CONDITIONS OF THE FERROWOLLASTONITE-FERROHEDENBERGITE INVERSION IN THE SKAERGAARD INTRUSION, EAST GREENLAND

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ABSTRACT

Rocks from the late stages of fractionation of the Skaergaard intrusion contain ferrohedenbergites inverted from ferro-wollastonite solid solutions (Upper Zone c) and quartz inverted from tridymite (Upper Border Group 'Y'). Experiments determining the pressure-temperature conditions of the hedenbergite-wollastonite solid-solution inversion for an analyzed Skaergaard ferrohedenbergite (EG 4471), combined with published data on the quartz-tridymite inversion, show that the pressure was 600 ± 100 bars and that the temperature range included the span 980 to 950°C during the late stages of crystallization of the Skaergaard intrusion. The oxygen fugacity under these conditions is calculated to have ranged from $10^{-13.8}$ to $10^{-13.6}$ atm. These values are about one and one-half orders of magnitude below those of the fayalite-magnetite-quartz buffer, and essentially coincide with those of the wüstite-magnetite buffer. The absence of inverted ferro-wollastonite solid solutions in the Bushveld intrusion is ascribed to higher pressure prevailing during the crystallization of that body relative to the Skaergaard intrusion.

INTRODUCTION

The clinopyroxenes crystallized during the late stages of fractionation of the Skaergaard intrusion and of the Bushveld intrusion have closely similar compositional trends (Wager and Brown, 1968, pp. 39; 391). A minor but significant difference between them is the presence in the Skaergaard intrusion of green hedenbergitic pyroxenes (Hdss) that are believed to have inverted form ferro-wollastonite solid solutions (Woss) Wager and Deer, 1939, p. 111; Muir, 1951, pp. 708–709; Brown and Vincent, 1963, pp. 186–190; Wager and Brown, 1968, pp. 41–42). Lindsley (1967, pp. 232–234) proposed that the absence of inverted WOss from the Bushveld intrusion resulted from crystallization of that body at somewhat higher pressures than prevailed during the late crystallization stages of the Skaergaard intrusion. In this paper we report experiments on the Hdss-Woss inversion in several analyzed Mg-poor clinopyroxenes from the Skaergaard intrusion and one from the Bushveld intrusion. The pressure-dependence of the inversion temperature in one inverted WOss (from Skaergaard sample EG 4471), combined with data in the quartz-tridymite inversion (Tuttle and Bowen, 1958, pp. 30–32) yields the temperature range and pressure that must have prevailed at some stage during crystallization of Upper Zone c (Fig. 1) of the Skaergaard intrusion. Thus it is possible to adduce data on some of the intensive parameters that controlled late-stage crystallization of that intrusion. Our results corroborate, but do not prove conclusively, the inference that the late stages of the Skaergaard intrusion crystallized at lower pressures than did the equivalent portions of the Bushveld intrusion.
tain green pyroxene rimmed by or intergrown with the brown variety. Note that EG 4471 and 1881 are crystal accumulates, where EG 4330 probably represents a liquid. Photomicrographs showing the pyroxenes from these three rocks are given in Figure 3. Chemical analysis of the pyroxenes are given in Brown and Vincent (1963, Table 1). Analyses of similar examples of inverted ferriferous wollastonites are also given by Muir (1951), his EG 1974 being comparable with EG 4471, and his EG 4131 being intermediate between EG 4471 and EG 1881. (Structural heights given for Muir’s specimens have been revised by Wager and Brown, 1968.)

The cumulate rocks from Upper Zone c all contain cumulus fayalitic olivine and intercumulus quartz. Rocks immediately overlying this zone (Upper Border Group γ, approximately 100 m thick) contain quartz paramorphs after tridymite, coexisting with primary quartz (for example, EG 3021, Fig. 4). If both pairs of minerals—Hdₖs, Woss and quartz-tridymite—occurred in the same layer, then at some time during its crystallization history that layer must have been at a pressure and temperature corresponding to the intersection of the appropriate inversion curves in P-T space. At the coexisting pairs occur at slightly different levels, an estimate of the pressure and temperature differences between the two levels will indicate how close the crystallization sequence came to the region of intersection.

