American Mineralogist, Volume 67, pages 142–148, 1982

Contact metamorphic effects of the Stillwater Complex, Montana: the concordant iron-formation: a discussion of the role of buffering in metamorphism of iron-formation

B. RONALD FROST
Department of Geology
University of Wyoming
Laramie, Wyoming 82071

Abstract

This paper argues that the presence of external control of fluid composition during metamorphism of iron-formation should be indicated by the occurrence of high-grade rocks which either lack the buffering assemblages such as olivine–magnetite–quartz or by the presence of such assemblages in which the silicates show a very restricted range in composition. A review of high-grade iron-formations from contact and regional metamorphic terrains, including the Stillwater iron-formation, the Biwabik iron-formation and iron-formations from Western Australia, Labrador and Southwestern Montana, shows that all were metamorphosed under a variety of oxygen fugacities and that all had buffered the fluid composition during metamorphism.

Introduction

In their recent paper on the metamorphism of iron-formation at the base of the Stillwater complex, Vaniman *et al.* (1980) argue that the oxygen fugacity of the iron-formation was controlled by fluids moving out from the Stillwater intrusion. Furthermore, because of this effect, which they say is also present around the Duluth gabbro (*cf.* Simmons *et al.* 1974), iron-formations metamorphosed by mafic intrusions equilibrated at lower oxygen fugacities than those which underwent regional metamorphism. The authors base their argument on the fact that regionally metamorphosed iron-formation commonly contains hematite-bearing assemblages and rarely contains fayalite, while both the Gunflint and Stillwater iron-formations lack hematite and contain rocks whose oxygen fugacity was close to that of the quartz–magnetite–fayalite (QMF) buffer (see Vaniman *et al.*, 1980, Fig. 9). From the earliest studies of fluids in metamorphism, metamorphosed iron-formation has been used as an example of internal control of fluid composition (Eugster 1959, Klein 1973, Frost 1979), thus, it is important to scrutinize the arguments of Vaniman *et al.* (1980) closely.

Controls of mineral composition in high-grade metamorphosed iron-formation

A simplified picture of the controls of metamorphism in iron-formation was presented by Frost (1979) for the Mg-free system. He noted that the path of metamorphism is dependent on the original bulk composition of the iron-formation and that internal control can lead to two possible high-grade assemblages. Beds which were originally rich in hematite and poor in siderite and silicates would end up at highest grades with the assemblage hematite–quartz±magnetite while those with abundant silicates or siderite would have the assemblage quartz–magnetite–fayalite at the highest grades, even if they contained hematite originally (see also Frost, 1980).

The major effect of adding magnesium to the simplified system is to add an extra degree of freedom to all equilibria listed by Frost (1979) and to stabilize orthopyroxene at the expense of olivine. We can consider the effect of Mg on the equilibria in high-grade iron-formations if we disregard grunerite, which is present as a prograde phase in most high-grade iron-formations, and consider only the anhydrous phases. By doing so we can write three equilibria which control oxygen fugacity and which are independent of the CO_2 or H_2O content of the attendant fluid. These are:

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{3SiO_2} = \underset{\text{olivine}}{3Fe_2SiO_4} + O_2 \quad (1)$$

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{6SiO_2} = \underset{\text{opx}}{3Fe_2Si_2O_6} + O_2 \quad (2)$$

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{opx}}{3Fe_2Si_2O_6} = \underset{\text{fayalite}}{6Fe_2SiO_4} + O_2 \quad (3)$$

0003–004X/82/0102–0142$02.00

By considering that iron may occupy two sites in olivine and orthopyroxene, by combining the activity coefficient for both sites as a single term, and by taking magnetite as a pure substance (as it nearly is in iron-formation), we can obtain the following expressions for the equilibrium constants:

$$K_1 = (f_{O_2})\,(X_{Fe}^{ol})^6(\gamma_{Fe}^{ol})^3 \qquad (4)$$
$$K_2 = (f_{O_2})\,(X_{Fe}^{opx})^6(\gamma_{Fe}^{opx})^3 \qquad (5)$$
$$K_3 = (f_{O_2})\,(X_{Fe}^{ol})^{12}(\gamma_{Fe}^{ol})^6/(X_{Fe}^{opx})^6(\gamma_{Fe}{}^{opx})^3 \qquad (6)$$

