OBSERVATIONS ON THE DISTRIBUTION OF TRACE ELEMENTS IN THE PERTHITE PEGMATITES OF THE BLACK HILLS, SOUTH DAKOTA

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ABSTRACT

The trace-element contents of the Black Hills perthites have been determined spectrographically. Their chief trace elements are found to be Rb, Ba and Sr. The distribution and relative proportions of the different trace elements are discussed. They seem to support the metasomatic derivation of the perthites from the schists of the country rocks in which the pegmatites occur.

STATEMENT OF PROBLEM

The perthite pegmatites of the Black Hills, South Dakota, have been considered by the writer (Higazy, 1949) to have been formed not by magmatic crystallization but mainly by replacement processes. The chemical composition of these perthites as well as their textural and microscopic features support their metasomatic derivation. Moreover, field observations seem also to be in favor of the replacement origin of these pegmatites. The trace-element contents of the perthites and of some of the country rocks were determined spectrographically in order to study the significance of such elements in the petrogenesis of these perthites.

SPECTROGRAPHIC ANALYSIS AND DATA OBTAINED

Portions of the powders used previously for chemical analysis were spectrographically analyzed by the writer at the Macaulay Institute for Soil Research at Aberdeen, Scotland, using the semiquantitative method described in detail by Mitchell (1948). The determined trace elements, and the wave lengths of their respective diagnostic lines have already been recorded by the writer (Higazy, 1952a).

The trace-element contents of the analyzed perthites and cleavelandite are listed in Table 1; and those of the other country rocks are given in Table 2. For the exact location of these rocks, and their chemical composition and petrographic description, reference should be made to an earlier paper (Higazy, 1949, Fig. 1, p. 556, p. 559 and pp. 562–564).

MAJOR ELEMENTS

The average ratio Or:Ab:An in the analyzed perthites is 75.8:22.4:1.8 (Higazy, 1949, p. 561). The most important major elements in their composition are, therefore, Si, Al and K. Sodium and Ca may also be

significant but not to the extent of that of K. The ranges of K_2O, Na_2O and CaO in these perthites are 10.58–15.62, 0.38–3.29 and 0.15–0.82 per cent, respectively.

Small amounts of Mg and Fe are usually present in the composition of perthites. MgO and total iron oxides (as Fe_2O_3) in the perthites of the Black Hills vary from 0.00–0.12 and 0.06–0.13 per cent, respectively. The exact mode of occurrence of these elements, namely, Mg, Fe^2 and Fe^3, in the structure of potash feldspar is not yet perfectly known. Among the major elements of the perthite, Na possesses the closest ionic radius (0.98 Å) to that of Mg (0.78) and that of Fe^2 (0.83). It is not certain that Mg and/or Fe^2 replace Na in the feldspar lattice since (*a*) Na usually has a higher coordination number and (*b*) Mg and Fe^2 appear to have much higher activation energy values (E-value). Magnesium is known to replace Al in biotite and hornblende. Although these species have different structures from that of the feldspars, yet the possibility of such replacement in the latter should not be disregarded. If, however, Mg and Fe^2 have no definite position in the structure of the feldspar, it may then be conjectured that they are either dispersed through the structure or present in minute mineral inclusions in the perthite. A combination of these two alternatives is also a possibility.

Fe^3 has an ionic radius of 0.67 Å, not very different from that of Al^3 (0.57), and both have the same valency. If the feldspar lattice is favorable for the admission of Fe^3, it may be surmised that it replaces Al, since Wickman (1943, p. 381) points out that Fe^3 may be considered as so immobile that it could be incorporated in a suitable lattice under any conditions.

TRACE ELEMENTS

The different trace elements in the perthite pegmatites are classified according to their abundance into four categories: abundant, present in small amounts, rare and very rare.

ABUNDANT: Rb, Ba and Sr.
PRESENT IN SMALL AMOUNTS: Li, Pb, Ga and Tl.
RARE: Mn, V, Cu; Be, Ge and Zr.
VERY RARE: Cr, Co, Ni, Sc; Sn, Ag, Mo; La, Y and In.

Rubidium, barium and strontium

The Rb content in the analyzed perthites (Nos. 1–15) varies from 600 to 9500 ppm. and the average is 2665 ppm. (Table 1). The average in the two analyzed microcline-perthites from the Hugo pegmatite is 3600 ppm. The Rb content of the potash feldspar of the Caledonian granodioritic rocks of Scotland studied by Nockolds and Mitchell (1948); Table XXI, p. 571) varies from 60 to 800 ppm., the highest being in potash feldspar from aplite, Garabal Hill-Glen Fyne Complex, Scotland.

