OXYGEN FUGACITIES OF THE LAYERED SERIES OF THE SKAERGAARD INTRUSION, EAST GREENLAND

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ABSTRACT. The oxygen fugacities (f$_{O_2}$) of bulk rock samples and mineral separates from the Layered Series of the Skærgaard intrusion have been measured between 800° and 1200°C under ambient pressure by using the solid-electrolyte double-cell method. The f$_{O_2}$ values, measured reversibly upon temperature cycling, are half-way between those of the iron-wüstite and wüstite-magnetite assemblages throughout the crystallization sequence. The f$_{O_2}$ of Fe–Ti oxide separates are generally higher than those of bulk rock samples and silicate separates, suggesting selective postcumulus oxidation of the oxides.

The Lower Zone and Middle Zone samples underwent irreversible self-reduction when heated to temperatures above 1120°C, a behavior previously observed in natural and synthetic samples containing graphite. The crystallization f$_{O_2}$ of these samples, estimated on the basis of observed pre-reduction log f$_{O_2}$–(1/T) relations and inferred temperatures of crystallization, agree with the f$_{O_2}$ of the C–(CO$_2$ + CO) system under the inferred pressures of crystallization. These observations point strongly to the carbon control of the f$_{O_2}$ of the Skærgaard magma during the early stages of crystallization. It is probable that the low f$_{O_2}$ of the Skærgaard magma and the ensuing iron-enrichment differentiation trend were caused by the initial presence of carbon in the magma, combined with a low H$_2$O content and a relatively greater depth of crystallization, factors that retard the oxidation due to H$_2$ loss.

INTRODUCTION

Being one of the world's best exposed, preserved, and studied layered intrusions, the Skærgaard intrusion provides material ideally suited for the study of the redox behavior of a basaltic magma during subterranean crystallization differentiation. Many petrographic, mineralogical, and chemical data have been published and subsequently summarized (Wager and Brown, 1967). Using these data, several investigators have made estimates of the oxygen fugacities under which this intrusion crystallized. Buddington and Lindsley (1964) have estimated the f$_{O_2}$ of the Skærgaard rocks by their magnetite–ilmenite method. Lindsley, Brown, and Muir (1969) have used the quartz–magnetite–fayalite equilibrium relation in conjunction with estimated activities of the solids. Williams (1971) has also used the quartz–magnetite–fayalite equilibrium relation to estimate the f$_{O_2}$ of the Skærgaard rocks from several structural levels. These estimates are subject to uncertainties caused by post-crystallization changes of the oxides and incomplete knowledge of the solid solution behavior of the magnetite–ulvöspinel system at low magnetite compositions. We have tried the more direct solid-electrolyte oxygen cell method on the samples of the Layered Series, kindly provided by Professor A. R. McBirney of the University of Oregon. The oxygen fugacity data obtained indicate much more reducing conditions for the crystallization of the Skærgaard magma than those previously estimated.

METHOD

General background.—We used the solid-electrolyte double-cell method originally developed by Sato (1972) and improved by Sato, Hick-

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ling, and McLane (1973). This method is briefly described below for those who are not familiar with it. A small capsule containing a rock or mineral sample is placed at the closed end of a long tube of zirconia-based ceramic, which conducts electricity by oxide ion migration. The tube is evacuated, filled with an inert gas, and sealed tightly. The closed-end side of the tube is then heated in a vertical tubular furnace. Reactive gases such as H₂O and CO₂, existing as impurities in the inert gas or evolving from the sample upon heating, equilibrate with the sample and attain an f₀₂ which is equal to that of the sample. The amount of the reactive gases is normally so small that the intrinsic f₀₂ of the sample is considered virtually unchanged. An emf is developed across the wall of the electrolyte tube as a function of both the temperature and the logarithm of the ratio of the f₀₂ of the inner gas and that of the outer gas (furnace gas). The emf is picked up by the inner and outer inert metallic electrodes and read by a high-impedance electrometer. This assembly constitutes the sample cell. It is easy to see that by knowing or measuring the temperature of the sample and the f₀₂ of the furnace gas at this temperature, the f₀₂ of the sample can be determined from the measured emf. If the electrolyte tube were completely impervious to gases, air could be used as the furnace gas. In reality, however, leakage of gases through the tube wall occurs at high temperatures. When air is used as the furnace gas, a rock sample is oxidized slowly but steadily. To minimize the gas leakage effect on the sample f₀₂, oxidizing and reducing gases are mixed automatically in such a way that the f₀₂ of the furnace atmosphere follows that of the sample closely throughout the f₀₂ measurements. An additional cell is required to determine the f₀₂ of the furnace gas. Air is circulated through the interior of the second oxygen cell to act as the f₀₂ reference. In practice, the emf's of the two cells are added because the emf of the sample cell is not always zero due to an error in the f₀₂ matching.

The solid-electrolyte double-cell method is not only direct and applicable to wide ranges of f₀₂ and temperature but is also a very sensitive method. An invisibly thin coating of ferric oxide weighing about 3 × 10⁻¹⁶ g would produce a sustained emf reading for an hour (Sato, 1972). This high sensitivity may become a disadvantage, because sometimes the cell emf responds to the presence of minute contaminants more than to the predominant sample material proper. For example, a thin limonite coating on mineral grains formed by weathering would produce a high f₀₂ for hours during the initial heating at subsolidus temperatures simply because the inner gas phase responds directly to the surface rather than to the interior of the mineral grains. Organic contaminants, such as residues of heavy liquids used for separation or hydrocarbons absorbed by a powdered sample from polluted urban atmosphere in storage, would give an extremely low f₀₂ reading at several hundred degrees C by evolving reducing gases upon pyrolysis. Fortunately, it is possible to differentiate such abnormal readings from the true sample f₀₂ in most cases by monitoring the steadiness (or unsteadiness) of the emf at a constant tem-
temperature. Contaminants such as those described above produce constantly drifting emf's, because they react with the bulk of the sample steadily until exhausted. The emf eventually approaches a steady value, which can be reproduced in subsequent temperature cycling. Admittedly, a contaminated sample should not give exactly the same $f_{O_2}$ as that of an uncontaminated sample even after the contaminants are exhausted. In reality, however, whether the result obtained with a slightly contaminated sample should be completely discarded or partly saved depends on the judgement of the experimenter. In many cases, a slight contamination does not produce a significant difference in reproducible $f_{O_2}$ once the contaminants are reacted out, as the difference depends on the change in the bulk composition of the sample due to the reaction with the contaminants. The $f_{O_2}$ values measured during the temporary domination of the gas phase $f_{O_2}$ by the contaminants should be discarded, as the departure could be as large as several log $f_{O_2}$ units.

If a rock has undergone a substantial post-crystallization oxidation or reduction, the solid-electrolyte method is subject to the modification like any other method. An important advantage of this method is, however, the freedom of choice of the phases to examine. Mineral separates such as oxides, olivine, and pyroxenes can be used just as well as the bulk rock, and the results can be compared. If the oxides have been altered by a subsolidus oxidation process, the bulk of the silicates may have escaped the oxidation, owing to slower reaction rates. This point will be demonstrated later.

