The heat-capacity of ilmenite and phase equilibria in the system Fe-Ti-O*

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Abstract—Low temperature adiabatic calorimetry and high temperature differential scanning calorimetry have been used to measure the heat-capacity of ilmenite (FeTiO₃) from 5 to 1000 K. These measurements yield \( S_{298} = 108.9 \) J/(mol·K). Calculations from published experimental data on the reduction of ilmenite yield \( \Delta G^\circ_{\text{red}}(298) = 1153.9 \) kJ/(mol·K). These new data, combined with available experimental and thermodynamic data for other phases, have been used to calculate phase equilibria in the system Fe-Ti-O. Calculations for the subsystem Ti-O show that extremely low values of \( f_0\) are necessary to stabilize TiO₂, the mineral baronite reported from the Tsoo district in China. This mineral may not be TiO₂ and it should be re-examined for substitution of other elements such as N or C. Consideration of solid-solution models for phases in the system Fe-Ti-O allows derivation of a new thermometer/oxybarometer for assemblages of ferro-pseudobrookite-pseudobrookite, and hematite-ilmenite. Preliminary application of this new thermometer/oxybarometer to lunar and terrestrial lavas gives reasonable estimates of oxygen fugacities, but generally yields subsolidus temperatures, suggesting re-equilibration of one or more phases during cooling.

INTRODUCTION

ILMENITE, FeTiO₃, occurs as an accessory phase in a wide variety of igneous and metamorphic rocks. In combination with other phases it has thermometric, barometric, and oxy-barometric significance (e.g. SPENCER and LINDSLEY, 1981; BOHLEN et al., 1983). However, thermodynamic data for ilmenite are incomplete. Heat-capacity measurements by SHOMATE et al. (1946) were only performed down to 51 K, ROBIE (1965) and ULBRICH and WALDBAUM (1976) noted that magnetic transitions below 50 K often make significant contributions to the entropies of transition metal phases. Because ilmenite has a paramagnetic-antiferromagnetic transition near 55 K (ISHIKAWA and AKIMOTO, 1957; STICKLER et al., 1967), heat-capacity measurements are needed to much lower temperatures for adequate extrapolation to 0 K. We have remeasured the heat-capacity of ilmenite from 5 to 1000 K which allows more accurate calculation of phase relations of ilmenite and other minerals in the system Fe-Ti-O.

SAMPLE DESCRIPTION

A 6.9363 g sample of ilmenite was synthesized for low-temperature adiabatic measurements. Merck "Ultrapure" grade Fe₂O₃, TiO₂, and Fe metal reagents were used as starting materials. Stoichiometric mixtures of these reagents were reacted for 4 days in evacuated silica tubes at 1065°C. The resultant material formed a dark grey powder. The lattice parameters of the sample were refined by powder diffraction methods using a scan speed of 3° degree per minute and fluorite as an internal standard. Refinement was performed by least-squares using 16 measured reflections on the hexagonal unit cell. The resulting values are \( a = 5.086(1) \) Å, and \( c = 14.077(7) \) Å, close to those of the National Bureau of Standards (MORRIS et al., 1978; \( a_0 = 5.0884(2) \) Å, \( c_0 = 14.0932(6) \) Å). The slight differences may either be due to a small amount of Fe₂O₃ in our sample or TiO₂ in the NBS standard.

Mössbauer spectra of ilmenite were obtained at room temperature by Dr. S. R. Bohlen (now at SUNY, Stony Brook) in W. Dollase's laboratory at the University of California, Los Angeles using a constant acceleration, mechanically driven Mössbauer spectrometer in order to check the material for the presence of Fe³⁺. Samples of 70–90 mg were used with a 10 cm Cs²⁵Co in Pd source. Duplicate spectra were recorded in 512 channels of a multichannel analyzer using a velocity increment of 0.01 mm per channel. Counting times were sufficient to obtain several million counts per channel and peak dips of approximately 10⁵ counts. The spectra were fitted with Lorentzian doublets that in most cases were constrained to equal widths and areas for the low- and high-velocity components. Chi-squared and additional goodness-of-fit parameters (RUBY, 1973) were calculated for each fitted spectrum.

The Mössbauer spectrum of ilmenite consists of a single ferrous doublet and a very small, poorly defined ferric doublet that appears in the spectrum as a low intensity "shoulder" on the low-velocity part of the ferrous doublet. For the octahedrally coordinated ferrous iron in ilmenite the measured average isomer shift (relative to Fe⁰) and quadrupole splitting (IS = 1.058 mm/sec; Qe = 0.657 mm/sec) are similar to previously reported values (RUBY and SHIRANE, 1961; SYONO et al., 1981). Observed peak widths are 0.28 mm/sec. The intensity of the peaks attributable to ferric iron is so low that the location of the ferric doublet had to be constrained to be consistent with the isomer shifts and quadrupole splittings of octahedrally coordinated Fe³⁺ in other similar Fe phases in order to obtain...
convergence in the fitting procedure. The relative areas of the ferrous and ferric count dips suggest that approximately 3 ± 1.5% of the iron is present as Fe²⁺. A slight, but significant difference was noted in the areas of the two components of the ferrous doublet. At first this was thought to be the result of preferred orientation of the platy ilmenite grains. However, similar ferrous doublets with unequal areas are observed when efforts have been made to eliminate the preferred orientation. Relaxation of the constraint of equal area results in a slightly better fit to the data but does not change the relative amounts of inferred Fe³⁺. The relative areas of the ferrous count dips differ by 3 ± 0.1%. The cause of this difference has not been determined.

