

Phase relations of orthopyroxene, olivine, and grunerite in high-grade metamorphic iron-formation

TAKASHI MIYANO¹ AND CORNELIS KLEIN

Department of Geology
Indiana University
Bloomington, Indiana 47405

Abstract

The phase relations of orthopyroxene, olivine, and grunerite, in the presence of magnetite, are quantitatively evaluated using an ideal-solution model for the silicates. The evaluations are directly applicable to estimates of the physicochemical conditions of high-grade metamorphism of iron-formations and associated retrograde reactions.

Standard thermodynamic properties for ferrosilite and grunerite were calculated and estimated from published experimental and petrologic data. S°_{298} , $\Delta H^{\circ}_{f,298}$, and $\Delta G^{\circ}_{f,298}$ of ferrosilite are 93.05 ± 0.3 J/mol · K, -1194.872 ± 1.0 kJ/mol, -1117.124 ± 1.0 kJ/mol, respectively; those of grunerite 721.8 ± 10.0 J/mol · K, -9648.304 ± 20 kJ/mol (minimum), and -8988.759 ± 20 kJ/mol (minimum), respectively.

The phase relations are evaluated on $\log f_{O_2}$ - T diagrams, at constant pressure. The stability field of orthopyroxene is restricted within a narrow range of f_{O_2} in fayalite-bearing systems. Because of the compositional limit ($X_{Fe}^{Ol} > 0.8$) of olivine in iron-formations, an upper f_{O_2} limit for olivine may be set. At the same P and T , orthopyroxene is stable at higher f_{O_2} conditions than olivine. Consequently the phase relations for iron-formations may be classified into three types: (I) olivine-free, (II) olivine- and quartz-bearing, and (III) olivine-bearing and quartz-free relations. Each type may or may not include grunerite. Its presence is strongly influenced by the magnitude of f_{H_2O} . Grunerite in type (I) assemblages tends to have lower X_{Fe}^{Gru} , and is related to higher f_{H_2O} than that of type (II).

The retrograde changes of (1) olivine $\rightarrow$ grunerite, (2) orthopyroxene $\rightarrow$ grunerite, and (3) olivine $\rightarrow$ orthopyroxene relate directly to the phase relations discussed in this study. Reactions (1) and (3) may never take place in assemblages of type (I) but may be observed in the rocks of types (II) and (III). The formation of retrograde grunerite appears to be dependent upon f_{H_2O} rather than on the lowering of T .

Introduction

Phase relations of orthopyroxene, olivine, and grunerite are an important tool in the analysis of the physicochemical conditions during high-grade metamorphism of iron-formations. They are, however, poorly understood because of experimental difficulties. Although many workers have attempted to evaluate such phase relations (*e.g.*, Morey *et al.* 1972; Burt, 1972; Mel'nik and Sirosh-tan, 1973; Bonnichsen, 1975; Miyano, 1976; Floran and Papike, 1978; Frost, 1979), most of the stability fields of grunerite and orthopyroxene are known qualitatively only. Recently, Miyano and Klein (1981) have semiquantitatively evaluated the stability relations of orthopyroxene, olivine, and grunerite in the presence of magnetite. Here we discuss such phase relations more quantitatively

on the basis of newly estimated thermodynamic properties for ferrosilite and grunerite, some existing experimental data, and naturally occurring assemblages in metamorphic iron-formations. We will also evaluate the physicochemical conditions of high-grade metamorphism of several iron-formations, applying the phase relations presented here.

Mineral assemblages

The high-grade metamorphic mineral assemblages in iron-formations as discussed here, are restricted to those in the system Fe-Mg-Si-O-H and include the stability relations of olivine (fayalite-forsterite series), orthopyroxene (ferrosilite-enstatite series), and clino-(Ca-free) amphibole (grunerite-cummingtonite series). The assemblages reported in iron-formations may be conveniently grouped into three types (see Table 1 and Fig. 1); (I) olivine-free; (II) olivine- and quartz-bearing; and (III) olivine-bearing and quartz-free assemblages. Those of

¹Permanent address: Institute of Geoscience, University of Tsukuba, Ibaraki 305, Japan.

Table 1. Simplified mineral assemblages in high-grade metamorphic iron-formations in the system Fe–Mg–Si–O–H. If = iron-formation.

Regional metamorphism	
Klein (1966); Wabush IF, Labrador, Type I (ankerite, siderite, calcite)* Opx+Gru+Qtz±Mt, Gru+Qtz±Mt	
Butler (1969); Wabush IF, Labrador, Type I (ankerite, siderite, calcite, hematite, graphite)* Opx+Gru+Qtz±Mt, Opx+Qtz±Mt	
Klein (1978); Mount Reed IF, Labrador, Type I (ankerite, calcite, magnesite, hematite)* Opx+Gru+Qtz±Mt, Opx+Qtz±Mt, Opx+Gru+Mt	
Chakraborty (1966); Wabush IF, Labrador, Type I (carbonates)* Opx+(Gru)+Qtz±Mt (silicate facies), Opx+Gru±Mt (carbonate facies), Gru+Qtz±Mt (oxide facies)	
Immega and Klein (1976); Southwestern Montana, Type I (calcite, hematite)* Opx+(Gru)+Qtz±Mt, Opx+Gru+Mt	
Dahl (1979); Southwestern Montana, Type I (calcite, hematite)* Opx+Qtz±Mt, (Gru)+Qtz±Mt±Opx	
Haase (1979); Negaunee IF, Northern Michigan, Type II (calcite, hematite)* Ol+(Gru)+Qtz±Mt, Gru+Qtz±Mt	
Gole and Klein (1981); Archean, Western Australia, Type II Ol+Opx+Gru±Qtz±Mt, Ol+Gru+Qtz±Mt, Opx+(Gru)+Mt±Qtz	
Contact metamorphism	
Gundersen and Schwartz (1962); Biwabik IF, Mesabi, Type II (carbonates, graphite)* Ol+(Opx)+(Gru)+Qtz±Mt, Opx+(Gru)+Qtz±Mt Ol+Opx+Qtz±Mt	
French (1968); Biwabik IF (zone 4), Mesabi, Type II (calcite, graphite)* Ol+(Gru)+Qtz±Mt, Ol+Qtz±Mt Ol+Opx+Qt±Mt	
Bonnichsen (1969,1975), Biwabik IF, Dunka River, Type II (calcite, graphite)* Ol+(Opx)+Qtz±Mt, Ol+(Opx)+Mt Ol+Opx+(Gru)±Mt, Ol+Opx+(Gru)+Qtz±Mt Opx+(Gru)+Qtz±Mt, Ol+(Gru)±Mt Ol+Qtz±Mt, Gru+Qtz±Mt	
Morey et al. (1972), Biwabik IF, Mesabi, Type II (calcite)* Ol+(Gru)±Qtz±Mt, Gru±Qtz±Mt Ol±Qtz±Mt	
Simmons et al. (1974), Gunflint IF, Minnesota, Type II Ol+(Opx)+Qtz±Mt, Opx+(Gru)±Qtz±Mt Ol+(Gru)±Qtz±Mt	
Floran and Papike (1978); Gunflint IF, Min.-Ont., Type II Gru+Qtz±Mt, Ol+(Gru)+Qt±Mt	
Vaniman et al. (1980); Stillwater IF, Montana, Type III Opx+(Gru)+Qtz±Mt, Ol+(Opx)+Mt Ol+Qtz±Mt (rare assemblage)	

Most mineral assemblages listed are regarded as stable in the presence of magnetite (in the absence of graphite and hematite). Types I, II, and III refer to olivine-free, olivine and quartz-bearing, and olivine-bearing and quartz-free relations, respectively (see text). *Minerals in parentheses may be part of the assemblage, however, hematite and graphite occur only locally and are insignificant in amount.

Abbreviations (used through the text)
Fa, fayalite; Fs, orthoferrosilite; Ol, olivine; Opx, orthopyroxene; Gru, grunerite; Qtz, quartz; Mt, magnetite; Sd, siderite; QFM, quartz-fayalite-magnetite; HM, hematite-magnetite; W, water; Mi, minnesotaite. (Opx) or (Gru) implies that the orthopyroxene or grunerite may be a retrograde product, respectively.

type (I) are common in regionally metamorphosed iron-formations, those of type (III) in contact metamorphosed iron-formations, and those of type (II) occur in both regionally and contact metamorphosed settings. Representative mineral assemblages of types (I) and (II) consist of orthopyroxene (Opx)–quartz (Qtz)–magnetite (Mt) and olivine(Ol)–Qtz–Mt, respectively. The latter may also include orthopyroxene. Assemblages of type (III) are Opx–Qtz–Mt and/or Ol–Opx–Mt, in which quartz coexists with orthopyroxene but not with olivine. Grunerite may or may not be present in the assemblages, and its appearance or disappearance is mainly controlled by the magnitude of the partial pressure of water. Magnetite is a common mineral and is generally present in all types of assemblages. In most high grade metamorphic iron-formations, where silicate minerals (other than olivine) and carbonates are abundant, quartz is scarce and often absent.

In the subsequent section the Fe–Mg distributions between the following mineral pairs, orthopyroxene–olivine, grunerite–olivine and grunerite–orthopyroxene, in iron-formations are summarized from published data.

Orthopyroxene–olivine pairs

Compositional data on orthopyroxene–olivine pairs in iron-formations are given by Bonnichsen (1969), Vaniman et al. (1980), and Gole and Klein (1981) and are plotted in Figure 2A. This shows that the mole fraction (X_{Fe}^{Ol}) of olivine coexisting with orthopyroxene ranges from > 0.8 to < 0.95. X_{Fe}^{Ol} in quartz-bearing pairs is, however, more restricted than in quartz-free pairs and ranges from 0.89 to 0.95 (Bonnichsen, 1969; Vaniman et al. 1980). Experimental data on the stability of orthopyroxene–olivine–quartz (Smith, 1971; Bohlen and Boettcher, 1981) show that a decrease of X_{Fe}^{Ol} to less than 0.8 is unlikely in the P – T regime associated with high-grade metamorphism

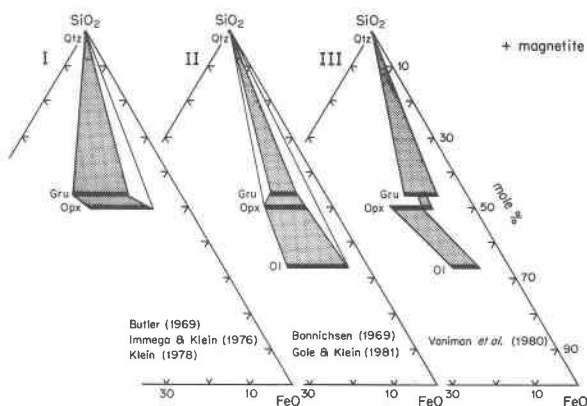


Fig. 1. Compositional ranges of olivine, orthopyroxene, and grunerite in high-grade metamorphic magnetite-rich iron-formations. I: olivine-free assemblages (type I), II: olivine- and quartz-bearing assemblages (type II), III: olivine-bearing and quartz-free assemblages (type III).

