

*Aspects of the geochemistry of arsenic and antimony,
exemplified by the Skaergaard intrusion*

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Summary. The distribution of As and Sb in a series of Skaergaard rocks and some of their minerals has been investigated using neutron activation analysis, and the geochemical behaviour of these elements during the fractionation of a basic magma is discussed.

It is concluded that As^{3+} is probably accepted into octahedral lattice sites usually occupied by Fe^{3+} , Mg^{2+} , Ti^{4+} , and Al^{3+} , and that there is also some substitution of As^{5+} for Si^{4+} and Al^{3+} in tetrahedral sites. There is a strong tendency for the element to concentrate in both interstitial and late-stage liquids.

Sb seems to show a marked preferential entry into early (magnesian) olivines, as in the case of Ni. The analytical results indicate that the substitution of Sb^{3+} for Fe^{2+} probably accounts for most of the Sb in silicate and oxide minerals. The tendency for Sb to concentrate in the residual Skaergaard liquids is less marked than in the case of As, but greater than in the cases of V, Cr, and Ni.

As and Sb have also been determined in four chondritic meteorites, in which the As/Sb ratio ranges from 8.5–12.4. Analyses for As and Sb in the standard rock powders G-1 and W-1 have also been made.

PRIOR to the work of Onishi and Sandell (1955), very little was known about the geochemistry of arsenic and antimony in silicate rocks and their constituent minerals. The colorimetric methods used by Onishi and Sandell enabled them to determine arsenic (at the ppm level) in individual samples of a wide range of rocks and minerals, and to discuss its geochemical distribution and behaviour. In the case of antimony (generally < 1 ppm) the analytical method limited much of their work to composite samples, so that only a broad picture of its distribution could be obtained.

The development of neutron activation analysis has facilitated the determination of arsenic and antimony in the submicrogram range (Smales and Pate, 1952; Smales *et al.*, 1957, 1958). This very sensitive technique is used in the present work to obtain accurate analyses for arsenic and antimony in a series of rocks and some separated minerals from the Skaergaard intrusion, and an attempt is made to account for their behaviour during the fractional crystallization of a basic magma.

Sample Preparation. Rock powders passing 120-mesh were prepared by crushing in a hardened steel percussion mortar, and there was no

evidence of contamination by arsenic or antimony. Samples of the constituent minerals were obtained by means of a hand-magnet, an a.c. electromagnet, a magnetic separator in which the brass chute was replaced by one made of Perspex, and micropanning with bromoform.

Analytical method. The procedures used for both elements were modifications of the neutron activation methods described by Smales and Pate (1952) and Smales *et al.* (1957, 1958).

A typical batch of samples and standards for irradiation consisted of 15 to 20 100-mg portions of rock powder, three 10 mg portions of As_2O_3 , and three 0.1–0.2 g portions of a dilute Sb solution (10 μg Sb/g of solution). Samples and standards were sealed in short lengths of polythene tubing (the Sb solution being evaporated to dryness before sealing), packed into a $3'' \times 1''$ AERE aluminium can and irradiated for 3 days in the Harwell reactor BEPO at a flux of about 10^{10} neutrons/cm² sec.

After irradiation, the samples together with 50 mg amounts of As_2O_3 and Sb_2O_3 carriers were decomposed by sintering with 2g Na_2O_2 in nickel crucibles at $490 \pm 10^\circ \text{C}$ (Rafter, 1950). Samples and standards were then treated as described by Smales *et al.* (1957, 1958), thioacetamide being used instead of H_2S to precipitate the sulphides. The activities of the final precipitates were measured by means of an end-window G.M. tube and scaler, and the radiochemical purity of each was checked by plotting decay curves. In some cases, β -ray absorption curves and γ -spectrometry were used as additional checks. The few radiochemically impure samples were either repurified or discarded.

For most of the samples, it was possible to record 10 000 counts in less than 30 min.

Arsenic and antimony in the rocks and minerals

Wager and Deer (1939) gave a detailed description of the geology and petrology of the Skaergaard intrusion, and, partly in the light of new analyses, Wager (1960) has recently reassessed the layered series and revised the earlier estimates of the average composition of the hidden layered series and of the successive residual liquids. Useful summaries of the main features of the intrusion and the origin and sequence of the chief rock types are given in papers by Wager and Mitchell (1951) and Wager, Vincent, and Smales (1957).

In the present work, arsenic and antimony have been determined in twenty-five Skaergaard rocks representative of the significant horizons in the strongly differentiated sequence, including four marginal rocks, fourteen from the exposed layered series, three from the upper border

group and four transgressive acid granophyres. The individual minerals in three rocks of the layered series, one from each of the three main zones, have also been analysed for both elements. Arsenic has been determined in one sample of apatite and one of pyrrhotine from later rocks in the sequence.

Fig. 1 (from Wager, 1960) recalls the main variations in occurrence and composition of the mineral phases throughout the intrusion, and indicates the positions, on the adopted structural height scale, of the rocks analysed for arsenic and antimony. The results for the whole rocks are listed in table I.

Figs. 2 and 3 respectively represent the distribution of arsenic and antimony in the rocks of the layered part of the intrusion. The postulated distributions of these elements in the hidden layered series and in the successive liquids at various stages in the sequence of crystallization were constructed by the graphical method used by Wager (1960) for the major constituents.

Arsenic in the rocks. In the rocks of the exposed layered series, representing the final 30 % of the magma (Wager, 1960), arsenic shows a remarkably smooth variation, only one result falling appreciably off the curve obtained by plotting ppm As against estimated percentage of magma crystallized (fig. 2).