**CALORIMETRIC TECHNIQUE**

Heat-capacity measurements were made in the Mark II adiabatic cryostat over the temperature range 3 to 320 K. Cryostat construction and measurement-circuit calibration are described in Westrum et al. (1968). A gold-plated copper calorimeter (laboratory designation W-34) weighing 10.448 g, with an internal volume of 6.567 cm³ and an axial entrance well for the thermometer assembly was used. The calorimeter was evacuated and then filled with 20 torr of He gas to enhance thermal contact and reduce equilibration times. A capsule was evacuated and then filled with 20 torr of He gas to enhance thermal contact and reduce equilibration times. A capsule-

**RESULTS**

Smoothed low-temperature data (Table 4) show a distinct λ-type transition at approximately 57.2 ± 0.1 K (Table 1), in fair agreement with the Néel point temperatures of 55 K determined by Ishikawa and Akimoto (1957) and 56 K determined by Stickers et al. (1967). The differences are consistent with the small amount of ferric iron in our sample (Ishikawa and Akimoto, 1957), but the possible effects of TiO₂ in either of the measured samples are unknown. Heat-capacity in this temperature region is composed of contributions from the crystal lattice, from the magnetic transition, and from electronic disorder (the Schottky contribution). The lattice heat-capacity of ilmenite was estimated from that of MnTiO₃ (pyrophanite; Stephens and Smith, 1968). The Cₜ (lattice) function for MnTiO₃ was adjusted for mass and volume following the Lindemann relation:

\[ \Thetaₜ = B \frac{T_m}{M(T_m)}^{1/2} \]  

where \( B \) is a constant, \( T_m \) is the melting temperature, \( M \) is the mean atomic weight, and \( V \) the molar volume of the phase in question. For two minerals we obtain:

\[ \frac{Θₜ(M)}{Θₜ(Pyr)} = \left( \frac{M(Pyr)}{M(Ill)} \right)^{1/2} \cdot \left( \frac{V(Pyr)}{V(Ill)} \right)^{1/3}. \]  

The melting points of FeTiO₃ and MnTiO₃ are poorly known, and depend on \( f_O₂ \) (Levin et al., 1969; Lindsey, 1976). Because \( T_m \) for Fe₂TiO₄ and MnTiO₃ are similar, they will be ignored. Using mean atomic weights and molar volumes from Robie et al. (1978) this yields:

\[ \Thetaₜ(Fe₂) \]  

The lattice heat-capacity of ilmenite is obtained by taking the estimated lattice \( Cₜ \) of pyrophanite at some temperature \( T₁ \), multiplying \( T₂ \) by 1.0834, and using the resulting \( Cₜ(T₂) \) as the \( Cₜ \) model for ilmenite. The derived \( Cₜ \) (lattice) for ilmenite is a good match for the measured data at high temperature (Fig. 1), but shows that there is significant non-lattice heat-capacity below 300 K.

The non-lattice heat-capacity (excess heat-capacity) is caused by magnetic and electronic disordering. To calculate the total excess entropy \( δS^α \) from \( Cₜ(Pyr) \) data, we used the method of Simpson et al. (1974). For convenience in our calculations, below 20 K \( Cₜ \) was assumed to follow the relation \( Cₜ = T^2 \) which yields:

\[ 5δS^α(20) - 5δS^α(0) = 1/3Cₜ(20 K) = 0.63 J/(mol·K). \]  

For numerical integration points were chosen at 5 K intervals from 20 to 50 K. Across the transition, from 50 to 70 K points were chosen at 1 K increments, and points were spaced every 10 K from 70 K to 300 K. These calculations yield \( 5δS^α = 19.12 J/(mol·K) \).

The magnetic contribution to excess entropy derives from disorder of magnetic moments of Fe atoms as the Néel tran
The temperature is raised, the sixth d-electron will tend to disorder over the lower energy orbitals. The Schottky effect generates an excess entropy which iron is found splits the 3d orbitals into a lower energy pair \( d_x^2 \) and \( d_y^2 \) and a higher energy orbital \( d_z^2 \). As temperature is raised, the sixth d-electron will tend to disorder over the lower energy orbitals. The Schottky effect generates an excess entropy of 5.73 J/(mol·K).

The remaining excess entropy is 5.73 J/(mol·K). This excess may be ascribed to disorder of electrons between orbitals (the Schottky effect; GOPAL, 1966; WOOD, 1981). At 0 K, the sixth d-electron in ferrous iron is assumed to reside in the lowest energy d-orbital. In ilmenite, distortion of the octahedra in which iron is found splits the 3d orbitals into a lower energy pair \( d_x^2 \) and \( d_y^2 \) and a higher energy orbital \( d_z^2 \). As temperature is raised, the sixth d-electron will tend to disorder over the lower energy orbitals. The Schottky effect generates an excess entropy of 5.73 J/(mol·K).

### Table 2: Experimental high-temperature heat capacities (J/C) for ilmenite

<table>
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<tr>
<th>( T ) (K)</th>
<th>( C_p ) (J/mol·K)</th>
<th>( T ) (K)</th>
<th>( C_p ) (J/mol·K)</th>
<th>( T ) (K)</th>
<th>( C_p ) (J/mol·K)</th>
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<td>740.2</td>
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The close agreement suggests that we have a reasonable model of the lattice heat-capacity of ilmenite, and have accounted for all other entropy contributions below 360 K. As the magnetic contribution cannot be calculated as a function of temperature, the possibility that this agreement is fortuitous cannot be evaluated.

Comparison of our heat-capacity data with that previously reported by SHOMATE et al. (1946) and later used by KELLEY and KING (1961) and ROBIE et al. (1978) at 50 K, the lower limit of the older data, our results are 0.2 J/(mol·K) higher than they report, and at the peak of the transition our data are 2.9 J/(mol·K) higher than theirs. Between 150 and 298.15 K our results increased gradually to 0.7 ± 0.1% higher than SHOMATE et al.'s. and our measured value of \( S^{\text{ex}}_{\text{mol}} \) (108.9 J/(mol·K)) is 3.0 J higher than the earlier value. This difference is due to our somewhat greater values of \( C_p \) or all temperatures below 298 K, our sharper magnetic anomaly, and to errors in their extrapolation from 50 to 0 K.

