer. H. Holland (Personal communication) has applied this to two of the pegmatites that have been investigated during this research, the Beartooth pegmatite

(2700 m.y.) and the Peerless pegmatite (1650 m.y.). The Na-K ratio of muscovite from the Beartooth beryl indicated a temperature of 460° C., whereas the relationship for the wall zone of the Peerless pegmatite indicates a temperature of 550° C. The Na-K ratios for two additional muscovites were also determined. According to the same criteria one of the Greer Lake, Manitoba pegmatites (B4) was emplaced at 520° C. and the Beryl Mt. pegmatite at 540° C. (see appendix). Thus, for these pegmatites Cherdyntsev and Kozak's observation is not correct. Certainly there is no evidence that pegmatites were formed at progressively increasing temperatures in geologic time and so this hypothesis need not be considered further in this connection.

Lord Rayleigh (1933) not having the information now available, favored a nuclear hypothesis to explain the excess inert gases in beryl. Nevertheless, he did point out that the accidents of uncovering of pegmatites favor the exposure of shallow seated young pegmatites and deep seated Archean pegmatites. Deeper burial would provide higher hydrostatic pressures forcing more of the gases into the beryl structure. But the fact that there is no significant variation in the total volume of the volatile constituents, other than helium and argon, eliminates pressure as a direct cause of the age correlation. A 100-fold difference in burial is impossible and even if attained would result in an increase in all the volatile constituents.

It is possible that the quantity of gas occluded by beryl and cordierite may yield valuable information concerning temperature-pressure conditions during pegmatite formation. However, it will be necessary to synthesize beryl and cordierite in the presence of these gases under controlled laboratory conditions in order to obtain this information.

CONCLUDING REMARKS

Minerals such as beryl and cordierite provide a most effective method for sampling the volatiles which are present in the environment during the process of regional metamorphism and pegmatite formation. As might be expected, these volatiles consist primarily of water, carbon dioxide, nitrogen and the inert gases.

The excess helium and argon appear to have been trapped at the time of mineral formation and are related to their partial pressures in the immediate environment. The surprising amount of helium and argon in the oldest minerals was not so readily anticipated. Having examined various possibilities it is concluded that the origin of this age effect must be sought in a more extensive mobilization of the lower crust and mantle in the past with a consequent greater rate of degassing of the inert gases than at present. Additional evidence for this greater degassing in earlier

times (based upon the isotopic composition of the inert gases, rates of leakage, and present atmospheric abundances), has been treated in another paper (Damon and Kulp, 1957).

There are other minerals which contain "holes" large enough to accommodate helium and argon atoms. Amphibole has been previously mentioned. The structure of the newly discovered mineral osumilite (Miyashiro, A., 1956) is based on a double hexagonal ring, $(Si, Al)_{12}O_{30}$. Unfortunately not enough of this mineral was available for this study. Milarite (Belov and Tarkhova, 1949) and osumilite are isostructural. According to Belov (1942) the Si_6O_{18} ring is also observed in dioptase.

The minerals beryl and cordierite also provide an excellent source for studying nuclear processes occurring in nature which produce the inert gases as end products. Thus in addition to He^3, it is quite certain that nucleogenic Ne^{21}, A^{36}, A^{38} and fissiogenic krypton and xenon isotopes are present in smaller quantities than were observable during this investigation.

Description of Samples

B1   Beryl-collected by Mr. Rae Harris (PD-56-23); one quarter mile south of Black-
       stone Lake, Bear Tooth, Mont.; orthoclase-quartz pegmatite about 150 ft. long
       and 10 ft. thick at the widest part; albite and book muscovite 6″ in diameter also
       occur in the pegmatite; according to Dr. Heinrich Holland of Princeton University,
       the Na-K ratio for the muscovite indicates that the temperature of formation was
       about 450° C. Age = 2750 m.y. (Gast and Kulp, 1957).

B2   Collected by Dr. F. D. Eckelmann (DE-39-56); grey-white opaque beryl from
       Huron claim; in potash feldspar-quartz pegmatite containing thin veins of colum-
       bite-tantalite; may be followed for 1000 ft. on strike with the Silverleaf-Bear Claim
       pegmatite about 25′ wide; age 2600 m.y.; see Eckelmann and Kulp (1957) for
       discussion. Age = 2650 m.y. (Gast and Kulp, 1957).

B3a   Collected by Dr. F. D. Eckelmann (DE-130-56); light colored opaque beryl with
       yellow-pink tint from S.E. corner of Greer Lake in S.E. Manitoba; south pit of
       potash feldspar-quartz-biotite, uraninite bearing pegmatite. Age = 2650 m.y. as
       above.

B3b   Same as (DE-130-56) but from north pit, color is white.

B4   Collected by Dr. F. D. Eckelmann (DE-135–56); located about 3000 ft. S.W. of
       samples B3 (a and b) and part of same pegmatite swarm, about 1000 ft. south of
       the center of Greer Lake; beryl forms small, euhedral crystals in an elongate band;
       greenish in color but color varies within mineral and markedly within area of
       10×10 ft. Associated muscovite alkali content is $Na_2O = 1.43\%$, $K_2O = 9.58\%$,
       $Rb_2O = 1.11\%$, indicated temperature = 520° C.

