

A review of graphite-sulfide-oxide-silicate equilibria in metamorphic rocks

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ABSTRACT. — Opaque phases are important monitors of fluid composition in metamorphic rocks. It has long recognized that graphitic rocks will be reduced during metamorphism due to graphite-fluid equilibria. In other rock types the T - f_{O_2} path followed during metamorphism will be governed by oxide-silicate equilibria. In iron-formation, where magnetite is a product phase of the buffering reactions, prograde metamorphism will lead to relative reduction while in metaperidotites, where magnetite is a reactant, progressive metamorphism will lead to oxidation. In most other rock types the equilibria controlling oxygen fugacity is not known. It is distinctive that many amphibolite-grade non-graphitic rock types, including metabasite, metapelite, and metabauxite, equilibrated at oxygen fugacities of the ilmenite-hematite solvus, about three to four log units of f_{O_2} above that of the FMQ buffer. Many of these rocks contained Ti-free hematite at lowest metamorphic grades and, therefore, seem to have been reduced during metamorphism. Basalt that has not been subjected to surface oxidation, however, seems to undergo relative oxidation during low-grade metamorphism from oxygen fugacities near FMQ to those of the ilmenite-hematite solvus. Because H_2S is the dominant sulfur species in most metamorphic rocks the T - f_{O_2} path followed by a rocks during metamorphism governs the sulfur fugacity of the rock and, hence the stable sulfide assemblage. Relatively reducing rocks, such as graphitic schists and serpentinites have low-sulfur assemblage dominated by graphite-free pelites and amphibolites.

Introduction

Although volumetrically minor in most rocks, opaque phases, most importantly, Fe-Ti oxides, and Fe sulfides, are petrologically significant because they can be used to monitor the oxygen and sulfur fugacities of the attendant fluid phase. In addition some opaque assemblages may also used as a geothermometer or geobarometer (BUDDINGTON and LINDSLEY, 1964; HUTCHEON, 1978, 1980). Although opaque minerals provide important information independent of the associated silicate assemblage, they are even more powerful when they are studied in conjunction with the coexisting silicates and carbonates. For example, in graphite-bearing rocks, the silicate and carbonate assemblages may be used along with the graphite-fluid equilibria to constrain the composition of the C-O-H fluid that may have been present (OHMOTO and KERRICK, 1977; FROST, 1979a). In addition, the $Fe/(Fe + Mg)$ ratio of silicates from low-variance assemblages containing Fe-Ti oxides or Fe sulfides can be used as sensitive monitors of changes in oxygen or sulfur fugacity (FROESE, 1971, 1977; THOMPSON, 1972; FROST, 1982; NESBITT, 1986a, b).

Despite the usefulness of opaque phases in

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understanding the petrologic evolution of metamorphic rocks, our knowledge of the behavior of oxides and sulfides during metamorphism is meager at best. Almost thirty years ago EUGSTER (1959) introduced the concept of oxygen buffers to metamorphic petrology and established that oxygen fugacity in metamorphic rocks is internally controlled. Since then, however, little progress has been made in understanding the factors that control the composition and occurrence of opaque phases in metamorphic rocks. Only in rocks that are chemically simple do we have adequate knowledge of the factors that control the composition and occurrence of the opaque phases. This paper will review the studies that have been made to date and will attempt to present a coherent model for the oxygen and sulfur fugacity trajectories followed during metamorphism of some common protoliths. In the process it is hoped that it will identify numerous problems which should be addressed in future studies.

Phase equilibria

The way that the compositions of oxides, silicates, and sulfides in a given assemblage are inter-related can be understood by considering the phase equilibria as consisting of four separate processes: oxide-oxide equilibria, oxide-silicate or oxide-carbonate equilibria, graphite-fluid equilibria, and silicate-oxide-sulfide equilibria.

Oxide-Oxide Equilibria

The factors that control the composition of magnetite relative to other oxides can be understood by considering the systems Fe-Al-Cr-O and Fe-Ti-O. In ultramafic rocks the major diluting components in magnetite are Al_2O_3 and Cr_2O_3 . In general, spinel is closest to Fe_3O_4 in serpentinites and becomes progressively diluted, first with Cr_2O_3 , then with Al_2O_3 , as metamorphic grade increases (EVANS and FROST, 1975). This variation in spinel composition is well reflected in studies of magnetic susceptibility. Serpentinites tend to be strongly magnetic (CARMICHAEL, 1982) while mantle peridotites are paramagnetic (WASILEWIKI et al., 1979).

The oxide relations in most other crustal rocks can be described in the system Fe-Ti-O. Under metamorphic conditions, the phase tie-lines for this system have two distinct configurations (RUMBLE, 1976). At low temperatures magnetite and rutile may coexist, while at higher temperatures ilmenite and hematite solid solutions occur instead (Fig. 1). The exact temperature at which the reaction that separates these assemblages:

$\text{Fe}_3\text{O}_4 + \text{TiO}_2 = \text{FeTiO}_3 + \text{Fe}_2\text{O}_3$ (1)
magnetite rutile ilmenite hematite
occurs is not well constrained. LINDSLEY and LINDH (1974) maintain that at 1 kilobar it lies below 550°C . This is consistent with field evidence indicating that it occurs in upper greenschist facies (BRAUN & RAITH, 1985; FEENSTRA, 1985).

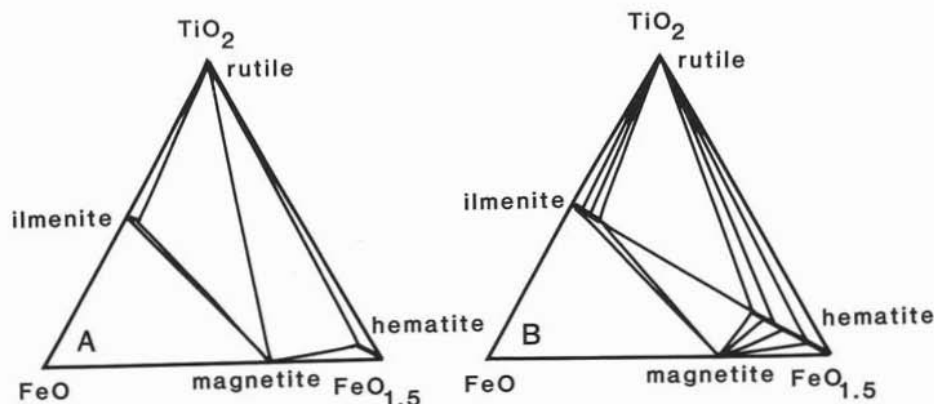


Fig. 1. — Chemographic diagrams showing phase relations among the Fe-Ti oxides in metamorphic rocks after RUMBLE (1976). A. greenschist and lower amphibolite facies. B. middle and upper amphibolite facies.