TABLE 1. TRACE-ELEMENT CONTENTS IN PPM. OF THE ANALYZED
PERTHITES AND CLEAVELANDITE

Element	Sensitivity	1	2	3	4	5	6	7	8	9	10	11
Rb	1	2800	1500	2500	5000	1000	600	800	5000	9500	6000	800
Li	1	40	4	9	7	25	3	2	170	300	100	8
Ba	5	45	80	25	260	200	400	1%	1000	20	830	1500
Sr	5	1500	12	20	180	45	70	750	400	600	90	60
Cr	1	*	*	*	*	*	*	*	*	5	3	3
Co	2	*	*	*	*	*	*	*	*	*	*	*
Ni	2	*	*	*	*	*	*	*	*	*	*	*
Zr	10	*	*	*	*	300	*	*	*	*	*	*
La	30	*	*	*	*	*	*	*	*	*	*	*
Y	30	*	*	*	*	*	*	*	*	*	*	*
Cu	3	3	3	4	5	4	3	3	3	4	4	3
V	5	5	5	*	5	*	5	5	5	20	10	10
Ga	1	35	30	40	35	50	30	30	40	45	30	30
Tl	30	30	*	30	65	40	*	*	140	150	80	*
Sn	5	*	*	*	*	*	*	*	*	*	*	*
Pb	10	10	18	15	50	15	30	35	20	40	10	40
Sc	10	*	*	*	*	*	*	*	*	*	*	*
Mn	5	8	10	10	10	10	12	8	7	8	10	10
Mo	1	*	*	*	*	*	*	*	*	1	*	*
Ge	10	*	*	*	*	*	*	*	15	10	*	*
Be	5	8	*	*	10	*	*	*	*	8	*	8
Ag	1	*	*	*	*	1	*	*	*	1	1	3
In	10	*	*	*	*	*	*	*	*	*	*	*

Nos. 1 to 11 correspond to numbers of chemical analyses by R. A. Higazy recorded by
the writer (Higazy, 1949, p. 559).

Spectrographic analyst: R. A. Higazy.

* Element if present is in amounts below its limit of sensitivity.

But the perthite found as phenocrysts in the granites of the Glendale
area of the Black Hills (analysis 13, Table 1) has 900 ppm. Rb. On the
whole, the Rb content of the Black Hills perthites seems to be higher
than that of the Caledonian feldspars.

Ahrens (1945b) examined the Rb content of 67 specimens of potash
feldspars (microcline, orthoclase and perthite). Most of these, however,
were collected from pegmatites of widely different occurrence. Their Rb
content varies from 40 to 2560 ppm., with an average of 295 ppm. The
range in the 16 green microcline (amazonite) examined also by him, is
from 640 to 11,880 ppm., with an average of 3670 ppm. The average in
perthites of the Black Hills (2665 ppm.) is not appreciably lower than
that of the green microcline. Among the fifteen analyzed perthites of

TABLE 1. TRACE-ELEMENT CONTENTS IN PPM. OF THE ANALYZED PERTHITES
AND CLEAVELANDITE—(*Continued*)

Element	Sensitivity	12	13	14	15	Average	16	17	Cleavelandite
Rb	1	2000	900	1000	600	2665	1200	6000	2
Li	1	130	25	55	2	60	35	160	150
Ba	5	100	150	200	100	965	30	550	5
Sr	5	240	25	50	35	270	800	90	100
Cr	1	3	1	3	1	1.5	1	1	1
Co	2	*	*	*	*	*	*	*	*
Ni	2	*	*	*	*	*	*	*	*
Zr	10	*	*	*	*	*	*	*	30
La	30	*	*	*	*	*	*	*	*
Y	30	*	*	*	*	*	*	*	*
Cu	3	3	5	4	3	4	4	4	5
V	5	5	5	8	5	6	5	15	10
Ga	1	30	30	35	30	35	35	40	70
Tl	30	45	*	*	*	39	*	80	*
Sn	5	*	*	*	*	*	200	*	*
Pb	10	20	25	20	450	53	10	10	*
Sc	10	*	*	*	*	*	*	*	*
Mn	5	15	10	12	10	10	12	8	40
Mo	1	*	*	*	*	*	*	1	*
Ge	10	10	*	*	*	*	*	10	20
Be	5	*	*	*	*	*	8	*	120
Ag	1	*	1	4	1	1	3	1	*
In	10	*	*	*	*	*	*	*	*

Nos. 12 to 17 correspond to numbers of chemical analyses by R. A. Higazy recorded by the writer (Higazy, 1949, p. 559).

Spectrographic analyst: R. A. Higazy.

* Element if present is in amounts below its limit of sensitivity.

the Black Hills, one is grayish in color (No. 9), five are grayish-white (Nos. 2, 4, 8, 10 and 12) and the other nine are pinkish (Higazy, 1949, p. 563). The grayish perthite is relatively the richest in Rb (9500 ppm.). The average Rb content of the six grayish and grayish-white samples is 4835 ppm., while that of the nine pinkish perthites is only 1220 ppm. This seems to be a fairly reliable indication that the pink varieties of potash feldspar contain relatively less Rb than the grayish types. The average Rb of the grayish perthites (4835 ppm.) lies within the range given by Ahrens (1945 *b*, p. 229) for amazonite (4570–5485 ppm.) and closer to the minimum limit, while the average for the pink types is notably less than for the green species being, only 1220 ppm.

