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A Comparative Study of the Geochemistry of Arsenic, Antimony and Bismuth in Minerals from a Fractionated Sequence

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Abstract : A comparative study of the group V elements As, Sb, and Bi in minerals from a complete fractionation sequence as exemplified by the Skaergaard intrusion reveals that their geochemical behaviour is governed chiefly by their chemistry. Arsenic shows a predominance of the As^{5+} ion in the magma. In the minerals, it exists both as As^{3+} and As^{5+} substituting for other cations of suitable size and charge. The tendency of arsenic to form complex oxyions enables it to act as a network former in silicates. It acts as a network modifier when free ions are formed. This dual behaviour characterizes the geochemistry of arsenic. Antimony on the other hand shows a $\frac{Sb^{5+}}{Sb^{3+}}$ ratio varying from 0.05 to 0.2 indicating the predominance of the Sb^{3+} ion. It is very likely that it is mainly the Sb^{3+} ion which substitutes for major element cations of similar ionic radius even though some pentavalent antimony may form complex ions and become enriched in the residual liquid. The last of the group V elements, bismuth, shows no Bi^{5+} ion in nature, its geochemistry being entirely that of the Bi^{3+} ion. Bismuth prefers to enter the oxide minerals such as magnetite and ilmenite as against the silicates, and substitutes mainly for the Fe^{2+} ion. Accordingly, bismuth silicate minerals are extremely rare while bismuth oxide minerals are common.

1. Introduction

The geochemistry of the group V elements As, Sb and Bi is not well known due to the dearth of information regarding their distribution in rocks and minerals. Much of the earlier data obtained by colorimetric, polarographic and spectrographic techniques,[2,3,4,13,16,19] can be considered as only being semi-quantitative since the detection limits of these techniques for As, Sb and Bi are relatively higher when compared to their abundance in rocks and minerals. Very few analyses by the precise and highly sensitive analytical techniques such as neutron activation analysis and isotope dilution analysis have been made.[6,8,11,12,17,18]

This work deals with a comparative study of the group V elements in the minerals of the Skaergaard intrusion of East Greenland (Figure 1) by far the best testing grounds for theories on trace element behaviour.[21] Since the publication of the classic paper on the distribution of trace elements in the Skaergaard intrusion by Wager and Mitchell,[22] which included the study of 18 trace elements, more work on the geochemical distribution of some elements not hitherto studied has been carried out. A total of more than 60 elements have been now studied from the point of view of their geochemical distribution, thereby making the Skaergaard intrusion the best documented layered igneous complex. This study highlights the behaviour of As, Sb and Bi in the minerals as influenced by their chemical properties.

2. Experimental

2.1 Arsenic and Antimony

As and Sb in the Skaergaard samples have been determined by Esson *et al.*[8] using modifications of neutron activation methods.[17,18] Briefly, the procedure is as follows:—

100 mg portions of the powdered rocks and minerals are irradiated in a nuclear reactor for 3 days at a flux of about 10^{10} neutrons/cm^2 sec along with 10 mg portions of As_2O_3 and 0.1 g to 0.2 g portions of a dilute Sb solution (10 μg Sb/g of solution) to serve as standards. After irradiation, the samples together with 50 mg amounts of As_2O_3 and Sb_2O_3 carriers are decomposed by sintering with 2 g Na_2O_2 in nickel crucibles at 490°C ± 10°C. The samples and standards are then subjected to a chemical separation process,[17] finally the As and Sb being precipitated as sulphides using thioacetamide. The activities of the final precipitates are measured and the radiochemical purity checked by decay curves.

2.2 Bismuth

Bismuth in the Skaergaard samples were determined by Dissanayake,[6] using sub-stoichiometric isotope dilution analysis.[10,15]

Approximately 100 mg samples are decomposed with a HF—$HClO_4$ mixture spiked with Bi^{207} tracer. The bismuth is converted to the iodide and extracted with methyl isobutyl ketone. The extract is washed with acidiodide and the bismuth brought into the aqueous phase before being complexed with a known sub-stoichiometric amount of EDTA. The excess bismuth is then extracted as the iodide and the Bi^{207} in the aqueous phase EDTA complex counted and the specific activity determined. The bismuth contents of the samples are derived using a calibration curve obtained by carrying standard bismuth solutions through the same procedure as the samples.

3. Results and Discussion

3.1 The Chemistry of As, Sb and Bi

Before considering the comparative behaviour of As, Sb and Bi, it would be profitable to outline some of their more important chemical properties as they could influence the gross geochemical behaviour (Table 1).

From the above table of properties it can be seen that while arsenic and antimony form the M^{5+} ion, the Bi^{5+} ion is not known in nature. The tendency to form compounds with electropositive elements decreases markedly from arsenic to bismuth. Similarly, the covalent nature of bonds decreases down the group with bismuth showing increased cationic behaviour. In the +5 state all three elements are predominantly non-metallic and acidic but as this state is less readily attained as

the atomic weight increases from As to Bi, there is a marked decrease in the acidic character down the group as shown by the fact that bismuth forms the most basic compounds. The tendency to form oxyanions decreases from As to Bi with the latter forming no oxyanions in nature.

TABLE 1. Chemical data for arsenic, antimony and bismuth.

