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 ($FeTiO_3$) from 5 to 1000 K. These measurements yield $S^0_{298} = 108.9$ J/(mol·K). Calculations from published experimental data on the reduction of ilmenite yield $\Delta G^0_{298}(II) = -1153.9$ 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 fO_2 are necessary to stabilize TiO, the mineral hongquiite reported from the Tao district in China. This mineral may not be TiO, 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 ferropseudobrookite-pseudobrookite$_{ss}$ and hematite-ilmenite$_{ss}$. 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, $FeTiO_3$, 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 Fe_2O_3, TiO_2, 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 ¼ 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 Fe_2O_3 in our sample or Ti_2O_3 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 Fe^{3+}. Samples of 70–90 mg were used with a 10 m Ci ^{57}Co in Pd source. Duplicate spectra were recorded in 512 channels of a multichannel analyzer using a velocity increment of 0.03 mm per channel. Counting times were sufficient to obtain several million counts per channel and peak dips of approximately 10^5 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 Fe^0) and quadrupole splitting (IS = 1.058 mm/sec; Qs = 0.637 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 Fe^{3+} in other similar Fe phases in order to obtain

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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 Fe^{3+}. 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 even after 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 Fe^{3+}. 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 5 to 350 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 cm^3 and an axial entrant 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-type platinum resistance thermometer (A-5) calibrated by the National Bureau of Standards and referred to the IPTS-48 temperature scale (STIMSON, 1961) above 90.18 K and the NBS 1955 provisional scale at lower temperatures was used for temperature measurements.

A molar mass of 151.7452 g, corresponding to the formula $FeTiO_3$ was used to calculate the apparent molar heat-capacity. Measured heat-capacity values were corrected for the heat-capacity of the empty calorimeter, which was measured separately, and for the differences in helium content between the empty and loaded calorimeter. Data are presented in Table 1.

Heat-capacities from 340 to 1000 K were measured with a Perkin-Elmer differential scanning calorimeter (model DSC-2) in R. A. Robie and B. S. Hemingway's laboratory at the U.S. Geological Survey in Reston, Virginia. A 31.952 mg sample was measured as described by HEMINGWAY et al. (1981). Experimental and smoothed results are listed in Tables 2 and 3.

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 STICKLER 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 Ti_2O_3 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 $MnTiO_3$ (pyrophanite; STEPHENSON and SMITH, 1968). The C_p (lattice) function for $MnTiO_3$ was adjusted for mass and volume following the Lindemann relation:

$$\Theta_T = B\left[\frac{T_m}{MV^{2/3}}\right]^{1/2} \quad (1)$$

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:

$$\frac{\Theta_T^{(II)}}{\Theta_T^{(Pyro)}} = \left[\frac{T_m(II)}{T_m(Pyro)}\right]^{1/2} \cdot \left[\frac{M(Pyro)}{M(II)}\right]^{1/2} \cdot \left[\frac{V(Pyro)}{V(II)}\right]^{1/3}. \quad (2)$$

The melting points of $FeTiO_3$ and $MnTiO_3$ are poorly known,

Table 1: Unsmoothed low-temperature Heat Capacity data

T (K)	Cp (J/(mol·K))	T (K)	Cp (J/(mol·K))	T (K)	Cp (J/(mol·K))
Series 1		196.35	78.09	15.14	1.06
260.84	93.82*	206.60	80.80	16.31	1.31
270.91	93.74	216.67	83.34	17.66	1.59
Series 2		Series 7		19.09	2.04
258.60	86.29	47.61	24.24*	20.61	2.56
272.36	95.77	51.78	30.32*	22.45	3.23
Series 3		55.27	35.95*	24.48	4.15
130.72	54.29	55.75	36.81	26.58	5.22
139.48	57.98	56.25	37.91	28.92	6.63
148.32	61.58	56.36	38.95*	31.27	8.67
157.29	64.98	56.66	39.61	34.71	10.97
166.50	68.51	Series 8		37.95	4.82
176.19	71.88	54.09	33.53*	41.44	17.38
Series 4		54.61	34.57	45.07	21.2?
55.50	36.13	55.12	35.57	48.87	15.80*
59.95	25.80	Series 9		52.13	30.30*
64.93	25.26	208.65	81.35	55.07	35.39*
70.10	26.75	219.65	83.94	55.57	36.19*
76.16	29.27	229.50	86.63	56.07	37.46*
84.44	33.35	239.60	89.12	56.55	39.11*
Series 5		249.57	91.17	57.02	40.30*
50.96	28.59*	259.93	93.26	57.49	38.20*
52.48	30.86	270.68	95.29	57.99	30.26*
53.91	33.34*	281.28	97.44	58.51	26.58*
55.26	35.93*	291.70	99.25	59.04	25.61*
56.54	39.09*	302.10	100.81	59.57	25.05
57.78	34.08*	312.31	102.26	60.10	24.80*
59.12	25.40	322.42	104.00	60.62	24.74
Series 6		332.46	106.11	Series 12	
57.83	32.06*	342.38	111.34	56.14	37.63*
63.40	24.96*	Series 10		56.32	38.27*
69.20	26.50	5.32	0.34*	56.51	38.89*
75.55	29.00	7.24	0.09*	56.54	39.76*
82.65	32.46	8.66	0.14*	56.87	39.78*
91.00	36.41	9.89	0.36	57.05	40.17*
86.48	34.33	Series 11		57.23	40.54
96.33	38.75	5.33	0.01*	57.41	39.22
106.51	43.41	6.81	0.00*	57.59	36.70
115.93	47.77	7.72	0.00*	57.78	32.83
124.80	51.64	8.49	0.02*	57.98	29.88
132.78	55.15	9.16	0.02	58.17	27.73
142.50	59.17	9.91	0.28	56.12	30.87
152.83	63.31	10.80	0.47	Series 13	
163.83	67.44	11.88	0.55	54.44	33.07*
175.02	71.38	12.91	0.69		
185.83	74.96	13.91	0.84		

