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Fe-Ti Oxide Minerals from Regionally Metamorphosed Quartzites of Western New Hampshire

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Abstract. The assemblages rutile-hematite, hematite, hematite-magnetite, hematite-ilmenite-magnetite, and ilmenite-magnetite occur in sillimanite- and kyanite-grade quartzites exposed in western New Hampshire. Different assemblages are found in interlayered sedimentary beds of single outcrops. Magnetites are nearly pure Fe_3O_4 and contain trace amounts of Al, Si, Ti, V, Cr, Mn, and Ni. Magnetites in contact with hematites contain up to 0.4 weight % MnO, but magnetites in contact with ilmenites containing up to 2.3 weight % MnO have no detectable Mn. Ilmenite is enriched in Mn relative to coexisting hematite, and hematite is so enriched with respect to magnetite. Systematic partitioning of elements between oxide minerals and absence of crossing tie lines suggest that the minerals attained chemical equilibrium during regional metamorphism. None of the assemblages are divariant because of the presence of components in addition to FeO, Fe_2O_3, and TiO_2; therefore, none of them constitute oxygen buffers. Nevertheless, gradients in μ_{O_2} between adjacent sedimentary beds can be measured using variations of oxide mineral composition in trivariant and quadrivariant phase assemblages. Oxygen behaved as an "initial value" component or "inert" component during regional metamorphism. It is likely that the μ_{O_2} gradients are due to differences in bulk composition of sedimentary beds at the time of deposition.

Introduction

The status of the volatile component oxygen as an "inert" (Korzhinskii, 1959), "buffered" (Eugster, 1959), or "initial value" (Zen, 1963) component of metamorphic rocks is an accepted principle of metamorphic petrology. That oxygen behaves in this way was first suggested by the petrographic observation of intercalated two-phase assemblages of hematite and magnetite and one-phase assemblages of hematite or magnetite (James and Howland, 1955; Thompson, 1957; Eugster, 1959). The two-phase assemblage hematite-magnetite defines the chemical potential of oxygen at fixed T and P by the condition of heterogeneous equilibrium:

$$\mu_{O_2} = 6\mu_{Fe_2O_3,\ \text{hematite}} - 4\mu_{Fe_3O_4,\ \text{magnetite}}. \tag{1}$$

The two-phase assemblage is invariant at constant P and T provided the mineral compositions lie wholly on the join Fe_2O_3-Fe_3O_4. If there were an "external reservoir" with which the buffer assemblages were in equilibrium with respect to μ_{O_2}, then the reservoir would necessarily have the same value of μ_{O_2} as the buffer assemblages. Such a coincidence is unlikely, and Zen (1963) concluded that the observed assemblages could not have been in equilibrium with an external reservoir. There are two essential steps in the logical structure of this argument: (1) The mineral assemblages must have been in chemical equilibrium during metamorphism. Such criteria as absence of crossing tie lines (Greenwood, 1967) and systematic partitioning of elements between minerals (Kretz, 1959) may be used to test for the attainment of equilibrium. (2) The status of a given assemblage as an oxygen buffer or nonbuffer must be established by evaluating its variance. In the absence of divariant buffer assemblages, the conditions of equilibrium with respect to μ_{O_2} may be evaluated by measuring mineral compositions of trivariant assemblages that are isothermal, isobaric functions of μ_{O_2} (Butler, 1969). Most workers have chosen to bypass these two logical steps. Accepting petrographic observation of presumed oxide buffer assemblages at face value, they have focused their efforts on variation in silicate mineralogy and composition as a function of observed oxide parageneses (see Chinner, 1960; Mueller, 1960; Klein, 1966).

The purpose of this paper is to present a systematic body of data on the chemical compositions of coexisting oxide minerals and to test the data to determine whether the hypothesis of attainment of chemical equilibrium is justified. The variance of oxide mineral assemblages will be evaluated in order to determine whether divariant oxygen buffers are present. In the absence of oxygen buffers, variations in oxide mineral composition in trivariant assemblages will be used to measure gradients in μ_{O_2} between adjacent rock layers.

Area and Rocks Studied

The quartzites and quartz mica schists of this study belong to the Clough Formation of late Early Silurian age (Billings, 1937; Boucot and Thompson, 1963) and are exposed in western New Hampshire (Fig. 1). The formation consists of conglomerates, quartzites, current-bedded quartzites, quartz-mica schists, and mica schists that rest unconformably upon amphibolites, mica schists, and granites of Ordovician age (Thompson *et al.*, 1968; Naylor, 1969). The Clough Formation is overlain by calcareous rocks of the Upper Silurian Fitch Formation and pelitic rocks of the Lower Devonian Littleton Formation. The Ordovician, Silurian, and Devonian rocks were regionally metamorphosed, recumbently folded, and refolded into anticlinoria and synclinoria during post-Lower Devonian, pre-Triassic time (Thompson *et al.*, 1968).

Method of Study

Electron microprobe[1] measurements of chemical composition were made using the data-reduction scheme and matrix corrections of Boyd (1969, pp. 63–69). The calculated precision of the analyses of elements present in concentrations greater than 1.0 weight % is 1.0% of the amount present; the accuracy of the analyses is estimated to be 3.0% of the amount present. The calculated detectability limit of elements present in amounts less than 0.10 weight % is 100–200 ppm.

Hematite and ilmenite grains commonly contain lamellae of each other too small to be resolved for individual analysis by the microprobe. To determine the bulk compositions of single mineral grains showing such lamellae, a beam diameter of 20–30 µm and counting

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[1] MAC electron microprobe purchased with the assistance of the National Science Foundation under grant GP 4384.