Two adjacent lower-zone olivine-gabbros, both at a structural height of 280 metres, contain 0.22 ppm As. Both these rocks are plagioclase (c. An_{60})–augite–olivine (c. Fo_{60}) orthocumulates (terminology from Wager, Brown, and Wadsworth, 1960), are reasonably representative of their horizon, and contain appreciable amounts of intercumulus (pore) material representing up to about 30 % of trapped liquid. It is thought likely that similar orthocumulates may also exist in the hidden zone (Wager, 1960), so that an arsenic content of 0.2–0.3 ppm may apply to these rocks also. Two marginal border rocks, a gabbro-picrite 4526 (40 m from the northern margin) and a coarse olivine-gabbro 4443 (65 m from the western margin), contain 0.23 and 0.28 ppm As respectively. These rocks are interpreted as having been formed by the gravitative accumulation of early olivine, pyroxene, and plagioclase. In this respect, they may approximate in composition to some of the early rocks of the hidden layered series (Wager, 1960) and the position of the early part of the distribution curve for arsenic in the rocks is based on these two values.

The gabbros of the middle zone (800–1575 m) contain very little intercumulus material and are adcumulates of plagioclase (An_{53} – An_{44}), augite, ilmenite, and titaniferous magnetite. They are almost olivine free,

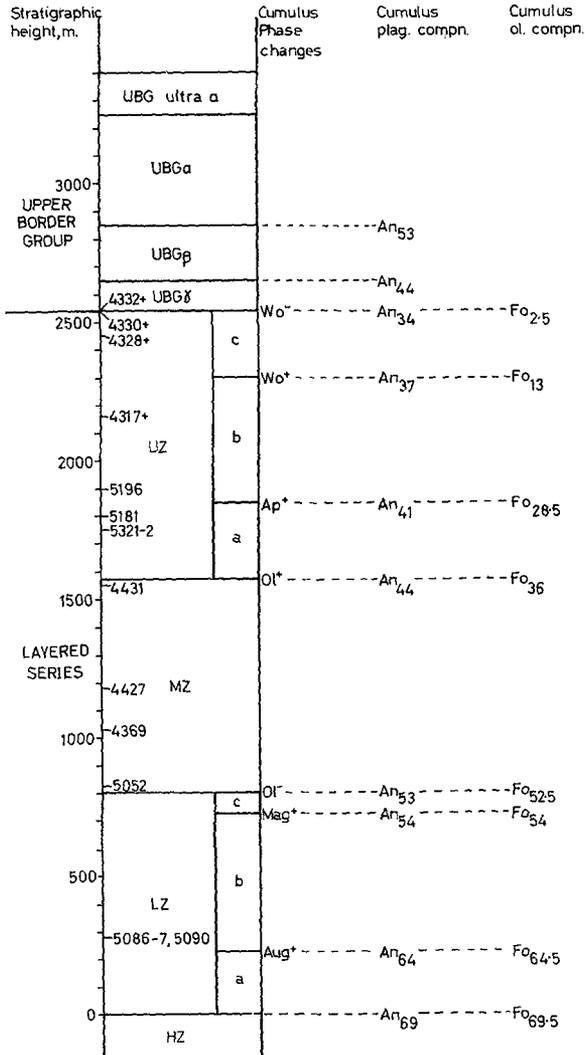


FIG. 1. The main variation in occurrence and composition of the mineral phases with the structural heights of the rocks analysed for As and Sb.

generally containing less than 3 % by weight, and much of this is in the form of reaction rims between augite and ore crystals. The lowest arsenic content of all the rocks analysed is found in the two early-middle-gabbros 5052 (825 m) and 4369 (1025 m), with 0.091 and 0.066 ppm As respectively. These two samples are petrographically fairly representative of the middle zone.

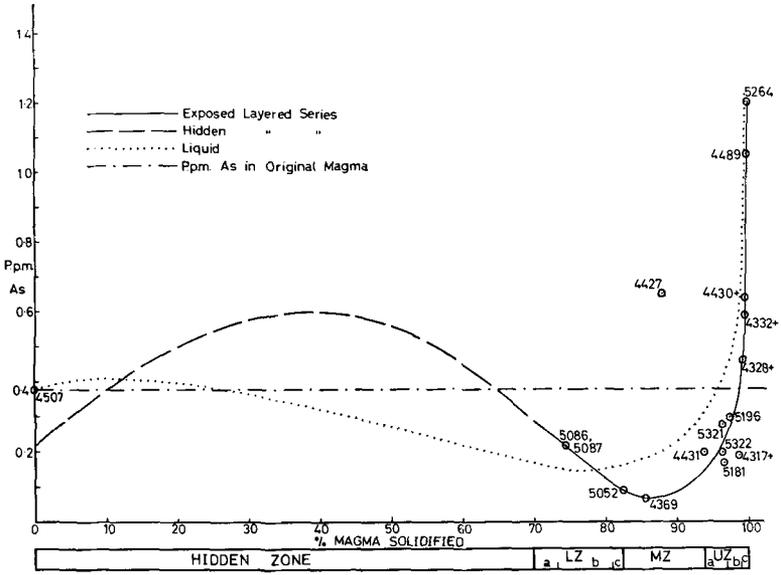


FIG. 2. The variation of arsenic in the Skaergaard rocks and successive liquids.

