Armalcolite in crustal paragneiss xenoliths, central Mexico

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ABSTRACT

Aluminous armalcolite has been found in two sillimanite-bearing xenoliths that were recently exhumed from the lower crust of central Mexico. The ranges of compositions are 

\[(\text{Fe}^{3+}0.38-0.66 \text{Mg}_{0.18-0.28} \text{Al}_{0.15-1.18} \text{V}_1^{0.06-0.10} \text{Ti}_{0.64-1.18}^{4+} \text{O}_3 \) \]

and 

\[(\text{Fe}^{2+}_{0.20-0.5} \text{Mg}_{0.18-0.28} \text{Al}_{0.16-0.19} \text{V}_1^{0.02-0.06} \text{Fe}_{0.30-0.81}^{3+} \text{Ti}_{1.49-1.71}^{4+} \text{O}_3 \) \]

The occurrence of armalcolite is unusual in crustal paragneisses because most terrestrial armalcolite occurs in volcanic rocks that are derived from partial melting in the Earth's mantle. Textures suggest that armalcolite is a late product formed by the reaction rutile + ilmenite \( \rightarrow \) armalcolite during rapid transport of the xenoliths to the surface. Phase equilibria in the system \( \text{MgO-FeO-Fe}_2\text{O}_3-\text{TiO}_2 \), which indicate that armalcolite is stable in the crust at 900-1200 °C, are consistent with this interpretation.

Thermodynamic properties are estimated for oxides in the system \( \text{MgO-FeO-Fe}_2\text{O}_3-\text{TiO}_2 \) to constrain activity-composition relations for armalcolite and conditions of formation. Activity coefficients calculated for armalcolite range from 0.27 to 1.36, depending on the ilmenite model used, at temperatures between 1000 and 1300 °C. Depth of formation of armalcolite in the crust is not well constrained. Thermodynamic calculations at 800-1200 °C for the compositions observed indicate that the armalcolite in one xenolith would have been in equilibrium with rutile at values of \( f_{O_2} \) between the hematite + magnetite buffer (HM) and the fayalite + magnetite + quartz (FMQ) buffer, and that armalcolite in the other xenolith would have been in equilibrium with rutile and ilmenite at values of \( f_{O_2} \) between FMQ and two log units below the FMQ buffer.

INTRODUCTION

Armalcolite (\( \text{Fe}_8\text{Mg}_5\text{Ti}_3\text{O}_{12} \)) has been observed most commonly in lunar rocks that equilibrated under reducing conditions, although occurrences of armalcolite in terrestrial rocks have been reported by von Knorring and Cox (1961), Ottemann and Frenzel (1965), Cameron and Cameron (1973), Haggerty (1975), Velde (1975), El Gorisy and Chao (1976), Tsyymbal et al. (1980), Pedersen (1981), and Mets et al. (1985). Armalcolite was discovered in two crustal xenoliths of paragneiss from central Mexico (cf. Hayob et al., 1989). The Mexican occurrence is unusual because the majority of terrestrial, armalcolite-type minerals reported thus far have been found in volcanic rocks.

CRYSTAL CHEMISTRY OF ARMALCOLITE

Armalcolite (\( \text{Mg}_6\text{Fe}_3\text{Ti}_5\text{O}_{18} \)) forms a complete solid solution series between an Fe end-member (\( \text{Fe}^{2+}\text{Ti}_3\text{O}_9 \)) and a Mg end-member (\( \text{MgTi}_3\text{O}_9 \)) at high temperatures (Akimoto et al., 1957; Bowles, 1988). Armalcolite is isostructural with pseudobrookite (Psb: \( \text{Fe}^{3+}\text{Ti}_3\text{O}_9 \)), which is widespread in terrestrial volcanic rocks. Whereas Bowles's (1988) definitions of armalcolite and pseudobrookite have been accepted by the International Mineralogical Association, the definitions appear to violate the currently accepted procedure for symmetrical subdivisions of ternary composition space (Nickel, 1992). A bizarre result of Bowles's definitions is that pure \( \text{Fe}^{2+}\text{Ti}_3\text{O}_9 \) can be regarded as either pseudobrookite or armalcolite (Fig. 1). Nonetheless, the authors will provisionally apply the definitions of Bowles for solid solutions in the pseudobrookite group until the IMA reevaluates this system. Pseudobrookite will be used as a group name (sensu lato) as well as for a specific compositional range (sensu stricto).

Available crystal-chemical data indicate that pseudobrookite and armalcolite are entropy stabilized and therefore are expected to form at high temperatures (Navrotsky, 1975). Pseudobrookite and armalcolite have two crystallographically distinct octahedral sites, M1 (Wyckoff notation 4c) and M2 (Wyckoff notation 8f) (Smyth, 1974). Analogous to an inverse spinel structure, \( \text{Fe}^{3+} \) in ordered pseudobrookite (\( \text{Fe}_5\text{Ti}_3\text{O}_9 \)) is distributed equally between M1 and M2, and \( \text{Ti}^{4+} \) is incorporated into M2 (Lind and Housley, 1972; Brigatti et al., 1993). In ordered armalcolite, \( \text{Mg}^{2+} \) and \( \text{Fe}^{2+} \) are incorporated into M1, and \( \text{Ti}^{4+} \) is incorporated into M2 (Lind and Housley, 1972; Smyth, 1974; Wechsler et al., 1976; Brown and Navrotsky, 1989; Wechsler and von Dreule, 1989). There is, however, substantial cation disorder in most natural

Fig. 2. P-T diagram showing loci of Rt + Gk = Mg-Arm and Rt + Ilm = Fe-Arm calculated from thermodynamic data in Tables 4 and 5 (solid curves). Loci of Rt + Gk = Mg-Arm calculated from thermodynamic data of Chase et al. (1985, long dashes) and Knacke et al. (1991, short dashes) are also shown. Arrows denote experimental reversals of Lindsley et al. (1974), and the solid circle is from experiments of Haggerty and Lindsley (1969). Armalcolite (MgFeO5TiO5) breaks down to rutile + ilmenite, at 1010 °C at 1 bar (not shown; Haggerty and Lindsley, 1969). Rt = rutile, Gk = geikielite, Ilm = ilmenite, Fe-Arm = FeTiO3, and Mg-Arm = MgTiO'.