Barium in the Black Hills perthites is less abundant than Rb except

TABLE 2. CHEMICAL COMPOSITION AND TRACE-ELEMENT CONTENTS OF
THE COUNTRY ROCKS

	A Biotite-schist	B Perthite-schist	C Granite	D Albitite
	Chemical composition as weight per cent of the oxide			
Oxide				
SiO_2	68.83	70.85	73.48	69.93
TiO_2	0.46	0.21	0.10	0.00
Al_2O_3	14.63	15.48	15.10	17.84
Fe_2O_3	1.42	0.64	0.41	0.14
FeO	3.83	1.09	0.82	0.20
MnO	0.05	0.01	0.02	0.01
MgO	2.24	0.83	0.60	0.54
CaO	0.52	0.38	0.80	0.59
Na_2O	1.05	2.16	3.34	9.68
K_2O	5.01	6.45	4.31	0.42
P_2O_5	0.17	0.45	0.13	0.51
H_2O	1.52	1.18	0.94	0.23
H_2O^-	0.14	0.08	0.08	0.06
	Trace elements as parts per million of the element			
Element				
Rb	240	600	240	1
Li	30	70	150	10
Ba	2000	3500	750	25
Sr	35	150	50	5
Cr	80	60	3	4
Co	10	3	*	2
Ni	40	20	*	*
Zr	220	250	250	50
La	30	30	30	*
Y	120	60	40	30
Cu	9	3	8	6
V	50	60	20	12
Ga	35	40	50	60
Tl	*	*	*	*
Sn	5?	*	5?	*
Pb	12	18	12	*
Sc	*?	*	*	*
Mo	1	*	*	*
Ge	*?	*	*	*
Be	5	8	25	10
Ag	<1	<1	<1	<1
In	*	*	*	*

Chemical and Spectrographic analyst: R. A. Higazy.
Chemical analyses A, B and D are taken from Higazy (1949, p. 560).
* Element if present is in amounts below its limit of sensitivity given in Table 1.

in the perthite porphyroblast (No. 7) found in the perthitized schist. It is interesting to notice that the color of this Ba-rich perthite is salmon red and that it contains 0.13 per cent of total iron oxides as Fe_2O_3, an amount similar to that of perthite No. 15, which is pinkish. Moreover, perthites Nos. 10 and 11 are grayish-white and deep pink, respectively; yet each has 0.09 per cent Fe_2O_3. But the Ba content of the grayish-white perthite (380 ppm.) is less than that of the deep pink (1500 ppm.). The reddish coloration, therefore, seems to be related to relative enrichment in Ba rather than in Fe.

The Ba content ranges from 20 to 10,000 ppm. The highest abundance for the pegmatitic perthites excluding the perthite porphyroblast of the schist is 1500 ppm., while the average is 965 ppm. The average Ba content of the microcline-perthites of the Hugo pegmatite is 290 ppm. In the potash feldspars of the Caledonian granodioritic rocks Ba ranges from 2000 to 8000 ppm. and is more abundant than Rb, as in the porphyroblast of the perthitized schist of the Glendale area of the Black Hills. But the Ba content (50 ppm.) of the potash feldspar from aplite, Garabal Hill-Glen Fyne Complex, (Nockolds and Mitchell, 1948, p. 571) is lower than that of Rb (2000 ppm.), as in the pegmatitic perthites and the perthite phenocryst of the granite of the Black Hills. Although the data for the Black Hills perthites do not show a regular relationship between Rb and Ba, yet they suggest that the relatively Rb-rich perthite (No. 9) possesses a relatively low content of Ba.

Strontium varies from 20 to 1500 ppm., with an average of 270 ppm. It is less abundant than Ba in most of the analyzed perthites, as in the potash feldspars of the Caledonian rocks and those of the pre-Cambrian granites of Boulder Creek, Overland Mtn. and Silver Plume, Jamestown, Colorado, examined by Bray (1942).

That Rb, Ba and Sr are concentrated in the K-rich feldspars is very obvious, especially when comparison is made with the content of these three elements in cleavelandite. This Na-rich species has only 0.09 per cent K_2O and its Rb, Ba and Sr contents are 2, 5 and 100 ppm., respectively. Rubidium and Ba are thus present in negligible amounts compared with their respective average abundances in the perthites. Strontium however, is relatively high. But cleavelandite has 0.50 per cent CaO. Its Or:Ab:An ratio is 0.6:97.0:2.4 (Higazy, 1949, p. 561). It is quite likely that Sr (1.27 Å) substitutes for Ca (1.06) in cleavelandite.

Lithium, lead and gallium

Lithium is present in all the analyzed perthites but in widely variable amounts, the range being from 2 to 300 ppm. and the average 60 ppm. It seems that the relatively Rb-rich perthites (Nos. 8, 9 and 10 of Glen-

dale area pegmatites and No. 16 of the Hugo pegmatite) are also rich
in Li. But this relationship cannot be generalized since perthite No. 12
has 2000 ppm. Rb and 130 ppm. Li, while perthite No. 4 has 5000 ppm.
Rb and only 7 ppm. Li. Moreover, the potash feldspar of the adamellite,
Morven-Strontian Complex, Scotland (Nockolds and Mitchell, 1948),
has 600 ppm. Rb and 8 ppm. Li, while the range of the Rb content of
the other Caledonian potash feldspars is from 60 to 2000 ppm., and
their Li is below its limit of sensitivity (1 ppm.).

