

## Stability of Fe–Mg amphiboles with respect to oxygen fugacity

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### Abstract

The stability of amphiboles on the join  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  has been hydrothermally investigated at 2 kbar fluid pressure as a function of oxygen fugacity and temperature. At  $f_{\text{O}_2}$  defined by the MH buffer, the maximum extent of solution of Fe end-member in amphibole is 14 and 22 mole percent at 725° and 630°C respectively; amphibole is unstable below 630°C, being replaced by the assemblage talc + quartz + magnetite + hematite. At  $f_{\text{O}_2}$  defined by the NNO buffer the extent of solid solution expands to 54, 62, and 65 mole percent Fe end-member at 725°, 625°, and 600°C, respectively.

Results obtained in this study have been combined with previously published data to produce a  $T$ – $X$  section of the upper thermal stability of amphibole at 2 kbar and  $f_{\text{O}_2}$  defined by the FMQ buffer. Temperatures for the reaction: amphibole → pyroxene + quartz + vapor decrease from ~765°C for the pure Mg end-member to ~710°C for 62 mole percent Fe end-member. The breakdown reaction: amphibole → olivine + quartz + vapor, was observed for the more iron-rich amphiboles, and takes place at ~675°C for amphibole of 73 mole percent Fe end-member.

Comparison of the experimental results to selected natural cases shows good agreement in maximum iron contents for the appropriate oxygen fugacity range. Estimates of temperatures of crystallization of metamorphic and igneous Fe–Mg amphiboles are also consistent with prior reports.

### Introduction

The  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  series is the simplest chemically of all amphiboles and thus can provide valuable information for the understanding of more common and complex members of this important group of rock-forming minerals. Determination of phase relations along the  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  join has been hampered by sluggishness of reaction. Boyd (1955) reported synthesis at 1 kbar and about 800°C of some compositions on this join between  $\text{Mg}_{3.5}$  ··· and about  $\text{Mg}_6$  ··· but was unable to crystallize amphibole from its high-temperature breakdown products, hypersthene and quartz.

Hinrichsen (1967) synthesized orthorhombic amphiboles on the join at  $P_{\text{H}_2\text{O}} = 1$  kbar, 500°–700°C and at  $f_{\text{O}_2}$  purportedly defined by the iron–wustite (IW) and iron–magnetite (IM) buffers. Recently,

Cameron (1975) determined the upper thermal stability of an intermediate orthorhombic amphibole of 50 mole percent Fe end-member.

Several studies, while not restricted chemically to the Fe–Mg amphiboles, have presented results relevant to amphiboles on the join. Cameron (1975) investigated the join  $\text{Mg}_{3.5}\text{Fe}_{3.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Ca}_2\text{Mg}_{2.5}\text{Fe}_{2.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$  at  $P_{\text{H}_2\text{O}} = 2$  kbar,  $f_{\text{O}_2}$  defined by the FMQ buffer, and 500°–800°C. Schurmann (1974) has investigated the joins ferrotremolite–grunerite, and ferrotremolite<sub>50</sub>–grunerite<sub>50</sub>–tremolite<sub>50</sub>–anthophyllite<sub>50</sub> in the range  $P_{\text{H}_2\text{O}} = 1$ –6 kbar, 450°–700°C, and  $f_{\text{O}_2}$  defined by the IW and IM buffers. For a further summary of previous experimental studies, the reader is referred to Popp *et al.* (1976).

Despite the results of the above-mentioned studies, phase relations of the Fe–Mg amphiboles are still poorly understood. This paper describes the results of a hydrothermal investigation of the phase relations of amphiboles on the join at  $P_{\text{H}_2\text{O}} = 2$  kbar, in the temperature range 600°–700°C, and a range of oxy-

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gen fugacities defined by the MH, NNO, and FMQ buffers.

### Experimental methods

Starting materials for runs consisted of:

- (1) amphiboles: synthesized to yields of >95 percent (see Popp *et al.*, 1976);
- (2) magnetite + SiO<sub>2</sub> glass: mixed together in appropriate amounts to yield an Fe:Si ratio equivalent to pure iron end-member amphibole. Magnetite: recrystallized from Fisher reagent grade Fe<sub>3</sub>O<sub>4</sub> at 700°C, 2 kbar in Au capsules;
- (3) products of previous runs.

The buffer techniques of Eugster (Huebner, 1971) were used to define  $f_{O_2}$  at the equilibria magnetite-hematite (MH), nickel-nickel oxide (NNO), and fayalite-magnetite-quartz (FMQ). Solid starting materials plus a measured amount of distilled H<sub>2</sub>O were sealed into Ag<sub>70</sub>Pd<sub>30</sub> capsules, or into Pt capsules when the Ni-NiO buffer was employed. These capsules were then sealed into large Au capsules along with the appropriate solid buffer assemblage plus H<sub>2</sub>O. Runs were carried out in standard hydrothermal vessels. Temperature fluctuations of  $\pm 3^\circ$  and pressure variations of  $\pm 20$  bar were typical. All runs were checked for the presence of H<sub>2</sub>O in the inner and outer capsules upon opening. All buffers were checked by either optical or X-ray methods. Further description of the apparatus and procedures is included in Popp *et al.* (1976).

### Phase identification and characterization

Run products were examined with the petrographic microscope and by X-ray powder diffraction using a Norelco (Ni-filtered CuK $\alpha$  radiation) diffractometer equipped with a graphite monochromator.

Amphiboles occurred as needle-like grains averaging 1–2 $\mu$  by 10–15 $\mu$  often intergrown as fibrous masses. Compositions were determined by the X-ray method described by Popp *et al.* (1976). X-ray scans for compositional determination were run at 0.5°2 $\theta$ /min using synthetic MgAl<sub>2</sub>O<sub>4</sub> spinel ( $a = 8.0831 \text{ \AA}$ ) as an internal standard. Centers of peaks were located at 2/3 peak height. In most runs, sufficient amphibole was present to allow for the 040, 420, and 440 peaks to be used in the determination, and therefore compositions are assumed accurate to between 2 and 4 mole percent Fe end-member.

In a small number of the runs at the MH buffer, especially those in which there was considerable reaction of amphibole, inclined extinction of 0°–10° was

observed on a small proportion of the grains (1–5% of total amphibole). Thus clin amphibole appears to be nucleating from the decomposition of orthoamphibole. Since the total percentage of monoclinic amphibole was small and the molar volumes (*i.e.*, unit-cell parameters) of the synthetic orthoamphiboles are roughly equivalent to the natural C2/m monoclinic amphiboles, the determinative curves should still reflect the appropriate chemical composition, provided there is no strong preferential segregation of Fe and Mg between the two structure types.

Depending upon  $f_{O_2}$ , magnetite or hematite occurred in run products as equant grains ranging in size from 30 $\mu$  down to <1 $\mu$ . Very small grains often coated and in some cases appeared to be included within amphibole. Magnetite was always anhedral to subhedral, whereas the larger hematite grains commonly occurred as hexagonal plates.