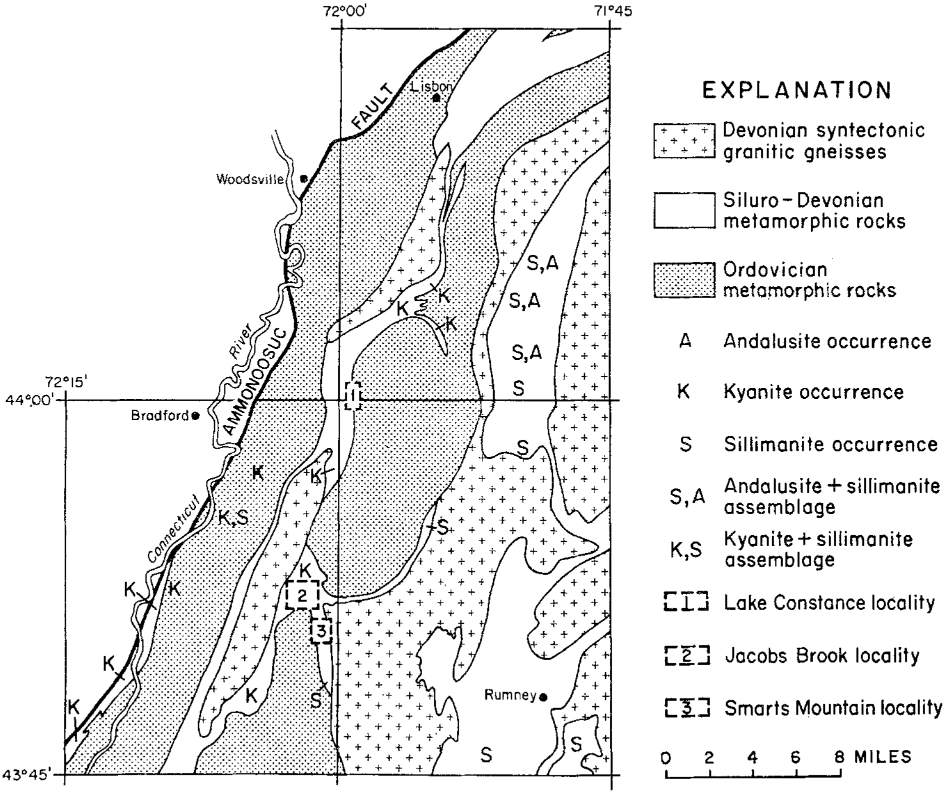

Fig. 1. Geological map of western New Hampshire after Billings (1956) and Rumble (1971c) showing aluminium silicate occurrences and sample localities

times of 50 sec were used and twenty measurements were made per grain. These conditions of analysis considerably reduce calculated standard deviations compared with measurements made with smaller beam diameters or shorter counting times, or with fewer measurements per grain. The calculated precision of the analyses for major elements is 3.0% of the amount present. Major element concentrations determined for adjacent grains in the same thin section agree within 3.0–6.0% of the amount present.

In order to estimate the amount of ferric iron in the Fe-Ti oxides, microprobe analyses were recalculated in the following way: The number of cations was normalized to its ideal value of 3 for magnetites and 2 for rhombohedral minerals. For the latter, Mn is assigned to $MnTiO_3$, Al to $FeAlO_3$, Si to $FeSiO_3$, the remaining Ti to $FeTiO_3$, and the remaining Fe to Fe_2O_3. For magnetites, Mn is assigned to $MnFe_2O_4$, Si to Fe_2SiO_4, Ti to Fe_2TiO_4, and the remaining Fe to Fe_3O_4. The Fe^{2+}:Fe^{3+} ratio is obtained by adding the numbers of these cations in each component. Cation-deficient magnetites correspond to those whose oxides total less than 100%. Within the limits of uncertainty of microprobe analysis, none of the magnetites are detectably cation deficient.

Fe-Ti Oxide Mineral Assemblages

Oxide mineral assemblages found in the rocks of the Clough Formation are given in Table 1. No graphite and only one grain of pyrrhotite have been found. Two-

Table 1. Silicate and oxide mineral assemblages

A. Lake Constance locality

	68–20	68–20A	68–20R	68–20X	70–129	70–129B	70–176	70–176A
quartz	+	+	+	+	+	+	+	+
muscovite	+	+	+	+	+	+	+	+
kyanite							+	
staurolite		+						
chloritoid							+	
garnet							+	
chlorite						+	+	
biotite								
plagioclase								
tourmaline				+				
rutile								
titanhematite			+	+	+			+
ilmeno-hematite	+	+					+	
hemo-ilmenite		+						
ferrianilmenite								
magnetite	+	+	+		+	+	+	+

B. Jacobs Brook locality

	66-7-11A	66-7-90	66-15A	66-16A	66-24C	66-25B	66-25C	66-57A	66-111B	66-127
quartz	+	+	+	+	+	+	+	+	+	+
muscovite	+	+	+	+	+	+	+	+	+	+
kyanite									+	
staurolite	+			+		+		+		+
garnet	+	+		+	+		+		+[a]	
chlorite	+	+		+	+	+		+	+	+
biotite	+	+		+	+	+		+		+
plagioclase				+						
tourmaline				+			+	+		

rutile										
titanhematite										
ilmeno-hematite			+				+		+	
hemo-ilmenite			+							
ferrianilmenite	+	+		+	+	+		+		+
magnetite			+		+	+	+	+		

C. Smarts Mountain locality

	66-76A	66-76B	66-76C	66-127	66-128A	68-277	68-277A	68-278A
quartz	+	+	+	+	+	+	+	+
muscovite	+	+	+	+	+	+	+	+
kyanite	+	+						
staurolite				+		+		+
chloritoid		+	+					
garnet	+	+	+		+	+	+	
chlorite	+	+		+		+		
biotite				+		+		
plagioclase								
tourmaline			+					
rutile	+		+					
titanhematite	+							
ilmeno-hematite		+	+				+	+
hemo-ilmenite							+	+
ferrianilmenite				+	+	+		
magnetite					+		+	+