PREVIOUS STUDIES AND GEOLOGIC SETTING

Armalcolite was first identified in lunar samples from Apollo 11 (Anderson et al., 1970). Experimental data (Akimoto et al., 1957; Haggerty and Lindsley, 1969; Hartzman and Lindsley, 1973; Lindsley et al., 1974; Friel et al., 1977) and thermodynamic calculations (Navrotsky, 1975; Anovitz et al., 1985) indicate that FeTiO3 is stable only at relatively low pressures and high temperatures (Fig. 2). Armalcolite occurs in lunar basalts and terrestrial volcanic rocks, consistent with an origin at low pressure and high temperature. Substitution of Al3+, Cr3+, and Ti4+ stabilizes armalcolite to lower temperature (Kesson and Haggerty, 1975), whereas addition of Zr4+ appears to restrict armalcolite to higher temperature (Friel et al., 1977).

Figure 1 is a diagram showing observed compositions for the system Fe2TiO5-MgTiO3-FeTiO3-TiO2 compiled for natural samples of pseudobrookite and armalcolite, excluding those with > 5 mol% MnTiO3, CaTiO3, FeZrO3, and Cr2O3, and > 10 mol% Al2O3 (Smith, 1965; Levy et al., 1972; Peckett et al., 1972; Reid et al., 1973; Tsyymbal et al., 1980; Mets et al., 1985; Varlamov et al., 1993). Experimental results of Friel et al. (1977) suggest that CaO may not be incorporated into pseudobrookite or armalcolite, and that ZrO2 has a saturation limit in armalcolite of approximately 4 wt% at 1200–1300 °C and 1 atm, so it is uncertain whether so-called armalcolite with high CaO and ZrO2 contents (Smith, 1965; Levy et al., 1972; Peckett et al., 1972; Reid et al., 1973) is really armalcolite. Compositions of lunar armalcolite plot near the MgTiO3-FeTiO3 binary or at more reducing conditions in the TiO2 field. Terrestrial
armalcolite typically contains a significant amount of Fe³⁺ (Fig. 1).

Several terrestrial occurrences of armalcolite and fero-
sous pseudobrookite are known (Fig. 1). The substance is
erite, reported from Janovsky by Schaller (1912), may
be armalcolite or FeTiO₃, although Janovsky considered it
to be an intergrowth of rutile and Fe₂⁺ or Ti₃⁺ (wüstit or mag-
netite?). Von Knorring and Cox (1961) described armal-
colite-pseudobrookite solid solutions in the Karroo vol-
canoic rocks of southern Rhodesia that contain
approximately equal amounts of Fe₂⁺, Fe³⁺, FeTiO₃, and
Mg₂TiO₄. Ottemann and Frenzel (1965) analyzed several
pseudobrookite samples and an armalcolite from Ger-
many. Rice et al. (1971) reported an analysis of armal-
colite from lamproites in Montana. Armalcolite that is associ-
ated with native iron in trachybasalts from the Ukraine
was also discovered by Tysmbil et al. (1982). Lorand and
Cottin (1987) discovered armalcolite in ultrabasic cu-
mulates from the Laouni layered intrusion in Algeria;
their armalcolite analyses are similar to Velde’s (1975)
analyses of armalcolite from lamproites in Montana.

Armalcolite was observed in two paragneiss xenoliths
(samples ET11 and ET42 of Hayob et al., 1989) from a
Quaternary cinder cone, El Toro, located in the Central
Mexican Plateau (CMP) near the city of San Luis Potosi.
El Toro is one of several volcanic centers in the CMP
that contain xenoliths from the deep crust and upper
mantle (cf. Aranda-Gómez and Ortega-Gutiérrez, 1987;
Hayob et al., 1989). The CMP is an elevated region of
high heat flow, bounded to the west by the Sierra Madre
Occidental and to the east by the Sierra Madre Oriental.
The western mountains are part of an extensive, mid-
Tertiary ignimbrite province, and the eastern mountains are composed of Mesozoic sediments that were deformed
during the Laramide Orogeny. The younger Quaternary
volcanism erupted through the CMP and alluvial cover,
transporting xenoliths from the lower crust and upper
mantle to the surface. More detailed field relations are
given elsewhere (Aranda-Gómez, 1982; Aranda-Gómez
and Ortega-Gutiérrez, 1987; Luhr et al., 1989).

PETROLOGY

The armalcolite-bearing xenoliths from El Toro con-
tain primary garnet + sillimanite + quartz + plagioclase
+ mesoperthite + rutile + graphite ± ilmenite. Data for
most of these minerals have been reported previously
(Hayob et al., 1989) and will be discussed only briefly
here. The mesoperthites consist of regular intergrowths
of coarse (approximately 20 μm) alkali feldspar and plagi-
oclass lamellae that are unusually rich in ternary feld-
spar components (Hayob et al., 1989, 1990). On the basis
of reintegrated compositions of the mesoperthites, feld-
spar thermometry (Fuhrman and Lindsley, 1988) indi-
cates that the peak of metamorphism was at T ≥ 1025
°C (ET42) and T ≥ 1075 °C (ET11). Compositions of
coeexisting host and lamellae indicate that the xenoliths
last equilibrated at about 890 °C (ET42) and 880 °C (ET11)
(Fuhrman and Lindsley, 1988). The garnet + sillimanite
+ quartz + plagioclase barometer (GASP, Kozol and
Newton, 1988) yields pressures of 10.0 ± 1.0 kbar at 880
°C (ET11) and 8.9 ± 1.0 kbar at 890 °C (ET42) assuming
the garnet is in equilibrium with the exsolved plagioclase.