It is important to note that while lowest oxygen fugacity at which hematite may occur in Ti-poor rocks, such as iron-formations and metaperidotites, is the hematite-magnetite buffer (see EUGSTER, 1959), this is not so in Ti-bearing systems. The solution of Ti into hematite expands its stability field down to oxygen fugacities of the hematite-ilmenite solvus. Although the assemblage ilmenite-hematite without rutile or magnetite is not an oxygen buffer, at fixed temperature and pressure it is restricted to occur at a fixed oxygen fugacity. Unfortunately the location of the solvus in T - f_{O_2} space is not well known; SPENCER and LINDSLEY (1981) place it 3 to 4 log units of f_{O_2} above FMQ (see Fig. 2), but this estimate is not exact.

At temperatures above reaction (1) the oxide assemblage in most rocks is ilmenite and magnetite (with or without hematite). This is, of course the two-oxide geothermometer (BUDDINGTON and LINDSLEY, 1964) but several factors make it of limited use in most

metamorphic rocks. First, in rock metamorphosed at temperatures below 500-600°C, the Ti-content of magnetite is so low that analytical error makes the geothermometer impractical (cf. Fig. 2). Second, many mafic rocks equilibrated along the ilmenite-hematite solvus, outside the range of calibration of the geothermometer. Because the ilmenite isopleths might have strong curvature near the solvus, application of the geothermometer to hematite-bearing assemblages is subject to errors of large magnitude (SPENCER & LINDSLEY, 1981).

Despite the problems, composition of the phases in the assemblage ilmenite-hematite + /— magnetite are temperature-dependent and can be used to indicate relative differences in temperature between assemblages (cf. BRAUN & RAITH, 1985; FEENSTRA, 1985). Indeed, if the solvus can be determined experimentally, this assemblage will become a valuable geothermometer.

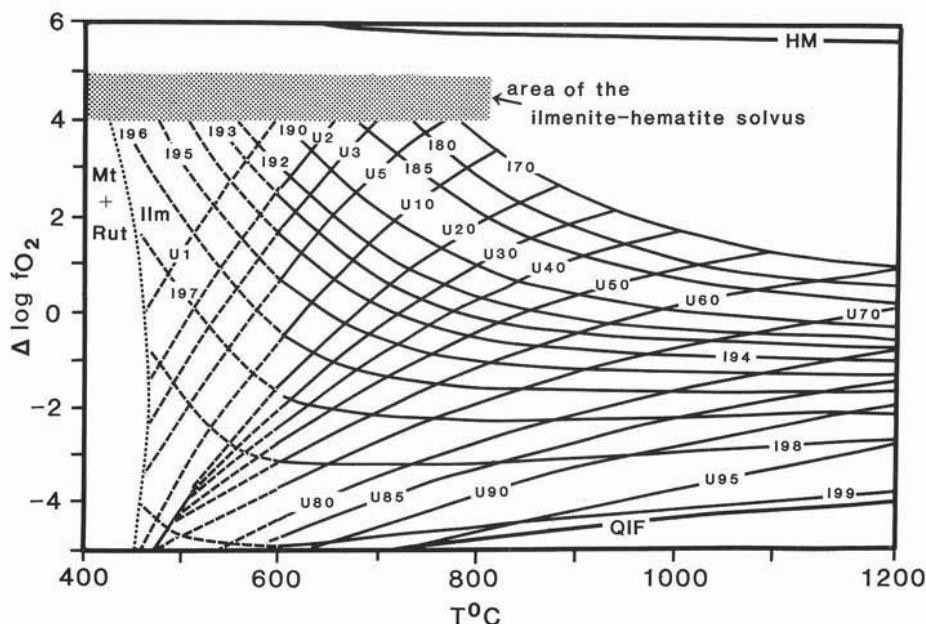


TABLE 1
Equilibria in the System Fe-Si-C-O-H

PHASE COMPOSITION			
Fayalite (F): Greenalite (Gre): Gruenerite (Gru): Hematite (H):	Fe_2SiO_4 $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$ $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ Fe_2O_3	Iron (I): Minnesotaite (Mi): Quartz (Q): Vapour (V):	Fe $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ SiO_2 H_2O
Equilibria			
2. $2 \text{ M} + 3 \text{ Q} = 3 \text{ F} + \text{O}_2$ 3. $2 \text{ Gru} = 7 \text{ F} + 9 \text{ Q} + 2 \text{ H}_2\text{O}$ 4. $3 \text{ Gru} + 3 \text{ O}_2 = 7 \text{ M} + 24 \text{ Q} + 3 \text{ H}_2\text{O}$ 5. $2 \text{ Gru} + 6 \text{ M} = 16 \text{ F} + 3 \text{ O}_2 + 2 \text{ H}_2\text{O}$ 6. $\text{F} = 2 \text{ I} + \text{Q} + \text{O}_2$ 7. $2 \text{ Gru} = 14 \text{ I} + 16 \text{ Q} + 2 \text{ H}_2\text{O} + 7 \text{ O}_2$ 8. $2 \text{ Gru} + 18 \text{ I} + 9 \text{ O}_2 = 16 \text{ F} + \text{H}_2\text{O}$ 9. $7 \text{ Mi} = 3 \text{ Gru} + 4 \text{ Q} + 4 \text{ H}_2\text{O}$ 10. $2 \text{ Mi} + \text{O}_2 = 2 \text{ M} + 8 \text{ Q} + 2 \text{ H}_2\text{O}$ 11. $12 \text{ Mi} + 2 \text{ M} = 6 \text{ Gru} + \text{O}_2 + 6 \text{ H}_2\text{O}$ 12. $2 \text{ Min} = 6 \text{ I} + 8 \text{ Q} + 3 \text{ O}_2 + 2 \text{ H}_2\text{O}$ 13. $4 \text{ Mi} + 2 \text{ I} + \text{O}_2 = 2 \text{ Gru} + 2 \text{ H}_2\text{O}$ 14. $9 \text{ Mi} + 4 \text{ F} = 5 \text{ Gru} + 4 \text{ H}_2\text{O}$		15. $6 \text{ Mi} + 10 \text{ M} = 24 \text{ F} + 6 \text{ H}_2\text{O} + 5 \text{ O}_2$ 16. $2 \text{ Mi} + 10 \text{ I} + 5 \text{ O}_2 = 8 \text{ F} + 2 \text{ H}_2\text{O}$ 17. $3 \text{ Gre} = \text{Mi} + 6 \text{ F} + 9 \text{ H}_2\text{O}$ 18. $4 \text{ Gre} + \text{O}_2 = 2 \text{ Mi} + 2 \text{ M} + 6 \text{ H}_2\text{O}$ 19. $6 \text{ Gre} + 2 \text{ M} = 12 \text{ F} + 12 \text{ H}_2\text{O} + \text{O}_2$ 20. $2 \text{ Gre} + 2 \text{ I} + \text{O}_2 = 4 \text{ F} + 4 \text{ H}_2\text{O}$ 21. $4 \text{ Gre} = 2 \text{ Mi} + 6 \text{ I} + 6 \text{ H}_2\text{O} + 3 \text{ O}_2$ 22. $\text{M} = 3 \text{ I} + 2 \text{ O}_2$ 23. $\text{Gre} + 2 \text{ Q} = \text{Min} + \text{H}_2\text{O}$ 24. $2 \text{ Gre} + \text{O}_2 = 2 \text{ M} + 4 \text{ Q} + 4 \text{ H}_2\text{O}$ 25. $6 \text{ H} = 4 \text{ M} + \text{O}_2$ 26. $4 \text{ Gre} + 3 \text{ O}_2 = 6 \text{ H} + 8 \text{ Q} + 8 \text{ H}_2\text{O}$ 27. $2 \text{ Gre} = 6 \text{ I} + 4 \text{ Q} + 4 \text{ H}_2\text{O} + 3 \text{ O}_2$	