* Data not fitted to smoothed curve

and depend on fO_2 (LEVIN et al., 1969; LINDSLEY, 1976). Because T_m for $FeTiO_3$ and $MnTiO_3$ are similar, they will be ignored. Using mean atomic weights and molar volumes from ROBIE et al. (1978) this yields:

$$\frac{\Theta_T^{(II)}}{\Theta_T^{(Pyro)}} = 1.00834 \quad (3)$$

The lattice heat-capacity of ilmenite is obtained by taking the estimated lattice C_p of pyrophanite at some temperature T_1, multiplying T_1 by 1.00834, and using the resulting (C_p, T_2) as the C_p model for ilmenite. The derived C_p (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.

Non-lattice heat-capacity (excess heat-capacity) is caused by magnetic and electronic disordering. To calculate the total excess entropy S^{ex}, C_p vs. T was integrated using the Simpson 3-point method. For convenience in our calculations, below 20 K C_p^{ex} was assumed to follow the relation (LYON and WESTRUM, 1974):

$$C_p^{ex} = T^3 \quad (4)$$

which yields:

$$S^0(20) - S^0(0) = 1/3 C_p (20 \text{ K}) = 0.63 \text{ J/(mol·K)}. \quad (5)$$

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 to 300 K. These calculations yield $S^{ex} = 19.12$ J/(mol·K).

The magnetic contribution to excess entropy derives from disorder of magnetic moments of Fe atoms as the Néel tran-

Table 2. Experimental high-temperature heat capacities (DSC) for ilmenite

T	c_p	T	c_p	T	c_p
K	J/(g·K)	K	J/(g·K)	K	J/(g·K)
Series 1		Series 4		Series 8	
340.2	0.6902	659.4	0.8291	819.1	0.8649
360.2	0.7091	679.4	0.8306	829.0	0.8669
380.1	0.7275	699.3	0.8349	839.0	0.8716
400.0	0.7426	719.3	0.8400	848.0	0.8721
420.0	0.7553	739.3	0.8454		
440.0	0.7657	748.2	0.8473	Series 9	
459.9	0.7751				
		Series 5		868.9	0.8780
Series 2				878.9	0.8828
		659.4	0.8330	888.9	0.8838
420.0	0.7566	679.4	0.8332	897.9	0.8834
440.0	0.7669	699.3	0.8378		
459.9	0.7756	719.3	0.8429	Series 10	
479.9	0.7831	739.3	0.8492		
499.8	0.7901	748.2	0.8510	928.8	0.8906
519.8	0.7965			938.8	0.8918
539.7	0.8041	Series 6		947.8	0.8944
548.7	0.8069				
		769.2	0.8603	Series 11	
Series 3		798.1	0.8649		
				968.7	0.8966
519.8	0.7933	Series 7		978.7	0.9033
539.8	0.8023			988.7	0.8999
559.7	0.8090	769.2	0.8512	997.5	0.9004
579.6	0.8142	798.1	0.8559		
599.6	0.8207				
619.5	0.8245				
639.5	0.8257				
648.5	0.8288				

sition is crossed (GOPAL, 1966). For $FeTiO_3$, which has one iron atom per mole, the total molar entropy from this transition is:

$$S^{ex}_{mag} = R \ln 5 = 13.39 \text{ J/(mol·K)}. \qquad (6)$$

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 $3t_{2g}$ orbitals into a lower energy pair (d_{xz} and d_{yz}) and a higher energy orbital (d_{xy}). 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:

$$S^{ex}_{Schottky} = R \ln 2 = 5.76 \text{ J/(mol·K)}. \qquad (7)$$

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) shows that 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^0_{298} (108.9 J/(mol·K)) is 3.0 J greater 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 (TiO_2), hongquiite (TiO), the Magneli phases Ti_2O_3, Ti_3O_5, Ti_4O_7, Ti_5O_9, $Ti_{11}O_{20}$, and Ti_6O_{11}, hematite (Fe_2O_3), magnetite (Fe_3O_4), wüstite ($Fe_{0.947}O$), ilmenite ($FeTiO_3$), ulvöspinel (Fe_2TiO_4), pseudobrookite (Fe_2TiO_5), and ferropseudobrookite ($FeTi_2O_5$). All calculations assume that these phases have stoichiometric cation/anion ratios. Possible non-