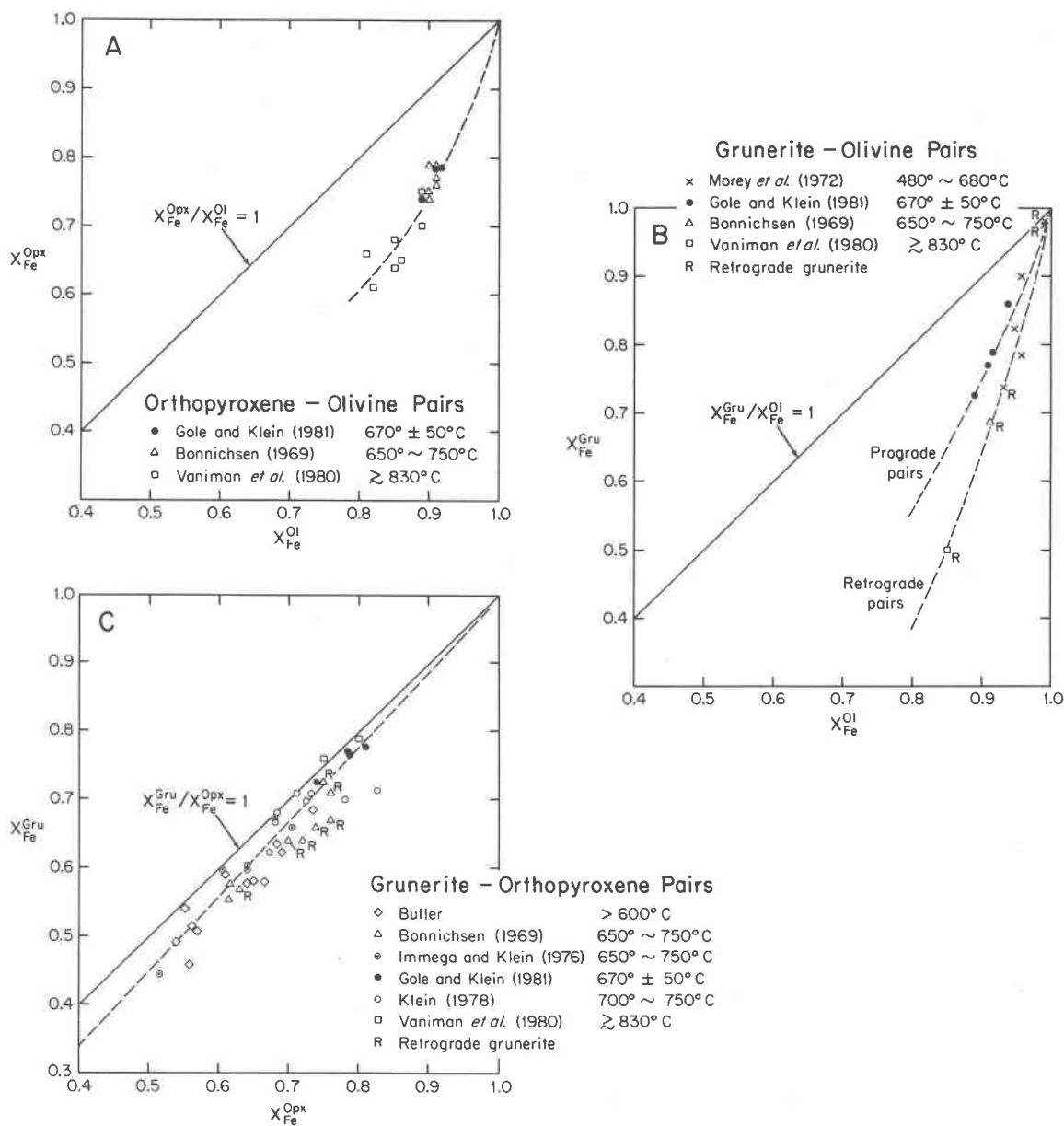


Fig. 2. Element distribution among silicates in high-grade iron-formations. A. X_{Fe}^{Opx} and X_{Fe}^{Ol} distribution for orthopyroxene–olivine pairs. B. X_{Fe}^{Gru} and X_{Fe}^{Ol} distribution for grunerite–olivine pairs. C. X_{Fe}^{Gru} and X_{Fe}^{Opx} distribution for grunerite–orthopyroxene pairs.

($\approx 800^\circ C$ and ≈ 1 kbar). A similar compositional limit for olivine is also suggested in some of the theoretical diagrams of Olsen and Mueller (1966), Wood and Strens (1971), Kurepin (1971), and Perchuk (1977).

Although there are a considerable number of experimental studies on the Fe–Mg distribution between coexisting olivine and orthopyroxene (*e.g.*, Nafziger and Muan, 1967; Medaris, 1968; Kitayama and Katsura, 1968; Larimer, 1968; Kitayama, 1970; Williams, 1971; Matsui and Nishizawa, 1974), none of these studies assesses the Fe–Mg distribution between Fe-rich olivine and Fe-rich

orthopyroxene. Bohlen *et al.* (1980) and Sack (1980) reviewed the available data on iron-rich compositions and found that the Fe–Mg distribution constant between Opx–Ol pairs is dependent upon composition and temperature. More recently, Bohlen and Boettcher (1981) determined such a distribution constant on the basis of experiments at 800 – $1000^\circ C$. Their $X_{Fe}^{Ol} / X_{Fe}^{Opx}$ relation is nearly consistent with that extrapolated by least squares from natural pairs, given in Figure 2A. This curve shows essentially no temperature dependence for the small range (650 – $850^\circ C$) for which a limited amount of data is available.

Grunerite-olivine pairs

The association of grunerite and olivine is commonly observed in contact metamorphic iron-formations (French, 1968; Bonnicksen, 1969, 1975; Morey *et al.*, 1972; Simmons *et al.*, 1974; Floran and Papike, 1980). Recently Haase and Klein (1978) and Gole and Klein (1981) reported such associations from regionally metamorphosed iron-formations as well. In contact metamorphosed iron-formations, retrograde grunerite is commonly found to replace fayalite (*e.g.*, Bonnicksen, 1969; Morey *et al.*, 1972; Simmons *et al.*, 1974; Floran and Papike, 1978; Vaniman *et al.*, 1980). The $X_{\text{Fe}}^{\text{Gru}}$ in retrograde grunerite is generally lower than that of prograde grunerite (see Fig. 2B).

Grunerite-orthopyroxene pairs

Such assemblages occur in both contact and regionally metamorphosed iron-formations (*contact*: Bonnicksen, 1969; Simmons *et al.*, 1974; Vaniman *et al.*, 1980; *regional*: Kranck, 1961; Klein, 1966, 1978; Butler, 1969; Immege and Klein, 1976; Gole and Klein, 1981). In prograde assemblages, $X_{\text{Fe}}^{\text{Gru}}$ is slightly lower than $X_{\text{Fe}}^{\text{Opx}}$ (Fig. 2C). Some retrograde grunerite coexisting with orthopyroxene has also been reported from these iron-formations. According to Bonnicksen (1969), $X_{\text{Fe}}^{\text{Gru}}$ of the early cumingtonite (prograde?) is about 0.6 (or less) and generally lower than that of the later (retrograde) variety which replaces orthopyroxene.

Estimation of thermodynamic properties

Ferrosilite

Thermodynamic properties for ferrosilite have been published by several workers. Those recently reported by Helgeson *et al.* (1978) and Bohlen and Boettcher (1981), were calculated from experimental data for the equilibrium reaction



Helgeson *et al.* (1978) calculated the standard enthalpy and heat capacity from the data of Akimoto *et al.* (1965) and Smith (1971), using an estimated standard entropy of ferrosilite ($S_{298}^{\circ} = 94.6 \text{ J/mol} \cdot \text{K}$). However the equilibrium data for the reaction were revised to somewhat lower pressure by Bohlen *et al.* (1980); these data reflect fairly well the phase transition of α - and β -quartz. Bohlen and Boettcher (1981) calculated, from Bohlen *et al.*'s (1980) data, the standard entropy of orthoferrosilite to be $95.4 \text{ J/mol} \cdot \text{K}$ (at 25°C) by extrapolation from the entropy change (ΔS_r°) at temperatures of 700°C to 850°C , assuming $\Delta S_r^{\circ}/\Delta T_r = 10 \text{ bar}^{\circ}\text{C}$. Based on the standard entropies of orthoferrosilite and clinoferrosilite of this study (Table 4), the ferrosilite entropy of Bohlen and Boettcher (1981) is, however, greater than that of orthoferrosilite ($92.89 \text{ J/mol} \cdot \text{K}$) and close to that of clinoferrosilite ($94.66 \text{ J/mol} \cdot \text{K}$) (see Table 4). From the same data of Bohlen *et al.* (1980), Wood (1981) calculated the entropy of ferrosilite to be $93.3 \text{ J/mol} \cdot \text{K}$, essentially equivalent to that of orthoferrosilite. The recalculated entropy ($93.54 \text{ J/mol} \cdot \text{K}$) from $\Delta H_{\text{f},298}^{\circ}$ and $\Delta G_{\text{f},298}^{\circ}$ of Bohlen and Boettcher (1981) is close to that of orthoferrosilite. The magnitude of the difference between the two values for orthoferrosilite and clinoferrosilite, however, causes greater uncertainties ($\approx 2 \text{ kbar}$ at least) in the equilibrium pressure than are reported for experimental conditions ($\pm 0.1 \text{ kbar}$, Bohlen *et al.* 1980). We will therefore compute both S_{298}° and $\Delta H_{\text{f},298}^{\circ}$ for ferrosilite from the data of Bohlen *et al.* (1980) on the basis of an estimation of the standard heat capacity of ferrosilite.

The standard free energy change (ΔG_r°) of Reaction (1) can be evaluated from the equilibrium P - T brackets. Because there is no complete set of data on thermal expansion (α) and compressibility (β), we used the following approximation (Carmichael *et al.* 1974) for computing volume (V_T^P) of a solid phase, at arbitrary P and T ,

$$V_T^P = V_{298}^{\circ} (1 + \alpha \Delta T) (1 - \beta P) \quad (2)$$

where α and β are assumed to be independent of P and T .