Chemical analyses of coexisting oxides were obtained
with a Cameca Camebax electron microprobe (Tables 1–
3). A focused beam with an accelerating potential of 15
kV and a sample current of 0.010 μA were standard oper-
ating conditions. Well-characterized natural and syn-
thetic materials were used as standards. Counting times of
30 s or 40000 total counts were used for all major elements
in standards and unknowns. Analytical data were correct-
ed using the Cameca PAP program. Ratios of Fe²⁺/Fe³⁺.
and Ti\textsuperscript{3+}/Ti\textsuperscript{4+} were calculated by charge-balance requirements with mineral formulae normalized about cations. In sample ET11, ilmenite occurs primarily as partial rims or overgrowths on rutile (Fig. 3a). One ilmenite crystal was observed in the matrix that is not associated with rims or overgrowths on rutile (Fig. 3a). One ilmenite crystal was observed in the matrix that is not associated with rims or overgrowths on rutile (Fig. 3a). Rutile or armalcolite, although it appears to be a fine intergrowth, contains varying amounts of Fe and Mg. All Fe in ilmenite is contained in varying amounts of Fe and Mg. All Fe in ilmenite is contained in ilmenite + plagioclase + quartz barometer (GRIPS, Bohlen and Liotta, 1986), and 8.0 ± 1.0 kbar is obtained with the garnet + rutile + sillimanite + ilmenite + quartz barometer (GRAIL, Bohlen et al., 1983) at 880 °C. These pressures are consistent with results obtained from the GASP barometer. Textural relations suggest that ilmenite that forms rims on rutile is secondary (Fig. 3a). Pressures of 11–12 kbar (GRIPS) and 9–10 kbar (GRAIL) are obtained at 880 °C using compositions of ilmenite rims (X\textsubscript{Mg} = 0.83–0.88), indicating that the GRIPS and GRAIL barometers are quite robust with respect to moderate changes in ilmenite composition (Table 2). Ilmenite is not present in sample ET42, but limits of pressure of >8 kbar and >7 kbar, respectively, are obtained with the GRIPS and GRAIL barometers at 880 °C assuming a X\textsubscript{Mg} = 0.83–0.88.

In sample ET11, armalcolite is associated with ilmenite that either mantles or is intergrown with rutile (Fig. 3a). Textures suggest that the armalcolite formed by decomposition, as there is no evidence of injection of the basalt host near the crystals of rutile and ilmenite. Armalcolite is opaque in transmitted light and has a reflectivity similar to that of ilmenite. Minor amounts of either Fe\textsuperscript{3+} or

### Table 2. Representative electron microprobe analyses of ilmenite from sample ET11

<table>
<thead>
<tr>
<th>wt% oxide</th>
<th>ET11A</th>
<th>ET11B*</th>
<th>ET11C</th>
<th>ET11</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>0.01</td>
<td>0.09</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>0.02</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>CrO\textsubscript{2}</td>
<td>0.03</td>
<td>0.06</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>V\textsubscript{2}O\textsubscript{5}</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>0.05</td>
<td>0.08</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MgO</td>
<td>3.68</td>
<td>3.68</td>
<td>2.56</td>
<td>3.90</td>
</tr>
<tr>
<td>MnO</td>
<td>0.67</td>
<td>0.61</td>
<td>0.60</td>
<td>0.68</td>
</tr>
<tr>
<td>CaO</td>
<td>0.09</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Formulae normalized to 2 cations**

| Zr         | 0.000 | 0.001 | 0.001 | 0.001 |
| Si         | 0.001 | 0.001 | 0.001 | 0.001 |
| Ti\textsuperscript{3+} | 0.992 | 0.972 | 0.982 | 0.986 |
| Ti\textsuperscript{4+} | 0.008 | 0.008 | 0.008 | 0.008 |
| Al         | 0.001 | 0.001 | 0.001 | 0.001 |
| Cr         | 0.001 | 0.001 | 0.001 | 0.001 |
| V          | 0.010 | 0.010 | 0.010 | 0.010 |
| Fe\textsuperscript{3+} | 0.845 | 0.827 | 0.872 | 0.959 |
| Fe\textsuperscript{2+} | 0.000 | 0.000 | 0.002 | 0.002 |
| Mg         | 0.134 | 0.134 | 0.095 | 0.091 |
| Mn         | 0.014 | 0.013 | 0.014 | 0.014 |
| Ca         | 0.013 | 0.013 | 0.013 | 0.013 |

**Note:** all analyses are from different crystals. Rim = rim on rutile. Xr = discrete, homogeneous grain. X\textsubscript{Mg} = Mg/(Mg + Fe\textsuperscript{2+} + Mn + 0.5Fe\textsuperscript{3+} + 0.5V + 0.5Cr + 0.5Al + 0.5Si). Fe\textsuperscript{2+} and Ti\textsuperscript{3+} were calculated from charge balance. * Rim on rutile garnet.
Fig. 3. Back-scattered electron (BSE) images of oxide textures. Scale bars are 50 μm. (a) Rutile (dark) partially rimmed by armalcolite (medium) and ilmenite (bright) from sample ET11. (b) Ilmenite crystal from sample ET11; light and dark regions are ilmenite that contains varying amounts of Fe and Mg. (c) Rutile (dark) rimmed by armalcolite (bright) from sample ET42. (d) Primary graphite (dark) included in garnet from sample ET11.
Table 4. Thermal expansion and compressibility data for phases used in this study