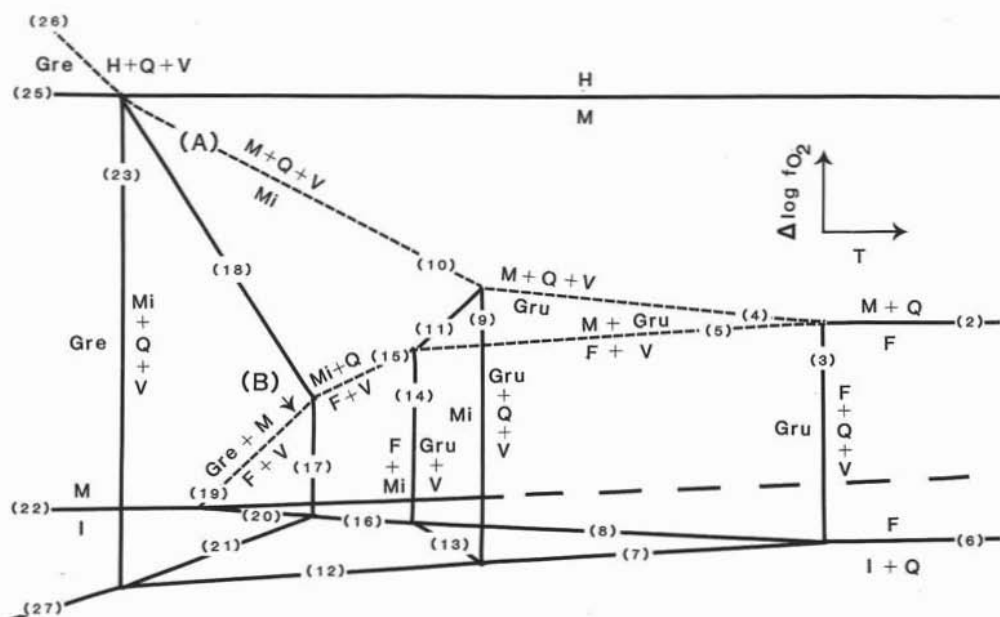


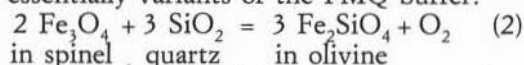
Fig. 3. — Isobaric $\Delta \log f_{\text{O}_2}$ - T diagram showing phase relations in the system Fe-Si-O-H. Equilibrium surface marked by A is an example of a reaction where magnetite is a product and which, therefore produces relative reduction during metamorphism. Equilibrium surface marked by B is an example of a reaction where magnetite is a reactant and which produces relative oxidation during metamorphism. Modified from FROST (1985) and ENGI (1986).

Silicate-Oxide and Silicate-Oxide-Carbonate Equilibria

There are two general types of equilibria between Fe oxides and Fe-Mg silicates or Fe-Mg carbonates: (1) oxidation-reduction equilibria, in which Fe^{3+} in the oxides is reduced to Fe^{2+} in the silicates or carbonates and (2) equilibria in which Fe^{3+} in the oxides reacts to form Tschermak's molecule in the silicates.

Oxidation-reduction equilibria

Oxidation-reduction equilibria are essentially variants of the FMQ buffer:



A series of equilibria involving magnetite, native iron, and Fe-silicates have been generated for the system Fe-Si-O-H (FROST, 1979b, 1985; ENGI, 1986) (see Table 1 and Figure 3). Important features of this diagram can be seen by comparing reaction surfaces (A) and (B). Magnetite is a product of the reactions on surface (A), while it is a reactant on surface (B). As a result, during prograde metamorphism a rock with a buffering assemblage on equilibrium surface (A) will undergo relative reduction while one with an assemblage on equilibrium surface (B) will be relatively oxidized. As will be discussed below,

it is probably equilibrium relations such as shown in Figure 3 that account for changes in relative oxygen fugacity during metamorphism. It should be noted, however, that, due to the fact that O_2 is only a minute proportion of the fluid phase, only petrographically insignificant amounts of magnetite can be produced by these buffering reactions (see FROST, 1982). In magnesium-bearing systems the isobarically univariant curves in Figures 3 will become divariant surfaces that slope to higher oxygen fugacity as the silicates become enriched in Mg. Apart from the stabilization of orthopyroxene at the expense of olivine + quartz, however, the topology of isopotential $\text{MgFe}_{-1}\text{-T-log } f_{\text{O}_2}$ sections in the system Fe-Mg-Si-O-H does not differ greatly from relations shown in Figure 3 (see FROST, 1985). It is possible to derive diagrams that show how the oxygen fugacity of buffering assemblage varies as a function of the Fe/Mg ratio of the silicates (FROESE, 1977; NESBITT, 1986b). Unfortunately, our knowledge of the thermodynamic properties of most phases, particularly the energetics of the Fe-Mg exchange, is still poor. As a result, such diagrams are subject to considerable error.

Even if one cannot calculate the oxygen fugacity directly for a given buffering assemblage, one can still monitor changes in oxygen fugacity by comparing the

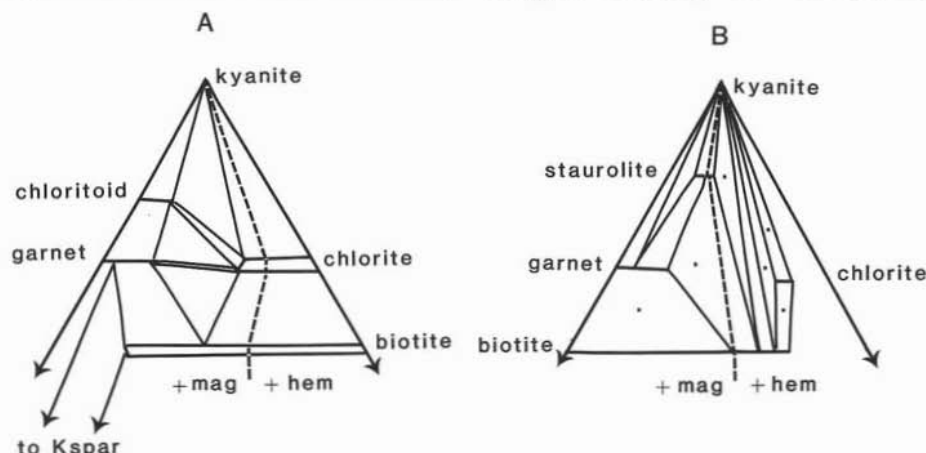


Fig. 4. — Chemographic projections from muscovite, quartz, and an Fe-oxide. A. Projection from muscovite, quartz, magnetite, and vapor in the system $\text{K}_2\text{O-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (modified after THOMPSON, 1972). B. phase relations in amphibolite-grade pelites. Fernleigh, Ontario. Dots show assemblage encountered by HOUSLOW and MOORE (1976).