Equation (2) is nearly equal to equation $V_T^P = V_T^{\circ} + V_{298}^P - V_{298}^{\circ}$ which Bohlen and Boettcher (1981) used. However, this same equation may fail to properly estimate the volume of a mineral which has a phase transition (*e.g.*, quartz). According to the volume estimate of Helgeson *et al.* (1978) for α -quartz at an arbitrary P and T , the volume is more positive, by about $0.5 \text{ cm}^3/\text{mol}$, than that computed by using $V_T^P = V_T^{\circ} + V_{298}^P - V_{298}^{\circ}$. Figure 3 demonstrates the volume changes for reaction (1) estimated by both methods. In the calculation we used thermal expansion data for fayalite, orthoferrosilite, and β quartz from Smyth (1975), Sueno *et al.* (1976), and Skinner (1966), respectively. Compressibility data for fayalite are from Yagi *et al.* (1975). The compressibility (β) of orthoferrosilite was estimated to be 0.9×10^{-6} on the basis of the assumption (*e.g.*, Olinger, 1977) that orthoferrosilite may be more compressible than enstatite ($\beta = 0.75 \times 10^{-6}$) and probably bronzite (0.88×10^{-6}). This assumption is contrary to that of Bohlen and Boettcher (1981). The volume of α -quartz at P and T was calculated using the equation of Helgeson *et al.* (1978).

By measuring graphically the area under the curve in Figure 3, one can calculate the free energy change of Reaction (1) according to the following relation at equilibrium,

$$\begin{aligned} \Delta G_r^{\circ} &= - \int_1^P \Delta V_T^P dP \\ &\approx - \int_1^P \Delta V_{298}^{\circ} (1 + \Delta \alpha \Delta T) (1 - \Delta \beta P) dP, \end{aligned} \quad (3)$$

where ΔV refers to the volume change of Reaction (1). The results are in close agreement with those estimated

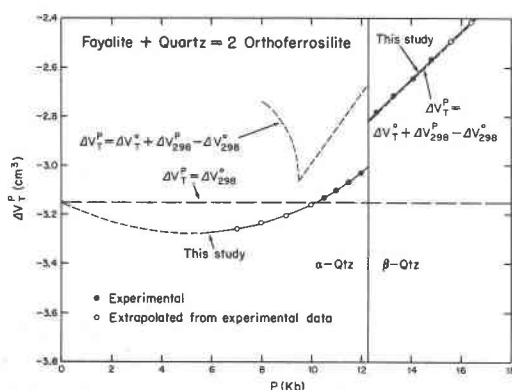


Fig. 3. Volume change for the reaction fayalite + quartz = 2 orthoferrosilite at equilibrium pressure and temperature. Equilibrium (P , T) brackets used for approximation of ΔV_T^P were taken from Bohlen *et al.* (1980). The relation $\Delta V_T^P = \Delta V_T^0 + \Delta V_{298}^P - \Delta V_{298}^0$ is inappropriate for a reaction including a mineral with a transition within the temperature range considered. See text for explanation.

by the relation $\Delta G_T^0 \approx -\Delta V_{298}^0(P - 1)$ as shown in Table 2. This means that the volume change of Reaction (1) is nearly constant over the specified range of temperature and pressure, but calculated uncertainties (less than ± 0.3 kbar) in equilibrium pressure are still larger than experimental ones (± 0.1 kbar, Bohlen *et al.* 1980).

The heat capacity of ferrosilite can be approximated by the following relation, as suggested by Helgeson *et al.* (1978):

$$C_P(\text{FeSiO}_3) = C_P(\text{MgSiO}_3) - C_P(\text{MgO}) + C_P(\text{FeO}) \quad (4)$$

Using heat capacity data for clinoenstatite (Robie *et al.* 1978) and orthoenstatite (Krupka *et al.* 1979) allows for the estimation of the heat capacities for clinoferrosilite and orthoferrosilite. The differences between the two values are fairly small (5 J/mol · K at 300°C and 6 J/mol · K at 700°C). Because heat capacity data for orthoenstatite are only available up to 727°C, the heat capacity value for orthoferrosilite above 727°C is somewhat uncertain. A polynomial heat capacity function (with T^2 term) for orthoenstatite is not appropriate for extrapolation to high temperatures as pointed by Day and Halbach (1979) and Holland (1981). (Indeed, the difference between the two values of clinoferrosilite and orthoferrosilite is 13 J/mol · K at 1000°C and 22 J/mol · K at 1200°C). Because of difficulties in the extrapolation of C_P we chose the heat capacity function of clinoferrosilite for ferrosilite. As we used data from two different sources (Robie *et al.*, 1978 and Helgeson *et al.*, 1978), we have listed the mean values of the coefficients of heat capacity in Table 3.

The standard enthalpy ($\Delta H_{f,298}^0$) and entropy (S_{298}^0) of ferrosilite (which hereafter refers to FeSiO_3 in its stable form at all temperatures and pressures) can be evaluated from a pair of equilibrium P - T brackets of Bohlen *et al.*

(1980), by using thermodynamic data taken from Robie *et al.* (1978) except for the heat capacity of ferrosilite, which is from this study. The values are:

$$S_{298}^0 = 93.05 \pm 0.23 \quad \text{J/mol} \cdot \text{K}$$

$$\Delta H_{f,298}^0 = -1194,872 \pm 10 \quad \text{J/mol}$$

The uncertainties (1σ) were derived by averaging computed $\Delta H_{f,298}^0$ and S_{298}^0 values, and were found to be very small. The calculated S_{298}^0 value is in good agreement with orthopyroxene entropy values, 92.9 J/deg. mol of Wood (1981) and 92.84 J/deg. mol of Mel'nik (1972). The $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ values are comparable with published data (Mel'nik, 1972; Helgeson *et al.*, 1978) and are in excellent agreement with those of Bohlen and Boettcher (1981). If, however, the entropy estimated by Bohlen and Boettcher is accepted, their $\Delta H_{f,298}^0$ value should be less negative by 600 J/mol.

Therefore, the error in the estimated heat capacity may only be as much as or less than ± 3 J/mol · K. This error causes uncertainties of about ± 1.0 kJ/mole in ΔH_f^0 and ΔG_f^0 of ferrosilite.

The free energy change of Reaction (1) was recalculated by using the newly estimated thermodynamic properties for ferrosilite. The results are in good agreement with the values obtained by Equation (3) within uncertainties of ± 33 joules (± 0.1 kbar) as shown in Table 2.

Grunerite

Thermodynamic properties of grunerite have been reported by several workers (*e.g.*, Mel'nik, 1972; Miyano, 1978; Popp *et al.*, 1977b) but these show considerable uncertainty for lack of sufficient experimental data. Be-

Table 2. The Gibbs free energy change of the reaction fayalite + quartz = 2 orthoferrosilite.

$P\#$ (Kb)	$T\#$ (°C)	$-\int_1^P \Delta V_T^P dP$ (J)	$-\Delta V_{298}^0 (P-1)$ (J)	$\Delta G_T^0 (T)^*$ (J)
10.5	700	3397	3314 (83)**	3368 (29)**
11.0	750	3552	3473 (79)	3548 (4)
11.5	800	3707	3628 (79)	3720 (-13)
12.0	850	3858	3787 (71)	3891 (-33)
12.6	900	4033	3975 (58)	4063 (-30)
13.3	950	4226	4213 (13)	4234 (-8)
14.1	1000	4439	4452 (13)	4410 (29)
14.8	1050	4623	4686 (-63)	4590 (33)

equilibrium P - T brackets for reaction (1) from Bohlen *et al.* (1980).

* recalculated free energy change of reaction (1) on the basis of estimated thermodynamic properties for ferrosilite of this study.

** values in parentheses show differences from values listed in the third column.

Table 3. Summary of estimated thermodynamic properties of iron-bearing silicates at 25°C and 1 bar and coefficients of their heat capacity power functions.

	S_{298}° (J/mol·K)	$\Delta H_{f,298}^{\circ}$ (KJ/mol)	$\Delta G_{f,298}^{\circ}$ (KJ/mole)
Ferrosilite FeSiO_3	93.05 (1)	-1194.872 (1)	-1117.124 (1)
Fayalite Fe_2SiO_4	148.32 (2)	-1479.360 (2)	-1379.375 (2)
Grunerite $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	721.8 (1)	-9648.304 (1, -9626.338) (1)	-8988.759 (1) (-8966.793) (1)
Minnesotaite $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	350.8 (1)	-4822.989 (3)	-4474.788 (3)
Greenalite $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$	304.5 (1)	-3301.000 (3)	-3003.000 (3)

	V_{298} (cm ³ /mol)	$C_p(\text{J/mol}\cdot\text{K})^*$				
		a	b(x10 ³)	c(x10 ⁻⁵)	d(x10 ⁶)	e(x10 ⁻³)
Ferrosilite	32.96 (4)	159.268	6.723	-1.760	0	-1.146 (1)
Fayalite	46.39 (2)	172.76	-3.4055	-36.299	22.411	0 (2)
Grunerite	278.73 (5)	769.479	354.343	-156.691	0.1255	0 (1)
Minnesotaite	148.5 (6)	395.262	182.632	-71.421	-55.898	0 (6)
Greenalite	115.0 (7)	269.324	287.022	-37.405	-118.114	0 (6)

(1) this study; (2) Robie *et al.* (1978); (3) adjusted for new entropy (on the basis of low-temperature phase relations of Miyano (1976, 1978); (4) Sueno *et al.* (1976); (5) Klein and Waldbaum (1967); (6) Miyano (1978); (7) Helgeson *et al.* (1978). $C_p(T) = a + bT + cT^{-2} + dT^{-2} + eT^{-0.5}$. For grunerite, $\Delta H_{f,298}^{\circ}$ and $\Delta G_{f,298}^{\circ}$ values represent minima and maxima (see text). The maximum values are in parentheses.

cause of experimental difficulty in this system as noted by Forbes (1977), any thermodynamic properties estimated so far for grunerite can not be tightly constrained by experimental data. However, the upper stability limit of minnesotaite, which decomposes to grunerite + quartz + water, was calculated to be 310°C and 1 kbar by Miyano (1978), using thermodynamic properties of grunerite and minnesotaite predicted by Mel'nik (1972) and Miyano (1978). This upper limit is in fairly good agreement with published values of 300 ~ 350°C and 1 to 2 kbar (James, 1955; James and Clayton, 1962; Forbes 1971; French, 1973; Kretschman and Scott, 1976; Klein, 1983). In Mel'nik and Miyano, the standard entropies and heat capacity functions of minnesotaite and grunerite were approximated by means of an oxide summation method. However, the thermodynamic properties of minnesotaite and grunerite can be revised using the method of Helgeson *et al.* (1978). Furthermore the observed heat capacity of amosite (Bennington *et al.*, 1978) can be used for that of grunerite. The difficulty in the estimation of the heat capacity of amphibole using a method of oxide summation is probably due to the difficulty of evaluating the heat capacity of its constituent water. Estimated heat capaci-

ties of the water from various amphiboles, whose heat capacity values are experimentally known, are very diverse as shown in Figure 4. The heat capacity for water from amosite may be used for that of pure grunerite. This results in a somewhat higher value for the C_p of grunerite than that of amosite (Fig. 5).