	As	Sb	Bi
Outer electronic configuration	$3d^{10}\ 4s^2\ 4p^3$	$4d^{10}\ 5s^2\ 5p^3$	$5d^{10}\ 6s^2\ 6p^3$
Sum of the first three ionization potentials ev	59.0	52.3	52.0
Electronegativity	2.20	1.82	1.67
Ionic radii[24]	As^{5+} (0.42°A)	Sb^{3+} (0.85°A) Sb^{5+} (0.69°A)	Bi^{3+} (1.10°A)
Covalent radii (for trivalent type)	1.21	1.41	1.52
Main oxidation states	+3 +5	+3 +5	+3
Oxides formed	As_4O_6, As_2O_5	Sb_4O_6, Sb_2O_5	Bi_2O_3
Heat of vaporization kgcal/g atom	7.75	46.6	42.7

3.2 The behaviour of As, Sb and Bi in the Skaergaard fractionation

Figure 2 shows the variation of As, Sb and Bi during fractionation. Arsenic shows a marked increase in the last stages of the fractionation sequence indicating its tendency to remain preferentially in the liquid. Antimony and bismuth, too, show somewhat similar curves even though the concentration of arsenic relative to antimony changes from about 1 to 5 during progressive fractionation. Bismuth, on the other hand, does not show an enrichment in the last stages of fractionation as arsenic, even though it is greater than that of antimony. This relative variation of the three elements during increasing solidification of the magma is illustrated in Figure 2.

It can be seen that both liquid and solid trends are very similar. The liquid trend observed for As, Sb and Bi shows an order of enrichment as follows :-

0% to 40% solidification : As > Bi > Sb
40% to 80% solidification : Bi > Sb > As
80% to 100% solidification : As > Sb > Bi

Figure 1 shows the minerals present and their compositions in the fractionation sequence. The early liquid is rich in Sb and as stated by Esson *et al.*,[8] it becomes concentrated in the early magnesian olivines and the amount of antimony in the olivines decreases as differentiation causes a progressive change in the olivine composition from Fo_{70} to Fo_2. In the case of bismuth, there seems to be very little tendency to enter the early formed minerals.

