

Mercury in rocks and minerals of the Skaergaard intrusion, East Greenland

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SUMMARY. Mercury has been determined by radiochemical neutron-activation analysis in nineteen representative rocks from the Skaergaard intrusion and in the separated cumulus minerals of five. The chilled marginal gabbro contains 0.23 ppm Hg, values in the Layered Series rocks ranging from 0.07 to 0.34 ppm, in one exceptional case reaching 1.23 ppm Hg. There is a tendency for mercury to be more abundant in leucocratic than in average or melanocratic rocks at a similar horizon. Somewhat higher levels of mercury are found in the granophyric rocks at the top of the intrusion.

Apart from a weak and sporadic tendency to be preferentially enriched in plagioclase, the distribution of mercury between the various cumulus phases is fairly uniform and it is thought to occur as uncharged atoms mainly occupying spaces resulting from lattice defects and imperfections rather than in specific structural sites.

The distribution pattern of mercury in the intrusion appears to be determined by its high volatility and chemical inertness; no real evidence of any chalcophile character is observed.

MOSTLY due to the lack of reliable analytical data, little is known of the behaviour of mercury in igneous rocks; earlier spectrographic and colorimetric determinations could be regarded at best as semi-quantitative. In the present work, neutron-activation analysis has been used, the rocks and minerals of the Skaergaard intrusion providing a useful suite of samples in which to study the behaviour of mercury during the fractional crystallization of a basic magma.

The composition of the initial Skaergaard magma (Wager and Brown, 1968) is considered to be that of a dry, highly reduced, tholeiitic basalt with a high alumina content. The chilled marginal gabbro, number E.G. 4507 from the Southern Border Group of the intrusion, has been widely used as representing the best approximation available to the initial magma, but its composition is in some ways anomalous and its petrogenetic status must therefore be regarded with caution. Within the estimated 500 km³ of tholeiitic magma, extreme crystal fractionation produced rocks ranging in composition from ultrabasic to acid (although extensive contamination by the gneisses of the local metamorphic basement complex has probably played a significant part in the development of the latest acid fractions).

Wager (see, for example, Wager and Brown, 1968) estimated on the basis of field observations, chemistry, and mineralogy of the rocks that some 70 % of the lower and earlier products of solidification of the magma remain unexposed at the present level of erosion. Chayes (1970) presented cogent arguments for raising the estimate of this Hidden Zone to 80 %; while more recent and as yet unpublished geophysical and geochemical work by McBirney, Goles, *et al.* (pers. comm.) casts doubt upon the

existence of any very large Hidden Zone immediately underlying the exposed part of the Skaergaard intrusion.

In the present work, nineteen rocks from the exposed Layered Series were studied; their locations within the differentiated sequence are shown in fig. 1, on which is also indicated the steady compositional variations observed in the cumulus mineral phases, and their appearance and disappearance. The rocks analysed for mercury range from olivine gabbros, through olivine-free gabbros to ferrodiorites and acid granophyres.