<table>
<thead>
<tr>
<th>Phase</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>Ref</th>
<th>e</th>
<th>f</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile</td>
<td>-5.684x10^-2</td>
<td>2.453x10^-3</td>
<td>1.573x10^-4</td>
<td>1.247x10^-1</td>
<td>1</td>
<td>0.4541</td>
<td>0.5698</td>
<td>2</td>
</tr>
<tr>
<td>Geikielite</td>
<td>-1.123x10^-1</td>
<td>4.442x10^-4</td>
<td>1.020x10^-5</td>
<td>-1.104x10^-1</td>
<td>3</td>
<td>0.5917</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>-6.830x10^-2</td>
<td>2.834x10^-3</td>
<td>8.168x10^-4</td>
<td>8.620x10^-1</td>
<td>5</td>
<td>0.5863</td>
<td>1.3006</td>
<td>5</td>
</tr>
<tr>
<td>MgTiO₃</td>
<td>-1.253x10^-1</td>
<td>5.066x10^-3</td>
<td>-5.125x10^-4</td>
<td>3.118x10^-3</td>
<td>6</td>
<td>0.5917</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>FeTiO₃</td>
<td>-6.132x10^-2</td>
<td>3.468x10^-4</td>
<td>-6.064x10^-4</td>
<td>3.314x10^-3</td>
<td>3</td>
<td>0.5863</td>
<td>1.3006</td>
<td>8</td>
</tr>
<tr>
<td>Fe₂TiO₅</td>
<td>8.381x10^-2</td>
<td>4.494x10^-3</td>
<td>-6.145x10^-3</td>
<td>3.227x10^-3</td>
<td>3</td>
<td>0.5863</td>
<td>1.3006</td>
<td>9</td>
</tr>
</tbody>
</table>

Note: \( V_2 = V_{298} + \left[ V_{298}(100)-(a + bT + cT^2 + dT^3) \right] \left( \text{T} \cdot \text{C} \right) \); \( V_1 = \frac{V}{(1 \times 10^{-6}P - f \times 10^{-4}P^2)} \) (P kbars). References are as follows: 1 = Skinner (1966); 2 = Hazen and Finger (1981); 3 = this study (see text); 4 = Liebermann (1978); 5 = Wechsler and Prewitt (1984); 6 = Brown and Navrotsky (1989); 7 = set equal to geikielite; 8 = set equal to ilmenite; 9 = set equal to hematite (Robinson et al., 1982).

\* Valid only for \( T = 700-1200 \text{ } \text{C} \).

Ti³⁺ are required in armalcolite analyses to satisfy charge balance, whereas ilmenite analyses require a small amount of Ti⁴⁺. The apparent need for trivalent ions in ilmenite may be the result of small systematic errors in the microprobe data, particularly since Ti³⁺ is preferentially partitioned into armalcolite rather than ilmenite (Lindsley et al., 1974; Kesson and Lindsley, 1975). In sample ET42, armalcolite is associated only with rutile (Fig. 3c). In this sample, there is also no evidence of injection of the basalt host near the crystals of rutile and armalcolite, although both are associated with quenched isochemoical melt that rims garnets. It is possible that the armalcolite formed by the reaction of rutile with Fe from the nearby garnet or from ilmenite that is no longer present. Variable but substantial amounts of Fe³⁺ are needed in this armalcolite to maintain neutrality (Table 3). The \( \chi_{Fe}^{\text{Mg}} \) in sample ET11 ranges from 0.09 to 0.13 and the \( \chi_{Fe}^{\text{Mg}} \) ranges from 0.18 to 0.28 (Tables 2 and 3), corresponding to a range in \( K_0 \) of 2.2-2.6 [\( K_0 = (\text{Fe}/(\text{Mg/Fe})^\text{Mg} \text{TiO}_3 \text{)} \text{Mg} \text{TiO}_3 \text{)} \text{Mg} \text{TiO}_3 \text{)} \text{Mg} \text{TiO}_3 \text{)}].

In contrast, experimental results of Lindsley et al. (1974) at 1 bar suggest that the distribution coefficient between armalcolite and ilmenite has a value between 3.6 and 4.8 for temperatures of 900-1140 °C. Their data predict the ilmenite with 9-13 mol% MgTiO₃ should be in equilibrium with armalcolite that contains 30-40 mol% MgTiO₃. The discrepancy in \( K_0 \) predicted from the experiments and that observed for the Mexican samples may result from errors in the experiments, disequilibrium in the natural samples, or both. Upper limits of pressure can nonetheless be estimated for the formation of armalcolite from the reaction

\[ \text{TiO}_2 + \text{MgTiO}_3 = \text{MgTi}_2\text{O}_5 \]  

which has been located for the range \( T = 950-1200 \text{ } \text{C} \) by Lindsley et al. (1974) (Fig. 2). If the rutile, ilmenite, and armalcolite were in equilibrium, pressures can be estimated from values of \( \ln K \) for Equilibrium 1. Use of Equilibrium 1 for barometry of natural samples, however, requires knowledge of the thermodynamic properties of pure MgTiO₃ and activity relations for armalcolite solid solutions.

**Thermodynamic Properties of Oxides in the System MgO-FeO-Fe₂O₃-TiO₂**

Data are not available for the thermal expansion of MgTiO₃ or for the compressibility of MgTiO₃. Therefore, the coefficients of thermal expansion \( (a, b, c, \text{ and } d) \) for geikielite were estimated from the equation in Table 4 and

\[ V(\text{MgTiO}_3) = V(\text{FeTiO}_3) + V(\text{MgO}) - V(\text{FeO}). \]

Thermal expansivities of FeO (stoichiometric) and MgO were obtained from Fei and Saxena (1986). Thermal expansion coefficients for MgTiO₃ were derived from high-temperature in situ diffraction data of Brown and Navrotsky (1989) for the temperature range 700-1200 °C and may not be valid outside of this range. The compressibility of MgTiO₃ was set equal to that of MgTiO₃ because compressibility data are not available.