Table 3: Smoothed High-Temperature Thermochemical Data for Ilmenite ($FeTiO_3$)

Temp.	Heat Capacity	Entropy	Enthalpy Function	Gibbs Energy Function	Gibbs Energy of formation
T	c_p	$S^0_T - S^0_0$	$(H^0_T - H^0_{298})/T$	$-(G^0_T - H^0_{298})/T$	ΔG^{elem}_f
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	kJ/mol
298.15	99.15	108.9	0.000	108.9	-1153.9
300	99.44	109.5	0.612	108.9	-1153.4
350	106.3	125.3	15.241	110.1	-1140.6
400	111.6	139.4	26.965	112.9	-1127.8
450	115.8	153.3	36.609	116.7	-1115.1
500	119.2	165.7	44.701	121.0	-1102.5
550	122.0	177.2	51.602	125.6	-1090.0
600	124.3	187.9	57.566	130.3	-1077.6
650	126.3	197.9	62.780	135.1	-1065.2
700	128.1	207.3	67.358	139.9	-1052.9
750	129.7	216.2	71.489	144.7	-1040.6
800	131.2	224.6	75.176	149.5	-1028.4
850	132.6	232.5	78.514	154.1	-1016.2
900	134.0	240.3	81.558	158.7	-1004.0
950	135.3	247.5	84.353	163.2	-991.9
1000	136.7	254.5	86.936	167.6	-979.7

$$c_p \text{ (J/g·K)} = 1.73094 - 5.2713 \cdot 10^{-4} \cdot T + 2.2325 \cdot 10^{-7} \cdot T^2$$
$$- 16.725 \cdot T^{-0.5} + 2522 \cdot T^{-2}$$

Table 4. Smoothed low-temperature thermodynamic data

T	C_p	$S^o_T-S^o_0$	$(H^o_T-H^o_0)/T$	$-(G^o_T-H^o_0)/T$
K	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/(mol·K)
5	(0.04)	(0.013)	(0.05)	(0.004)
10	0.31	0.10	0.79	0.025
15	1.02	0.35	3.92	0.088
20	2.33	0.81	12.04	0.205
25	4.41	1.54	28.55	0.393
30	7.35	2.59	57.57	0.669
35	11.21	4.00	103.6	1.038
40	15.85	5.79	171.0	1.515
45	21.51	7.96	263.2	2.109
50	27.30	10.49	383.9	2.816
57.25	40.54	14.96	624.2	4.058
65	25.25	18.30	827.7	5.573
70	26.75	20.23	957.4	6.552
80	31.12	24.07	1245	8.502
90	35.93	28.02	1581	10.45
100	40.60	32.05	1964	12.41
110	45.09	36.13	2392	14.38
120	49.51	40.24	2866	16.36
130	53.87	44.38	3383	18.35
140	58.15	48.23	3943	20.36
150	62.26	52.68	4545	22.38
160	66.15	56.83	5183	24.40
170	69.75	60.95	5867	26.43
180	73.05	65.02	6581	28.46
190	76.11	69.04	7327	30.49
200	78.99	73.01	8102	32.52
210	81.71	76.94	8906	34.53
220	84.27	80.79	9736	36.56
230	86.73	84.60	10591	38.56
240	89.08	88.37	11470	40.56
250	91.25	92.05	12372	42.55
260	93.34	95.65	13295	44.52
270	95.20	99.20	14238	46.48
273.15	95.85	100.33	14539	47.09
280	97.11	102.72	15200	48.43
290	98.91	106.15	16181	50.39
298.15	100.25	108.91	16992	51.92
300	100.54	109.54	17178	52.27
310	102.05	112.84	18191	54.17
320	103.47	116.11	19218	56.09
330	105.44	119.33	20262	57.93
340	109.62	122.55	21334	59.78

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 SLAUGHTER 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 SCHMALZREID, 1964; LEVITSKII et al., 1969, 1970; TAYLOR et al., 1972; SATO et al., 1973; MERRITT and TURNBULL, 1974; SAHA and BIGGAR, 1974; SIMONS and WOERMANN, 1978) on the reaction (Fig. 2):

Ilmenite = Iron + Rutile + O_2

$$FeTiO_3 = Fe + TiO_2 + 1/2O_2. \qquad (8)$$
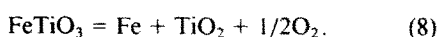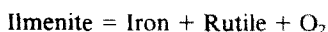
The calculated position of the reaction fits the exper-

imental data well, except for the data of TAYLOR et al. (1972). As the amount of Ti_2O_3 component present in the experimental ilmenites is in most cases unknown, no correction for its effects could be made, and they were assumed to be minimal. The calculated Gibbs energy of formation is -1153.9 kJ/mol at STP (1 bar and 298.15 K). This value is 5.9 kJ/mole smaller than that reported by ROBIE et al. (1978).