Fe/(Fe + Mg) ratio of the silicates. One way to do this chemographically is by projecting from Fe-oxide. This technique was used by FROST (1982) to compare the oxygen fugacity at which iron-formations have crystallized. A similar diagram is shown schematically in Figure 4 for pelitic schists in upper amphibolite facies (THOMPSON, 1972). In such a diagram the two-phase tie-lines are isobars of oxygen fugacity. Thus a decrease in Fe/(Fe + Mg) ratio of silicates from a buffering assemblage will reflect an increase in oxygen fugacity. At some value of Fe/(Fe + Mg) hematite will become the stable oxide in place of magnetite. This is shown in Figures 4 A and B the heavy line. The way diagram can be used to compare the oxygen fugacity of crystallization in the amphibolite-grade metapelites is shown in Figure 4 B (see also HUTCHON, 1979).

Enlarging the system to include carbon adds two more phases: siderite-magnesite solid solution and graphite. In addition, one must also consider the presence of reduced carbon species, mainly methane in the fluid phase. Although experimental results are conflicting (cf. FRENCH, 1971; WEIDNER, 1972), the occurrence of fayalite + siderite in nature (FLORAN and PAPIKE, 1978) leads FROST (1979b) to argue that graphite is incompatible with the assemblage magnetite + quartz. This being so, then silicate-carbonate-magnetite equilibria for quartz-saturated rocks can be considered to have formed in the presence of a $\text{CO}_2\text{-H}_2\text{O}$ binary fluid (FROST, 1979b). Such simplification cannot be made for quartz-free assemblages containing magnetite and a Fe-bearing carbonate, indeed some carbonate-bearing assemblage in serpentinites may have considerable amounts of methane (see FROST, 1985). One important generalization that can be made for all assemblages with magnetite and a Fe-bearing carbonate, is that those assemblages which crystallized at higher X_{CO_2} will also be more oxidized (FROST, 1985).

Equilibria involving Tschermak's substitution

Equilibria between Fe oxides and Fe^{3+} in the silicates may be important in reactions

involving Fe-oxides and silicates containing significant Tschermak's component. Because such equilibria can operate without any change in the oxidation state of iron, they may have a major control on the abundance of Fe-oxides in metamorphic rocks. For example it is observed that hematite in contact metamorphosed slates and red sandstones decreases markedly in abundance when biotite appears (BEST and WEISS, 1964; RIKLIN, 1983). Detailed studies by RIKLIN (1983) shows that this decrease is not due to a change in the oxidation state of iron but rather is related to incorporation of Fe^{3+} into biotite. Similar equilibria are probably important in mafic rocks as well. JOLLY (1980) documents that hematite disappears from metabasalts during the transition from greenschist to amphibolite facies. This is probably due to Fe^{3+} substitution into hornblende, for it is well known that amphiboles in mafic rocks become more tschermakitic with increasing metamorphic grade (LAIRD, 1981).

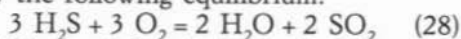
Graphite-Fluid Equilibria

The equilibria between graphite and a C-O-H fluid phase is important because it is one of the major processes of reduction in petrology (FRENCH, 1966; OHMOTO and KERRICK, 1977; FROST, 1979a; HOLLOWAY, 1984). This is a manifestation of the fact that the graphite-saturation surface in the system C-O has relatively more reducing slope with increasing temperature than do the oxide-silicate or oxide-oxide buffers. The saturation surface in the C-O system gives the maximum oxygen fugacity at which graphite may occur. The presence of diluting species in the fluid, such as H_2O and CH_4 , will cause the surface to fall to lower f_{O_2} . In pelitic rocks, where the silicate relations are governed by dehydration equilibria, the fluid composition is likely to follow a path on the graphite-saturation surface that is marked by the locus of points where $X_{\text{H}_2\text{O}}$ is at a maximum, i.e. $X_{\text{H}_2\text{O}}^{\text{max}}$ (OHMOTO and KERRICK, 1977). This forms a curve that lies one half to one log unit below the graphite-saturation curve in the pure C-O system. Any graphite-bearing rock undergoing metamorphism with concurrent

dehydration will follow a buffering path marked by $X_{\text{H}_2\text{O}}^{\text{max}}$ rather by the graphite-saturation surface in the pure C-O system. This will lead to a marked reduction of oxygen fugacity. With increasing temperature such a process will also cause the fluid phase (which initially is very rich in H_2O) to become progressively enriched in CO_2 and CH_4 (OHMOTO and Kerrick, 1977; FROST, 1979a).

Silicate-Oxide-Sulfide Equilibria

Phase relations involving sulfides, silicates and oxides are complicated by the fact that the fugacity of sulfur is a function of oxygen fugacity. In metamorphic environments S_2 is only a minor sulfur species. The dominant species are H_2S and SO_2 , which are related by the following equilibrium:



We can define the locus of points at which the fugacities of H_2S and SO_2 are equal as the sulfate-sulfide fence. At oxygen fugacities above this fence SO_2 will be the dominant species, while at lower oxygen fugacities, H_2S will dominate. The sulfate-sulfide fence, like the graphite-saturation surface has a more reducing slope with increasing

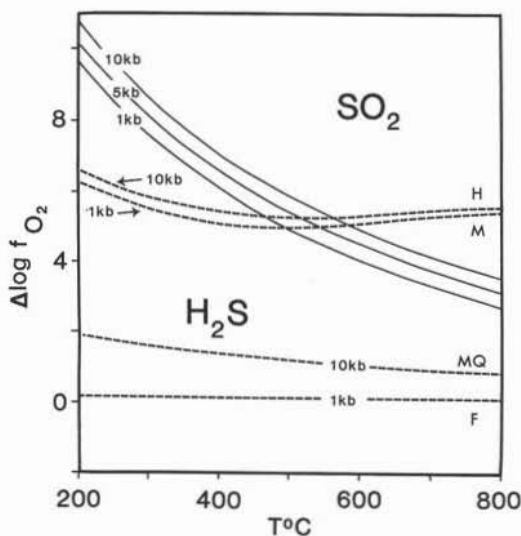


Fig. 5. — The position of the sulfide-sulfate fence (i.e. the locus of points where the fugacities of H_2S and SO_2 are equal) as a function of T , $\Delta \log f_{\text{O}_2}$ and pressure.