High-temperature, in situ X-ray powder diffraction data of Brown and Navrotsky (1989) indicate that disorder in MgTiO₃ increases continuously from 500 to 1200 °C (and probably up to 1500 °C). Disorder in MgTiO₃, above about 1000 °C; however, is not preserved in quenched samples (Wechsler and Navrotsky, 1984; Brown and Navrotsky, 1989; Wechsler and von Dreele, 1989). Entropy coefficients of MgTiO₃ are derived from high-temperature heat content data of MgTiO₃ (Brown and Navrotsky, 1989) using transposed temperature-drop calorimetry (Table 5). Thus, the entropy coefficients for MgTiO₃ derived from those enthalpy data should include any contributions to entropy that result from disorder. The \( S_{298} \) of MgTiO₃ is from Kelley and King (1961) with an additional 10.5 J/(mol·K) added for the third law entropy at 0 K (Table 5), which was estimated from cation distribution data on samples quenched from 973 K (Brown and Navrotsky, 1989). However, these entropy coefficients are valid only for the temperature range of the enthalpy measurements (700-1500 °C) and should not be used outside of this range. Thus, standard free energies of formation cannot be estimated at 298.15 K for pseudobrookite from the data in Tables 4 and 5. In contrast, thermochemical data and room-temperature Rietveld re-
The structure of the system of FeTiO₃, MgTiO₃, and Fe₂TiO₅ is calculated using the Gibbs free energy method. The equilibrium constant for the reaction

$$\text{Fe}_2\text{TiO}_5 + \text{FeTiO}_3 \rightarrow 2\text{FeTiO}_4$$

is calculated at high temperature and low pressure. The calculated data are compared with experimental data obtained by other authors.

The molar volume, entropy, and entropy coefficients for phases used in this study are given in Table 5. The molar volume, entropy, and entropy coefficients for the phases are given in Table 5.

$$(V, S, S_0)_{MgTiO_3} = S_0(\text{MgTiO}_3) + 2.5V_0$$

$$(V, S, S_0)_{FeTiO_3} = S_0(\text{FeTiO}_3) + 2.5V_0$$

The molar volume of FeTiO₃, MgTiO₃, and Fe₂TiO₅ are estimated from values and equations in Table 4 and

$$V(\text{Fe}_2\text{TiO}_5) = V(\text{MgTiO}_3) + V(\text{FeO}) - V(\text{MgO})$$

Thermal expansion and compressibility data for FeO (stoichiometric) and MgO (Fei and Saxena, 1986) were refit to the equations given in Table 4.

Anovitz et al. (1985) estimated the entropy of Fe₂TiO₅ from those of pseudobrookite, hematite, and ilmenite. They assumed that Fe₂TiO₅ and FeTiO₃ were completely ordered (normal pseudobrookite structure of TiFe₂O₅) and did not account for entropy from magnetic effects. Their analysis yields a value of $S_0^{298} = 156.1 \text{ J/mol.K}$. Because most crystals of pseudobrookite contain a substantial amount of disorder at $T > 700 \text{ °C}$ (Brown and Navrotsky, 1989; Brigatti et al., 1993), a better approximation of $S_0^{298}$ and entropy coefficients ($A, B, C, D$) of FeTiO₃ can be estimated from

$$S_0(\text{FeTiO}_3) = S_0(\text{MgTiO}_3) + S_0(\text{FeO}) - 2.5V_0$$

(Fyfe and Verhoogen, 1958) and

$$V(\text{Fe}_2\text{TiO}_5) = V(\text{MgTiO}_3) + V(\text{FeO}) - V(\text{MgO})$$

(Table 5). An estimate of $S_0^{298} = 172.4 \text{ J/mol.K}$ is obtained for Fe₂TiO₅, significantly higher than the value estimated by Anovitz et al. (1985). Inherent in Equation 5 is the assumption that Fe₂TiO₅ and MgTiO₃ exhibit similar degrees of disorder with increasing temperature. There are no in situ cation distribution data available for Fe₂TiO₅, but a comparison of cation distribution data for synthetic, quenched samples of Fe₂TiO₅ and MgTiO₃ suggests that Fe₂TiO₅ has similar amounts of cation ordering (Lind and Housley, 1972; Grey and Ward, 1973; Virgo and Huggins, 1975; Brown and Navrotsky, 1989; Wechsler and von Dreele, 1989). Ilmenite (Ishikawa and Akimoto, 1957; Stickler et al., 1967) and pseudobrookite (Akimoto et al., 1957; Muranaka et al., 1971) are paramagnetic at room temperature and become antiferromagnetic at low temperature. As a first approximation, con-
tributions to the configurational entropy of FeTiO₃, resulting from magnetic transitions at low temperature are accounted for in Relation 5 because magnetic effects are included in the entropy data of ilmenite (Anovitz et al., 1985). Heat capacity, transposed drop calorimetry, and in situ cation distribution data at high temperature are necessary for a more accurate determination of the thermodynamic properties of FeTiO₃.

Thermodynamic data used for pseudobrookite are given in Tables 4 and 5. The thermal expansion of Fe₂TiO₅ was estimated from

\[ \Delta V(\text{Fe}_2\text{TiO}_5) = \Delta V(\text{Fe}_3\text{Ti}_2\text{O}_9) + \Delta V(\text{Fe}_2\text{O}_3) - \Delta V(\text{Fe}_3\text{Ti}_2\text{O}_7) \]

(Table 4). The compressibility of pseudobrookite was set equal to that of hematite. Thermodynamic data of Robinson et al. (1982) were used for hematite. The \( S^0_{298} \) of pseudobrookite was estimated from

\[ S^0(\text{Fe}_2\text{TiO}_5) = S^0(\text{Fe}_3\text{Ti}_2\text{O}_9) + S^0(\text{Fe}_2\text{O}_3) - S^0(\text{Fe}_3\text{Ti}_2\text{O}_7) + 2.5 \]

(Fyfe and Verhoogen, 1958). Using entropy coefficients estimated from FeTiO₃, Fe₂O₃, and Fe₃O₇, values of \( S^0 \) calculated for pseudobrookite are slightly lower than published values of \( S^0 \). Therefore, entropy coefficients for pseudobrookite were taken directly from the published values of Bonnickson (1954).