Quartz, where formed as a product of amphibole decomposition, ranged from very small (<1 $\mu$ ) anhedral grains to doubly-terminated prisms up to 30 $\mu$  in length. SiO<sub>2</sub> glass + magnetite was added to a number of runs, and quartz which crystallized from silica glass occurred as equant anhedral grains up to 40 $\mu$ . This quartz generally could be distinguished from quartz formed by amphibole decomposition.

Talc occurred only in the lower-temperature runs. Optically it appeared as small shred-like grains often intergrown in larger clumps. When finely dispersed it was almost impossible to distinguish from fine-grained quartz, and thus X-ray methods were primarily used for its identification. When sufficient amounts were present, iron content was estimated using the location of the 003 peak (Forbes, 1969).

Olivine occurred as a high-temperature decomposition phase of the most Fe-rich amphiboles. It occurred as equant grains generally 1–10 $\mu$ , but up to 50 $\mu$  in certain runs. The amount of olivine in any run was not sufficient to allow estimation of composition by X-ray methods.

Pyroxene was a high-temperature decomposition product of amphiboles across most of the join. It always was much coarser-grained than amphibole, often occurring as 300 $\mu$   $\times$  30 $\mu$  laths and rarely up to 1 mm in length. All pyroxene observed had parallel extinction and was assumed orthorhombic.

### Phase equilibria

#### *Magnetite-hematite buffer*

The phase relations on the Fe–Mg amphibole join were investigated at oxygen fugacities defined by the MH buffer at 2 kbar in the range 600°–725°C. Reac-

tion rates at lower temperatures are too slow for experiments to be practical. At temperatures higher than 725° diffusion of H<sub>2</sub> through the large outer Au capsules is so rapid that the buffer can not be maintained longer than three to four days. Critical run data are summarized in Table 1 and phase relations are shown in Figures 1 and 2.

Steepness of the curve separating the field of amphibole from Amph + Qtz + Hm + Mt (Fig. 1) necessitated determination by monitoring changes in amphibole composition. Runs starting with essentially all amphibole (>95%) in the Amph + Qtz + Hm + Mt field reacted to yield Mg-enriched amphibole, quartz, hematite, and magnetite, while those in the amphibole field showed no shift in composition outside of experimental error. Even though small amounts of quartz, hematite, and magnetite were observed optically, runs #436 and #460 (Table 1) are interpreted as lying in the amphibole field because the amphiboles show no significant shift in composition. The starting materials for these two runs contained ~2 percent quartz + pyroxene + olivine in addition to amphibole. Neither pyroxene nor olivine was observed in the run products, and the presence of iron oxides is attributed to oxidation of these phases.

Runs starting with the assemblage amphibole + magnetite and SiO<sub>2</sub>-glass in amounts chemically equivalent to an amphibole composition of Fe:Si = 7:8 permit the starting amphiboles to react to more Fe-rich compositions. A reversal was determined at 650°C, and the phase boundary was inferred at higher temperatures.

Figure 2 is a condensed *T-X* section of the phase relations on the join at 2 kbar. Pertinent reversals for other reactions are shown by the rectangular symbols. Since the reaction talc + hematite + magnetite + quartz → amphibole is isothermal (as it does not depend on composition), the high-temperature side can be located by a decrease in the amount of talc present rather than by its complete disappearance (*cf.* runs #461, #546, Table 1).

The phase relations shown in the Mg-rich portion of the join were constructed by combining the data of this study with previously published data to produce one possible set of internally consistent phase relations. The breakdown temperature of the Mg<sub>7</sub>-amphibole was taken as the center of Greenwood's (1963) reversal bracket. The slope and shape of the Amph + Tc + Ol loop were estimated from the phase diagram of Hinrichsen (1967). Curve *d-e* represents the maximum Fe/(Mg + Fe) of olivine at 2 kbar and the MH buffer as determined by Fisher (1967). Line *a-b-c* indicates the composition of olivine in equilib-

Table 1. Runs at *f*<sub>O<sub>2</sub></sub> defined by MH buffer, 2 kbar

Run #	T (°C)	Duration (days)	Reactants <sup>b</sup>	Products <sup>a</sup>
303	725	15	A(28.6)	A(16,2) <sup>c</sup> +Q+H+M
315	702	15	A(28.6)	A(19,2)+Q+H+M
397	676	21	A(28.6)	A(20,2)+Q+H+M
409	651	20	A(28.6)	A(23,2)+Q+H+M
436	724	14	A(14.3)	A(14,3)+[q+h+m] <sup>d</sup>
460	651	16	A(14.3)	A(12,2)+[q+h+m] <sup>d</sup>
521	698	20	A(14.3)+M+Q	A(13,3)+Q+H+M
545	649	23	A(14.3)+M+Q	A(19,2)+Q+H+M
424	625	21	A(14.3)	A+Q+H+M+T
381	625	21	A(28.6)	A+Q+H+M+t?
371	623	23	A(42.9)	A+Q+H+M+T
461	650	16	A+Q+H+M+T-(14.3) <sup>e</sup>	A+[q+h+m]
546	650	23	A+Q+H+M+T-(42.9) <sup>e</sup>	A+Q+H+M+t?

a - Abbreviations: A - amphibole, Q - quartz, H - hematite, M - magnetite, T - talc. Lower case symbols indicate phase present in minor amounts. [ ] indicate presumed metastability.

b - Starting amphibole composition indicated in mole % Fe end-member.

c - Numbers in parentheses indicate amphibole composition (mole % Fe) and uncertainty (follows comma).

d - Only very minor amounts of quartz, hematite, and magnetite. May represent breakdown of the non-amphibole phases in the starting material (see text).

e - Represents bulk composition of the run, rather than only the amphibole composition.

rium with amphibole and talc for bulk compositions within the Tc + Ol + Amph field. For segment *a-b*, it is assumed that iron is preferentially segregated into olivine over talc. At point *b* olivine coexists with the most iron-rich talc stable at that temperature and oxygen fugacity (Forbes, 1969), and thus at lower temperatures olivine is rapidly enriched in iron (segment *b-c*). At the temperature of intersection of curves *b-c* and *d-e* the solubility of iron in olivine is exceeded, and tie-line switch occurs (Fig. 3e,f), resulting in the set of phase assemblages shown by the dashed lines (Fig. 2).