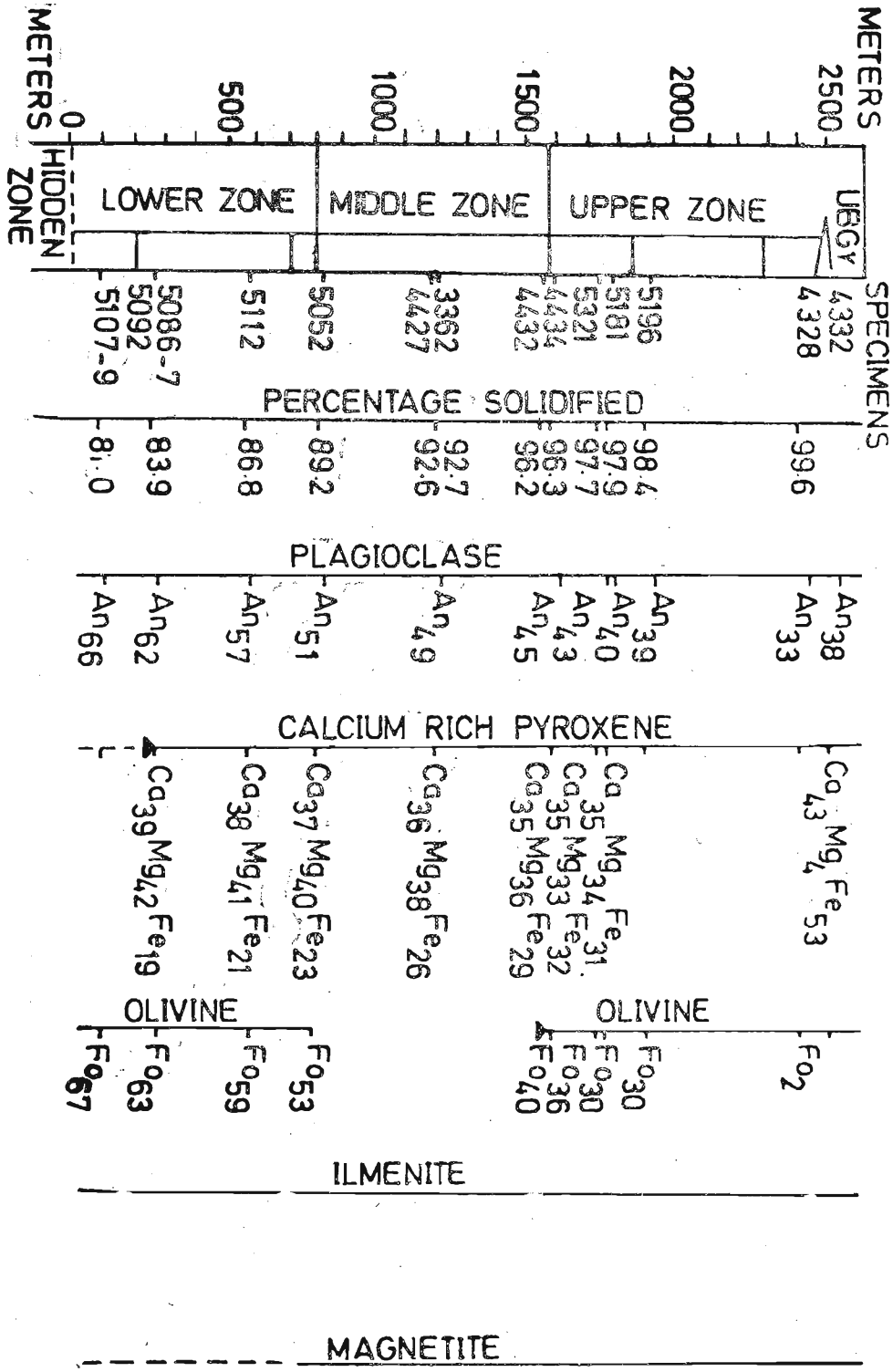

Figure 1. Minerals present in the various rocks of the Layered Series of the Skaergaard ntrusion. Discontinuous vertical lines relate to intercumulus minerals or those of indeterminate status.

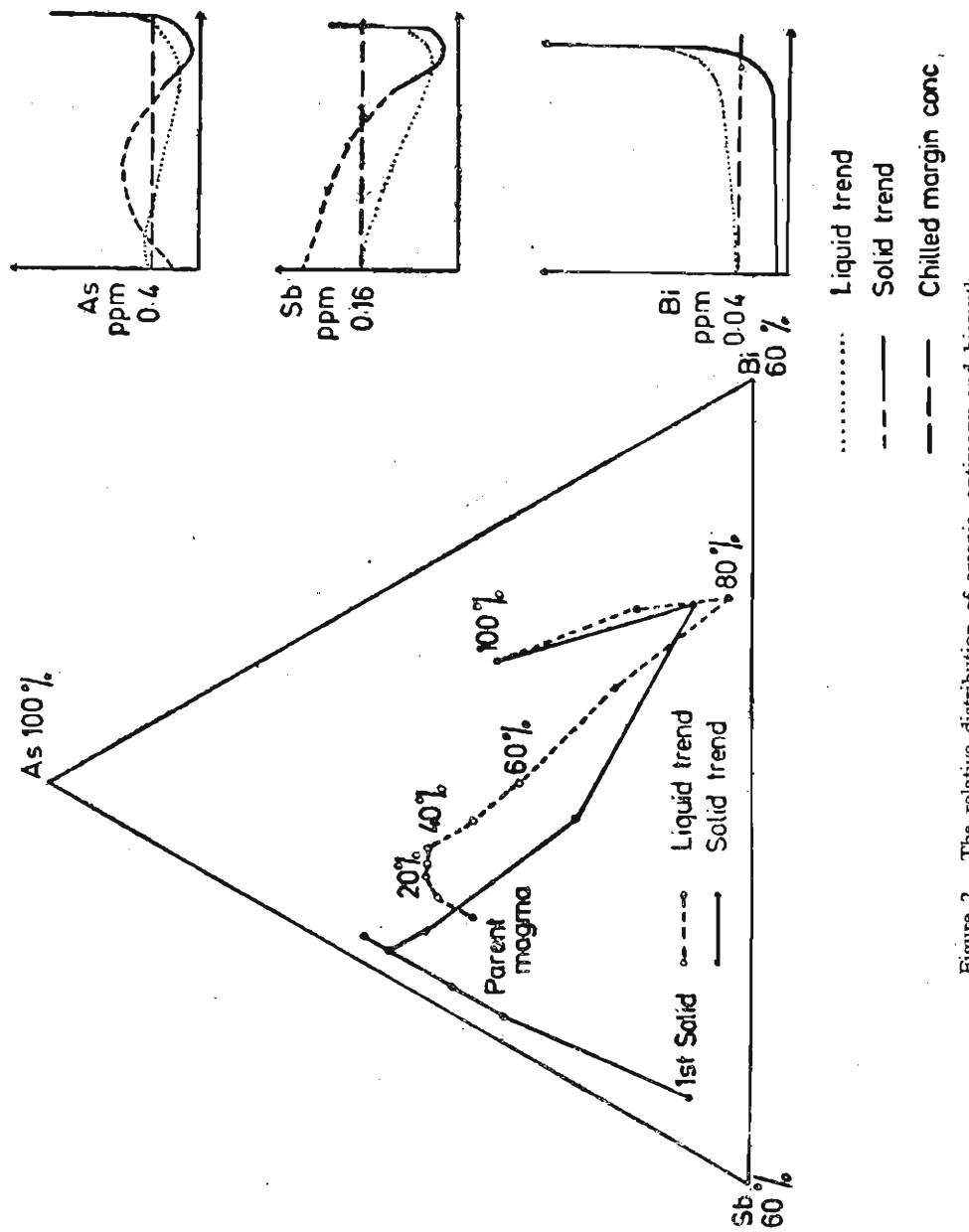

Figure 2. The relative distribution of arsenic, antimony and bismuth.

From about 40 % to 80 % solidification a distinct trend towards the bismuth corner is seen (Figure 2). While the antimony concentration changes only within narrow limits, arsenic shows a rapid decrease in both solid and liquid. Thus, it is at about 40 % solidification that bismuth shows signs of incorporation in the solid corresponding to the enrichment in the liquid.

