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Preliminary observations on the distribution of trace elements in the rocks of the Skaergaard intrusion, Greenland.

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1. Introduction.

THE Skaergaard intrusion of Kangerdlugssuak, East Greenland (68° 10' N., 31° 40' W.) contains a series of gabbros and related rocks—the layered series—which has been interpreted as the result of fractional crystallization of a fairly normal gabbro magma (Wager and Deer, 1939).¹ Analysis of these rocks and of some of the constituent minerals by Dr. W. A. Deer has shown a considerable and systematic variation in the major constituents (1939, table XXXVI and pp. 67–84)² and it was considered therefore that it would be of value to determine the variation in some of the rarer elements.

The work of Goldschmidt and his collaborators on the distribution of trace elements in minerals (summarized in Goldschmidt, 1937) combined with our recently acquired knowledge of many crystal structures has made clearer the factors controlling the distribution of the trace constituents in minerals. Where the minerals are the result of fractional crystallization, the variation in the trace constituents should be systematic and more readily understood than in minerals of more obscure origin, and hence the particular interest of work on the layered series of the Skaergaard intrusion. It was decided that this work should consist of two parts: first, analysis of selected rocks; and second, analysis of the more important mineral species separated from the rocks. The distribution of trace elements in the more important minerals of the rocks should provide a secure basis for understanding the variation in the rocks themselves. Only the first part of this programme has been carried through, namely, analysis of the rocks for trace elements. Pending the further work on the minerals, which cannot be undertaken at present, it is proposed to present here the results of the analysis of the rocks. These will be compared with the few available analyses for similar rocks

¹ See list of references at end of this paper.

² Where no author is mentioned, the paper referred to is that by Wager and Deer, 1939.

and a preliminary discussion will also be given of the probable factors controlling the variation in the amounts of the trace constituents during differentiation.

Whilst the variety among the rocks of the Skaergaard intrusion is largely due to differentiation by fractional crystallization, a minor part of the variation is believed to be the result of admixture with the surrounding metamorphic complex. In proving such admixture and estimating its extent, analyses for trace constituents may be of more value than analyses for major constituents. In furtherance of this line of investigation, determinations of the trace constituents in two samples of the dominant rock of the metamorphic complex, the 'grey gneiss', have also been made and are recorded here.

The analyses for trace elements are the work of one of the authors (R. L. M.), while the discussion of the results is largely the work of the other (L. R. W.). We are greatly indebted to Dr. W. G. Ogg for allowing the determinations to be made at the Macaulay Institute for Soil Research, Aberdeen.

2. *Methods of analysis and statement of results.*

Determinations of the trace element contents of the rocks have been made by the cathode-layer-arc spectrographic technique previously described (Mitchell, 1940). This method, similar to that employed by Goldschmidt and his collaborators, gives results which are reasonably accurate when the amounts of the trace constituent are near to the minimum value which can be observed, but when the content is some 50 times this value the results are less satisfactory. Hence values for SrO above 1000 p.p.m., say, or CoO above 100 p.p.m., are less reliable than those below these contents. The values quoted for CuO are questionable, owing to the presence of variable traces of copper in the electrodes employed.

The results of the analyses for trace elements are presented in parts per million in table I (heavy type); with them are incorporated the results of Deer's analyses for the major constituents (normal type), taken from the previous work (1939, table XXXVI). The analyses are presented in terms of the oxides in which the particular element has the valency it usually has in igneous rocks. The order adopted in the table is that of increasing ionic radius [Column A, taken from Goldschmidt (1926 and 1938)]. This order is adopted because ionic size is considered to be the chief factor controlling the distribution of trace constituents in the various crystal phases of the rocks.

For one or two of the rocks, analyses for trace elements by ordinary chemical means had already been undertaken by Deer (1939, table XXXVI). These earlier results, although not identical, are of the same general order as those now found. Only for copper is the difference significant, and whilst the presence of copper in the electrodes detracted from the precision of the results obtained spectrographically, the copper content of the rocks appears to be higher than that found chemically. The presence of this electrode impurity is the reason for no data being quoted for rocks of low copper content, and for no estimate of the sensitivity being given. For the trace constituents the results of spectrographic analysis only are considered, so that comparisons are homogeneous throughout.

3. *Composition of the original Skaergaard magma.*

An olivine-gabbro of constant composition is found as a chilled facies at all marginal contacts of the Skaergaard intrusion and this rock, typified by specimen

1724 (table I, column 1) is regarded as having essentially the composition of the original basic magma which filled the space now occupied by the intrusion (1939, pp. 137-144). The varied rocks of the intrusion have been mainly developed by differentiation from this magma, but contamination with the 'grey gneiss' of the surrounding metamorphic complex has also contributed.