B5   American Museum of Natural History collection (A.M.N.H. 24878); from Erä-
       järvi, Viitaniemi, Finland; white, translucent, cesium beryl; many thin sericite-
       muscovite veinlets may be seen in thin section; age from location in fennoscandian
       shield 1800 m.y.

B6a   Collected by Mr. L. Long (LL-11a-56); white beryl from single 2 ft. long crystal
       (see fig. IV-2); from Peerless Mine, Keystone, S. D. Age from micas dated by Mr.
       Long etc. is 1630 m.y.

B6b   As above (LL-11b-56).

B6c   As above (LL-11c-56).

B7   Collected by Dr. S. Schaffel from Keystone, S. D. region, white beryl (SS-D-3).

B8   Collected by Dr. K. Turekian (KT-D-3a); from Etta Mine, Keystone, S. D.;
       milky white; small amount of sericite-muscovite inclusions in thin section.

B9   Columbia University Collection (CU-D-11), from Harding, N. M., piece of large,
       massive, white specimen, age 1600 m.y. (Faul, 1954, p. 278).

B10   Collection of Mineralogiska Advelningen Natur Historiska Riksmuseet, Stock-
       holm; from Sorkallen near Ranea, Norbotten, Sweden; massive green specimen
       from large crystal, age thought to be about 1300 m.y. (Dr. F. E. Wickman, per-
       sonal communication).

B11a   Collected by author (BMD-9), Beryl Mt., N. H. pegmatite; this specimen is an
       aquamarine; the beryl bearing pegmatite has a core of white and rose quartz
       flanked by a unit 25 to 50 ft. wide consisting of perthite and quartz with large
       books of muscovite and large circular diameter crystals of albite. Biotite, black
       tourmaline and garnet are present near the wall zones; for further description of
       pegmatite see Cameron et al. (1954). This particular specimen contained a large
       number of tourmaline inclusions visible in thin section; clear translucent and with
       very little muscovite. Age = 323 m.y. (Damon and Kulp, 1957). Associated mus-

covite alkali content is $Na_2O = 1.66\%$, $K_2O = 10.09\%$, $Rb_2O = 0.21\%$, indicated temperature $= 540°$ C.

B11*b*   Same as above (BMD-2D), yellow-brown beryl intimately intergrown with quartz and muscovite. Veinlets of sericite-muscovite observed in thin section; also peculiar mosaic structure in thin section but no bubbles. The radioactivity of this beryl was exceptionally high (4.92α/mg. hr.) leading to the supposition that the mosaic structure was due to metamictization. This crystal when heated to 600° C. in vacuum lost its opaqueness and took on a pleasing blue coloration. All beryl (also amazonite) studied, when heated to 1000° C. in vacuum, became opaque white.

B12   A.M.N.H. collection (No. 23798); aquamarine from Rumney, N. H. region; crystal about 4 cm. long embedded in milky quartz. Probably same age as Beryl Mt. pegmatite.

B13*a,b*   Columbia University collection (CU-D-4); from Stoneham, Maine; aquamarine, 6 cm. in length; see Cameron et al. (1954). Probably same age as Beryl Mt. pegmatite.

B14   Columbia University collection (CU-D-1); from Haddam, Conn., Gillette quarry; transparent aquamarine, crystal 6 in. long; Cameron et al. (1954), usual muscovite inclusions in thin section; hand specimen veined with quartz. Age $= 280$ m.y. (H. Faul, p. 267).

C1   Cordierite collected by members of Geological Survey of So. Rhodesia (GB-18); foliated metabasite composed of about $\frac{1}{3}$ cordierite and $\frac{2}{3}$ anthophyllite with sprinkling of opaque accessory minerals; 39 miles E. by N. of Fort Victoria, Ndanga District, Lat. 19° 58' S., Long. 31° 25' E., perhaps Sebakwian in age $(2,700 + $m.y.); thought to be a metamorphosed basalt.

C2   Cordierite A.M.N.H. No. 10404 from Orijärvi, Finland; hand specimen is clear, almost transparent blue-grey; crystals and veins of pyrite visible in chips under low magnification, some muscovite on crystal surfaces; muscovite-sericite inclusions visible in thin section; age 1800 m.y. from position in fennoscandian shield; for geological description of the area see P. Eskola (1914).

C3   Collected by Dr. A. Poldervaart; cordierite schist from Geelkop in the Orange R. Valley; according to Dr. Poldervaart, the schist is the result of high grade metamorphism (600°–650° C.). Estimated age $= 1100$ m.y.

C4   Cordierite (M-D-3) from Kragero, Norway; translucent blue, free of microscopic impurities; age probably 1300 m.y. (from archaeozoic gneiss) (from A.M.N.H. Collection).

C5   A.M.N.H. (17768) from Rakinankaratra, Madagascar; dark blue, translucent, granular cordierite; altered on surfaces; probably late Precambrian in age.

T1   Tourmaline collected by L. Long (LL-12-56) from Peerless mine, Keystone, South Dakota; black tourmaline associated with cleavelandite from quartz-muscovite zone.

T2   Tourmaline collected by L. Long (LL-30-56) from Hugo Mine, Keystone, S. D.; black tourmaline from quartz, plagioclase, muscovite wall zone.

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