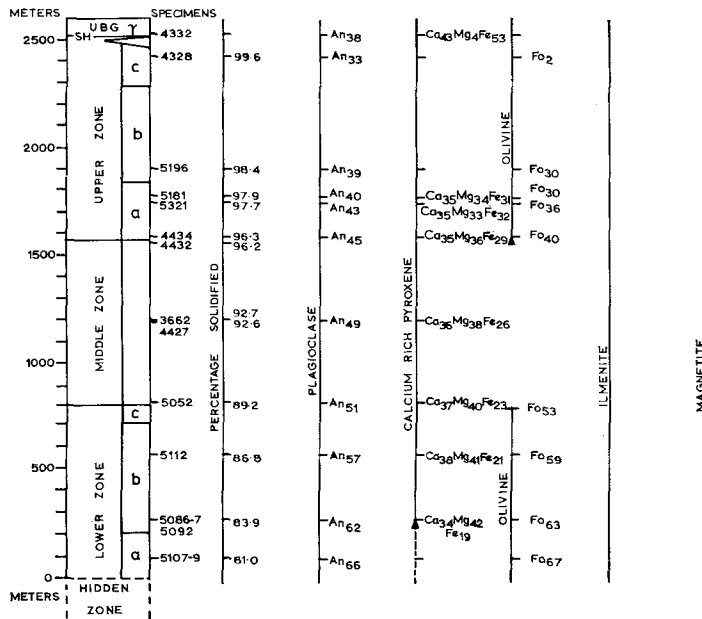


FIG. 1. Mineralogical changes in the Skaergaard Layered Series. Discontinuous vertical lines relate to intercumulus minerals or those of indeterminate status. Positions of analysed rocks indicated. (Simplified after Wager and Brown, 1968, fig. 14.)

Analytical method

The abundances of mercury in rocks are very low and the element highly volatile, so that the avoidance of sample contamination in the laboratory is important. Samples were crushed for analysis as gently as possible using hard-steel percussion and agate mortars. Mineral separations were achieved by means of an isodynamic magnetic separator and by centrifuging in heavy organic liquids; the use of Clerici's solution (a notorious source of contamination) was avoided. Crushing and separating were carried out in a laboratory in which no mercury or mercury compounds had been used. Figures for mercury in U.S. Geological Survey reference rock samples (McNeal *et al.*, 1972) indicate considerable inhomogeneities in its distribution within a sample, and in the present work all whole-rock powders were homogenized as well as possible by tipping on to a sheet of glazed paper and thoroughly mixing with a platinum spatula

before weighing portions of 0.1–0.5 g into acid-cleaned, weighed quartz-glass vials for analysis. The preparation of the quartz vials, flux monitor standards, and carriers followed the methods described by Ehmann and Lovering (1967). The samples and flux monitor vials were irradiated together in the UKAEA Herald reactor, Aldermaston, in a thermal neutron flux of approximately $5 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$ for 3 days. After the elapse of 3 days, to allow short-lived radioisotopes to decay, radiochemical separations were carried out, taking appropriate safety precautions for handling millicurie quantities of radioactivity.

The radiochemical separations, used for both samples and flux monitor standards, were based upon the methods described by Marowski (1971), care being taken throughout the processing to avoid the use of high temperatures and the consequent loss of mercury through volatilization.

Each irradiated sample was transferred from the quartz vial to a teflon basin, 20 ml of 60 % HF and a few drops of conc. H_2SO_4 added, together with 30 mg of inactive mercury carrier, and the whole warmed carefully under an infra-red lamp kept about 20 cm above the basin. Hot aqua regia was added to the empty quartz vial. After two further additions of HF to the sample, followed by evaporation, 5 ml of aqua regia, together with the vial wash solution, were added to the residue and again evaporated gently. The final residue was dissolved in 20 ml of 0.5M HCl.

Ilmenite and magnetite samples were dissolved as follows: 15 ml of 60 % HF, a drop of conc. H_2SO_4 , and 30 mg of inactive mercury carrier were added. After evaporating to a volume of about 1 ml, 15 ml of 6 to 8M HCl were added and the whole again warmed under the infra-red lamp until the residue slowly dissolved. The final solutions were then made in 0.5M HCl as in the case of the silicate samples.

The solutions were then passed through an 0.6×10 cm column of Dowex 1 \times 4 ion-exchange resin (50–100 mesh, Cl^- form), which had previously been washed with 0.5M HCl. Elution with 0.5M HCl removed the bulk of the radioactivity due to the sample matrix, and was followed by elution with 0.1M HCl and de-ionized water for further purification.

The mercury was finally eluted from the column with 50 ml of 0.1M thiourea in 0.01M HCl, and precipitated at 80 °C in strong ammonia solution as HgS. After dissolving the precipitate in a few drops of aqua regia, holdback carriers for Cr, Au, and Ir were added and the ion-exchange purification repeated. Final HgS precipitates, the yields of which varied between about 60 and 90 %, were prepared from samples and flux monitor standards and submitted to gamma-ray spectrometry.