Considering the major constituents only, the original Skaergaard magma had a fairly typical olivine-gabbro composition, which is close to that of a mixture of two parts of the porphyritic central magma of Mull (SiO_2 48%) and one part of the Mull normal magma (SiO_2 47%), (1939, pp. 142-143). The original Skaergaard magma differed in the two following respects from this theoretical mixture of Mull magmas and, indeed, from the average composition of olivine-gabbros: (1) the content of potassium was much lower; (2) a larger proportion of the iron was in the ferrous state. It is considered that the special trend of differentiation shown by the Skaergaard magma is not due to these differences in composition from normal olivine-gabbro magma (1939, pp. 309-313), but to special conditions during differentiation.

No equally satisfactory standard of comparison with other gabbros is available in respect of the trace constituents. The best is derived from analyses, by different workers, of the trace constituents of a specially prepared mixture of eleven German gabbros (Noll, 1934). Of the eleven rocks of this mixture six were classified as gabbros, four as olivine-gabbros, and one as norite. Thus, the mixture represents a somewhat more acid material than the original Skaergaard magma and one which would crystallize at a somewhat lower temperature. The amounts of certain trace constituents in Noll's average gabbro are given in table I, column C, where figures for the average amounts of the major constituents in gabbro, taken from Daly (1937), are also given. Comparison of the amount of trace constituents in the Skaergaard magma with these average figures shows fairly close similarity, except in the case of strontium. Thus, the values for the Skaergaard rock are not more than four times and not less than one-third the average value (or, where sensitivity does not allow this to be stated, the figures are not excluded from being within these limits) for the following elements: B, Ga, Cr, Sn, Li, Ni, Co, Yt, La, Ba, and Rb. The amount of strontium falls outside these limits, there being ten times more SrO in the Skaergaard magma than in Noll's average gabbro. Thus, as far as data are available, the amounts of the trace elements in the Skaergaard magma are, within certain broad limits, similar to those for average gabbro, except in the case of strontium.

The amount of SrO in the Skaergaard magma is 0.2%; this value is surprisingly high, being equal to the amount of K_2O . The volume of magma originally occupying the Skaergaard intrusion was about 150 cubic kilometres, and it is a reasonable hypothesis that the Skaergaard magma represents an important rock type within the earth in this part of East Greenland. In table I, the amount of SrO in the 'grey gneiss', the dominant rock of the upper crust in this part of East Greenland, is also given, and is ten times that in Noll's average of 14 German granites, and six times that of average diorite (table II). This evidence suggests that both the acid and basic outer parts of the earth in this part of East Greenland are richer in strontium than the average.

The case of barium is also of interest, although the evidence is not so clear. The BaO content of the Skaergaard magma is only half that in the average

TABLE I. ANALYSES OF ROCKS OF THE SKAERGAARD INTRUSION

(Analyst for trace elements, R. L. Mitchell;

A.		B.	C.	1.	2.	3.	4.	5.
Ionic radii in Å.		Sensitivity.	Average of Noll's 11 gabbros and Daly's average gabbro.	Marginal olivine-gabbro 1724.	Gabbro-picrite 1682.	LAYERED SERIES.		
					Olivine-gabbro 4077.	Middle gabbro 3662.	Hortonolite-ferrogabbro 1907.	
CO ₂	..	0.15	—	100	—	—	300	—
B ₂ O ₃	..	0.20	3	*	*	*	*	*
SO ₂	..	0.30	—	6,200	—	—	3,500	—
P ₂ O ₅	..	0.33	2,800	600	200	600	500	800
BeO	..	0.34	30	*	*	*	*	*
SiO ₂	..	0.39	482,400	478,300	412,700	463,700	481,500	448,100
GeO ₂	..	0.44	15	*	*	*	*	*
Al ₂ O ₃	..	0.57	178,800	186,200	87,100	168,200	180,200	139,600
Ga ₂ O ₃	..	0.62	7	33	13	27	20	27
Cr ₂ O ₃	..	0.64	1	900	1,500	300	*	*
TiO ₂	..	0.64	—	9,700	12,900	15,400	7,900	26,400
V ₂ O ₅	..	0.66	7	225	150	300	375	60
Fe ₂ O ₃	..	0.67	—	31,600	11,600	26,900	15,200	25,200
MoO ₃	..	0.68	1	—	*	*	*	37,500
SnO ₂	..	0.74	13	10	*	*	*	*
Li ₂ O	..	0.78	6	20	10	20	6	20
MgO	..	0.78	—	75,100	79,200	270,900	96,100	52,500
NiO	..	0.78	1	200	120	750	250	30
CoO	..	0.82	2	100	75	100	90	50
CuO	..	—	—	—	400	600	400	1,200
FeO	..	0.83	—	59,500	88,700	105,200	104,400	95,000
ZnO	..	0.83	350	—	*	*	*	166,600
Sc ₂ O ₃	..	0.83	—	30	+++	+++	+++	+
ZrO ₂	..	0.87	13	—	25	40	40	25
Sb ₂ O ₃	..	0.90	350	—	*	*	*	*
MnO	..	0.91	—	1,300	900	1,600	900	1,200
Na ₂ O	..	0.98	—	25,500	25,400	6,900	24,500	34,600
CeO ₂	..	1.02	600	*	*	*	*	*
CdO	..	1.03	350	*	*	*	*	*
Yt ₂ O ₃	..	1.06	15	3	*	*	*	*
CaO	..	1.06	—	109,900	105,900	65,900	112,900	101,700
ThO ₂	..	1.10	60	—	*	*	*	*
Ag ₂ O	..	1.13	1	—	3	*	*	*
La ₂ O ₃	..	1.22	15	10	*	*	*	*
SrO	..	1.27	10	200	2,000	100	2,000	1,000
PbO	..	1.32	30	—	*	*	*	1,500
K ₂ O	..	1.33	—	8,900	2,000	1,300	2,000	1,400
BaO	..	1.43	10	70	30	10	50	30
Rb ₂ O	..	1.49	50	20	*	*	*	*