Specimen EG 3021 occurs less than 100 m above EG 4330 and 200 m above EG 1881, corresponding to maximum pressure differences of about 30 and 60 bars, respectively. Crystallization at each level took place over a
temperature range, or course, but it is nevertheless meaningful to estimate differences in the temperatures at which the clinopyroxene now present in each layer first crystallized or, say, at which fifty percent of the pyroxene had crystallized in each layer. We may refer to these as “average” temperature differences. An estimate of the “average” temperature difference between EG 1881 and EG 3021 may be made as follows. On the basis of the compositions of clinopyroxene and of olivine, EG 3021 probably crystallized at about the same time, and hence over approximately the same temperature interval, as rocks in the layered series between EG 4318 and EG 4471 (Fig. 1). Tilley, Yoder, and Schairer (1963, p. 78, 80; 1964, p. 94) determined the liquidus temperatures and temperatures of first appearance of Wo$_{ss}$ (or H$_{ss}$) in two Skaergaard specimens that have approximately the same stratigraphic separation as do EG 1881 and the layered equivalent of EG 3021 (see Fig. 1). For specimen EG 4472 (same level as EG 4471) the temperatures are: liquids, 1035°C; first appearance of H$_{ss}$ and Wo$_{ss}$ 1010°C. For EG 4330, the liquidus is at 1020°C and the first appearance of H$_{ss}$ and Wo$_{ss}$ at 995°C. The difference in liquidus temperatures, and also the difference in the temperatures of first appearance of H$_{ss}$ + Wo$_{ss}$, is 15°C. Thus a reasonable estimate of the “average” temperature difference between EG 1881 and EG 3021 is 15°C; 30°C would be a maximum difference. These experiments were performed in vacuum, and the temperatures determined may differ somewhat from those that prevailed at pressure in nature; however, the temperature differences at pressure were probably similar to those obtained in vacuum. Note that the liquidus temperature for EG 4472 must be a maximum inasmuch as that specimen is
a crystal accumulate and therefore did not crystallize from a liquid of its own bulk composition. We conclude that the pressure and "average" temperature differences between EG 1881 and EG 3021 were not more than 60 bars and 30°C, respectively. Therefore, the intersection in pressure-temperature space of the quartz-tridymite and Hds-Wo inversions should give a close estimate of the pressure and temperature during crystallization of the late stages of the Skaergaard intrusion.

PREVIOUS EXPERIMENTAL WORK ON THE Hds-Wo Inversion

The pioneering study on synthetic Ca-Fe pyroxenes was made by Bowen, Schairer, and Posnjak (1933). Their discovery that hedenbergitic pyroxenes invert to Wo upon heating to temperatures well below the metasilicate solidus was the basis for Wager and Deer’s conclusion that the mottled green ferrohedenbergites from the Skaergaard intrusion had initially crystallized as ferro-wollastonite solid solutions. Bowen, Schairer, and Posnjak (1933, p. 213) showed an inversion loop between Hds and Wo with a minimum at approximately WoFs (mole %), and they indicated that the composition of Hds coexisting with Wo + fayalite + tridymite is about WoFs. Lindsley and Munoz (1969) redetermined the subsolidus relations for the join Hds-Fs using much longer run durations and hydrothermal experiments to demonstrate equilibrium. They found that only the hedenbergite-rich half of the Hds-Wo inversion loop of Bowen, Schairer, and Posnjak represents stable equilibrium and that the maximum solubility of FeSiO3 in Hds and Wo is somewhat less than that given by Bowen, Schairer, and Posnjak. A revised diagram for the join Hds-Fs, incorporating the subsolidus data of Lindsley and Munoz with the melting data of Bowen, Schairer, and Posnjak is given in Figure 5. At 940°C, fayalite and silica can coexist with Hds (WoFs) and Wo (WoFs). This result is consistent with the fact that the green, inverted Wo is slightly richer in FeSiO3 than is the brown, primary Hds from the Skaergaard intrusion (Muir, 1951, p. 708; Brown and Vincent, 1963, pp. 181, 183).