**Activity-composition relations of armalcolite**

Activity-composition (a-X) relations have been evaluated for ilmenite-geikielite-hematite solid solutions (Andersen and Lindsley, 1988; Ghiorso, 1990; Andersen et al., 1991), although some discrepancies remain in these values that may be traced to the mixing properties assumed for olivine. No mixing data are available for orthorhombic oxides in the ternary system FeTiO₃-MgTiO₃-Fe₂O₃. The Fe-Mg exchange equilibrium between stoichiometric armalcolite (i.e., Fe₀.₃Mg₀.₇TiO₃) and ilmenite

\[ \text{MgTiO}_3 + \text{FeTiO}_3 = \text{FeTiO}_3 + \text{MgTiO}_3 \]

was located at 1010 °C at 1 bar by Lindsley et al. (1974). The composition of ilmenite in equilibrium with Fe₀.₃Mg₀.₇TiO₃ is Fe₀.₃Mg₀.₇TiO₃ (their Fig. 1), although exact compositions or chemical analyses are not given. They studied the equilibrium distribution of Fe²⁺ and Mg between armalcolite and ilmenite for a range of bulk compositions at 1 bar and 900–1140 °C. A value of \( K_\phi \) between 3.6 and 4.8 is calculated from their data. Friel et al. (1977) determined the location of Equilibrium 9 for stoichiometric armalcolite for the temperature range 1000–1200 °C as a function of pressure, although they did not report the composition of ilmenite in equilibrium with Fe₀.₃Mg₀.₇TiO₃. On the basis of the \( K_\phi \) data of Lindsley et al. (1974), Fe₀.₃Mg₀.₇TiO₃ should have equilibrated with Fe₀.₃2Mg₀.₇5TiO₃ at 1100 °C and with Fe₀.₃Mg₀.₇5TiO₃ at 1200 °C, if the \( K_\phi \) is independent of pressure.

Mixing relations can be estimated for FeTiO₃-MgTiO₃ solutions using experimental results for Equilibria 1, 3, and 9 if the following are accurately known: (1) volume data of all phases at \( P \) and \( T \), (2) a-X relations of ilmenite-geikielite solutions, and (3) \( K_\phi = (\text{Mg/Fe})^{\alpha\text{Mg}}/(\text{Mg/Fe})^{\alpha\text{Mg}} \) as a function of \( P \) and \( T \). Volume data used in this study are given in Tables 4 and 5. Mixing relations of Andersen et al. (1991) and Ghiorso (1990) were used for ilmenite-geikielite solid solutions, and an ideal model was assumed for rutile. The \( K_\phi \) was estimated as a function of temperature from the data of Lindsley et al. (1974). Activity coefficients for FeTiO₃ and MgTiO₃, calculated from

\[ \int_P^P \Delta V \frac{dP}{P} = -RT \ln \frac{K_\phi}{K_\phi} \]

are given in Table 6. The prime refers to the standard state, chosen to be either MgTiO₃ or FeTiO₃ for armalcolite at \( T \) of interest, where \( P \) is defined by the locus of Equilibrium 1 or 3, respectively. Assuming a molecular activity model (i.e., \( a_{\text{MgTiO}_3} = \gamma_{\text{MgTiO}_3} \alpha_{\text{MgTiO}_3} \)), negative deviations from ideality are necessary for MgTiO₃, and positive deviations are required for FeTiO₃, for the shifted loci of Equilibria 1 and 3 to be coincident with the locus of Equilibrium 9 (Table 6). Regardless of the ilmenite model used, the calculated activity coefficients of MgTiO₃ and FeTiO₃ decrease with increasing temperature.

**Barometry**

Pressures were estimated from Relation 10 with \( P' \) defined by the locus of Equilibrium 1 or Equilibrium 3 for rutile-armalcolite ± ilmenite pairs from samples ET 11 and ET 42, assuming various activity models for armalcolite and ilmenite (Hayob, 1994). Attempts to use the derived thermodynamic values to estimate pressure of formation of armalcolite were not successful. It is likely that the ilmenite and armalcolite did not equilibrate in sample ET 11, on the basis of low values obtained for the \( K_\phi \) in comparison with data of Lindsley et al. (1974). Upper limits of pressure estimated from armalcolite compositions are not useful because of the substantial dilution of the MgTiO₃ and FeTiO₃ components, and it is difficult to evaluate the effect of additional components such as Al on the stability of armalcolite in the xenoliths. The depth in the crust at which armalcolite formed in the xenoliths cannot be well constrained. However, by anal-

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**Table 6.** Calculated activity coefficients for armalcolite (Fe₀.₃Mg₀.₇TiO₃) on the basis of a molecular activity model

