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Crystal chemistry and petrology of coexisting galaxite and jacobsite and other spinel solutions and solvi[1]

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Abstract

Galaxite (*Gx*:$MnAl_2O_4$) and jacobsite (*Jb*:$MnFe_2O_4$)-rich spinels occur together in the metamorphosed manganese deposit near Bald Knob, North Carolina. They show limited mutual solubility with 12–19% *Jb* in *Gx* and 19–22% *Gx* in *Jb*. The implied solvus is consistent with syntheses of Ishida *et al.* (1977) along the *Gx–Jb* pseudobinary. Refinement of the structure of one galaxite ($Gx_{85}Jb_{10}Sp_4Gh_1$) reveals that Mn is located on tetrahedral sites and Al on octahedral sites and that galaxite is therefore a normal spinel. All available data suggest that jacobsite is also a normal spinel at low temperatures, and the solvus between galaxite and jacobsite does not seem to be caused by differences in normality/inverseness. Chemical and experimental data available for $(Mg,Zn,Mg,Fe^{2+})(Fe^{3+},Al)_2O_4$ spinels suggest that the ferrites (jacobsite, franklinite, magnesioferrite and magnetite) show extensive solid solution and are separated from aluminate solid solutions (galaxite, gahnite, spinel (*s.s.*) and hercynite) by wide solvi at metamorphic temperatures.

Introduction

The manganese deposit near Bald Knob, North Carolina contains a wide range of unusual manganese minerals which have equilibrated under amphibolite facies metamorphic conditions (Winter *et al.*, 1981). The deposit was originally described by Ross and Kerr (1932). We have subsequently carried out extensive mineralogical–petrological studies of the several mineral groups occurring there (Peacor *et al.*, 1974; Winter *et al.*, 1981, in prep.; Simmons *et al.*, 1981). The spinel group minerals (galaxite and jacobsite) found at Bald Knob are relatively simple in composition and therefore serve as a source of insights into the crystal-chemical and phase relations of spinels. This paper is a description of the mineralogy and petrology of those manganese spinels.

Only a limited amount of experimental data are available regarding the nature of solvi among spinels at low to moderate temperatures. Turnock and Eugster (1962) experimentally determined the magnetite–hercynite solvus showing complete solid solution above 870°C and a wide miscibility gap below 600°C. These two spinels are largely inverse and normal, respectively. The area of complete solution probably represents a continuum of cation distributions, but the occurrence of the solvus must be related in part to ordering into the inverse versus the normal cation distribution. Experiments on the binaries Fe_3O_4–Fe_2TiO_4 (Vincent *et al.*, 1957; Price, 1981; Lindsley, 1981) and Fe_3O_4–$ZnFe_2O_4$ (Valentino and Sclar, 1982) suggest that the solvus observed in natural materials must form below 500–600°C. Experiments in the systems $MnFe_2O_4$–$MnAl_2O_4$ (Ishida *et al.*, 1977) and $ZnFe_2O_4$–$ZnAl_2O_4$ (Carvalho, 1978) reveal extensive miscibility gaps at metamorphic temperatures of 500–700°C with the crest of the solvi located at 900–1100°C. Experiments of Muan *et al.* (1972) on the ternaries $FeAl_2O_4$–Fe_2TiO_4–$FeCr_2O_4$ and $MgAl_2O_4$–Mg_2TiO_4–$MgCr_2O_4$ show solvi extending to more than 1300°C between the aluminate and titanate species but with complete solution at $T > 1000$°C engendered with addition of 30–40% of the chromites. There are no experiments on the join $MgAl_2O_4$–Fe_3O_4 and one must turn to natural occurrences to estimate the form of this solvus.

Surprisingly few examples exist of observations on naturally occurring two-phase spinels despite the fact that such observations may have the advantage of demonstrating equilibrium cation distributions at relatively low temperatures. Studies of minerals in lunar basalts have revealed high-temperature solvi in the system $(Mg,Fe^{2+})Al_2O_4$–$(Mg,Fe^{2+})Cr_2O_4$–$(Mg,Fe^{2+})_2TiO_4$ (Haggerty, 1971, 1972a,b,c; El Goresy *et al.*, 1972, 1976; Nehru *et al.*, 1974). Muir and Naldrett (1973) and Berg (1976) analyzed coexisting spinels and magnetites from igneous rocks, finding a wide miscibility gap in the system Fe_3O_4–$MgAl_2O_4$ which contracts with increasing Cr in solid solution. Plaksenko (1980) describes incipient exsolution in chrome spinels from ultramafic rocks. Kuno