A surprisingly high arsenic content, 0.65 ppm, is found in the rock 4427, which, at 1180 m, is but 155 m above 4369. This is the only result falling far from the smooth curve that can be drawn through the results for the whole of the exposed layered series, and there seems to be no really satisfactory explanation for this anomalously high value. The rock is similar to 5052 and 4369, except that it is somewhat more melanocratic, the olivine reaction rims around magnetite are more frequent and more pronounced, and there may have been rather more trapped liquid (but certainly not more than a few per cent). As can be seen from the results of the individual mineral analyses (table II), the dark minerals do not themselves generally contain sufficient arsenic to cause such a sudden increase. Indeed, very melanocratic rocks later in the sequence (5322 and 5196) carry similar amounts of arsenic to their

TABLE I. Arsenic and antimony in the Skaergaard rocks

Rock no., classification, and type	Field locality	As content of replicates, ppm	Ave. As content, ppm	Sb content of replicates, ppm	Ave. Sb content, ppm
<i>Late Differentiates</i>					
3058 T.Gr. } Transgressive	Tinden Hill	0.25, 0.26, 0.25	0.25	0.52, 0.44, 0.36	0.44
5259 T.Gr. } acid granophyres	"	0.49, 0.50	0.50	0.039, 0.095, 0.10	0.096
5260 T.Gr. }	"	0.41, 0.31, 0.23, 0.49, 0.43, 0.36	0.36	0.16, 0.16, 0.15	0.16
4515 T.Gr. } Acid granophyre	"	0.28, 0.33, 0.29	0.30	0.12, 0.07, 0.09	0.09
4439 UBG } Early trans. granophyre	"	1.06, 1.03	1.05	0.12, 0.12	0.12
5264 UBG-y } Melanogranophyre	"	1.21, 1.17, 1.26	1.21	—	—
4332+ UBG-y } "	"	0.57, 0.61	0.59	0.19, 0.22	0.21
<i>Layered Series</i>					
	Structural Height (m)	% Magma Solidified			
4330+ UzC } Ferrodiorite	2540	99.5	0.64	0.14, 0.089, 0.096	0.10
4328+ UzC } Fayalite ferrodiorite	2450	99.3	0.46	0.19, 0.19	0.19
4317+ UzB } Ferrodiorite	2160	98.7	0.19	0.031, 0.025, 0.029	0.028
5196 UzB } Hornomolite ferrodiorite, melano.	1900	97.4	0.30	0.23, 0.21, 0.17, 0.16	0.19
5181 UzA } " " "	1800	96.6	0.17	0.17, 0.18, 0.17	0.17
3322 UzA } " " melano.	1750	96.3	0.20	0.030, 0.029	0.030
5321 UzA } " " leuco.	1750	96.3	0.28	—	—
4431 MZ } Middle gabbro, olivine free	1550	93.8	0.20	0.16, 0.20	0.18
4427 MZ } " " " "	1180	88.0	0.65	0.16, 0.16	0.16
4369 MZ } " " " " "	1025	85.7	0.066	0.022, 0.025, 0.029	0.025
5052 MZ } " " "	825	82.5	0.091	{*(a) 0.042, 0.026, 0.033}	0.025
5097 LZb } Lower olivine gabbro, ave.	280	74.3	0.22	{*(b) 0.017, 0.014, 0.016}	0.039
5086 LZb } " " "	280	74.3	0.22	0.13, 0.15	0.14
5090 LZb } Inclusions in plag. cumulate	(280)	(74.3)	0.10	0.053	0.053
<i>Marginal Rocks</i>					
4507 SBG } Chilled olivine gabbro	1 m from S. margin	{*(a) 0.30, 0.30}	0.38	{*(a) 0.13, 0.13}	0.16
4526 NBG } Gabbro-plitte	40 m from N. margin	{*(b) 0.45, 0.47}	0.23	{*(b) 0.20, 0.16, 0.18}	0.24
4443 WBG } Coarse olivine gabbro	65 m from W. margin	0.22, 0.24	0.27	0.24, 0.26, 0.22, 0.22	0.24
5076 WBG } Perpendicular feldspar rock	W. border group	0.27, 0.28	0.27	0.043, 0.050	0.046
		0.08, 0.10, 0.11, 0.13, 0.12	0.11	0.034, 0.028, 0.031	0.031

* (a) and (b) represent different powder samples of the same rock.

leucocratic (5321) and average (5181) neighbours. However, evidence from the mineral analysis of three other rocks and from the differentiated series as a whole, shows that arsenic concentrates quite strongly in the residual liquids and in some secondary minerals. Thus, the high concentration of arsenic in the rock 4427 could be due to very little arsenic having been removed from the magma by the early-middle-gabbros (5052 and 4369), because of their containing virtually no pore material and hence very little late-stage or secondary mineral formation, with the result that the next higher rocks to show these features would be much richer in arsenic.

Rock 4431 (1550 m), from near the top of the middle zone, contains 0.20 ppm As and thus reverts to the smooth variation pattern.

At 1575 m in the layered series, olivine once again becomes a primary (cumulus) phase and the rocks are classified as upper-zone ferrodiorites (Wager and Vincent, 1962). In the first upper zone (UZa, 1575–1850 m), plagioclase (An_{44} – An_{41}), augite, olivine ($Fe_{0.36}$ – $Fe_{0.28.5}$), and ore minerals constitute the main primary minerals. At 1850 m, primary apatite appears and the UZb extends from 1850–2300 m. The rocks of Upper Zone c (2300–2540 m) are characterized by the occurrence of ferrowollastonite, now inverted to ferrohedenbergite. Throughout the upper zone, small amounts (up to 0.4 % by weight) of copper-rich sulphide minerals are important accessories in some of the rocks, while a fairly narrow band at about 2450 m contains larger amounts (up to 2 % by weight) of iron sulphides (Wager, Vincent, and Smales, 1957).

A leucocratic rock (5321) from a height of 1750 m in UZa contains 0.28 ppm As, while a melanocratic rock (5322) from the same horizon has 0.20 ppm and average material (5181) from 1800 m 0.17 ppm. UZb rocks continue the slight upward trend in arsenic content, with 0.30 ppm in a melanocratic band (5196, 1900 m) and 0.19 ppm in a more average rock (4317+, 2160 m). The increase in arsenic becomes much more apparent in UZc, where 4328+ (2450 m) and 4330+ (2540 m) contain 0.46 and 0.64 ppm As respectively.