The 279.1 keV gamma rays of ^{203}Hg ($t_{1/2} = 47$ days) were used for radiometric assay, the operation being carried out using a sophisticated spectrometer, with Ge (Li) detector and dedicated PDP 10 computer, in the Oxford University Department of Nuclear Physics. Peaks in the gamma-ray spectrum were identified by calibration against sources of known energy: ^{137}Cs , ^{60}Co , ^{57}Co , and ^{22}Na . Although the 77.6 keV peak of ^{197}Hg offers rather greater sensitivity, X-rays of Tl generated by internal conversion of the gamma rays of ^{203}Hg fall between the ^{197}Hg peak and the associated Au- $K\beta_2$ X-rays at 80.1 keV, so that adequate base-line correction is difficult. The ^{203}Hg peak, on the other hand, is a 'clean' peak, easily identified and measured on the

almost radiochemically pure HgS precipitates obtained in the present work, and, following Ehmann and Lovering (1967) was chosen in preference to the ^{197}Hg peak. The total peak area, as discussed by Yule (1968), was automatically computed following standard programmes of the Oxford Department of Nuclear Physics.

The assessment of over-all errors in the analyses is difficult. It was impracticable to carry out more than duplicate determinations for each sample and calculation of the standard error of the mean is pointless when dealing with only duplicate analyses and at the very low levels of concentration of mercury involved. As regards the ^{203}Hg peak areas in the gamma-ray spectrum, comparing samples and flux monitor standards, most measurements were reproducible to 1 or 2 %, except in a few samples with the lowest mercury contents, where the spread of individual assays of the same sample rose to a maximum of 14 %.

Results and discussion

With an outer electronic configuration of $5d^{10}6s^2$, mercury has unusually high ionization potentials and a high positive standard electrode potential. These properties, together with its low vaporization energy and general chemical inertness are attributed to the 'inert pair' effect (Cotton and Wilkinson, 1967). The element has a low affinity for oxygen and mercuric oxide decomposes at about 400 °C. Mercury combines with sulphur directly, but the sulphide again decomposes at about 600 °C. Many mercury compounds are found in the vapour phase above this range of temperature.

In order to understand the geochemical behaviour of mercury in the present context it is useful to gain some idea of its state of oxidation and this can be done, admittedly very roughly, by assuming activities to be more or less proportional to concentrations, even in the magmatic environment, and calculating the oxidation potential of the latter from its observed ferric:ferrous iron ratio. If, for example, we substitute the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratio for the Skaergaard UZb liquid (Wager and Brown, 1968, fig. 14) in the expression $E_h = -E^0 + RT/nF \ln \text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ [where E^0 (for $\text{Fe}^{2+} = \text{Fe}^{3+} + e$) = -0.771V ; $R = 8.314$ absolute joules per degree-mole; $T = 1273$ °K; $n = 1$ (number of electrons transferred in the reaction); $F = 96\,500$ coulombs], we derive a value for the oxidation potential E_h of the liquid of 0.555V . For the reaction $\text{Hg} = \text{Hg}^{2+} + 2e$, $E^0 = -0.854\text{V}$, $n = 2$, and on substitution in the above equation we find $\text{Hg} \sim 10^2 \text{Hg}^{2+}$, a magnitude that holds good for all zones in the Skaergaard Layered Series taking the appropriate estimated $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratios of the various liquids into account. The existence of the mercurous ion, Hg^+ , in any significant proportion is similarly unlikely, the number of stable mercurous compounds being in any case rather restricted. Goldschmidt (1954), too, remarks that 'at magmatic temperatures the redox potential of the ferrous iron in magmas must in most cases be sufficient to transform mercury compounds into mercury and thus force the metal into the gaseous exhalation products . . .'. In interpreting the Skaergaard results for mercury, therefore, the chief factors to be taken into account are that it most probably existed throughout mainly, if not entirely, in the elemental state, and that its behaviour was largely controlled by its extremely volatile character.