In the last 20 % of solidification, arsenic once again shows the highest enrichment in the liquid. This is mainly due to its strong tendency to remain in the liquid rather than entering the iron rich silicate and oxide mineral phases. The arsenic contents of the minerals contribute little to the total arsenic content of the rocks, the rest being contributed by the trapped liquids. Further, arsenic shows a greater tendency than antimony and bismuth to enter the minor iron sulphide phase which appears in the last stages of the fractionation sequence. At these stages, Sb and Bi show a very similar trend, both elements tending to enter the primary minerals rather than remaining in the interstitial liquid as As does. Thus in the final stages of fractionation the order of enrichment in the liquid is As > Sb > Bi. It is of interest to note that this order is the same as the order for the tendency to form complex oxyanions which tend to accumulate in the late stage liquids. While the lithophile tendency increases in the order Bi > Sb > As, the chalcophile tendency increases in the reverse order.

3.3 Distribution of As, Sb and Bi in minerals

Tables 2 and 3 illustrate the As, Sb and Bi contents of the minerals separated from rocks. The entry of As, Sb and Bi into the cationic sites of the rock forming minerals can best be discussed in the light of the theory of Ringwood.[14]

Ringwood[14] considers 2 groups of ions. (*a*) Free ions which act as network modifiers, and (*b*) complex ions which act as network formers. According to him, the group into which any ion falls depends on the affinity of that ion for oxygen as governed by its ionic potential $\frac{\text{(cationic changes)}}{\text{(ionic radius)}}$. Accordingly, ions with low ionic potential (less than 2.7) enter cationic sites in the structure thereby becoming network modifiers while those with high ionic potential (greater than 4.8) form the centres of complex oxyions and are network formers. Examples of the latter type are

Be^{2+}, B^{3+}, Al^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, P^{5+}, As^{5+}, Ta^{5+}, Mo^{6+}, etc.

Between these two groups there is an intermediate group of ions which maintain an equilibrium between complex and non-complex positions. Generally, these are present as free ions in the magma until when the pegmatitic stage is reached these intermediate ions form complexes with the volatile elements not readily accepted into the silicate structures, thereby accumulating in the residual liquids.

TABLE 2.* Arsenic and Antimony in Constituent Minerals of the Rocks 5181, 5052 and 5086

Rock No. and Description	*Mineral*	*Modal % by weight*	*As PPM*	*As content contributed to rock*	*Sb PPM*	*Sb content contributed to rock*
5181	Plagioclase An_{40}	54.4	0.019	0.0103	0.23	0.1278
Hortonolite	Pyroxene $Ca_{35}Mg_{34}Fe_{31}$	21.9	0.066	0.0145	0.10	0.0230
ferrodiorite	Magnetite	4.5	0.20	0.0095	0.082	0.0045
	Ilmenite	5.5	0.11	0.0061	0.27	0.0121
	Olivine Fo_{30}	13.2	0.17	0.0224	0.20	0.0271
				0.0628		0.1945
	Whole rock (average)	0.17			0.17	
	Fine dust from mineral separation		0.24		0.069	
5052	Plagioclase An_{51}	42.2	0.027	0.0114	0.032	0.0135
Middle gabbro	Pyroxene $Ca_{37}Mg_{40}Fe_{23}$	29.4	0.048	0.0141	0.026	0.0076
	Magnetite	9.5	0.089	0.0086	0.025	0.0024
	Ilmenite	14.6	0.021	0.0031	0.150	0.0212
	Olivine Fo_{53}	3.3	0.086	0.0029	1.17	0.0386
				0.0401		0.0833
	Whole rock (average)	0.091			0.046	
	Fine dust		0.11		0.042	
5086	Plagioclase An_{62}	46.1	0.021	0.0097	0.036	0.0166
Lower Olivine	Pyroxene $Ca_{47}Mg_{34}Fe_{19}$	25.6	0.107	0.0256	0.032	0.0081
gabbro	Magnetite	1.8	3.6	0.0648	0.11	0.0017
	Olivine Fo_{53}	25.7	0.074	0.0193	1.37	0.3500
				0.1194		0.3764
	Whole rock (average)	0.22			0.14	
	Fine dust		0.29		0.12	