This steep rise is maintained in the upper border group (UBG) of the late differentiates. These UBG rocks are intermediate in character and have been classified as melanogranophyres. One of the earliest (4332+) contains 0.59 ppm As, while a later example (5264) has 1.21 ppm, more than any other analysed rock from the intrusion. The latest rocks of the UBG grade upwards into a transgressive granophyre, supposedly produced by filter-press action. One example (4489) contained 1.05 ppm As.

The latest rocks of the whole complex are found in a transgressive acid granophyre sheet (the Tinden Sill), the last product of the filter press process and probably also involving some assimilated acid gneiss of the basement complex. Various specimens (4515, 5260, 5259, and 3058) from this sill contain between 0.25 and 0.50 ppm As, which is appreciably lower than in the rocks of the UBG and is possibly due to the incorporation of country rock rather than a genuine decline of arsenic content in the magma. Indeed, one rock (5090, from the lower zone of the layered series) with country rock inclusions in the plagioclase cumulate contains only 0.11 ppm As. However, it is not impossible that some arsenic may have escaped with volatiles at this stage, and a few of the acid granophyres, e.g. 4489, do show evidence of slight hydrothermal alteration.

Sporadic patches of iron sulphides appear in the UBG, but the amount is generally only about 0.01 % (Wager, Vincent, and Smales, 1957). The transgressive acid granophyres may contain up to about 1 % of sulphide minerals. It was thought that arsenic, well known as a chalcophile element, would in all probability be concentrated in these sulphides. However, due to the difficulty of separating the minute sulphide globules from the enclosing rocks, it only proved possible to obtain sufficient material (pyrrhotine) for analysis from one rock (5275), and this contained about 6 ppm of arsenic. Thus, it seems that, while arsenic is relatively enriched in the sulphide phase, only a minor percentage of the arsenic in the whole rock is in fact contained in accessory sulphides. This conclusion is confirmed by the rocks of the layered series, where the arsenic content of material with a few tenths per cent of sulphides falls on the same distribution curve as material with virtually no sulphides (e.g. rocks 4330+, 4328+, 5196, 5181, and 5322 contain appreciably more sulphide than 4317+, 5321, and 4431).

Four of the marginal border rocks were analysed for arsenic. The most significant is the chilled marginal gabbro 4507, taken at one metre from the contact with the basalts at the southern margin of the intrusion. This rock is taken to represent perhaps the best estimate of the composition of the original 300 km³ of magma from which the rocks crystallized, and it contains 0.38 ppm As. The composition of this rock is one of the three factors used to estimate the overall composition of the hidden zone (70 % of the intrusion; Wager, 1960). The other two factors are the estimated relative volumes of the exposed and hidden parts of the intrusion, and the overall composition of the exposed rocks. Fig. 2 shows the estimated distribution of arsenic throughout the hidden

zone, assuming a smooth variation and also that, during the formation of the layered series, the crystallizing system remained closed with respect to arsenic. The justification for this assumption is that there is no major hydrothermal stage associated with the intrusion, and that only two of the analysed rocks (5052 and 4369) contain very much less arsenic than the original magma (as represented by the chilled marginal gabbro 4507).

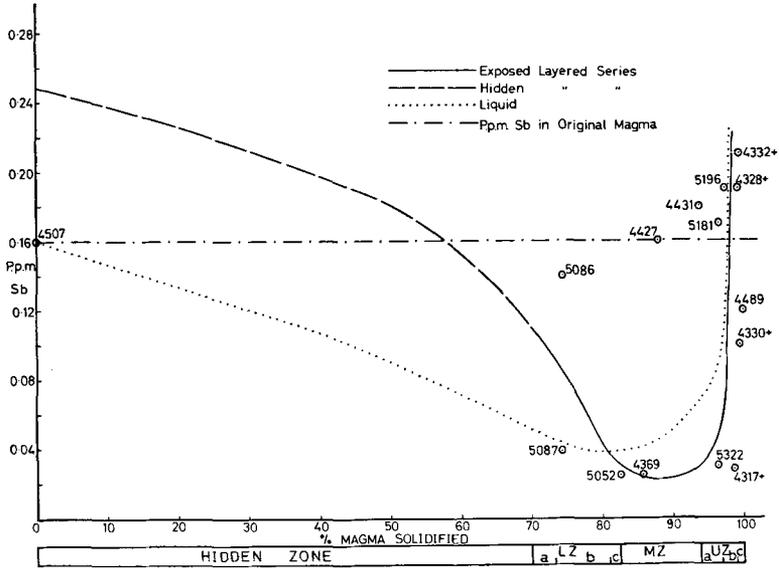


FIG. 3. The variation of antimony in the Skaergaard rocks and successive liquids.

Two of the other marginal border rocks, the gabbro-picrite (4526) and a coarse olivine-gabbro (4443) have already been discussed in connexion with the likely composition of the hidden layered series. The rock 5076, from the outer part of the western marginal border group, is an olivine-gabbro petrographically similar to the chilled margin 4507, except that it has lath-shaped crystals of plagioclase oriented with their length at right angles to the nearby intrusion wall. It has the low arsenic content of 0.09 ppm.

Antimony in the rocks. The antimony contents of the Skaergaard rocks examined in this work are listed in table I, and fig. 3 represents the variation in antimony content of the rocks and of the residual liquid with progressive crystallization. The idealized distribution of antimony

throughout the intrusion, as depicted by the smooth curve, is similar to that of arsenic, except for the estimated distribution in the early parts of the hidden layered series. In addition, the rocks 5086, 4427, and 4431 seem to have anomalously high antimony contents.