A serious drawback of the present solid-electrolyte double-cell method is the restriction on pressure. It is not possible to conduct $f_{O_2}$ measurements at the same pressure as that under which the rocks crystallized at depth. An equilibrium assemblage under a high pressure may not be in equilibrium at all at the ambient pressure, and an internal redox reaction may occur. In the present study, we have encountered a problem of this nature with certain samples. Pronounced self-reduction at high temperatures has marred our attempt to determine the intrinsic $f_{O_2}$ values of these samples at high temperatures and has forced us to extrapolate the the low temperature values to such temperatures. As will be discussed later, the observed self-reduction has been interpreted to have been caused by the presence of graphite, the oxidation $f_{O_2}$ of which is highly pressure-dependant.

In addition to the occurrence of pressure-sensitive reactions such as the one discussed above, there is a problem of pressure-dependency of the intrinsic $f_{O_2}$ arising from the volume change of the condensed phases under pressure. Iron-bearing oxygen buffer assemblages show some pressure-dependency ranging from 0.04 to 0.07 log $f_{O_2}$ units per kilobar at 1000°C (Eugster and Wones, 1962). At subsolidus temperatures the equilibrium $f_{O_2}$ of a basaltic rock sample can be considered as being controlled by reactions similar to those for the standard buffer assemblages, because the rock contains mineral phases with a fixed activity of either fayalite, silica, magnetite, et cetera, or a combination of these. It
is highly probable that the bulk-rock $f_{O_2}$ increases with increasing pressure in a manner similar to the standard iron-bearing buffer assemblages, and that the relative change of the bulk-rock $f_{O_2}$ with respect to those of the buffers for a pressure of a few kilobars is negligible. At temperatures higher than the solidus of the rock sample (which may be very different from that of the magma), a complication may arise because of the formation of a liquid, which reacts with the surrounding gas much faster than the solids and thus takes over the control of the gas $f_{O_2}$ that is being measured. In an undifferentiated lava or dike rock, the $f_{O_2}$ of the liquid probably recapitulates the natural path of crystallization of the magma. In a highly differentiated and layered rock, the liquid produced may have no resemblance to the liquid from which the orthocumulates had crystallized. In fact, in a rock composed predominantly of orthocumulus ferrous silicates, the liquid is expected to have a lower Fe$_2$O$_3$/FeO ratio, and hence a lower $f_{O_2}$, than the liquid from which the orthocumulates had crystallized as the degree of melting advances. In such a case, the intrinsic $f_{O_2}$ of each orthocumulate mineral is a more reliable indicator of the crystallization $f_{O_2}$, provided that the pressure effect is negligible and the temperature remains below its melting point. The pressure dependency of the intrinsic $f_{O_2}$ of a single mineral phase is difficult to evaluate (Sato, 1972), but it may be approximated by the following model. Olivine, for example, is known to contain a finite concentration of ferric iron, though it may be extremely small. Natural olivine, therefore, may be regarded as a solid solution of fayalite, forsterite, and trace amounts of silica and magnetite. Partial molar volumes of silica and magnetite in the olivine are difficult to assess but may be approximated as close to those of the pure components. The pressure effect on the intrinsic $f_{O_2}$ in such a case would not differ much from that of the fayalite–quartz–magnetite buffer, which is $+0.07 \log f_{O_2}$ unit per kilobar. For a pressure less than a few kilobars, the pressure effect may be neglected.

Experimental procedure.—Flat-bottomed $Y_2O_3$ (10 mole percent)-stabilized zirconia tubes $^1$ (9.5 mm OD) were used for both the reference cell and the sample cell. The sample cell was placed below the reference cell in a upside-down position. A small silica glass capsule (6 mm OD and 6 mm high) containing 50 to 100 mg of a crushed rock or mineral sample and capped by a tadpole-shaped piece of Ag$_{40}$Pd$_{60}$ foil was placed at the top interior of the sample tube. The capsule was firmly supported by a Vycor tube having an 1 mm bore. The AgPd foil acted as the internal metallic contact of the solid-electrolyte tube. For olivine separates, the silica capsule was lined with AgPd foil to prevent a possible reaction. A platinum wire connected the foil electrically with an external elec-

$^1$According to Professor G. C. Ulmer of Temple University, Philadelphia, yttria-stabilized zirconia tubes manufactured in U.S.A. after 1976 are either too sensitive to thermal shock (nuclear grade) or so high in iron content that erroneous emfs are produced (electrochemical grade). An effort to rectify this problem is being excrated by the manufacturer. The tubes used in this study were made before 1976 and showed no sign of misbehavior when calibrated with standard buffers such as iron-wüstite and Ni-NiO.
trometer circuit through the Vycor tube and a Teflon high vacuum connector which sealed the sample cell. After the loading of the sample, the air in the cell interior was evacuated and replaced by pure argon.

For the furnace gas, a mixture of 1 percent CO₂ in N₂ and 1 percent H₂ in N₂ were blended through a servo-controlled valve in such a way that the f₀₂ of the gas mixture closely followed that of the sample during a series of measurements to prevent oxidation or reduction of the sample by gas diffusion through the electrolyte. The temperature was changed stepwise between 800° and 1200°C in both directions at temperature intervals of about 40°C and at time intervals of about 1.5 hrs. The emf difference between the two cells and the temperature within the reference cell were read near the end of each isothermal period from a digital recording tape.

Great care was exercised in the preparation of the samples. For bulk-rock samples, the fresh interior of a lump was coarsely crushed in a synthetic sapphire mortar and used unsieved. For single mineral samples, the rocks were crushed to -60 to +200 mesh size, magnetically separated, and hand-picked under stereomicroscope. Heavy liquids were never used. The use of pre-powdered samples was discontinued after a few preliminary measurements because of a suspicion of organic contamination.

The double-cell apparatus was periodically calibrated by using the Ni-NiO and Fe-FeO buffers for f₀₂ and gold melting for temperature. The instrumental accuracy is conservatively estimated at ± 0.1 log f₀₂ (bar) unit for f₀₂ and ± 2°C for temperature.

RESULTS

The results obtained show much lower f₀₂ conditions throughout the major crystallization sequence of the Skaergaard magma than those previously estimated. Both bulk-rock samples and separated minerals consistently showed f₀₂ conditions lower than those of the magnetite-wüstite buffer. The results are described below for each submember of the Layered Series starting from the top of the Layered Series. This inverse manner of presentation of the stratigraphic sequence is necessitated by the complexity of the data of the lower horizons.

It was observed in a number of cases that the log f₀₂ values of a sample below a certain temperature showed a linear relation to the reciprocal absolute temperature, (1/T), when plotted graphically. There is no a priori reason to assume the linearity, but for the convenience of numerical presentation of the data, linear regression (least squares fit) of the data points below the temperature at which the linearity ceases has been performed to obtain an equation of the form: log f₀₂ = a + b/T. These equations are summarily tabulated in table 1, together with McBirney's sample identification number, stratigraphic horizon, the number of data points, correlation coefficient (r²), and the temperature range. No attempt has been made to describe the petrology of the rock sample nor the exact location of the sample. References shall be made
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to Professor Mc Birney's papers (that is, Mc Birney, 1975) for information. The inferred nature of the temperature at which the linearity ceases is discussed below for each sample.