Yoder, Tilley, and Schairer (1963, p. 91) inverted ferrohedenbergites separated from Skaergaard specimens EG 4471, 4472, and 4143 to Wo at 970° ± 5°C in evacuated tube experiments. They did not reverse the inversion, however, so their results give only a maximum temperature for the beginning of the inversion in vacuum.

Turnock has shown that the temperature of the Hds-Wo inversion strongly increases with increasing Mg-content for the join Ca0.5Mg0.5SiO3—Ca0.5Fe0.5SiO3 (1962, p. 81) and the join Ca0.4Mg0.6SiO3—Ca0.4Fe0.6SiO3 (personal communication, 1968). Compositions of late-stage Hds from the Skaergaard intrusion lie close to the Fe-rich end of the latter join.

Lindsley (1967, p. 234) found that the temperature of the Hds-Wo inversion on the join Hds increases sharply with pressure. For example, pure hedenbergite inverts to Wo at 965°C at one atmosphere but at approximately 1200°C at 10 kbars.

INVERSION OF GREEN FERROHEDENBERGITE FROM EG 4471

To locate an appropriate Hds-Wo inversion interval for the Skaergaard intrusion we have investigated the pressure-temperature relations for the green Hds from EG 4471.
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4471 at pressures from 0 to 5 kbar. The starting material was a split of the mineral separate analyzed by Brown and Vincent (1963); part of the material was initially inverted to Wo as in vacuum at 1000°C to permit reversal of the reaction. Details of the experimental techniques employed and the experimental data are given in the Appendix. Our results are summarized in Figure 6.

We are uncertain of the exact nature of the transition from primary Wo as to Hd as in EG 4471. There are several possibilities: (1) Transition of Wo as to Hd as of the same composition; this is a true inversion, and will take place over a temperature interval. (2) Reaction of Wo as to Hd as + FeSiO3-rich pyroxene. Bown and Gay (1960, p. 386) found that the green Hd as of EG 1974 and EG 1881 are single phases, but that of EG 4143 shows exsolution of FeSiO3-rich clinopyroxene. This metastable reaction also would take place over a temperature interval. We cannot tell which of these three processes took place in nature or in our experiments, but in keeping with past usage we will refer to the transition as an inversion, and to the necessary temperature interval as an inversion interval.

The inversion interval shown in Figure 6 is applicable directly only to the green, inverted Wo as from EG 4471; later hedenbergites from the Skærgaard intrusion would presumably invert over a lower temperature range and earlier hedenbergites would invert, if at all, over a higher temperature range. However, it is possible qualitatively to relate other late-stage Skærgaard rocks to the diagram. EG 4471 originally precipitated Wo as and quartz, and is therefore shown in the P-T region where those fields overlap. Because EG 1881 occurs later in the crystallization sequence and at a higher stratigraphic level than does EG 4471, it must have been precipitated over a lower temperature range and at a lower pressure. EG 1881 contains inverted Wo as, primary Hd as, and quartz, so it is shown in Figure 6 as lying in the quartz field and within the Wo as + Hd as field (the assumption being that the inversion interval for EG 1881 is not much different from that for EG 4471).

EG 4330, containing primary Hd as and quartz is still later in the crystallization sequence, and must have crystallized over a lower temperature interval and at a lower pressure than did EG 1881; the Hd as in EG 4330 formed below its own inversion interval and therefore below that shown for EG 4471 in Figure 6. Finally, because of its higher elevation, EG 3021 must have crystallized at still lower pressures; but the Fe/Mg ratios of its clinopyroxene and olivine reflect a higher temperature range than any of the other three samples. EG 3021 contains both inverted tridymite and primary quartz, so it must lie at lower temperatures not more than 30°C above and at pressures not more than 60 bars below EG 1881. The distribution of pressures and temperatures shown in Figure 6 for these four rocks is the only one mutually consistent with the textural, mineralogical, and stratigraphic evidence, and with the available experimental data. We conclude that the rocks formed during the late crystallization stages of the Skærgaard intrusion (Upper Zone c and Upper Border Group γ) crystallized at 600 ± 100 bars and over a temperature interval that must have spanned the range 950–980°C.