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(1960) and Bowman (1978) report analytical data on metamorphic spinel–magnetite pairs which equilibrated at *ca.* 700°C and show even less mutual solution. The system $MgAl_2O_4$–Fe_3O_4 appears to have a wide, symmetrical miscibility gap from temperatures of less than 1100°C. Manganese and zinc spinels have both ferrite and aluminate representatives in nature but the solubilities involving Mn *vs.* Zn, and Al *vs.* Fe^{3+} are still poorly understood. Franklinite ($ZnFe_2O_4$) has extensive miscibility at high temperatures with jacobsite ($MnFe_2O_4$) and magnetite (Deer *et al.*, 1963). Frondel and Klein (1965) and Carvalho (1978) have described exsolution blebs of gahnite in franklinite consistent with the existence of a low-temperature solvus in this system. We have examined many franklinite samples and found one with similar blebs with compositions of a complex aluminate $(Mg,Zn,Mn,Fe^{2+})(Al,Fe^{3+})_2O_4$ in a matrix of franklinite $(Zn,Mn)Fe_2O_4$; the phases are thus multi-component and do not contribute to general conclusions regarding solvi.

Galaxite ($MnAl_2O_4$) is known from only a few localities and only limited data are available on its miscibility with other spinels. Hirowatari (1969) and Chopin (1980) have reported the existence of two-phase jacobsite–galaxite mixtures. At Bald Knob galaxite is restricted to carbonate-rich rocks undersaturated in silica which also contain tephroite or the Mn-humites—manganhumite, alleghanyite or sonolite (Ross and Kerr, 1932; Winter *et al.*, 1983). The color of galaxite is variable in thin-section and ranges from golden-yellow to deep red to red-black apparently as a function of iron content. When deep red it is easily confused with associated pyrophanite but that mineral is anisotropic and has higher reflectivity. While routinely examining polished sections, we noticed a second ten to twenty micron-sized opaque phase with higher relief and higher reflectivity coexisting with galaxite. Qualitative microprobe analysis suggested that it was jacobsite with some Al in solution. The mineral assemblages noted in each sample are:

635: manganhumite–sonolite–spessartine–kutnahorite–galaxite–kellyite–jacobsite

BK6: alleghanyite–kutnahorite–galaxite–jacobsite–pyrophanite–alabandite–cattierite–kellyite–stilpnomelane–fluorapatite

BK11: alleghanyite–kutnahorite–galaxite–jacobsite–pyrophanite–alabandite–cattierite–caryopilite–kellyite

Table 1. Electron microprobe analyses of jacobsite and galaxite from near Bald Knob, N. C.

Sample	635	BK6-1		BK6-2		BK11		BK14	BK22	
Mineral	Gx	Gx	Jb	Gx	Jb	Gx	Jb	Gx	Gx	Jb
Oxide Wt%										
TiO_2	<0.05	<0.05	0.37	0.67	9.4	0.13	0.38	<0.05	<0.05	0.34
Al_2O_3	56.3	49.4	10.4	49.3	6.2	44.5	8.14	50.5	45.1	9.7
V_2O_3	0.14	0.14	0.66	0.87	0.58	n.d.	n.d.	0.20	0.25	0.39
$^1Fe_2O_3$	46.0	14.5	57.6	12.5	44.2	18.7	59.5	9.0	16.6	57.6
^1FeO	0.0	1.4	3.3	5.8	5.9	0.7	0.5	5.9	1.4	3.1
MnO	39.1	33.5	29.8	32.1	33.5	36.3	32.1	30.4	35.7	29.2
ZnO	0.43	0.97	<0.05	<0.05	0.62	n.d.	n.d.	0.61	0.10	0.13
CoO	0.25	0.70	0.21	0.62	0.71	n.d.	n.d.	1.07	0.84	0.62
MgO	0.83	1.47	0.02	1.30	0.19	1.44	0.03	0.92	0.53	<0.05
sum	101.7	102.1	102.4	103.2	101.3	101.8	100.6	98.6	100.5	101.1
Cations/3 Cations										
Ti	0.00	0.00	0.01	0.01	0.26	0.00	0.01	0.00	0.00	0.01
Al	1.90	1.77	0.43	1.70	0.27	1.57	0.35	1.80	1.62	0.38
V	0.00	0.00	0.01	0.02	0.01	n.d.	n.d.	0.00	0.00	0.01
$^1Fe^{3+}$	0.10	0.23	1.55	0.27	1.20	0.42	1.62	0.20	0.38	1.46
$^1Fe^{2+}$	0.00	0.03	0.10	0.14	0.18	0.02	0.02	0.15	0.04	0.09
Mn	0.95	0.86	0.90	0.79	1.03	0.92	0.99	0.77	0.92	0.83
Zn	0.01	0.02	0.00	0.00	0.02	n.d.	n.d.	0.01	0.00	0.00
Co	0.00	0.02	0.00	0.01	0.02	n.d.	n.d.	0.03	0.02	0.02
Mg	0.04	0.07	0.00	0.06	0.01	0.07	0.01	0.04	0.02	0.00