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[a] Garnet contains 37 mole % *spessartine* component.

phase mineral grains of ilmeno-hematite[2] and hemo-ilmenite probably resulted from cooling and exsolution of one-phase grains of titanhematite and ferrianilmenite, respectively. According to this interpretation, the bulk compositions of ilmeno-hematite and hemo-ilmenite grains in contact with each other represent the binodal composition of titanhematite and ferrianilmenite on the ilmenite-hematite solvus under the conditions of recrystallization. Titanhematite lamellae in hemo-ilmenite are narrower and less abundant than ferrianilmenite lamellae in ilmeno-hematite, suggesting that the solvus may be asymmetric toward $FeTiO_3$-rich compositions. Rutile forms thin selvages between grains of ilmeno-hematite and magnetite. The intergrowth may be the result of the reaction

$$\text{Ilmenite (lamellae)} + \text{hematite (host)} = \text{rutile} + \text{magnetite}$$

proceeding as grains of ilmeno-hematite in contact with magnetite are cooled (cf. Mielke and Schreyer, 1972; Southwick, 1968). Magnetite porphyroblasts are euhedral and may reach a size of 5 mm on a side. The subhedral hematite and ilmenite grains have the form of flat plates; their rectangular cross-sections measure up to 40×90 μm. The hematite and ilmenite plates show a strong preferred orientation parallel to the schistosity defined by the mica grains of the quartz-mica schists. No traces of relict detrital mineral grains are present.

Magnetite may be partially or wholly altered to hematite, forming martite pseudomorphs. Ferrianilmenite may be partially or wholly altered to aggregates of rutile and hematite, a texture characteristic of beach-sand alteration (Bailey *et al.*, 1956). This alteration is probably a form of weathering, since it is most intense along joints in deeply weathered out-crops. Furthermore, the intensity of the alteration varies greatly within a single polished thin section; the most altered oxide minerals are found along grain boundaries of silicates or enclosed in cracked silicates.

Silicate mineral assemblages are also listed in Table 1. The minerals rich in ferrous iron, staurolite, chloritoid, biotite, and almandine occur with ilmenite or ilmenite-magnetite, not with rutile-hematite or hematite-magnetite assemblages. The minerals poor in ferrous iron, kyanite, chlorite, and spessartine are commonly associated with rutile-hematite or hematite-magnetite assemblages (cf. Chinner, 1960; Mueller, 1960).

Chemical Compositions of Minerals

The Fe-Ti oxide minerals analyzed in this study lie almost wholly within the system Fe-Ti-Mn-O (Table 2). They are not measurably inhomogeneous within a single sedimentary bed. Magnetites are nearly pure Fe_3O_4. Ilmenite and hematite are approximately ternary solutions on the join $FeTiO_3$-Fe_2O_3-$MnTiO_3$. Fig. 2 shows compositions of coexisting oxide minerals projected onto an isothermal, isobaric μ_{O_2} vs. $Fe/(Fe+Ti)$ phase diagram. No two-phase assemblages of titanhematite-magnetite or ferrianilmenite-magnetite plot within the three-phase field defined by compositions of coexisting hemo-ilmenite, ilmeno-hematite, and magnetite. This observation suggests that the compositions $70Fe_2O_3$-$30FeTiO_3$

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[2] The terminology of Buddington *et al.* (1963) and Anderson (1968) has been adopted to describe the intergrowths of Fe-Ti oxide minerals.

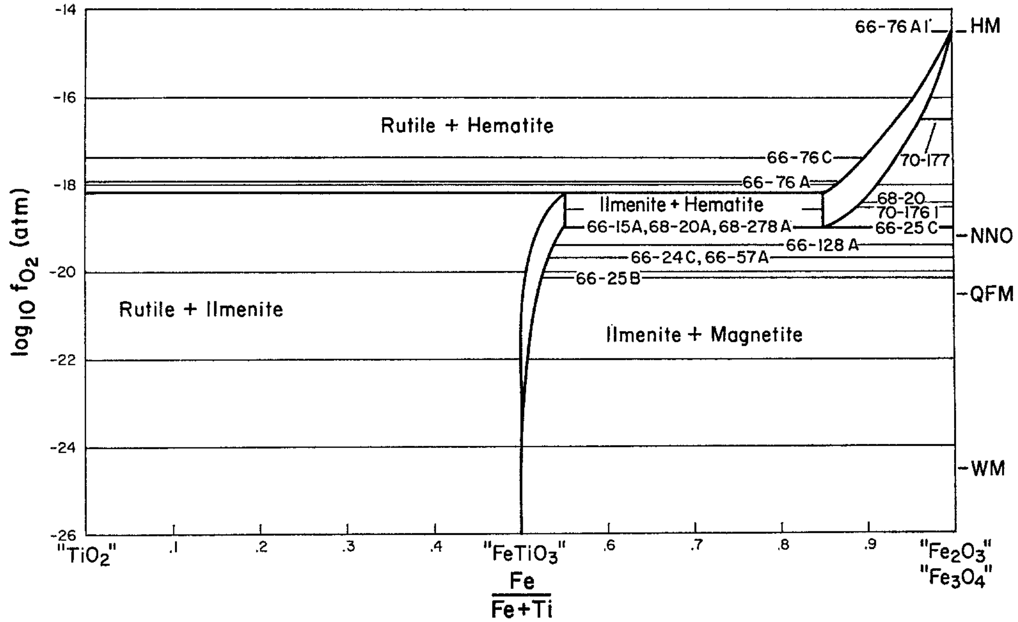

Fig. 2. f_{O_2} vs. Fe/(Fe+Ti) diagram for phases in the system Fe-Ti-O at 600°C and 1 kbar. Tie lines joining the Fe/(Fe+Ti) ratios of coexisting minerals listed in Table 2 are labelled by sample number. f_{O_2} of ilmenite coexisting with magnetite estimated from Fig. 5 of Buddington and Lindsley (1964)