If we regard changes in the equilibrium coefficient as being a secondary function, we can rearrange the expressions 4 to 6 to the form:

$$\log f_{O_2} = \log K_1 - 6 \log (X_{Fe}^{ol}) \qquad (7)$$
$$\log f_{O_2} = \log K_2 - 6 \log (X_{Fe}^{opx}) \qquad (8)$$
$$\log f_{O_2} = \log K_3 - 12 \log (X_{Fe}^{ol}) + 6 \log (X_{Fe}^{opx}) \qquad (9)$$

Since X_{Fe}^{ol} or X_{Fe}^{opx} is always less than 1.00, $\log f_{O_2}$ in expressions 7 and 8 increases as Mg is added to the system. Likewise, since $(X_{Fe}^{ol})^{12}$ is always greater than $(X_{Fe}^{opx})^6$, then $\log f_{O_2}$ for expression 9 will also increase as Mg increases, albeit at a slower rate than for expressions 7 and 8. These relations are shown on Figure 1. The significant feature to note here is that, although equilibrium 3, (Q), is more reducing than equilibrium 2, (OL), it is less reducing than equilibrium 1, (OPX) because it is constrained to lie at higher Mg contents.

Expressions 7–9 show that there are only three ways in which equilibrium can be maintained in a buffered assemblage. The Fe/Mg ratio of the silicates may remain fixed and thus, dictate the attendant oxygen fugacity; if so, the fluid is internally controlled. The oxygen fugacity may be held fixed and the Fe/Mg ratios of the silicates altered until they are in equilibrium with it; in such systems the fluid is said to be externally controlled. Finally, it is also possible for both f_{O_2} and X_{Fe} to vary. When this occurs the system is considered to have undergone imperfect external control. We can thus use the compositions of olivine and pyroxene from the buffered assemblages as an indicator of the processes under which the rocks came to equilibrium. This has been done in a graphical form in Figures 1, 2 and 3 by projecting from magnetite onto the FeO–MgO–SiO$_2$ plane.

In systems that are internally controlled it is the Fe/Mg ratio of the silicates which control the oxygen fugacity of the fluid. However, before we can use Figures 2 and 3 to compare the metamorphic conditions of regionally metamorphosed and con-

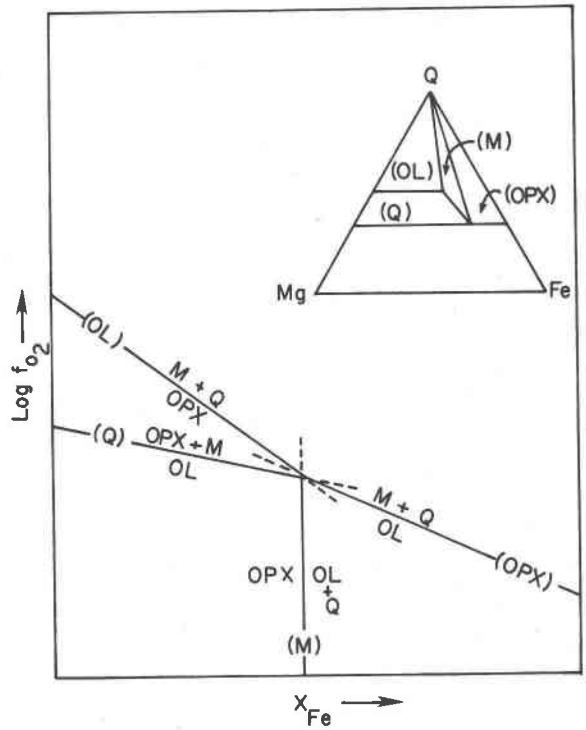

Fig. 1. Isobaric, isothermal log f_{O_2}–X_{Fe} diagram showing phase relations among magnetite, olivine, orthopyroxene and quartz in high-grade metamorphosed iron-formation. Equilibria (Q) and (M), although actually divariant, are shown as univariant curves in this projection to emphasize the topologic relations. The chemographic triangle is a projection from magnetite onto the SiO$_2$–FeO–MgO plane. The divariant fields in this projection labeled (OL), (OPX), and (Q) show where assemblages buffered by these curves would plot on the projection. The field labeled (M) is, of course, invariant in this projection.