Mercury in the rocks. The observed mercury contents of the whole-rock samples are given in Table I, and plotted in fig. 2 as a function of the percentage magma solidified, following the estimate of Chayes (1970) for the magnitude of the Hidden Zone. For many trace elements previously studied it can reasonably be assumed that the Skaergaard intrusion behaved to all intents and purposes as a closed system. For the highly volatile mercury this assumption is invalid and the method described by Wager and Brown (1968) for estimating the mercury contents of the Hidden Zone and of

TABLE I. *Mercury in rocks of the Skaergaard intrusion, East Greenland*

Rock No. E.G.	Rock type	% magma crystallized (Chayes, 1970)	Hg, ppm duplicate analyses	Mean Hg, ppm
5259	Acid granophyre	—	0·70 0·75	0·73
4489	" "	—	0·02 0·03	0·03
4332	Melanogranophyre	—	0·35 0·40	0·38
4328	Fayalite ferrodiorite, UZc	99·6	0·27 0·27	0·27
	Hortonolite ferrodiorite:			
5196	(melanocratic), UZb	98·4	0·27 0·24	0·26
5181	(average), UZa	97·9	1·26 1·20	1·23
5321	(leucocratic), UZa	97·7	0·27 0·30	0·29
4434	(average), UZa	96·3	0·11 0·16	0·14
	Olivine-free gabbro:			
3662	(leucocratic), MZ	92·7	0·34 0·34	0·34
4427	(melanocratic), MZ	92·6	0·19 0·22	0·21
5052	(average), MZ	89·2	0·11 0·10	0·11
	Lower olivine gabbro:			
5112	(average), LZb	86·6	0·07 0·07	0·07
5092	(melanocratic), LZb	83·9	0·18 0·14	0·16
5087	(average), LZb	83·9	0·06 0·08	0·07
5086	(average), LZb	83·9	0·25 0·25	0·25
5109	(leucocratic), LZa	81·0	0·13 0·13	0·13
5108	(melanocratic: olivine cumulate), LZa	81·0	0·10 0·09	0·10
5107	(average), LZa	81·0	0·12 0·12	0·12
4507	Chilled marginal gabbro, SBG	00·0	0·21 0·24	0·23

successive magmatic liquids cannot be applied, so that no curve for the liquids is shown in fig. 2. While all the analyses taken together show a considerable scatter in the diagram, it is none the less possible to draw a reasonable distribution curve through most of the values obtained from the analysis of rocks of 'average' composition as regards proportions of their constituent minerals; most of the aberrant points in fig. 2 refer to contrasted Layered Series rocks representing decidedly leucocratic or melanocratic facies. The distribution of mercury in average rocks shows a very distinct increase in concentration of the element in the latest magmatic fractions, as might be expected, while on the Wager-Chayes model adopted here, the lowest concentrations of the element would be expected in the rocks of the Hidden Zone.

The chilled marginal gabbro (4507) considered by Wager and his co-workers to represent the best approach to the initial magma contains 0·23 ppm of mercury.

Because the Skaergaard is a high-level intrusion, it is possible that the chilled gabbro, too, has lost some of its mercury and the parental magma may originally have contained more than 0.23 ppm. This value is in any case already higher than the average estimate (Taylor, 1964; Saukov, 1946) of 0.080 ppm for mercury in surface rocks. Ehmann and Lovering (1967) found remarkably high mercury contents (of the order of 1 ppm) in samples of peridotitic and eclogitic inclusions from South African