Upper Zone

1. UZc subzone.—The bulk-rock $f_{O_2}$ values are plotted on a log $f_{O_2}$ vs $(1/T)$ diagram in figure 1A. The values measured during the first heating cycle showed a good linear relation to the maximum heating temperature of 1112°C, but those obtained during the first cooling cycle showed appreciable departure toward higher $f_{O_2}$ in the temperature range of 950° to 850°C (max 865°C). Below 800°C, the $f_{O_2}$ returned to the linear relation. The cause for this apparently anomalous behavior has not been ascertained, but one speculation is that the rapid cooling rate in the laboratory had caused the fractionation of the melted sample, and the residual liquid (perhaps a few percent of the total), enriched in ferric iron, dominated the gas phase $f_{O_2}$ as discussed earlier. When the residual liquid had crystallized at lower temperatures, the majority of the crystallized sample regained the control of the gas $f_{O_2}$. In lieu of experimental confirmation of this interpretation, all the 11 data points were included in the regression analysis, the result of which is tabulated in table 1.

The $f_{O_2}$ values of Fe–Ti oxides (a mixture of titaniferous magnetite and ilmenite), separated magnetically after crushing the rock sample, are shown in figure 1B. During the first heating cycle, log $f_{O_2}$ followed a linear relation against $(1/T)$ up to about 1200°C, where a downward drift began. Below 1030°C, log $f_{O_2}$ returned to the initial linear relation. During the second heating cycle, the deviation from the linearity began

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<th>McBirney Sample No.</th>
<th>Stratigraphic Horizon</th>
<th>Sample Type</th>
<th>Fig. No.</th>
<th>$\log f_{O_2}$ (least-squares fit)</th>
<th>No. of Data Points</th>
<th>Correlation Factor ($r^2$)</th>
<th>Temperature Range (°C)</th>
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* Before the onset of self-reduction
at about 1100°C. During the second cooling cycle, log $f_{o_2}$ returned to the linear relation at 1030°C as before. This behavior is highly suggestive of partial melting of the oxides. A similar behavior was observed in the past on the fayalite-magnetite-quartz buffer at temperatures above 1140°C, the solidus of the assemblage. Because a mixture of pure Fe–Ti oxides should not melt at 1030°C, it is likely that some silicates (plagioclase, fayalitic olivine) remained unseparated within the oxide grains and produced a low-melting liquid with the oxides. The liquid probably leaked out at about 1200°C during the first heating and gained control of the gas $f_{o_2}$. As the liquid probably formed at the surface of the oxide grains during the second heating cycle, the deviation from the linearity began at lower temperatures. (Unfortunately, we did not have time to make a more thorough separation and test this hypothesis.) The result of the least squares fit of 15 data points measured at and below 1030°C is tabulated in table 1.

2. UZb subzone.—The bulk-rock $f_{o_2}$ values showed a systematic scatter as shown in figure 2A. The first cooling cycle values were consistently higher than the first heating cycle values. The departure was at maximum at 980°C. At lower temperatures, the two sets of values became close again, and the second heating cycle values fell between the two

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**Fig. 1.** Measured $f_{o_2}$ of the bulk-rock sample from the Upper Zone c horizon of the Skærgaard intrusion. The bold solid line represents the linear log $f_{o_2}$ versus $(1/T)$ equation tabulated in table 1. The symbols discriminating the data points stand for those obtained during the first heating cycle △, the first cooling cycle ▽, the second heating cycle △, the second cooling cycle ▽, the third heating cycle △, and the third cooling cycle ▽, wherever applicable from figure 1A through figure 7. Data points with an arrow pointing down or up indicate those that failed to reach a steady value within and equilibration period of about 1.5 hrs and are considered to be unreliable. The fine solid lines, when drawn in a figure, show the log $f_{o_2}$–$(1/T)$ trace after partial melting or self-reduction, covering the data points that are not considered to be useful in inferring the magmatic $f_{o_2}$ at the time of crystallization of the orthocumulates. The dotted lines are for the WM (wüstite-magnetite) and IW (iron-wüstite) $f_{o_2}$ buffers. (B) Measured $f_{o_2}$ of Fe-Ti oxides separated magnetically from the UZc rock sample.
sets of values. The similarity of the pattern to that of the UZc bulk-rock sample suggests that the cause for the systematic scatter was also similar. The higher temperature for the maximum deviation, presumably caused by a differentiated residual liquid, is in line with the earlier crystallization of UZb. The result of the least squares fit of 15 data points obtained between 690° and 1110°C (4 points obtained below 800°C are not shown in fig. 2A) is tabulated in table 1.

The oxide separate showed a behavior characteristic of a sample contaminated by a thin oxidation film, as discussed earlier. During the first heating cycle, the fO₂ kept drifting down and did not stabilize within the programmed equilibration periods (about 1.5 hrs) until heated to 1200°C. Subsequent cooling and heating showed a reproducible and linear relation as shown in figure 2B. Because the fO₂ of the oxide separate after the cessation of the constant drifting is very similar to that of the bulk rock, and the bulk rock sample did not show such a behavior, it is likely that the presumed oxidation film was a product of weathering or some other low-temperature process and of very local nature. The constantly drifting nature disqualifies the validity of the data obtained during the first heating cycle below 1200°C. Table 1 lists the result of the least squares fit of 24 data points obtained between 857° and 1204°C, which exclude those of the first heating cycle mentioned above.

3. UZa subzone.—The bulk rock sample showed a constant downward drifting of fO₂ during the first heating cycle up to about 1000°C, due probably to the presence of traces of oxidized matter of unknown origin. Stable and reproducible values were obtained above this temperature during the first heating cycle and at all temperatures of fO₂ measurement (803°-1211°C) during the second heating and cooling cycles. The log fO₂-(1/T) plots are linear below 1030°C, but at higher tem-

![Fig. 2. (A) Measured fO₂ of the bulk-rock sample from UZb horizon. (B) Measured fO₂ of the oxide separate from UZb horizon. For symbols used, see figure 1A.](image-url)
peratures they follow, reproducibly, a concave-upward curve which increasingly deviates from the linear relation toward lower $f_{O_2}$ with increasing temperature, as shown in figure 3A. Judging from the reproducibility of the non-linear segment, it is likely that the deviation from the linearity was caused by the formation of a liquid in which the $Fe^{3+}/Fe^{2+}$ ratio decreased with increasing temperature as more ferrous silicates dissolved. The initial liquid formed at 1080°C was probably of intercumulus nature. This "solidus" temperature, therefore, should be lower than the crystallization temperature of the cumulus minerals, but the difference between the two temperatures is probably small, because the UZa rock represents about 95 percent crystallization level of the Skaergaard magma (Wager and Brown, 1967), and most of the $H_2O$ originally present in the intercumulus liquid was probably lost during the post-crystallization cooling. The result of the least squares fit of the 9 data points obtained below 1030°C, which exclude those of the first heating cycle below 1000°C for the reason of incomplete internal equilibration of the sample as reflected by the unsteadiness of the readings, is given in table 1. Above 1030°C, the $f_{O_2}$ of the liquid of this rock composition follows the curve shown in figure 3A. The liquid curve does not necessarily represent the $f_{O_2}$ of the magma from which the orthocumulates had crystallized, however. It is more likely that the intrinsic $f_{O_2}$ of the cumulus silicates, which should better reflect the magmatic $f_{O_2}$ at the crystallization temperature, lies closer to the high-temperature extension of the linear relation.

The magnetic separate (oxides) from UZa rock sample failed to produce stable $f_{O_2}$ readings during the initial heating cycle, a behavior similar to that of the UZb oxides. The $f_{O_2}$ kept drifting down until the temperature reached about 1200°C. Partial oxidation of the oxide(s) during subsolidus cooling of the intrusion or upon exposure to the

![Image](image_url)

**Fig. 3.** (A) Measured $f_{O_2}$ of the bulk-rock sample from UZa horizon. (B) Measured $f_{O_2}$ of the oxide separate from UZa horizon.
weathering environment of the rock is a possible reason for this behavior, as discussed earlier. Reproducibility was good in the subsequent heating and cooling cycles. Only the \( f_{O_2} \) values obtained after the initial heating and cooling cycles are shown in figure 3B. The result of the least squares fit of 28 data points obtained between 993° and 1206°C, which exclude those of the first heating and cooling cycles, is given in table 1.