* After Esson *et al.*

TABLE 3. Bismuth in Minerals of the Skaergaard Intrusion

Mineral	*Modal wt.%*	*Bi (ppm) Replicate analyses*		*Average Bi (ppm)*	*Contribution to whole Bi (ppm)*	*% Contribution to whole rock B*
5181 *Upper Zone a* (UZa)						
Plagioclase An_{40}	54	0.17	0.14	0.15	0.08	28.5
Pyroxene $Ca_{55}Mg_{34}Fe_{31}$	23	0.13	0.15	0.14	0.03	10.7
Olivine Fa_{70}	13	0.32	0.39	0.35	0.05	17.8
Magnetite	4.5	0.38	0.32	0.35	0.01	3.5
Ilmenite	5.5	0.46	0.46	0.46	0.02	7.1
					0.19	67.6
				Whole rock	0.28	
4427 *Middle Zone* (MZ)						
Plagioclase An_{49}	26.7	0.03	0.04	0.04	0.01	7.1⅓
Pyroxene $Ca_{36}Mg_{38}Fe_{26}$	36.0	0.04	0.03	0.04	0.01	7.1
Magnetite	12.4	0.28	0.21	0.24	0.03	21.4
Ilmenite	22.6	0.27	0.23⅔	0.25	0.06	42.8
					0.11	78.4
				Whole rock	0.14	
5052 *Middle Zone* (MZ)						
Plagioclase An_{51}	48.0	0.06	0.05	0.06	0.03	18.7
Pyroxene $Ca_{37}Ma_{40}Fe_{23}$	29.0	0.05	0.05	0.05	0.01	6.2
Magnetite	9.0	0.32	0.35	0.34	0.03	18.7
Ilmenite	14.0	0.28	0.24	0.26	0.04	25.0
					0.11	68.6
				Whole rock	0.16	
5112 *Lower Zone* (LZb)						
Plagioclase An_{57}	37.2	0.10	0.10	0.10	0.04	28.5
Pyroxene $Ca_{/23/}Mg_{41}Fe_{21}$	45.0	0.08	0.07	0.08	0.03	21.4
Olivine Fa_{43}	14.7	0.09	0.10	0.09	0.01	7.1
					0.08	57.0
				Whole rock	0.14	
5092 *Lower Zone* (LZb)						
Plagioclase An_{62}	19.5	0.06	0.05	0.06	0.01	7.6
Pyroxene $Ca_{39}Mg_{42}Fe_{19}$	31.2	0.04	0.08	0.06	0.02	15.3
Olivine Fa_{37}	47.8	0.11	0.14	0.12	0.06	46.1
				Whole rock	0.09	69.0
4507* *chilled marginal gabbro*						
Plagioclase An_{72}	51.3	0.10	0.12	0.11		
Pyroxene $Ca_{37}Mg_{40}Fe_{23}$†	27.9	0.17	0.10	0.13		
Olivine Fa_{41}	19.0	0.12	0.13	0.13		
4314 Apatite		0.09	0.08	0.09		
5275 Pyrrhotite		0.41	0.38	0.40		

*Represents 'parent' magma

†Not pure.

The case of arsenic is interesting if one considers the following criteria for the diadochy between trace element complex ion and the tetrahedral complex ion SiO_4^{4-}.[14]

(*a*) The substituting ion must be of tetrahedral configuration ; any others will tend to accumulate in residual liquid fractions.

(*b*) The central cation in the complex must have a radius close to that of Si^{4+}.

(*c*) The ionic potential of the central cation should not be higher than that of Si^{4+} since the cation—oxygen bond would then have a greater covalent character than the Si—O bond. This makes substitution unlikely. A good example is tetrahedral PO_4^{3-} which is never known to substitute for SiO_4^{4-} due to the former having a much higher ionic potential.

Arsenic shows the dual behaviour of a network former and a network modifier.

(a) In pyroxene :

Pyroxene consists of parallel straight chains of SiO_4^{4-} tetrahedra, the oxygens being shared to form repeating units of $(Si_2O_6)^{4-}$, the adjacent chains being linked mainly by cations such as Ca^{2+}, Mg^{2+} and Fe^{2+} even though Fe^{3+}, Al^{3+}, Na^+, and Ti^{4+} may also be found to some extent. Since the latter group of ions are known to occur in the pyroxene structure, it is possible for As^{3+} to enter the sites, thereby occupying a network modifying position. The Mg^{2+} and Fe^{2+} ions are mostly in tetragonally distorted octahedral coordination (M_1 position) and the Ca^{2+} ions are surrounded by 6 to 8 oxygens (M_2 position) irregularly. Arsenic will enter only the M_1 position since it cannot enter the M_2 position by substituting for the larger Ca^{2+} ions.

(b) In feldspar :

Here the structure consists of a 3 - dimensional network of SiO_4^{4-} and AlO_4^{5-} tetrahedra, all the oxygens being shared. Cations Na^+, K^+, Ca^{2+} within the structure maintain electrical neutrality. Since As^{3+} and As^{5+} are too small to substitute for the larger Na^+, K^+ and Ca^{2+} ions, arsenic could enter the network as AsO_4^{3-} groups replacing SiO_4^{4-} tetrahedra. This seems reasonable since like the SiO_4^{4-} group, AsO_4^{3-} is tetrahedral in configuration and has an effective radius of 2.48°A as for SiO_4^{4-}. Further, the radii of the central cations As^{3+} and As^{5+} are similar to that of Si^{4+} and also the degree of covalent character in the bonds.

Thus arsenic could enter the structure of a silicate mineral as a network former and as a network modifier.

As shown in Table 2, arsenic shows no very marked preference for light or dark minerals. The concentrations of arsenic in the various mineral phases are mainly of the same order of magnitude except for the magnetite, ilmenite and olivine from the latest of the three rocks, i.e. 5181. While there is an increase in the arsenic content of magnetite, ilmenite and olivine with increasing differentiation, it seems to have had no effect on the As contents of plagioclase and pyroxene. Only about half the arsenic content appears to be 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.