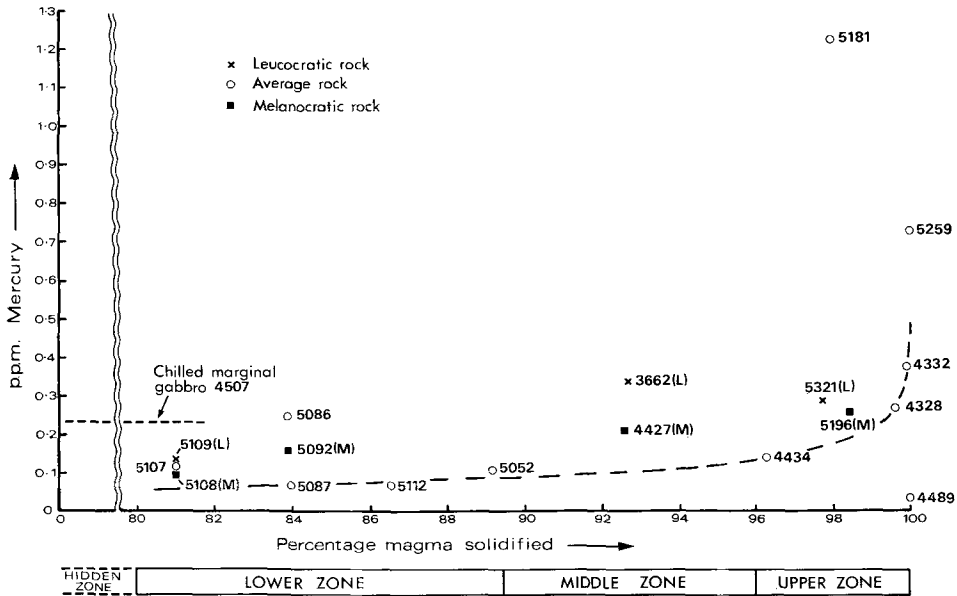


FIG. 2. Distribution of mercury in the Skaergaard rocks.

kimberlites and Australian alkali-basalts, possibly indicating a general increase in mercury content with depth, and remarked 'If the high values found in these inclusions are characteristic of the continental lower crust and the upper mantle, it will be necessary to drastically revise current estimates of the over-all terrestrial abundance of mercury.'

While many trace elements in the Skaergaard rocks show distribution profiles similar to that of fig. 2, due to their general inability readily to enter diadochically the crystal structures of the various cumulus phases, it seems that in the case of mercury the dominant factor may well be the movement of the element upwards in the layered sequence along with the more volatile constituents. Such a process leads to a general enrichment in the latest magmatic rocks (though some proportion will be lost by diffusion into the surrounding country rocks); some of the variation in the mercury contents of different cumulate rocks from the same horizon in the Layered Series may similarly be due to the retention of differing proportions of intercumulus liquids.

Many of the Skaergaard rocks carry minute traces of sulphide minerals, but these only become noteworthy constituents at two rather narrow horizons within the

Layered Series: some of the more melanocratic hortonolite ferrodiorites of UZa (fig. 1) carry up to about 0.4 % by weight of copper and copper-iron sulphide, and some of the fayalite ferrodiorites of UZc up to about 2 % by weight of iron sulphides (mostly marcasite after pyrrhotine (Wager, Vincent, and Smales, 1957)). While the behaviour of mercury in low-temperature ore deposits is mostly determined by its volatility and by its chalcophile character, it appears to show no tendency in the Skaergaard case to become concentrated in the accessory copper sulphides. Indeed, of two UZa rocks analysed, the melanocratic example, 5196, carries *c.* 0.4 % of sulphide minerals (900 ppm S) and has a mercury content of 0.25 ppm, while the average example, 5181 (with 54 % by weight of feldspar and 160 ppm S) has a mercury content of 1.22 ppm, the highest found among the Skaergaard rocks. Neither is there much evidence that mercury is appreciably concentrated in the accessory iron sulphide minerals in UZc. The fayalite ferrodiorite 4328 carries sporadic sulphide blebs amounting to 1 or 2 % by weight of the rock; its mercury content of 0.27 ppm is not abnormally high, however.

One of the most striking features of the distribution of mercury in the Layered Series is the definite tendency (fig. 2; Table I) for the element to be present in higher concentrations in feldspathic rocks as compared with average or melanocratic rocks at the same horizon. This is unexpected since, with the possible exception of that from the UZa rock 5181 (see below) the separated plagioclases analysed contain much the same quantities of mercury as do the other cumulus minerals. Possibly even within each rhythmic layered unit the tendency for mercury to migrate upwards towards slightly lower temperatures is sufficiently marked for the element to become appreciably enriched in the mesostasis of the uppermost leucocratic member of the unit, the actual amount of this mesostasis (Henderson, 1970) being perhaps of lesser importance in any individual case. Unfortunately, the plagioclases separated for analysis were all taken from average or rather melanocratic facies rocks and no direct evidence is available to show whether the actual feldspar crystals in the leucocratic facies do or do not carry more mercury than those in the adjacent average facies.