**Middle Zone**

One set of measurements of the bulk rock \( f_{O_2} \) produced reproducible and linear log \( f_{O_2}-(1/T) \) plots as shown in figure 4A. The result of the least squares fit of 14 data points obtained between 763° and 1205°C is given in table 1. Another experiment using a different batch of the sample produced unstable readings below 1050°C and a sudden drifting down above about 1120°C. After heating to 1156°C, the \( f_{O_2} \) became stable and settled to a trace very close to the iron-wüstite buffer curve during subsequent cooling and heating cycles. The probable cause for this behavior and similar behavior observed on other samples of the Middle Zone and the Lower Zone will be discussed below.

The \( f_{O_2} \) of the oxide separate was steady at each temperature step and showed a high degree of linearity in the log \( f_{O_2}-(1/T) \) plot up to 1120°C during the first heating cycle, as shown in figure 4B. The correlation coefficient for the linear regression analysis was very high (table 1). Above this temperature, the \( f_{O_2} \) drifted downward and assumed a new linear trace during the first cooling and the second heating cycles. When the temperature exceeded about 1140°C, the \( f_{O_2} \) again shifted to lower values. The downward shift of the log \( f_{O_2}-(1/T) \) trace in the present case differs from the case of liquid formation discussed earlier in that the departure from the initial linear trace is irreversible when the tempera-

![Fig. 4. (A) Measured \( f_{O_2} \) of the bulk-rock sample from MZ horizon. (B) Measured \( f_{O_2} \) of the oxide separate from MZ horizon. Self-reduction occurred at temperatures above 1120°C.](image-url)
ture was lowered. This fact indicates that the process that caused the $f_{O_2}$ drift was not an equilibrium (or quasi-equilibrium) process, such as partial melting, but a redox reaction that occurred as a result of a chemical disequilibrium within the sample system. The reduction of the sample was not induced externally, because the Upper Zone samples did not show this behavior when heated to as high as 1200°C under identical experimental conditions. Contamination by organic matter can be excluded, because the temperature at which the $f_{O_2}$ began drifting was too high for organic matter, as discussed earlier. The most reasonable explanation appears to be that an internal disequilibrium was created by a change in an environmental parameter, namely pressure, and the rise in temperature kinetically triggered the redox reaction to reach a new equilibrium state. In fact, this “self-reduction” behavior has been observed rather commonly on rocks and minerals formed under pressure, such as mantle-derived nodules (Sato, 1978a and unpub data). Some of the nodules that showed this behavior contain macroscopic graphite flakes. The oxidation $f_{O_2}$ of graphite is highly pressure dependent (French, 1966), and when the $CO_2 + CO$ pressure exceeds a few hundred bars, graphite can coexist with a basaltic magma without precipitating metallic iron (Sato, Hickling, and McLane, 1973). The slow reaction rate of graphite with a basaltic glass at temperatures below 1120°C was demonstrated experimentally by Sato (1977). The pattern of the irreversible $f_{O_2}$ shift observed in the above experiment was almost identical to that of the present case. Although the occurrence of graphite in the lower horizons of the Skaergaard intrusion has not been described in the literature, the self-reduction behavior observed in the present sample and the randomness of the occurrence of the self-reduction among different batches of the Middle Zone bulk rock sample may best be explained by assuming that elemental carbon existed as sparsely distributed minute flakes in these samples. Carbon is an efficient reducing agent; 100 ppm C can reduce at least as much as 0.13 wt percent $Fe_2O_3$ to FeO.

**Lower Zone**

The $f_{O_2}$ measurements of the Lower Zone samples were plagued by the self-reduction behavior presumably due to the presence of graphite, as discussed for some of the Middle Zone samples.

1. **LZc.**—A typical behavior of the bulk rock $f_{O_2}$ of the LZc samples is shown in figure 5A. The initial heating to about 1120°C produced a linear trace which follows the equation tabulated in table 1. A drastic downward shift of the trace, amounting to more than 1.5 log $f_{O_2}$ unit, occurred at higher temperatures, and on cooling the $f_{O_2}$ followed a path that is comparable to those of lunar basalts. For reasons discussed earlier, the $f_{O_2}$ data obtained after the occurrence of the high-temperature reduction should be considered as experimental artifacts and, hence, should be ignored.

An oxide separate showed a similar behavior, although less pronounced than for the bulk rocks, as shown in figure 5B. The initial heat-
ing produced a linear trace up to about 1120°C following the relation tabulated in table 1. Self-reduction occurred at higher temperatures, and the $f_{o_2}$ during the first cooling and second heating cycles (below 1120°C) followed another linear relation. A slight reduction again occurred at higher temperatures during the second heating.

An olivine separate also showed a similar self-reduction behavior at high temperatures as shown in figure 5C. During the first heating cycle, the $f_{o_2}$ of the olivine did not follow a linear log $f_{o_2}$ vs (1/T) relation below about 950°C but started out at a value identical to that of the post-reduction value at the same temperature (856°C), which is about 0.5 log $f_{o_2}$ unit lower than that of the iron–wüstite buffer. The $f_{o_2}$ drifted upward with increasing temperature and at above 950°C stopped drifting.

Fig. 5. (A) Measured $f_{o_2}$ of the bulk-rock sample from LZc horizon. Self-reduction occurred at temperatures above 1120°C. (B) Measured $f_{o_2}$ of the oxide separate from LZc horizon. (C) Measured $f_{o_2}$ of the olivine separate from LZc horizon. (D) Measured $f_{o_2}$ of the plagioclase separate from LZc horizon.
and settled on a linear relation listed in table 1 up to about 1120°C. A slight reduction again occurred at temperatures above 1145°C during the second heating cycle, presumably because carbon remained partly unreacted during the first heating.

A plagioclase separate produced very low $f_{O_2}$ readings throughout the first heating cycle and subsequent heating cycles, as shown in figure 5D. These values are comparable to those of lunar rocks. Plagioclase has a low iron content (generally less than 1 percent in basaltic rocks) and a rather open crystal structure, and thus its intrinsic $f_{O_2}$ may have been altered easily by a subsolidus reduction caused by the presence of graphite or CO. The behavior of the olivine $f_{O_2}$ at the initial stage of the first heating cycle described above is also suggestive of a slight post-crystallization surface reduction. The cause for such a reduction remains uncertain at present. We do not believe that the plagioclase data reflect the initial magmatic $f_{O_2}$ condition, however.

2. LZb subzone.—The results obtained on samples of this subzone do not appear to be reliable. Except for one olivine separate run, the bulk rock, plagioclase, and olivine separates all gave $f_{O_2}$ values equal to or lower than those of the iron-wüstite buffer. The results obtained on the olivine separate are shown in figure 6. It showed the self-reduction behavior at high temperatures. The five data points measured during the first heating cycle below 1120°C appeared to be strongly curved. When a linear fit is forced upon these points on the basis of the behavior of other samples, the equation given in table 1 is obtained.