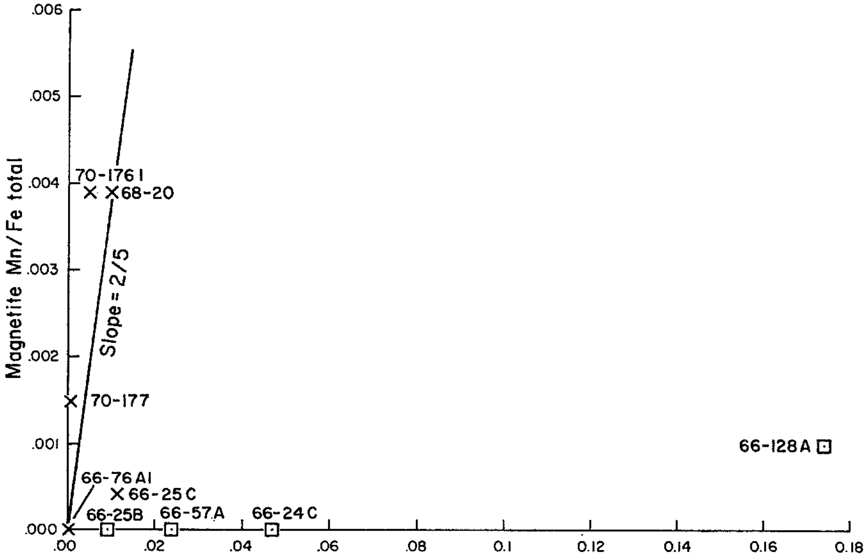

Fig. 3. Distribution of Mn in magnetite-hematite or magnetite-ilmenite assemblages

Table 2. Electron microprobe analyses of Fe-Ti oxide minerals

A. Lake Constance locality

	68–20		68–20A		
	Hematite	Magnetite	Hematite	Ilmenite	Magnetite
SiO_2	0.42	0.09	0.32	0.28	0.09
TiO_2	10.94	0.04	14.21	46.10	0.03
Fe_2O_3	77.94	67.43	71.21	10.14	68.56
Al_2O_3	0.10	0.06	0.48	0.34	0.14
V_2O_3	n.a.[b]	0.09	n.a.	n.a.	0.15
Cr_2O_3	0.05	0.00	0.05	0.01	0.06
FeO[a]	8.77	30.39	12.83	39.41	31.26
MnO	0.77	0.32	0.32	2.25	0.00
MgO	0.02	0.00	0.02	0.05	0.01
NiO	0.01	0.04	0.00	0.01	0.06
CaO	0.00	0.00	0.01	0.00	0.01
ZnO	0.03	0.04	0.00	0.03	0.00
Total	99.05	98.50	99.45	98.62	100.37

B. Jacobs Brook locality

	66-15A		66-24C		66-25B	
	Hematite	Ilmenite	Ilmenite	Magnetite	Ilmenite	Magnetite
SiO_2	0.21	0.20	0.30	0.17	0.16	0.13
TiO_2	15.22	47.23	49.19	0.08	48.84	0.17
Fe_2O_3[a]	68.52	6.26	4.33	67.87	2.74	67.51
Al_2O_3	0.18	0.09	0.11	0.25	0.17	0.39
V_2O_3	n.a.	n.a.	n.a.	0.18	n.a.	n.a.
Cr_2O_3	0.09	0.03	0.00	0.03	0.00	0.05
FeO[a]	13.71	40.92	42.43	31.33	45.68	31.28
MnO	0.31	1.76	2.14	0.00	0.43	0.00
MgO	n.a.	n.a.	0.00	0.00	n.a.	n.a.
NiO	0.00	0.00	0.01	0.06	0.00	0.00
CaO	n.a.	n.a.	0.01	0.00	n.a.	n.a.
ZnO	n.a.	n.a.	0.00	0.00	0.00	0.00
Total	98.24	96.49	98.52	99.97	98.02	99.53

C. Smarts Mountain locality

	66-76A		66-76AI		66-76C	
	Hematite	Rutile	Hematite	Magnetite	Hematite	Rutile
SiO_2	0.67	0.92	0.13	0.60	0.68	0.66
TiO_2	13.30	95.41	0.04	0.05	11.06	96.52
Fe_2O_3[a]	71.56	—	99.48	67.20	76.70	—
Al_2O_3	0.24	0.18	0.08	0.00	0.16	0.00
V_2O_3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cr_2O_3	0.15	0.07	0.07	0.06	0.10	0.03
FeO[a]	12.65	1.52[c]	0.18	31.68	10.11	1.23[c]
MnO	0.09	0.00	0.00	0.00	0.60	0.00
MgO	0.00	n.a.	n.a.	n.a.	n.a.	n.a.
NiO	0.00	0.00	0.00	0.12	0.04	0.00
CaO	n.a.[b]	n.a.	n.a.	n.a.	n.a.	n.a.
ZnO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	98.66	98.12	99.98	99.71	99.46	98.45

[a] Recalculated electron microprobe analysis, see text.