$^1Fe^{2+}/Fe^{3+}$ calculated to yield O=4
n.d. = not determined

BK14: manganhumite–sonolite–kutnahorite–galaxite–(jacobsite) – alabandite – stilpnomelane – caryopilite – kellyite–fluorapatite

BK22: alleghanyite–kutnahorite–galaxite–jacobsite–alabandite–cattierite–cobaltite–kellyite–fluorapatite.

A consideration of the solubility limits of galaxite and jacobsite as represented by those Bald Knob samples, their cation distribution and the nature of the solvus between them comprises the subject matter of this note.

Chemical analysis

Electron microprobe analyses were obtained under operating conditions of an accelerating potential of 15 kV, an emission current of 150 nA, a sample current of 0.01 μA and using digitized beam current. Standards used were synthetic TiO_2, Al_2O_3, V_2O_5, Mn_2O_3, $MgAl_2O_4$, Fe_2O_3, Co_3S_4, ZnS and NiS. Spectrometer data were corrected for atomic number, fluorescence, absorption and drift effects using the program EMPADR VII written by Rucklidge and Gasparrini (1969). Analyses of the spinels are given in Table 1. The totals deviate by 2–3% from 100% when Fe^{2+} is estimated by the equation $Fe^{2+} = ⅓(Al + V + \Sigma Fe) + 4/3(Ti) - ⅔(Mn + Mg + Zn + Co)$ generating four oxygens for spinels normalized to three cations. While imperfect, these estimates and totals are judged adequate for the purposes of this paper.

The jacobsite and galaxite show a relatively symmetrical miscibility gap with about 12–20% mutual solution of each component. Only minor amounts of additional components are generally present in solid solution. We have plotted our analyses along with those reported by Hirowatari (1969) and Chopin (1980) in the system $MnAl_2O_4$–$MnFe_2O_4$–$MgAl_2O_4$–$MgFe_2O_4$ (Fig. 1). They define a reasonable miscibility gap when the analyses are combined with the binary experiments of Kwestroo (1959) and of Ishida *et al.*, (1977). Ross and Kerr's (1932) analysis of Bald Knob galaxite falls slightly within the inferred solvus. Few other analyses are available which are reasonably represented by the composition space of Figure 1. Most jacobsites have either Fe_3O_4, $ZnFe_2O_4$, or Mn_3O_4 in solid solution. Spinel analyses are also plotted in the composition space $MnAl_2O_4$–$MnFe_2O_4$–$ZnAl_2O_4$–$ZnFe_2O_4$ (Fig. 2). A relatively symmetrical solvus separating Mn, Zn aluminates from Mn, Zn ferrites can be inferred by combining our data with the binary experiments and observations of Ishida *et al.* (1977) and of Carvalho (1978). Ignoring the substantial Fe^{2+}, the titanian jacobsite of BK-6 is plotted in the composition space $MnAl_2O_4$–$MnFe_2O_4$–Mn_2TiO_4 for comparison with data of Fukuoka and Hirowatari (1980) and of Fukuoka (1981) (Fig. 3). It can be seen that there is substantial solution between $MnFe_2O_4$ and Mn_2TiO_4 at metamorphic temperatures. It is anticipated that a new spinel mineral species with dominant Mn_2TiO_4 will eventually be found in a metamorphosed titaniferous manganese deposit.