The two lower-zone olivine-gabbros 5086 and 5087 differ in antimony content, 0.14 and 0.039 ppm Sb respectively, by a factor of 3, although they are both from the same differentiation stage in the intrusion (structural height 280 m), do not differ greatly in mineralogical composition, and are identical in arsenic concentration. These two rocks, however, have also been found to differ unexpectedly in their gold and cadmium contents (Vincent and Crocket, 1960; Vincent and Bilefield, 1960), although in the latter case it is 5087 that is high. Thus, it seems that this pair of very similar rocks from the same structural height in the intrusion show some appreciable and not readily explicable differences in trace element content.

In addition to an unexpectedly high concentration of arsenic, the middle-gabbro 4427 (1180 m) also has an unaccountably high antimony content, 0.16 ppm. Another middle-gabbro, 4431 (1550 m), from near the top of the middle zone, contains 0.18 ppm Sb but the amount of arsenic reverts to the lower level of the two early-middle-gabbros 5052 and 4369. It is not possible to assess the significance of these two high values for antimony, but it seems fairly certain that the behaviour of antimony during fractionation of the Skaergaard magma does not follow such a simple pattern as that of arsenic.

In the latest, upper zone, rocks of the layered series the antimony concentration increased sharply as the last 5 % of the liquid crystallized, thus following the marked trend shown by arsenic. The transgressive acid granophyres tend to show lower concentrations of antimony than the UBG rocks, as is the case with arsenic.

The two most important marginal border rocks, the chilled gabbro 4507 and the gabbro-picrite 4526, contain 0.16 and 0.24 ppm Sb respectively.

Arsenic in the minerals. The results for arsenic in the rocks suggest that this element shows no very marked preference for light or dark minerals, and this is confirmed by analyses for arsenic made on the constituent minerals separated from rocks at three different horizons of the intrusion. In all but two cases, the analysed minerals were > 99 % pure, and the results are given in table II.

In an attempt to obtain a semi-quantitative estimate of the amount of arsenic contained in the interstitial material of these three rocks,

analyses were also made of the < 200 -mesh dust produced when the rocks were first crushed prior to mineral separation. The whole rock samples were first reduced to < 40 mesh in a steel percussion mortar, and the fine dust removed by sieving through 200-mesh nylon cloth.

The results in table II show that the concentrations of arsenic in the various mineral phases are mainly of the same order of magnitude,

TABLE II. Arsenic in constituent minerals of the rocks 5181, 5052, and 5086

Rock no. and description	Mineral	Modal %		As content
		by weight	As content, ppm	contributed to rock, ppm
5181 (1800 m), hortonolite ferrodiorite	Plagioclase, An_{40}	54.4	0.019, 0.019	0.0103
	Pyroxene, $Ca_{27}Mg_{31}Fe_{31}$	21.9	0.064, 0.068, 0.067	0.0145
	Titaniferous magnetite	4.5	0.21, 0.20, 0.21	0.0095
	Ilmenite	5.5	0.11, 0.09, 0.12	0.0061
	Olivine, Fo_{40}	13.2	0.16, 0.19, 0.15	0.0224
				$\Sigma = 0.0628$
	Whole rock (average)		0.17	
	Fine dust from mineral separation		0.24	
5052 (825 m), middle gabbro	Plagioclase, An_{50}	42.2	0.027, 0.026, 0.029	0.0114
	Pyroxene, $Ca_{27}Mg_{31}Fe_{23}$	29.4	0.049, 0.047	0.0141
	Titaniferous magnetite	9.5	0.083, 0.087, 0.098	0.0086
	Ilmenite	14.6	0.019, 0.023	0.0031
	Olivine, Fo_{53}	3.3	0.094, 0.088, 0.077	0.0029
				$\Sigma = 0.0401$
	Whole rock (average)		0.091	
	Fine dust		0.11	
5086 (280 m), lower olivine- gabbro	Plagioclase, An_{62}	46.1	0.021, 0.021	0.0097
	Pyroxene, $Ca_{17}Mg_{31}Fe_{19}$	25.6	0.097, 0.112, 0.112	0.0256
	Titaniferous magnetite	1.3	3.4, 3.8	0.0648
	Olivine, Fo_{63}	25.7	0.069, 0.080	0.0193
				$\Sigma = 0.1194$
	Whole rock (average)		0.22	
	Fine dust		0.29	

except for the magnetite, ilmenite, and olivine from the latest of the three rocks (5181) and the magnetite of the earliest rock (5086). Progressive differentiation seems to have no significant effect on the arsenic content of plagioclase and augite, but it seems that increasing differentiation causes an increase in the arsenic content of magnetite, ilmenite, and olivine. The occurrence of 3.6 ppm of arsenic in the magnetite from the rock 5086 is probably due to the fact that the magnetite in this rock is intercumulus, having been formed by crystallization from a comparatively large amount (30 %) of trapped liquid. In such a case it is likely that some of the arsenic accumulating in the liquid was incorporated into the small amount of late magnetite, behaviour that is akin to the

increased concentration of arsenic in late-stage rocks and minerals. Similar behaviour is expected in the hidden layered rocks, which probably contain small amounts of intercumulus magnetite formed from 30–40 % of trapped liquid.

It was considered possible that there might be some correlation between arsenic and phosphorus, due to phosphate–arsenate isomorphism, in the rocks above a structural height of 1850 m, where apatite becomes a primary mineral phase. However, a sample of apatite extracted from the rock 4312 (1920 m) contains 0.40 ppm of arsenic, which is of the same order of magnitude as the arsenic content of the whole rocks from this horizon. In addition, the distribution of arsenic in the rocks is quite different from that of phosphorus (Wager, 1960), so that there seems in the present case to be no correlation between the two elements.

It was remarked earlier that there are small amounts of sulphide minerals present in some of the later rocks. One sample of pyrrhotine (from the granophyre 5275) contained about 6 ppm of arsenic, indicating an expected preference of arsenic for the sulphide phase. Thus, it is likely that arsenic is relatively enriched in all of the sulphides but the total amount carried by the small modal percentages of sulphides in these rocks is insignificant compared with that contained in the oxide and silicate minerals.