The S^0_{298} value for ulvöspinel (titanomagnetite) (KELLEY and KING, 1961; 168.9 J/(mol·K)) and used by ROBIE et al. (1978) contained $R \ln 2$ added as "an allowance for randomness in the structure". This is half the additional entropy expected from total disorder of iron and titanium over two octahedral sites, an arbitrary choice (KELLEY and KING, 1961). This was removed, and calculations were performed for both totally ordered and totally disordered ulvöspinel. Figure 3 shows experiments (SCHMAL et al., 1960; NOVOKHATSKII et al. 1966; WEBSTER and BRIGHT, 1966; TAYLOR et al., 1972; LEVITSKII et al., 1972; SATO et al., 1973; SAHA and BIGGAR, 1974; MERRITT and TURNBULL, 1974; SIMONS and WOERMANN, 1978) on the reaction:

Ulvöspinel = Ilmenite + Iron + O_2

$$Fe_2TiO_4 = FeTiO_3 + Fe + 1/2O_2 \qquad (9)$$
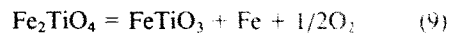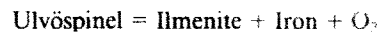
Derived values for the Gibbs energies of ordered and disordered ulvöspinel at STP are -1413.9 kJ/mol and -1402.8 kJ/mol respectively. The differences between the calculations for ordered (solid line) and disordered (dashed line) ulvöspinel are small (Fig. 3). Only results for the ordered phase will therefore be considered in further calculations.
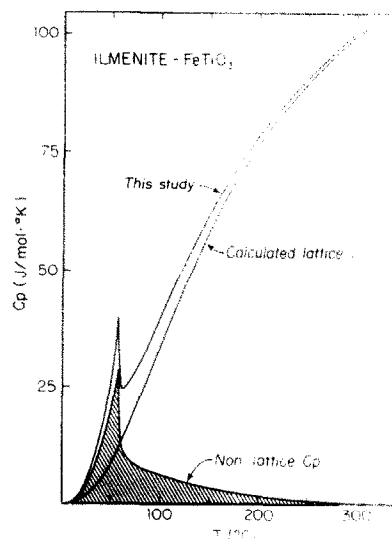

FIG. 1. Heat capacity of ilmenite as a function of temperature from 0 to 300 K. The measured heat capacity, as well as calculated lattice and non-lattice contributions are shown. The shaded area was integrated to obtain non-lattice contributions to the total entropy.

TABLE 5: Sources of data used in the calculations presented here

PHASE	FORMULA	ABR	VOL	TEXP	COMP	S	ΔG
α-Iron	Fe	α-Fe	1	1	1	1	1
γ-Iron	Fe	γ-Fe	1	1	1	1	1
α-Titanium	Ti	α-Ti	2	3	4	2	2
β-Titanium	Ti	β-Ti	2	3	4	2	2
α-Hematite	Fe_2O_3	α-Hm	1	1	1	1	1
β-Hematite	Fe_2O_3	β-Hm	1	1	1	1	1
α-Magnetite	Fe_3O_4	α-Mt	1	1	1	1	1
β-Magnetite	Fe_3O_4	β-Mt	1	1	1	1	1
Wüstite	$Fe_{0.947}O$	Wu	1	1	1	1	1
Ti_2O_3	Ti_2O_3	Ti_2O_3	-	-	-	2	2
Ti_3O_5	Ti_3O_5	Ti_3O_5	-	-	-	2	2
Ti_4O_7	Ti_4O_7	Ti_4O_7	-	-	-	2	2
Ti_5O_9	Ti_5O_9	Ti_5O_9	-	-	-	5*	6
$Ti_{11}O_{20}$	$Ti_{11}O_{20}$	$Ti_{11}O_{20}$	-	-	-	5*	6
Ti_6O_{11}	Ti_6O_{11}	Ti_6O_{11}	-	-	-	5*	6
Rutile	TiO_2	Ru	2	3	4	2	2
Ulvöspinel(Ord)	Fe_2TiO_4	Uv	2	7	7	2*	5
Ulvöspinel(Dis)	Fe_2TiO_4	Uv	2	7	7	2*	5
Ilmenite	$FeTiO_3$	Il	5	8	4	5	5
Pseudobrookite	Fe_2TiO_5	Psb	2	9	9	2	5
Ferropseudobrookite	$FeTi_2O_5$	Fpb	10	9	9	5*	5