Explanation of table I.

Figures in heavy type show the amount of the trace elements determined spectrographically; others are those given by chemical analysis.

* indicates that the amount is less than the sensitivity (column B).

+, ++, +++, used for Sc₂O₃ only, for which comparison standards were not available, indicate respectively: spectrum lines weak but visible, moderate, and strong.

— indicates that data are lacking.

Column A, Ionic radii from Goldschmidt (1926 and 1938).

AND COMPARISONS (EXPRESSED AS PARTS PER MILLION).

for other elements, W. A. Deer.)

LAYERED SERIES.				D. Average of Noll's 14 granites and Daly's average granite.	10. 11. 'Grey gneiss' of metamorphic complex		CO ₂ B ₂ O ₃ SO ₂ P ₂ O ₅ BeO SiO ₂ GeO ₂ Al ₂ O ₃ Ga ₂ O ₃ Cr ₂ O ₃ TiO ₂ V ₂ O ₅ Fe ₂ O ₃ MoO ₃ SnO ₂ Li ₂ O MgO NiO CoO CuO FeO ZnO Sc ₂ O ₃ ZrO ₂ Sb ₂ O ₃ MnO Na ₂ O CeO ₂ CaO Yt ₂ O ₃ CaO ThO ₂ Ag ₂ O La ₂ O ₃ SrO PbO K ₂ O BaO Rb ₂ O
6. Ferrohortonolite- ferrogabbro 4145.	7. Fayalite- ferrogabbro 4142.	8. Basic hedenbergite- granophyre 4137.	9. Acid granophyre 3058.		1865.	1867.	
400	—	—	—	—	—	..	
*	*	*	*	10	*	3 ..	
7,700	—	—	—	1,900	—	..	
18,500	16,100	7,000	200	1,900	3,100	..	
*	*	*	*	20	*	..	
446,100	441,300	521,300	750,300	701,800	681,700	..	
*	*	*	*	5	*	..	
117,000	178,800	158,700	131,700	144,700	161,300	..	
20	27	27	20	20	33	27 ..	
*	*	*	4	3	4	15 ..	
24,300	24,800	11,400	3,100	3,900	6,300	..	
*	*	*	15	—	45	75 ..	
20,500	40,500	56,100	15,600	15,700	5,800	..	
*	*	*	4	—	*	1 ..	
*	*	*	*	100	*	..	
40	20	400	15	400	200	100 ..	
17,100	2,500	11,100	1,500	8,800	—	18,200 ..	
*	*	4	6	3	13	10 ..	
40	4	25	4	10	20	7 ..	
2,500	600	1,200	—	—	—	..	
226,800	266,300	111,700	5,800	17,800	—	20,900 ..	
*	*	*	*	—	*	..	
++ +	++	++	*	2	*	..	
55	40	250	400	—	200	250 ..	
*	*	*	*	—	*	..	
2,100	4,800	3,000	100	1,200	—	500 ..	
29,500	21,500	36,300	42,400	34,800	—	44,000 ..	
*	*	*	*	—	*	..	
*	*	*	*	—	*	..	
*	*	*	40	15	*	..	
87,100	100,300	58,000	6,900	19,900	—	20,700 ..	
*	*	119	110	—	60	80 ..	
*	*	*	*	—	*	..	
*	*	*	40	50	70	30 ..	
1,000	1,500	2,000	300	100	1,000	3,000 ..	
*	*	*	*	—	*	..	
3,500	4,700	13,800	38,500	41,100	—	32,200 ..	
100	200	600	2,000	500	3,000	3,000 ..	
*	*	200	1,000	600	1,000	1,500 ..	

Column C, Figures in heavy type are for average gabbro material prepared by Noll from 11 different German gabbros. The other figures are taken from Daly's average for gabbro.

Column 1, Marginal olivine-gabbro, which is considered to represent the composition of the original Skaergaard magma.

Columns 2-9, Skaergaard rocks in order of differentiation.

Column D, Figures in heavy type are for average granite material prepared by Noll from 14 German granites. The other figures are taken from Daly's average for granite.