In Figure 6, EG 3021 falls in the Wo as field as determined for the inverted Wo as from EG 4471. It is necessary to pos-

It is worth reemphasizing here that all the rocks crystallized over a temperature range: the temperatures indicated in Fig. 6 might well correspond to those at which approximately half the pyroxene now present in each rock had crystallized. Likewise, of the four specimens, only EG 4330 and EG 3021 crystallized at a fixed pressure. EG 1881 and EG 4471 are crystal accumulates, and the minerals now present in them crystallized over a possible pressure range that at a maximum corresponds to the thickness of the remaining magma through which they sank, that is, to the difference in elevation between each layer and its equivalent in the Upper Border Group. The pressure range cannot exceed approximately 85 bars for EG 4471 (based on a layer of liquid plus crystals with a maximum thickness of 280 m and a specific gravity of 3.0); for EG 1881 the pressure range is less.
Fig. 7. Hypothetical and highly schematic diagrams showing the authors' interpretation of the relationship between the clinopyroxene (Cpx)-Wo₃ inversion intervals and the crystallization curves for the Skaergaard and Bushveld magmas. Dotted lines: crystallization curves; approximate temperature range over which liquid of a given Fe/Mg ratio precipitated metasilicates. Dashed lines: approximate boundaries of Cpx-Wo₃ inversion intervals. During the bulk of Skaergaard crystallization (a) Wo₃ was not stable. However, as the Fe/Mg ratio of the liquid increased with continuing fractionation, the crystallization curve intersected the Cpx (Hd₃,-)-Wo₃ inversion interval. Wo₃ was the only metasilicate precipitated (e.g., Eg 4471, 1974) in the interval where the crystallization curve lay completely above the Cpx-Wo₃ inversion. With increasing Fe/Mg ratio of the liquid Cpx and Wo₃ co-precipitated (e.g., EG 4471, 1974) and finally only Wo₃ precipitated (EG 4330). According to this interpretation there should also be at least a narrow layer immediately underlying EG 4471 and 1974 in which Cpx and Wo₃ co-precipitated. Such a layer has not yet been reported.

The effect of increasing pressure on the temperatures of the Cpx-Wo₃ inversion and of magmatic crystallization is unequal; the increase of the former is greater. Accordingly, in the Bushveld intrusion (b), which is thought to have crystallized at a higher pressure than did the Skaergaard intrusion, the crystallization curve never intersected the Wo₃ field.

In order to precipitate the primary Hd₄⁺ occurring in EG 3021 contains too much Mg for Wo₃ to have precipitated in its place. This conclusion is consistent with available experimental data on the Di-Hd join (Turnock, 1962) that the inversion temperature increases with increasing Mg/Fe ratio, and with the observation that the green, inverted Wo₃ contains less Mg than would a Hd₃⁺ in the same position in the Skaergaard layered series (Muir, 1951, p. 708; Brown and Vincent, 1963, p. 181, 183). We tested this hypothesis by holding analyzed Hd₄⁺ from EG 3021, 4332, and 4318, all of which contain somewhat more MgSiO₃ than that from EG 4471 (Fig. 1), at 1000°C for 40 days in evacuated silica glass tubes. Also included in this experiment were the green, inverted Wo₃ from EG 4471 as a control; the brown, nearly Mg-free Hd₄⁺ from EG 4330; and a pale green Hd₄⁺ from the Bushveld intrusion whose composition (SA 1149, Wager and Brown, 1968, Table 28) is closely similar to that from EG 4330. The first three more magnesian samples failed to invert; the latter three did invert to Wo₃, although SA 1149 inverted only partially. These results are not definitive; the failure of the three samples richest in Mg to invert suggests, but does not prove, that their Hd₄⁺ was still stable. However, these experiments are consistent with our conclusion that only briefly during the crystallization history of the Skaergaard intrusion were the activity of MgSiO₃ and the pressure sufficiently low, while the temperature was sufficiently high, to permit primary precipitation of Wo₃. In the Bushveld intrusion, on the other hand the pressure was too high to permit the precipitation of Wo₃ at any time. These interpretations are illustrated schematically in Figure 7.