Table II shows that, in all three cases, the arsenic determined in the minerals is insufficient to account for the observed arsenic content of the whole rock. The amount accounted for ranges from 40 % in the rocks 5052 and 5181 to 54 % in 5086, which seems to concur with the results of leaching experiments carried out on various rocks by Onishi and Sandell (1955*a*). These authors estimate that about 50 % of the arsenic is in the interior of the silicate and oxide minerals, the remainder being in the interstitial material and the outer zones of crystals, much of which is usually lost during mineral separation. In the present work, the fine dusts collected prior to mineral separation all show a greater arsenic content than the whole rocks from which they are derived (table II). This may constitute somewhat more positive evidence that arsenic shows some concentration in trapped liquids, small amounts of reaction minerals, and possibly in the outer zones of primary mineral crystals.

Little is known about the presence of arsenic in the principal rock-forming minerals. Onishi and Sandell (1955*a*) consider a number of ways in which arsenic could enter silicate rocks and minerals, and mention the following as probably being the most important: As^{3+} , As^{5+} substituting

for Al^{3+} ; As^{3+} for Fe^{3+} and Ti^{4+} ; As^{5+} for Si^{4+} (ionic radii, Ahrens, 1952, As^{3+} 0.58, As^{5+} 0.46, Al^{3+} 0.51, Si^{4+} 0.42, Fe^{3+} 0.64, and Ti^{4+} 0.68 Å).

Onishi and Sandell assume that the amount of As^{5+} present in magmas is low, especially when the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ is high. However, experimental work on arsenic in silicate glasses shows that the pentavalent state is by far the predominant form in glass melts (Close, Shepherd, and Drummond, 1958; Baak, 1959) and thus it may be reasonable to assume that both valence states of arsenic are about equally important in magmas, even when $\text{Fe}^{2+}/\text{Fe}^{3+}$ is high. A rough oxidation-potential calculation for the Skaergaard magma, based on the ferrous-ferric iron ratio (Vincent and Crockett, 1960), gave a value of about 2 for the ratio $\text{As}^{5+}/\text{As}^{3+}$ in the magma at various stages of fractionation.

Consideration of ionic radii shows that arsenic can only enter the plagioclase structure by the substitution of As^{3+} or As^{5+} , or both, for Si^{4+} or Al^{3+} in tetrahedral sites, or As^{3+} for Al^{3+} in octahedral sites. As^{3+} is probably somewhat too large to form a tetrahedral complex similar to SiO_4^{4-} and AlO_4^{5-} , but As^{5+} readily exists as AsO_4^{3-} (AsO_4^{3-} is, like SiO_4^{4-} and AlO_4^{5-} , a network former (Ringwood, 1955)). However, the comparatively low concentrations of arsenic found in plagioclase leave little doubt that both the entry of As^{3+} into octahedral and As^{5+} into tetrahedral sites are unfavourable to the structure.

The pyroxenes analysed contain from 2 to 5 times as much arsenic as the plagioclase from the same rock, and this is probably due to the presence of a larger number of smaller cations in the structure. The acceptance into octahedral sites of such cations as Mg^{2+} , Al^{3+} , Fe^{3+} , and Ti^{4+} (radii 0.66, 0.51, 0.64, and 0.68 Å) may also provide an opportunity for the entry of As^{3+} (0.68 Å), in addition to some substitution of As^{5+} for Si^{4+} and Al^{3+} in tetrahedral sites.

The arsenic found in olivine, ilmenite, and magnetite probably results from a straightforward substitution of As^{3+} for Ti^{4+} and Fe^{3+} . In the case of olivine, there is also the possibility of some substitution of Si^{4+} by As^{5+} .

Thus we conclude that most of the arsenic present in rock-forming minerals is in the trivalent state, while there is a general tendency for it to concentrate, as AsO_4^{3-} or some other As^{5+} complex, in the residual solution.

Antimony in the minerals. In each of the three sets of Skaergaard minerals analysed, the sum of the amounts of antimony contributed to the rock by the minerals exceeds the concentration determined in the whole rock (table III). There is quite close agreement for the rock 5181,

but for 5051 and 5086 the discrepancy is by a factor of about 2. This may be due to contamination of mineral samples during separation (despite precautions), or it may not be significant because rock and mineral analyses were unfortunately made on different samples of the same rocks.

TABLE III. Antimony in constituent minerals of the rocks 5181, 5052, and 5086

Rock no.	Mineral	Sb content, ppm	Sb contributed to rock, ppm
5181	Plagioclase, An ₄₀	0.24, 0.23	0.1278
	Pyroxene, Ca ₃₅ Mg ₃₁ Fe ₃₁	0.11, 0.10	0.0230
	Titaniferous magnetite	0.088, 0.077	0.0045
	Ilmenite	0.27	0.0121
	Olivine, Fo ₄₀	0.19, 0.22	0.0271
			$\Sigma = 0.1945$
	Whole rock (average)	0.17	
	Fine dust	0.069	
5052	Plagioclase, An ₅₀	0.032	0.0135
	Pyroxene, Ca ₃₇ Mg ₄₁ Fe ₂₂	0.026	0.0076
	Titaniferous magnetite	0.023, 0.028	0.0024
	Ilmenite	0.13, 0.16	0.0212
	Olivine, Fo ₅₃	1.17	0.0386
			$\Sigma = 0.0833$
	Whole rock (average)	0.046	
	Fine dust	0.042	
5086	Plagioclase, An ₆₂	0.040, 0.032	0.0166
	Pyroxene, Ca ₄₇ Mg ₃₄ Fe ₁₉	0.029, 0.035	0.0081
	Titaniferous magnetite	0.11	0.0017
	Olivine, Fo ₆₃	1.32, 1.43	0.3500
			$\Sigma = 0.3764$
		Whole rock (average)	0.14
	Fine dust	0.12	

The fact that a similar effect is not apparent for arsenic may indicate that this element is more uniformly distributed within the rocks, which seems a reasonable assumption because arsenic, unlike antimony, shows no strong preference for any particular mineral. This difference in behaviour between the two elements may partly account for the closeness of arsenic in the analysed rocks to a smooth distribution curve, whereas the antimony contents of the rocks are more scattered.