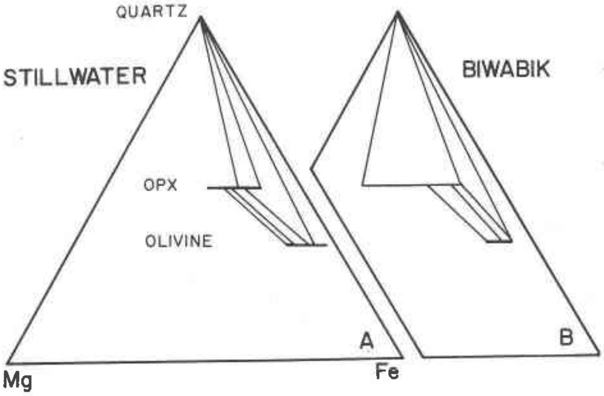

Fig. 2. Mineral assemblages in high-grade contact metamorphosed iron-formation as projected from magnetite. The Fe/Mg ratio of the silicates coexisting with magnetite and quartz is an indicator of oxygen fugacity at which the assemblage equilibrated (see the text for discussion). A. Assemblages from the Stillwater iron-formation (Vaniman *et al.*, 1980). B. Assemblages from the Biwabik iron-formation (Bonnichsen, 1969).

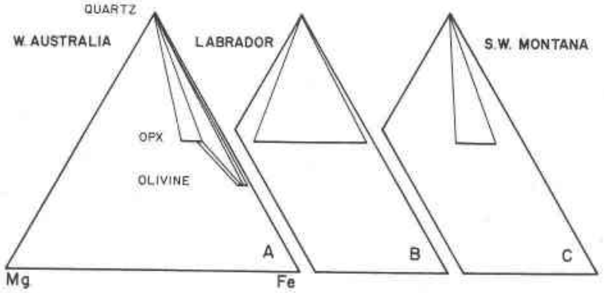

Fig. 3. Mineral assemblages in high-grade regionally metamorphosed iron-formation as projected from magnetite. A. Assemblages from Western Australia (Gole and Klein, 1981). B. Assemblages from iron-formations in Labrador (Butler, 1969; Klein, 1978). C. Assemblages from iron-formations in southwest Montana (Gillmeister, 1971; Immega and Klein, 1976). Note that there are assemblages in all localities which were metamorphosed at oxygen fugacities equal to or lower than those involved in the contact metamorphosed iron-formations in Fig. 2.

tact-metamorphosed iron-formations, it must be shown that changes in pressure and temperature will have no effect on the pyroxene and olivine compositions from the buffering assemblages. This can be done using the technique pioneered by Greenwood (1974). Consider the equilibrium:

$$\underset{\text{in silicates}}{3\,FeO} + H_2O = \underset{\text{magnetite}}{Fe_2O_3} + H_2 \qquad (10)$$

This is the major equilibrium controlling the oxygen fugacity in an iron-silicate–magnetite–quartz assemblage in the presence of an aqueous fluid. From the QMF expression of Chou (1978) and the fugacity coefficients in Shaw and Wones (1964), one can calculate that at 800° C and 2 kbar an aqueous fluid coexisting with the QMF buffer will have $X_{H_2} = 0.0025$. Using equation 4 of Greenwood (1975) and the stoichiometry of equation 10 above, it can be shown that buffering one mole of pure water to this fluid composition will produce .0025 moles of magnetite.

Walther and Orville (1980) estimate that metamorphism of pelitic rocks will evolve about .5 moles of H_2O for every 100 cc of rock. If metamorphism of iron-formation will evolve the same amount of fluid, then only .056 cc of magnetite would be produced in every 100 cc of rock during prograde metamorphism. This amount of magnetite would not be enough to alter the bulk Fe/Mg of the silicates (unless, of course, there was an extremely small quantity of silicate present), nor incidently, would it be enough to be seen petrographically.