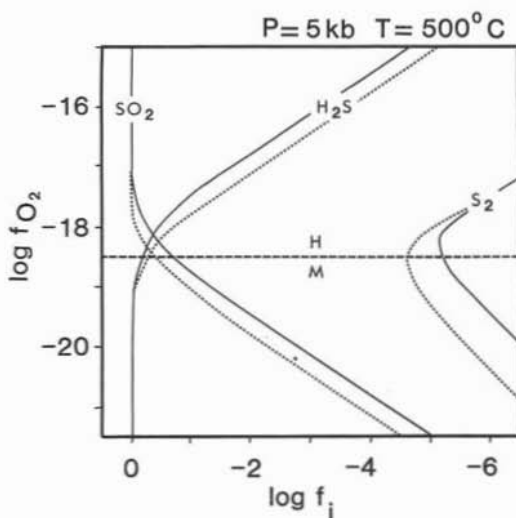
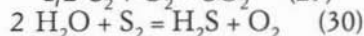
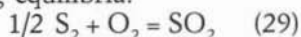


Fig. 6. — Diagram showing the effect of changes in $X_{\text{H}_2\text{O}}$ on the fugacity of the sulfur species. Solid line: $X_{\text{H}_2\text{O}} = 1.0$; dotted line: $X_{\text{H}_2\text{O}} = 0.2$.

temperature than do the oxide-oxide or oxide-silicate buffers (Fig. 5). From the stoichiometry of equilibrium (28) it is evident that the location of the sulfate-sulfide fence is dependent on the composition of the attendant fluid. This effect, however is not large, for example, at 500°C and $X_{\text{H}_2\text{O}} = 0.8$, the sulfate-sulfide will lie 0.4 log units lower in f_{O_2} than it would if the fluid were pure H_2O (Fig. 6). From Figures 5 and 6 it is evident that H_2S will be the dominant sulfur species in all metamorphic rocks, apart from those metamorphosed at high temperatures and under relatively oxidizing conditions or in the presence of a carbonic fluids phase. Thus, although, it is entirely valid to write reactions in terms of S_2 when balancing equilibria, when one is considering a process, the reactions must be written with H_2S as the sulfur species.

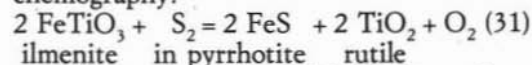
Within the sulfide or sulfate field the sulfur fugacity of the fluid is controlled by the following equilibria:



The way in which the fugacity of the sulfur species is related to f_{O_2} and the mole fraction of H_2O is shown in Figure 6. This Figure shows clearly that f_{S_2} is strongly dependent on oxygen fugacity and that it

reaches a maximum on the sulfate-sulfide fence. Furthermore, sulfur fugacity is also dependent on X_{H_2O} . All other factors being equal, sulfur fugacity will be higher in a rock that has equilibrated with a CO_2 -rich fluid than in one with a H_2O -rich fluid.

In rocks containing pyrite or pyrrhotite and a source or sink for oxygen, generally magnetite or graphite, a series of equilibria can be written relating the composition of the Fe-Mg silicates to sulfur fugacity (see NESBITT, 1986a). By projecting from Fe-sulfide, one obtains a chemography that is similar in appearance to the Fe-oxide projection (Figure 4) except in this projection tie-lines are isobars of sulfur fugacity rather than oxygen fugacity. At sufficiently high sulfur fugacities (as monitored by X_{Fe} of the silicates) one is likely to encounter pyrite rather than pyrrhotite (see Figure 7). In addition, in highly reduced rocks containing graphite, the following reaction can also be shown on the chemography:



Such diagrams are useful in pelites where the fluid is either buffered to compositions near $X_{H_2O}^{max}$, or can be assumed to be nearly pure H_2O (Fig. 7). However, if samples with variable X_{H_2O} are plotted on such a diagram the results may be confusing. For example BUTLER (1969) found that in high-grade iron-formations containing the oxygen-dependent assemblage quartz-orthopyroxene-magnetite, the pyrite-pyrrhotite transition was not restricted to lie at a fixed X_{Fe}^{Opx} . Rather pyrite or pyrrhotite occurred with orthopyroxene that had X_{Fe} values that overlapped over a wide range. A close look at the assemblage involved indicates that the pyrite-bearing assemblages that occur with orthopyroxene that is apparently too iron-rich probably came from rocks that equilibrated at a higher X_{CO_2} than pyrrhotite-bearing rocks with equivalent X_{Fe}^{Opx} .

Effect of prograde metamorphism on various protoliths

During prograde metamorphism of most rocks, the path followed by the fluid

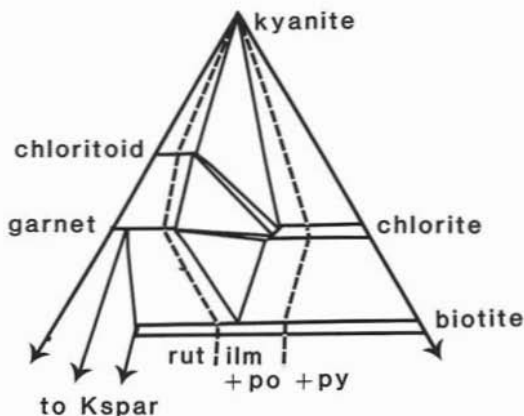


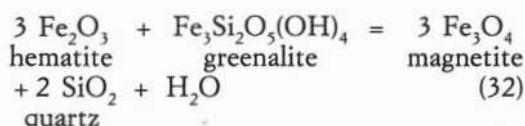
Fig. 7. — Chemographic projection from muscovite, quartz, graphite and Fe-sulfide showing how Fe/Mg ratio of the silicates reflect sulfur fugacity.

composition is essentially determined by the bulk composition of the protolith. The bulk composition will determine the mineral assemblages present at any given point on the P-T path of a rock, and these assemblages will dictate the path followed by the fluids. Although the behavior of the fluids during prograde metamorphism has not been determined for all rock types, a rough summary of some protoliths is given below.

Metaperidotite and Iron-formation

These protoliths can be discussed together because the behavior of both can be closely approximated by the Fe-Mg-Si-C-O-H system (see Fig. 3). Because most iron-formations are saturated with respect to magnetite and quartz, they will lie on surfaces (appropriately displaced because of magnesium substitution) that are equivalent to curve (A) in Figure 3.

Progressive metamorphism of these rocks will lead to relative reduction (see FROST, 1979b). These is strong evidence (see HAN, 1978) that the lowest grade iron-formations contain the assemblage greenalite-hematite-quartz (with or without siderite). Buffering by oxide-silicate-quartz equilibria will drive oxygen fugacity to the hematite-magnetite buffer (Fig. 3, 8). At this point hematite can be converted to magnetite by the oxygen-conserving reaction:



At temperature above this intersection the fluid in a hypothetical Mg-free rock will be buffered by the solid curve in Figure 8 until, in the highest grade rocks, the FMQ buffer surface is reached. The presence of Mg in natural system will cause the buffering surface to be displaced to higher f_{O_2} . In addition, sufficient Mg will stabilize orthopyroxene at the expense of favalite + quartz. Most iron-formations contain silicates that are only moderately magnesian and, therefore, lie at oxygen fugacities that deviate only slightly from the solid line in Figure 8. Some iron-formations, however, contain silicates that are relatively strongly magnesian, for example the orthopyroxene with $X_{\text{Mg}} = 0.23$ reported by BUTLER (1969). To account for this compositional variation the f_{O_2} trajectory on Fig. 8 is shown in a stippled pattern with the density of the pattern representing the approximate frequency of occurrence.