For each of the three rocks 5086, 5052, and 5181 the antimony content of the fine dust, representing pore material and outer zone crystal material, is lower than that of the whole-rock, perhaps indicating that there is a tendency for antimony to enter into the primary minerals, rather than remain in the interstitial liquid like arsenic.

Despite the doubts expressed above, the following remarks on antimony in the minerals may be valid:

The most striking feature of the antimony content of the minerals analysed (table III) is that the amount of antimony in olivines seems to decrease steadily as differentiation causes a progressive change in olivine composition, from Fo_{70} to $\text{Fo}_{2.5}$, throughout the exposed layered series. There is apparently a marked preferential entry of antimony into early magnesian olivines. This effect is shown in table IV and may account for the relatively high antimony concentrations deduced for the hidden layered series (fig. 3), since it is likely that these rocks contain

TABLE IV. Apparent variation in Sb content with composition of olivine

Rock	Olivine composition	Average Sb content of olivine, ppm
5181	Fo_{46}	0.205
5052	Fo_{53}	1.17
5086	Fo_{63}	1.375

olivines even more forsterite-rich, Fo_{70} – Fo_{80} (Wager and Deer, 1939; Wager, 1960), than the earliest rocks of the exposed layered series.

Ilmenite appears to be the next most favourable host for antimony, presumably due to the straightforward substitution of Sb^{3+} for Fe^{2+} (ionic radii 0.76 and 0.74 Å respectively). This substitution also offers an explanation of the small amounts of antimony found in pyroxene and magnetite. In the case of plagioclase, it is likely that Sb^{3+} or Sb^{5+} , like Fe^{3+} , enters octahedral sites normally occupied by Al^{3+} .

There would seem to be little doubt that, in magmas, the ratio $\text{Sb}^{5+}/\text{Sb}^{3+}$ is fairly small. In silicate glass melts it varies between 0.06 and 0.3 (Close, Shepherd, and Drummond, 1958), and the rough oxidation potential calculation for the Skaergaard magma at various stages gives values between 0.05 and 0.2. Thus, perhaps, some of the antimony in magmas is in the pentavalent state while the larger part is trivalent. The ionic radii and electronegativities of Sb^{5+} and Fe^{3+} are similar (ionic radii 0.62, 0.68 Å, electronegativities both 1.6–1.7), so they may possibly occupy similar sites in rock-forming minerals.

Very little is known about the behaviour of antimony during magmatic crystallization, except that it tends to become concentrated in residual granitic magmas and appears in ore deposits related to them (Rankama and Sahama, 1950). This behaviour is in accordance with considerations of electronegativities and ionic radii (Ringwood, 1955),

and with the increase observed in the late-stage Skaergaard rocks. Thus, the high antimony content of the early magnesian olivines, and that deduced for the early rocks of Skaergaard would seem to represent anomalous behaviour, unless the early removal of some antimony from the liquid does not necessarily preclude a later enrichment in more acid liquids.

Ni, V, and Cr are largely removed from magmas at a fairly early stage, but sometimes tend to become concentrated in later residual acid liquids. Nickel shows a strong tendency to enter olivines and pyroxenes, and the nickel content of the Skaergaard magma reached a very low level at an intermediate stage of differentiation (Wager and Mitchell, 1951; Wager, Vincent, and Smales, 1957). In the case of Skaergaard, differentiation later gave rise to a small amount of granophyre and the nickel content began to increase again. Cr, V, and Sb show similar behaviour (fig. 4).

Ringwood (1955) divides ions into three classes, according to their ionic potentials and behaviour in magmas. The two main groups are termed network-forming (e.g. Si^{4+} , Al^{3+}) and network-modifying (e.g. Na^+ , Ca^{2+}), and the third group consists of ions of intermediate size (e.g. Fe^{2+} , Mg^{2+} , Fe^{3+}), which act as network-formers and modifiers. Ni^{2+} , Cr^{3+} , V^{3+} , and Sb^{3+} fall into this intermediate category, and their behaviour in magmas will depend on whether they exist as free ions or as complex ions.

In a basic magma such as Skaergaard, the initial concentration of volatiles is probably quite low and, according to the principles discussed by Ringwood, the intermediate ions would exist as free ions. As crystallization proceeds, there is probably an increase in the concentration of volatiles in the remaining liquid. Thus, it would be possible for the intermediate ions to change from being network-modifiers to network-formers, and hence become concentrated in the residual liquid. The present work on the Skaergaard intrusion seems to provide direct evidence of the dual behaviour of antimony during differentiation. Such behaviour may partly account for some of the observed discrepancies between the antimony content of some Skaergaard rocks and the idealized distribution of antimony throughout the intrusion (fig. 3).

As/Sb ratios for the rocks and successive liquids, from figs. 2 and 3, show that As and Sb follow each other very closely during differentiation, but there is a steady concentration in the liquid of As relative to Sb. For the liquids the ratio changes steadily from 2.4 to 5.5, and for the rocks from 0.9 to 5.1.