Our calculated enthalpy for ilmenite is 1.9 percent higher at 1000 K than the value given by NAYLOR and COOK (1946) and used by ROBIE et al. (1978). The calorimeter used by Naylor and Cook was essentially the same as that used by O'BRIEN and KELLEY (1957). ANOVITZ et al. (in prep.) have argued that the temperature scale used by O'Brien and Kelley for their drop calorimeter was in error by 7 K at 1000 K. If we assume that the same systematic error existed in the calorimetric system of Naylor and Cook and correct for the assumed error in the temperature scale, the difference in the calculated enthalpy at 1000 K is reduced to 0.9 percent. This corrected result is within the combined experimental error in the data.

### PHASE EQUILIBRIA

The ilmenite data presented above permit accurate calculation of the phase relations for the system Fe-Ti-O. The following phases have been considered: iron (Fe), titanium (Ti), rutile (TiO₂), hongquartz (TiO₂), the Magneli phases \( Ti_2O_5, Ti_3O_7, Ti_4O_9, Ti_5O_11 \), and \( Ti_6O_{17} \), hematite \( Fe_2O_3 \), magnetite \( Fe_3O_4 \), wustite \( FeO \), ilmenite \( FeTiO_3 \), ulvöspinel \( Fe_2TiO_4 \), pseudobrookite \( Fe_3TiO_4 \), and ferroepidotebrookite \( Fe_5TiO_4 \). All calculations assume that these phases have stoichiometric cation/anion ratios. Possible non-

### Table 3: Smoothed High-Temperature Thermochemical Data for Ilmenite (FeTiO₃)

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( C_p ) (J/mol·K)</th>
<th>( dH^{\text{mol}} ) (J/mol·K)</th>
<th>( dS^{\text{mol}} ) (J/mol·K)</th>
<th>( dG^{\text{mol}} ) (J/mol·K)</th>
<th>( dG^{\text{mol}} ) (J/mol·K)</th>
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\[ C_p (J/mol\cdot K) = 1.73094 - 5.2713 \times 10^{-4} T + 2.2325 \times 10^{-7} T^2 \]

\[ C_p (J/mol\cdot K) = 16.765 T^{-0.5} - 2522 T^{-2} \]
Table 4. Smoothed low-temperature thermodynamic data

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<tr>
<th>T (°C)</th>
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</table>

Stoichiometry and disorder should be carefully evaluated in phases formed at high temperatures before using the equilibria presented here. Sources for all thermodynamic data taken from the literature are listed in Table 5.

Phase equilibria presented here were calculated using the FORTRAN program EQUILI (Wall and Essene, unpublished data) which is similar to that of Slaughte et al. (1976). All calculations were performed using a second order approximation in which the thermal expansion of each phase at $P/T$ is assumed equal to that at 1 bar. $T$, and the compressibility of each phase at $P/T$ is assumed equal to that at 298 K and $P$.

The Gibbs energy of ilmenite was derived from published experiments (Shomate et al., 1946; Lenev and Novokhatskii, 1964; Taylor and Schmalz-Reid, 1964; Levitskii et al., 1969, 1970; Taylor et al., 1972; Sato et al., 1973; Saha and Biggar, 1974; Merritt and Turnbull, 1974; Simons and Woermann, 1978) on the reaction:

$$\text{Fe}_2\text{TiO}_4 = \text{Fe} + \text{TiO}_2 + \frac{1}{2}\text{O}_2$$

Derived values for the Gibbs energies of ordered and disordered ulvöspinel at STP are $-1413.9$ kJ/mol and $-1402.8$ kJ/mol respectively. The differences between the calculations for ordered (solid line) and disordered (dashed line) ulvöspinel are small (Fig. 3). Only results for the ordered phase will therefore be considered in further calculations.
The Gibbs energy of pseudobrookite was derived from the reversal by HAGGERTY and LINDSLEY (1969) on the reaction:

\[
Pseudobrookite = 
\text{Hematite} \mid \text{Rutile}
\]

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

at 585°C and 1 bar which yields \(-1624.94\) kJ/mol at STP. NAVROTSKY (1975) notes that her measured enthalpy for pseudobrookite, together with the reversal of Haggerty and Lindsey, yields an entropy value in good agreement with the measured data. This may be fortuitous as neither order-disorder nor magnetic transition effects have been accounted for (NAVROTSKY, 1975). The entropy of pseudobrookite may contain \(2R\ln 2\) due to disorder, \(2R\ln 5\) due to magnetic effects, and \(2R\ln 2\) or \(2R\ln 3\) from Schottky effects depending on site distortions and crystal field effects. Because of the inherent uncertainties in the available data, and because of the agreement between the measured entropy data and Navrotsky's calculated entropy, all calculations in this paper will be based on the published entropy data without additions. Accurate low-temperature heat-capacity data are necessary if magnetic effects are to be understood and separated from the potential effects of disorder.

The entropy of ferropseudobrookite was estimated from the approximation (FYFE and VERHOOGEN, 1958):

\[
S^0(\text{Fpb}) = S^0(\text{H}) + S^0(\text{Psb}) - S^0(\text{Hm}) + 2.5\ C^\beta
\]  

Above the Néel point of hematite the \(S\) vs. \(T\) slopes of hematite and ilmenite are parallel. Below this temperature, however, the entropy of hematite changes more rapidly than that of ilmenite. In order to avoid systematic errors in the estimated entropy of ferropseudobrookite, the entropy of hematite below its Néel point was assumed to parallel that of ilmenite, offset by the difference in their entropies at the transition temper-
ature for the estimation. This yields an estimated value of \( S_{\text{Fpb}} = 156.1 \) J/(mol·K). As the entropy of ferropseudobrookite is based on that of pseudobrookite, ferropseudobrookite will also be treated as an ordered compound. As in the case of pseudobrookite, accurate low-temperature heat-capacity data are necessary if the effects of magnetic transitions and potential disorder are to be evaluated. The Gibbs energy at STP \( (AG_{\text{Fpb}}) = -2038.9 \) kJ/mol of ferropseudobrookite was derived from the reversal at 1140°C by HAG-GERTY and LINDSLEY (1969) on the reaction:

\[
\text{Ferropseudobrookite} = \text{Ilmenite} + \text{Rutile} \\
\text{Fe}_{3}\text{TiO}_8 = \text{FeTiO}_3 + \text{TiO}_2. \tag{12}
\]

The result of Haggerty and Lindsey has been chosen because the ferropseudobrookite used appeared to be free of a TiO component, while that of EL GOREY and WOERMANN (1976) contained 13.5 mole percent TiO.