The position of Li in the feldspar lattice is debatable. Lithium feldspars
do not exist in nature, and according to Ahrens (1945 a, p. 82), a Li
content greater than 2–5 ppm. is exceptional in the feldspars. However,
the Li content of the micas is generally appreciable. There are good
grounds for assuming that Li replaces Mg in biotite. Both elements have
the same ionic radius (0.78 Å) and the same coordination number. On
the other hand, muscovite does not usually contain Mg. But Hendricks
(1939, p. 763) mentions that Li can enter the muscovite structure giving
rise to lithium muscovite. Moreover, Ahrens finds as much as 1.2 per
cent Li_2O in the muscovites of Uranoop River Area, Namaqualand, S.
Africa (Ahrens, 1945a). He suggests that Al may be replaced by Li in
the muscovite structure providing that electrostatic balance is restored
by a concomitant replacement elsewhere in the lattice. The proposed
substitution of Al by Li in muscovite may possibly imply that such
replacement could also take place in the feldspar lattice, as Lundegårdh
suggests (1947, p. 108). It should also be mentioned that Li (0.78 Å)
may replace Na (0.98). Cleavelandite has 150 ppm. Li, but this Na-rich
species also possesses a high amount of Al. On the other hand the
analyzed albitite (Table 2) is relatively poor in Li (10 ppm.). This makes
the replacement of Na by Li rather uncertain.

Lead is present in all the analyzed perthites. Omitting No. 15 it
ranges from 10 to 40 ppm., with an average of 25 ppm. Perthite No. 15
is exceptionally high in Pb (450 ppm.) and if it is taken into account, the
average rises to 53 ppm. It is interesting to notice that the total of Rb,
Ba and Sr in the exceptionally high Pb perthite (No. 15) is the lowest
among all the samples tested. Pb ores were not detected microscopically
in the thin section of this perthite. Lead is below its limit of sensitivity
(10 ppm.) in cleavelandite. It is most likely replacing K in the lattice
of the potash feldspars; the association of Pb and K in silicic rocks has
been pointed out by Sandell and Goldich (1943, p. 169).

Gallium occurs in the analyzed samples rather uniformly, the range
being from 30 to 50 ppm. and the average is 33 ppm. Cleavelandite has
70 ppm. Ga. The geochemical relationship between Ga and Al is unique.

Gallium feldspars, $KGaSi_3O_8$ and $NaGaSi_3O_8$, in which Ga completely replaces Al, have been synthesized by Goldsmith (1950).

Thallium

The abundance of Tl in the perthites of the Black Hills is very interesting. The average Tl content of the fifteen perthites of the Glendale area is 39 ppm. It is found in amounts below its limit of sensitivity (30 ppm.) in some perthites and in others it may be present up to 150 ppm. Shaw (1952, p. 128) reports 84 and 21 ppm. Tl in the microcline-perthites of Custer Mt. and the High Climb pegmatites of the Black Hills, respectively. The microcline of the Hugo pegmatite has 80 ppm. Tl. In the five perthites which possess less than 1000 ppm. Rb (Nos. 6, 7, 11, 13 and 15) Tl is below its limit of sensitivity. Moreover, the lepidomelane-skarn of Co. Donegal, Ireland, examined by the writer (Higazy, 1952a) has as much as 800 ppm. Rb and its Tl content is undetectable. Of the four perthites (Nos. 2, 5, 14 and 16) in which Rb varies from 1000 to 1500 ppm. thallium is present in detectable amount (40 ppm.) only in No. 5. All the remaining perthites (Nos. 1, 3, 4, 8, 9, 10, 12 and 17) contain appreciable amounts of Tl together with at least 2000 ppm. of Rb. This clearly shows that there is a geochemical relationship between Rb and Tl as suggested by Ahrens (1948). It should be stated that Cs (8079.02 Å line) was detected qualitatively in only the spectrum of the perthite No. 9 which possesses the relatively highest contents of both Rb (9500 ppm.) and Tl (150 ppm.). There may be, therefore a relationship between Cs on the one hand and Rb and Tl on the other, especially if we consider that the cesium mineral pollucite examined by Ahrens (1945b) also contains appreciable amounts of both Rb and Tl. However, more data from several other Rb-rich potash feldspars are needed to establish the suggested relationship.

The Rb/Tl ratio in the perthites of the Black Hills varies from 25 to 93 with a mean of 60. Ahrens (1945b) concluded that the mean weight ratio Rb_2O/Tl_2O is 110 and that the limits of variation are 30 and 650. He also mentions that this ratio can vary in the same type of mineral from one area to another. The mean value of this ratio for the perthites of the Black Hills is 64, with variation from 28 to 98. The log. per cent relationship between Rb_2O and Tl_2O is represented graphically in Fig. 1. The results are practically the same as those plotted by Ahrens (1945b, Fig. 3) and the slope of the graph in both cases is nearly 45°.