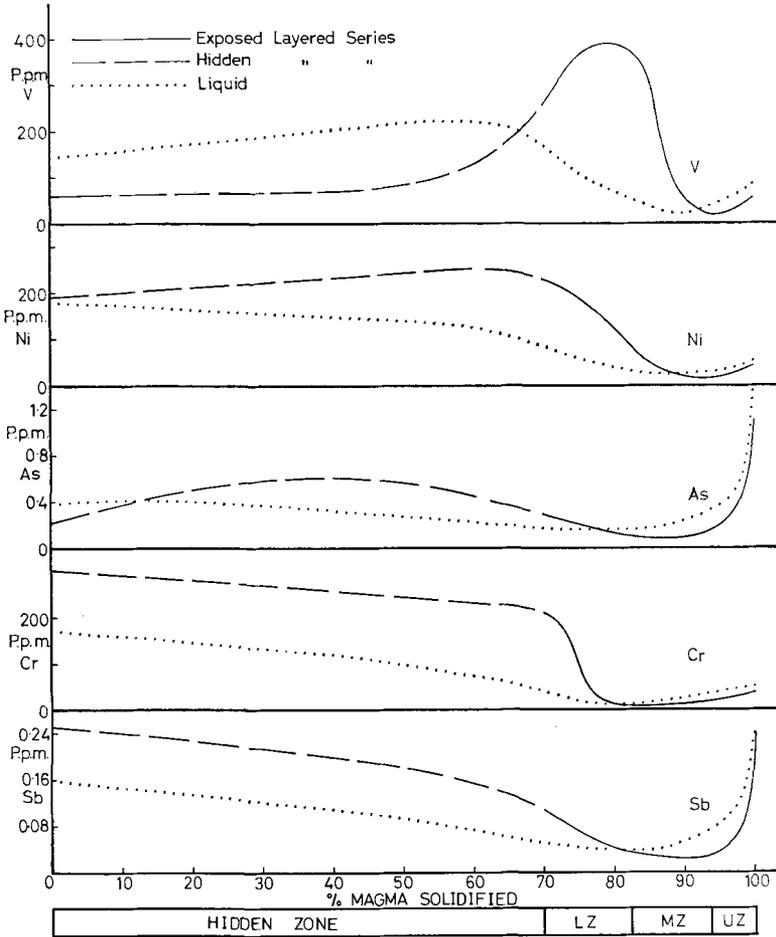


FIG. 4. The variations of V, Ni, As, Cr, and Sb in the Skaergaard rocks and successive liquids.

The presence of small amounts of sulphides, relatively enriched in As, in the rocks probably contributes to the observed deficiency of As in the separated minerals compared with the whole rock (pp. 98-99).

The partition coefficients for As and Sb between the various minerals and the estimated liquid from which they crystallized have been calculated from figs. 2 and 3 and tables II and III. For As the coefficients

are all < 0.5 except for the magnetite 5086, confirming that As prefers to remain in the liquid. Sb shows no marked preference for solid or liquid phase (coefficients close to 1), except in the olivines 5086 and 5052.

As and Sb in chondritic meteorites

The results of analyses for arsenic and antimony made on four stone meteorites (table V) are somewhat lower than the composite values, 2.2 and 0.1 ppm for As and Sb respectively, obtained by Onishi and Sandell (1955). Three of the four chondrites analysed in the present

TABLE V. As and Sb in chondritic meteorites

Meteorite	As content, ppm	Sb content, ppm	As/Sb
Bjurböle	0.78, 0.79	0.062, 0.065	12.4
Château Renard	0.57, 0.65, 0.71	0.084, 0.065	8.5
Ochansk	1.44, 1.43	0.13, 0.14	10.6
Chandrakapur	0.75, 0.71	0.076, 0.069	9.9
Ave. chondrite values of Onishi and Sandell (1955)	2.2	0.1	22

work contain very similar amounts of As and Sb, while the Ochansk chondrite contains about twice as much of each element. This may possibly be accounted for by the fact that this meteorite contains about 18 % of metal phase, whereas the other three contain only 7–8 %. It is known (Onishi and Sandell, 1955) that the metal phase of chondrites generally contains much higher concentrations of As and Sb than the silicate phase. The As/Sb ratio found in our work is fairly constant at about 10, compared with the value of 22 found by Onishi and Sandell.

As and Sb in the standard rocks G-1 and W-1

Table VI compares the results obtained in the present work with earlier analyses. There is little doubt that the neutron activation results are preferable to those obtained by colorimetry. The most interesting aspect of the present study is the small systematic differences in As and Sb content of different bottles of G-1 and W-1 powders. Indications of the inhomogeneity of these two powders with respect to some trace elements have already been recorded by Fleischer and Stevens (1962).

TABLE VI. Summary of As and Sb determinations in G-1 and W-1

Rock	As content, ppm	Ave. As, ppm	Sb content, ppm	Ave. Sb, ppm	Method
G-1	1.0, 1.0	1.0	—	—	Colorimetric (1)
W-1	1.8, 1.8	1.8	—	—	
G-1	—	—	Individual values not given	0.6	Colorimetric (2), Ave. of 4.
W-1	—	—		1.2	
G-1	0.64, 0.67, 0.69	0.67	0.20, 0.30, 0.34	0.28	Neutron activation (3)
W-1	1.9, 2.2, 2.4	2.2	0.74, 1.0, 1.1	0.95	
G-1 (a)	0.83, 0.81, 0.82, 0.83	0.75	0.37, 0.36, 0.37, 0.38	0.30	Neutron activation, present work.
G-1 (b)	0.70, 0.70, 0.62, 0.73				
W-1 (a)	2.55, 2.49, 2.50, 2.58	2.38	1.2, 1.0, 1.1, 1.2, 0.97, 1.0	1.03	
W-1 (b)	2.14, 2.25, 2.34, 2.23				

(a) and (b) signify different bottles of G-1 and W-1.

(1) Onishi and Sandell, 1960.

(2) Ward and Laikin, 1954.

(3) Hamaguchi *et al.*, 1961.

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