There are a number of factors that could complicate or alter the phase relations shown in the Mg-rich end of the join. The possible appearance of pyroxene at high temperature has been neglected, since no data on its stability at *f*<sub>O<sub>2</sub></sub> defined by the MH buffer are available. Pyroxene is expected to be a high-temperature breakdown phase of amphibole, but it could possibly occur in the system at lower temperatures as a product of the oxidation of amphi-

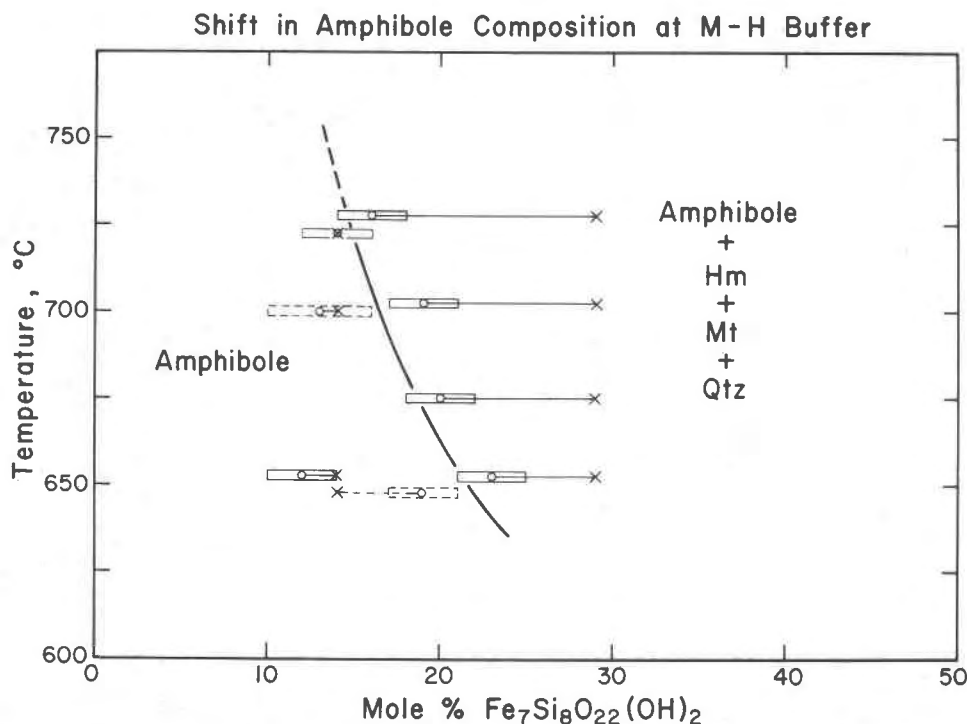


Fig. 1. Shift in amphibole composition at  $f_{\text{O}_2}$  defined by magnetite-hematite (MH) buffer. Error bars represent uncertainty in amphibole composition. Starting amphibole composition denoted by X: solid lines = amphibole +  $\text{H}_2\text{O}$ ; dashed lines = amphibole + magnetite + silica glass +  $\text{H}_2\text{O}$ .

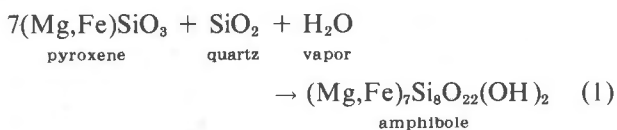
bole. The occurrence of minnesotaite, the iron analog of talc, would also alter the configuration of the system. However, lattice spacings of the 003 reflection indicate very low iron contents, consistent with the findings of Forbes (1969). These complications would alter only the Mg-rich side of the join and have no effect on the data original to this study.

Figure 3 shows schematic isothermal sections of the lower-temperature phase relations inferred from Figure 2, and the observation that amphibole breaks down at high temperature to pyroxene plus quartz (Greenwood, 1963; Cameron, 1975; and this study). Phases are shown projected from an  $\text{H}_2\text{O}$  apex onto a ternary molar ratio Si-Mg-Fe plane. The ranges of olivine (Ol), amphibole (Amph), and talc (Tc) solid solutions (indicated by the heavy dark bars) have been expanded over those shown in Figure 2 to facilitate viewing, while the geometric details have been preserved. The range of pyroxene (Px) solution is hypothetical, but was estimated assuming Fe to be preferentially segregated into pyroxene over amphibole, and into olivine over pyroxene (Ramberg, 1952). The pyroxene is presumed to be unstable in the presence of vapor at lower temperature, where it reacts to olivine plus amphibole. Bulk compositions

of runs lie on the amphibole join but coexist with a free vapor phase.

Reactions (1)–(7), given below, account for the tie-line shifts shown graphically in Figure 3. For reactions (6) and (7), compositions of phases and temperatures were estimated from Figure 2 and molecular coefficients are rounded off to the nearest 0.01. The remainder are written as reactions between solid solutions of unknown Fe:Mg ratios. Reactions (3) and (4) are schematic only because they cannot be balanced without knowledge of the precise compositions of the silicate phases. It is important to note that temperature estimates for reactions (2)–(4) are hypothetical, but must lie between  $765^\circ$  and  $660^\circ\text{C}$ . Hematite could also be added as an indifferent phase on the reactant side of the equations involving magnetite.

Between  $\sim 765^\circ$ – $740^\circ\text{C}$



Between  $\sim 765^\circ$ – $740^\circ\text{C}$

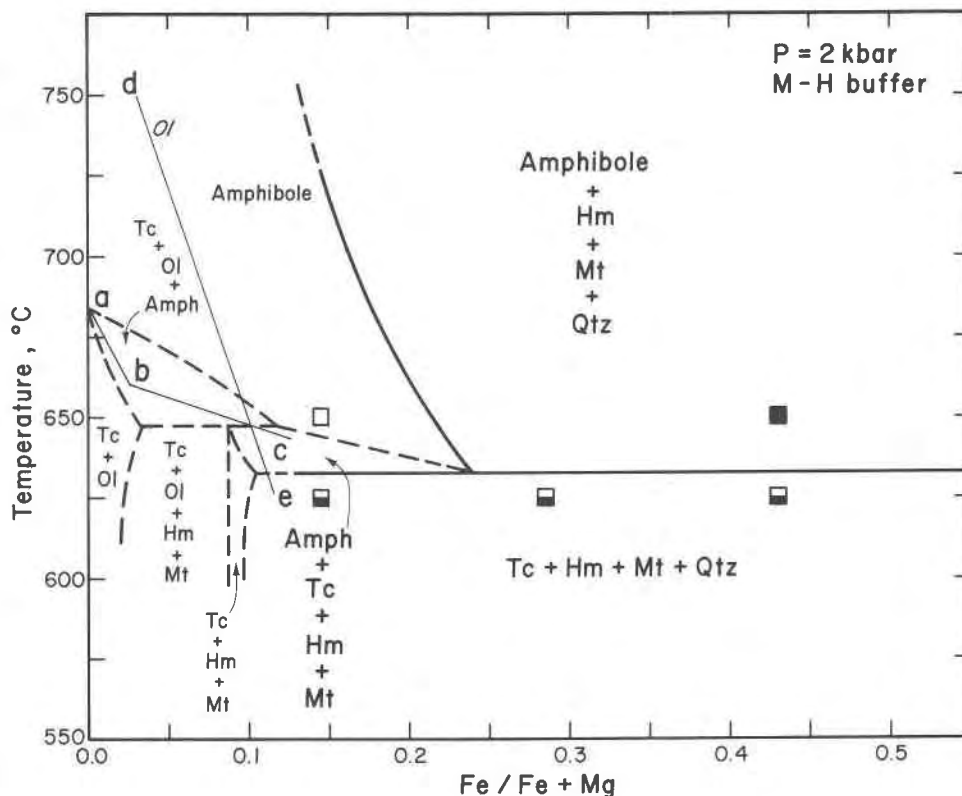
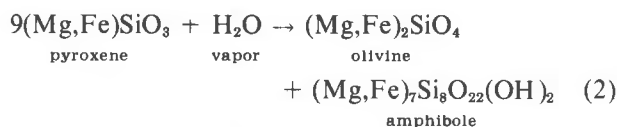
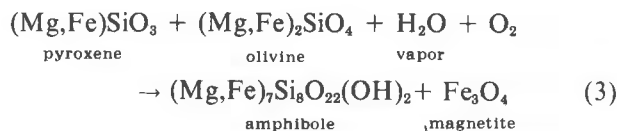