The standard entropy of silicates can be approximated with considerable accuracy by the following relation developed by Helgeson *et al.* (1978):

$$S_{i,298}^{\circ} = \frac{S_{i,s}^{\circ}(V_{i,s}^{\circ} + V_{i,298}^{\circ})}{2V_{i,s}^{\circ}} - n\gamma \quad (5)$$

where S_s° and V_s° are simply-summed entropy and volume of the i th mineral, respectively, in a suitable reaction for the estimation of molar entropy $S_{i,298}^{\circ}$ of the mineral. $V_{i,298}^{\circ}$ is the molar volume of the mineral, n is the number of moles of ferrous iron oxide in one mole of the mineral, and γ is a correction factor when FeO is used in the reaction. γ was determined to be equivalent to 8.4 J/mol · K (2 cal/mol · K) by Helgeson *et al.* (1978), which reflects the crystal field effect and electronic entropy of Fe^{2+} in a mineral site (Wood and Strens, 1972; Wood, 1981).

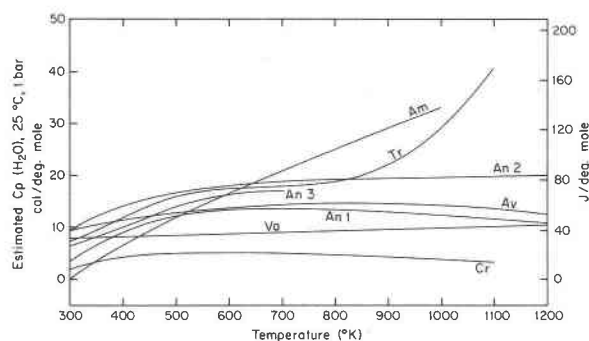


Fig. 4. Estimated molar heat capacity of water from observed heat capacity values of amphiboles, as a function of temperature. $C_p(\text{H}_2\text{O})$ was calculated from the relation $C_p(\text{H}_2\text{O}) = C_p(\text{amphibole}) - \sum C_p(\text{oxide})$. Heat capacity data for oxides are taken from Helgeson *et al.* (1978) and Robie *et al.* (1978); for SiO_2 (average heat capacity) from Miyano (1978). Abbreviations: Am, amosite (Bennington, *et al.* 1978); An 1, anthophyllite (Goranson, 1942); An 2, anthophyllite (Day and Halbach, 1979; Hemley *et al.*, 1977); An 3, anthophyllite (Krupa *et al.* 1979); Av, average heat capacity of H_2O (Miyano, 1978); Cr, crocidolite (Bennington *et al.*, 1978); Tr, tremolite (Robie *et al.*, 1978); Va, vapor (H_2O) (Robie *et al.*, 1978).

Generally, the entropy of an Mg-bearing silicate as estimated from the exchange with an Fe^{2+} -bearing silicate is somewhat greater, by about 2 J/mol · K, than that determined experimentally. The differences between estimated and observed entropy values of Mg-bearing silicates as determined from the following exchange reaction, (Mg) silicate + $\text{FeO} = (\text{Fe}^{2+})$ silicate + MgO , often exceed 4 J/mol · K. This difference may be amplified by using a smaller standard entropy for FeO (59.8 J/mol · K, Robie *et al.*, 1978; 59.0 J/mol · K, Wood, 1981) than that of Helgeson *et al.* (60.8 J/mol · K). This implies that the “FeO” correction factor in Equation (5) is not the same in both directions of the exchange reaction. We have used the FeO value of Robie *et al.* (1978) and redetermined the “FeO” correction factor (γ) to be 7.2 J/mol · K ($7\gamma \approx 50$ J/mol · K) for positive n and 6.7 J/mol · K ($7\gamma \approx 46$ J/mol · K) for negative n . By using these correction factors, the standard entropy value of an iron-bearing mineral computed from Equation (5) becomes consistent with others from different exchange reactions as shown in Table 4. Standard entropy values of clinoferrrosilite and orthoferrrosilite estimated in this study were also used to calculate entropies of other iron-bearing silicates listed in Table 4. Maximal uncertainties by this revised method are estimated to be about $\pm 2\%$ of the predicted entropy.

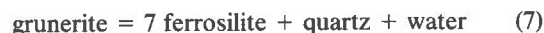
Consequently the standard entropy of grunerite is approximated as 721.8 J/mol · K, which is comparable to the observed value of 706.3 ± 21 J/mol · K for amosite (including about 80% of the grunerite molecule) by Bennington *et al.* (1978).

Using the revised entropies for minnesotaite and grunerite and heat capacity power function for grunerite, the

minimum and maximum $\Delta G_{f,298}^\circ$ values of grunerite were evaluated as -8988.759 (-9648.304 for $\Delta H_{f,298}^\circ$) kJ/mol and -8966.793 (-9626.338 for $\Delta H_{f,298}^\circ$) kJ/mol, respectively, on the basis of the upper stability limit of minnesotaite. When these values are compared with reported $\Delta H_{f,298}^\circ$ and $\Delta G_{f,298}^\circ$ values of grunerite, both minimum and maximum $\Delta H_{f,298}^\circ$ values fall within the uncertainty range of the experimental value obtained by Popp *et al.* (1977b), and the $\Delta G_{f,298}^\circ$ values are comparable with -8979 kJ/mol of Miyano (1978) and -8958 kJ/mol of Mel'nik (1972). In order to evaluate which of these $\Delta G_{f,298}^\circ$ values of grunerite is the best estimate, we have plotted the published P - T estimates for several high-grade metamorphic iron-formations (see Fig. 6). Although these P - T conditions were determined independently of the stability relations of the iron-silicates in this study, the rocks contain mineral assemblages defined by the following reactions,



and



The upper stability limit of minnesotaite is represented by the reaction



The univariant curves for Reactions (6), (7), and (8) are labelled (a), (b), and (c), respectively, in Figure 6. Reaction (7) (for pure phases) becomes metastable at low pressures with respect to Reaction (6). Both Reactions (6) and (7) aid in constraining the upper stability limit of grunerite as discussed below.

The maximum $\Delta G_{f,298}^\circ$ (or $\Delta H_{f,298}^\circ$) value of grunerite is estimated from the $\Delta G_{f,298}^\circ$ value of minnesotaite giving the same low-temperature stability relations as those shown by Miyano (1976). The $\Delta G_{f,298}^\circ$ value used for minnesotaite is -4475 kJ/mol which is nearly equivalent

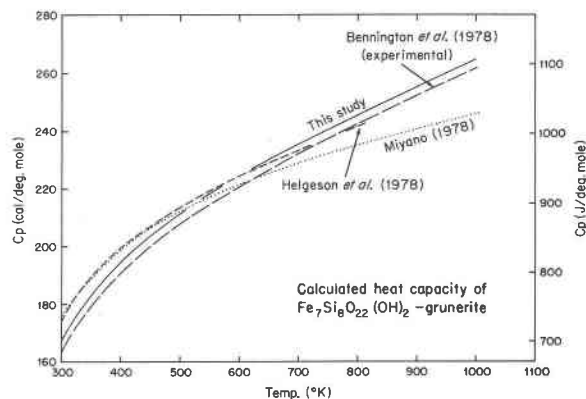


Fig. 5. Estimated molar heat capacity of grunerite as a function of temperature. The heat capacity power function of grunerite was adjusted from that of amosite (Bennington *et al.*, 1978) using the method of oxide summation (see text).

Table 4. Estimated standard third-law entropies of iron-bearing silicates from Equation (5).

Orthoferrosillite (FeSiO ₃)	$V_{298}^O = 32.961 \text{ cm}^3/\text{mol}$ (1)	Iron-Anorthophyllite (Fe ₇ Si ₈ O ₂₂ (OH) ₂)	$V_{298}^O = 278.7 \text{ cm}^3/\text{mol}$ (4)
92.91	MgSiO ₃ ^{or} - 0.5 Mg ₂ SiO ₄ + 0.5 Fe ₂ SiO ₄	712.3	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{an} - 3.5 Mg ₂ SiO ₄ + 3.5 Fe ₂ SiO ₄
92.87	MgSiO ₃ ^{or} - MgO + FeO	712.2	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{an} - 7 MgO + 7 FeO
92.89	Average	712.4	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{an} - 7 MgSiO ₃ ^{cl} + 7 FeSiO ₃ ^{cl}
		712.7	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{an} - 7 MgSiO ₃ ^{or} + 7 FeSiO ₃ ^{or}
		712.4	Average
Clinoferrosillite (FeSiO ₃)	$V_{298}^O = 32.943 \text{ cm}^3/\text{mol}$ (2)	Minnesotaitaite (Fe ₃ Si ₄ O ₁₀ (OH) ₂)	$V_{298}^O = 148.5 \text{ cm}^3/\text{mol}$ (5)
94.67	MgSiO ₃ ^{cl} - 0.5 Mg ₂ SiO ₄ + 0.5 Fe ₂ SiO ₄	350.7	Mg ₃ Si ₄ O ₁₀ (OH) ₂ - 1.5 Mg ₂ SiO ₄ + 1.5 Fe ₂ SiO ₄
94.65	MgSiO ₃ ^{cl} - MgO + FeO	350.8	Mg ₃ Si ₄ O ₁₀ (OH) ₂ - 3 MgO + 3 FeO
94.66 (94.56)	Average	350.8	Mg ₃ Si ₄ O ₁₀ (OH) ₂ - 3 MgSiO ₃ ^{cl} + 3 FeSiO ₃ ^{cl}
Cummingtonite (Mg ₇ Si ₈ O ₂₂ (OH) ₂)	$V_{298}^O = 264.68 \text{ cm}^3/\text{mol}$ (2)	350.9	Mg ₃ Si ₄ O ₁₀ (OH) ₂ - 3 MgSiO ₃ ^{or} + 3 FeSiO ₃ ^{or}
529.2	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂ - 2 CaO + 2 MgO	350.8 (348.4)	Average
529.4	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂ - 2 CaSiO ₃ + 2 MgSiO ₃ ^{cl}		
529.3 (526.1*)	Average		
Grunerite (Fe ₇ Si ₈ O ₂₂ (OH) ₂)	$V_{298}^O = 278.73 \text{ cm}^3/\text{mol}$ (3)		
721.7	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{cum} - 3.5 Mg ₂ SiO ₄ + 3.5 Fe ₂ SiO ₄	Greenalite (Fe ₃ Si ₂ O ₅ (OH) ₄)	$V_{298}^O = 115.0 \text{ cm}^3/\text{mol}$ (6)
721.7	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{cum} - 7 MgO + 7 FeO	304.5	Mg ₃ Si ₂ O ₅ (OH) ₄ - 1.5 Mg ₂ SiO ₄ + 1.5 Fe ₂ SiO ₄
721.8	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{cum} - 7 MgSiO ₃ ^{cl} + 7 FeSiO ₃ ^{cl}	304.4	Mg ₃ Si ₂ O ₅ (OH) ₄ - 3 MgO + 3 FeO
722.0	Mg ₇ Si ₈ O ₂₂ (OH) ₂ ^{cum} - 7 MgSiO ₃ ^{or} + 7 FeSiO ₃ ^{or}	304.5	Mg ₃ Si ₂ O ₅ (OH) ₄ - 3 MgSiO ₃ ^{cl} + 3 FeSiO ₃ ^{cl}
721.8 (716.6*)	Average	304.6	Mg ₃ Si ₂ O ₅ (OH) ₄ - 3 MgSiO ₃ ^{or} + 3 FeSiO ₃ ^{or}
		304.5 (303.8)	Average
Anorthophyllite (Mg ₇ Si ₈ O ₂₂ (OH) ₂)	$V_{298}^O = 264.43 \text{ cm}^3/\text{mol}$ (2)		
519.8	Mg _{6.3} Fe _{0.7} Si ₈ O ₂₂ (OH) ₂ ^{an} - 0.35 Fe ₂ SiO ₄ + 0.35 Mg ₂ SiO ₄		
519.7	Mg _{6.3} Fe _{0.7} Si ₈ O ₂₂ (OH) ₂ ^{an} - 0.7 FeO + 0.7 MgO		
519.7	Mg _{6.3} Fe _{0.7} Si ₈ O ₂₂ (OH) ₂ ^{an} - 0.7 FeSiO ₃ ^{cl} + 0.7 MgSiO ₃ ^{cl}		
519.7	Mg _{6.3} Fe _{0.7} Si ₈ O ₂₂ (OH) ₂ ^{an} - 0.7 FeSiO ₃ ^{or} + 0.7 MgSiO ₃ ^{or}		
519.7 (538.1)	Average		