With the exception of the mineralogically more or less average UZa hortonolite ferrodiorite, 5181, which appears to have an abnormally high mercury content, the highest concentrations are to be found in the melanogranophyre, 4332, and the transgressive acid granophyre, 5259. The melanogranophyres are considered by Wager and Brown (1968) probably to represent material produced by fractional crystallization of the original basic magma; in the genesis of the acid granophyre assimilation of basement complex gneisses has probably been an important factor. Iron sulphide minerals (pyrrhotine and pyrite) are sporadically present also in these latest granophyres; very little sulphide can be detected microscopically in the rock 4489, which has the extremely low mercury content of 0.03 ppm. These iron-sulphide traces can sometimes be separated for analysis, but none has been analysed for mercury; possibly they may provide, at these extreme stages in the petrogenetic sequence, a more positive repository for the potentially chalcophile mercury than do the iron sulphides or copper sulphides in the UZ rocks of the rather earlier Layered Series proper.

It seems that mercury tends to migrate upwards in the intrusion, with the potentially

volatile phases of the magma, as solidification proceeds, and that in general its rather sporadic distribution is to be attributed more to the movement and concentration of the magmatic residue and vapours than to any very positive crystal-chemical behaviour of the element itself. Eshelman *et al.* (1971) have detected mercury as a component of the volcanic gases at Hawaiian volcanoes, and state that 98 % of the mercury issuing from fumaroles is either in the form of a gas or of particles less than 0.3 μm in diameter.

Mercury in the minerals. Table II shows the mercury contents of separated mineral fractions from five rocks spanning Lower, Middle, and Upper Zones of the Layered Series: no particular general distribution pattern of the element between one mineral and another is apparent, but the relatively high level of mercury in all the minerals of the UZa ferrodiorite 5181 is noteworthy.

Accepting that mercury occurs mainly in the elemental state, with the large atomic radius of about 1.6 Å, it can scarcely be expected to occupy specific structural sites in most rock-forming minerals, but rather to be distributed in more random fashion in lattice defects, dislocations, and imperfections, and perhaps along grain boundaries. Similar behaviour was postulated in the case of the noble metal gold in the Skaergaard minerals (Vincent and Crocket, 1960).

In a series of heating experiments on rocks and minerals, Reed and Jovanovic (1967) observed that most samples lost mercury within two distinct temperature ranges: 0 to 450 °C, and above 450 °C. This division at about 450 °C represents the difference between mercury loosely held in labile sites, which can easily escape and is volatilized at a few hundred degrees, and mercury trapped in more retentive sites in crystal structures or held in solid solution, which requires a higher temperature to bring about its diffusion to surfaces, in a manner analogous to the escape of trapped gases.

If the mercury contents of the Skaergaard minerals are multiplied by their modal fractions in each rock, and the sum of these compared with the independent analysis for mercury of the whole rock sample (Table II), it is seen that in three cases out of five the contribution from the mineral fractions accounts for more than 80 % of the total mercury found in the rock. The figure for the MZ gabbro 5052 is 59 %, and that for the LZb rock 5112 only 34 %. Minor amounts of intercumulus ilmenite and magnetite present in the latter rock were not separated for analysis, and it could be that the intercumulus material for some reason remained particularly rich in mercury in this rock. Much of the crystallized products of the intercumulus magma is, of course, lost in the mechanical process of crushing the rock and separating the minerals for analysis.

With the exception of rock 5112, then, it appears that by far the greater part of the mercury present in the minerals is due to the retentive fraction of Reed and Jovanovic, the labile fraction being rapidly lost by upwards diffusion and migration. As regards the manner of mercury retention in the minerals, reference may be made to the work of Du Fresne and Anders (1962) and Lancet and Anders (1973) on the retention of noble gases in meteorites, and in the magnetite structure. In most meteorite minerals, lattice