By using the Modified Relich-Kwong expression (Holloway, 1977; Flowers, 1979) to obtain γ_{H_2} it can be shown that an aqueous fluid coexisting with the QMF buffer at 7 kbar and 800° will have $X_{H_2} = 0.001$. From the same arguments used above it is clear that if two rocks with the same bulk X_{Fe} were subjected to metamorphism under widely different pressures and temperatures, the processes involved in internally controlling the fluid phase would not significantly alter the bulk X_{Fe} of either rock. It should be noted here that the buffering of the fluid from high X_{CO_2} values to water-rich compositions, such as might happen during the breakdown of grunerite (*cf.* Frost, 1979, Fig. 9), will have a similar effect as the examples given above, with the production of a minuscule amount of magnetite being associated with the buffering process.

The above arguments indicate that, once the assemblages olivine–magnetite–quartz, orthopyroxene–magnetite–quartz, or orthopyroxene–olivine–magnetite have formed, the X_{Fe} of the silicates will remain unchanged, regardless of the changes in temperature or pressure. However, in this regard it should be noted that most high-temperature iron-formations, including many of the samples plotted on Figures 2 and 3 contain grunerite in addition to fayalite and orthopyroxene. Since any grunerite present will contain some of the Mg in the system, the plot of X_{Fe} in olivine and pyroxene from a grunerite-bearing assemblage will not reflect accurately the bulk X_{Fe} of the rock. Fortunately, grunerite contains only slightly more Mg than does coexisting orthopyroxene, which means that the X_{Fe} of olivine or pyroxene from a grunerite-bearing rock will be only slightly higher than the values from a rock with the same $X_{Fe}^{silicate}$ in which grunerite is absent.

The presence or absence of grunerite in high-grade metamorphosed iron-formation has important implications concerning the question of internal control of fluid composition. The stability of grunerite is a function of both X_{CO_2} (*cf.* Frost, 1979) and of X_{Fe} (*cf.* Morey *et al.*, 1972), with low X_{CO_2} and low X_{Fe} favoring its stability. A high-grade iron-formation in which the fluid compositions were internally controlled would have a distinct layering produced by changes in the abundance of the Fe–Mg silicates, magnetite, and quartz. Grunerite-rich beds may be present in layers which originally were poor in CO_2 (*i.e.*, low in primary siderite) while those beds which were originally carbonate-rich may be expressed as layers rich in olivine or pyroxene. (Note that in high-grade iron-formation the fluid may be rich in CO_2 without a carbonate being present.) Furthermore, the compositions of the olivine and pyroxene from the grunerite-poor beds would display a range of X_{Fe} values which would reflect the compositional variability of the original sediment.

In a system that is externally controlled it is the f_{O_2} of the incoming fluid which determines the composition of the silicates. If the fluid has an oxygen fugacity below that of the QMF buffer, magnetite will be consumed by reactions 1, 2, and 3 producing the assemblages orthopyroxene–quartz, orthopyroxene–olivine, orthopyroxene–olivine–quartz, olivine–quartz, or olivine–magnetite, depending on the original MgO, Fe-total, and silica content of the rock (*cf.* Fig. 1). It should be noted that the assemblage orthopyroxene + magnetite will not form because it is equivalent to the more-reduced assemblage olivine or olivine–quartz. Thus external imposition of an oxygen fugacity below that of QMF will not only destroy any buffered assemblages which were originally present by removal of magnetite, it will also produce the assemblage olivine + quartz at the expense of orthopyroxene + magnetite, even in assemblages which were originally quartz-free.