(in J/mol·K). Superscripts: cl, or, cum, and an, refer to clinopyroxene, orthopyroxene, cummingtonite, and anorthophyllite, respectively. Standard entropies of orthoenstatite and anorthophyllite (Mg_{6.3}Fe_{0.7}Si₈O₂₂(OH)₂) were taken from Krupka et al. (1979), and all other entropies from Robie et al. (1978). (1) Sueno et al. (1976), (2) Robie et al. (1967), (3) Klein and Waldbaum (1967), (4) predicted on the basis of volume of grunerite, (5) Miyano (1978), (6) Helgeson et al. (1978). Values in parentheses next to average values are from Helgeson et al. (1978).

*Corrected volume was used.

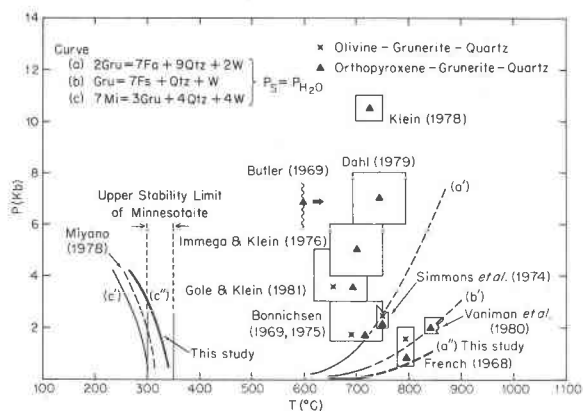


Fig. 6. Published metamorphic P - T conditions for various high-grade metamorphic iron-formations. Curves ((a') and (a'')), (b'), and ((c') and (c'')) are equivalent to reactions (a), (b), and (c), respectively. Curves (a'), (b'), and (c') are based on the maximum $\Delta H_{f,298}^\circ$ (or $\Delta G_{f,298}^\circ$) value of grunerite. Curves (a'') and (c'') are calculated using the minimum $\Delta H_{f,298}^\circ$ (or $\Delta G_{f,298}^\circ$) value of grunerite. See text for further explanation.

to -4476 kJ/mol of Mel'nik (1972). The upper stability limit of minnesotaite, using this maximum $\Delta G_{f,298}^\circ$ value, is shown in Figure 6 (curve (c')), and lies at lower temperatures than that of Miyano (1978). When one considers the common substitution by Mg in minnesotaite, the upper stability limit shifts to higher temperatures by 30 to 50°C. The upper stability limits of grunerite, defined by curves (a') and (b'), lie on the low temperature side of the P - T conditions estimated for grunerite formation on the basis of natural occurrences (Fig. 6). Because such naturally occurring Fe amphiboles are not pure phases ($\text{Fe}/(\text{Fe}+\text{Mg}) < 1.0$), the univariant curves for pure phases (at $P_{\text{H}_2\text{O}} = P_s$) must be located at higher temperatures than those shown in Figure 6. This is also supported by the experimental results of Popp *et al.* (1977a).

The minimum $\Delta G_{f,298}^\circ$ (or $\Delta H_{f,298}^\circ$) value of grunerite is estimated from the $\Delta G_{f,298}^\circ$ value (-4485 kJ/mol, Miyano, 1978) of minnesotaite (see curve (c'') in Figure 6 for the upper stability limit). Curve (a''), calculated on the basis of this minimum value, is nearly parallel to the temperature axis and represents the high temperature limit for the metamorphic P - T conditions of grunerite production as shown in Figure 6. Using the $\Delta G_{f,298}^\circ$ value of minnesotaite, Fe-rich minnesotaite would coexist with hematite at temperatures below 250°C ($P_{\text{H}_2\text{O}} = P_s$). This is inconsistent with hematite-free and magnetite-bearing assemblages in very low-grade metamorphic iron-formations.

As such the minimum and maximum $\Delta G_{f,298}^\circ$ values of grunerite produce some inconsistencies with respect to the upper stability limits of minnesotaite and grunerite in natural occurrences. It should be noted, however, that some of the grunerite-containing assemblages which are plotted in Figure 6, contain retrograde grunerite, and the

optimum formation temperature of such grunerite would be lower than that of the peak temperature. In high-grade contact metamorphic iron-formations, grunerite may have formed during retrograde metamorphism from pyroxenes and fayalite (Bonnichsen, 1969, 1975; Floran and Papike, 1978). If much of the grunerite in contact metamorphic rocks (*e.g.*, French, 1968; Vanniman *et al.* 1980) is retrograde, the upper stability limit of grunerite may be close to that (curve (a')) calculated from the maximum $\Delta G_{f,298}^\circ$ value of grunerite in this study. Further evaluation of textural relations is, however, needed in order to be able to justify using the maximum $\Delta G_{f,298}^\circ$ value for calculation of the phase relations. In subsequent discussion, the minimum $\Delta G_{f,298}^\circ$ value of grunerite will be used to estimate the minimum $f_{\text{H}_2\text{O}}$ for formation of prograde grunerite during metamorphism.

The estimation of the uncertainties in the minimum and maximum $\Delta H_{f,298}^\circ$ and $\Delta G_{f,298}^\circ$ values of grunerite is not straightforward, because many factors are involved. If, however, one considers only the uncertainties caused by the upper stability limit of minnesotaite, and by the entropy and heat capacity of grunerite, they can be estimated to be about ± 20 kJ/mol at a maximum.

A summary of thermodynamic properties for ferrosilite and grunerite (minimum and maximum) is given in Table 3.

Phase relations

The newly estimated thermodynamic properties for ferrosilite and grunerite allow for the construction of phase relations of iron-bearing silicates (orthopyroxene, olivine, and grunerite) at high temperatures and high pressures. In this treatment, all the iron-bearing silicates are assumed to be ideal solid solutions between Mg- and Fe-end members because thermodynamic data are lacking for other compositional substitutions. The following paragraph evaluates this assumption on the basis of several publications.

According to activity-composition relations of Saxena and Ghose (1971) and Sack (1980), orthopyroxene (Fe, Mg) SiO_3 may be slightly non-ideal in a macroscopic sense at temperatures above 800°C. Furthermore, Sack (1980) shows in his calculated activity-composition diagram that iron-rich orthopyroxene ($X_{\text{Fe}}^{\text{Opx}} > 0.6$) behaves as a nearly ideal solution at a temperature of 600°C. However, Bohlen and Boettcher (1981) note, on the basis of their experimental data, that olivine is slightly non-ideal (with a negative deviation) provided that orthopyroxene is really ideal as Sack (1980) concluded. Engi (1980) computed the solid-solution behavior of olivine (Fe, Mg) SiO_4 in the temperature range from 500 to 1500 K. His results indicate that olivine is nearly ideal at temperatures above 1000 K and that olivine with $X_{\text{Fe}}^{\text{Ol}} > 0.5$ may be regarded as nearly an ideal solution at 800 K. Recently Ghose (1981) reviewed several existing models for Fe-Mg distribution in the cumingtonite-grunerite series, and concluded

from amphiboles in metamorphosed iron-formation that the Fe-Mg ion exchange between "V sublattice" (M4) and "W sublattice" (M1, M2, M3) (Mueller, 1962) may be regarded as ideal at temperatures of 600 to 700°C. Popp *et al.* (1977b) examined three mixing models for the Fe-Mg distribution in Fe-Mg amphiboles (simple ideal solution, ideal sublattice of "V" and "W" solution, and symmetrical regular solution) by computing an equilibrium constant (at 700°C, $P_S = P_{H_2O} = 2$ kbar) for the reaction $\text{grunerite} + \text{O}_2 = \text{magnetite} + \text{quartz} + \text{H}_2\text{O}$, based on their own experimental data. The results showed that no significant differences, caused by use of various models, are detectable and that the differences may be within the uncertainties of the experiments.

In resume, a small deviation from ideality seems to be present in all of the Fe-Mg bearing silicates mentioned. Such a deviation, however, will have a trivial effect on the present analysis of the phase relations because any uncertainty in estimated parameters such as temperature and pressure will cause much larger errors than minor non-ideality. In this study we therefore treat the silicates as ideal solutions at the temperatures (>650°C) of high-grade metamorphism of iron-formation. We also assume the activities of magnetite and quartz to be unity.

Metamorphic reactions

Possible reactions during high-grade metamorphism of iron-formations have been deduced from mineral assemblages by many workers (*e.g.*, Kranck, 1961; Gundersen and Schwartz, 1962; French, 1968, 1973; Klein, 1973, 1983; Mueller, 1973; Bonnicksen, 1975; Floran and Papike, 1978; Haase, 1979). In the simple systems Fe-Si-O-H and Fe-Mg-Si-O-H, which are used in this study, simplified reactions have been proposed for the construction of phase relations by Burt (1972), Mel'nik and Siroshtan (1973), Miyano (1976), Floran and Papike (1978) and Frost (1979). In addition to these reactions, some mineral assemblages reported by Vaniman *et al.* (1980) from the Stillwater iron-formation suggest that the following reaction may have taken place in quartz-free systems:



On the basis of the phase rule and consideration of the above reactions, an additional reaction can be deduced.



This reaction constrains the low temperature limit of orthopyroxene in $\log f_{\text{O}_2}$ - T space as will be discussed later. Natural assemblages which may support Reaction (9) have been reported from Mount Reed (in the Labrador Trough) by Klein (1978). All the reactions are listed in Table 5.