TABLE II. *Mercury in minerals from the Skaergaard intrusion, East Greenland*

Rock No. and mineral	Modal Wt. %	Hg, ppm (duplicate analyses)	Mean Hg, ppm	Contribution to whole rock Hg, ppm	% contribution to whole rock Hg	
<i>5181, UZA</i>						
Plagioclase, An ₄₀	54	1.30	1.33	1.32	0.71	57.7
Pyroxene, Ca ₃₅ Mg ₃₄ Fe ₃₁	23	0.99	1.00	1.00	0.23	18.7
Olivine, Fa ₇₀	13	0.23	0.25	0.24	0.03	2.4
Ti-magnetite	4.5	0.57	0.61	0.59	0.03	2.4
Ilmenite	5.5	0.36	0.37	0.37	0.02	1.6
					1.02	82.8
				Whole rock	1.23	
<i>4427, MZ</i>						
Plagioclase, An ₄₀	27	0.10	0.09	0.10	0.03	14.3
Pyroxene, Ca ₃₆ Mg ₃₈ Fe ₂₆	36	0.41	0.43	0.42	0.15	71.4
Ti-magnetite	12.5	0.17	0.13	0.15	0.02	9.5
Ilmenite	22.5	n.d.				
					0.20	95.2
				Whole rock	0.21	
<i>5052, MZ</i>						
Plagioclase, An ₅₁	48	0.08	0.08	0.08	0.04	36.4
Pyroxene, Ca ₃₇ Mg ₄₀ Fe ₂₃	29	0.06	0.03	0.05	0.01	9.1
Ti-magnetite	9	0.06	0.04	0.05	0.005	4.5
Ilmenite	14	0.05	0.05	0.05	0.01	9.1
					0.065	59.1
				Whole rock	0.11	
<i>5112, LZb</i>						
Plagioclase, An ₅₇	37	0.01	0.01	0.01	0.004	5.7
Pyroxene, Ca ₃₈ Mg ₄₁ Fe ₂₁	45	0.03	0.03	0.03	0.01	14.3
Olivine, Fa ₄₃	15	0.05	0.04	0.05	0.01	14.3
Ti-magnetite	1	n.d.				
Ilmenite	2	n.d.				
					0.024	34.3
				Whole rock	0.07	
<i>5092, LZb</i>						
Plagioclase, An ₆₂	20	0.12	0.12	0.12	0.02	12.5
Pyroxene, Ca ₃₉ Mg ₄₂ Fe ₁₉	31	0.06	0.07	0.07	0.02	12.5
Olivine, Fa ₃₇	48	0.18	0.19	0.19	0.09	56.3
					0.13	81.3
				Whole rock	0.16	

defects are the probable loci of the gas atoms; in magnetite anion vacancies are considered the most likely trapping sites. If a mineral with volatiles in structural sites or defects is heated, the volatiles will not all be driven off at once but will diffuse at a rate that depends on the activation energy for the particular site and the temperature, in general the activation energy being lower for the defects, so that these would lose gas more rapidly than the structural sites at any given temperature. Some minerals (e.g. beryl, tourmaline, cordierite) have open structures with holes large enough to

hold foreign atoms or molecules: the loss of gas from these will be diffusion-controlled in the same way as for a gas occupying lattice sites.

Feldspars are known to be capable of taking up, and holding, up to twice their own volume of gas; Lancet and Anders (1973), for example, state that albite has the capacity to hold 3×10^{18} atoms Ar/g at 1000 °C and 2000 bars. The size of the hole in the 12-membered ring of the feldspar framework is about that of an oxygen ion and would not require very much distortion to enable it to accommodate mercury atoms of radius 1.6 Å. This might explain, for instance, the high mercury content of the 5181 plagioclase (1.31 ppm) and the higher mercury contents observed in the feldspathic rocks in general. The magma at the stage represented by the ferrodiorite 5181 seems to have been particularly rich in volatiles, as noted by Gay and Muir (1962) in a study of the feldspars, and by Wager (1960), who showed that water determinations in the whole rocks reached a peak at the same stage. Barker (1968), too, noted that the total volume of gases evolved on heating Skaergaard plagioclases *in vacuo* increased upwards in the intrusion, the Upper Zone plagioclases having the highest gas contents. Doubtless the high mercury contents of all the minerals of the rock 5181 reflect the richness of the magma in volatile components, including mercury, at that particular stage in its evolution.

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