If the incoming fluid has an oxygen fugacity slightly above that of the QMF buffer, the response of the rocks will depend on their bulk composition. Silicates which were too iron-rich for this fluid would react to form magnetite + quartz with the reaction proceeding until X_{Fe} of the silicate is in equilibrium with the oxygen fugacity of the fluid. Likewise, magnetite + quartz will be consumed in layers whose silicates are more magnesian than the equilibrium value until the silicates attain the equilibrium X_{Fe}. If the oxygen fugacity of the fluid was high enough to stabilize orthopyroxene at the expense of olivine + quartz, external control of oxygen fugacity could lead to the formation of either the orthopyroxene–olivine–magnetite or the orthopyroxene–magnetite–quartz assemblage, depending on the silica content of the rocks (*cf.* Fig. 1). If this were to occur, however, one would not find any occurrence of the assemblage olivine–magnetite–quartz.

Since an infiltrating fluid would impose a fixed X_{CO_2} content on the rocks as well as a fixed oxygen fugacity, external control of fluid composition should have a distinct effect on the distribution of grunerite. If the fluid composition was too CO_2 rich or too reducing for grunerite, grunerite should not occur in any magnetite-bearing sample. However, if the fluid had a composition under which grunerite was stable, then some amount of grunerite should appear in every sample containing magnetite.

The following petrologic features would, therefore, indicate that the fluids associated with an iron-formation were subjected to external control during metamorphism:

1. Widespread occurrence of magnetite-free assemblages or of the assemblage olivine–magnetite.
2. Widespread occurrence of the assemblage olivine–magnetite–quartz with the olivine being restricted to a narrow range of composition.
3. The occurrence of the assemblage orthopyroxene–olivine–magnetite and the assemblage orthopyroxene–magnetite–quartz with the X_{Fe}^{opx} of the former assemblage consistently showing a lower value than that from the latter assemblage.
4. The widespread occurrence of the assemblage grunerite–magnetite–quartz with the X_{Fe}^{gru} being fixed within a narrow range of values.

Even in rocks where external control is incomplete, the effect of partial external control should be shown by the mineral assemblages present. If the infiltrating fluid was more reducing than the QMF buffer, the following features should be present in the iron-formation:

1. There should be a distinct tendency for X_{Fe} values to cluster near 1.00 for any buffered assemblages, resulting in the elimination of orthopyroxene from most samples.
2. Magnetite-free assemblages should be common, but the assemblage quartz–magnetite–fayalite or any magnetite-bearing assemblage with orthopyroxene should be rare.

If the fluid had an oxygen flugacity above that of the QMF buffer, the following should be observed:

1. There should be a distinct tendency for X_{Fe} of orthopyroxene or olivine from the buffering assemblage to cluster around the X_{Fe} value dictated by the fluid, with the result that a very restricted set of assemblages should be encountered.
2. Those layers in which magnetite or quartz was depleted during the attempts to equilibrate with the fluid should contain a silicate with X_{Fe} which is less than that which would have been in equilibrium with the fluid.

With these considerations in mind, let us now compare iron-formations which have undergone high-temperature contact metamorphism with those from regional metamorphic terrains.

A comparison of high-grade metamorphosed iron-formation

Stillwater iron-formation

Figure 2A shows the composition of the orthopyroxene and olivine from quartz-free and quartz-bearing layers within the Stillwater iron-formation (Vaniman *et al.*, 1980). Compared to many of the iron-formations the minerals do show a restricted range of composition. However, there is no tendency for the mineral compositions to cluster near a value which can be taken as being the end-product of external control. From Figure 9 in Vaniman *et al.* (1980) one might assume that the authors believe that the controlling oxygen fugacity lay slightly below the QMF buffer. This conclusion, however, is not supported by the mineralogic data because there is widespread occurrence of the assemblage orthopyroxene–magnetite (with either olivine or quartz) while there is a distinct under-representation of the more reducing assemblage olivine–magnetite–quartz or the highly reduced assemblage fayalite–quartz. One might say, therefore, that the fluid might have been slightly more oxidizing than the QMF buffer and that equilibration with it forced the occurrence of the relatively more common assemblages orthopyroxene–magnetite–quartz and orthopyroxene–olivine–quartz and that the single occurrence of the assemblage olivine–quartz–magnetite came from a rock which simply did not equilibrate fully with the fluid. However, this is not consistent with those quartz-free rocks which contain very iron-rich olivine since quartz would have only been depleted from rocks which were forced to increase their ferrous iron content during equilibration. The quartz-free assemblages, therefore, could only have formed due to a silica-poor primary bulk composition. There is no compelling reason to assume that other assemblages also were not internally controlled.