Columns 10 and 11, 'Grey gneiss', the dominant acid gneiss forming the country-rock of the Skaergaard intrusion.

gabbro quoted, but this is probably to be accounted for by the more olivine-rich character of the Skaergaard magma than the average gabbro with which it is compared. The grey gneiss is six times as rich in BaO as average granite and ten times as rich as average diorite (table II). It may well be that the basic outer part of the earth in east Greenland has about the normal content of BaO, while the acid part is markedly richer in BaO than the average acid crust of the earth. Holmes and Harwood (1932) have commented on what seems to be a fundamental heterogeneity in the crust in respect of SrO and BaO. The data they assembled indicated that the area east of the Rocky Mountains from Colorado to Montana is unusually rich in both oxides, while the pre-Cambrian rocks of Southern Rhodesia are probably rich in SrO. In contrast, their data indicated that the rocks of eastern Australia are poor in both SrO and BaO. Holmes and Harwood have emphasized that the distribution of trace constituents in rocks should some day provide a valuable aid in understanding the fundamental petrogenetic processes involved in the development of the major units of the outer earth. It is clear that the fascinating problem of the distribution of BaO and SrO in the outer part of the earth could appropriately be followed up among the well-characterized rocks which build up East Greenland.

TABLE II. Amounts, in parts per million, of certain oxides in the Skaergaard rocks compared with values from Noll (1934), Engelhardt (1936), and Daly (1933).

	Olivine-gabbro, 1724, representing Skaergaard magma.	Average gabbro (Noll, Engelhardt, & Daly).	Average diorite (Noll, Engelhardt, & Daly).	'Grey gneiss' average of 1865 & 1867 representing dominant country-rock of intrusion.	Average granite (Noll, Engelhardt, & Daly).	Charnockite (Engelhardt).
CaO	106,000	110,000	61,000	21,000	20,000	—
SrO	2,000	200	300	2,000	100	—
K ₂ O	2,000	9,000	21,000	32,000	41,000	—
BaO	30	70	300	3,000	500	2,000

In view of the unusual trend of differentiation of the Skaergaard magma to give ferrogabbros, the question whether the original magma had peculiarities in composition which might have caused this trend was carefully considered in the earlier paper (1939, pp. 309-313). The low K₂O content and the reduced state of the iron were noted as the only peculiarities in composition indicated by analyses for the major constituents. Work on the trace constituents indicates that there was a further peculiarity, namely, high SrO content which is ten times normal. As with the peculiarities previously noted, it is not considered that the high SrO content is likely to have been responsible for the unusual trend of differentiation of the magma to give ferrogabbros.

4. Variation of the trace constituents during differentiation.

The bulk of the layered series is the result of what has been called non-selective gravitational differentiation (1939, p. 282). Thus, the rocks consist of a precipitate of all the solid phases separating at a particular time from the magma, together with about 20% of the magma then existing, the latter filling the inter-

stices of the crystal precipitate (1939, pp. 127-128). Five rocks of the layered series representing this best-defined stage of the differentiation of the Skaergaard magma have been analysed (table I, columns 3 to 7). In order from the earliest to the latest, these are: olivine-gabbro, 4077; olivine-free gabbro, 3662, belonging to the 'middle' gabbro series; hortonolite-ferrogabbro, 1907; ferrohortonolite-ferrogabbro, 4145; and fayalite-ferrogabbro, 4142. Superimposed on the non-selective gravitational differentiation there was an effect due to the different densities of the crystals and this gave rise to what has been called rhythmic layering (1939, pp. 30-37). As a result of this, a single specimen of the rock, even when carefully selected, can represent only an approximation to the average composition of the rocks forming at that particular time, because of the partial sorting into layers of the heavy and light constituents. Of the rocks analysed for trace constituents only the middle gabbro, 3662, is considered to depart significantly from the average appropriate to the horizon, and this differs by being richer in plagioclase than the average. Among the major constituents the effect of this is seen in the rather low values for MgO and FeO; among the trace constituents this divergence from the average has probably been responsible for the amounts of NiO and CoO being less by 20 or 30 p.p.m. than would probably be found for a more average rock of this horizon.

Two of the analysed rocks of the layered series are considered to have resulted from strong selective gravitational differentiation whereby some of the separating crystal phases have sunk and others risen. Thus the gabbro-picrite, 1682 (table I, column 2), from the northern margin is apparently the original magma, having the composition of the chilled marginal gabbro, 1724, enriched by early olivine which sank into it. At the other end of the differentiation series, the basic hedenbergite-granophyre, 4137 (table I, column 8), which occurs at the top of the layered series, is considered to be the result of some of the heavier constituents being removed by sinking, leaving a granophyric residue.

In the latest stages of solidification of the Skaergaard intrusion, veins of acid granophyre were formed in small quantities. This material is regarded as a residual magma produced by filter-press action, and an example, 3058, has been analysed (table I, column 9). The 'grey gneiss' of the metamorphic complex, which partly surrounds the Skaergaard intrusion, was incorporated to some extent into the rocks of the intrusion and material derived from this source may have contributed significantly to the acid granophyres, such as the analysed rock, 3058.