$\log f_{\text{O}_2}$ - T diagrams

Table 5. Possible reactions in the system Fe-Mg-Si-O-H at high-grade metamorphism

(1)	3 grunerite + 3.5 O ₂ = 7 magnetite + 24 quartz + 3 H ₂ O
(2)	2 grunerite + 6 magnetite = 16 olivine + 2 H ₂ O + 3 O ₂
(3)	2 magnetite + 3 quartz = 3 olivine + O ₂
(4)	3 grunerite + magnetite = 24 orthopyroxene + 3 H ₂ O + 0.5 O ₂
(5)	2 magnetite + 6 quartz = 6 orthopyroxene + O ₂
(6)	6 orthopyroxene + 2 magnetite = 6 olivine + O ₂
(7)	2 grunerite = 7 olivine + 9 quartz + 2 H ₂ O
(8)	grunerite = 7 orthopyroxene + quartz + H ₂ O
(9)	grunerite + olivine = 9 orthopyroxene + H ₂ O
(10)	olivine + quartz = 2 orthopyroxene
grunerite (FeMg) ₇ Si ₈ O ₂₂ (OH) ₂ , orthopyroxene (FeMg)SiO ₃ , olivine (FeMg) ₂ SiO ₄	

The phase relations in the system Fe-Mg-Si-O-H were calculated on the basis of the thermodynamic properties of the iron-silicates in Table 3 and the metamorphic reactions in Table 5. These are illustrated in $\log f_{\text{O}_2}$ - T diagrams, in the presence of magnetite, in Figures 7 to 12. The calculated $\log K$ (T , 1) values for the metamorphic reactions used in the construction of the $\log f_{\text{O}_2}$ - T diagrams are listed in Table 6 for a temperature range from 500 to 900°C. The pressure effects on the reactions in Figures 7 to 10 were calculated assuming

$$\int_1^P \Delta V_T^P dP \approx \Delta V_{298}^P (P-1).$$

The equilibrium temperature for the assemblage orthopyroxene-olivine-quartz, at a specific pressure, was estimated from the experimental data of Bohlen and Boettcher (1981).

High-pressure phase relations

High-pressure and high temperature regionally metamorphosed iron-formation assemblages have been observed in the Gagnon, Mount Reed, and Lac des Silicates areas of the Labrador Trough, Canada (Klein, 1978). The P - T conditions of the metamorphism of the Gagnon-Mount Reed region were estimated to be 10–11 kbar and 700–750°C by Klein (1978). Mineral assemblages in these iron-formations, which directly apply to the chemical system of this study, are Gru-Opx-Qtz-Mt and Opx-Qtz-Mt (see Table 1). Olivine is absent in all of the iron-formation assemblages. Using Klein's compositional data on orthopyroxene ($X_{\text{Fe}}^{\text{Opx}}$) and grunerite ($X_{\text{Fe}}^{\text{Gru}}$), the phase relations for such iron-formations are shown in Figure 7 for a given temperature and pressure (=10 kbar). In this diagram, the assemblage orthoferrosilite-fayalite-quartz (pure phases) located at invariant point D, occurs within the stability field of grunerite. The absence of olivine in the natural assemblages can be explained by the fact that the f_{O_2} (dotted area) for this type of metamorphism is much higher than that defined by the compositional limit

Table 6. Calculated equilibrium constants and volume changes of Reactions (1) to (6) at 500 to 900°C.

reaction	ΔV_s° (25°C, cm ³)	log K (T, 1)				
		500	600	700	800	900
(1)	19.990	83.79 (88.25)	73.30 (77.24)	65.31 (68.85)	58.72* (61.92*)	53.12* (56.05*)
(2)	-82.364	-71.59 (-68.76)	-58.31 (-55.85)	-48.19 (-46.03)	-40.09* (-38.19*)	-33.47* (-31.78*)
(3)	-17.942	-23.90	-20.10	-17.20	-14.86	-12.92
(4)	-89.650	-13.95 (-9.50)	-9.23 (-5.29)	-5.66 (-2.12)	-2.89* (0.32*)	-0.72* (2.22*)
(5)	-27.410	-24.44	-20.63	-17.74	-15.40	-13.46
(6)	-8.474	-23.36	-19.56	-16.66	-14.31	-12.37

Temperature in °C.
*for grunerite, extrapolated from the estimated heat capacity within a temperature range of 298 to 1000°K.
Values in parentheses are calculated from the maximum $\Delta H_{f,298}^\circ$ (or $\Delta G_{f,298}^\circ$) value of grunerite (see Table 3).

of olivine ($X_{Fe}^{Ol} = 0.8$, see curve (3)). From the X_{Fe}^{Gru} of grunerite coexisting with orthopyroxene the minimum water fugacity (f_{H_2O}) during metamorphism can be calculated to have ranged from about 2040 ($X_{Fe}^{Gru} = 0.71$) to about 3700 ($X_{Fe}^{Gru} = 0.63$) bars at 725°C.

Medium-pressure phase relations

This type of metamorphism has been observed in regional metamorphism of most iron-formations (e.g., Kranck, 1961; Klein, 1966, 1983; Butler, 1969; Dahl, 1979; Immea and Klein, 1976). Among these, the P - T conditions of metamorphism in southwestern Montana were estimated to be 4–6 kbar and 650–750°C for the Tobacco Root Mountains by Immea and Klein (1976) and to be 6–8 kbar and $745 \pm 50^\circ\text{C}$ for the Ruby Range (Kelly area) by Dahl (1979). The mineral assemblages and phase relations in these areas are very similar to those for high-pressure metamorphism (Fig. 7), as shown in Figure 8 (also Table 1). However, X_{Fe}^{Opx} and X_{Fe}^{Gru} in Figure 8 are more Mg-rich than those in Figure 7. The orthopyroxene–olivine–quartz assemblage (X_{Fe}^{Ol} , $X_{Fe}^{Opx} > 0.8$; point D) is again located within or near the grunerite field. Curve (3), with the compositional limit for olivine of $X_{Fe}^{Ol} = 0.8$, lies far below the $\log f_{O_2}$ region (dotted area) appropriate for the iron-formation. The minimum f_{H_2O} was calculated to range from about 630 ($X_{Fe}^{Gru} = 0.67$) to about 1540 ($X_{Fe}^{Gru} = 0.56$) bars at 700°C.

Low-pressure phase relations (I)

These types of phase relations occur in both contact and regionally metamorphosed iron-formations. Mineral assemblages in such iron-formations have been studied by French (1968), Bonnichsen (1969, 1975), Morey *et al.* (1972), Simmons *et al.* (1974), Floran and Papike (1978),

Haase and Klein (1978), and Gole and Klein (1981) (also see Table 1). Representative mineral assemblages are:



with local assemblages such as $\text{Opx} + \text{Qtz} + \text{Mt}(\pm \text{Gru})$ and $\text{Opx} + \text{Fa} + \text{Mt}(\pm \text{Gru})$. Using the P - T conditions (3–5 kbar, $670 \pm 50^\circ\text{C}$) estimated by Gole and Klein (1981), for regionally metamorphosed iron-formations, the calculated phase relations are shown in Figure 9. The pressure estimate by Gole and Klein was adjusted to 3 kbar within the error of the new experimental data of Bohlen and Boettcher (1981). The $\log f_{O_2}$ region in Figure 9 (dotted area) is defined by two curves on the basis of the compositional data for olivine and orthopyroxene. Reaction (5) defines the upper and Reaction (3) the lower limit. The assemblage orthopyroxene–olivine–quartz is located at invariant point D (within the dotted area). In this type of iron-formation, the orthopyroxene field is restricted to a narrow f_{O_2} range and is located only at point D in the presence of grunerite (Fig. 9). The phase relations of iron-formations described by French (1968), Morey *et al.* (1972), and Floran and Papike (1978), contain assemblages that may be located along curve (3) at a somewhat higher T and f_{O_2} than those of point D. On the other hand, the phase relations for the iron-formations reported by

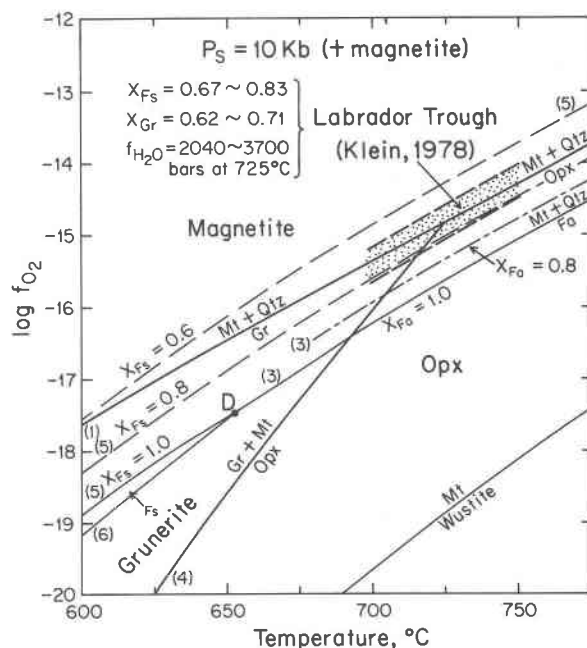


Fig. 7. $\log f_{O_2}$ - T conditions for regionally metamorphosed Proterozoic iron-formation in the Mount Reed area of the Labrador Trough region (high pressure phase relations, ~10 kbars). Point D marks the coexistence of the pure phases $\text{Fs} + \text{Fa} + \text{Qtz}$, which is unstable in this diagram. X_{Fs} , X_{Fa} , and X_{Gru} in Figures 7 to 10 refer to X_{Fe}^{Opx} , X_{Fe}^{Ol} , and X_{Fe}^{Gru} , respectively. f_{H_2O} in Figures 7 to 10 are minimum values (see text).

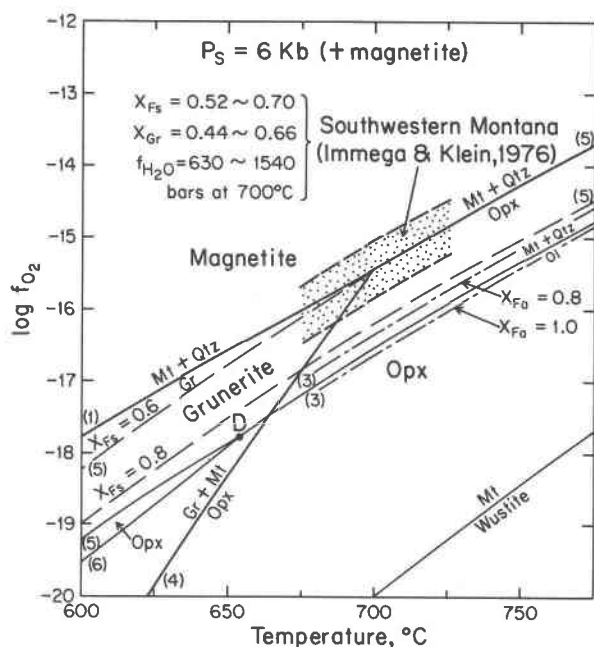


Fig. 8. Log f_{O_2} - T conditions for some regionally metamorphosed Archean iron-formations of Southwestern Montana (medium pressure phase relations, ~ 6 kbars). Point D represents assemblage Opx + Ol ($0.9 < X_{Fe}^{Ol} < 1.0$) + Qtz and is unstable in this diagram.