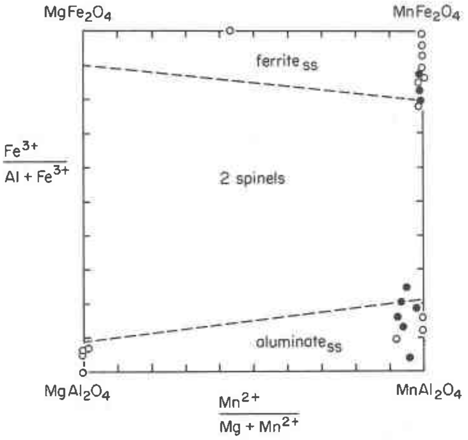

Fig. 1. The composition space $MnAl_2O_4$–$MnFe_2O_4$–$MgAl_2O_4$–$MgFe_2O_4$ with spinel analyses plotted. Closed circles: data on Bald Knob spinels; open circles: data from other occurrences. References: Ross and Kerr (1932) Stillwell and Edwards (1951), Lee (1968), Kuno (1960), Deer *et al.*, (1962), Berg (1976), Bowman (1978), Carvalho (1978), Chopin (1978), Fukuoka and Hirowatari (1980), Fukuoka (1981). Spinels with >0.05 Zn, Fe^{2+}, Mn^{3+} or Ti per four oxygens are excluded.

Cation ordering

A yellow-colored galaxite from Bald Knob, sample no. 635 (collection of D. R. Peacor), was analyzed and found to contain approximately 92 mol% component $MnAl_2O_4$ (Table 1), making it the purest naturally occurring galaxite which we have been able to obtain. Because we wished to determine its cation distribution in detail, crystals were separated for single-crystal X-ray diffraction. Film data confirmed the existence of extinctions as consistent with the usual space group for spinels, *Fd*3*m*. The unit translation was determined to be $a = 8.181(2)$Å

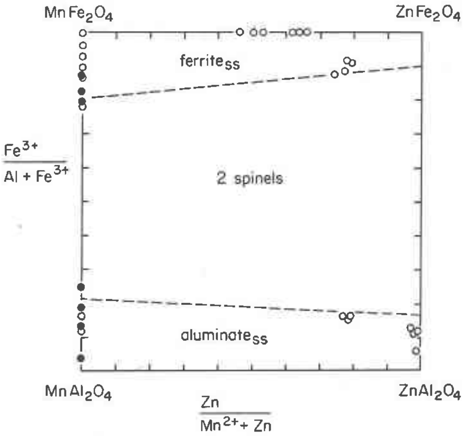

Fig. 2. The composition space $MnAl_2O_4$–$MnFe_2O_4$–$ZnAl_2O_4$–$ZnFe_2O_4$ with spinel analyses plotted. Symbols and references the same as for Fig. 1, with additional references: Palache (1935), Kayupova *et al.* (1970), Vogel *et al.*, (1976). Spinels with >0.05 Mg,Fe^{2+},Mn^{3+} or Ti per four oxygens are exluded.

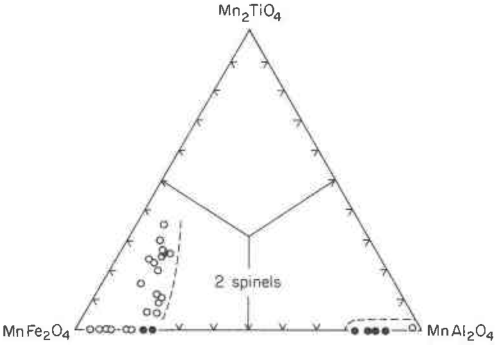

Fig. 3. The composition space $MnAl_2O_4$–$MnFe_2O_4$–Mn_2TiO_4 with spinel analyses plotted. Symbols and references the same as for Figure 1. Spinels with >0.30 Fe^{2+}, or 0.10 Mg, Zn, Mn^{3+} are excluded.

using data from an internally standardized powder diffractometer pattern.