1) Robinson et al. (1982), 2) Robie et al. (1978), Skinner (1966),
4) Birch (1966), 5) This study, 6) Anderson and Khan (1970),
7) Compressibility set equal to that of magnetite, 8) Thermal
expansion set equal to hematite, 9) Thermal expansion and
compressibility set equal to that of ulvöspinel, 10) Lindsley et
al. (1974). VOL = molar volume, TEXP = thermal expansion, COMP =
compressibility, S = entropy, ΔG = Gibbs' free energy. *) see text.

The Gibbs energy of pseudobrookite was derived from the reversal by HAGGERTY and LINDSLEY (1969) on the reaction:
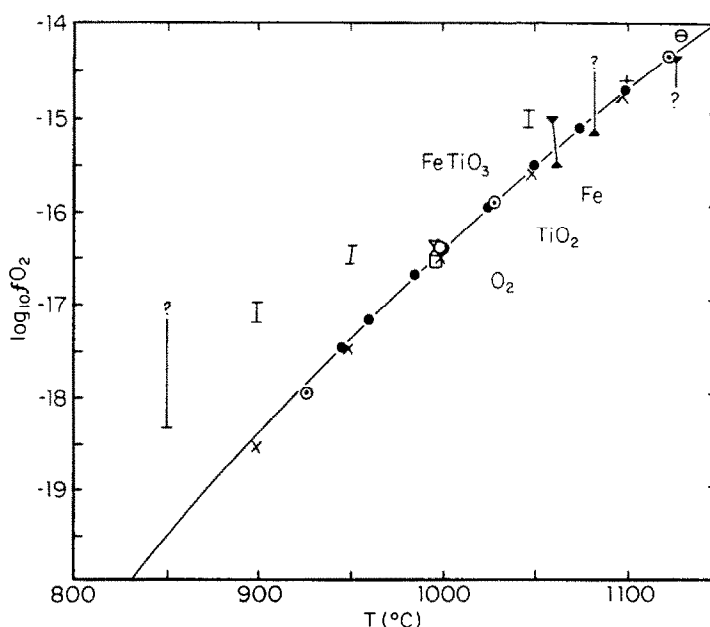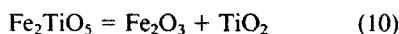
Pseudobrookite = Hematite + Rutile

$$Fe_2TiO_5 = Fe_2O_3 + TiO_2 \qquad (10)$$

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 Lindsley, 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):

$$S^0(Fpb) = S^0(Il) + S^0(Psb) - S^0(Hm) + 2.5V^0. \qquad (11)$$

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-
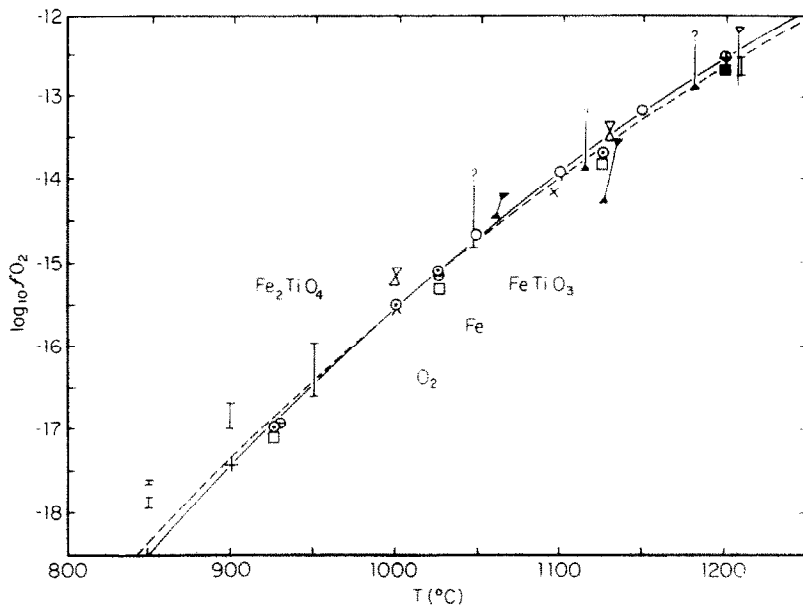

FIG. 2. Experimental data on the reaction Il = Fe + Ru + O_2: (●) SHOMATE et al. (1946), H_2-H_2O; (□) LENEV and NOVOKHATSKII (1964), CO-CO_2; (+) TAYLOR and SCHMALZREID (1964), emf; (×) LEVITSKII et al. (1969), CO-CO_2; (⊙) LEVITSKII et al. (1970), emf; (l) TAYLOR et al. (1972), CO-CO_2; (○) SATO et al. (1973), buffer unknown; (⊖) MERRITT and TURNBULL (1974), emf; (⵶) SAHA and BIGGAR (1974), H_2-CO_2; (⵶) SIMONS and WOERMANN (1978), CO-CO_2. The solid line represents the calculated position of this reaction.

