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## SCANDIUM IN BIOTITE AS A GEOLOGIC THERMOMETER

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The main features of the geochemistry of scandium are known through the work of V. M. Goldschmidt and Cl. Peters (1), who also utilized older data especially from the publications of G. Eberhard (2). The principal result of the investigations of Goldschmidt and Peters was that, contrary to earlier views, the amount of Sc present in the Earths' crust is concentrated largely in the ferromagnesian minerals of basic rocks, particularly in the augites, which contain on the average about 0.01 % Sc. Some data confirming this have also been published by A. Kvalheim and L. W. Strock (3). The explanation offered is that  $\text{Sc}^{3+}$  replaces  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  in the crystal lattices, the sizes of these ions being very nearly equal.<sup>1</sup> Of the other ferromagnesian minerals contributing considerably to the material of the Earths' crust the few amphiboles examined were found to contain somewhat variable amounts of Sc; some of them were quite as rich in Sc as the augites of basic eruptive rocks, as were also the pyrope-almandite garnets of eclogite rocks. These garnets were usually somewhat richer in Sc than the pyroxenes of the same rocks. The olivines, however, turned out to be unexpectedly poor in Sc, containing at most 0.001 % Sc. Of biotite only two specimens (not from common rocks) were examined by Goldschmidt and Peters; they contained very little Sc (0.0005 % and less). On the other hand it is known from the work of Eberhard (2) that mica minerals — not only biotite but also muscovite and zinnwaldite — may in some cases contain relatively very high percentages of Sc. I have had the opportunity of examining by the

<sup>1</sup> Radii according to V. M. Goldschmidt:  $\text{Sc}^{3+}$  0.83Å,  $\text{Fe}^{2+}$  0.83Å,  $\text{Mg}^{2+}$  0.78Å.

method described below two specimens from Eberhards' research material, namely a colourless mica from Ytterby, Sweden, and a biotite from Nuolaniemi, Finland.<sup>1</sup> In both of them I found about 0.05 % Sc, which agrees well with Eberhards' own estimates. Eberhard also examined two biotites from thortveitite-bearing pegmatites (4) and found about 0.1 % Sc in both of them. As will be seen below, this figure is also in perfect agreement with results found by myself. I have further during earlier spectrographic work observed Sc-concentrations as high as 0.1 % and more in certain other micas (6). Obviously a study of the contents of Sc in a larger number of micas from different kinds of deposits would be of interest.

### Analytical method.

The concentrations of Sc were determined by semi-quantitative spectrochemical analysis. The powdered substances were mixed with about equal quantities of powdered purified carbon and packed into cylindrical bores in purified carbon cathodes, the dimensions of which were in all cases the same (diameter of carbon 3.5 mm, diameter of bore 1.5 mm, depth of bore 4 mm). The carbon arc was kept burning at about 120 V, 5 A until the sample was completely consumed, which required in all cases about 3 minutes, this being also the exposure time. The spectrograms were taken with a large two-prism glass spectrograph<sup>2</sup> giving in the spectral region in question a dispersion corresponding to about 1 mm to 6 Å on the films. The image of the arc was focussed onto the slit of the spectrograph and the "Glimmschicht"-effect thus utilized. The films (Agfa "Normal") were developed for about 2<sup>1</sup>/<sub>2</sub> minutes at 18° C in a metol-hydroquinone developer. As a source of Sc for the preparation of the standard mixtures was used thortveitite from Iveland, assumed, according to analyses published by J. Schetelig (4), to contain about 27 % Sc. This was diluted with ordinary potash feldspar to give a series of powder mixtures ranging in concentration from 1 % Sc down to 0.0001 % Sc. In the feldspar itself no trace of Sc could be detected. As the mixtures were designed chiefly for com-

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<sup>1</sup> These specimens were found among the material used by J. Schetelig for his studies on thortveitite.