We can determine a third intensive parameter that prevailed during these late stages of Skaergaard crystallization, the oxygen fugacity (fₒ₂), as follows: Specimen EG 1974 (= EG 4471) contains a titaniferous magnetite whose bulk composition (Vincent and Phillips, 1954, p. 12) recalculates to the binary composition M₁⁺₄.₃₂US₈.₅₂ (see Buddington and Lindsley, 1964, p. 314-328 for the justification of this recalculation). The experimental data show that the maximum fₒ₂ at which a spinel of this composition can be stable is 10⁻³⁻⁵.₅ bar at 950°C and 10⁻¹⁻₃.₅ bar at 980°C, the values for the wüstite-magnetite buffer (Buddington and Lindsley, 1964, Fig. 2, 5). An additional constraint results from the fact that EG 1974 contains fayalitic olivine and quartz as well as titaniferous magnetite. This assemblage defines the equilibrium oxygen fugacity through the relation:

\[ 3\text{Fe}_2\text{SiO}_3 + \text{O}_2 = 2\text{FeO} + 3\text{SiO}_2 \]

and therefore

\[ K_T = \frac{(\alpha_{\text{Fe}_2\text{O}_3})^3(\alpha_{\text{SiO}_2})^3}{(\alpha_{\text{FeO}})^3 f_{\text{O}_2}} \]

where \( \alpha_{\text{Fe}_2\text{O}_3} \) is the activity of Fe₂O₃ in titaniferous magnetite, etc. The equilibrium constant \( K_T \) equals \( 1/f_{\text{O}_2} \) when the activities of all the solid phases are unity, and it can be evaluated from the data of Eugster and Wones (1962, p. 90):

\[ K_T = 10^{11.97} \text{ at } 950^\circ\text{C and } 10^{11.45} \text{ at } 980^\circ\text{C.} \]

The activities of the solid phases are estimated as follows: As a first approximation the activity of Fe₂O₃ is taken as equal to the mole fraction 0.145; note that any departure from ideality is likely to be positive since the Fe₂O₃-Fe₃O₄-TiO₂ series has a miscibility gap at lower temperatures. The coexisting olivine in EG 1974 contains 98 percent Fe₃SiO₄ (Fig. 1), so to a good approximation \( \alpha_{\text{Fe}_3\text{SiO}_4} = 0.98. \) Quartz apparently was not a cumulus phase in EG 1974, but inasmuch as it is a fairly abundant intercumulus phase, the activity of silica must have been essentially unity during precipitation of the olivine and titaniferous magnetite. Using these estimates we calculate the \( f_{\text{O}_2} \) at 600 bars as 10⁻¹⁻₃.₅ bar at 950°C and 10⁻¹⁻₃.₁ bar at 980°C. These must be minimum values, since any positive deviation from ideality of \( \alpha_{\text{Fe}_2\text{O}_3} \) would yield higher values for \( f_{\text{O}_2}. \) This close correspondence between the calculated maximum and minimum values probably owes at least as much to good fortune as to experimental virtuosity. Nevertheless it is reasonable to conclude that the oxygen fugacity during the late stages of Skaergaard fractionation ranged from approximately 10⁻¹⁻₃.₀ (at 980°C) to 10⁻¹⁻₃.₅ bar (at 950°C) which happen to coincide with the values for the wüstite-magnetite buffer.

Evidently conditions became oxidizing relative to that
buffer at lower temperatures, since the titaniferous magnetite from EG 1974 contains ilmenite lamellae. On the basis of coexisting ilmenite and titaniferous magnetite in EG 4142 (= EG 1881), Buddington and Lindsley (1964, p. 331) derived a temperature of 890 ± 50°C and an fO₂ of 10⁻¹⁵.² ± 1.⁹, conditions that probably reflect the cessation of granule-“exsolution” of ilmenite upon oxidation of the magnetite (p. 322–324). Although this value of fO₂ is numerically similar to that calculated above for EG 1974, it is oxidizing relative to the wüstite-magnetite buffer since it obtained at a lower temperature.