Biwabik iron-formation

Only a single sample of the high-grade Gunflint iron-formation has been studied (Simmons *et al.*, 1974) and, therefore, the moderately large number of samples required to determine whether external control was present are not available. However, Bonnichsen (1969) lists a significant number of assemblages from the correlative Biwabik iron-formation in the Dunka River area. In this area the iron-formation is locally in direct contact with the Duluth complex. The Biwabik, therefore, lies far closer to the mafic intrusion than does the Stillwater iron-formation and if external control were to operate around the margins of mafic intrusions, one should certainly see the effects in the metamorphism of the Biwabik iron-formation. However, Figure 2B shows that the Fe/Mg variability in silicates from the Biwabik iron-formation is far greater than it is in those from the Stillwater. Furthermore, a quick look at the many analyses by Bonnichsen (1969) shows that there is no tendency for any particular X_{Fe} value to dominate. The conclusion that oxygen fugacity was internally controlled in these rocks is unmistakable.

Western Australia

The metamorphosed iron-formation from Western Australia is of great interest because it contains the first recorded instance of an assemblage containing olivine–orthopyroxene from regionally metamorphosed iron-formations (Gole and Klein, 1981). The orthopyroxene and olivine coexisting with magnetite and quartz are considerably richer in Fe than are minerals from similar assemblages in contact metamorphic iron-formations (*cf.* Figures 2 and 3). This is not surprising considering the fact that the assemblage olivine–quartz is progressively restricted as pressure increases (Smith, 1971). However, it is significant to note that the metamorphic conditions of these rocks were as reducing or locally more reducing than those assemblages from either the Stillwater or the Biwabik iron-formations and that there are no outside sources to which this reduction can be attributed.

Another significant occurrence in these rocks is the silica-poor assemblage clinopyroxene–orthopyroxene–grunerite–fayalite–magnetite (sample 1A). This rock is important because it indicates that quartz-free assemblages are not restricted to contact metamorphic environments and therefore, that they are not produced by any process unique to contact metamorphism. The quartz-free assemblages are more likely to represent layers in the original sediment which were unusually rich in carbonate and poor in quartz.

Iron-formations of the Labrador Trough

Unlike the Stillwater, Biwabik and Gunflint iron-formations, high-grade metamorphosed iron-formation from the Labrador Trough does contain hematite in some assemblages (Butler, 1969; Klein, 1978). However, Figure 2B shows that the silicate-bearing iron-formations were metamorphosed at a variety of oxygen fugacities, some of which were, despite the lack of olivine, more reducing than those which accompanied metamorphism of the Biwabik and Stillwater iron-formations.

Iron-formation in southwestern Montana

Interpreting the significance of assemblages from southwestern Montana is tricky because Immega and Klein (1976) report the presence of hematite in most assemblages listed. Two factors indicate that this hematite is retrogressive and that its presence doesn't indicate anything about the oxygen fugacity at the time of metamorphism. First, Klein (1978) reports that orthopyroxene with $X_{Fe} = .243$ coexists with magnetite and quartz without any hematite present. The orthopyroxenes reported by Immega and Klein (1976) and Gillmeister (1971) all are much richer in iron and, therefore, all must have formed well below the hematite–magnetite buffer. Secondly, the habit of the hematite described by Immega and Klein (1976) with the hematite occurring as oriented lamellae concentrated on the margins of the magnetite grains, implies a secondary origin for hematite. If the hematite is accepted as being secondary, then a simple picture of the metamorphism of these rocks is obtained (Figure 2C) with an internal control of oxygen fugacity ranging down to fairly reducing conditions.