<sup>2</sup> Constructed by dr. R. Mannkopff, Göttingen.

parison with biotites it was originally intended to use a biotite as a base substance; however, nearly all biotites contain appreciable amounts of Sc. The potash feldspar was then thought to be sufficiently similar to the micas in composition, in spite of the absence of Mg and Fe. As will be seen below, the values found for the contents of Sc in pyroxenes &c by means of these mixtures agree very well with those given by Goldschmidt and Peters (1); the agreement with Eberhards' values for some unusually Sc-rich micas has already been mentioned. This shows that the mixtures may be used fairly safely for comparison even with minerals which differ very considerably from potash feldspar in composition. The concentrations of Sc were estimated by direct visual comparison of corresponding Sc-lines in the mineral spectra and the standard mixture spectra. The most sensitive Sc-line in the spectral region used is 4246.83; it is also quite undisturbed by other lines under the given conditions. A number of other Sc-lines were also utilized: 4314.12—4320.80—4325.00—4400.42, and in the cases of very high Sc-concentrations 4743.82—4741.03—4354.62. The line Sc 4246 was distinct at 0.0005 %; at 0.0001 % it was no longer visible. The spectra of the standard mixtures show that the Sc-lines are fairly sensitive to variations in the concentration: a concentration of a certain value is generally readily distinguished from that of the double value by means of the intensities, and it seems to be possible to distinguish even smaller differences. In the following tables the correct values may therefore largely be assumed to lie between  $\frac{2}{3}$  and  $\frac{3}{2}$  of the figures given.

### Results of the Sc-determinations.

The tables give the concentrations of Sc in grams per ton and with the probable accuracy just mentioned.

Table 1.

*Sc-concentrations in ferromagnesian minerals of common rocks.*

	Pyroxene	Amphibole	Biotite
Eruptive rocks, Oslo Region:			
Augite Porphyrite, Holmestrand .....	150		
Pyroxenite, Randviksholmen .....	100		7
Pyroxenite, Filtvet, Vestby * .....	100		
Pyroxenite, Brandbukampen .....	100		
Kjelsåsité, Sørkedalen .....	70		
Larvikite, Tjølling .....	150		5
Lardalite, Løvemoen .....	100		<3
Nordmarkite, Grorud .....			10
Granitite, Heggedal .....			10
Granitite, Bjørgeseter .....			10
Eruptive rocks, Caledonian Range:			
Diorite, pegmatitic, Opdal—Inset .....		70	10
Opdalite, Austberg, Rennebu .....	+		10
Trondhjemite, Støren (2 samples) .....			5
Trondhjemite, Sognefjord .....			10
Granite (Bergen—Jotun—kindred), Årdal .....	+		10
Archaean rocks, Southern Norway:			
Amphibolite, Ertveit, Iveland .....		50	
Amphibolite, Feitedalen, Iveland .....		150	
Amphibolite, Mykland .....		100	
Amphibolite, Tørdal, Telemark .....		100	
Amphibolite, i. Torungen, near Arendal .....		100	
Biotite Schist, i. Torungen .....			20
Biotite Schist, Fossingfjord, Bamble .....			10
Hornblende Gabbro, Høydalen, Tørdal .....		50	5
Hornblende Rock, Berg—Sponvik, Østfold .....		70	50
Hornblende Gneiss (quartz diorite), Gurskøy .....		40	10
Farsundite (quartz monzonite), Spind .....		50	15
Gneiss, light grey, Ljan, near Oslo .....			25
Granite, Iddefjord .....			30
Granite, Tørdal, Telemark .....			30
Granite, Fevik, main type .....			30
Granite, Fevik, dark types .....		+	7

Remarks. A + in a column means that the mineral in question (pyroxene or amphibole) was present in the rock, but could not be isolated for examination.

For the samples of amphibole and biotite from farsundite, which were already isolated from the rock, I am indebted to Professor Tom. Barth.

In a biotite (lepidomelane) from nepheline syenite pegmatite, Langesundsfjord, was found a Sc-content of at most 3 g/t, in agreement with the result of Goldschmidt and Peters.

Biotite from the foliated allanite-bearing granite pegmatite at Eidsbugaren (Melkedalen) contains about 10 g/t Sc, like most of the biotites from Caledonian rocks.