Considering the ionic radii and changes, one could expect the following substitutions:

(*a*) As^{3+}(0.58°A), As^{5+}(0.42°A) for Al^{3+}(0.47°A).

(*b*) As^{3+} for Fe^{3+} (0.57°A) and Ti^{4+}(0.61°A).

(*c*) As^{5+} for Si^{4+} (0.34°A).

Onishi and Sandell[13] assume that the amount of As^{5+} is low, particularly when the $\frac{Fe^{2+}}{Fe^{3+}}$ ratio is high. Experimental work[1,5] on silicate glasses however shows that the +5 state of arsenic is by far the predominant form in glass melts even when the $\frac{Fe^{2+}}{Fe^{3+}}$ ratio is high. It is of interest to note that some recent work on the activities of trace elements in silicate melts[9] shows that there is an increased stability of the higher oxidation states of altervalent trace elements in silicate melts with increasing basicity.

If it is assumed that activities are more or less proportional to concentrations even in the magmatic environment, the oxidation potential of the liquid is given by

$$Eh = -E^\circ + \frac{RT}{nF} \ln \frac{Fe^{3+}}{Fe^{2+}}$$

where E° (for $Fe^{2+} = Fe^{3+} + e$) $= -0.771$ V
R = 8.314 absolute joules per degree
T = 1273°K
n = 1 (number of electrons transferred in reaction)
F = 96500 C

Substituting for the Fe^{3+}/Fe^{2+} ratio for the UZb liquid of the Skaergaard Layered Series (Figure 1)[21] we obtain Eh — 0.555 V. On substituting the E° value for the reaction $As^{3+} = As^{5+} + 2e$ in the equation, one arrives at $\frac{As^{5+}}{As^{3+}} \simeq 2$ indicating the predominance of the pentavalent state over the trivalent state. It is of interest to note that in the case of mercury, $Hg \simeq 10^2\ Hg^{2+}$,[7] and for gold, $Au \simeq 10^4\ Au^{+}$.[20]

Considering the individual minerals, arsenic can only enter the plagioclase structure by the substitution of As^{3+} and/or As^{5+} for Si^{4+} and Al^{3+} in tetrahedral sites, or as As^{3+} in octahedral sites. Esson *et al.*[8] think however, that both the entry of As^{3+} into octahedral and As^{5+} into tetrahedral sites would be unfavourable to the structure.

The fact that pyroxene had 2 to 5 times as much arsenic as the plagioclase from the same rock could be explained in terms of the greater number of sites available for substitution.

As^{3+} for Mg^{2+}, Al^{3+}, Fe^{3+} and Ti^{4+}; octahedral sites.

As^{5+} for Si^{4+} and Al^{3+} ; tetrahedral sites.

In the case of opaque oxide minerals, ilmenite and magnetite, the arsenic found in the structure probably resulted from a straightforward substitution of As^{3+} for Ti^{4+} and Fe^{3+}, respectively. In olivine, substitution of As^{5+} for Si^{4+} is also a possibility. The work of Esson *et al.*[8] also indicates that AsO_4^{3-} probably increases more strongly in the last liquids than As^{3+} showing that the tendency for As^{3+} to replace small cations is greater than the tendency for AsO_4^{3-} to enter the silicate structures in place of SiO_4^{4-}.

In contrast to arsenic, the $\frac{Sb^{5+}}{Sb^{3+}}$ ratios for the Skaergaard magmas vary from 0.05 to 0.2 indicative of the fact that Sb^{3+} is the predominant ion in the basic magmas. It is important to bear in mind the greater stability of the trivalent ion in group V as one moves down from As to Bi. Unlike arsenic, antimony (Sb^{5+}) is unable to form tetrahedral oxyions such as SbO_4^{3-} due to the larger size of Sb^{5+} not being conducive to the formation of small stable coordination groups with oxygen, even though pentavalent groups may form complex ions such as $(Sb_2O_6)^{2-}$ $(SbCl_6)^-$ $(SbF_6)^-$ etc, which generally accumulate in the residual magma. Further, the higher charge of Sb^{5+} would hinder the simple substitution of Sb^{5+} for Mg^{2+}, Fe^{3+}, etc., even though the ionic radii may be similar. Therefore, it is very likely that it is mainly the Sb^{3+} ion which substitutes for major element cations of similar ionic radius even though a little pentavalent antimony may form complex ions and become enriched in the residual liquid.

In the Skaergaard samples, the amount of Sb in olivines seems to decrease steadily as differentiation causes a progressive change in olivine composition from Fo_{70} to Fo_2. Ilmenite is the next favourable host, the substitution presumably being Sb^{3+} for Fe^{2+}. The same explanation can be held for pyroxene and magnetite. In the case of plagioclase it is likely that Sb^{3+} enters octahedral sites normally occupied by Al^{3+}.