3. LZa subzone.—The measurements on these samples were troubled by self-reduction behavior. Several runs produced $f_{O_2}$ values lower than those of the iron-wüstite buffer, even from the start of the first heating cycle. This was particularly true with plagioclase separates, though the $f_{O_2}$ was reproducible. One bulk rock run produced results that did not

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**Fig. 6.** Measured $f_{O_2}$ of the olivine separate from LZb horizon.

**Fig. 7.** Measured $f_{O_2}$ of the bulk-rock sample from LZa horizon.
appear to have been affected by the self-reduction nor by accidental oxidation during the first heating cycle below 1120°C. The plots of $f_{O_2}$ vs. $(1/T)$ are linear below this temperature, as shown in figure 7. The result of the least squares fit of 6 data points obtained below 1120°C is given in table 1.

**DISCUSSION**

Two major points are indicated by the results of our direct $f_{O_2}$ measurements on bulk rock samples and mineral separates. The first point is that the $f_{O_2}$ values measured reproducibly (or measured before the onset of self-reduction in the Lower Zone and Middle Zone samples) are all lower than those of the wüstite–magnetite buffer, contrary to previous estimates. The second point is that the presence of graphite or some other form of reduced carbon in the magma during the early stages of crystallization is indicated by the self-reduction behavior of the samples of the lower levels.

**Discordancy with Previous Estimates**

Inasmuch as we are faced with a substantial disagreement with the $f_{O_2}$ estimates of Buddington and Lindsley (1964), Lindsley, Brown, and Muir (1969), Williams (1971), and Morse, Lindsley, and Williams (1980), we feel that critical examinations of the methods used are necessary.

As discussed briefly in the Method Section, the solid electrolyte method is subject to kinetic effects and contamination problems. Because the emf reading of the double-cell arrangement depends on the $f_{O_2}$ of the gas phase inside the sample compartment, whatever controls this $f_{O_2}$ more quickly has a dominant effect on the measured $f_{O_2}$ initially. Rust or organic material may thus produce an $f_{O_2}$ reading far removed from that of the uncontaminated sample. A problem of this nature can easily be deciphered from continuous drifting of $f_{O_2}$ at a constant temperature. A liquid formed by partial melting of intercumulus material in a differentiated, layered rock may produce an $f_{O_2}$ reading slightly different from that of the magma at the crystallization temperature of the cumulus minerals. The liquid formation can often be inferred from a reversible change in the $f_{O_2}$–$T$ trace as discussed earlier. Other problems such as a failure of the furnace gas supply or an unnoticed crack in the electrolyte tube which permitted air to diffuse into the sample cell before the start of the measurements also occurred in the present study, but these problems could be readily seen during the experiment, and the results set aside. Other than paying due caution to the existence of these problems, the solid electrolyte method is not prejudicial. The method measures the $f_{O_2}$ of a sample system in the cell automatically, regardless of what the sample is. The redox history of a rock, such as postcumulus oxidation, may be deciphered by the choice of the sample, that is, by loading the bulk rock, handpicked orthocumulates, or separated intercumulus minerals.

It may be argued that the intrinsic $f_{O_2}$ measured under low ambient pressure would not reflect those under higher pressures which prevailed
during the crystallization of the Skaergaard magma. It is difficult to believe that the intrinsic $f_{O_2}$ of a rock or a mineral is multifold more sensitive to pressure than the $f_{O_2}$ of an all-solid buffer assemblage, however. As discussed earlier (see Method Section), a more reasonable assumption is that the positions of the measured intrinsic $f_{O_2}$ of the Skaergaard samples with respect to the $f_{O_2}$ of the iron-bearing $f_{O_2}$ buffers remained virtually unchanged within the pressure range of a few kilobars. In summary, it is difficult to change the overall picture, that the $f_{O_2}$ values of the Skaergaard rocks fall half-way between those of the wüsite-magnetite and iron-wüsite buffers, by blaming the method. If the rocks truly had $f_{O_2}$ higher than the wüsite-magnetite buffer, the method would have measured higher $f_{O_2}$ values, as demonstrated with an Etna hawaiite lava (Sato and Moore, 1978).

The previous $f_{O_2}$ estimates of the Skaergaard magma all relied on the compositions of the Fe–Ti oxides. There are at least two possible sources of error for such estimates. The magnetite-ilmenite method of Buddington and Lindsley (1964) is vulnerable to the subsolidus re-equilibration of the oxides. Rapid re-equilibration of the two oxides was documented by Grommé, Wright, and Peck (1969) on the drill core samples of Hawaiian lava lakes, in which a more dominant ilmenite-hematite phase was believed to have forced the oxidation of the magnetite-ulvöspinel phase at subsolidus temperatures. Similar oxidation of the magnetite-ulvöspinel phase may have contributed to the higher maximum $f_{O_2}$ estimate (10–13.6 bar at 980°C) for UZc by Lindsley, Brown, and Muir (1969).

Another possible source of error involved in the oxide methods is the higher susceptibility of the Fe–Ti oxides to postcumulus oxidation processes. The exposed Skaergaard rocks have higher $Fe_3O_4/FeO$ ratios than those that can be accounted for by crystallization differentiation (Wager, 1960). Constant loss of hydrogen from the magma was suggested to be the cause (Wager and Deer, 1939). Even though the Skaergaard magma has been considered to be relatively dry, it is still likely that some water existed in the interstitial liquids. When the liquids finally solidified and the water vapor pressure abruptly increased, hydrogen probably escaped by osmosis. Subsolidus oxidation of basalt, probably caused by this mechanism, has been observed in Hawaiian lava lakes (Sato and Wright, 1966) and in the interior of a thick Icelandic lava flow (Watkins and Haggerty, 1967). If a similar subsolidus oxidation occurred in the Skaergaard intrusion, it is likely that intercumulus minerals were more oxidized than the cumulus minerals. Among the intercumulus minerals, the oxides probably underwent oxidation more intensely than the silicates, because the oxides are known to react more readily to changing $f_{O_2}$ than the silicates. In our study, the Fe–Ti oxides of UZa and MZ showed definitely higher $f_{O_2}$ than those of corresponding bulk rocks and silicates. It is less clear with samples of other subzones, but the tendency appears to be general. Because both cumulus and intercumulus oxides were
picked up by our magnetic separation method indiscriminately, and because the iron oxides crystallized late (Wager and Brown, 1967), the oxide separates undoubtedly had a larger fraction of intercumulus material, which probably suffered from post-cumulus oxidation of the sort discussed above.

The most important source of error involved in the \( f_{O_2} \) estimation on the basis of the activities of \( SiO_2 \), \( Fe_2SiO_4 \), and \( Fe_3O_4 \) (Lindsley, Brown, and Muir, 1969; Williams, 1971) is the assumption of near-ideal solution behavior for the magnetite-ulvöspinel series. A separate study by the present authors has indicated that the solution series show a pronounced negative deviation from ideality at least between 1000°C and 1200°C. The activity coefficient of magnetite is about 0.3 where magnetite mole fraction is less than 0.18, and hence the ideal solution assumption gives more than an order of magnitude higher \( f_{O_2} \) when the oxide solution is rich in ulvöspinel as in the Skaergaard rocks. A more detailed discussion will be made elsewhere regarding a close agreement between the intrinsic \( f_{O_2} \) values of Fe-Ti oxides measured in the present study and the theoretical \( f_{O_2} \) values based on the activities of magnetite determined experimentally.