Rubidium and Tl have the same ionic radii (1.49 Å) and are concentrated in potash-rich minerals, where they enter into the lattices with about the same ease, replacing K.
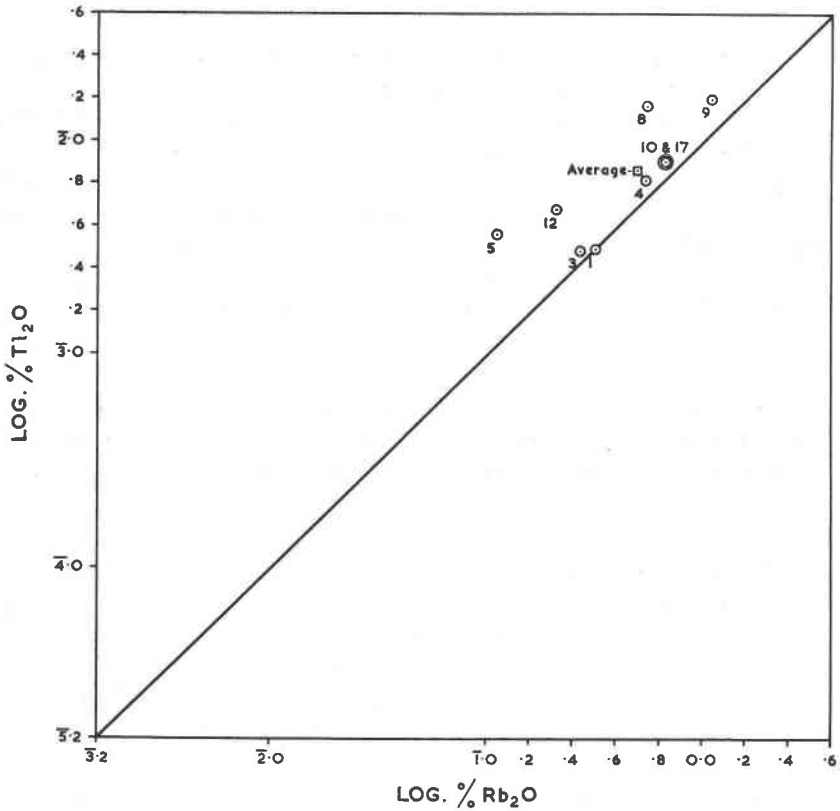
FIG. 1. Relationship between Rb and Tl in the analyzed perthites of the Black Hills.

Manganese, vanadium and copper

Each of the elements Mn, V and Cu is found in almost uniform amounts. Manganese varies from 7 to 15 ppm. with an average of 10 ppm.; V from amounts below its limit of sensitivity (5 ppm.) to 20 ppm., with an average of 6 ppm.; and Cu from 3 to 5 ppm. with an average of 4 ppm. The exact position of each of these elements in the lattice of the potash feldspar is not known. Judging from the ionic radii of Mn^2 and Cu^2, 0.91 and 0.83 Å, respectively, it may be surmised that they replace Na (0.98), and that V^3 (0.65) substitutes for Al (0.57).

The contents of V (10) and Cu (5 ppm.) in cleavelandite are within the range of these elements in the perthites. However, the Mn content in this Na-rich feldspar (40 ppm.) is much higher than in any of the perthites.

Beryllium and germanium

Be is found in all the analyzed perthites except one (No. 6). It varies from 5 to 8 ppm. Germanium, however, is found in only five perthites of the Glendale area and in the microcline of the Hugo pegmatite. Its range is 10 to 15 ppm. It is likely that both Be and Ge replace Si in the feldspar lattice, since the ionic radius of Be (0.34 Å) and that of Ge (0.44) are close to the radius of Si (0.39). Moreover, Ge feldspars, in which Ge completely replaces Si, have been synthesized by Goldsmith (1950). Cleavelandite is richer in both Be and Ge than the perthites, having as much as 120 ppm. of Be and 20 ppm. of Ge.

Zirconium

Zirconium is found only in one perthite (No. 5) and there it is present in rather high amount (330 ppm.). This makes it very likely that minute inclusions of zircon are responsible for the Zr present in No. 5.

The very rare trace elements

Among the very rare trace elements in the analyzed perthites are Cr, Co and Ni. Chromium is found in eight perthites in amounts varying from 1 to 5 ppm., but below its limit of sensitivity in the others. Cobalt and Ni, if present at all, are below their limits of sensitivity (2 ppm.) in all the analyzed samples. In six of the perthites it can be stated that the relative distribution of Cr, Co and Ni is $Cr > Co = Ni$.

Scandium, if present is in amounts below its limit of sensitivity in all the perthites. Chromium, Co, Ni and Sc are elements which generally replace Mg, Fe^2 and Fe^3 in crystal lattices. The relative deficiency of the perthites in these major elements explains the impoverishment of their replaceable trace elements.

Silver is present in most of the analyzed perthites in amounts ranging from <1 to 4 ppm. The ionic radius of Ag is 1.13 Å, very close to that of K. It is possible that the relatively small amount of this trace element replaces K in the lattice.

Tin is found in detectable amount in only one sample (No. 16), collected from the Hugo pegmatite. The high content of Sn (200 ppm.) present in this perthite appears to be accidental, being attributable to very minute inclusions of Sn minerals, possibly cassiterite.

Molybdenum is found in one perthite from the Glendale area and in another from the Hugo pegmatite, the Mo content in each being only 1 ppm.

Lanthanum, Y and In, if present, are each in amounts below the respective limit of sensitivity.

SIGNIFICANCE OF THE DISTRIBUTION OF THE TRACE ELEMENTS

The petrogenetic significance of the distribution of the various determined elements in the perthites can be studied with regard to (*a*) the composition of the different perthites, and (*b*) the trace-element contents of the associated country rocks: namely, the unaltered schist (quartz-muscovite-biotite-schist), the perthitized schist, the granite and the perthite pegmatites.