The discussion thus far highlights a decreasing tendency for

(*a*) complex ion formation,

(*b*) M^{5+} formation as against M^{3+} formation,

(*c*) entering the structure as a network former,

as one moves from As to Sb with increasing atomic weight. Accordingly, one could predict that bismuth should almost entirely be Bi^{3+} and that its tendency for complex oxyion formation should be negligible. This is in fact observed. Neither does Bi^{5+} exist in nature nor does bismuth form a complex ion capable of replacing SiO_4^{4-} tetrahedra. Hence, the geochemistry of bismuth is almost entirely that of the Bi^{3+} ion. If this be the case, the only sites available for Bi^{3+} substitution would be the cation sites linking the tetrahedra in silicates and the normal cation sites in the oxide minerals. Since the substituted cations in silicates and oxides (mainly Fe^{2+}) do not show any great disparity as regards their coordination, it seems logical that the preferential entry of bismuth into the oxides is related to the presence or absence of Si^{4+}, O^{2-} or SiO_4^- tetrahedra. It appears that the explanation lies on a possible tendency for Bi^{3+} to establish links with oxygen, the ease of which seems obviously to be hampered by the presence of Si^{4+} which would compete for the O^{2-} ions, In both magnetite and ilmenite, Fe^{2+} positions are more suitable than Fe^{3+} and Ti^{4+} for the linking with O^{2-} ions due to the preferred size of the former. It is also of importance to bear in mind that bismuth is the most electropositive element in group V. The 'oxide preferring' property of bismuth as against a 'silicate preferring' tendency is illustrated by the fact, while bismuth silicate minerals are very rare (the only examples being eulytite ($Bi_4(SiO_4)_2$) and bismutoferrite ($BiFe_2(SiO_4)_2(OH)$), there are numerous oxide compounds with bismite (Bi_2O_3) as one of the commonest bismuth minerals. An interesting feature in the bismuth silicate mineral eulytite is the occurrence of BiO_6 groups.

Since the geochemistry of bismuth is almost completely that of the Bi^{3+} ion, it is of interest to discuss in detail how the Bi^{3+} ion enters cationic sites in the rock forming minerals as exemplified by those from the Skaergaard intrusion.

Table 3 shows the bismuth contents of the minerals separated from rocks of the Lower, Middle and Upper Zones of the fractionation sequence. It can be seen that magnetite, ilmenite and olivine show an enrichment of bismuth, while pyroxene and plagioclase carry lesser amounts. The distribution of bismuth in the oxide minerals ilmenite and magnetite and the silicate minerals, plagioclase and pyroxene is put in perspective if one compares the ratios of the bismuth contents in these minerals (Table 4).

TABLE 4. Distribution Coefficients for Bismuth in Coexisting Minerals

ROCK	*Plagioclase Pyroxene*	*Ilmenite Magnetite*	*Ilmenite Plagioclase*	*Ilmenite Pyroxene*	*Magnetite Plagioclase*	*Magnetite Pyroxene*
5181	1.1	1.3	3.0	3.3	2.2	2.5
4427	1.1	1.0	6.2	6.9	6.1	6.8
5052	1.1	0.8	4.6	5.4	6.0	7.0
5112	1.3	—	—	—	—	—
5092	0.9	—	—	—	—	—
AVERAGE	1.1	1.0	4.6	5.2	4.7	4.5

Two features are immediately apparent.

(*a*) The remarkable constancy of the distribution coefficient for the oxide mineral pair, ilmenite and magnetite and also for the silicate mineral pair plagioclase and pyroxene, their average values being 1.0 and 1.1, respectively.

(*b*) The distribution coefficient of approximately 5 for oxide/silicate pairs as shown by the last column of Table 4.

At this point of the discussion, one can safely conclude that bismuth shows a distinct preference for the oxide minerals as against the calcium bearing silicate minerals. Olivine has not been considered in a similar manner, due to the fact that only one set of data is available where olivine and the oxide minerals coexist. However, judging by the bismuth contents of the olivines analysed, it appears that olivine incorporates less bismuth than the oxide minerals.

The uptake of bismuth from the liquid into the available sites in the structures of the minerals studied can best be discussed if one considers the equilibrium constants of partition K.

The replacement of a cation Y^+ in a mineral structure by a trace element cation X^+ is governed by the equilibrium,

$$X^+_{\text{eq.liq.}} + Y^+Z^-_{\text{eq.}(XY)+Z^-} \underset{\text{cryst.}}{\rightleftharpoons} Y^+ + X^+Z^-_{\text{eq}(XY)^+Z^-\ \text{cryst.}}$$

where each component is considered to be in the actual environment afforded by the liquid or solid of equilibrium composition.[23] The partition coefficient K of bismuth with respect to another element Y has been calculated for the different minerals, K being defined as

$$K = \frac{Bi^{3+}\ \text{mineral}}{Bi^{3+}\ \text{liquid}} \times \frac{Y^+\ \text{liquid}}{Y^+\ \text{mineral}}$$

where $Y^+ = Ca^{2+}$, Fe^{2+}, Fe^{3+}, Mg^{2+} and Ti^{4+} depending on the presence of these ions as major element cations in the structure of the minerals concerned. It is to be noted however, that in this work the activities have been replaced by concentrations.

Table 5 shows the calculated partition coefficients of bismuth against the major cations in the minerals studied. The partition coefficient K of bismuth with respect to Ti^{4+} in ilmenite, shows the lowest value, while that for Fe^{2+} in magnetite shows the highest. However, except for a single K value of 1.02 for Fe^{2+} in magnetite, all other K values in Table 5 are less than unity. This indicates the fact that bismuth prefers to remain in the liquid as against the mineral phases. A better idea of the relative partition coefficients of bismuth with respect to the major element cations could be obtained if the K values are recalculated taking the average K value for Ti^{4+} (which is the least) as unity (Table 5). When the other K values are divided by the average K Ti^{4+} one arrives at the following decreasing order for the partition coefficients.