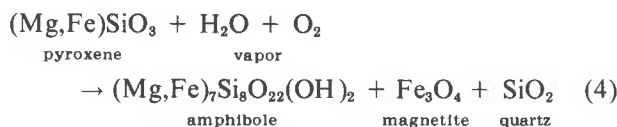
Fig. 2. Condensed  $T$ - $X$  section of phase relations on the  $Mg_7$ - $Fe_7Si_8O_{22}(OH)_2$  join at 2 kbar and  $f_{O_2}$  defined by magnetite-hematite (MH) buffer. Symbols: solid and open, growth of high-temperature assemblages at the expense of talc; half shaded, growth of talc. Size of box represents uncertainty. See text for discussion.



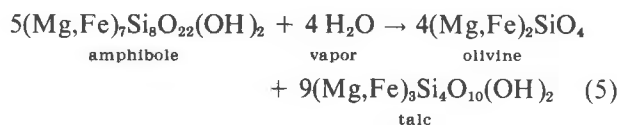
Between  $\sim 740^\circ$ - $730^\circ\text{C}$



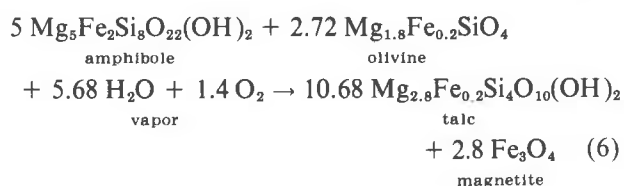
Between  $\sim 730^\circ$ - $725^\circ\text{C}$



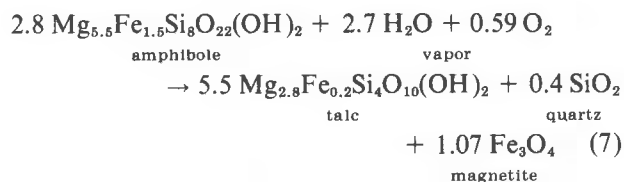
Between  $\sim 725^\circ$ - $660^\circ\text{C}$



Between  $\sim 660^\circ$ - $635^\circ\text{C}$



$\sim 630^\circ\text{C}$



Nickel-nickel oxide buffer

As a result of the loss of iron from charges to platinum capsules at the NNO buffer, runs could not effectively be maintained on the amphibole join at this buffer. However, location of the curve representing oxidation of amphibole to magnetite, quartz, and

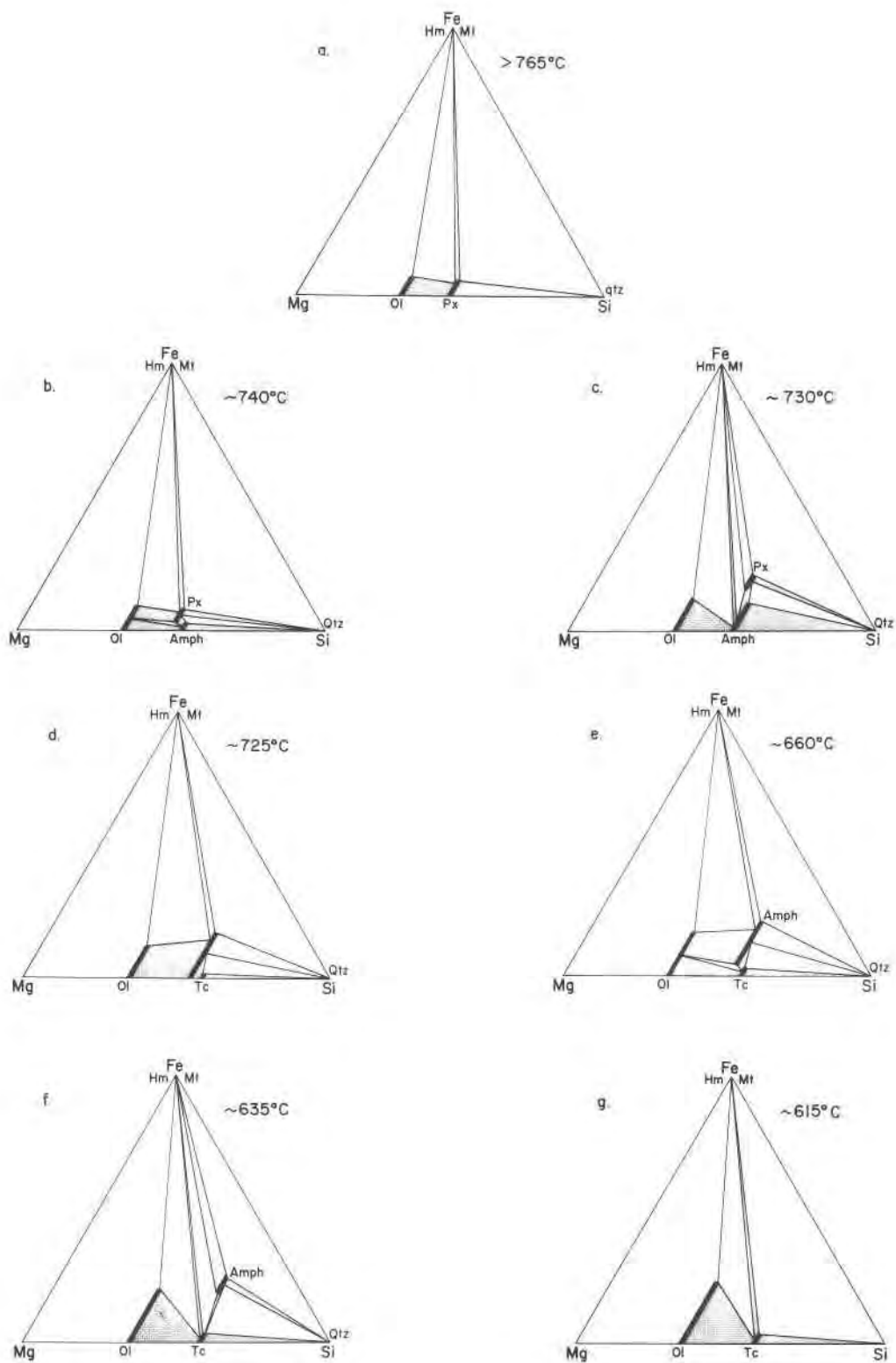


Fig. 3 Isothermal sections at 2 kbar and  $f_{O_2}$  defined by magnetite-hematite (MH) buffer. Phases are projected from an  $H_2O$  apex onto an atomic ratio Mg-Fe-Si plane.