(*a*) *The composition of the different perthites*

Bray (1942) estimated certain trace elements in the potash feldspars of both Pre-Cambrian granites and their corresponding pegmatites. These rocks were supposed to be of magmatic origin. He (Bray, 1942, p. 797) remarked that the pegmatite minerals usually contain less of almost every minor element than the corresponding minerals from the parental granitic rocks. The statement that pegmatitic minerals should be relatively less enriched in almost every minor element, is too broad a generalization; it is not in complete harmony with Goldschmidt's principles of the replacement of major by trace elements (Goldschmidt, 1937 and 1945), replacement being a process which is mainly governed by the electrostatic charges and the ionic radii of the elements concerned. According to these principles, there should be certain elements which become relatively concentrated in the pegmatite minerals, provided that such minerals also occur in the parental rocks. In such cases the ratio of the content of the trace element to that of its replaceable major element should be higher in the pegmatite mineral. Rubidium is an example of this, since its ionic radius (1.49 Å) is greater than that of K (1.33). The potash feldspar of aplite from the Garabal Hill-Glen Fyne Complex in Scotland has 2000 ppm. Rb, while the average of this element in the potash feldspars of the granodioritic rocks supposed to have crystallized earlier from the magma is only 425 ppm. (Nockolds and Mitchell, 1948). Moreover, the average Rb_2O content of the potash feldspars from granites studied by Ahrens (1948) is 0.0073 per cent, while that of the pegmatitic species is 0.0319 per cent and that of the hydrothermal microclines from pegmatites is as high as 0.433 per cent. Amongst the perthites of the Black Hills Nos. 6 and 15 have the lowest Rb_2O content, 0.066 per cent. The perthite phenocryst (No. 13) from granite, however, has a higher Rb_2O content (0.099 per cent). The Rb/K ratio of the phenocryst (9.4) is also higher than that of the perthites Nos. 6 and 15 (6.1). Moreover, the perthite porphyroblast of the schist has 0.088 per cent Rb_2O and its Rb/K ratio is 7.7. Supposing, for the sake of the argument, that these perthites were derived from strictly magmatic sources, that is by differentiation of a basic magma,

then their Rb contents, as well as the values of their Rb/K ratio, would seem to imply that the pegmatite perthites were formed at an earlier stage than the perthite phenocryst from the granite, and that the porphyroblast was developed at an intermediate stage—conclusions that are obviously not feasible.

There are other pegmatitic perthites, especially Nos. 4, 8, 9 and 10 of the Glendale area and No. 17 of the Hugo pegmatite, which have unusually high Rb contents. These perthites cannot be considered as primary products of magmatic crystallization since such products generally have a much lower Rb content. The relatively high Rb and Li contents in these perthites may support the hypothesis that the latter were formed at the hydrothermal stage during which replacement processes become dominant.

There are also certain features in the distribution of the other trace elements which are not in favor of the magmatic mode of genesis. The Ba content of the phenocryst from granite and the value of its Ba/K (1000Ba/K = 1.6) are much lower than those of (*a*) most of the pegmatitic perthites (1000Ba/K ranges from 1.9 to 14.7), and (*b*) of the perthite porphyroblast of the schist (100Ba/K = 97.0). But according to Goldschmidt's principles, divalent Ba should be more concentrated relative to K in the early formed crystals. Moreover, Engelhardt (1936) has pointed out that Ba is relatively enriched in potash feldspars which form at the earlier stages of crystallization compared with those formed later.

It is important to trace the source of the replacing materials which gave rise to the pegmatitic perthites. They may be the residual hydrothermal solutions which usually remain at the end of the magmatic history. These solutions subsequently replace the magmatic minerals of the pegmatites. But the relative distribution of Cr, Co and Ni leads to the belief that such magmatic hydrothermal solutions cannot be responsible for the development of the Black Hills perthites. It has been found that the relative abundances of these trace elements in the rocks that form during the end stages of magmatic crystallization is Co > Ni > Cr (Ludegardh, 1949, p. 21), or Ni > Co > Cr (Higazy, 1952*b*). Consequently the hydrothermal magmatic solutions as well as the magmatic pegmatites, or even the granites that crystallized immediately before the hydrothermal stage, should have a lower Cr content than that of either Co or Ni. The question now arises, why the Black Hills pegmatites and granite, if of strictly magmatic ancestry, have the relative distribution Cr > Ni ≧ Co which is inconsistent with this mode of origin. Why do we find wide fluctuations in the Rb, Li and Ba contents of the different perthites? It may be argued that the composition of the hydrothermal replacing solutions varies from place to place in the same locality, that is

to say, the solutions may have been Rb-rich in one part of the country rocks and Li-rich in another. But then the separation of such differing solutions from the original magmatic liquor calls for explanation. These problems seem to find their solution if we seek the origin of the replacing material in the country rock itself. In the first place, the analyzed schist has the relative distribution $Cr > Ni > Co$, like that of the associated granite and pegmatites. In the second place, the trace-element contents in the country schists are quite likely to differ from one part to another. Landergren (1945), studying the boron content of sediments, points out that this content varies horizontally as well as vertically in the stratigraphic column from one district to another. Such local differences in the trace-element contents of the country rocks would undoubtedly show up in the corresponding granitization products. This would be so quite apart from the fact that the mobilities of the different elements also vary and would therefore tend to give rise to different concentrations of such elements in the various parts of the rocks through which they pass. Moreover, it seems that each element would tend to follow preferential paths determined by the structural features of the area and therefore, for this additional reason, the relative concentrations would vary in different parts of the same locality.

(b) The trace-element contents of the various country rocks

The chemical composition and the trace-element contents of the country rocks, namely, the unaltered schist, the perthite-schist, the granite and the albitite are recorded in Table 2.