(1)	Magnetite	Fe^{2+}	(6)	Pyroxene	Ca^{2+}
(2)	Ilmenite	Fe^{2+}	(7)	Olivine	Mg^{2+}
(3)	Pyroxene	Fe^{2+}	(8)	Pyroxene	Mg^{2+}
(4)	Plagioclase	Ca^{2+}	(9)	Magnetite	Fe^{3+}
(5)	Olivine	Fe^{2+}	(10)	Ilmenite	Ti^{4+}

TABLE 5. Equilibrium Constants for Partition (K)

ROCK	*Il* Ti^{4+}	*Mag* Fe^{3+}	*Pyrox* Mg^{2+}	*Ol* Mg^{2+}	*Pyrox* Ca^{2+}	*Ol* Fe^{2+}	*Plag* Ca^{2+}	*Pyrox* Fe^{2+}	*Il* Fe^{2+}	*Mag* Fe^{2+}
5181	0.07	0.07	0.07	0.16	0.24	0.41	0.55	0.45	0.61	0.70
4427	0.07	0.07	0.06	—	0.10	—	0.21	0.21	0.43	0.64
5052	0.09	0.12	0.12	—	0.18	—	0.33	0.36	0.52	1.02
5112	—	—	0.20	0.10	0.30	0.30	0.65	0.67	—	—
5092	—	—	0.19	0.16	0.18	0.47	0.36	0.58	—	—
Average	0.07	0.08	0.12	0.14	0.20	0.39	0.42	0.45	0.52	0.78
Relative	1.00	1.14	1.71	2.00	2.85	5.57	6.00	6.42	7.42	11.14

K values taking K for Ti^{4+} in ilmenite as unity.

From these decreasing order of K values, a few salient features emerge which are worthy of note.

(*a*) The relatively high placings for the Fe^{2+} sites in minerals.

(*b*) The very low placing for the triple and quadruple charged Fe^{3+} and Ti^{4+}.

(*c*) The higher placing for Fe^{2+} sites as against the Mg^{2+} sites for both pyroxene and olivine.

(*d*) The higher placing for the plagioclase Ca^{2+} as against the pyroxene Ca^{2+}.

From Table 6 where the ratios of the partition coefficients are shown, it is at once apparent how much in the oxide minerals (which are the best hosts for Bi), bismuth shows greater preference for the Fe^{2+} sites as against the Fe^{3+} and Ti^{4+} sites.

TABLE 6. Partition Coefficient Ratios for the Different Cations

ROCK	$\frac{Mag\ Fe^{2+}}{Mag\ Fe^{3+}}$	$\frac{Il.Fe^{2+}}{Il.Ti^{4+}}$	$\frac{Pyrox.Fe^{2+}}{Pyrox.Mg^{2+}}$	$\frac{Ol.Fe^{2+}}{Ol.Mg^{2+}}$	$\frac{Mag.Fe^{2+}}{Pyrox.Fe^{2+}}$	$\frac{Pyrox.FeCa^{2+}}{Pyrox.Ca^{2+}}$	$\frac{Plag.Ca^{2+}}{Pyrox.Ca^{2+}}$	$\frac{Pyrox.Mg^{2+}}{Ol.Mg^{2+}}$	$\frac{Mag.Fe}{Il.Fe^{2}}$	$\frac{Pyrox.Fe^{2+}}{Ol.Fe^{2+}}$
5181	10.00	8.71	6.42	2.56	1.55	1.87	2.29	0.43	1.14	1.09
4427	9.14	6.14	3.50	—	3.04	2.10	2.10	—	1.48	—
5052	8.50	5.77	3.00	—	2.83	2.00	1.83	—	1.96	—
5112	—	—	3.35	3.00	—	2.23	2.16	2.00	—	2.23
5092	—	—	3.05	2.93	—	3.22	2.00	1.18	—	1.23
Average	9.21	6.87	3.86	2.83	2.47	2.28	2.07	1.53	1.52	1.51

4. Conclusions

From the above discussion the following conclusions could be arrived at:

(1) A smooth variation of the geochemical behaviour exists as the atomic weight increases from As to Bi.

(2) The geochemical behaviour of arsenic is characterized by the predominance of the As^{5+} ion and the dual ability to act as a network former and a network modifier.

(3) In the minerals, arsenic substitutes for Al^{3+}, Fe^{3+}, Ti^{4+} and Si^{4+}.

(4) Antimony also contains both the tri- and pentavalent ions in the minerals even though the Sb^{3+} ion predominates over the Sb^{5+} ion.

(5) The stability of the trivalent ion is highest in bismuth, where it shows preferential entry into the oxide minerals as against the silicate minerals. Within the oxide minerals Bi prefers the Fe^{2+} sites to Fe^{3+} and Ti^{4+} sites.

The group V elements provide a very good example of how the geochemical distribution follows the trends expected from their electronic configuration, ionic size and general chemical properties.

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