70–176 I		70–177	
Hematite	Magnetite	Hematite	Magnetite
0.06	0.09	0.09	0.09
11.39	0.03	3.89	0.01
77.14	67.75	91.09	68.45
0.12	0.10	0.41	0.06
n.a.	0.16	n.a.	0.13
0.01	0.02	0.03	0.04
9.96	30.59	3.69	31.06
0.36	0.39	0.02	0.14
0.01	0.00	0.00	0.01
0.00	0.06	0.00	0.00
0.01	0.01	0.01	0.01
0.00	0.00	0.00	0.00
99.06	99.20	99.23	100.00

66-25C		66-57A	
Hematite	Magnetite	Ilmenite	Magnetite
0.61	0.24	0.14	0.11
16.09	0.08	47.95	0.08
67.93	68.17	6.41	66.82
0.12	0.10	0.13	0.39
n.a.	n.a.	n.a.	0.16
0.09	0.00	0.01	0.07
14.18	31.36	42.12	30.82
0.84	0.04	1.14	0.00
n.a.	n.a.	0.02	0.01
0.00	0.09	0.03	0.03
n.a.	n.a.	0.00	0.01
n.a.	n.a.	0.03	0.00
99.86	100.08	97.95	98.49

66-128A		68-278A			67-53		
Ilmenite	Magnetite	Hematite	Ilmenite	Magnetite	Hematite	Ilmenite	Magnetite
0.68	0.13	0.42	0.28	0.17	0.27	0.12	0.13
48.55	0.12	13.73	46.36	0.04	14.98	46.26	0.04
6.46	68.08	70.61	10.69	68.29	68.46	10.31	67.30
0.00	0.16	0.42	0.13	0.12	0.08	0.09	0.19
n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.38
0.23	0.00	0.08	0.04	0.03	0.14	0.03	0.23
37.05	31.12	12.51	39.99	31.19	13.55	40.28	31.06
7.37	0.09	0.33	2.01	0.00	0.24	1.42	0.00
n.a.	n.a.	n.a.	n.a.	n.a.	0.00	0.02	0.00
0.00	0.04	0.00	0.00	0.12	0.00	0.00	0.00
n.a.	n.a.	n.a.	n.a.	n.a.	0.00	0.00	0.00
n.a.	n.a.	n.a.	n.a.	n.a.	0.00	0.00	0.00
100.34	99.74	98.10	99.50	99.96	97.72	98.56	99.34

[b] n.a., not analyzed. [c] Total Fe as FeO.

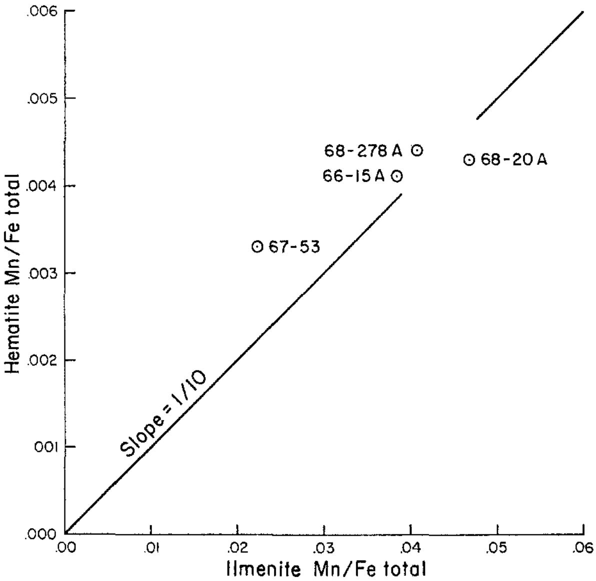

Fig. 4. Distribution of Mn in assemblages of ilmeno-hematite and hemo-ilmenite

and $10Fe_2O_3$-$90FeTiO_3$ have real significance as the binodal compositions of the hematite-ilmenite solvus (cf. Kretschmar and McNutt, 1971, p. 954). The absence of primary rutile-magnetite assemblages is emphasized in Fig. 2; such assemblages stand in reaction relationship to binodal hematite-ilmenite assemblages.

The partitioning of Mn between ilmenite, hematite, and magnetite is shown in Figs. 3 and 4. The ratios Mn/(Fe total) are plotted in order to prevent the scheme of recalculation of microprobe analyses from introducing additional uncertainty. Magnetites in contact with hematite (Fig. 3) may contain up to 0.4 weight % MnO. Magnetites in contact with ilmenites contain no detectable Mn, except where the whole rock is unusually rich in Mn (66–128). Mn is enriched in ilmenite with respect to coexisting hematite (Fig. 4).

Traces of Ni are present in magnetites but not in hematite or ilmenite. Other elements such as Al, Si, and Cr are present in such low concentrations that any systematic partitioning would be masked by analytical uncertainties.

Attainment of Chemical Equilibrium

Systematic partitioning of elements between oxide minerals, absence of crossing tie lines, and homogeneity of analyzed minerals in a given assemblage suggest that the minerals attained chemical equilibrium. As Zen (1963) has pointed out, these criteria are necessary but not sufficient conditions for the attainment of chemical equilibrium.

The binodal compositions $70Fe_2O_3$-$30FeTiO_3$ and $10Fe_2O_3$-$90FeTiO_3$ measured in this study do not agree with the ilmenite-hematite solvus determined by Carmichael (1961). His binodal compositions (recalculated to 1 kbar) are $82Fe_2O_3$-$18FeTiO_3$ and $25Fe_2O_3$-$75TiO_3$ at 600° C, $85Fe_2O_3$-$15FeTiO_3$ and $21Fe_2O_3$-

79 $FeTiO_3$ at 500°C, and 88 Fe_2O_3-12 $FeTiO_3$ and 19 Fe_2O_3-81 $FeTiO_3$ at 400°C (Rumble, 1971b, Fig. 30). Carmichael's results may be in error, however, for Lindsley (1973, p. 858, Table 1) has succeeded in dissolving 30 mole-% $FeTiO_3$ in titanhematite at 600°C and 2 kbar without exsolution, an amount that is in agreement with the measurements of this study.