We do not conclude from these results that the entire Skaergaard intrusion crystallized under conditions of constant oxygen fugacity. Rather, we visualize crystallization of all but a minute fraction of this notoriously “dry” intrusion at oxygen fugacities whose numerical values were similar to those of the wüstite-magnetite buffer. Below 950°C, however, only minute amounts of liquid remained, and the activity of the dissolved water increased accordingly. Under these conditions the activity of hydrogen would also increase (see, for example, Eugster and Wones, 1962, Fig. 3). Hydrogen would therefore tend to escape preferentially by thermal diffusion, and the system would become more oxidizing (Presnall, 1966, p. 778–779; Buddington and Lindsley, 1964, p. 321). Because of a high molecular proportion of oxide phases to water, the extent of oxidation was not great. For example, of five titaniferous magnetite-ilmenite pairs from the Skaergaard intrusion, all indicate oxygen fugacities above those of the wüstite-magnetite buffer but still below those of the fayalite-magnetite-quartz assemblage (Buddington and Lindsley, 1964, p. 331).

Stoichiometric water is oxidizing with respect to the wüstite-magnetite buffer; at temperatures near 950°C and total pressures of 600 bars or less, a H₂O fluid in equilibrium with the wüstite-magnetite buffer has a H₂/O ratio of approximately 1 : 8. If the late-stage rocks of the Skaergaard intrusion exchanged oxygen isotopes with large volumes of meteoric groundwater (which would be essentially stoichiometric and hence oxidizing) as suggested by Taylor (1968, p. 60–62), most of the exchange must have taken place at temperatures below approximately 950°C.

**ACKNOWLEDGMENTS**

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**APPENDIX**

**Experimental techniques and data.** The results of critical experiments on the H₂O–WO₄⁻ inversion are given in Table 1. Three

### Table 1. Critical Experiments on Inverted WO₄⁻ from EG 4471

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<th>Pressure</th>
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<th>Products²</th>
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<td>Hdo</td>
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¹ Run #: “a” and “b” refer to experiments in which the run material is recycled; that is, reacted further at the same pressure and temperature.

² Pressure: 5 kbar, dry, or “load” pressure (piston-and-cylinder device); evac, experiment in evacuated silica-glass tube; 200, 400, 500 bar, water pressure (Tuttle press).

³ Temperature: 5 kbar, ± 10°C; evac and hydrothermal, ± 5°C.

⁴ Buffer: 5 kb, “Fe”, represents equilibrium with metallic iron (essentially fayalite-iron-quartz buffer); evac, no external buffer; hydrothermal, fayalite-magnetite-quartz buffer.

⁵ Products: percentages from visual estimates of optical mounts, corroborated by peak heights on X-ray diffractometer charts. Hdo, hedenbergite solid solution. WO₄⁻, ferriferous wollastonite solid solution.
types of apparatus (evacuated tubes, Tuttle press, and piston-and-cylinder; see Lindsley and Munoz, 1969, for descriptions) were employed to make the experiments, and in each a different method was used to control the oxidation state of the iron. For very low-pressure experiments the charges were wrapped in Ag-Pd foil and then sealed in evacuated silica-glass tubes. The solubility of iron in the silver-palladium alloy is very low under these conditions (Muan, 1963), and the foil prevents reaction between the charge and the silica tube. For 200- to 500-bar experiments the charges were sealed in Ag-Pd capsules with 5 to 10 percent water by weight; these capsules were then sealed in larger gold capsules together with a Fayalite-magnetite-quartz (or tridymite) buffer plus water. Because EG 4471 contains quartz, fayalite, and titaniferous magnetite, the foy* imposed by the buffer must be reasonably close to that prevailing during precipitation of the inverted Wos.

For experiments at 5 kbar the charges were confined in metallic iron capsules. Some reaction between ferric iron in the charge (1.25 wt %) and the iron capsule undoubtedly took place, with a resulting increase in the FeO content of the charge from 30.79 to 32.5 weight percent if all the ferric iron reacted. The resulting foy* would approximate that of the fayalite-iron-quartz buffer, well below that of methods 1 and 2, but similar to that of many experiments on synthetic pyroxenes in equilibrium with metallic iron. The slight charge in bulk composition, combined with the pressure uncertainties in the solid-media, piston-and-cylinder apparatus at 5 kbar, requires that the 5-kbar results be used with caution.