Table 2. Shift in amphibole composition at nickel-nickel oxide buffer (2 kbar)

Run #	T (°C)	Duration (days)	Starting Amphibole <sup>a</sup>	Final Assemblage
515	673	33	Mg <sub>3</sub> Fe <sub>4</sub>	A(56) + M + Q
516	600	33	Mg <sub>3</sub> Fe <sub>4</sub>	A(62) + M + Q
547	701	35	Mg <sub>2</sub> Fe <sub>5</sub>	A(59) + M + Q
548	603	35	Mg <sub>2</sub> Fe <sub>5</sub>	A(68) + M + Q
566	700	29	Mg <sub>3</sub> Fe <sub>4</sub>	A(57) + M + Q
573	650	28	Mg <sub>2</sub> Fe <sub>5</sub>	A(68) + M + Q
574	626	28	Mg <sub>4</sub> Fe <sub>3</sub>	A(50) + M + Q
575	725	28	Mg <sub>4</sub> Fe <sub>3</sub>	A(50) + M + Q

a - All runs started with amphibole + H<sub>2</sub>O + magnetite + silica glass.

b - Abbreviations: A - amphibole (numbers in parentheses represent composition expressed as mole % Fe end-member (±3)); M - magnetite; Q - quartz.

vapor (i.e., location of the most Fe-rich amphibole which is stable) could be determined. Magnetite and SiO<sub>2</sub>-glass in the proportion equivalent to an amphibole of composition Fe:Si = 7:8 were sealed in Pt

capsules with distilled H<sub>2</sub>O plus synthetic amphibole. As discussed in relation to experiments at the MH buffer, this assemblage allows the amphibole to shift to either more Mg-rich or Fe-rich compositions as dictated by the equilibrium assemblage. Sufficient magnetite and SiO<sub>2</sub> were added to assure that the initial bulk composition lay well within the amphibole + magnetite + quartz field (e.g., Fig. 3d). Even substantial loss of iron to the capsule from such compositions will change neither the equilibrium assemblage nor the amphibole composition.

Results of runs at the NNO buffer at  $P_{total} = 2$  kbar are summarized in Table 2, and shifts in amphibole compositions are plotted versus temperature in Figure 4. Comparison of the maximum Fe/(Fe+Mg) content of the amphibole solid solution with that of biotites (Wones and Eugster, 1965) and olivines (Fisher, 1967) at the MH and NNO buffers is shown in Figure 5. Curves plotted separate the fields of stable amphibole, biotite, or olivine solid-solution on the left from the fields in which they coexist with an

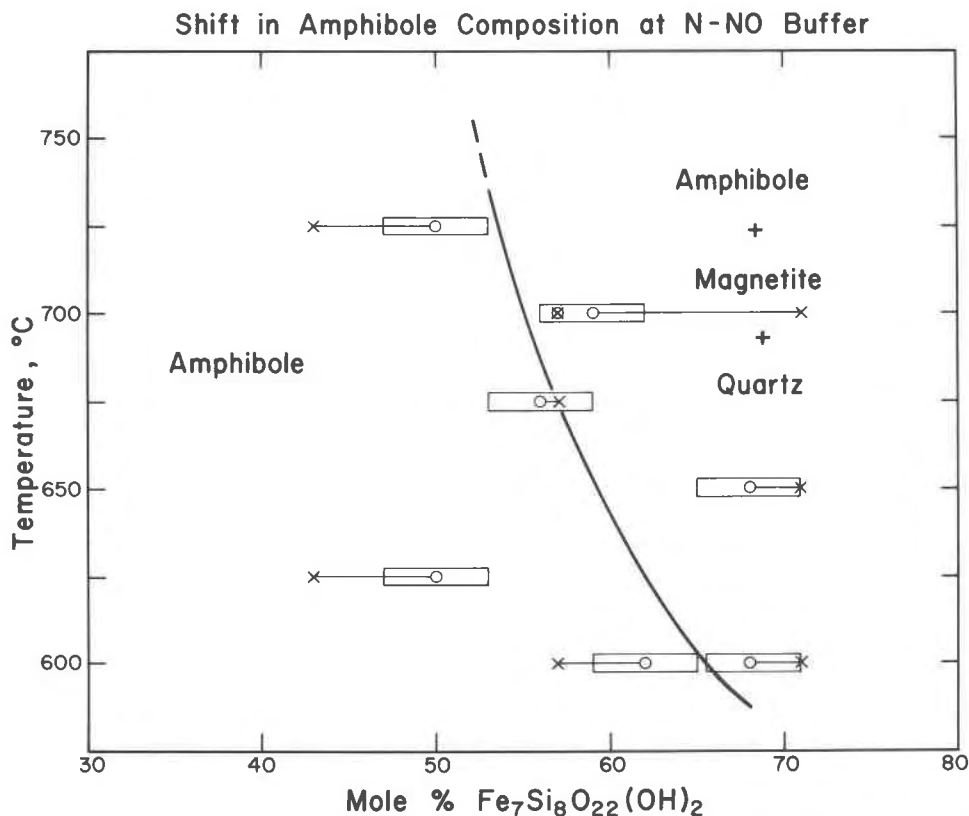


Fig. 4. Shift of amphibole composition at  $f_{O_2}$  defined by the nickel-nickel oxide (NNO) buffer. Starting materials for all runs were amphibole (composition denoted by X) + magnetite + silica glass + H<sub>2</sub>O. Error bars indicate uncertainty in measurement of amphibole composition.

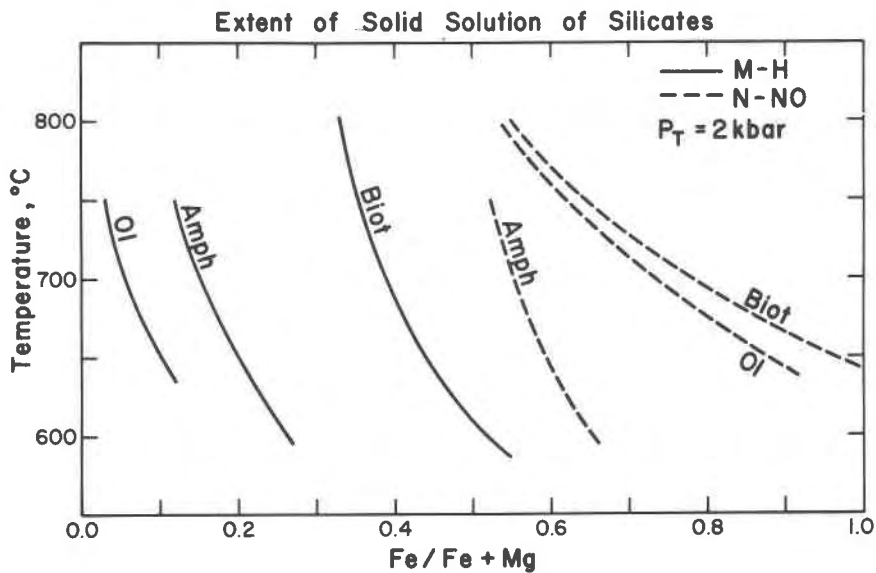


Fig. 5. Maximum Fe/(Fe + Mg) content of silicates as a function of temperature at oxygen fugacities defined by the M-H and N-NO buffers. Amphibole, this study; biotite, Wones and Eugster, 1965; olivine, Fisher, 1967.

iron oxide plus the appropriate breakdown assemblage. The compositional ranges of all three mineral groups greatly expand at lower  $f_{O_2}$ .