Calculations show that in the range 400–600°C and 1–5 kbar rutile-magnetite assemblages should be stable with respect to assemblages of hematite-ilmenite (Rumble, 1971a, Fig. 43). These phase compatibilities have not been observed in this study. The uncertainty in the calculations, however, is equal to the number of kilocalories by which hematite-ilmenite is metastable with respect to rutile-magnetite.

The magnetite-ilmenite tie lines reported here do not correspond to those shown in Fig. 5 of Buddington and Lindsley (1964) but do fall within the range of uncertainty for the NNO and QFM buffers at 550° and 600°C as represented in their Figs. 2 and 3.

Conditions of Metamorphism

It is difficult to estimate exactly the temperature and μ_{O_2} of metamorphism because of the great uncertainty in the experimentally measured location of magnetite compositions in equilibrium with ilmenite on the NNO and QFM buffers at 550° and 600°C (Buddington and Lindsley, 1964, Fig. 2). It is impossible to estimate the total pressure of metamorphism from oxide mineral compositions because they are insensitive to changes in pressure (Rumble, 1971a, Tables 6 and 7). Despite uncertainty concerning P and T conditions, the conditions of equilibrium with respect to μ_{O_2} may be evaluated for adjacent oxide mineral assemblages provided they are located close enough together to have been metamorphosed under identical P and T.

Fig. 2 is an attempted portrayal of the approximate magnitudes of gradients in μ_{O_2} (or f_{O_2}) that existed between adjacent assemblages during metamorphism. In the Smarts Mountain locality, a difference of approximately 10^{-4} atm f_{O_2} existed within a single thin section (66–77 Al, 66–76 A). Outcrop 66–25 in the Jacobs Brook locality contains two assemblages that differ by $10^{-1.5}$ atm in inferred f_{O_2} and are separated by 10 m. Outcrop 68–20 from the Lake Constance locality contains assemblages (68–20, 68–20A) that span a difference in f_{O_2} of 10^{-1} atm over a distance of 10 m. Not only do gradients in μ_{O_2} exist between adjacent assemblages but reversals of gradients exist within a single outcrop or outcrop area. Assemblages 66–76Al, 66–76A, and 66–76C illustrate reversals of gradients for an outcrop 5 m in diameter. Reversals of gradients in μ_{O_2} within the same outcrop area are illustrated by 66–24 and 66–25, separated by 20 m.

In Fig. 2 the presence of Mn in the oxide minerals is neglected. It might be argued that appropriate substitution of Mn in oxide minerals would make it unnecessary to postulate μ_{O_2} gradients despite differences in their Fe/(Fe + Ti) ratio (cf. for Mg substitution, Speidel, 1970). If the P and T of metamorphism and the equations of state of phases in the system Fe-Ti-Mn-O were known, values of μ_{O_2} could be calculated using Eq. 1 for each of the hematite (or ilmenite)-magnetite assemblages listed in Table 2. Since these data are unknown, a more general line of reasoning must be used. An expression for

$$[\partial \mu_{O_2}/(\partial X_{Fe_2O_3,\ \text{ilmenite or hematite}})]$$

as an isothermal, isobaric function of composition for hematite (or ilmenite)-magnetite assemblages must be found. Let phase A be ilmenite; phase B, magnetite. Let component 1 be $FeTiO_3$; component 2, Fe_2O_3; component 3, $MnTiO_3$; component 4, Fe_3O_4; component 5, $MnFe_2O_4$; and component 6, Fe_2TiO_4. X_{4B} is the mole fraction of Fe_3O_4 in magnetite. It is assumed that the phases are stoichiometric and show no cation deficiency.

For a two-phase assemblage we have two Gibbs-Duhem equations,

$$0 = \boldsymbol{S}_B dT - \boldsymbol{V}_B dP + X_{5B}(d\mu_5 - d\mu_4) + X_{6B}(d\mu_6 - d\mu_4) + d\mu_4 \tag{2}$$

$$0 = \boldsymbol{S}_A dT - \boldsymbol{V}_A dP + X_{3A}(d\mu_3 - d\mu_1) + X_{2A}(d\mu_2 - d\mu_1) + d\mu_1 \tag{3}$$

and two conditions of exchange equilibrium,

$$0 = (d\mu_6 - d\mu_4) + (d\mu_2 - d\mu_1) \tag{4}$$

$$0 = (d\mu_3 - d\mu_1) - (d\mu_5 - d\mu_4). \tag{5}$$

Differentiating Eq. 1 and substituting $d\mu_2 = (d\mu_2 - d\mu_1) + d\mu_1$,

$$0 = 4d\mu_4 - 6(d\mu_2 - d\mu_1) - 6d\mu_1 + 1\,d\mu_{O_2}. \tag{6}$$

Now we write the total differentials of $(d\mu_3 - d\mu_1)$ and $(d\mu_2 - d\mu_1)$ as functions of P, T, X_{2A}, and X_{3A} (cf. Prigogine and Defay, 1954, p. 279, eq. 18.44).

$$\begin{aligned} d(\mu_3 - \mu_1) = {} & (\partial(\mu_3 - \mu_1)/\partial T)_{P,X_{2A}X_{3A}}\, dT + (\partial(\mu_3 - \mu_1)/\partial P)_{T,X_{2A}X_{3A}}\, dP \\ & + (\partial(\mu_3 - \mu_1)/\partial X_{2A})_{P,T,X_{3A}}\, dX_{2A} + (\partial(\mu_3 - \mu_1)/\partial X_{3A})_{P,T,X_{2A}}\, dX_{3A} \end{aligned}$$