In metaperidotites the lowest oxygen fugacity will occur with the assemblage antigorite-olivine-brucite-magnetite (FROST, 1985). This assemblage lies four to five log units of oxygen fugacity below FMQ and commonly occurs with highly-reduced iron-nickel alloys. At temperatures above the stability of this assemblage, metaperidotites will be olivine-saturated and will lie on displaced equivalents of curve (B) in Fig. 3. Prograde metamorphism will lead to relative oxidation along this curve. Because the spinel phase in the highest grade rocks is dominated by Cr and Al rather than Fe^{3+} , oxygen fugacities in these rocks will be one to four log units above FMQ (see FROST, 1985) (Fig. 9).

In both iron formations and metaperidotites, carbonate-bearing assemblages will be more oxidized than carbonate-free rocks. This difference will be most pronounced in metaperidotites because of the extremely low oxygen fugacity of the carbonate-free assemblage (Fig. 8, 9). Thus, talc-magnesite rocks may have hematite, indicating an oxygen fugacity more than ten

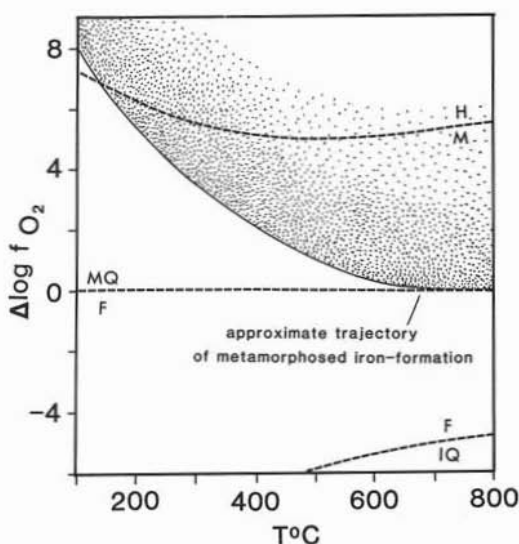


Fig. 8. — Approximate T - f_{O_2} trajectory followed during metamorphism of iron-formation. Density of stippling reflects frequency of occurrence.

log units higher than that in native-metal serpentinites (see ECKSTRAND, 1975). Because carbonate tends to be eliminated from these protoliths during prograde metamorphism, the T - f_{O_2} trends for carbonate-bearing iron-formations and metaperidotites will approach the trends for the carbonate-free assemblages (see Figure 9).

The changes in sulfur fugacity during prograde metamorphism of iron-formations and metaperidotites are not well characterized. Because the T - f_{O_2} path followed by iron-formations during metamorphism is roughly parallel to the trend of the sulfide-sulfate fence, one would assume that they would undergo only minor changes in relative sulfur fugacity. As a result, one would expect that the stability of pyrite as opposed to pyrrhotite in metamorphosed iron-formation will be more a function of the bulk composition of the rock than metamorphic grade. These inferences are substantiated by the fact that pyrite, which is the major sulfide in low-grade iron-formation (KLEIN and FINK, 1976) survives to upper amphibolite facies in Northern Michigan (JAMES, 1955) and into granulite facies in the Grenville Province (BUTLER, 1969). As noted above, there does seem to be a relation between sulfide

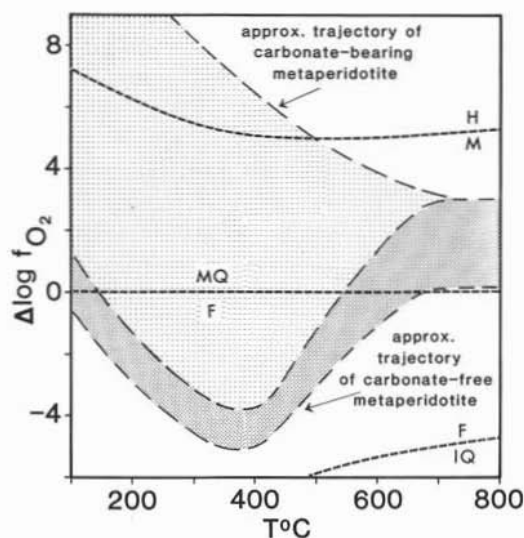


Fig. 9. — Approximate T - f_{O_2} path followed during metamorphism of serpentinite. Area in light stippling indicates carbonate-bearing rocks, dark stippling indicates carbonate-free assemblage. Modified after FROST (1985).

mineralogy and silicate composition, but whereas the stability of the sulfides is a function of X_{CO_2} as well as f_{O_2} , these controls are as yet not well delineated.

Unlike iron-formations, metaperidotites, which show strong oxidation during metamorphism, are likely to show major changes in sulfur fugacity. Although a detailed study of this problem is yet to be conducted, data from the Malenco serpentinite (TROMMSDORFF and EVANS, 1972; PERETTI, pers. comm.) indicates that the low-sulfur assemblages, indicated by the occurrence of native metals, tend to be restricted to the lowest metamorphic grades (antigorite-olivine-brucite). Because of the extreme change in f_{O_2} between carbonate-bearing and carbonate-free metaperidotites, especially at relatively low metamorphic grades, sulfide mineralogy in these rocks is more sensitive to the oxygen fugacity maintained by the silicate-oxide +/— carbonate assemblage present than to changes in metamorphic grade. For example, low-sulfur assemblages are found in carbonate-free serpentinites, while high-sulfur assemblages are characteristic of carbonate-bearing metaperidotites of equivalent metamorphic grade (ECKSTRAND, 1975).

Metabasites

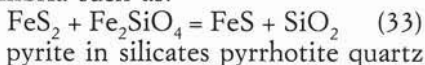
Little work has been done on the oxygen or sulfur fugacities of metabasites. To a large extent this is a consequence of the fact that it is difficult to characterize quantitatively any intensive parameter in these low-variance rocks. However, on the basis of petrologic studies and from studies of magnetic susceptibility a rough picture of the behavior of oxides during metamorphism of mafic rocks can be constructed (Fig. 10).

In weakly metamorphosed basalts it is common to recognize both oxidized, red-weathering, and reduced, green-weathering, horizons (cf. SURDAM, 1968), however it is impossible to make such distinctions in rocks that have been metamorphosed to grades above greenschist facies. Mafic rocks in amphibolite facies commonly have the relatively oxidized assemblage ilmenite-hematite (+/— magnetite) (BANNO and KANEHIRA, 1961; KANEHIRA et al., 1964; BRAUN and RAITH, 1985; PERETTI and KÖPPEL, 1986; LAIRD, pers. communication). This leads to the conclusion that the rocks that were originally hematite-rich were reduced to the hematite-ilmenite solvus during prograde metamorphism. Many metabasites, however, were not oxidized prior to metamorphism and began their metamorphic histories with iron-oxide assemblages indicative of oxygen fugacities near FMQ (see HAGGERTY, 1976). Many of these originally reduced rocks seem to end up with the hematite-ilmenite assemblage (cf. PERETTI and KÖPPEL, 1986). The exact process by which this oxidation takes place is not known, but it is probably related to reactions that consume magnetite. As noted above, if any of the ferric iron from the magnetite is reduced to Fe^{2+} during prograde metamorphism, the reactions involved will have a tendency to increase the oxygen fugacity of the attendant fluid.