The sequence of the differentiates from a rock approaching peridotite in composition, 1682, to a rock, 3058, approaching granite in composition is the sequence followed in table I (columns 2 to 9). In relation to the sequence of differentiation the amounts of the trace constituents can be seen to undergo a fairly regular variation, the chief features of which will now be summarized:

(1) Ga_2O_3 is present only in small amounts and shows little variation throughout the differentiation. The small variation found is approximately proportional to the amount of Al_2O_3 . The enrichment of Ga_2O_3 in late differentiates which has been noted by Goldschmidt (1937) is not apparent over the range of differentiation here considered.

(2) Cr_2O_3 is abundant in the gabbro-picrite, 0-15% being present; the amount then falls rapidly, there being less than 1 p.p.m. in the middle gabbro and later

ferrogabbros. This is in harmony with the well-known fact that chromium is normally associated with ultra-basic rocks (cf. Groves, 1937); Goldschmidt gives the average for peridotite as 0.5% and for gabbro 0.05%. Comparison of the figures for the amount of Cr_2O_3 in the original magma (column 1) and in the differentiates (columns 2 to 9) combined with data previously given on the relative volume of these rocks, suggests that a considerable precipitation of Cr_2O_3 must have occurred in the early, hidden layered rocks (cf. 1939, pp. 217-224).

(3) V_2O_5 reaches a maximum value in the middle gabbro where there is about 0.04%. If the V_2O_5 is mainly present in the iron ores, then it apparently occurs to a greater extent in those precipitated during the middle stages of differentiation, for iron ore increases during the differentiation up to the time of formation of the basic hedenbergite-granophyres, 4137, whereas the amount of V_2O_5 falls off in these later stages.

(4) SnO_2 is low throughout the whole series and even in the acid granophyre there is less than one-sixth of the average amount in granites. This provides another small piece of evidence that normal granites are not differentiates from gabbro magma, since even with strong crystal fractionation of this fairly typical gabbro magma, SnO_2 is not concentrated to anything like the same extent as in average granite.

(5) Li_2O remains low until the basic hedenbergite-granophyre, 4137, is reached when the Li_2O content rises abruptly to 0.04%. Stroock (1936) has shown that lithium tends to occur mainly in low-temperature, ferromagnesian minerals and not in the feldspars. The small amount of Li_2O in the latest differentiate, the acid granophyre, 3058, is no doubt the result of the small amount of ferromagnesian mineral present in it.

(6) NiO is abundant in the magnesium-rich rocks, the gabbro-picrite, 1682, containing 0.07% and the olivine-gabbro, 4077, 0.02%. Goldschmidt (1937) estimates that the average NiO content of peridotite is 0.40% and of gabbro is 0.02%. Thus the value for the gabbro-picrite lies between these amounts and rather closer to that for gabbro. It should be noted that the Skaergaard magma, as represented by 1724, column 1, although an olivine-gabbro in composition, has a lower content of NiO than Noll's average gabbro. It also has a lower content of CoO as shown below.

(7) CoO was present in the original magma, as represented by 1724, to about half the extent of the NiO , and it is more evenly spread than NiO through the basic rocks of the intrusion. The variation in the amount of Co and Ni and other elements entering olivine and pyroxene is more fully considered in the next section.

(8) CuO reaches a maximum of 0.25% in the ferrohortonolite-gabbro, which belongs to a later stage of the fractional crystallization than the gabbros where CoO reaches its maximum. Data for copper are, however, incomplete for the reasons already given (p. 284).

(9) ZrO_2 , as would be expected, is concentrated in the latest rocks, the basic hedenbergite-granophyre, 4137, and the acid granophyre, 3058. The amount in all the differentiates which have been examined exceeds that in the original magma, 1724. It is possible that this result is due to incorporation of 'grey gneiss' into the rocks of the Skaergaard intrusion. In the 'grey gneiss' there is ten times as much ZrO_2 as in the original olivine-gabbro magma, and thus the

incorporation of even small amounts of 'grey gneiss' might well produce a relatively conspicuous increase of ZrO_2 in the Skaergaard rocks.

(10) Yt_2O_3 , ThO_2 , and La_2O_3 are notably concentrated in the latest differentiates. For La_2O_3 slight concentration in granites relative to gabbros has already been shown by Goldschmidt (1937).

(11) SrO, as has already been noted, was particularly abundant in the original magma as represented by 1724 (p. 285). The amount is low in the gabbropicrite which confirms Noll's conclusion that SrO is present only in very small amounts in magnesian olivine. SrO is high in the gabbros and basic hedenbergite-granophyre, but falls again markedly in the acid granophyre.

(12) BaO is present only in small amount in the gabbropicrite and the early differentiates; it increases steadily as differentiation proceeds and reaches 0.2% in the acid granophyre. As with ZrO_2 it is possible that the incorporation of 'grey gneiss', which is rich in BaO, may contribute somewhat to the amount of BaO in the later differentiates.