LINDSLEY (1983) noted that calculations in log \( fO_2 - T \) space can be displayed more clearly by plotting the results relative to a standard buffer curve. The position of the hematite-magnetite (HM) buffer:

\[
\text{Magnetite} + O_2 = \text{Hematite} \\
4\text{Fe}_2\text{O}_3 + O_2 = 6\text{Fe}_3\text{O}_4 \tag{13}
\]

has been calculated from the data of ROBINSON et al. (1982). Other reactions will be plotted relative to this buffer. In order to facilitate calculation of the absolute log \( fO_2 \) value from that given here we have fit log \( fO_2 \) for the HM buffer as calculated from ROBINSON et al.'s data to the following equations:

\[
\begin{align*}
\log fO_2 &= -0.39824 \cdot T \\
&+ 0.16378 \cdot T^2 + 0.72703 \cdot 10^{-6} \cdot T^3 \\
&- 18.015 \cdot T^{0.5} - 253.08 \ (298.2-848.5 \ K) \\
\log fO_2 &= -0.21506 \cdot T + 0.49263 \cdot 10^{-6} \cdot T^2 \\
&- 5.6010 \cdot T^{0.5} \ (848.5-955.5 \ K) \\
\log fO_2 &= -0.13949 \cdot T + 0.11822 \cdot 10^{-6} \cdot T^2 \\
&- 8.9815 \cdot T^{0.5} - 167.75 \ (955.5-1700 \ K) \tag{14}
\end{align*}
\]

THE SYSTEM Ti-O

Four minerals have been reported in the system Ti-O: rutile, anatase, brookite, and hongquite. Data of NAVROTSKY and KLEPPA (1967), SCHUILING and VINK (1967), JAMIESON and OLINGER (1968) and MITSUHASHI and KLEPPA (1979) suggests that anatase and brookite are metastable, and they will therefore be excluded from this discussion. An additional phase, TiO-II has been synthesized at high pressures (DACHILLE and ROY, 1962; BENDELLIANI et al., 1966; MCQUEEN et al., 1967; JAMIESON and OLINGER, 1968; DACHILLE et al., 1968, LINDSLEY, 1976) but its stability field has not been well located and no thermodynamic data are available. Hongquite (TiO) has only been reported from one location, associated with platinum ores in garnet hornblende pyroxenites from the Tao district, China (YU et al., 1974; FLEISCHER et al., 1976).
The other phases in the Ti-O system are the Magneli phases, which have the generalized formula $\text{T}_{i+1} \text{O}_{2i+1}$. Thermodynamic data exist for six of these phases: $\text{Ti}_2 \text{O}_3$, $\text{Ti}_3 \text{O}_5$, $\text{Ti}_4 \text{O}_9$, $\text{Ti}_5 \text{O}_{11}$, $\text{Ti}_9 \text{O}_{20}$, and $\text{Ti}_3 \text{O}_{11}$. Entropy data for the last three of these were estimated from $\text{Ti}_3 \text{O}_5$ and rutile, and their Gibbs energies were calculated from the data of ANDERSON and KHAN (1970). As can be seen from its formula, $\text{Ti}_9 \text{O}_{20}$ is not an end-member of the Magneli series, and Anderson and Khan suggest that it is an ordered intergrowth of $\text{Ti}_5 \text{O}_5$ and $\text{Ti}_3 \text{O}_{11}$.

Phase equilibria for this system at 1 bar are shown in Fig. 4. The lower stability of rutile forms the upper limit of reaction in this system. It lies 2.8 log units below iron-wüstite at 1300 K, and 10.6 log units below iron-magnetite at 500 K. The stabilities of $\text{Ti}_5 \text{O}_5$, $\text{Ti}_9 \text{O}_{20}$, and $\text{Ti}_3 \text{O}_{11}$ are not shown in Fig. 4. Calculations based on the data of ANDERSON and KHAN (1970) suggest that $\text{Ti}_5 \text{O}_5$ becomes stable above approximately 1300°C, and that the lower stability limits of $\text{Ti}_9 \text{O}_{20}$ and $\text{Ti}_3 \text{O}_{11}$ lie at temperatures somewhat higher than that. As these temperatures represent long extrapolations of the estimated entropies of these phases, their stability fields cannot be predicted with any accuracy, and they have not been shown.