There is ample evidence indicating that the incorporation of ferric iron in amphiboles and chlorite has important effects on the reactions governing the prograde metamorphism of mafic rocks. Hematite seems to disappear or decrease in abundance with the appearance of hornblende (cf. BANNO and KANEHIRA, 1961; KANEHIRA et al., 1964; JOLLY, 1980).

In addition many metabasites are distinctly poor in magnetite, as indicated by their low magnetic susceptibility (POWELL, 1970; WILLIAMS et al., 1986). This suggests that reactions between Fe-oxides and Fe^{3+} in the silicates, rather than oxidation-reduction equilibria, may be the most important oxide-silicate equilibria in mafic rocks. There are several indications that the Fe^{3+} bound in silicates is released as magnetite during the transition from amphibolite to granulite facies. For example POWELL (1970) found mafic granulites to be distinctly more magnetic than amphibolite-grade equivalents. Furthermore, mass-balance calculations indicate that magnetite should be a product phase (RUSS, 1984) of hornblende-breakdown reactions. If magnetite is a product of hornblende breakdown, then buffering by the breakdown assemblage should lead to reduction (for example, see curve A in Fig. 3). Indeed, such reduction is indicated for mafic granulites. They generally contain oxide assemblages that equilibrated at oxygen fugacities one to two units above the FMQ buffer (cf. BOHLEN & ESSENE, 1977; etc.), well below those of the hematite-ilmenite solvus (Figure 10).

Judging from the relatively high oxygen fugacity of basic schists, one would conclude that sulfur fugacity in these rocks would also be relatively high. This is consistent with the findings of BANNO and KANEHIRA (1961) and KANEHIRA et al., (1964) who record pyrite-chalcocopyrite +/—bornite as a common assemblage in blueschists and amphibolites of the Sanbagawa belt. This assemblage is also common in ore deposits hosted in mafic rocks. Since metamorphism can be considered as a devolatilization process, one would expect ore deposits to become desulfurized during metamorphism. Although this seems to happen, the sulfur produced seems to be consumed locally. This can be modelled by equilibria such as:



In the relatively sulfur-rich rocks studied by BACHINSKI (1976) these reactions such as this seem to occur in lower amphibolite conditions. This is indicated by the fact that rocks in hornblende hornfels facies contain silicates

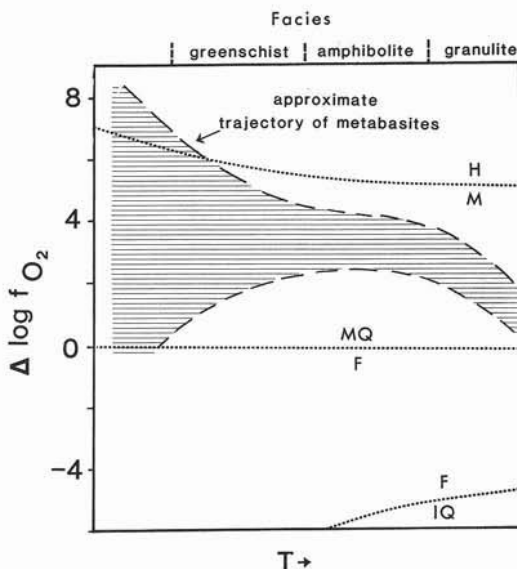


Fig. 10. — Approximate T - f_{O_2} path followed during prograde metamorphism of mafic rocks.

that are considerably more magnesian than those equivalent rocks in greenschist facies. Along with silica and magnesium, reactions such (33) will enrich the silicates in all other elements that are incompatible with sulfides. As a result, the high-grade described by BACHINSKI (1976) contain cordierite and look more closely related to a pelitic protolith than a mafic one (see MACRAE, 1974; NESBITT 1986b).

Graphite-Free Rocks with Fe-Ti Oxides

Information to date indicates that in the absence of graphite, the fluid composition of many rocks will be driven to oxygen fugacities of the hematite-ilmenite solvus. In addition to the metabasites noted above, this assemblage has been found in quartzites (RUMBLE, 1976), metamorphosed bauxites (FEENSTRA, 1985), metamorphosed sandstones (RIKLIN, 1983), and graphite-free pelitic schists (CHIDESTER, et al., 1960; HOUNSLOW & MOORE, 1967). It is not known exactly what equilibria control oxygen fugacity in most protoliths, but it is clear that at the lowest grades many rocks contain hematite. During metamorphism these must have been reduced to the ilmenite-hematite solvus as the hematite

was progressively enriched in titanium. This is particularly well demonstrated by the metabauxites studies by FEENSTRA (1985). These rocks have Ti-poor hematite + rutile at the lowest grades but contain magnetite + ilmenite in upper amphibolite facies.

Pelitic Schists

The major factor which determines the path followed by oxygen fugacity during metamorphism of pelitic schists is whether the protolith contained abundant organic matter. Those which were originally poor in organic matter evolve to become graphite-free metapelites. In amphibolite facies such rocks generally contain the assemblage ilmenite-hematite (+ /— magnetite) (CHINNER, 1960; HOUNSLOW & MOORE, 1967; HUTCHEON, 1979). Originally most of these rocks were probably hematitic. Like hematite-bearing mafic rocks and metabauxites noted above, they were probably reduced to their present assemblage during metamorphism, although the exact equilibria that were responsible have not yet been identified. In general pyrite survives to higher metamorphic grades in graphite-free schists than in graphite-bearing ones (see HUTCHEON, 1979). This simply reflects the fact that graphitic schists are more reducing, and hence have a lower sulfur fugacity than non-graphitic schists of the same metamorphic grade.

As would be expected, prograde metamorphism of graphitic schists is accompanied by marked reduction (Fig. 11). This is indicated by the fact that such rocks are distinctly lacking in magnetite and contain ilmenite and rutile as the sole oxides (see MOHR and NEWTON, 1984). Prograde metamorphism also leads to progressive desulfurization. Low-grade slates commonly contain pyrite but in graphitic rocks pyrrhotite appears in the lowest amphibolites facies. For example, in the southern Appalachians pyrrhotite appears in graphitic schists at grades slightly below those of the biotite isograd (CARPENTER, 1974) and pyrite disappears by the time the staurolite isograd is reached (NESBITT and ESSENE, 1983).

Pyrite, however, may not disappear at such low grades in all graphitic schists. In some sulfur-rich schists from eastern Maine it persists to upper sillimanite grades (GUIDOTTI, 1970) and in high-pressure rocks from Japan it is stable in epidote-amphibolite facies (KANEHIRA and BANNO, 1964).

Metasomatic movement of reduced carbon, sulfur, and oxygen

While the stability of oxides, sulfides, or graphite in most rocks is determined by the chemical characteristics of the protolith, there are many instances recorded in which carbon and sulfur, and to a lesser extent, oxygen have moved during metamorphism. Some occurrences are related to veins, where the effects of fluid movement is clear, but others occur in diffuse zones and could be confused with isochemical metamorphism. Indeed, it is in just such instances that sulfide-silicate-oxide equilibria allow one to recognize whether metasomatic process have occurred.