Table 3. Results of runs at  $f_{O_2}$  defined by the fayalite-magnetite-quartz buffer at  $P_{total} = 2$  kbar

Run #	T (°C)	Duration (days)	Composition (Mole % Fe <sub>7</sub> )	Starting* Material	Products
290	700	44	Mg <sub>6</sub> Fe <sub>1</sub> (14.3)	A + P + Q	A
128	750	48	Mg <sub>6</sub> Fe <sub>1</sub> (14.3)	A + P + Q	A + P + Q
577	752	22	Mg <sub>6</sub> Fe <sub>1</sub> (14.3)	A	A + P + Q
455	714	15	Mg <sub>5</sub> Fe <sub>2</sub> (28.6)	A	A
431	748	8	Mg <sub>5</sub> Fe <sub>2</sub> (28.6)	A	A + P + Q
368	750	5	Mg <sub>4</sub> Fe <sub>3</sub> (42.9)	A	A
399	761	10	Mg <sub>4</sub> Fe <sub>3</sub> (42.9)	A	A + P + Q
459	724	8	Mg <sub>3</sub> Fe <sub>4</sub> (57.1)	A	A
550	740	27	Mg <sub>3</sub> Fe <sub>4</sub> (57.1)	A	A + P + Q
457	751	16	Mg <sub>2</sub> Fe <sub>5</sub> (71.4)	A	A + P + Q
402	720	8	Mg <sub>2</sub> Fe <sub>5</sub> (71.4)	A	A + Ol + Q
576	648	26	Mg <sub>2</sub> Fe <sub>5</sub> (71.4)	A + Ol + Q	A

Abbreviations: A - amphibole; P - orthopyroxene; Q - quartz, Ol - olivine.

\* The single letter "A" as starting material or product indicates greater than 95% amphibole.

The extent of olivine and amphibole solution at the NNO buffer is such that the most Fe-rich amphibole coexists with magnetite and quartz rather than olivine and quartz over the range of temperatures in Figure 5. This is verified by the absence of olivine in run products. The absence of pyroxene in equilibrium with amphibole and quartz in run products indicates that the pyroxene solid solution cannot extend past approximately Fe/(Fe + Mg) = 0.65 at 700°C and 0.75 at 650°C.

#### Fayalite-magnetite-quartz buffer

A preliminary series of runs to determine the upper thermal stability of amphiboles on the join was carried out at oxygen fugacities defined by the FMQ buffer. Starting materials for all runs were either amphibole + H<sub>2</sub>O, or amphibole + decomposition products + H<sub>2</sub>O equivalent in bulk composition to amphibole + H<sub>2</sub>O. Results are given in Table 3 and plotted with previously published data in Figure 6.

The boundary separating the Amph and Amph + Px + Qtz fields was drawn to satisfy the reversal bracket of Greenwood, the high-temperature reversal at 14.3 mole percent Fe end-member of this study, and the low-temperature reversal of Cameron at 50 percent. The curve between the Amph + Px + Qtz and Px + Qtz fields satisfies Greenwood's bracket and the low-temperature reversal of Cameron, and has been extrapolated to more Fe-rich compositions. The isotherm limiting the upper stability of the Amph



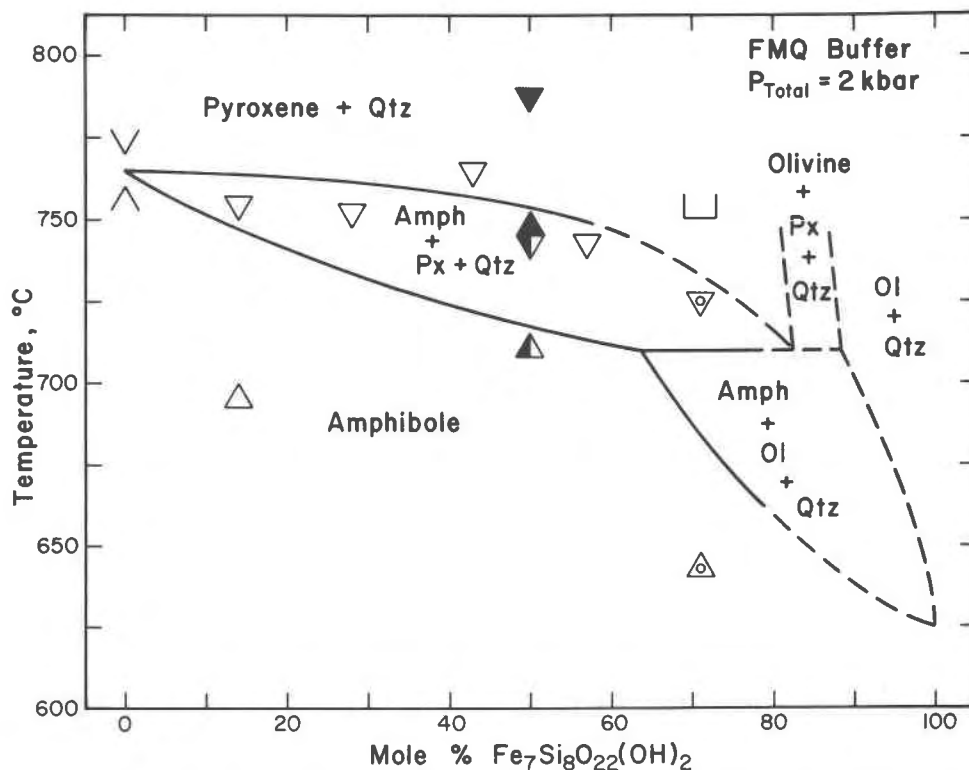


Fig. 6. Condensed  $T$ - $X$  section of phase relations on the  $Mg_7$ - $Fe_7$  join at  $f_{O_2}$  defined by the fayalite-magnetite-quartz (FMQ) buffer. Symbols: arrows, Greenwood (1963); solid and half-shaded triangles, Cameron (1975). This study: open triangles,  $Amph \rightleftharpoons Amph + Px + Qtz$ ; triangles with circles,  $Amph \rightleftharpoons Amph + Ol + Qtz$ ; square bracket,  $Amph + Ol + Qtz \rightarrow Amph + Px + Qtz$ . All pyroxene is orthorhombic.