**Graphite in the Skaergaard Rocks**

As mentioned earlier, we believe that the self-reduction observed at temperatures above about 1120°C of the rock and mineral samples from the LZ and MZ horizons was caused by the presence of graphite or some other forms of reduced carbon in these samples. This interpretation is not new. Sato (1977, 1978a, and unpub. data) has observed similar reduction behavior on terrestrial mantle-derived minerals and some lunar rocks and postulated that the reduction was caused by fine-grained graphite existing in these samples. To support this claim, Sato (1977) has demonstrated that, when about 1 percent graphite was added to a synthetic basaltic glass, the \( f_{O_2} \) of this mixture was identical to that of the pure synthetic glass below 1120°C, due probably to the extreme sluggishness of the reduction of graphite at lower temperatures. At higher temperatures the \( f_{O_2} \) decreased abruptly and irreversibly. Although the amount of the downshift of the log \( f_{O_2} - (l/T) \) trace of this synthetic mixture was much more drastic than the natural material suspected of containing graphite, the pattern of the shift was strikingly similar. The amount of graphite required to cause a substantial decrease in \( f_{O_2} \) can be very small, if the initial \( Fe^{3+}/Fe^{2+} \) ratio in a rock is rather small, as in the Skaergaard rocks. It takes only 100 ppm C to reduce more than 9.15 wt percent \( Fe_2O_3 \) to \( FeO \). Fedali (1965) has shown that \( f_{O_2} \) changes roughly in proportion to \( FeO_{1.5}/FeO \) mole ratio in a rock melt. The average content of \( FeO_{1.5} \) in the LZ rocks is 1.8 wt percent and that of \( FeO \) is 10.2 wt percent (Wager and Brown, 1967). A simple calculation shows that 500 ppm C can lower the \( f_{O_2} \) of a melt of this composition by more than 0.9 log \( f_{O_2} \) unit if reacted to form CO and by more than 2.5 log \( f_{O_2} \) units if oxidized to \( CO_2 \).
The presence of graphite in basaltic rocks has been reported by a few authors. Hoefs (1969) reports 110 to 290 ppm C for the concentration of elemental carbon in minerals from gabbroic and basaltic rocks. Lebedev (1957) believes that elemental carbon occurs as submicroscopic inclusions of graphite in Siberian basalts. Czamanske, Himmelberg, and Goff (1976) report that graphite has been found throughout the exposed portion of the La Perouse layered gabbro, Alaska, and that it occasionally occurs as nearly pure seams up to 0.3 m thick. It is likely that graphite is a common igneous mineral in many deep-seated basaltic intrusions that solidified under pressure. The reason that the occurrence of graphite in the Skaergaard rocks has not been reported is probably that nobody has looked for it. Graphite is opaque in thin sections and easily plucked away during polishing in polished sections. If very fine grained, the recognition of graphite by optical means will be very difficult. Detection of carbon by the electron microprobe method will also be difficult because of the small atomic number of carbon. A systematic search for graphite in the Skaergaard rocks is urgently needed, however.

Another indirect support for the presence of graphite in the Skaergaard magma during the early stages of crystallization comes from the agreement between the inferred crystallization $f_{O_2}$ of the LZ and MZ rocks and the oxidation $f_{O_2}$ of graphite. This argument rests on two basic assumptions. The first assumption is that the crystallization $f_{O_2}$ of the cumulus minerals can be obtained from the linear log $f_{O_2} - (1/T)$ relations observed before the onset of self-reduction and the estimated temperatures of crystallization. This assumption is justifiable because the intrinsic $f_{O_2}$ of the orthocumulates should coincide with the magmatic $f_{O_2}$ at the temperature of crystallization.

It has been found empirically (for example, Sato, 1972) that the intrinsic $f_{O_2}$ of various minerals, glassy materials, and the equilibrium $f_{O_2}$ of bulk rocks at subsolidus temperatures follow a linear log $f_{O_2} - (1/T)$ relation closely for a temperature span of a few hundred degrees. The second assumption is that the oxidized carbon gases (CO$_2$, CO) are the predominant gases in basaltic magmas at a depth where pressure is greater than a few hundred bars. The observations of Roedder (1965) and Moore, Buchelder, and Cunningham (1977) justify this assumption. It follows then that, if graphite was indeed present in the Skaergaard magma during the crystallization of the LZ and MZ cumulates, the magmatic $f_{O_2}$ should have been equal to the $f_{O_2}$ of the graphite–(CO$_2$ + CO) system under the existing pressure in the magma. This means that the inferred crystallization $f_{O_2}$ of the LZ and MZ cumulates should approximate the $f_{O_2}$ of the C–(CO$_2$ + CO) system under inferred load pressure.

To examine the above correspondence, the pre-reduction bulk-rock $f_{O_2}$ of LZa and that of LZc as well as the intrinsic $f_{O_2}$ of LZc olivine, all listed in table 1 in the form log $f_{O_2} = a + b/T$, are drawn on a log $f_{O_2}$–$(1/T)$ diagram in figure 8. Isobaric (in terms of total pressure) $f_{O_2}$ curves for the C–(CO$_2$ + CO) system, computed by the Modified Redlich-Kwong equation program of Holloway (1976), are also shown on the diagram.
In order to evaluate the above correspondence, it is necessary to know or estimate the temperature of crystallization.

Williams (1971) has estimated that the crystallization temperature for LZc (700 m level) was 1150°C on the basis of the olivine–pyroxene–magnetite–ilmenite equilibria. The bulk-rock $f_{O_2}$ of LZc corresponds to about 900 bars of gas pressure for the C–(CO$_2$ + CO) system, and the olivine $f_{O_2}$ corresponds to about 1.2 kb of the gas pressure at this temperature, as shown graphically in figure 8. Similarly, the bulk-rock $f_{O_2}$ of LZa corresponds to 1.5 to 2.2 kb between 1150° and 1200°C. Williams (1971) has estimated the total pressure of the Skaergaard intrusion at 2 kb at the base to 0.5 kb at the top. McBirney (1975) and W. P. Nash (personal commun.) have estimated the pressure at the base of LZa at 1.2 kb. Although not shown in figure 8, the bulk-rock $f_{O_2}$ of MZ (almost identical to that of LZc in the range of temperature under discussion) corresponds to about 600 to 900 bars between 1100° and 1150°C. Con-

![Fig. 8. Comparison of isobaric curves for the C–(CO$_2$ + CO) equilibrium with the pre-reduction log $f_{O_2} - (1/T)$ relations for the LZa bulk rock (A, solid line), LZc olivine separate (B, dashed line), and LZc bulk rock (C, broken line). If the carbon gases were the predominant gases in the magma and the magmatic $f_{O_2}$ was controlled primarily by the C–(CO$_2$ + CO) reaction, the crystallization $f_{O_2}$ of the cumulates should coincide with the $f_{O_2}$ of the C(CO$_2$ + CO) reaction for the corresponding pressure of crystallization.](image-url)
sidering the uncertainties in the \( f_{O_2} \) values, estimated crystallization temperatures, and fugacity coefficients for \( CO_2 \) and \( CO \), the agreement between the estimated pressure of crystallization of the LZ and MZ rocks and the \( (CO_2 + CO) \) gas pressure in equilibrium with graphite deduced from the experimental crystallization \( f_{O_2} \) of the rocks appears to be good. A better agreement is obtained, however, if the estimated 1-bar crystallization temperatures of the LZ and MZ rocks are lowered by a few tens of degrees.