Three-dimensional intensity data were measured using a Supper-Pace automated system, employing measurement of background on both sides of a peak and graphite monochromated Mo*Kα* radiation. The crystal used was an octahedron with an average edge length of approximately 0.11 mm which was obtained from the same area of the same specimen as the analyzed material. Data were corrected for Lorentz-polarization and absorption (μ = 66.5 cm^{-1}) effects. Up to six symmetry-related intensities were measured to a $\sin\theta$ limit of 0.60. Following averaging of symmetry related values, the final data set consisted of 82 structure amplitudes. Of these, one (044) was subsequently found to be seriously affected by extinction and excluded from the refinement, and seven were below minimum observable values. Refinement was carried out using the program RFINE (Finger and Prince, 1975) using neutral form factors of Doyle and Turner (1968). Form factors for Al and Mn were used both for the octahedral and tetrahedral sites, the small amount of Mg being represented by the Al form factor and the iron and traces of Co, Ti, V, and Zn by the Mn form factor. Refinement was carried out by varying the single oxygen coordinate, anisotropic temperature factors and the occupancies of the tetrahedral and octahedral sites. The final conventional unweighted R-value, excluding unobserved data, is 2.8%. Structure factors are listed in Table 2[2] and final atomic parameters in Table 3.

Occupancy values for the tetrahedral site are 0.11(3) and 0.89 for the Al and Mn form factors, respectively, and 1.03 and −0.03 for the octahedral site. The latter values are consistent with complete ordering of Al on the octahedral site, and those for the tetrahedral site also imply the presence of some Al, taking into consideration that each form factor represents minor amounts of elements other than Al and Mn. The total Al (plus Mg) required by these occupancies is slightly greater than that indicated by the analysis (1.94 Al + Mg, per 8 O). However, there is some variation in composition of different crystals within the specimen serving as a source for the crystal used for the diffraction data. The results of the refinement of the occupancy values can therefore be interpreted as consistent with a complete, or nearly complete normal cation distribution, with Al and Mn occupying only the octahedral and tetrahedral sites, respectively.

The cation ordering is also confirmed by the cation–oxygen distances which are 1.991 (1) and 1.927 (1)Å for the tetrahedral and octahedral sites respectively. This result differs somewhat from the study of Greenwald *et al.* (1954) who found that synthetic $MnAl_2O_4$ is approximately 70% normal. This exemplifies the importance of using natural materials to determine low-temperature ordering parameters where possible as synthetic materials may have metastable states of order due in part to relatively rapid rates of formation.

Prediction of cation ordering in jacobsite is somewhat uncertain. While some writers (Verwey and Heilman, 1947; Gorter, 1950, 1954; McClure, 1957; Dunn *et al.*, 1965; Burns, 1970; Strunz, 1970) regard jacobsite as probably inverse, measurements of synthetic materials show that it is approximately 80–90% normal (Hastings and Corliss, 1956; Harrison *et al.*, 1957; Butler and Büssem, 1962; Lotgering, 1964; Sawatzky *et al.*, 1967, 1969; Lotgering and Van Diepen, 1973; Brabers and Klerk, 1974). Jacobsite has extensive solution with frank-

Table 3. Atomic parameters for galaxite

Tetrahedrally coordinated site	
occupancy	0.89(3) Mn + 0.11 Al
temperature factor	β_{11} = 0.007171(15) B_{eq} = 0.46 Å
M-O = 1.991(1) Å	
Octahedrally coordinated site	
occupancy	1.03(2) Al - 0.03 Mn
temperature factors	β_{11} = 0.00105 (16) β_{12} = -0.00018(8) B_{eq} = 0.28 Å^2
M-O = 1.927(1) Å	
Oxygen	
x = 0.2655(2)	
temperature factors	β_{11} = 0.00230(19) β_{12} = -0.00011(15) B_{eq} = 0.62Å^2

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[2] To obtain a copy of Table 2, order Document AM-83-216 from the Business Office, Mineralogical Society of America, 2000 Florida Ave. N.W., Washington, D.C., 20009. Please remit $1.00 in advance for microfiche.

linite ($ZnFe_2O_4$) and studies show that these solutions are normal or close to normal (Knoavitch *et al.*, 1963; König 1966; König and Chol, 1968; Morrish and Clark, 1975; Korneev *et al.*, 1975; Vogel *et al.*, 1976). Jacobsite also has extensive solution with magnetite at high temperatures (Mason, 1947) but the cation ordering in these solutions is unknown. Natural jacobsites are most likely to be normal spinels; the solvus between jacobsite and galaxite (like that for franklinite and gahnite) involves two normal spinels and is not driven by differences in cation distributions.