It is important to notice that the schist does not lack any of the trace elements present in the granitic country rocks. Moreover, they all have $Cr > Ni > Co$ and $Ba > Sr$. This is the same relationship as that found in the psammo-pelitic schists of the different metamorphic zones of the Scottish Highlands (Higazy, 1952c). Here, also the relative distributions $Cr > Ni > Co$ and $Ba > Sr$ persist in the analyzed rocks of the chlorite-, biotite-, garnet-, staurolite- and sillimanite-zones.

The essential mineral constituents of granites, wherever they occur, are substantially the same. Yet the distribution of the rarer elements in these granites varies rather markedly. The trace-element contents of the Pre-Cambrian granites of the Black Hills (S. Dakota), the rapakivi granite of Finland and the Caledonian granites (adamellites) of Moy and Morven-Strontian (Scotland) are listed in Table 3. It will be noticed that the rapakivi granite has 1000 ppm. Rb, while the Scottish rocks have 500 and 400 ppm., and the Black Hills granite only 240 ppm. Furthermore, both the rapakivi and the Black Hills granites are relatively poor in Sr, having 39 and 50 ppm., respectively, while the Scottish

granites have 1200 and 1500 ppm. of this element. The values of Ba/Sr
in the granites of Finland (rapakivi), Black Hills, Moy and Morven-
Strontian are 12, 15, 2.5 and 1, respectively. These marked differences
cannot be entirely attributed to the different ages of these granites,
since Sahama and Rankama (1939, p. 8) point out that the Pre-Cambrian
granites in the different parts of Finland show a remarkable variation in
their rarer-element contents, a discovery which led them to the belief
that not all the granites could be of magmatic origin.

TABLE 3. TRACE-ELEMENT CONTENTS IN PPM. OF GRANITES

Element	Rapakivi granite[1]	Black Hills granite	Morven-Strontian, Scotland adamellite[2]	Moy, Scotland adamellite[2]	Average granite[3]
Ba	480	570	1500	3000	445
Sr	39	50	1500	1200	85
Rb	1000	240	400	500	550
Li	25	150	40	25	185
Co	0	<1	<1	10	8
Ni	0	<1	8	10	2
Cr	28	3	10	20	2
Ga	75	50	15	15	15
V	2	20	70	20	—

[1] Amounts taken from Sahama (1945, p. 59.)

[2] Amounts taken from Nockolds and Mitchell (1948, p. 549 and p. 550).

[3] Amounts taken from Wager and Mitchell (1943, p. 237).

— No data.

It is difficult to see how residual granitic melts which might form at
the late stages of differential crystallization of basic magma could exhibit
such wide variations in their trace-element contents from one geographi-
cal occurrence to another. It is a more reasonable inference from the
data available that the granites concerned formed either by metaso-
matic processes within the country rocks or by a further extension of
such processes—leading to refusion, whereby granitic ichors might be
formed. Moreover, if the normative composition of several granitic and
pegmatitic rocks supposed to have crystallized at the late stages of the
differentiation history of basic magma be plotted on the orthoclase-
albite-anorthite and the $NaAlSiO_4$–$KAlSiO_4$–SiO_2 equilibrium diagrams,
the distribution is inconsistent with the hypothesis of their derivation
from a differentiating basic magma (Higazy, 1950). The normative
feldspar contents lie in the orthoclase field of the orthoclase-albite-
anorthite equilibrium diagram and their salic normative constituents

place them outside the region of low temperature in the $NaAlSiO_4$–$KAlSiO_4$–SiO_2 equilibrium diagram. It has been generally assumed that the discrepancy between the chemical composition of such rocks and the results of high temperature studies of analogous systems is mainly due to the effect of water vapor which usually concentrates towards the end of the magmatic history. However, this explanation is considered, on theoretical grounds, to be inadequate (Higazy, 1949). Moreover, Bowen and Tuttle (1950, p. 497) have recently established that water vapor has no discernible effect on the fundamental course of crystallization in the albite-orthoclase binary system i.e., in the system which is the most important one concerned in the problem of the perthite.

The discrepancy between the normative composition of the Black Hills perthites and the orthoclase-albite-anorthite equilibrium diagram, together with the textural features, were considered as criteria supporting a metasomatic origin for these perthites (Higazy, 1949). Metamorphic differentiation, which is responsible for the development of the perthite porphyroblasts in the schist, was thought to give rise to chemically similar perthite pegmatites in parts of the country rock where favorable physical and structural conditions prevailed. Experimental data, given by Jagitsch, (1949) however, suggested that the depth affected by solid diffusion is only a few metres in 10^8 years. Although so slow a rate could satisfactorily account for the formation of the perthite porphyroblasts yet it cannot explain the development of large pegmatitic bodies by "solid" diffusion. But the state under which diffusion takes place may not necessarily be that of a perfect solid; moreover, we do not yet know the exact effect on diffusion rates of the very complicated pressures and stresses that attend orogenesis. Such conditions may change an apparently solid rock into a state concerning which our knowledge is so far negligible (Bridgman, 1951). However, it is quite common to find appreciable amounts of water in sediments and especially in the pelitic types. Garrels, Dreyer and Howland (1949) report a rate of penetration for ions during their diffusion through intergranular spaces in water-saturated rocks, of two and a half miles in a million years at a temperature of 100° C. Moreover, they mention that the rate of diffusion increases with temperature. These findings add strength to the view that water might have accelerated the reactions and transformations during the metamorphic differentiation of the country schist which is regarded as having given rise to the perthites (Higazy, 1949, p. 580).