(13) Rb_2O is present in amounts below the sensitivity in all except the two latest differentiates, the hedenbergite-granophyre and the acid granophyre; in the latter the amount is as much as 0.1%. Concentration of Rb_2O in granites relative to gabbros has been shown by Goldschmidt (1937).

5. *Variation of the trace constituents in relation to ionic size and charge.*

Elements present in small amount in a crystallizing magma do not form separate crystal phases but enter into crystals whose structure and essential nature is controlled by the major constituents of the magma. Furthermore, the trace constituents enter, with varying facility, into the crystal phases formed from the major constituents. From our present general knowledge of the structure of crystals, and from the particular work of Goldschmidt and his collaborators, we now have a general understanding of the main factors controlling the entry of the trace constituents into the crystal phase. The crystals separating from a magma behave towards the trace elements, to use Goldschmidt's descriptive phrase, as a sieving mechanism. Thus the trace elements do not enter in proportion to their abundance in the magma but only as they can be conveniently accommodated in the crystal lattice, and ease of accommodation depends on certain intrinsic properties of the ions of the trace elements. The factors chiefly involved are:

(a) The size of the ions. The crystal structure can tolerate substitution of some of its component ions by others provided they are of approximately similar size. Among ions of approximately similar sizes, the rather smaller ions enter more readily than the larger ions. Thus relative enrichment in the somewhat smaller ions takes place in the earlier crop of crystals formed during fractional crystallization, while enrichment in the larger ions is found in the later fractions.

(b) The ionic charge or valency. Substitution of ions of approximately the same size but of different ionic charge can occur provided that other adjustable substitution of ions can also take place to maintain a neutral total charge on the lattice. It has been shown that ions of appropriate size but of larger charge, relative to the ions being substituted, enter the crystal lattice more easily, and those of smaller charge less easily than the ions being substituted. Goldschmidt

has described the substitution which is controlled by ionic size as the camouflage effect, and that dependent on the ions with larger charge entering more easily he has called the capturing effect. It has not so far been possible to assess in a simple way the relative effects on substitution of size and charge.

The changes in the amounts of the trace elements during the differentiation of the Skaergaard magma provide examples of the above principles which may now be briefly considered. When analyses of some of the separate crystal phases present in the Skaergaard rocks can be carried out, it will be possible to test further some of the tentative conclusions about the location of the trace constituents in the various phases and their variation in amount during crystal fractionation.

The effects of ionic size and charge in controlling the amount of trace constituents is best shown by consideration of ions between 0.75 and 1.00 Å. in radius, as these are the constituents which play an important part in two of the chief materials, the olivines and pyroxenes. The ions in this group in order of size are Li^+ , Mg^{++} , Ni^{++} , Co^{++} , Cu^{++} , Fe^{++} , Zn^{++} , Sc^{+++} , Zr^{++++} , Sb^{+++} , Mn^{++} , Na^+ . The more abundant are Mg^{++} and Fe^{++} , which form olivine, pyroxene, and iron ore under the conditions of crystallization of the Skaergaard magma. Magnesium-rich olivine and pyroxene are present in the gabbro-picrite, 1682, and in the olivine-gabbro, 4077; olivine of moderate richness in iron is present in the middle gabbro, 3662, but no pyroxene; while increasingly iron-rich olivines and pyroxenes are present in the ferrogabbros, 1907, 4145, and 4142. The two iron ores, ilmenite and magnetite, present in small amounts in the gabbro-picrite and olivine-gabbro, are not considered to be primary phases (cf. 1939, p. 229), but become so in the middle gabbro and so remain throughout the rest of the layered series. Of the two iron ores, the ilmenite occurs in decreasing amount, and the magnetite in increasing amount, as the differentiation proceeds.

The divalent ions of the trace constituents Ni, Co, Cu, and Mn are probably mainly present in the olivine and pyroxene, replacing Mg and Fe ions. Since all these ions have the same charge, the main factor controlling the amount present in the olivines and pyroxenes at different stages of the crystal fractionation would be expected to be size. The ferrous iron ion, being larger than the magnesian ion, should enter less easily into the olivine and pyroxene crystals than the magnesian ion. Iron, therefore, should become gradually concentrated in the later, lower-temperature olivines and pyroxenes, an effect which was clearly shown by the previous studies of the Skaergaard intrusion (1939, Chap. VI) and which is in conformity with the experimentally established thermal behaviour for the olivines and for those pyroxenes so far investigated.

Ni^{++} has closely the same ionic size as Mg^{++} and it should therefore enter with about the same facility as Mg into the olivines and pyroxenes, the proportion between these being determined by the amount originally present in the magma. The ratio of NiO to MgO actually found for these constituents in the rocks examined is 1/600 for the original magma (1724), 1/400 for the gabbro-picrite, 1/700 for the olivine-gabbro, 1/500 for the middle gabbro, and less than 1/200 for the succeeding ferrogabbros. These figures suggest slight concentration of Ni in relation to Mg in the earlier ferromagnesian fractions. Perhaps the effective size of the Ni ion in these minerals is slightly smaller than the Mg ion, but separation and analysis of the various individual minerals, especially of the

olivine, pyroxene, and iron ores, is required before more detailed consideration of the behaviour of the Ni in relation to Mg can be made.