Status of jacobsite

The status of jacobsite as a distinct mineral has been questioned by Mason (1943, 1947) and by Van Hook and Keith (1958), who described jacobsite as an intermediate member of the magnetite-high hausmannite series based on experiments along the join Fe_3O_4–Mn_3O_4. Because jacobsite is a normal spinel, $(Mn^{2+})^{IV}\,(Fe^{3+})_2^{VI}O_4$, it is *not* a disordered solid solution $(Mn^{2+}_{.33}\ Fe^{3+}_{.67})^{IV}$ $(Mn^{2+}_{.67}Fe^{3+}_{1.33})^{IV}O_4$ *nor* a compound obtained by combination of ⅓ Mn_3O_4 and ⅔ Fe_3O_4, $(Mn^{3+}_{.33}Fe^{3+}_{.67})^{IV}$ $(Mn^{2+}_{.33}Fe^{2+}_{.67}Mn^{3+}_{.33}Fe^{3+}_{.67})^{VI}O_4$. It is a unique end-member with distinctive cationic valency and distribution. Mason's (1943) definitions of spinels on the Mn_3O_4–Fe_3O_4 join should be discarded and jacobsite accepted as a valid mineral.

Petrology

Galaxite should only be stable in undersaturated rocks for it should react to form spessartine and an aluminosilicate in the presence of quartz:

$$3MnAl_2O_4 + 5\ SiO_2 = Mn_3Al_2Si_3O_{12} + 2Al_2SiO_5 \quad (1)$$

The instability of galaxite with quartz is an important factor in explaining its scarcity. Reactions of galaxite with other manganese silicates may be considered:

$$MnAl_2O_4 + 4MnSiO_3 = Mn_3Al_2Si_3O_{12} + Mg_2SiO_4\ (2)$$

$$MnAl_2O_4 + 3MnSiO_3 + CO_2 = Mn_3Al_2Si_3O_{12} + MnCO_3 \quad (3)$$

Galaxite–rhodonite/pyroxmangite and tephroite–spessartine assemblages are both known at Bald Knob, and three samples (BK4, BK8, BK18) have all four phases apparently coexisting. Reaction (2) is apparently bridged by assemblages at Bald Knob presumably due to variable solid solution and could be of great use in metamorphosed manganese deposits once determined. Reaction (3) will limit spessartine-rhodochrosite to lower temperatures and/or CO_2-rich fluids, but the reaction cannot be located until adequate thermodynamic or experimental data are available for these phases.

Reactions involving jacobsite are complicated by possible variations in the oxidation state of iron and perhaps manganese. Jacobsite will be reduced to a manganwüstite at oxygen fugacities about one order of magnitude higher than the reduction of magnetite to wüstite (Ulrich *et al.*, 1966; Shchepetkin and Chufarov, 1972). Jacobsite will also oxidize to hematite$_{ss}$ and a more Mn-rich spinel:

$$O_2 + MnFe_2O_4 = (Fe,Mn)_2O_3 + (Mn,Fe)_3O_4 \quad (4)$$

The upper limit of oxygen fugacity permitted for jacobsite is about two orders of magnitude higher than that for magnetite-hematite (Ono *et al.*, 1971; Pelton *et al.*, 1979). Thus jacobsite has the same wide oxidation and reduction stability as magnetite but shifted to somewhat more oxidizing conditions. This is in qualitative agreement with the oxygen fugacities estimated at Bald Knob by Winter *et al.* (1981). More complicated reactions involving manganese silicates can be inferred for jacobsite:

$$MnFe_2O_4 + (Mn,Fe)SiO_3 = (Mn,Fe)_2SiO_4 + O_2 \quad (5)$$

$$MnFe_2O_4 + (Mn,Fe)SiO_3 + CO_2 = (Mn,Fe)_2SiO_4 + (Mn,Fe)CO_3 + O_2 \quad (6)$$

but present thermodynamic data are inadequate for calculation of these reactions. Winter *et al.* (1981) have shown that the Bald Knob rocks with jacobsite and galaxite have formed at relatively low oxygen fugacity (near quartz-fayalite-magnetite) and high sulfur fugacity (near pyrrhotite-pyrite) and with $X_{CO_2} = 0.5$ for $T = 575°C$ and $P = 5$ kbar. These conditions should be consistent with the left-hand side of reactions (4) and (5) since jacobsite is found with pyroxmangite at Bald Knob. Other more complicated oxidation-reduction–carbonation–hydration reactions may be balanced for various humites, pyroxenoids, carbonates and jacobsite. Such reactions probably buffered the ratios of various fluid species during metamorphism of the jacobsite-bearing rocks.

Note added in press:

The wt.% Fe_2O_3 of Gx635 in Table 1 should read 4.6 wt.%.

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