The significance of isotopic composition of the oxygen in silicate rocks in petrogenesis has been pointed out by Beartschi (1950). Silverman (1952) has recently determined the relative abundances of the oxygen isotopes in different types of rocks. He has found that granites have

higher O^{18} abundances compared to the basic rocks. This fact implies that the granites he investigated are not late crystallizing fractions of a differentiating basic magma. Furthermore, he finds that the rocks which are supposed to be the late differentiates have variable isotopic abundances which can be correlated with variation in their parental sedimentary materials (Silverman, 1952, p. 35). The variation in the trace-element contents of the perthites of the Black Hills and the appreciable differences of these contents in the granites of various geographical regions can also be ascribed to corresponding variations in the lithological and chemical constitution of the original country rocks already noted.

GAINS AND LOSSES OF THE TRACE ELEMENTS DURING THE METASOMATISM OF THE COUNTRY SCHIST

If the hypothesis of the metasomatic derivation of the Black Hills perthites is true, it is of special interest to ascertain the behavior of the trace elements during the reorganization of the atoms and molecules inside the schist to give rise to these perthites. The additions and subtractions of the major elements which were inferred to have taken place during the metasomatism have already been given by the author (Higazy, 1949, Table 8, p. 574).

The metasomatic alteration of the quartz-muscovite-biotite-schist to perthitic schist comprised:

> addition of K, Na, Al and Si,
> and subtraction of Mg, Fe^2, Fe^3 and Ca.

Reference to Table 2 shows that, as regards the trace elements, there was

> addition of Rb, Ba, Sr and Pb; Ga; Be; Li and Zr,
> and subtraction of Cr, Co, Ni, Cu and Mo; and Y.

Thus Rb, Ba, Sr and Pb behaved similarly to K, while Ga followed Al and Be most probably accompanied Si. Lithium usually follows Mg, but in this particular case Li was added while Mg was subtracted. It has already been mentioned that Li may replace Al in the feldspar lattice. Since we here find that both Li and Al were added, it appears that replacement of Al by Li is highly probable. Chromium, Co, Ni, Cu and Mo followed their replaceable major elements Mg, Fe^2 and Fe^3; and Y behaved similarly to Ca.

The geochemical changes of the major elements involved in the transformation of the country schist into average perthite are mainly the same as those concerned in the formation of the perthite-schist. Potassium, Na and Al were added; and Ca, Mg and Fe were subtracted. The K-replacing trace elements which were added are Rb, Sr, Pb and Tl. Again Tl shows its geochemical coherence to Rb. Barium, however, was

subtracted; but since Ba can substitute for both K and Ca it seems that it followed Ca in this case, particularly as the gain in K (8.83)* is far greater than the loss in Ca (0.13).* Similarly the total amount of added Rb, Sr, Pb and Tl is greater than the amount of the subtracted Ba. Chromium, Co, Ni, Cu, V and Mo followed Mg, Fe^2 and Fe^3 in being subtracted; and La and Y decreased with Ca.

During the formation of the Black Hills perthites the trace elements therefore behaved as they have been found to do (a) in the metasomatic-metamorphic development of skarn rocks from an epidiorite in the Malin Head district of Co. Donegal, Ireland (Holmes and Reynolds, 1947; Higazy, 1952a), and (b) in the development of the various metamorphic zones of the Scottish Highlands (Higazy, 1952c). It is important to mention that the diffusion coefficients (D, in cm^2/day) recorded by Garrels, Dreyer and Howland (1949, p. 1819) show that the trace elements have the same or very similar diffusion coefficients as those of their replaceable major elements. Considerable confidence can be placed, therefore, in suggesting the addition of diffusion coefficient as a new significant factor in controlling the distribution and behavior of the trace elements during the progress of metasomatic and metamorphic processes.

CONCLUSIONS

The Black Hills perthites contain appreciable amounts of Rb, Ba and Sr. These elements have approximately the same ionic radii as that of K and are known to substitute for it in the crystal lattices. Thallium is present in detectable amounts in the perthites which are relatively rich in Rb. Lithium, Pb and Ga are present in amounts notably less than those of Rb, Ba and Sr. Manganese, V, Cu, Be and Ge are relatively rare; and Ag, Cr, Co, Ni, Sc, Mo, La and Y are very rare. The pink and reddish perthites seem to be relatively poor in Rb but relatively rich in Ba, while the grayish types show the reverse relationship.

The trace-element contents are variable in the different perthites. The Black Hills granite and perthite pegmatities have $Cr > Ni > Co$ and $Cr > Ni = Co$, respectively, which is not consistent with either a magmatic or a hydrothermal mode of origin. The replacing materials seem to have been derived endogenetically from (within) the country schist which also has $Cr > Ni > Co$.

During the metasomatic development of the Black Hills perthites the trace elements behave similarly to the major elements which respectively have approximately the same diffusion coefficients, and ionic radii and are known to be replaced by them in favorable crystal lattices.

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* Amount of gain or loss is calculated from Barth's (1948) rock formulae (based on a unit cell for each rock of 160 oxygen atoms) and recorded by Higazy (1949, p. 574).

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