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ABL</th>
<th>G</th>
<th>ABL</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>1010</td>
<td>0.78</td>
<td>1.02</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1140</td>
<td>0.56</td>
<td>0.81</td>
<td>n.d.</td>
<td>1.36</td>
</tr>
<tr>
<td>1100</td>
<td>0.42</td>
<td>0.67</td>
<td>1.28</td>
<td>1.33</td>
</tr>
<tr>
<td>1300</td>
<td>0.27</td>
<td>0.50</td>
<td>1.21</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Note: ABL values calculated using a-X relations of ilmenite from Andersen et al. (1991); G values calculated using a-X relations of ilmenite from Ghiorso (1990); n.d. = not determined.
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Fig. 4. Log fo₂-T diagram at 1 bar total pressure and 800-1200 °C showing loci of Equilibria 11 and 12 (combined), 16, and 17. Equilibria 16 and 17 are metastable below 1140 °C, where FeTiO₃ breaks down to rutile + ilmenite. Lined field shows ranges in fo₂ calculated from Equilibrium 16 for sample ET11. Light stippled field represents ranges in fo₂ calculated from Equilibrium 17 for samples ET11 and ET42, and heavy stippled line is calculated from the Ti³⁺ content of armalcolite for sample ET11A (Stanin and Taylor, 1980: ST). The reactions hematite = magnetite + O₂, quartz + magnetite = fayalite + O₂, and wüstite = iron + O₂, were calculated from equilibrium expressions in Frost (1991); ilmenite = rutile + iron + O₂, was calculated from thermodynamic data referenced in this study. C = graphite, CO = carbon monoxide, CO₂ = carbon dioxide, Fa = fayalite, Fe = metallic iron, Fe-Arm = FeTiO₃, Hem = hematite, Ilm = ilmenite, Mag = magnetite, Psb = pseudobrookite, Qtz = quartz, Rt = rutile, Wus = wüstite.

Fig. 5. Log fo₂-T diagram at 10 kbar total pressure and 800-1200 °C. Stippled field shows range in fo₂, conditions for the peak of metamorphism. Magnetite + rutile = ilmenite was calculated from thermodynamic data referenced in this study and data for magnetite from Robie et al. (1978). Hematite = magnetite, quartz + magnetite = fayalite, ilmenite = rutile + Fe, and abbreviations as in Fig. 4.

assuming that P_fad = P_tot and P_H₂O has negligible contributions to total pressure. At 1 bar total pressure, the partial pressure of each gaseous species can be determined as a function of temperature from

$$\Delta G_f^\circ = -RT \ln K.$$  \hfill (14)

Gibbs free energy data from Robie et al. (1978) were used to calculate the location of Equilibria 11 and 12 for the range T = 800-1200 °C at 1 bar total pressure (Fig. 4), assuming an ideal model (P_i = f_i). Oxygen fugacities more reducing than those of the iron + wüstite (IW) buffer are necessary to stabilize graphite at high temperatures at 1 bar (Fig. 4).

Pressure has a large effect on the locations of Equilibria 11 and 12 in fo₂-T space (e.g., Nordstrom and Munoz, 1986). At P_tot > 1 bar,

$$\Delta G_f^\circ \approx -RT \ln K + \Delta V_p (\text{solids}) \Delta P.$$  \hfill (15)

An iterative method was used to calculate the fO₂ of Equilibria 11 and 12 using Assumption 13 and Expression 15 at 10 kbar total pressure (Fig. 5). Fugacities were calculated from fugacity coefficients for CO (Ryzhenko and Volkov, 1971) and CO₂ (Shmulovich and Shmonov, 1975) at P and T up to 10 kbar and 1200 °C. The calculations were reiterated until convergence was achieved between

ogy with other armalcolite occurrences and from textural criteria, it seems likely that the Mexican armalcolite formed during decompression.

IMPLICATIONS FOR REDOX CONDITIONS

Metamorphic peak fO₂

Primary graphite, occurring as flakes along grain boundaries and as inclusions in other primary minerals, is common in both xenoliths (e.g., Fig. 3d). In the presence of graphite (G₀ = 1), the partial pressure (and fugacity) of O₂ in equilibrium with graphite is buffered by the equilibria

$$C + \frac{1}{2}O_2 = CO \quad (11)$$
$$C + O_2 = CO_2 \quad (12)$$

and

$$P_{CO} + P_{CO_2} = P_{tot} \quad (13)$$
the initial and final values for the partial pressures of CO and CO₂. The calculated \( f_{\text{O}_2} \) for Equilibria 11 and 12 is not extremely sensitive to the values of fugacity coefficients for CO and CO₂ or to the ratio of CO/CO₂. For example, at 900 °C \( \gamma_{\text{CO}} = 11.31-15.02 \) if \( P_{\text{CO}} = 8-9 \) kbar (Shmulovich and Shmonov, 1975), and \( \gamma_{\text{CO}} = 1.87-1.37 \) if \( P_{\text{CO}} = 1-2 \) kbar (Ryzhenko and Volkov, 1971), resulting in a calculated range in \( -\log f_{\text{O}_2} \) of 12.87-12.79. Convergence is obtained at 900 °C and 10 kbar total pressure for values of \( P_{\text{CO}} = 1.57 \) kbar and \( P_{\text{CO}} = 8.43 \) kbar, corresponding to \( -\log f_{\text{O}_2} = 12.83 \). Figures 4 and 5 show the calculated locations of Equilibria 11 and 12 (combined) at 1 bar and 10 kbar, respectively, at 800-1200 °C. If other fluid species were present, the activities of CO and CO₂ would be reduced and the loci of the combined equilibria (from 11 and 12) would be shifted toward lower values of \( -\log f_{\text{O}_2} \) in Figures 4 and 5. Thus, the presence of primary graphite provides an upper limit for the \( f_{\text{O}_2} \) at which the xenoliths equilibrated at approximately 10 kbar total pressure (Fig. 5).

The presence of primary graphite, lack of metallic Fe, and pressure estimates of 10 kbar for the peak of metamorphism indicate that the xenoliths equilibrated at values of \( -\log f_{\text{O}_2} \) between 11 and 15 during the peak of metamorphism at 1025-1075 °C (Fig. 5), the minimum temperature for the peak of metamorphism estimated on the basis of feldspar thermometry in these samples (Hayob et al., 1989).