Bonnichsen (1969) and Simmons *et al.* (1974) occur at a slightly lower T and f_{O_2} than those of point D, in which Reactions (5) and (6) are involved. The presence of grunerite in any assemblage depends upon the magnitude of f_{H_2O} during metamorphism. Accordingly grunerite may or may not be present in the phase assemblages. The calculated minimum f_{H_2O} for the Archean iron-formations of Figure 9 ranges from 60 ($X_{Fe}^{Gru} = 0.86$) to 100 ($X_{Fe}^{Gru} = 0.72$) bars at 670°C, based upon the compositional data for grunerite coexisting with olivine and orthopyroxene, respectively.

Low pressure phase relations (II)

Low-pressure phase relations in iron-formations are formed at temperatures that are approximately 100–150°C higher than those discussed previously. An example of such an occurrence is the iron-formation in contact with the Stillwater Complex, Montana (Vaniman *et al.*, 1980). There the mineral assemblages are: Opx + Qtz + Mt($\pm$ Gru) and Ol + Opx + Mt. The former occurs in olivine-free rocks and the latter in quartz-free rocks (Vaniman *et al.*, 1980). These assemblages are equivalent to those located on the low T -log f_{O_2} side of point D in Figure 9. Figure 10 was calculated on the basis of the P - T conditions (~ 2 kbar, $\sim 800^\circ\text{C}$) estimated by Vaniman *et al.* (1980). The temperature range in Figure 10 is the minimum estimated by Vocke *et al.* (1981). The upper

limit of the f_{O_2} range can be restricted by solid curve (5) and the lower limit by solid curve (6) on the basis of the compositional data on orthopyroxene and olivine of Vaniman *et al.* (1980). In Figure 10 two dotted regions (labelled A and B) are shown. Because olivine does not coexist with quartz the assemblages in region B occur at a much lower T and f_{O_2} than those defined by the invariant assemblage of orthopyroxene-olivine-quartz. Vaniman *et al.* (1980) reported a rare assemblage of Ol-Qtz-Mt. According to Figure 10, this assemblage occurs close to curve (3) which is a metastable extension between curves (5) and (6) or between the two dotted areas A and B at this temperature. It is, however, unlikely to occur because the compositional ranges of X_{Fe}^{Opx} and X_{Fe}^{Ol} do not permit this association. Such an assemblage may be possible at higher temperatures where curves (5) and (6) (or both dotted areas) meet.

Although prograde grunerite does not coexist with olivine in the Stillwater iron-formation (Vaniman *et al.*, 1980), the f_{H_2O} for grunerite stability during prograde metamorphism may be evaluated from X_{Fe}^{Gru} of grunerite coexisting with orthopyroxene in the f_{O_2} range of the dotted area A (Fig. 10). The minimum f_{H_2O} values range from about 560 ($X_{Fe}^{Gru} = 0.72$) to 980 ($X_{Fe}^{Gru} = 0.64$) bars at 840°C on the basis of extrapolation of the C_P for grunerite. These values are approximately equivalent to $P_{H_2O} = 600$ –1150 bars. At 840°C such P_{H_2O} values would cause

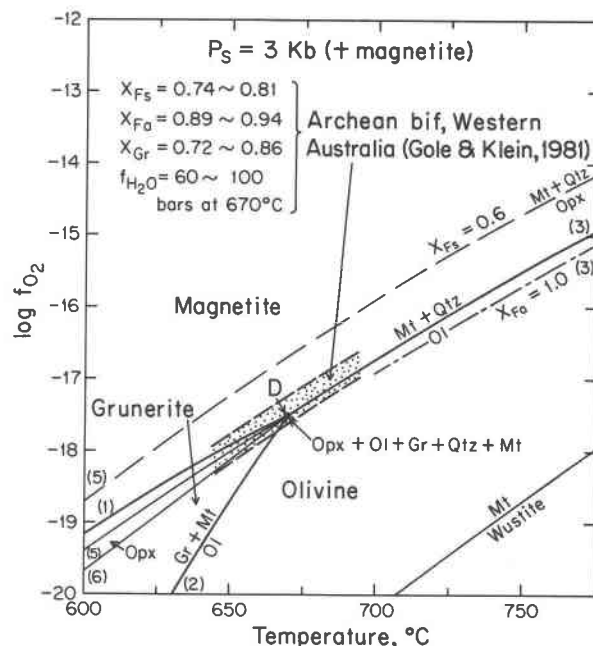


Fig. 9. Log f_{O_2} - T conditions for some regionally metamorphosed Archean iron-formations of Western Australia (low pressure phase relations, ~ 3 kbars). Point D represents assemblage Opx + Ol + Qtz + Mt + Gru. The Opx field is dependent upon the magnitude of f_{H_2O} . bif = banded iron-formation.

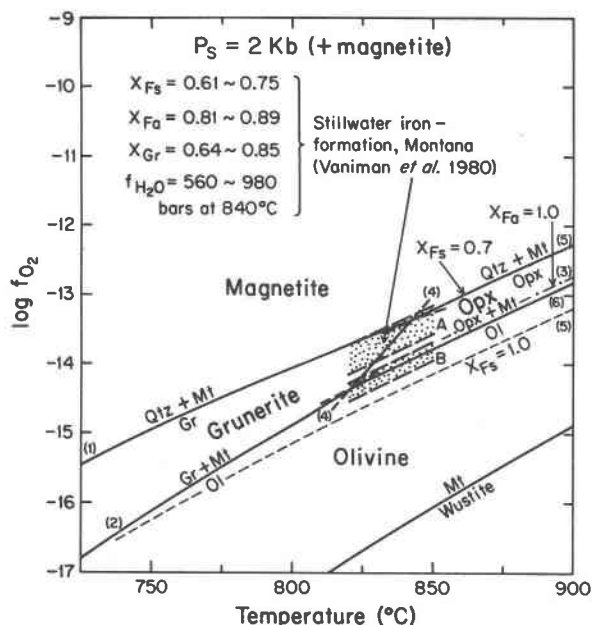


Fig. 10. Log f_{O_2} - T conditions for the contact metamorphosed Stillwater iron-formation in Montana (low pressure phase relations, <2 kbars). Assemblage Opx+Ol+Qtz is not shown in this diagram, and is probably stable at higher temperature. Metamorphic conditions for the Stillwater iron-formation are divided into two dotted zones, A and B. At a given temperature, grunerite forms more readily in zone A than in zone B in which a higher f_{H_2O} is required.

the formation of a melt. Although melting data on iron-formation rocks are lacking it is probable that the Stillwater iron-formation would indeed melt within such a P_{H_2O} - T range, similar to that for many rock types (e.g., Bailey, 1976; Wyllie, 1979). Because all evidence for melting is lacking, the grunerite here is probably of retrograde origin.

Summary of phase relations

All of the above phase relations may be summarized at fixed rock pressure (P_s) and water fugacity (f_{H_2O}), in the presence of magnetite, as shown schematically in Figure 11. This diagram depicts the relative magnitudes of temperature, f_{H_2O} , and f_{O_2} during metamorphism at constant pressure. The phase relations can be grouped into the same three types as the naturally occurring assemblages discussed earlier. Because the pressures for the various iron-formations are not the same, the three numbered regions reflect different T - f_{O_2} conditions. Those iron-formations having similar phase relations are grouped in boxes in Figure 11. They are (I) olivine-free relations, (II) olivine- and quartz-bearing relations, and (III) olivine-bearing and quartz-free relations. Quartz-free assemblages are not uncommon in some iron-formations (see Table 1), and these are also shown in Figure 11. Each of

the three types have quartz-free assemblages, which are typically defined by univariant curves (quartz-free reactions) (2), (4), and (6). (Also see Fig. 10 for location of Reaction (6); Table 5 lists the reactions). Type III assemblages may include olivine.

Type III assemblages are located at lower T - f_{O_2} conditions than those of type II. Type III associations are unlikely to occur because the grunerite field is extensive even with P_{H_2O} conditions as low as or less than 100 bars. It is therefore concluded that type III assemblages will occur only under very dry conditions, which may be attained at very high temperatures, such as in the contact metamorphism of the Stillwater iron-formation.

Figure 11 indicates that olivine is stable at lower f_{O_2} conditions than orthopyroxene at constant temperature. Because of the Fe-rich nature of olivine in metamorphosed iron-formations curve (3) represents the upper limit of f_{O_2} in association with olivine, with orthopyroxene becoming stable at higher f_{O_2} . Type I assemblages may be the equivalent of the upper region (highest f_{O_2} values) of type III associations as shown by the common assemblage Opx + Qtz + Mt (curve (5)). Orthopyroxene does not seem to coexist with olivine ($X_{Fe}^{Ol} > 0.8$) in these

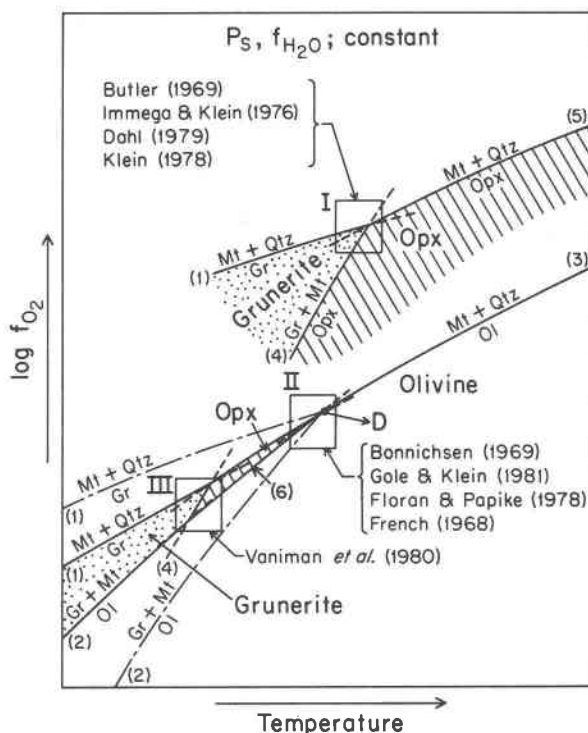


Fig. 11. Summary of the various types of phase relations in high-grade metamorphic iron-formations. Assemblages I, II, and III are equivalent to those in Figure 1 (see also Table 1 for a listing of types). Phase relations in type III reflect relatively low f_{H_2O} conditions which occur under dry conditions at high temperatures.

assemblages (see also Figs. 7 and 8). When orthopyroxene coexists with olivine, it is stable within a narrow range of f_{O_2} (Figs. 9, 10, 11) and at T - f_{O_2} conditions lower than those of point D (Fig. 11). Naturally occurring assemblages in the vicinity of point D may be highly variable because of the very narrow stability field of orthopyroxene. Such variability is shown by the assemblages reported by Bonnicksen (1969) for the Biwabik Iron Formation.