Most of the reactions shown in Fig. 4 lie well outside of usual terrestrial $f$O$_2$ values (though see ESSENE and FISHER, 1984). Even lunar samples seem commonly to have formed within the stability field of rutile (EL GORESY et al., 1974; MAO et al., 1974). The reported occurrence of hongquite is interesting as the upper limit of its stability as a pure phase lies 10 to 15 log units below iron-wüstite. The hongquite analysis given by YU et al. (1974), $(\text{Ti}_{0.99} \text{Fe}_{0.01})\text{O}$ suggests that solid-solution effects of cations will not account for its stabilization. The upper stability of hongquite at 1000 K lies at log $f$O$_2 = -36.4$. The data of ANOVITZ et al. (in prep.) show that almandine will break down to iron, sillimanite and quartz at log $f$O$_2 = -22.1$ at 1000 K. Thus the activity of almandine in garnet in equilibrium with hongquite can be no larger than log $a_{\text{Alm}} = -22.5$. Therefore, any garnet (and indeed any silicate) in equilibrium with TiO should have only some 10 atoms of Fe per mole of garnet! There is no indication of this in the brief description of silicates associated with hongquite (YU et al., 1974). We suspect that hongquite has been mischaracterized or that it is completely out of equilibrium with its associated minerals. The possibility that hongquite contains a light element other than oxygen, perhaps N or C, should also be evaluated. The unit cell volumes of TiN (osbornite) and TiC are sufficiently close to TiO to suggest that the X-ray patterns of these phases could be confused.

**THE SYSTEM Fe-Ti-O**

Phase relations in the system Fe-Ti-O are shown in Fig. 5 at 1 bar relative to hematite-magnetite. With the exception of the pseudobrookite reactions, the diagram is qualitatively symmetrical about the wüstite field. Reactions above this field are magnetite-bearing equivalents of iron-bearing reactions below it. Figure 5 has been calculated assuming that all phases remain pure end-members. Given the extensive solid-solutions present in magnetite, ilmenite, and pseudobrookite these curves only provide metastable limits on the positions of the actual reactions. Nevertheless, they provide a reference state from which the conditions of formation of phases containing solid-solutions inside and outside of the Fe-Ti-O system can be most easily calculated.

On the basis of a study of Apollo 17 samples EL GORESY et al. (1974) suggested that the reactions:

Ferro pseudobrookite + Ulvöspinel = Ilmenite

$$\text{FeTi}_2\text{O}_5 + \text{Fe}_2\text{TiO}_4 = 3\text{FeTiO}_3$$

Ferro pseudobrookite = Ulvöspinel + Rutile

$$2\text{FeTi}_2\text{O}_5 = \text{Fe}_2\text{TiO}_4 + 3\text{TiO}_2$$

control the stability of ferropseudobrookite in lunar rocks. Calculation of the end-member reactions, however, shows them to be metastable with respect to reaction (12). Lunar samples of magnesian ferropseudobrookite ("armacolite") contain approximately 50 percent replacement of Fe by Mg. In addition, the ulvöspinel reported by EL GORESY et al. are very chromian. The experimental work of LINDSLEY (1975) show that Mg$^{2+}$, Al$^{3+}$, Cr$^{3+}$, and Ti$^{3+}$ partition into ferropseudobrookite over ilmenite and rutile. This suggests that solid-solutions may stabilize reactions (15) and (16) in EL GORESY et al.'s samples.

Pseudobrookite and ferropseudobrookite are rare minerals. Occurrences of pseudobrookite are reported in high temperature contact aureoles (e.g. AGRELL and LANGLEY, 1958; SMITH, 1965; RUMBLE, 1976), oxidized basalts (e.g. HAGGERTY, 1976), and rhyolites and ignimbrites (e.g. DEUTSCH and SOMAYAJULU, 1970;
Lofkin, 1976; Haggerty, 1976). Ferropseudobrookite solid-solutions (armalcolite) are most commonly found as accessory phases in lunar basalts, but several terrestrial occurrences are known. The mineral "iserte" reported by Janovsky (1880) may be the first reported example. Schaller's (1912) analysis of iserte is close to the composition of ferropseudobrookite, but he considered it to be an intergrowth of iron and rutile. Smith (1965) concluded that the material may be ferropseudobrookite, but a reexamination of the sample is necessary to resolve the problem. Other terrestrial occurrences of ferropseudobrookite have been reported by Agrell and Long (1960), Haggerty (1973, 1975, 1983), Cameron and Cameron (1973), Velde (1975), Raber and Haggerty (1979), and Pederson (1979, 1981).

The limited terrestrial occurrences of pseudobrookite can be explained by its instability at low \( f_{O_2} \), low \( T \) and high \( P \). Reactions (10) and (12) calculated as a function of temperature and pressure and contoured for log \( K \) are shown in Fig. 6. Pseudobrookite is stable down to 585°C at 1 bar, but this minimum temperature increases rapidly with pressure. The minimum \( f_{O_2} \) at which pseudobrookite is stable lies slightly below the hematite-magnetite buffer. Thus pseudobrookite should occur only in oxidizing, low pressure, high temperature rocks of appropriate composition.

Ferropseudobrookite occurrences will be even more restricted in terrestrial rocks. While ferropseudobrookite is stable at \( f_{O_2} \) conditions commonly reported for terrestrial rocks, its low-temperature stability limit has a \( dP/dT \) slope (11.8 bars/°C) that is quite flat, similar to that for pseudobrookite (8.9 bars/°C in the hematite field). Unreasonably high temperatures would therefore be necessary to stabilize ferropseudobrookite in most rocks formed at medium to high pressures. The data of Lindley et al. (1974) and Kesson and Lindley (1975) on the magnesian equivalent of reaction (13) suggest a steeper slope of 25 bars/°C. Friel et al. (1977) studied the pressure-temperature stability of an armalcolite (50% Fe/Fe + Mg) and suggested a slope of 50 bars/°C with a 5 kb wide two-phase loop. These data suggest that reaction (12) should have a steeper slope than that found by Friel et al. rather than the flat slope calculated here. The difference may be due to the entropy estimate used for ferropseudobrookite, and clarification awaits careful measurements of its heat-capacity.

Pressure effects cannot, of course, explain the relative rarity of ferropseudobrookite in volcanic rocks. A survey of terrestrial basalts (Basaltic Volcanism Study Project, 1981) suggests that their average \( f_{O_2} \) values lie within ±2 log \( f_{O_2} \) units of the QFM buffer at temperatures of up to 1200°C, well within the stability field of ferropseudobrookite. Bulk composition may be a major controlling factor in the occurrence of ferropseudobrookite in terrestrial basalts.