\* From recently discovered essexite mass. See Olaf Holtedah, Vid.-Akad. Skr. Oslo, I, 1943. No. 2, p. 17.

Sc-determinations in eclogite from Almklovdalen agree well with those of Goldschmidt and Peters (Garnet 100 g/t, Pyroxene 50 g/t).

Sc-determinations in some ferromagnesian minerals from apatite deposits in Southern Norway gave the following results.

Ødegården, Bamble:	Enstatite	50 g/t,	Phlogopite	30 g/t
Regårdsheia, Søndeled:	Hornblende	70 -	—	7 -
Hovatn, Froland:	—	30 -		

Table 2.

*Sc-concentrations in micas from normal granite pegmatite.*

	Biotite	Muscovite
Hidra, near Flekkefjord .....	50	150
Eitland, near Farsund .....	50	400
Langeland, near Mandal .....	50	
Landsverk, Evje, Setesdal .....	3	
Høgetveit, Evje, Setesdal .....	100	
Birkeland, Iveland, Setesdal .....		5
Håverstad, Iveland .....	500	1000
Eptevann, Iveland .....	700	
Ljosland (Knipan), Iveland .....	700	
Ljosland (Torvelona), Iveland .....	1000	
Ljoslandsheia, Iveland .....	300	200
Ljoslandsheia, Iveland .....	100	
Rostadheia, Iveland .....	50	250
Ertveit, Iveland .....	200	
Nateland, Iveland .....	200	100
Tveit, Iveland .....		20
Grimstad (Fevik-granite pegm) .....	100	
Hella, near Arendal .....	50	
Garta, near Arendal .....	50	
Brokeland, Gjerstad .....	20	50
Karlshus, Råde .....	50	20
Sætregruben, Isesjøen, Østfold .....	100	
Kråkerøy, Fredrikstad .....	100	

Remarks. The biotite samples from Håverstad, Ljoslandsheia, and Nateland were more or less chloritized. The muscovite samples were taken from the same specimens. In the specimens from Rostadheia and Brokeland the biotite and muscovite were intergrown. Both minerals were quite fresh. The biotite from Karlshus did not belong to the pegmatite itself, but was taken from the biotitized amphibolite at the contact.

The pegmatites at Håverstad, Eptevann, Knipan, and Torvelona are thortveitite bearing. An ordinary green beryl from one of these (Ljoslandsknipan) was found to contain something like 10000 g Sc per ton (1%). The beryl was a quite fresh and pure crystal, and no trace of thortveitite could be seen in it nor in the specimen (potash feldspar) on the whole. Also Eberhard (4) had noticed that beryls from thortveitite-bearing pegmatites were rich in Sc. He examined a number of different minerals from such pegmatites, found traces of Sc in many of them, but summarized

his results in saying that the amount of Sc present in a pegmatite is largely concentrated in the biotite and the beryl, not counting the thortveitite. — As to the occurrence of Be in thortveitite I might add that I have taken a number of spectrograms (covering the region of the sensitive ultraviolet Be-lines) of thortveitites from the known localities in Iveland and from Madagascar. No trace of the Be-lines could be seen, except in one or two cases where the thortveitite crystals were seen or suspected to be intergrown with beryl. The content of Be in pure thortveitite, if at all present, must be very low indeed, certainly far below 0.001 % Be. This result agrees perfectly with that of the spectrographic investigations of Exner and Eberhard, however, not with the chemical analyses by Jan Sterba (see J. Schetelig, l. c. (4)).

Muscovites from the Caledonian pegmatites at Hundholmen, Tysfjord and Ørne-tind, Seiland in Northern Norway are poor in Sc, containing only 5–10 g/t.

Table 3.