Substituting:

$$(\partial(\mu_3 - \mu_1)/\partial T) = -(\boldsymbol{S}_{3A} - \boldsymbol{S}_{1A})$$

$$(\partial(\mu_3 - \mu_1)/\partial P) = (\boldsymbol{V}_{3A} - \boldsymbol{V}_{1A})$$

$$(\partial(\mu_3 - \mu_1)/\partial X_{2A}) = (\partial(\partial \boldsymbol{G}_A/\partial X_{3A})\, \partial X_{2A}) = (\partial^2 \boldsymbol{G}_A/\partial X_{2A}\, \partial X_{3A})$$

$$(\partial(\mu_3 - \mu_1)/\partial X_{3A}) = (\partial(\partial \boldsymbol{G}_A/\partial X_{3A})/\partial X_{3A}) = (\partial^2 \boldsymbol{G}_A/\partial X_{3A}^2)$$

and similarly for $d(\mu_2 - \mu_1)$ we obtain:

$$\begin{aligned} 0 = {} & -(\boldsymbol{S}_{3A} - \boldsymbol{S}_{1A})\, dT + (\boldsymbol{V}_{3A} - \boldsymbol{V}_{1A})\, dP - (d\mu_3 - d\mu_1) + \boldsymbol{G}_{23A}\, dX_{2A} \\ & + \boldsymbol{G}_{33A}\, dX_{3A} \end{aligned} \tag{7}$$

$$\begin{aligned} 0 = {} & -(\boldsymbol{S}_{2A} - \boldsymbol{S}_{1A})\, dT + (\boldsymbol{V}_{2A} - \boldsymbol{V}_{1A})\, dP - (d\mu_2 - d\mu_1) + \boldsymbol{G}_{22A}\, dX_{2A} \\ & + \boldsymbol{G}_{23A}\, dX_{3A} \end{aligned} \tag{8}$$

where $\boldsymbol{G}_{22A} \equiv (\partial^2 \boldsymbol{G}_A/\partial X_{2A}^2)$, $\boldsymbol{G}_{23A} \equiv (\partial^2 \boldsymbol{G}_A/\partial X_{2A}\, \partial X_{3A})$

$\boldsymbol{S}_{1A} \equiv$ partial molar entropy of $FeTiO_3$ in ilmenite, and

$\boldsymbol{V}_{1A} \equiv$ partial molar volume of $FeTiO_3$ in ilmenite.

At constant P, T, and X_{3A}, the seven equations may be divided through by dX_{2A} and solved for $(\partial\mu_{O_2}/\partial X_{2A})_{P,T,X_{3A}}$ using Cramer's rule.

$$(\partial\mu_{O_2}/\partial X_{2A})_{P,T,X_{3A}} = (6 - 6X_{2A} - 4X_{6B})\,G_{22A} + G_{23A}(4X_{5B} - 6X_{3A}) \qquad (9)$$

For stable ternary solutions, $G_{22A} > 0$ and $G_{23A} < (G_{22A}G_{33A})^{\frac{1}{2}}$ (Prigogine and Defay, 1954, p. 253, eq. 16.79). The coefficient of G_{22A} is positive and ranges in value from 5.3 to 5.6 for ilmenite-magnetite assemblages and from 0.0 to 3.0 for hematite-magnetite assemblages. The coefficient of G_{23A} is negative (except for 70–177) and ranges in value from -0.05 to -0.3 (excluding 66–128) for ilmenite-magnetite assemblages and from -0.1 to $+0.1$ for hematite-magnetite assemblages. These observations suggest but do not prove that the right-hand side of Eq. 9 is positive. If it is positive, then for assemblages with comparable Mn contents an increase in X_{2A} measures an increase in μ_{O_2}. It is likely, therefore, that the presence of Mn in the minerals does not eliminate the necessity of postulating μ_{O_2} gradients between adjacent mineral assemblages.

Owing to the existence of the hematite-ilmenite solvus, μ_{O_2} is not a single-valued function of X_{2A} (cf. Rumble, 1971a, Fig. 37). In order to properly evaluate μ_{O_2} gradients, only assemblages located on the same side of the solvus should be compared.

That oxygen behaved as an "inert" or "initial value" component during regional metamorphism has been confirmed for the rocks of this study. As Mueller (1967) has pointed out, such behavior is a consequence of the low concentrations of molecular oxygen, which prevent the rocks from attaining equilibrium with respect to diffusion of oxygen. Equilibrium with respect to μ_{O_2} may also be achieved by disassociation of H_2O and diffusion of H_2 (Eugster, 1959). There was not a sufficient amount of fluid phase available in the rocks of this study to attain equilibrium by this mechanism (cf. Sobolev, 1972, p. 140). Caution is indicated in inferring the existence of oxygen buffer assemblages on the basis of petrography alone. The three-phase assemblage hematite-ilmenite-magnetite, divariant in the three-component system Fe-Ti-O, is in fact at least trivariant because of the presence of additional components.

It is likely that the μ_{O_2} (f_{O_2}) gradients of the Clough Formation originated from differences in rock bulk composition at the time of sedimentation. The oxidized nature of the mineral assemblages from the conglomeratic, current-bedded Clough Formation correlated with its deposition in a transgressive, beach-sand environment. Gradients in μ_{O_2} also exist between the Clough Formation, considered as a whole, and the mica schists that overlie it. The mica schists contain the reduced assemblage rutile-ilmenite, with or without graphite and pyrrhotite; their parent sediments were probably shales and sandstones deposited under marine conditions that were more reducing than those of the beach-sand environment.