**THERMOMETRY**

The most widely used application of phase equilibria in the system Fe-Ti-O is undoubtedly magnetite-ilmenite thermometry (Lindley, 1963; Buddington and Lindley, 1964; Spencer and Lindley, 1981). Rumble (1971) and Powell and Powell (1977) noted that the temperatures derived may be represented as the temperature dependence of log \( K \) for the exchange reaction:

\[
\text{Ilmenite + Magnetite} \rightarrow \text{Hematite + Ulvospinel} \\
\text{FeTiO}_3 + \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{Fe}_2\text{TiO}_4, \tag{17}
\]

Once temperature is known, \( f_{O_2} \) may be found from any of the following reactions:

\[
\text{Magnetite} + \text{O}_2 \rightarrow \text{Hematite} \\
4\text{Fe}_2\text{O}_3 + \text{O}_2 \rightarrow 6\text{Fe}_3\text{O}_4, \tag{18}
\]

\[
\text{Ulvospinel} + \text{O}_2 \rightarrow \text{Ilmenite} + \text{Magnetite} \\
6\text{Fe}_2\text{TiO}_4 + \text{O}_2 \rightarrow 6\text{Fe}_3\text{O}_4 + 2\text{Fe}_2\text{O}_3, \tag{19}
\]

\[
\text{Ulvospinel} + \text{O}_2 \rightarrow \text{Ilmenite} + \text{Hematite} \\
4\text{Fe}_2\text{TiO}_4 + \text{O}_2 \rightarrow 4\text{Fe}_3\text{O}_4 + 2\text{Fe}_2\text{O}_3, \tag{20}
\]
Reaction (17) is extremely sensitive to values and equation used for the various thermodynamic parameters, as are most exchange reactions. Until these values are accurately known it is not possible to calibrate a thermometer in this manner without careful experiments.

The problem may be reformulated by noting that any two of reactions (18), (19), and (20) represent independent equations in \( \log K \), the third being the sum of the first two. At fixed \( f_{O_2} \) and temperature these represent two equations in four unknowns as:

\[
\log K(18) = 6 \log (a_{\text{hm}}) - 4 \log (a_{\text{mb}}) - \log f_{O_2} \tag{21}
\]

\[
\log K(19) = 6 \log (a_{\text{al}}) + 2 \log (a_{\text{bm}}) - 6 \log (a_{\text{mb}}) - \log f_{O_2} \tag{22}
\]

\[
\log K(20) = 4 \log (a_{\text{al}}) + 2 \log (a_{\text{al}}) - 4 \log (a_{\text{al}}) - \log f_{O_2}. \tag{23}
\]

If activity-composition relations are known along the magnetite-ulvöspinel and ilmenite-hematite joins the problem becomes one of four equations in four unknowns which may be solved explicitly. This approach may be used to formulate mixing models the problem is non-linear and must be solved numerically.

This analysis may be extended to the system pseudobrookite-ferropseudobrookite vs. ilmenite-hematite. The following reactions control the solid-solutions of the coexisting phases:

Pseudobrookite + Ilmenite

\[
\text{Fe}_2\text{TiO}_4 + \text{FeTiO}_3 = \text{Fe}_2\text{Ti}_2\text{O}_5 + \text{Fe}_2\text{O}_3 \tag{24}
\]

Ilmenite + \( O_2 \)

\[
\text{Fe}_2\text{TiO}_3 + \text{O}_2 = 2\text{Fe}_2\text{Ti}_2\text{O}_5 + 2\text{FeTi}_2\text{O}_5 \tag{25}
\]

Ilmenite + \( O_2 \) = Hematite + Ferropseudobrookite

\[
8\text{FeTiO}_3 + \text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{FeTi}_2\text{O}_5 \tag{26}
\]

Hematite + Ilmenite + \( O_2 \) = Pseudobrookite

\[
2\text{Fe}_2\text{O}_3 + 4\text{FeTi}_2\text{O}_5 + \text{O}_2 = 4\text{Fe}_2\text{Ti}_3\text{O}_5 \tag{27}
\]

Hematite + Ferropseudobrookite + \( O_2 \)

\[
6\text{Fe}_2\text{O}_3 + 4\text{FeTi}_2\text{O}_5 + \text{O}_2 = 8\text{Fe}_2\text{Ti}_3\text{O}_5. \tag{28}
\]

Reactions (25) and (26) were arbitrarily chosen for obtaining the solution. The model of SPENCER and LINDSLEY (1981) was used for the hematite-ilmenite solution, and ferropseudobrookite-pseudobrookite solutions were assumed to be ideal, where \( X_{\text{pb}} = X_{\text{fe}} - 1 = a_{\text{pb}}, \) and \( X_{\text{pfb}} = 1 - a_{\text{pb}} \). GREY and MERRITT (1981) suggest that pseudobrookite solid-solutions are significantly non-ideal, but their data are insufficient to allow formulation of a more accurate model. Reactions (25) and (26) have been fit to the equations:

\[
\log K(25) = 2.3571 \cdot 10^4/T(\text{K}) - 0.14081 \cdot P(\text{kb}) - 10.4861 (\pm 0.07) \tag{29}
\]

\[
\log K(26) = 2.3237 \cdot 10^4/T(\text{K}) - 0.13930 \cdot P(\text{kb}) - 10.5260 (\pm 0.07). \tag{30}
\]

If more accurate models for either solid-solution become available the results (Figs. 7 and 8) may be recalculated using these equations.