*Sc-concentrations in minerals from cleavelandite pegmatite.*

Landås, Iveland: (5).	
Muscovite, brownish, rich in Li.....	<3 g/t
Frikstad, Iveland: (5).	
Muscovite, brown, rich in Li (zinnwaldite?) .....	<3 -
Mørkhøgda, Gjerstad: (5).	
Muscovite.....	300 -
Skarsfjell, Tørdal: (6).	
Biotite from contact (biotitized amphibolite).....	100 -
Muscovite, yellow.....	500 -
Muscovite, greyish, rich in Li.....	400 -
Zinnwaldite (?), brown.....	2000 -
Topaz .....	3 -
Høydalen, Tørdal: (6).	
Muscovite, greyish, rich in Li.....	700 -
Lepidolite, reddish violet .....	5 -
Muscovite, pink .....	<3 -
Beryl, yellow.....	300 -
Beryl, pale blue.....	100 -
Beryl, pale pink to colourless.....	3 -
Cassiterite .....	100 -

Remarks. *Skarsfjell*: The greyish muscovite is younger than the zinnwaldite. Thortveitite has not been found in the deposit.

*Høydalen*: The lepidolite and the pink muscovite are younger than the greyish muscovite. The pink and colourless beryls are younger than the yellow and blue ones. The hornblende gabbro in the vicinity of the pegmatite is somewhat richer in Sc than usual (about 200 g/t in the amphibole).

The data given in Table 1 may be summarized as follows. The result found by Goldschmidt and Peters, that the concentration of Sc in the pyroxenes of basic igneous rocks is usually about 100 g/t, is confirmed by some additional evidence; this concentration is also

about the maximum value found in mineral constituents of common rocks. Similar Sc-concentrations are also found in the pyroxenes of some intermediate igneous rocks, in the amphiboles of amphibolites, and in eclogite garnet. Amphiboles of more acid rocks apparently tend to be somewhat poorer in Sc, however, this may not be sufficiently established. The biotites of common rocks are generally poor in Sc: the concentrations hardly exceed 30 g/t and are frequently much lower. The variations of the Sc-concentrations of these biotites seem to be regular in two ways: biotites from acid rocks are richer in Sc than those from more basic ones, and biotites from Archaean rocks are on the average richer in Sc than those from younger igneous rocks. A special feature, also pointed out by V. M. Goldschmidt, is the extremely low Sc-content of the biotite (lepidomelane) from the agpaite pegmatites of the Langesundsfjord; this also applies to the biotite of the mother rock, lardalite, in spite of the quite normal Sc-content of the pyroxene of this rock.

From the work of Goldschmidt and Peters we know that ordinary felsic rock constituents (feldspars &c.) do not contain appreciable quantities of Sc. It may be said, therefore, that practically the whole content of Sc in ordinary rocks is contained in pyroxene (amphibole) and biotite. The distribution of Sc between pyroxene (amphibole) and biotite within a rock obviously in most cases corresponds to a state of equilibrium analogous to the distribution of a soluble substance between two liquid phases. Naturally the coefficient of distribution will depend on the conditions of formation of the rock, and presumably mainly on the temperature, as all the rocks in question are products of more or less deep-seated igneous or metamorphic processes. From data contained in Table 1 we find the following approximate values for this coefficient of distribution:

Rock	Sc in pyroxene (amphibole)
	Sc in biotite
Farsundite .....	3
Hornblende Gneiss .....	4
Hornblende Gabbro.....	10
Diorite .....	7
Pyroxenite .....	15
Larvikite .....	30
Lardalite.....	30+

It is possibly also justified to combine the Sc-contents of the amphibole and biotite from Torungen, as the amphibolite and the biotite schist belong to the same metamorphic complex and the two specimens were taken in the close vicinity of each other. If we do this we find a coefficient of distribution of about 5. The dependency of these figures on the temperature seems quite obvious: at high temperature (crystallization of magmas) the coefficient of distribution is large (about 10—30), at lower temperatures (regional metamorphic processes) it is much smaller (5 and less). Applying this to the hornblende rock from Berg—Sponvik it would seem that the biotite has been formed at a rather low temperature, perhaps by reaction of some potassium compound with the amphibole. Likewise the apatite deposits examined seem to have been formed at low to moderate temperatures. However, it must not be forgotten that the assumed simple dependency of the coefficient of distribution on the temperature may not be valid over a wide range of different rocks, as minerals like pyroxene, amphibole, and biotite may vary considerably in composition and physical properties. Nevertheless the rule seems to give correct results in most cases, if not taken too literally.