### Armalcolite formation \( f_{\text{O}_2} \)

Phase equilibria involving armalcolite can be used to constrain \( f_{\text{O}_2} \) conditions if the armalcolite + rutile ± ilmenite were in equilibrium. In an oxidizing atmosphere at high temperature and low total pressure, ilmenite forms an armalcolite-pseudobrookite solid solution

\[
3\text{FeTiO}_3 + \frac{5}{2}\text{O}_2 = \text{Fe}_2\text{TiO}_5 + \text{FeTi}_2\text{O}_5
\] (16)
and FeTi₂O₅ oxidizes to form rutile + pseudobrookite

\[
2\text{FeTi}_2\text{O}_5 + \frac{1}{2}\text{O}_2 = 3\text{TiO}_2 + \text{Fe}_5\text{Ti}_2\text{O}_9
\] (Anovitz et al., 1985).These O₂ buffers are located within one log unit of each other at 1 bar total pressure between the hematite + magnetite (HM) and FMQ buffers (Fig. 4). Equilibria 16 and 17 are metastable below 1140 °C at 1 bar because FeTi₂O₅ is not stable.

It is difficult to estimate the temperature of formation of armalcolite in the xenoliths. The high Fe²⁺ content of armalcolite in sample ET11 suggests that armalcolite formed at fairly high temperature; however, Ti³⁺ and Al should stabilize armalcolite to lower temperatures (Kesron and Lindsley, 1975). The effect of V⁺ on the stability of armalcolite has not been studied experimentally but (by analogy with other trivalent ions) V should stabilize armalcolite. Two-feldspar thermometry of the exsolved feldspars indicates that the xenoliths did not cool below 900 °C until after eruption (Hayob et al., 1989, 1990). Data from Beard et al. (1993), which compare the feldspar thermometer of Elkins and Grove (1990) with experimental results on Kilbourne Hole xenoliths, suggest that feldspar thermometry has an accuracy of better than \( \pm 50 \) °C. The thermometer of Elkins and Grove (1990) yields temperatures that are similar to the models of Fuhrman and Lindsley (1988) and Lindsley and Nekvasil (1989) that were used by Hayob et al. (1989). Melting experiments conducted by Beard et al. (1993) on a pelite (their sample KH-12) from Kilbourne Hole at 900-1000 °C produced no melt, indicating that pelites may be quite refractory and stable to temperatures > 1000 °C. There is no textural evidence of reheating of the xenoliths during decomposition. Rims of quenched melt that formed upon decompression (Hayob et al., 1989) surround garnet in both samples and a small amount of melt (<1% by volume) is present along some grain boundaries. However, zoning is absent in all minerals, and if reheating occurred, it happened rapidly enough such that the compositions of the primary minerals were not affected. Thus, it is reasonable to assume that armalcolite formed at about 900-1000 °C at pressures lower than the peak of metamorphism (10 kbar).

Incorporation of activity coefficients has a negligible effect (e.g., \( \pm 0.1 \) log unit) on the calculated values of \( f_{\text{O}_2} \) (±0.1 log unit) for ET11 and ET42 in comparison with the effect of chemical heterogeneity in the oxides. Therefore, ideal molecular activity models were used for all phases (i.e., \( a_{\text{FeTiO}_3} = X_{\text{FeTiO}_3} \)). Values of \( f_{\text{O}_2} \) estimated at 1 bar from Equilibrium 16 for sample ET11, which contains ilmenite, and Equilibrium 17 for ET11 and ET42 are shown in Figure 4. At 10 kbar, Equilibria 16 and 17 are shifted +1.2 and 0.0 log units, respectively, from the 1 bar loci. The range of \( f_{\text{O}_2} \) indicated for each sample represents variations in \( f_{\text{O}_2} \) resulting from chemical heterogeneity in the coexisting oxides (Tables 1-3). In sample ET42, the mole fraction of FeTiO₃ is diluted sufficiently that armalcolite is stable to temperatures <800 °C (e.g., Fig. 2). Armalcolite from sample ET11, however, is not stable below 900 °C (Fig. 4) on the basis of values of \( \log K \) for Equilibrium 3. Equilibria 16 and 17 cannot be applied to armalcolite ET11A, which lacks a pseudobrookite component and contains a small amount of Ti^{3+}. Stanin and Taylor (1980) formulated an O₂ barometer for lunar basalts on the basis of the amount of Ti^{3+} in armalcolite and proposed that Ti^{3+}-rich armalcolite typically equilibrates at values of \( f_{\text{O}_2} \) between IW and 1.5 log units below IW. Their results are consistent with experiments of Friel et al. (1977) in which armalcolite reacted to form ilmenite + reduced armalcolite at values of \( f_{\text{O}_2} \) below \(-10.5 \) at 1200 °C and 1 bar. From the expression

\[
\log f_{\text{O}_2} = -1.7 \left( \frac{X_{\text{Ti}^{3+}}}{X_{\text{Fe}^{2+}}} \right)
\] (Stanin and Taylor, 1980), a value for \( f_{\text{O}_2} \) of approximately 0.0 (Fig. 4) is obtained for armalcolite from ET11A (heavy shaded curve, Fig. 4), where the \( f_{\text{O}_2} \) is in log units relative to the iron + wüstite buffer. In Equation
18. \(Ti^3+\) is the mole fraction of TiO, and Fe\(^{2+}\) is the mole fraction of FeTiO, in armalcolite.

**DISCUSSION**

Chemical variation in armalcolite produces a large range in calculated \(f_{O_2}\) for both samples, which may indicate disequilibrium on the scale of a thin section. The range in \(f_{O_2}\) is typical, however, for crustal and mantle rocks and indicates that armalcolite solid solutions involving Fe\(^{2+}\) and Mg are stable in terrestrial rocks. The value of \(f_{O_2}\) near IW for sample ET11A is more typical of lunar rocks, but the calculated \(f_{O_2}\) is sensitive to small amounts of \(Ti^3+\). Armalcolite seems to be relatively rare, however, even in volcanic rocks, and bulk composition may be more important than \(P-T-f_{O_2}\) in controlling its stability (Anovitz et al., 1983).

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