Summary and conclusions

The data in Figures 2 and 3 show emphatically that both regionally metamorphosed and contact metamorphosed iron-formations were metamorphosed under a range of oxygen fugacity conditions and that there is no tendency for contact metamorphosed iron-formations to be more reducing than regionally metamorphosed ones. While it is true that hematite–quartz±magnetite is rare in contact metamorphosed iron-formations, this absence could have been produced by the fact that the parent sediment did not have the proper composition. The assemblage hematite–quartz or hematite–magnetite–quartz with only minor amounts of silicates or siderite is quite rare in the low-grade portions of the Biwabik and Gunflint iron-formations (French 1968, Floran and Papike 1975); hence, its absence in the contact aureole is not surprising.

One might still argue that the contact-metamorphosed iron-formations show a narrower range in Fe/Mg ratios because they underwent incomplete equilibration with a fluid phase. Vaniman *et al.* (1980) give the presence of Cu-sulfides and chromite in the Stillwater iron-formation as evidence for the occurrence of such a process. However, the presence of anomalously high copper concentrations (*cf.* Raymond *et al.* 1975, Appel 1979a) and of chromite (Appel 1979b) in other Archean iron-formations casts doubt on the validity of this argument. Furthermore, the assemblages in pelitic hornfelses, which lie between the mafic intrusion and the iron-formations along most of the contact of both the Duluth gabbro and Stillwater complex argue strongly against the transport of large volumes of fluid across the contact aureoles. In both areas the hornfelses contain the assemblage cordierite–biotite–plagioclase–quartz. At a P_{H_2O} above 2 kbar and temperatures of 700° C this assemblage will melt to give orthopyroxene and a granitic melt (Hoffer and Grant 1980). If we accept the temperature of above 800° C given by Vaniman *et al.* (1980) (although there is reason to suspect that the temperature estimate is too high (Frost 1979)), then the a_{H_2O} in the pelitic hornfelses must have been very low. Any water moving out from the mafic intrusions would have caused melting in the pelitic hornfelses. As soon as the melt formed, it would have consumed all free water in the system, making it impossible for the fluids in the iron-formation to have been in communication with those in the mafic intrusion.

In conclusion it must be stressed that there are more similarities among high-grade iron-formations than there are differences. Regardless of whether they come from regional or contact-metamorphic terrains, all high-temperature iron-formations show a wide variety of assemblages and mineral compositions. The variations in these assemblages generally reflect the primary compositional layering of the original sediment, indicating that the fluid composition differed from layer to layer. This striking feature has been traditionally taken as being evidence for internal control of the fluid composition (*cf.* Eugster, 1959; Klein, 1973). Since the compositions of minerals coexisting with magnetite and quartz from any iron-formation fail to cluster around any specific value of X_{Fe} and, indeed, since the iron-formations fail to fit any of the other criteria indicating the presence of a fixed fluid composition throughout the body, this author is forced to conclude that mineralogic evidence for external control is utterly lacking. Furthermore, it must be emphasized that there is no need to call upon an external reducing agent to produce the assemblages seen in high-temperature iron-formations since it has already been demonstrated that internal control of fluid composition during metamorphism of most primary assemblages in iron-formation will ultimately lead to assemblages which are nearly as reducing as the QMF buffer (Frost, 1979).

Acknowledgments

I would like to thank Cornelis Klein, Stephen Haase, Jonathan Myers, Hans Eugster and a discreetly anonymous reviewer for suggestions and comments which vastly improved the quality of this paper. It should be stressed that not all of the reviewers agreed with all the points presented here and that responsibility for any errors and misconceptions presented here are mine alone.

References

Appel, P. W. U. (1979a) Stratabound copper sulfides in a banded iron-formation and in basaltic tuffs in the early Precambrian Isua supra crustal belt, West Greenland. Economic Geology, 74, 45–52.

Appel, P. W. U. (1979b) Cosmic grains in an iron-formation from the early Precambrian Isua supracrustal belt, West Greenland. Journal of Geology, 87, 573–578.

Bonnichsen, B. (1969) Metamorphic pyroxenes and amphiboles in the Biwabik iron formation, Dunka River area, Minnesota. Mineralogical Society of America Special Paper 2, 217–239.

Butler, P. (1969) Mineral compositions and equilibria in the metamorphosed iron formation of the Gagnon region, Quebec, Canada. Journal of Petrology, 10, 56–101.