The cobalt ion and probably the copper ion lie between the Mg and Fe ions in size. In conformity with this, CoO is not markedly concentrated in the earlier differentiates but persists in considerable amount into the middle differentiates, while copper reaches its maximum amount in the late middle differentiates.

On the other hand, the divalent manganese ion is larger than the Fe^{++} ion and, in conformity with this, manganese increases in amount relative to magnesium and iron throughout the fractional crystallization. That this increase is due, at any rate partly, to substitution of Mn for Mg and Fe in the pyroxenes and olivines as fractionation proceeds, is apparent from the analysis of the separated minerals given in the earlier papers (1939, pp. 72-73, and Deer and Wager, 1939). CaO also enters the olivines to some extent as shown by the earlier analyses of separated olivine and, in conformity with the large size of the divalent Ca ion, it is in the latest olivine fraction that Ca becomes important.

Strock (1936) has shown that lithium, despite its being a monovalent alkali metal, tends to enter the ferromagnesian minerals rather than the feldspars. This he considers to be the result of the similarity in size between the ions of Li, Mg, and Fe. The ion of Li is smaller than that of Mg and the size factor should work in the direction of increasing the Li content of the pyroxenes of the early fractions. Strock, however, has given good evidence that Li tends to be concentrated in the later, more iron-rich pyroxenes. In this we apparently see the effects of the low charge on the monovalent lithium ion compared with that on the divalent iron and magnesian ions, an effect which tends to the exclusion of the ion of lower valency from the earlier fractions. Among the Skaergaard rocks, the highest concentration of Li_2O is found in the basic hedenbergite-granophyre; it seems likely that the Li_2O occurs in the iron-rich pyroxene of this rock and that this is another example of what Strock has found, namely, the substitution of Li for Mg and Fe in late pyroxene fractions. The low value of Li_2O in the latest differentiate, the acid granophyre, 3058, is probably to be correlated with the small amount of total ferromagnesian mineral in this rock. The acid granophyre has abundant feldspar and the low amount of Li is further evidence that Li does not readily replace K and Na in feldspars.

The tetravalent ion of zirconium belongs to the size group now being considered, but there is no evidence that this element enters to any significant extent into the ferromagnesian minerals, or indeed into the feldspars which are the other important primary crystals formed from the Skaergaard magma. The amount of Zr remains low till the basic hedenbergite-granophyre is reached, when the amount suddenly becomes five times that in the earlier rocks. This behaviour is similar to that of P_2O_5 and TiO_2 (1939, pp. 227-229 and plate 27) and it is probable that zirconia, which is apparently extremely insoluble in silicate melts, makes its appearance as a primary phase in the basic hedenbergite-granophyre and persists in the later differentiates, such as the acid granophyre, 3058.

The trace elements of the Skaergaard rocks, which commonly form ions belonging to the size group 0.5-0.75 Å, are, in order of size, Al, Ga, Cr, Ti, V, trivalent Fe, Mo, and Sn. The fairly constant ratio between Al_2O_3 and Ga_2O_3 suggests that the latter occurs camouflaged in aluminosilicates replacing Al_2O_3 ,

and that, over the range of differentiation seen in the Skaergaard intrusion, there is little tendency for the larger size of the Ga ion to result in concentration in the late fractions. The remaining elements, excluding Mo and Sn, probably occur largely in the magnetite or other spinel mineral, but some may also occur in the ilmenite. Cr is strongly concentrated in the earlier differentiates where a chromium-bearing spinel is presumably present. Since the Cr^{+++} ion is smaller than the Fe^{+++} ion, chromium would be expected to be concentrated in the earlier spinel fractions. V_2O_3 seems to be present in greater amount in middle stages of the differentiation. From the ionic size of V^{+++} this might be expected if the element is present in the spinel mineral, but analyses of separate minerals, particularly the iron ore, are required to decide the location of V_2O_3 and the other elements of this size group.

Of the remaining trace elements, only SrO, BaO, and Rb_2O of the size group 1.0–1.5 Å. will be considered in the present paper. Whereas the elements previously considered have probably been mainly present in the ferromagnesian minerals and iron ores, these three elements are present partly or mainly in the feldspars.

Rb_2O is markedly concentrated in the latest differentiate, the acid granophyre, 3058. The large Rb^+ ion is probably present in the feldspars. The increase in the amount of Rb^+ during differentiation of the Skaergaard magma is in sympathy with the increase in the amount of K^+ , but is many times more marked. It would be expected that Rb^+ , by virtue of its large ionic size, would tend to be concentrated in the latest orthoclase fractions.