Ideally the experiments should recreate as closely as possible the natural environment in which the green Hds from EG 4471 originally inverted from Wos. Not only the pressure and temperature, but the chemical potentials of all the constituents of the parent rock should be duplicated. With one major exception, the excess of water, our experiments at 200 and 500 bars probably met this specification reasonably well: however carefully made, mineral separates always contain minor amounts of the other minerals present in the rock. Inasmuch as it is the presence of these phases, rather than their abundance, that controls the chemical potentials, the Hds, and Wos should have experienced a similar environment of intensive parameters in nature and in our experiments. Despite abundant evidence that the Skaergaard magma had a very low water content, we chose to use water as a pressure medium and a catalyst on the assumption that a high activity of water would not affect the Hds-Wos equilibrium. This assumption seems justified on the grounds that neither the clinopyroxene nor the pyroxenoid structure is likely to accept much water of OH, and no hydrous phases were formed. (Sclar, Carrison, and Stewart, 1968, have reported the synthesis of hydrated magnesium orthosilicates that have pyroxene structures. Their experiments, however, involved different bulk compositions, much higher pressures, and lower silica activities from those reported here.)

The green inverted Wos, from specimen EG 4471, which coexists with fayalitic olivine (Fbo) and quartz, has a low Mg-content (1.2% MgS04). If the original Wos had been Mg-free, its composition would have fallen on curve 2 in Figure 5, neglecting for the moment the effect of pressure. If stable equilibrium had been maintained upon cooling, the Wos would have reacted to a Hds-, lying on curve 1 (Fig. 5) plus fayalite and silica. Cooling under conditions of metastable equilibrium might have resulted in (a) reaction to Hds, plus (metastable) ferrosilite solid solution, or (b) inversion to a (metastable) Hds of the same composition. In case (b) the inversion would have taken place over a temperature interval, whereas in the first two cases the inversion would have been isothermal. But in fact the inverted Wos, from EG 4471 contains Mg, and inasmuch as Wos and Hds coexisting at any given temperature have different Mg/Fe as well as Ca/Fe ratios, the inversion must take place over a temperature interval. Bown and Gay (1960, p. 386) found from X-ray analysis that the green inverted Wos, from EG 4143 contains a trace of FeSiO3-rich clinopyroxene. Bown and Vincent (1963, p. 190) noted that the inverted Wos is "cloudy with an indeterminate material which may have been exsolved on inversion" and suggested that exsolution of the small excess of FeSiO3 may have been necessary to permit inversion of the Wos over an inversion interval. The temperature range of the inversion as indicated in Figure 6 undoubtedly reflects this necessary temperature interval as well as experimental problems in achieving equilibrium. Presumably Skaergaard rocks that contain both green, inverted Wos and brown, primary Hds, (for example, EG 1881, EG 4143) reflect crystallization within such a temperature interval.

Quartz-tridymite inversion. Application of experimental data on the quartz-tridymite inversion to the Skaergaard intrusion requires the following assumptions: (1) that the clusters of acicular quartz present in specimens such as EG 3021 originally crystallized as tridymite; (2) that the tridymite crystallized stably; (3) that the tridymite crystallized as a primary phase from the Skaergaard magma; and (4) that the quartz-tridymite inversion curve determined for the simple system SiO2H2O is applicable to complex chemical environments. Assumption (1) is based on morphology of the acicular quartz, which is typical of tridymite and atypical of quartz (Fig. 4). Assumption (2) seems justified by the very slow cooling rate of the Skaergaard mass relative to the volcanic rocks in which tridymite may precipitate metastably. With regard to (3), Wager and Brown (1968, p. 54) tentatively suggested that the restriction of inverted tridymite to the Upper Border Group of the Skaergaard intrusion might have resulted from heating by the later Basitoppen sheet. However, the conclusion of Gay and Muir (1962, p. 577), that the occurrence of inverted tridymite reflects lower pressures prevailing during crystallization of the Upper Border Group, seems more plausible: it is unlikely that the Basitoppen sheet could have heated large portions of the Upper Group sufficiently to permit secondary formation of tridymite at pressures that would have prohibited magmatic precipitation of tridymite.