Eugster, H. P. (1959) Oxidation and reduction in metamorphism. In P. H. Ableson, Ed., Researches in Geochemistry, p. 397–426. John Wiley, New York.

Floran, R. J. and Papike, J. J. (1975) Petrology of the low-grade rocks of the Gunflint iron-formation, Ontario-Minnesota. Geological Society of America Bulletin, 86, 1169–1190.

French, B. (1968) Progressive contact metamorphism of the Biwabik iron-formation, Mesabi Range. Minnesota Geological Survey Bulletin, 45.

Flowers, G. C. (1979) Correction of Holloway's (1977) adoption of the modified Redlich-Kwong equation of state for calculation of the fugacities of molecular species in supercritical fluids of geologic interest. Contribution to Mineralogy and Petrology, 69, 315–318.

Frost, B. R. (1979) Metamorphism of iron-formation: Parageneses in the system Fe–Si–C–O–H. Economic Geology, 74, 775–785.

Frost, B. R. (1980) On the formation of magnetite in Biwabik iron-formation. (abstr.) Geological Society of America Abstracts with Programs, 12, 430.

Gillmeister, N. (1971) The petrology, stratigraphy and structure of the Precambrian metamorphic rocks of the central Tobacco Root Mountains with special emphasis on electron microprobe analyses of high grade mineral assemblages. Ph.D. Thesis, Harvard University, Cambridge, Massachusetts (not seen, extracted from Immega and Klein (1978), American Mineralogist, 61, 1107–1144).

Gole, M. J. and Klein, C. (1981) High-grade metamorphic Archean banded iron-formation Western Australia: assemblages with coexisting pyroxenes and fayalite. American Mineralogist, 66, 87–99.

Greenwood, H. J. (1975) Buffering of pore fluids by metamorphic reactions. American Journal of Science, 275, 573–593.

Hoffer, E. and Grant, J. A. (1980) Experimental investigation of the formation of cordierite-orthopyroxene parageneses in pelitic rocks. Contributions to Mineralogy and Petrology, 73, 15–22.

Holloway, J. R. (1977) Fugacity and activity of molecular species in supercritical fluids. In D. G. Fraser, Ed., Thermodynamics in Geology, p. 161–181. Reidel, Dordrecht, The Netherlands.

Immega, I. P. and Klein, C. (1976) Mineralogy and petrology of some metamorphic Precambrian iron-formations in southwestern Montana. American Mineralogist, 61, 1117–1144.

Klein, C. (1973) Changes in mineral assemblages with metamorphism of some banded Precambrian iron-formations. Economic Geology, 68, 1075–1088.

Klein, C. (1978) Regional metamorphism of Proterozoic iron-formation, Labrador Trough, Canada. American Mineralogist, 63, 898–912.

Morey, G. B., Papike, J. J., Smith, R. W., and Weiblen, P. W. (1972) Observation on the Contact Metamorphism of the Biwabik iron-formation, East Mesabi District, Minnesota. Geological Society of America Memoir 135, 225–262.

Raymond, W. H., King, R. U. and Norton, J. J. (1975) Anomalous concentrations of several metals in iron-formation of the Blue Lead Mountain area, Pennington County, South Dakota. U.S. Geological Survey Circular 707.

Simmons, E. C., Lindsley, D. H., and Papike, J. J. (1974) Phase relations and crystallization sequence in a contact-metamorphosed rock from the Gunflint iron formation, Minnesota. Journal of Petrology, 15, 539–565.

Smith, D. (1971) Stability of the assemblage iron-rich orthopyroxene–olivine–quartz. American Journal of Science, 271, 370–382.

Vaniman, D. T., Papike, J. J. and Labotka, T. (1980) Contact-metamorphic effects of the Stillwater complex, Montana: the concordant iron formation. American Mineralogist, 65, 1087–1102.

Walther, J. V. and Orville, P. M. (1980) Rates of metamorphism and volatile production and transport in regional metamorphism (abstr.). Geological Society of America Abstracts with Programs, 12, 544.

Manuscript received, February 16, 1981;
accepted for publication, July 14, 1981.