The implication of the above agreement is that graphite was present in the Skaergaard magma during the crystallization of the LZ and MZ rocks and was trapped in the crystallizing minerals. Graphite probably disappeared by the end of crystallization of the Middle Zone in the Skaergaard magma. The Upper Zone minerals did not show the self-reduction behavior even when heated to temperatures above 1120\(^\circ\)C. The \( f_{O_2} \)-pressure correspondence discussed above for lower-level rocks was not observed with the UZ samples.

*Oxygen fugacity of the Skaergaard magma.*—In order to assess the \( f_{O_2} \) of the Skaergaard magma at each stage of crystallization of the Layered Series from the observed \( f_{O_2}-T \) relations listed in Table 1, it is necessary to know the temperatures of crystallization. At present, no published experimental data are available on the liquidus temperatures of liquids which would produce the observed cumulus assemblages of the Skaergaard intrusion. Mc Birney (1975) discusses the complications involved in experimentally determining the liquidus temperatures of simulated magmatic liquids for the Skaergaard rocks. In lieu of firmly established experimental data, the temperature estimates of Williams (1971) are used primarily except for the Lower Zones. We feel that Williams' estimate of 1300\(^\circ\)C for the base of the Lower Zone is too high. By using the olivine–pigeonite–magnetite–ilmenite assemblage Williams (1971) obtained 1150\(^\circ\)C for the 700 m level (near the LZb–LZc boundary) as the maximum temperature. Olivine–pyroxene–plagioclase assemblages were observed to crystallize from similar tholeite magmas below 1170\(^\circ\)C by Peck, Wright, and Moore (1966) and Wright and Okamura (1977) in Hawaiian lava lakes. The pressure coefficient of the liquidus temperature of tholeite is 5\(^\circ\) to 11\(^\circ\)C per kilobar according to Green (1968). As discussed earlier, our experimental \( f_{O_2} \) data on the LZ rocks agree reasonably well with the \( f_{O_2} \) of the C–(\( CO_2 + CO \)) system for estimated pressures, if the crystallization temperatures are assumed to be lower than 1200\(^\circ\)C, preferably about 1170\(^\circ\)C for LZa and about 1140\(^\circ\)C for LZc. In view of these factors, the following mid-level temperatures are tentatively assigned for various subzones: LZa 1200\(^\circ\)C, LZc 1150\(^\circ\)C, MZ 1100\(^\circ\)C, UZa 1050\(^\circ\)C, UZb 1010\(^\circ\)C, UZc 980\(^\circ\)C. An error in the temperature estimate would result in an appreciable difference in the numerical value of \( f_{O_2} \), but the numerical value is not as relevant as the relative position of the \( f_{O_2} \) in reference to those of the iron-bearing \( f_{O_2} \) buffer assemblages in evaluating the redox state of a magma. Fortunately, the relative position would not change much even though the error in the temperature
estimate amounted to a hundred degrees, because the observed sub-solidus \( \log f_{O_2} - (1/T) \) relations of the Skaergaard rocks and minerals are nearly parallel to those of the iron-bearing buffers (figs. 1-7). The inferred \( f_{O_2} \) trends of the Skaergaard magma are shown in figure 9 (bottom) on the basis of the measured sub-solidus \( f_{O_2} \) values of bulk-rock samples (solid arrows) and Fe–Ti oxides (dashed arrows) using the above temperature estimates. The trends of the relative \( f_{O_2} \) in reference to the iron–wüstite buffer are shown in figure 9 (top). The logarithms of the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ionic ratio, computed from the composition of the Skaergaard liquids at various stratigraphic levels estimated by Wager (1960), are also plotted in figure 9 (top). The intrinsic \( f_{O_2} \) of an iron-bearing liquid is a function of the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) activity ratio and hence should correlate with the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ionic ratio if the activity coefficients remain reasonably constant. As seen in figure 9 (top), the bulk-rock \( f_{O_2} \) trend corresponds with the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio except for UZc, whereas the oxide \( f_{O_2} \) trend fails to do so. Mc Birney (1975) has estimated the composition of the Skaergaard liquids on the basis of the composition of the melted inter-

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**Fig. 9 (bottom).** \( f_{O_2} \) trends of the Skaergaard magma inferred on the basis of estimated temperatures of crystallization shown in the figure and the measured \( f_{O_2} \) of the bulk-rock samples (circles with solid line) and those of Fe–Ti oxide separates (squares with dashed line). (Top). Comparison of the trend of the log \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ionic ratios calculated from the liquid compositions estimated by Wager (1960) with the trend of relative \( f_{O_2} \) of bulk-rock samples (circles with solid line) and that of oxide separates (squares with dashed line).
cumulus material and crystallization experiments on simulated liquids. The two estimates appear to be concordant except for the last stages of crystallization of the Upper Zone, although Mc Birney (1975) makes no reference to the Fe\(^{3+} / Fe^{2+}\) ratio. If we accept the trend of the Fe\(^{3+} / Fe^{2+}\) ratio based on Wager's estimate as correct except for UZc, it follows that the bulk-rock \( f_{\text{O}_2} \) trend reflects the magmatic \( f_{\text{O}_2} \) trend more faithfully than the Fe–Ti oxides. The oxides fail to reflect the magmatic \( f_{\text{O}_2} \) probably because a significant fraction of the oxides have crystallized from intercumulus liquids and have been subjected to postcumulus oxidation caused by \( H_2 \) loss from the intercumulus liquids.

The trend of the \( f_{\text{O}_2} \) of the Skaergaard magma observed on bulk-rock samples suggests the following redox history of the magma. The magma probably contained carbon as fine suspension of graphite when generated by partial melting of the mantle. The mobility of elemental carbon in basaltic magmas could be surprisingly high due to the possibility of temporary formation, diffusion, and subsequent disproportionation of CO and COS. Friel, Goldstein, and Romig (1977) have observed that carbon redistributed evenly in 1 day at 875°C between carbon-bearing and carbon-free iron–nickel charges separately placed in an evacuated silica glass capsule. They have suggested a mechanism similar to the above. The \( f_{\text{O}_2} \) of the magma at the source region could have been higher than that of the wüstite–magnetite buffer, because the \( f_{\text{O}_2} \) of the C–(CO\(_2\) + CO) system increases much more rapidly than those of the iron-bearing buffers with increasing pressure (fig. 8). As the magma ascended from the source region and intruded into the Skaergaard magma chamber, the drastic pressure decrease probably caused partial reduction of the magma by carbon. The reduction continued throughout the crystallization of the lower layers (HZ, L.Za–L.Zc, and MZ), as indicated by the decreasing relative \( f_{\text{O}_2} \) of these zones (fig. 9B). Carbon was oxidized to CO\(_2\) and probably trapped partly as dense CO\(_2\) inclusions by the early minerals, as observed by Roedder (1965) in other rocks and minerals of deep origin.