The stability field of orthopyroxene will shrink in the presence of water because grunerite will then become stable. Orthopyroxene in type III assemblages will be replaced by those of type II with increasing water fugacity and temperature (Fig. 11).

Grunerite coexisting with both olivine and orthopyroxene may be stable up to the T - f_{O_2} conditions of point D. Under even higher T - f_{O_2} conditions, grunerite may coexist with either olivine (type II) or orthopyroxene (type I). f_{H_2O} conditions for grunerite stability are a function of X_{Fe}^{Gru} and f_{O_2} at constant P and T . Generally, f_{O_2} is proportional to f_{H_2O} at the upper stability limit of grunerite (curve (1)). With increasing f_{H_2O} curve (1) will move toward higher f_{O_2} , and at the same time curves (2) and (4) will move toward lower f_{O_2} values. The X_{Fe}^{Gru} is inversely proportional to f_{H_2O} . Because f_{O_2} is controlled by the composition (X_{Fe}^{Ol} and/or X_{Fe}^{Opx}) of olivine and/or orthopyroxene according to Reactions (3), (5), or (6), f_{H_2O} is a reflection of the composition of grunerite at a given f_{O_2} , P , and T .

The total range of computed values of f_{O_2} and f_{H_2O} for each of the metamorphic assemblages treated here, extends only over one order of magnitude. This range is probably a function of the inhomogeneity of the fluid fugacity in the rocks during metamorphism, as discussed by Eugster (1959), Butler (1969), and Klein (1978).

Retrograde phase relations

The above phase relations may also be applied to mineral assemblages formed during retrograde metamorphism of iron-formation. The following retrograde reactions have been deduced from mineral assemblages in high-grade metamorphic iron-formations:

(A) olivine $\rightarrow$ grunerite. (Gundersen and Schwartz, 1962; Bonnicksen, 1969; Morey *et al.*, 1972; Simmons *et al.*, 1974; Floran and Papike, 1978; Vaniman *et al.*, 1980.)

(B) orthopyroxene $\rightarrow$ grunerite. (Gundersen and Schwartz, 1962; Bonnicksen, 1969; Simmons *et al.*, 1974; Immega and Klein, 1976; Dahl, 1979; Gole and Klein, 1981.)

(C) olivine $\rightarrow$ orthopyroxene. (Simmons *et al.*, 1974; Bonnicksen, 1975; Vaniman *et al.*, 1980.)

Bonnicksen (1969) suggested that the retrograde reactions listed in (A) and (B), took place along various reaction paths with decreasing temperature. Here, we will attempt to examine some of these retrograde paths on the basis of the phase relations already presented. The

replacement of olivine and orthopyroxene by grunerite depends upon the availability of water as the temperature is lowered and upon the T - f_{O_2} conditions of the original assemblage. If one considers that f_{O_2} is buffered by a peak metamorphic assemblage such as Ol + Qtz + Mt, Opx + Qtz + Mt, or Ol + Opx + Mt, Figure 12 shows that temperature and f_{O_2} can be reduced along curves (3), (5), or (6). Reactions along these curves are based on the assumption that no compositional change has occurred in the silicates during cooling. If one supposes that the initial assemblage at peak temperature consists of Ol + Qtz + Mt, the appearance of retrograde grunerite may have taken place in two ways depending on the magnitude of f_{H_2O} . If f_{H_2O} was originally high, grunerite would directly replace olivine (change (A) $\rightarrow$ (B), Fig. 12a). If f_{H_2O} was small or virtually zero, orthopyroxene would have replaced olivine, which would be equivalent to a change (A) $\rightarrow$ (D) (Fig. 12b). With a further decrease in temperature along curve (5) or (6) (Fig. 12b), assuming appropriate f_{H_2O} conditions, grunerite replaces orthopyroxene (A $\rightarrow$ D $\rightarrow$ B for quartz-bearing assemblages or A $\rightarrow$ D $\rightarrow$ C for quartz-free assemblages). If the assemblage Ol + Opx + Qtz, which originally formed at point D (Fig. 12b) were to remain in equilibrium with decreasing temperature (as suggested by Simmons *et al.* (1974) and Bonnicksen (1969)) then f_{O_2} would be reduced along path D $\rightarrow$ D' with an increase in X_{Fe}^{Ol} and X_{Fe}^{Opx} . If olivine or quartz were exhausted at point D, T and f_{O_2} might decrease along path D $\rightarrow$ B at constant X_{Fe}^{Opx} , or path D $\rightarrow$ C at constant X_{Fe}^{Opx} and X_{Fe}^{Ol} respectively. Although the retrograde change in Figure 12c applies to two different assemblages, Opx + Qtz + Mt (A') and Ol + Opx + Mt (A''), the former might follow path A' $\rightarrow$ B (curve (5)) until grunerite appears with decreasing temperature. Much of the grunerite that is retrograde after orthopyroxene in regional metamorphic iron-formations may have followed this path. Some orthopyroxene coexisting with olivine (but lacking quartz in the assemblage) may be replaced by grunerite according to path A'' $\rightarrow$ C (curve (6); Figure 12c) as the temperature is lowered.

In summary, there are many possible paths for retrograde metamorphic reactions. The major factors in the formation of retrograde assemblages in iron-formations are P and T , the compositions of the associated silicates and the prevailing f_{H_2O} conditions.

Local presence of graphite and hematite

Small amounts of graphite have been reported from both contact and regionally metamorphosed, high-grade iron-formations (*e.g.*, Gundersen and Schwartz, 1962; French, 1968; Butler, 1969; Bonnicksen, 1975). Graphite-bearing assemblages in high-grade metamorphic iron-formations are of minor importance because of their restricted occurrence. f_{O_2} conditions estimated from such assemblages appear to be close to or below the lower limit of the dominant f_{O_2} range. Accordingly, the phase rela-

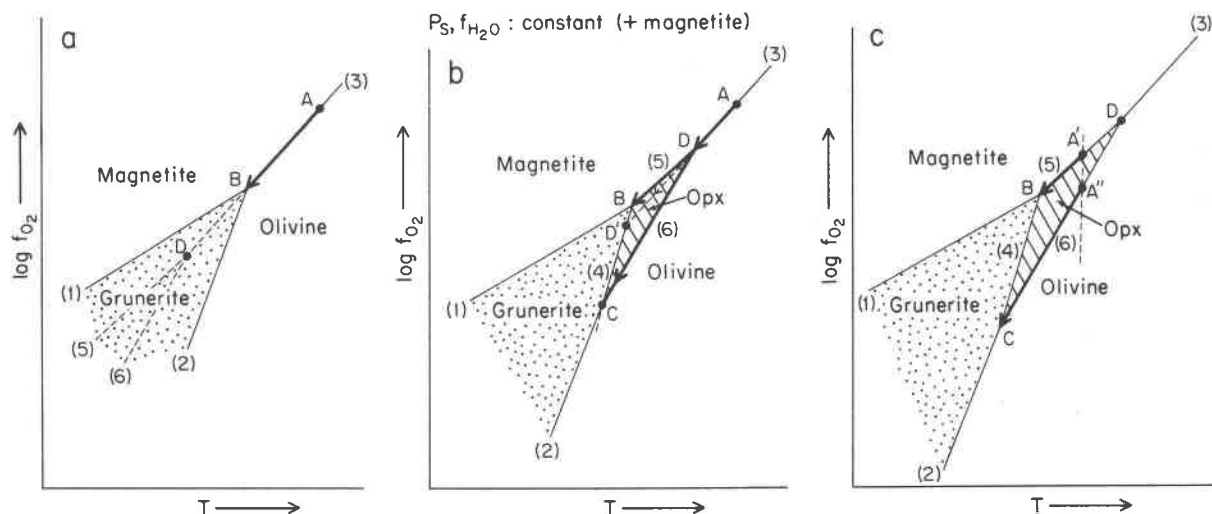


Fig. 12. Possible paths of retrograde metamorphism. Peak metamorphic conditions are represented by point A (or A' or A''). For significance of curves, 1, 2 and 3, see Figure 11. Solid arrows show possible paths of retrograde metamorphism toward the appearance of grunerite. Retrograde processes depend upon the initial conditions represented by point A. (a) Relatively high f_{H_2O} conditions. Opx is unstable. (b) Relatively low f_{H_2O} conditions. Opx is an essential retrograde mineral. If assemblage Opx + Ol + Qtz (point D) remains during cooling, Opx and Ol change their compositions and follow curve DD' (not an extension of curve AD). (c) Relatively low f_{H_2O} conditions. Opx is not retrograde.

tions presented in this study are unlikely to be seriously affected by the presence of graphite. Although our present knowledge of graphite-bearing assemblages is incomplete, graphite-bearing phase relations may be significant in medium-grade metamorphism of iron-formations. Evaluations of such graphite-bearing systems have been made by Burt (1972) and Frost (1979).

The local presence of primary hematite has been reported from some regionally metamorphosed iron-formations (e.g., Butler, 1969; Immega and Klein, 1976; Klein, 1966, 1978; Dahl, 1979). Hematite coexists commonly with quartz and magnetite, and in places with orthopyroxene and Mg-Fe clinoamphiboles. Generally these silicates are more Mg-rich ($X_{Fe}^{Opx} = 0.2-0.5$) than those in hematite-free rocks, and f_{H_2O} values defined by such hematite-containing assemblages can be much higher than those deduced above for equilibria with magnetite as the only Fe-oxide. In contrast to the presence of graphite, hematite is an indicator of the maximum fugacity values for fluids such as H_2O , CO_2 , and O_2 (or the minimum values of reducing species).

Conclusions

The phase relations for olivine, orthopyroxene, and grunerite were quantitatively evaluated in the system Fe-Mg-Si-O-H on the basis of (1) newly estimated thermodynamic properties for ferrosilite and grunerite, (2) mineral assemblages in high-grade metamorphic iron-formations, and (3) some published experimental data. It has been shown that the phase relations are directly applicable to estimates of physicochemical conditions during

high-grade metamorphism of iron-formations as well as to the retrograde reactions in the same rocks. No evaluations were made for high-grade metamorphic carbonate-bearing iron-formation, but some aspects of the physicochemical conditions of such occurrences may be estimated in the system Fe-Mg-Si-C-O-H (graphite-free) on the basis of the phase relations in the Fe-Mg-Si-O-H system.

The local presence of graphite or hematite (these define the lower and upper parts of the phase regions, types I, II, III in Figure 11) can be used to define the minimum and maximum limits of fluid fugacities and the compositions of iron-bearing silicates during high-grade metamorphism. Although the phase relations presented here relate to a rather simplified chemical system, the results obtained reflect to a large extent naturally-occurring mineral assemblages and allow for a reasonable assessment of mineralogical changes during metamorphism.

Acknowledgments

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