Since the Sc-concentration in rockforming pyroxenes and amphiboles is rather uniform (about 100 g/t), we may with nearly the same result base our temperature scale on the absolute Sc-contents of the biotites: high temperature biotites are the poorest in Sc.

If no pyroxene or amphibole is present in the rock the biotite is on the average distinctly richer in Sc than in the presence of one of these minerals (Table 1: nordmarkite, granitite, Archaean gneiss and granite). There are probably two cooperating reasons for this. Firstly Sc presumably enters more abundantly into biotite when there is no other mineral present into which it would have preferably entered, and secondly the absence of pyroxene and amphibole in many cases means that the rock is more or less acid and therefore has been formed at a comparatively low temperature.

When biotite is the only ferromagnesian constituent of a rock there is reason to believe that its lattice was in many cases *saturated* with Sc when formed. The main argument in favour of this view follows from Bowens' reaction principle, which is generally recognized in the case of igneous rock series: In the reaction series biotite is immediately preceded by amphibole, and this in turn by pyroxene. During the replacement of pyroxene by amphibole the Sc-concentra-



tion is largely unaffected; the replacement of amphibole by biotite, however, is apparently always accompanied by a very considerable loss of Sc. This obviously means that the biotite lattice was not able to take up all the Sc supplied from the amphibole, i. e. the biotite as formed by this process was saturated with Sc. Provided that the original Sc-concentration of the biotite has been preserved during the later history of the rock we may thus use the Sc-concentration itself as an indication of the temperature of crystallization. If biotites from magmatic granites &c. (e. g. Oslo Region) are saturated with Sc it is seen from Table 1 that biotites from pyroxene- or amphibole-bearing rocks cannot be very far from saturation, and that biotites from presumably palingenetic granites contain considerably more Sc than would saturate a biotite from a magmatic granite. The temperature scale based on absolute concentrations of Sc in biotite would be about as follows.

Rockforming processes	Sc in biotite, g/t
Crystallization of magmas:	
Basic and intermediate.....	5±
Acid .....	10±
Regional metamorphic processes .....	20±

Table 1 would seem to show, therefore, that the Archaean massive granites of Southern Norway have solidified at lower temperatures than truly magmatic granites. Their palingenetic character is thus confirmed.

Considering now the biotites from Archaean granite pegmatites (Table 2), we see that they are on the average much richer in Sc than those from ordinary rocks and that their Sc-content is highly variable. The maximum values observed (500—1000 g/t) obviously mark the maximum extent to which Sc is able to enter into the biotite lattice under the conditions of formation of normal (magmatic) granite pegmatites, as in these cases the pegmatites are thortveitite-bearing. If the temperature may be taken as the deciding factor,<sup>1</sup>

<sup>1</sup> Provided that the supply of Sc is sufficient to "saturate" the biotite, it is conceivable that also the large quantities of mineralizers present in a pegmatitic magma may favor high Sc-concentrations in the biotite.

the maximum Sc-content of the biotite thus affords a very sensitive geologic thermometer in the temperature region corresponding to the solidification of granitic magmas and their residual liquids: this maximum content increases from about 10 g/t to about 1000 g/t during these latest stages of magmatic activity. — From Table 2 it is seen that also muscovite from Archaean granite pegmatite may be very rich in Sc. The maximum content, found in thortveitite-bearing pegmatites and thus probably representing the “saturating” concentration, is about the same as found for biotite, about 1000 g/t. But in other cases, where saturation is not reached, it is seen that muscovite may be considerably richer or poorer in Sc than biotite from the same dike. This may indicate minor differences in temperature &c. between the different dikes, but on the other hand the muscovite is often distinctly younger than the biotite of the same dike, so that the distribution of Sc between the two minerals may depend on a variable supply of Sc to the pegmatite during its period crystallization, and not correspond to a simple equilibrium.