+ Ol + Qtz field was located at a temperature which is lower than the high-temperature side of the reaction (square bracket, Fig. 6), but which confines the field to the more Fe-rich side of the join. The lower thermal stability of the Amph + Ol + Qtz field was drawn to satisfy the reversal bracket of this study and was extrapolated to a hypothetical breakdown temperature of  $\sim 625^\circ\text{C}$  for the Fe end-member. Forbes (1971) synthesized Fe end-member grunerite at  $610^\circ\text{C}$  at the iron-magnetite buffer and at  $555^\circ\text{C}$  at the NNO buffer. The higher-temperature phase relations in the most Fe-rich portion of Figure 6 are hypothetical. The slopes of the curves limiting the Ol + Px + Qtz field assume olivine to be the high-temperature phase rather than pyroxene.

#### Geological applications

The results of this study can be applied to some natural amphibole-bearing assemblages if certain assumptions are made and a number of precautions noted. The amphiboles investigated have orthorhombic symmetry but space-group symmetry apparently

different from any known amphibole (Popp *et al.*, 1976). If energy differences among the structure types of synthetic amphibole, anthophyllite, and cummingtonite-grunerite are small, the experimental results may closely reflect the stabilities of chemically equivalent members of both natural groups. Rare nucleation of small amounts of monoclinic amphibole during breakdown of the synthetic material supports this assumption.

Experiments were all carried out under conditions of  $P_{H_2O}$  essentially equal to  $P_{total}$ , whereas natural amphibole assemblages have generally equilibrated with a vapor phase of unknown composition, but probably containing at least the components H-O-C-S. Under conditions of  $P_{H_2O} = P_{total}$ , experimental results such as those depicted in Figure 6 indicate maximum temperatures for amphibole stability; under conditions of  $P_{H_2O} < P_{total}$ , temperatures of thermal decomposition will in general be expected to decrease.

The chemical complexity of most natural assemblages generally requires that possible effects of other

components on phase relations be ascertained before applying the experimental data.

#### Metamorphosed iron formations

Iron-magnesium amphiboles are important constituents of regionally metamorphosed iron formations in the Labrador Trough (Mueller, 1960; Kranck, 1961; Klein, 1966; Butler, 1969). From the results of this study, estimates of temperatures of formation can be made for certain assemblages, and compositional limits compared.

Mueller (1960) reported cummingtonite [ $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.23$ ,  $\text{Mn}/(\text{Fe} + \text{Mg} + \text{Mn}) = 0.02$ ] coexisting with hematite (Hm) + magnetite (Mt) + quartz (Qtz) + talc (Tc) + actinolite from the Bloom Lake area, Labrador. Cameron (1975) has estimated temperatures of metamorphism in the range  $550^\circ\text{--}600^\circ\text{C}$  based on coexisting cummingtonite-actinolite compositions. At  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  and  $f_{\text{O}_2}$  defined by the MH buffer, amphibole reacts to form talc below  $\sim 630^\circ\text{C}$  (Fig. 2). The maximum extent of solid solution at this temperature [ $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.24$ ] agrees well with the observed natural composition. The presence of talc may indicate either amphibole breakdown or a bulk composition which lies off of the join investigated.

Klein (1966) reported both anthrophyllite and cummingtonite from the Wabush Lake area, approximately 20 miles northeast of Bloom Lake. Klein's  $T$ - $P$  estimate for metamorphism of  $<\sim 600^\circ\text{C}$  and 6-10 kbar has been revised by Cameron (1975) to  $550^\circ\text{--}600^\circ\text{C}$  and  $<5$  kbar, based on coexisting cummingtonite-actinolite and the aluminum silicate phase diagram of Richardson *et al.* (1969). Anthrophyllite [ $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.19$ ,  $\text{Fe}/(\text{Fe} + \text{Mg} + \text{Ca} + \text{Mn}) = 0.18$ ] rimmed by talc coexists with Hm + Qtz at the Smallwood mine. If the talc rims are taken to represent amphibole breakdown, a temperature of  $<\sim 630^\circ\text{C}$  is implied from Figure 2. Depletion of iron below the 0.24 atomic ratio value in this amphibole may be the result of a higher  $f_{\text{O}_2}$  as indicated by the absence of magnetite. Klein also reported manganian cummingtonite [ $\text{Fe}/(\text{Fe} + \text{Mg} + \text{Mn}) = 0.20$ ,  $\text{Mn}/(\text{Fe} + \text{Mg} + \text{Mn}) = 0.25$ ] coexisting with Hm + Mt + Qtz from the Wabush #4 deposit. This composition suggests that the extent of solid solution of Fe end-member at the HM buffer is apparently little affected by the addition of Mn to the amphibole. Only one assemblage reported by Klein contains Ca-free orthopyroxene: 25 percent cummingtonite,  $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.78$ ; 25 percent orthopyroxene,  $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.80$ ; 25 percent

siderite; 25 percent quartz. The presence of the carbonate indicates  $P_{\text{H}_2\text{O}} < P_{\text{total}}$ , a conclusion also necessitated by the assemblage Amph + Opx + Qtz at temperatures in the range of  $600^\circ\text{C}$  (Figs. 3, 4, 6).

The amphibole composition from an additional assemblage at the Wabush #6 deposit consisting of anthrophyllite [ $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.24$ ,  $\text{Fe}/(\text{Fe} + \text{Mg} + \text{Ca} + \text{Mn}) = 0.17$ ] + Hm + Mt + Qtz (Chakraborty, 1963) is also in good agreement with experimentally determined compositions at  $f_{\text{O}_2}$  defined by the MH buffer.

Somewhat more intense conditions of metamorphism have been estimated in the area of Mt. Reed and Gagnon, Quebec, areas approximately 70 miles southwest of Bloom Lake. Based on the occurrence of granitic migmatites and on the assemblage muscovite + quartz, Butler (1969) estimated temperatures of  $600^\circ\text{--}700^\circ\text{C}$  in the Gagnon area. The occurrence of kyanite implies pressures of  $\sim 5.5$  kbar at  $600^\circ\text{C}$  and  $\sim 7.5$  kbar at  $700^\circ\text{C}$  (Richardson *et al.*, 1969). Kranck (1961) and Butler (1969) report common assemblages of grunerite [ $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.45$  to 0.70], orthopyroxene, clinopyroxene, quartz, and calcite. Under conditions of  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  the somewhat higher pressures in the Gagnon region as compared to those of the experimental conditions would increase the upper thermal stability of amphibole; however, the presence of carbonate again implies  $P_{\text{H}_2\text{O}} < P_{\text{total}}$ . Applying the phase relations of Figure 6, minimum temperatures in the range  $715^\circ\text{--}725^\circ\text{C}$  are obtained for the assemblage amphibole + pyroxene for  $P_{\text{H}_2\text{O}} = P_{\text{total}}$ . However, under conditions of  $P_{\text{H}_2\text{O}} < P_{\text{total}}$  this temperature can be considerably lower. Although such estimates may not be quantitatively exact, the common occurrence of cummingtonite + orthopyroxene + quartz generally indicates higher temperatures of metamorphism as compared to the Wabush Lake area, a conclusion also reached by Butler (1969) and Cameron (1975). A carbonate-free assemblage of cummingtonite [ $\text{Fe}/(\text{Fe} + \text{Mg} + \text{Ca} + \text{Mn}) = 0.50$ ], magnetite, and quartz, also reported by Butler, can be used to estimate  $f_{\text{O}_2}$ . In the range  $600^\circ\text{--}700^\circ\text{C}$  such amphibole compositions are appropriate to the oxygen fugacity range of the NNO buffer (Fig. 4). It is important to note, however, that gradients in  $f_{\text{O}_2}$  may exist over distances on the order of centimeters in metamorphic terranes, and thus estimates of  $f_{\text{O}_2}$  apply only to the specific assemblage. The absence of orthopyroxene from the cummingtonite + magnetite + quartz assemblage may also indicate a higher  $P_{\text{H}_2\text{O}}$  as compared to the orthopyroxene-bearing assemblages.