The region of \( \Delta \log f_{O_2} - T \) space covered by this thermometer is shown in Fig. 7. As expected, pseudobrookite and hematite solutions dominate at high \( f_{O_2} \) values, and ferropseudobrookite-ilmenite compositions at low \( f_{O_2} \). Unfortunately, this thermometer allows large temperature variations with small changes in composition. Thus temperatures obtained from this calibration will be inaccurate, and it will be most useful as an oxygen barometer. The position of the hematite-ilmenite solvus is calculated from the SPENCER and LINDSLEY (1981) solution model. The top of the solvus lies just below 700°C, in agreement with the data of BURTON (1982, 1984) and of ESSENE et al. (1983). The stability of the assemblage ferropseudobrookite-ilmenite, is limited by reaction (12), which represents the lower bound to the region of applicability of this system to oxygen-barometry/thermometry (Fig. 7).
FIG. 8. Temperature and log $f\text{O}_2$ estimates for samples from Iceland and Hawaii reported by HAGGERTY (1971) and ANDERSON and WRIGHT (1972) respectively. Contours show the effects of $\pm 2$ (solid field) and $4$ mole percent (hachured field) errors in the estimated mole fractions of ilmenite and ferropseudobrookite.

The calibration in Fig. (7) must be regarded as preliminary. An experimental calibration, similar to that for the magnetite-ilmenite thermometry is necessary to refine the model. Outside of the direct uses of this oxygen-bometer/thermometer, such a calibration would serve to provide an independent check on the activity/composition models of SPENCER and LINDSLEY (1981). Errors in their magnetite-ulvöspinel model may be tied to errors in their ilmenite-hematite model in such a way that they reproduce the data but are incorrect if applied to one sol ation in the absence of the other (SPENCER and LINDSLEY, 1981). Simultaneous modeling of both the magnetite-ilmenite and pseudobrookite-hematite thermometers should yield more precise activity/composition models for ilmenite-hematite solutions, especially for hematite-rich compositions where calculations for Fig. 7 necessitated extrapolation of Spencer and Lindsley's model outside of the composition range to which it was fitted.

Unpublished experimental data (LINDSEY, written commun., 1984) on the effects of solid-solution along the join ferropseudobrookite-ilmenite, showed that the model of ANDERSON and WRIGHT (1972) agrees with their calculations. The four experiments in which the three-phase assemblage $\text{Fpb}_\text{m} - \text{Ilm}_\text{m} - \text{Ru}$ is stable fall nicely within the three-phase field suggested by Fig. 7. A fourth experiment, however, at $750^\circ\text{C}$ showed the three-phase assemblage stable at $X_{\text{Fpb}} = 0.7$, while our calculations would limit this assemblage to compositions between $X_{\text{Fpb}} = 0.77$ and $X_{\text{Ilm}} = 0.95$. Because of the low angle of intersection of the isopleths with the "limit" curve, small errors in the position of either could account for the discrepancy.

As noted above, the solution of the equations leading to Fig. 7 requires that the activity of ferropseudobrookite is known at a given temperature and activity of pseudobrookite. In our model $a_{\text{Fpb}} = X_{\text{Fpb}}$ and $a_{\text{Pb}} = X_{\text{Pb}}$ and therefore $a_{\text{Fpb}} = 1 - X_{\text{Pb}}$. If pseudobrookite solid-solutions exhibit a positive deviation from ideality, $a_{\text{Fpb}} > X_{\text{Fpb}}$, $a_{\text{Pb}} > X_{\text{Pb}}$ and $a_{\text{Pb}} > 1 - a_{\text{Pb}}$. This would stabilize the three-phase assemblage over the $X_{\text{Fpb}}$ field relative to the positions of these fields calculated from the ideal model, bringing the calculated results into better agreement with Lindsley's experimental data.

The effects of pressure may be calculated from Eqs. (24) and (25). For the pseudobrookite-hematite thermometer, temperature increases approximately $10^\circ\text{C}$/kbar and log $f\text{O}_2$ increases approximately $0.16$ log units/kbar over a $10$ kbar pressure range. If rutile is present pressure may be determined from the assemblage rutile + pseudobrookite + hematite. Contours of log $K$ for reactions (10) and (12) are shown in Fig. (6). The $P/T$ conditions for this assemblage must lie along one of these contours. Initial pressure and temperature estimates may be obtained from Figs. 6 and 7 and corrected by an iterative procedure. Because relatively small changes in log $K$ for reactions (10) and (12) have large effects on the calculated pressures, the results obtained may not be very accurate, but pressure ranges of $\pm 1-2$ kbars should be obtainable.

APPLICATIONS

The magnetite-ilmenite thermometer/oxygen-bometer of BUDDINGTON and LINDSLEY (1964) and SPENCER and LINDSLEY (1981) has gained wide recognition through successful application to a wide variety of igneous and metamorphic rocks. Other assemblages may also yield information on the $f\text{O}_2$-$I'$ state of rocks. Applications involving the assemblages pseudobrookite-hematite and ferropseudobrookite-ilmenite will be considered below. Appropriate analyses from the references cited are listed in Table 5.

Ferropseudobrookite-ilmenite

The assemblage ferropseudobrookite + ilmenite + rutile has been reported from Apollo 17 samples (EL GORESY et al. 1974: MAO et al. 1974). As noted by MAO et al., this assemblage must lie on the reaction:

$$\text{FeTi}_2\text{O}_5 + \text{Fe} + 1/2\text{O}_2 = \text{FeTiO}_3 \quad (31)$$

and on reactions (12) and (32):

$$\text{Rutile} + \text{Fe} + 1/2\text{O}_2 = \text{FeTiO}_3 \quad (32)$$

SATO et al. (1973) experimentally calibrated reactions (31) and (32), and found that they intersect at approx-
System Fe-Ti-O

Table 4. Formulas of Iron-Titanium Oxides from the Literature

<table>
<thead>
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<th>Phase</th>
<th>FeO</th>
<th>MnO</th>
<th>FeTiO3</th>
<th>TiO2</th>
<th>FeTiO2</th>
<th>MgO</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>Cr2O3</th>
<th>ZrO2</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>P2O5</th>
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(1-2) El Goresy et al. (1974); (3-4) Meyer and Rook (1972); (5-6) Pedersen (1981); (7-8) Anderson and Wright (1972); (9) Haggerty (1972).