The formation of Sc-rich micas may also continue during part of the hydrothermal-pneumatolytic phase of the granite pegmatite (Table 3). The material so far surveyed seems to show that Sc enters easily into the comparatively Fe-rich muscovites and lithium micas (muscovite-protolithionite-zinnwaldite) formed during the earlier stages of the hydrothermal-pneumatolytic period. Thus the brown Li-rich mica from Skarsfjell shows a higher Sc-content than even the micas from thortveitite-bearing normal pegmatites, indicating that the ability of the mica lattices of taking up Sc still continues increasing with falling temperature. On the other hand the nearly Fe-free micas formed at later stages (lepidolite and pink muscovite, Høydalen) are extremely poor in Sc. This may mean that further sinking of the temperature puts a stop to the entering of Sc into mica minerals, or it may mean that Sc follows the Fe-content of the mica (which seems to be partly true); but the main reason for the absence of Sc in these youngest micas is probably that no more Sc was available during their crystallization. This is supported by a look at the Sc-contents of the beryls from Høydalen: the older beryls are rather rich in Sc, the youngest are practically Sc-free. Also, in the two deposits at Landås and Frikstad there seems to have been no supply of Sc at all during the hydrothermal-pneumato-

lytic phase, as the brownish Li-rich micas from these localities are closely related to the brown Li-rich mica from Skarsfjell, apart from their extremely different contents of Sc.

It follows from the material surveyed that Norwegian granite pegmatites are usually more or less enriched in Sc as compared with ordinary granites. The Sc enters into mica minerals, beryl and some rarer minerals, and in extreme cases forms thortveitite. The correct explanation of this enrichment seems to be the following. As pointed out by V. M. Goldschmidt (7) the Sc is probably not an original constituent of the pegmatite magma, but has been extracted from amphiboles in the country rock of the pegmatite. A necessary condition should be, therefore, that the pegmatite cuts through amphibolite or similar rocks, and this condition is fulfilled by most granite pegmatites (8). Now it is well known that potassium compounds supplied from the pegmatite or granite magma frequently alters the amphibolite at the immediate contact into a biotite rock which forms a zone of varying thickness along the boundary. If this process takes place at an early stage or at great depth the temperature may be so high that only part of the Sc-content of the amphibole is able to enter into the biotite replacing it. The Sc thus set free must, in the shape of some compound, enter into the pegmatite magma. When, at later stages or nearer the surface, the pegmatite magma begins to crystallize, Sc-rich minerals may form, for instance micas formed at lower temperatures, which may contain considerable amounts of Sc. The Sc-contents of two specimens of biotitized amphibolite from pegmatite contacts are given above (Table 2, Karlshus and Table 3, Skarsfjell). The values do not differ notably from the usual concentrations in amphibole, which would seem to indicate that the temperature was in these cases sufficiently low to enable the biotite to take over all the Sc from the amphibole.

### SUMMARY

It is found that the concentration of Sc in rockforming biotites is fairly constant within certain groups of rocks, and that it varies systematically when passing from one of these groups to another. It is made probable that the concentration is in each case determined mainly by the temperature of crystallization of the biotite: Starting with the high temperature biotites of basic and intermediate igneous rocks and passing through those of younger granites &c. to those of Archaean granites

and gneisses, we find a gradual increase of the Sc-concentration from well below 10 g/t to about 30 g/t. During further sinking of the temperature the ability of the biotite to take up Sc apparently increases very rapidly: in biotite from thortveitite-bearing granite pegmatite the concentration may be as high as 1000 g/t. In granite pegmatite the muscovite may be quite as rich in Sc as the biotite, and muscovite formed during the later hydrothermal-pneumatolytic period (cleavelandite-pegmatite) may even show a further increase in the Sc-content. — The Sc-content of the granite pegmatite magma probably has been extracted from the basic country rock at the contact as a consequence of the alteration of amphibole to biotite at a comparatively high temperature, corresponding to a Sc-concentration in the biotite lower than about 100 g/t.

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Oslo, Mineralogisk-geologisk museum, June 1943.