Considerable attention has been directed to mineral assemblages produced in iron formations by contact metamorphism associated with emplacement of the Duluth Gabbro in northern Minnesota (e.g., Gunderson and Schwartz, 1962; French, 1968; Bonnicksen, 1969; Simmons *et al.*, 1974). Retrograde assemblages of cummingtonite replacing orthopyroxene and olivine have been reported adjacent to the contact with the gabbro in the Biwabik and Gunflint iron formations. Primary textural relations are normally unclear and commonly complicated by exsolution features in pyroxenes and amphiboles. In addition, presence of significant Ca in certain phases complicates interpretation. Nevertheless, Figure 6 can be applied to these assemblages in a general way. Retrograde cummingtonite in the compositional range  $Fe/(Fe + Mg + Ca) = 0.6-0.8$ , orthopyroxene in the range  $Fe/(Fe + Mg + Ca) = 0.6-0.8$ , and olivines in the range  $Fe/(Fe + Mg) = 0.75-0.95$  are reported by Bonnicksen (1969) and Simmons *et al.* (1974). From Figure 6, at  $P_{H_2O} = P_{total}$  and  $f_{O_2}$  defined by the FMQ buffer, the coexistence of amphibole, orthopyroxene, and olivine of such compositions indicates a temperature of 715°C. Estimates of  $P_{total}$  somewhat greater than 2 kbar,  $P_{H_2O} < P_{total}$ ,  $f_{O_2}$  close to the FMQ buffer, and  $T > 800^\circ C$  have been placed on the conditions of metamorphism at the gabbro contact by Simmons *et al.* (1974). Oxygen isotope ratios of quartz-magnetite pairs (Perry and Bonnicksen, 1966) indicate temperatures of 700°–750°C for the contact with the Biwabik formation. However, these temperatures represent the minimum temperature of isotopic equilibration. Since cummingtonite-orthopyroxene-olivine represents a retrograde assemblage, the estimate of ~715°C for this assemblage is consistent with the higher temperature estimates for the peak of metamorphism.

#### Regional metamorphism

Rocks of the granulite facies are commonly defined by the appearance of orthopyroxene in place of Ca-free amphiboles such as gedrite, cummingtonite, or anthophyllite (e.g., Winkler, 1967, Ch. 11). Thus the breakdown of amphibole to pyroxene + quartz + H<sub>2</sub>O shown in Figure 6 could be taken to represent the transition from the amphibolite to the granulite facies. Winkler (1967) suggests that  $P_{H_2O} < P_{total}$  generally prevails for the formation of granulite rocks, and thus only maximum possible temperatures of formation can be determined. Because the actual value of  $P_{H_2O}$  is generally unknown for granulite facies rocks, only a single example is discussed below.

Retrograde reaction of orthopyroxene to cummingtonite in basic rocks of the granulite facies in the Granite Falls-Montevideo area, Minnesota, was reported by Himmelberg and Phinney (1967). Chemical analyses of two coexisting pairs are reported: cummingtonite [ $Fe/(Fe + Mg) = 0.43$ ]-orthopyroxene [ $Fe/(Fe + Mg) = 0.61$ ]; cummingtonite [ $Fe/(Fe + Mg) = 0.43$ ]-orthopyroxene [ $Fe/(Fe + Mg) = 0.50$ ]. Maximum temperature estimates for these assemblages of ~725°C at  $P_{H_2O} = 2$  kbar are inferred from Figure 6. The natural pyroxenes are not as iron-rich as those predicted from the diagram. However, the limiting experiments shown are not sharply defined compositionally. The resulting temperature estimates are not drastically affected by this uncertainty.

In summary, the results of this study can be used to estimate temperatures of formation of natural metamorphic assemblages provided assumptions concerning  $P_{H_2O}$  can be made. At oxygen fugacities defined by the FMQ buffer, the assemblage Fe-Mg amphibole + orthopyroxene + olivine + quartz is stable only at a single temperature for constant  $P_{H_2O}$  (Fig. 6), and thus should be useful in limiting temperature of metamorphism. Figure 6 can also be used in placing approximate temperatures on progressive metamorphism based on general diagrams such as that of French (1968, Fig. 23) depicting the appearance of orthopyroxene and fayalite in cummingtonite-grunerite assemblages with increasing grade of metamorphism.

#### Extrusive igneous rocks

Ewart *et al.* (1971) have reported phenocrysts of cummingtonite, hypersthene, quartz, and plagioclase in rhyolitic volcanic rocks of the Taupo region of New Zealand. Chemical analyses indicate amphiboles of  $Fe/(Fe + Mg + Ca) = 0.34-0.39$ ,  $Ca/(Fe + Mg + Ca) = 0.03-0.04$ ; and orthopyroxene of  $Fe/(Fe + Mg) = 0.44-0.55$ . Conditions of formation of the phenocrysts were inferred to be 735°–780°C (final equilibration temperatures from oxygen isotopic studies), ~1.5–2.3 kbar  $P_{H_2O}$ , and oxygen fugacities approximately equivalent to that of the NNO buffer. The breakdown of amphibole to Opx + Qtz was not investigated at the NNO buffer in this study. At  $P_{H_2O} = 2$  kbar and the slightly lower  $f_{O_2}$  defined by the FMQ buffer, synthetic amphiboles chemically equivalent to the natural phenocrysts coexist with Opx + Qtz at 725°–735°C (Fig. 6), which is in good agreement with the above temperature estimates. Under conditions of  $P_{H_2O} = P_{total}$ , this temperature range

lies approximately 50°C above the granite minimum-melting curve at 2 kbar (Tuttle and Bowen, 1958).

### Acknowledgments

The authors thank F. D. Bloss, G. V. Gibbs, D. A. Hewitt, and P. Toulmin, III, for helpful discussion and review of the manuscript. This research was supported by N.S.F. grants DES72-01587 A01 and GA12479-A#1.

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Manuscript received, September 22, 1975; accepted for publication, September 13, 1976.