Imatimately 1025°C rather than at 1140°C as suggested by the data of Haggerty and Lindsley (1969). This discrepancy may result from the very low angle of intersection of these reactions, or from the presence of a TiO2 component in the ferrous pseudobrookite used in SATO et al.'s experiments. Indeed, SIMONS and Woermann (1978) suggest that at these temperatures equilibrium ferrous pseudobrookite contains significant TiO2. Without a direct measurement on SATO et al.'s materials, however, no correction may be attempted.

Assuming that the four phases reported by MAO et al. (1974) represent an equilibrium assemblage, they can be used to fix fO2 and T. As MAO et al. give no analyses, compositions must be estimated from other work on material from the Apollo 17 collections. Rutile and native iron are assumed to be pure, and ferrous-pseudobrookite and ilmenite analyses were taken from the average grey armalcolite and primary ilmenite analyses reported by EL GORESY et al. (1974). The data of LINDSLEY et al. (1974) and KESSON and LINDSLEY (1975) suggest that this assemblage equilibrated at approximately 925 ± 25°C at 1 bar. Assuming ideal mixing, log fO2 = -14.7, approximately 11 log units below hematite-magnetite. LINDSLEY et al. (1974) and HAGGERTY (1983) note that the rutile in armalcolite + ilmenite + rutile assemblages may be due to subsolidus reequilibration, and thus the temperature and fO2 conditions calculated above probably represent a point in the cooling history of the rock, rather than the crystallization conditions.

A similar assemblage, ilmenite + armalcolite + rutile + iron is reported from a dacite (sample GGU 176466, rock C) from Disko Island, Greenland (PEDERSON, 1981). The data of LINDSLEY et al. (1974) and of KESSON and LINDSLEY (1975) suggest a temperature of equilibration for this sample of approximately 950 ± 50°C. The large inferred error is due to the uncertain effects of Al11, Cr31, and Ti41 solid-solutions. This temperature is well below what Pederson infers from coexisting pyroxenes, and suggests that this assemblage equilibrated during subsolidus cooling. Assuming ideal mixing as before, log fO2 = -17.5, 10.7 log units below hematite-magnetite.

MEYER and DOCTOR (1974) report the assemblage ulvöspinel + ilmenite + iron in rock 75035 (Apollo 17) which represents the reaction:

$$\text{Ulvöspinel} + \text{Ilmenite} + \text{Iron} = \text{FeTiO}_3 + \text{Fe} + \frac{1}{2}\text{O}_2$$

(33)

While this reaction does not permit temperatures to be calibrated, it fixes fO2 for this rock as a function of temperature. Reaction (33) yields:

$$\log K(33) = \log (\alpha_\text{Fe} \cdot \alpha_\text{FeTiO}_3) + \log f_\text{O}_2.$$  

(34)

For the compositions given by MEYER and DOCTOR (1974, Table 6):

$$\log (\alpha_\text{Fe} \cdot \alpha_\text{FeTiO}_3) = 0.03$$

(35)

assuming ideal mixing. This implies that the rock equilibrated at fO2 conditions nearly identical to those calculated from reaction (33) (Fig. 5).

**Pseudobrookite-hematite**

HAGGERTY (1971) graphically reports analyses for two pseudobrookite-hematite pairs in a specimen of Icelandic basalt. A sharp difference in the slopes of the reported tie-lines suggests different temperatures of equilibration or analytical errors. Haggerty notes that submicroscopic exsolutions of rutile make the reported analyses at best qualitative, which may account for the scatter in the tie-lines. Taking the most similar slopes allowed by the error brackets, the pseudobrookite-hematite geothermometer yields T = 900°C and fO2 1.5 log units below hematite-magnetite for the more ferrous pair, and T = 880°C, fO2 0.8 log units below HM for the more ferric pair.

**ANDERSON and WRIGHT (1972)** report the assemblage ilmenite + pseudobrookite + magnetite in a basalt from Kilauea, Hawaii. While this cannot be an equilibration assemblage in the Fe-Ti-O system, it is probably stabilized by additional components. This assemblage allows the pseudobrookite-hematite system to be compared with the magnetite-ilmenite system. The magnetite-ilmenite pairs yield temperatures of 1100°C and $\Delta \log f_\text{O}_2 = -5.0$, while the pseudobrookite-hematite pairs yield 900°C and $\Delta \log f_\text{O}_2 = -3.0$. The source of this discrepancy remains unclear. The compositions of some of the oxide grains may have reset on cooling of the rock, the effects of solid-solutions outside of the Fe-Ti-O system may not
have been properly accounted for, or there may be errors in the calculations used.

Small analytical errors may lead to large errors in the temperatures calculated from pseudobrookite-
hematite or ferropseudobrookite-hematite pairs. A

A good microprobe analysis with errors of ±2 percent of the amount present for the major elements Fe and Ti yields errors of 1 to 4 mole percent in the estimated mole fractions of ilmenite and ferropseudobrookite. Figure 8 shows the effects of variations of ±2 (solid shading) and 4 mole percent (hachured field) on the calculated temperature and \( \Delta \log f_O \). While \( \Delta \log f_O \) varies by less than ±0.5 log units, temperature may vary by several hundred degrees. A typical mag- netite/ilmenite pair (sample SR-31, BOHLEN and ES- SENE, 1977), which yields a temperature of 690°C from the SPENCER and LINDSLEY (1981) thermometer, has an error of ±100°C and ±1 log unit \( \Delta \log f_O \) with a ±2 mole percent error in the measured ilmenite and magnetic compositions. Users of either thermometer should therefore be careful to evaluate the potential effects of analytical errors on the results obtained.

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