BaO shows a steady increase during fractional crystallization of the Skaergaard magma, the latest differentiate, the acid granophyre, being 200 times as rich in BaO as the earliest, the gabbro-picrite. It is likely that BaO is mainly present in the feldspars, but the apparently simple variation in the amount of Ba is probably the result of a complex interplay between effects due to the size and valency of the Ba ion relative to the size and valency of the other positive ions in the feldspars, Na^+ , Ca^{++} , and K^+ . The larger size of the Ba^{++} should produce concentration in the later feldspars, while the divalent character should tend in the other direction. Von Engelhardt (1936) believes that the higher Ba content in granites compared with the later pegmatites is due to the divalent Ba entering the earlier orthoclase rather than the later, the result of valency dominating over size. This degree of fractionation is not encountered among the Skaergaard rocks as there is an increase in Ba content throughout all the Skaergaard differentiates. It appears that, over the range of differentiation shown by the Skaergaard rock, the greater size of the Ba ion relative to that of Ca, Na, and K leads to concentration of Ba in the later differentiates. In the Skaergaard rocks BaO shows a markedly sympathetic variation with K_2O . Thus potassium is low compared with average basalt in the original Skaergaard magma and in the earlier Skaergaard differentiates, and so also is barium. Only a small amount of K_2O separated from the magma in the early stages and, in sympathy with this, only a small amount of BaO was separated. This resulted in a concentration of both K_2O and BaO in the later differentiates, the intensity of concentration for K_2O being 30 times and for BaO 200 times. Despite the relatively low amount of BaO in the original Skaergaard magma, there is about four times as much BaO in the latest Skaergaard differentiate, the acid granophyre, as in average granite. This

amount is about the same as is present in average syenite according to von Engelhardt's estimates (1936).

From Noll's investigations (1934) of the occurrences of SrO in magmatic minerals, it may be surmised that the SrO in the Skaergaard rocks is mainly present in the feldspars, but a significant amount probably also occurs in the pyroxenes. The low value for SrO in the gabbro-picrite is partly accounted for by the small amount of Sr in olivines and perhaps partly by the early plagioclase and early pyroxene having less SrO than the later because of the larger size of the Sr ion compared with the Ca ion. Even taking into consideration these factors, the particularly low value for SrO in the gabbro-picrite (100 p.p.m.) is unexpected and further investigation of the SrO content of the early fractions is desirable. The other analysed rocks have a fairly constant SrO content, except for the acid granophyre, where the SrO content is only about one-sixth that of the preceding differentiate, the basic hedenbergite-granophyre. It may be surmised that the Sr ion, being smaller than the Ba ion, has less tendency to become concentrated in the latest differentiates. It has been remarked above that von Engelhardt found that the amount of BaO decreased in the feldspar of the pegmatites, the latest differentiates he examined. It appears from the Skaergaard data that a decrease in the SrO content occurs at an earlier stage of the crystal fractionation process than is the case with BaO. This behaviour should be expected, as the somewhat smaller size of the Sr ion compared with the Ba ion should result in concentration of strontium in earlier differentiates than is the case with barium.

In the present section of this paper, the particular crystal phases in which the trace elements are located have had to be deduced by analogy with previous work and from general geochemical considerations. As soon as conditions permit, it is hoped that much of what has been tentatively suggested will be placed on a firmer basis by separation of the various crystal phases found in the successive differentiates of the Skaergaard intrusion and their separate analysis for trace constituents.

6. *Summary.*

A series of rocks from the Skaergaard intrusion, East Greenland, has been analysed spectrographically for certain trace elements. One of the rocks analysed is the chilled, marginal gabbro considered to represent in composition the undifferentiated olivine-gabbro magma from which the varied rocks of the intrusion have developed. The amounts of the trace elements present in this rock (table I, column 1) show relatively good agreement with the best available comparison analyses of an average gabbro prepared by Noll (table I, column C), except in the case of SrO which is ten times as abundant as in the average. The acid gneiss which is the dominant rock surrounding the intrusion is also shown to be richer in SrO and BaO (table I, columns 10 and 11) than average granite (column D). It is tentatively suggested that the outer layers of the earth in this part of east Greenland contain an amount of strontium and barium which is above the average.

The majority of the rocks analysed for trace elements, which range from gabbro-picrite, through normal olivine-gabbro, ferrogabbro, basic hedenbergite-granophyre, to a normal acid granophyre (table I, columns 2-9), were produced by fractional crystallization from a fairly normal olivine-gabbro magma. In this

series of rocks chromium and nickel tend to be concentrated in the earlier differentiates, vanadium and cobalt in the early middle differentiates, copper and lithium in the late middle differentiates, while molybdenum, zirconium, thorium, lanthanum, and rubidium are concentrated in the latest differentiate, the acid granophyre. Of the other elements for which the data are satisfactory, strontium occurs in considerable amount except in the first differentiate, the gabbro-picrite, and the last, the acid granophyre, while barium shows a continuous and marked increase in amount throughout the whole range of the differentiation series.

The probable location of the trace constituents in the various minerals of the rocks is briefly considered and in the case of certain of the elements the variation is shown to be related to ionic size and charge.

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