Increasing escape of \( H_2 \) after intrusion and increasing H\(_2\)O content of the liquid due to crystallization accelerated the reaction of carbon with H\(_2\)O: C + 2H\(_2\)O = CO\(_2\) + 2H\(_2\), and eventually oxidized all carbon (MZ–UZa) and partially dehydrated the magma. This dehydration may have caused, at least partly, the magma to absorb vaporized meteoric water from the heated surrounding rocks producing a lower O\(^{18}/\)O\(^{16}\) ratio as found by Taylor and Epstein (1963). Wager and Brown (1967, p. 187) consider that the amount of water that would have to be absorbed to produce the excess of ferric iron found in the exposed Layered Series rocks calculated on the basis of the amount in the chilled marginal gabbro (about 1.2 wt percent) is an order of magnitude too low to account for the change in oxygen–isotope ratios by the loss of H\(_2\) alone. The low \( f_{\text{O}_2} \) values of the Skaergaard magma found in the present study suggest that the ferric iron content of the magma during the crystallization of the rocks of the lower horizons was probably a fraction
of a percent in view of the experimental results of Fudali (1965). Taylor and Epstein (1963) suggest subsolidus oxidation of the chilled marginal gabbro, an interpretation which is compatible with the present argument. The reaction of carbon with water and the loss of H₂ and CO₂ would have enhanced the incorporation of a larger amount of meteoric water after the outward flow of CO₂ had diminished by the exhaustion of carbon at around the MZ stage.

Meanwhile, the temperature decrease caused a magnetite–ulvöspinel phase to crystallize in spite of the low fO₂ of the magma. Thompson (1975) has shown that the stability boundary of magnetite in contact with basaltic liquids sharply extends to lower fO₂ as temperature decreases. The high ulvöspinel content of magnetite–ulvöspinel in the Skaergaard rocks (up to 90 mole percent, Williams, 1971) are compatible with the low fO₂ of the magma presented in this study. According to Webster and Bright (1961), when ulvöspinel content is greater than 85 mole percent, the spinel is stable at fO₂ lower than that of the iron–wüstite buffer at 1200°C.

The relative fO₂ path of figure 9 (top) indicates that oxidation of the magma occurred after the crystallization of the MZ rocks. As discussed above, perhaps this was the stage when meteoric water moved into the magma and reacted with it generating H₂. The light, mobile H₂ continuously escaped from the roof of the magma chamber and resulted in the oxidation of the magma. Continuous monitoring of hydrogen now underway in active basaltic volcanic areas indicates that H₂ indeed escapes from a magma reservoir (Sato, unpub. data). The crystallization and separation of ferrous silicates also contributed to the increase of relative fO₂ of the magma by increasing the Fe³⁺/Fe²⁺ ratio of the liquid.

After the crystallization of UZb, the relative fO₂ decreased according to our results. This is the stage where our fO₂ trend and the Fe³⁺/Fe²⁺ ratio trend of Wager (1960) are discordant. The liquid composition trend of McBurney (1975) also disagrees with Wager's composition trend. The maximum ulvöspinel content in magnetite reaches the maximum at the UZc level (Williams, 1971). In view of these factors, we assume that the Skaergaard magma was reduced after the crystallization of UZb in accordance with our measured fO₂. The cause for this reduction was probably the dominant crystallization of cumulus magnetite. Comparison of the composition of the Skaergaard liquid (Wager, 1960) with that of magnetite–ulvöspinel (Vincent and Phillips, 1954) throughout the crystallization sequence of the Layered Series suggests that magnetite partitions ferric iron preferentially even when the ulvöspinel content exceeds 70 mole percent. In lieu of more reliable experimental data, we assume that this was true at least through the crystallization of the upper UZb rocks. The dry Skaergaard magma thus followed a low fO₂ path at least through the crystallization of UZc and followed the well-known iron-enrichment differentiation course, as argued by Wager and Brown (1967, p. 242).
The low $f_{O_2}$ of the Skaergaard magma compared to subaerial basalts and andesites (for example, Fudali, 1965) could be accounted for by the combination of the following three factors: the initial presence of carbon in the magma, low initial water content, and larger depth of crystallization. The initial presence of carbon in the magma is necessary to reduce the magma upon ascent from the source region, where the $f_{O_2}$ is presumably a little higher. The amount of water is very important in determining the $f_{O_2}$-T path of a magma (Sato, 1978a). In the absence of water, reduction by carbon would continue and eventually precipitate metallic iron as in lunar basalts. A higher water content in a magma would result in earlier disappearance of carbon and also in a higher $H_2$ loss caused by higher $f_{H_2O}$ and $f_{H_2}$. Alkali basalts, which are richer in $H_2O$ than tholeiitic basalts, thus would eventually have higher $f_{O_2}$ because of more rapid escape of $H_2$. The depth of crystallization also relates to the rate of $H_2$ loss. In a magma chamber shallower than the Skaergaard intrusion hydrogen would escape more easily. We believe that the role played by gas-forming elements in controlling the redox state of basaltic magmas is decisively important.

The post-cumulus oxidation of the iron oxides, as indicated by the relatively higher intrinsic $f_{O_2}$ of the magnetically separated oxides in figure 9, probably occurred when water was concentrated in the last residual fraction of the intercumulus liquids at temperatures comparable to the crystallization temperature of the granophyre phase. The increased water vapor pressure presumably accelerated the hydrogen loss and resulted in local oxidation.

CONCLUSIONS

The following conclusions may be drawn from the results of the present study.

1. The $f_{O_2}$ of the Skaergaard magma remained between those of the wustite-magnetite and the iron-wustite buffers throughout the crystallization of the exposed Layered Series.

2. The self-reduction behavior observed on Lower Zone and Middle Zone rocks at temperatures above 1120°C suggests the presence of elemental carbon (probably graphite) in these samples.

3. The estimated $f_{O_2}$ of the crystallization of the cumulates of the lower horizon rocks suggests that, during the crystallization of the lower horizon rocks, the magma contained graphite (perhaps as finely suspended particles) and that the magmatic $f_{O_2}$ was controlled by the oxidation reaction of graphite. Graphite in the magma probably disappeared after the crystallization of the MZ rocks due to the reactions with ferric iron and $H_2O$ in the magma.

4. The low $f_{O_2}$ of the Skaergaard magma was probably caused by a combination of the following three factors: (i) the initial presence of elemental carbon which probably reduced the magma during the ascent and the early stages of crystallization; (ii) the low initial content of water, which limited the water-carbon reaction and the extent of oxidation
due to hydrogen loss; (iii) the comparatively greater depth of crystallization, which hindered the hydrogen loss.

5. The high ulvöspinel content of the Skaergaard magnetite is the result of the low $f_{O_2}$ of the Skaergaard magma. The TiO$_2$, which would enter ilmenite in a more oxidized magma, was incorporated into the spinel phase.

6. Caution is required in estimating $f_{O_2}$ on the basis of Fe–Ti oxides, as the oxides are vulnerable to late stage oxidation due to hydrogen loss and to subsolidus re-equilibration. The non-ideal solution behavior of magnetite–ulvöspinel phase should be critically examined.

ACKNOWLEDGMENTS

This work would not have materialized without the generous offer of the Skaergaard rock samples by Professor A. R. Mc Birney, University of Oregon. Initially one of the authors (MS) planned to combine efforts with Professor Mc Birney using his powdered samples, but the preliminary results which showed self-reduction were considered to be puzzling then. After requesting block samples, the puzzle of self-reduction still remained unsolved. Years passed before the carbon reduction hypothesis was formulated from work by MS on lunar samples. The second author (MV) performed most of the experimental work presented in this paper while he was a visiting scientist at the U.S. Geological Survey in Reston on a grant provided by the National Research Council of Italy. The manuscript was reviewed by Drs. W. P. Nash, C. R. Thornber, R. J. Williams, and T. L. Wright. The paper has benefitted from their constructive criticisms. We also gratefully acknowledge personal communications provided by Drs. G. K. Czamanske, J. J. Friel, and G. C. Ulmer, and thank Dr. John Holloway for the use of his gas fugacity program.

REFERENCES


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