Metasomatic Graphite

Graphite veins are common and widespread

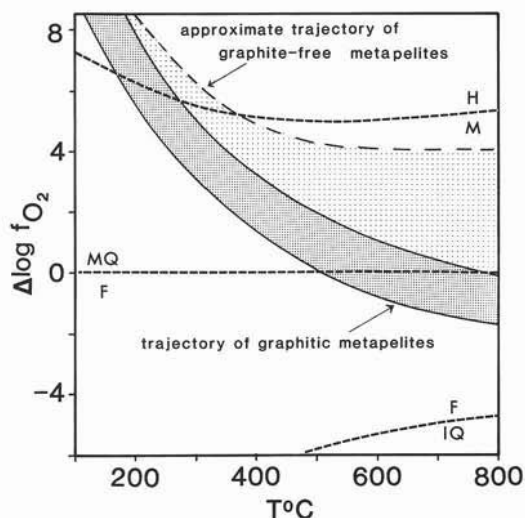


Fig. 11. — Approximate T - f_{O_2} paths followed during metamorphism of pelitic rocks. Cross-hatches area represent path followed by graphitic pelites, ruled area is for graphite-free rocks. Most graphite-free rocks probably equilibrated in the upper portion of the field shown.

and many theories have been put forth for their formation (see summary in FROST, 1979a). Recent work (DUKE and RUMBLE, 1986) has presented strong evidence that many veins have formed through the mixing of CO_2 -rich fluids from metamorphosed carbonated with CH_4 -bearing fluids from metapelites. Such mixing will precipitate graphite, even if neither of the primary fluids were graphite-saturated. Precipitation of disseminated graphite from fluids is difficult to detect, since it is likely to be recognized as having been metasomatically introduced only in rocks whose protoliths are not likely to have contained graphite. The most obvious rock type for this is serpentinite. Diagrams presented by FROST (1985) indicate that graphite can form in serpentinite only if carbon was introduced as CH_4 . In CO_2 bearing fluids, carbon would be consumed as carbonate. Such an origin for graphite in serpentinite is consistent with the graphitic serpentinites described by CHIDESTER et al. (1978), where graphite is enriched in the serpentinite bear the contact with pelitic schist.

Sulfur Metasomatism

Zones of sulfur metasomatism around metamorphosed sulfide bodies have been well described (see NESBITT, 1986b). For example the alteration halo around Ducktown Tennessee massive sulfide body shows a distinct gradient in both oxygen and sulfur fugacity which is reflected both by the opaque mineral assemblages and by the composition of the attendant silicates (NESBITT and Kelly, 1980). In such occurrences it is evident that sulfur diffusion was driven by chemical potential gradients, with sulfur moving from the areas of high sulfur fugacity in the ore body into the country rock.

Another type of sulfur movement is postulated by FROST (1985) to explain the mobilization of Ni-sulfides seen during metamorphism of ultramafic rocks (see BARRETT et al., 1977). In such a process sulfides are postulated to have dissolved in serpentinites, where they are relatively unstable because of the reducing conditions,

and to have been reprecipitated in bordering, more oxidized, rocks. At first glance this process seems to argue for transport against a chemical potential because f_{S_2} is surely much lower in the serpentinites, where native metals are often present, than in the ore zones. This apparent contradiction is resolved when one considers that the dominant sulfur in the fluid is H_2S , not S_2 . Because of the stoichiometry of the equilibrium relating $f_{\text{H}_2\text{S}}$ to f_{S_2} and $f_{\text{H}_2\text{O}}$ (equilibrium (29)), under highly reducing conditions the fugacity of H_2S in the fluid may be very high even though sulfur fugacity is low (see ROSSETTI and ZUCHETTI, this volume). Thus, the observed depletion of sulfur in olivine-bearing serpentinites and its accompanying enrichment in the carbonate-bearing metaperidotite or wall rocks (see ECKSTRAND, 1975) is a consequence of the extreme gradient in oxygen fugacity between the two environments (FROST, 1985).

Oxygen (or Hydrogen) Metasomatism

Because both O_2 and H_2 make up only vanishingly small proportions of the fluids in most metamorphic rocks it has argued that most graphite-free rocks have a nearly infinite buffering capacity for oxygen fugacity (FROST, 1982; 1985). This means that $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio of non-graphitic rocks should not change substantially during metamorphism, even if the relative oxygen fugacity changes by many orders of magnitude. To a certain extent this is an oversimplification. There are certainly instances in which net changes in the oxidation state of iron in a rock can occur during metamorphism, even without the participation of graphite. However, those rocks which do show changes in ferrous/ferric ratio must be associated with a source or sink for oxygen other than a simple O-H fluid. One process which is an exception to this statement is serpentinitization which is generally accompanied by the formation of magnetite and enrichment of the silicates in magnesium, (see references tabulated by FROST, 1985). Because serpentinitization takes place at oxygen fugacities 4 to 8 log units below FMQ, H_2

may make up between 0.1 and 1.0% of the fluid phase (FROST, 1985). In this situation there is probably sufficient H_2 in the fluid to account for the oxidation seen in the production of magnetite simply through the dissociation of H_2O . Rocks other than serpentinites have been metamorphosed at relatively higher oxygen fugacities where this process is an inefficient means of oxidation. In such rocks, therefore, some process other than the dissociation of H_2O must be responsible for any observed changes in the ferrous/ferric ratio.

Conclusion

The T - f_{O_2} trajectories presented here (Fig. 8-11) are admittedly crude. They have been constructed by applying liberal amounts of conjecture to a minimum amount of data. None the less, the author feels that they are of value to petrology if only because they will encourage future workers to test their veracity. Certainly once the T - f_{O_2} trends for the major rock types and the equilibria that control them have been determined they will prove invaluable to petrology. Not only will they help one understand the factors that control the stability of opaque phases in metamorphic rocks, they will also form an important basis for determining the factors that cause mobilization of ore minerals during metamorphism. In addition, if Fig. 10 correctly describes the T - f_{O_2} path followed during metamorphism of mafic rocks, it has important implications to experimental petrology. Most experimental works on amphibole stability are conducted in the presence of an externally controlled oxygen fugacity (GILBERT, 1966; LIOU et al., 1974; SPEAR, 1981). Clearly the ferric iron content of an amphibole and, hence the stoichiometry of the reaction that governs its stability, is strongly to be dependent on oxygen fugacity. Therefore, experiments done on amphibole stability at a controlled oxygen fugacity that differs markedly from that found in nature will have limited applicability to the natural amphibole-forming reactions.

Another important conclusion regards the

use of S_2 or H_2S as the sulfur species when writing chemical equilibria. Although it is perfectly valid to use S_2 as the sulfur when calculating mineral equilibria, because it is not the dominant sulfur species it is not valid to use it when modelling the processes that control sulfur mobility in metamorphic rocks. Only by using H_2S as the sulfur species can adequately determine the role that variations in f_{O_2} and f_{H_2O} have on the stability of sulfides.

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