There is widespread disagreement as to whether tridymite is stable as a pure phase in the unary system SiO2 (see Rockett and Foster, 1967, for a summary of the controversy). It appears to be impossible to synthesize tridymite except in the presence of other components—such as alkalies or water; whereas the Fenner-Roy school argues that the additional components merely catalyze the reaction to tridymite, the Floihe school maintains that the additional components actually stabilize tridymite by entering into its structure. If the latter were correct, then it is possible that the temperature of the quartz-tridymite inversion might vary, depending on the nature of the stabilizing substances, and assumption (4) would be invalid. Assumption (4) is valid, however, if the temperature of the quartz-tridymite inversion can be shown to be independent of the kind of components added, regardless of whether these components merely catalyze the inversion or cause it by stabilizing the tridymite structure. We had hoped to avoid this problem by determining the P-T inversion curve of quartz from EG 3021, since the same components that might have stabilized tridymite would still be present. Unfortunately, the quartz reacted with the coexisting feldspar remaining in the impure separate and with the water used as the pressure medium to produce liquid, and the quartz-tridymite inversion could not be observed. (We could have used an inert gas as a pressure medium, but then the inversion would probably have been too sluggish to detect.) We then added excess silica to glasses made from the quartz plus feldspar separated from EG 3021 to natural quartz (from Lisbon, Maryland) to one lot and pure silica glass, which was subsequently crystallized to tridymite by heating the mixture to 1350°C for six hours, to another
lot. With these starting materials we successfully duplicated Tuttle and Bowen's bracket at 4000 psi (276 bars) (1958, p. 30). At 900 ± 5°C tridymite partially inverted to quartz, and at 925 ± 5°C quartz partially inverted to tridymite, in each case in the presence of a water-rich, silica-feldspar liquid. This is not a conclusive experiment; it provides only the negative result that the presence of other components in addition to water did not in this case affect the quartz-tridymite inversion. Nevertheless, it provides permissive evidence that assumption (4) may be valid.

**Experimental difficulties.** The experiments were hampered by slow reaction rates. Evacuated tube experiments held at temperature for over 30 days may show only partial reaction. Our reversed point within the Hd−Wo+ inversion interval at 940°C in vacuum is based on 33-day experiments. The higher temperature for the beginning of the Wo+ inversion in vacuum obtained by Yoder, Tilley and Schairer (1963, p. 91) is probably for the beginning of the Wo− inversion interval at 940°C in vacuum is based on 33-day experiments. The higher temperature for the beginning of the Wo+ inversion in vacuum obtained by Yoder, Tilley and Schairer (1963, p. 91) is probably due to the shorter duration (7 days) of their experiments.

Hydrothermal experiments at 200 to 500 bars pressed the limits of the Tuttle (1948) press (with a pressure vessel of alloy R-41, heated by an external resistance furnace), and each point in Figure 6 represents a compromise between desirable run duration and the time (12 to 72 hours) a pressure vessel would operate without failure. It was usually impossible, therefore, to let the reaction go to completion, even when the run material was recycled at pressure and temperature. Most experiments in which reaction took place yielded the two reaction products Hdass + Woass, and the placement of boundaries for the inversion interval in Figure 6 is subjective. The lower boundary must lie below 965°C at 500 bars, for that is the lowest temperature at which Hdass even partially inverted to Woass; the failure of any Woass to form in an experiment of similar duration and at the same pressure but with a temperature 10°C lower suggests but does not prove that the lower boundary lies above 955°C. At the same pressure the upper boundary must lie above 965°C but below 1000°C (see Table 1). We suspect, but cannot prove, that the inversion interval is narrower than is shown in Figure 6. The inversion interval for the appropriate composition in the synthetic CaClO₃·FeSiO₄ system at one atmosphere is so narrow that Bowen, Schairer, and Posnjak (1933, p. 218) were unable to detect it. Furthermore, the small deviation in the composition of the green, inverted Woass (EG 4471) from the normal Skaergaard trend line (Fig. 2) suggests that the natural inversion interval is narrow in T-X sections.

**References**