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References

Anderson, A. T.: The oxygen fugacity of alkaline basalt and related magmas, Tristan da Cunha. Am. J. Sci. **266**, 704–727 (1968)

Bailey, S. W., Cameron, E. N., Spedden, H. R., Weege, R. J.: The alteration of ilmenite in beach sands. Econ. Geol. **51**, 263–279 (1956)

Billings, M. P.: Regional metamorphism of the Littleton-Moosilauke area, New Hampshire. Bull. Geol. Soc. Am. **48**, 463–566 (1937)

Billings, M. P.: Geology of New Hampshire, Part II, Bedrock geology. New Hampshire State Planning and Development Commission, 203 p. 1956

Boucot, A. J., Thompson, J. B., Jr.: Metamorphosed Silurian brachiopods from New Hampshire. Bull. Geol. Soc. Am. **74**, 1313–1334 (1963)

Boyd, F. R.: Electron-probe study of diopside inclusions from kimberlite. Am. J. Sci. **267**-A, 50–69 (1969)

Buddington, A. F., Fahey, J., Vlisidis, A.: Degree of oxidation of Adirondack iron oxides and Fe-Ti oxide minerals in relation to petrogeny. J. Petrol. **4**, 138–169 (1963)

Buddington, A. F., Lindsley, D. H.: Iron-titanium oxide minerals and synthetic equivalents. J. Petrol. **5**, 310–357 (1964)

Butler, P.: Mineral compositions and equilibria in the metamorphosed iron formation of the Gagnon Region, Quebec, Canada. J. Petrol. **10**, 56–101 (1969)

Carmichael, C. M.: The magnetic properties of ilmenite-hematite crystals. Proc. Roy. Soc. London, Ser. A, **263**, 508–530 (1961)

Chinner, G. A.: Pelitic gneisses with varying ferrous/ferric ratios from Glen Cova, Angus, Scotland. J. Petrol. **1**, 178–217 (1960)

Eugster, H. P.: Reduction and oxidation in metamorphism, In: Researches in geochemistry, P. H. Abelson, ed., vol. 1, p. 397–426. New York: John Wiley & Sons 1959

Greenwood, H. J.: The N-dimensional tie-line problem. Geochim. Cosmochim. Acta **31**, 465–490 (1967)

James, H. L., Howland, A. L.: Mineral facies in iron- and silica-rich rocks. Geol. Soc. Am. Bull. **66**, 1580–1588 (1955)

Klein, C.: Mineralogy and petrology of the metamorphosed Wabash Iron Formation, southwestern Labrador. J. Petrol. **7**, 246–305 (1966)

Korzhinskii, D. S.: Physicochemical basis of the analysis of the paragenesis of minerals. New York: Consultants Bureau 1959

Kretschmar, U. H., McNutt, R. H.: A study of the Fe-Ti oxides in the Whitestone Anorthosite, Dunchurch, Ontario. Can. J. Earth Sci. **8**, 947–960 (1971)

Kretz, R.: A chemical study of garnet, biotite, and hornblende from gneisses of southwestern Quebec, with emphasis on distribution of elements in coexisting minerals. J. Geol. **67**, 371–402 (1959)

Lindsley, D. H.: Delimitation of the hematite-ilmenite miscibility gap. Geol. Soc. Am. Bull. **84**, 657–662 (1973)

Meilke, H., Schreyer, W.: Magnetite-rutile assemblages in metapelites of the Fichtelgebirge, Germany. Earth Planet. Sci. Lett. **16**, 423–428 (1972)

Mueller, R. F.: Compositional characteristics and equilibrium relations in mineral assemblages of a metamorphosed iron formation. Am. J. Sci. **258**, 423–428 (1960)

Mueller, R. F.: Mobility of the elements in metamorphism. J. Geol. **75**, 565–582 (1967)

Naylor, R. S.: Age and origin of the Oliverian Domes, central-western New Hamshire. Bull. Geol. Soc. Am. **80**, 565–582 (1969)

Prigogine, I., Defay, R.: Treatise on thermodynamics, based on the methods of Gibbs and De Donder, vol. 1. tr. and rev. by D. H. Everett. London: Longmans, Green 1954

Rumble, Douglas, III: Thermodynamic analysis of phase equilibria in the system Fe_2TiO_4-Fe_3O_4-TiO_2. Carnegie Inst. Washington Year Book **69**, 198–207 (1971 a)

Rumble, Douglas, III: Fe-Ti oxide minerals and the behavior of oxygen during regional metamorphism. Carnegie Inst. Washington Year Book **70**, 156–165 (1971 b)

Rumble, Douglas, III: Recumbent and reclined folds of the Mt. Cube area, New Hampshire-Vermont, In: Guidebook for field trips in central New Hampshire and contiguous areas, J. B. Lyons and G. W. Steward, eds., p. 43–52. New England Intercollegiate Geological Society 1971 c

Sobolev, V. S., ed.: The facies of metamorphism, tr. by D. A. Brown, Canberra: Australian National University Press 1972

Southwick, D. L.: Mineralogy of a rutile- and apatite-bearing ultramafic chlorite rock, Hartford Co., Maryland. U.S. Geol. Surv. Profess. Paper **600**-C, C38–C44 (1968)

Speidel, D. H.: Effect of magnesium on the Fe-Ti oxides. Am. J. Sci. **268**, 341–353 (1970)

Thompson, J. B., Jr.: The graphical analysis of mineral assemblages in pelitic schists. Am. Mineralogist **42**, 842–858 (1957)

Thompson, J. B., Jr., Robinson, P., Clifford, T. N., Trask, N. J.: Nappes and gneiss domes in west-central New Hampshire, In: Studies of Appalachian geology, E-an Zen *et al.*, eds., p. 203–218, New York: John Wiley & Sons, 1968

Zen, E-an: Components, phases and criteria of chemical equilibrium in rocks. Am. J. Sci. **261**, 929–942 (1963)

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