FIG. 3. Experimental data on the reaction Uv = Il + Fe + O_2; (Θ) SCHMAL et al. (1960), CO-CO_2; (+) TAYLOR and SCHMALZREID (1964), emf; (■) WEBSTER and BRIGHT (1966), CO-CO_2; (□) NOVOKHATSKII et al. (1966), CO-CO_2; (I) TAYLOR et al. (1972), CO-CO_2; (O) SATO et al. (1973), buffer unknown; (X) MERRITT and TURNBULL (1974), emf; (⚡) SAHA and BIGGAR (1974), H_2-CO_2; (⊙) LEVITSKII et al. (1972), emf; (⚡) SIMONS and WOERMANN (1978), CO-CO_2. The solid line refers to ordered ulvöspinel, and the dashed line to disordered ulvöspinel.

ature for the estimation. This yields an estimated value of S^0_{298}(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 (ΔG^0_{298}(Fpb)) = −2038.9 kJ/mol) of ferropseudobrookite was derived from the reversal at 1140°C by HAGGERTY and LINDSLEY (1969) on the reaction:

Ferropseudobrookite = Ilmenite + Rutile

$$FeTi_2O_5 = FeTiO_3 + TiO_2. \quad (12)$$
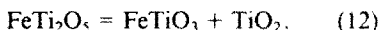
The result of Haggerty and Lindsley has been chosen because the ferropseudobrookite used appeared to be free of a Ti_3O_5 component, while that of EL GORESY and WOERMANN (1976) contained 13.5 mole percent Ti_3O_5.

LINDSLEY (1983) noted that calculations in log $f O_2$-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:

Magnetite + O_2 = Hematite

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \quad (13)$$

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 $f O_2$ value from that given here we have fit log $f O_2$

for the HM buffer as calculated from ROBINSON et al.'s data to the following equations:

$$\text{Log} f O_2 = -0.39824 \cdot T$$
$$+ -0.16378 \cdot 10^7/T^2 + 0.72703 \cdot 10^{-4} \cdot T^2$$
$$+ 18.015 \cdot T^{0.5} - 253.08 \quad (298.2-848.5 \text{ K})$$
$$\text{Log} f O_2 = -0.21506 \cdot T + -0.49263 \cdot 10^{-4} \cdot T^2$$
$$+ 5.6010 \cdot T^{0.5} \quad (848.5-955.5 \text{ K})$$
$$\text{Log} f O_2 = -0.13949 \cdot T + 0.11822 \cdot 10^{-4} \cdot T^2$$
$$+ 8.9815 \cdot T^{0.5} - 167.75 \quad (955.5-1700 \text{ K}) \quad (14)$$

THE SYSTEM Ti-O

Four minerals have been reported in the system Ti-O: rutile, anatase, brookite, and hongquiite. 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_2-II has been synthesized at high pressures (DACHILLE and ROY, 1962; BENDELIANI 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. Hongquiite (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 Ti_nO_{2n-1}. Thermodynamic data exist for six of these phases: Ti_2O_3, Ti_3O_5, Ti_4O_7, Ti_5O_9, $Ti_{11}O_{20}$, and Ti_6O_{11}. Entropy data for the last three of these were estimated from Ti_4O_7 and rutile, and their Gibbs energies were calculated from the data of ANDERSON and KHAN (1970). As can be seen from its formula, $Ti_{11}O_{20}$ is not an end-member of the Magneli series, and Anderson and Khan suggest that it is an ordered intergrowth of Ti_5O_9 and Ti_6O_{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 Ti_5O_9, $Ti_{11}O_{20}$, and Ti_6O_{11} are not shown in Fig. 4. Calculations based on the data of ANDERSON and KHAN (1970) suggest that Ti_5O_9 becomes stable above approximately 1300°C, and that the lower stability limits of $Ti_{11}O_{20}$ and Ti_6O_{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.
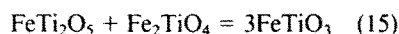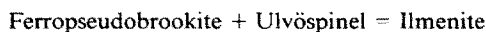
Most of the reactions shown in Fig. 4 lie well outside of usual terrestrial fO_2 values (though see ESSENE and FISHER, 1984). Even lunar samples seem commonly to have formed within the stability field of rutile (EL GORESY et al., 1974; MAO et al., 1974). The reported occurrence of hongquiite is interesting as the upper limit of its stability as a pure phase lies 10 to 15 log units below iron-wüstite. The hongquiite analysis given by YU et al. (1974), $(Ti_{0.99}Fe_{0.01})O$ suggests that solid-solution effects of cations will not account for its stabilization. The upper stability of hongquiite at 1000 K lies at $\log fO_2 = -36.4$. The data of ANOVITZ et al. (in prep.) show that almandine will break down to iron,

sillimanite and quartz at $\log fO_2 = -22.1$ at 1000 K. Thus the activity of almandine in garnet in equilibrium with hongquiite can be no larger than $\log a_{Alm} = -22.5$. 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 hongquiite (YU et al., 1974). We suspect that hongquiite has been mischaracterized or that it is completely out of equilibrium with its associated minerals. The possibility that hongquiite 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:

Ferropseudobrookite + Ulvöspinel = Ilmenite

$$FeTi_2O_5 + Fe_2TiO_4 = 3FeTiO_3 \quad (15)$$

Ferropseudobrookite = Ulvöspinel + Rutile

$$2FeTi_2O_5 = Fe_2TiO_4 + 3TiO_2 \quad (16)$$
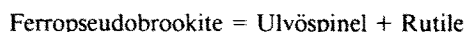
control the stability of ferropseudobrookite in lunar rocks. Calculation of the end-member reactions, however, shows them to be metastable with respect to reaction (12). Lunar samples of magnesian ferropseudobrookite ("armalcolite") contain approximately 50 percent replacement of Fe by Mg. In addition, the ulvöspinels reported by EL GORESY et al. are very chromian. The experimental work of LINDSLEY et al. (1974) and of KESSON and 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;
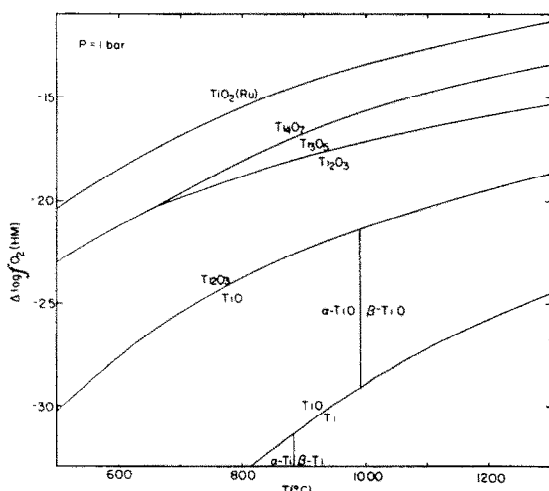

FIG. 4. Phase relations or the Ti-O system plotted relative to fO_2 for the hematite-magnetite (HM) buffer, calculated from the data in Table 5.
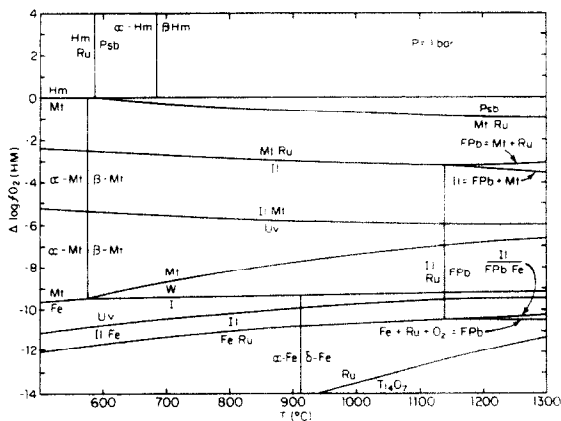
FIG. 5. Phase relations for the system Fe-Ti-O at 1 bar plotted relative to the hematite-magnetite buffer calculated from the data in Table 5.

LUFKIN, 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 "iserite" reported by JANOVSKY (1880) may be the first reported example. SCHALLER's (1912) analysis of iserite 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 fO_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 fO_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.
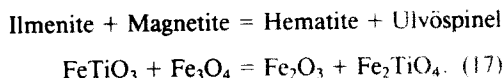
Ferropseudobrookite occurrences will be even more restricted in terrestrial rocks. While ferropseudobrookite is stable at fO_2 conditions commonly reported for terrestrial rocks, its low-temperature stability limit has a dP/dT slope (11.8 bars/°C) that is quite flat, similar to that for pseudobrookite (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 LINDSLEY et al. (1974) and KESSON and LINDSLEY (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 fO_2-T values lie within ±2 log fO_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 (LINDSLEY, 1963; BUDDINGTON and LINDSLEY, 1964; SPENCER and LINDSLEY, 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:

Ilmenite + Magnetite = Hematite + Ulvöspinel

$$FeTiO_3 + Fe_3O_4 = Fe_2O_3 + Fe_2TiO_4. \quad (17)$$

Once temperature is known, fO_2 may be found from any of the following reactions:

Magnetite + O_2 = Hematite

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \quad (18)$$

Ulvöspinel + O_2 = Ilmenite + Magnetite

$$6Fe_2TiO_4 + O_2 = 6FeTiO_3 + 2Fe_3O_4 \quad (19)$$

Ulvöspinel + O_2 = Ilmenite + Hematite
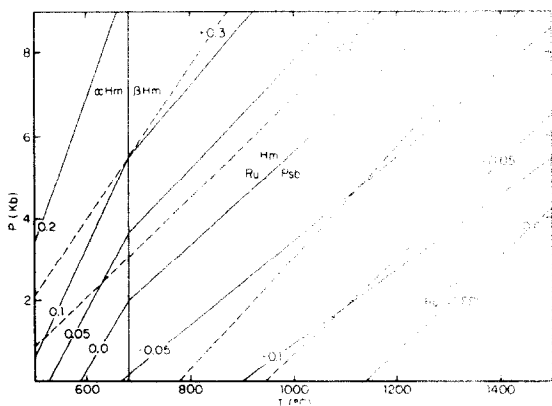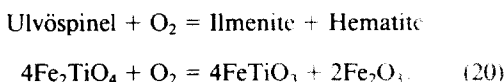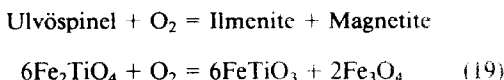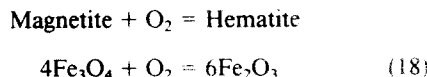
$$4Fe_2TiO_4 + O_2 = 4FeTiO_3 + 2Fe_2O_3 \quad (20)$$

FIG. 6. Calculated position of the reactions Psb = Hm + Ru (solid lines) and Fpb = Il + Ru (dashed lines) contoured for values of log K.

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 fO_2 and temperature these represent two equations in four unknowns as:

$$\log K(18) = 6 \log (a_{Hm}) - 4 \log (a_{Mt}) - \log fO_2$$
$$(21)$$

$$\log K(19) = 6 \log (a_{Il}) + 2 \log (a_{Mt})$$
$$- 6 \log (a_{Uv}) - \log fO_2 \quad (22)$$

$$\log K(20) = 4 \log (a_{Il}) + 2 \log (a_{Hm})$$
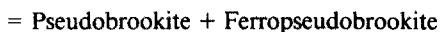$$- 4 \log (a_{Uv}) - \log fO_2. \quad (23)$$

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 obtain a diagram of the SPENCER and LINDSLEY (1981) type from thermodynamic data by contouring the calculated composition of phases from each join which are in equilibrium at a series of fO_2-T values. Unfortunately, because of the equations 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:
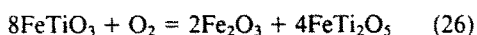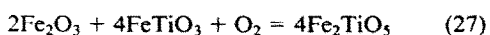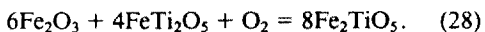
Pseudobrookite + Ilmenite

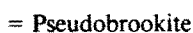= Ferropseudobrookite + Hematite

$$Fe_2TiO_5 + FeTiO_3 = FeTi_2O_5 + Fe_2O_3 \quad (24)$$

Ilmenite + O_2

= Pseudobrookite + Ferropseudobrookite

$$6FeTiO_3 + O_2 = 2Fe_2TiO_5 + 2FeTi_2O_5 \quad (25)$$
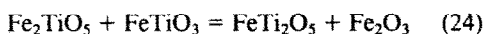
Ilmenite + O_2 = Hematite + Ferropseudobrookite

$$8FeTiO_3 + O_2 = 2Fe_2O_3 + 4FeTi_2O_5 \quad (26)$$

Hematite + Ilmenite + O_2 = Pseudobrookite

$$2Fe_2O_3 + 4FeTiO_3 + O_2 = 4Fe_2TiO_5 \quad (27)$$

Hematite + Ferropseudobrookite + O_2

= Pseudobrookite

$$6Fe_2O_3 + 4FeTi_2O_5 + O_2 = 8Fe_2TiO_5. \quad (28)$$

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 $X_{Psb} = X_{Fe} - 1 = a_{Psb}$, and $X_{Fpb} = 1 - X_{Psb}$. 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:

$$\log K(25) = 2.3571 \cdot 10^4/T \ (K)$$
$$- 0.14081 \cdot P \ (kb) - 10.4861 \ (\pm 0.07) \quad (29)$$

$$\log K(26) = 2.3237 \cdot 10^4/T \ (K)$$
$$- 0.13930 \cdot P \ (kb) - 10.5260 \ (\pm 0.07). \quad (30)$$

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 $\Delta \log fO_2$-T space covered by this thermometer is shown in Fig. 7. As expected, pseudobrookite and hematite solutions dominate at high fO_2 values, and ferropseudobrookite-ilmenite compositions at low fO_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$_{ss}$-ilmenite$_{ss}$ is limited by reaction (12), which represents the lower bound to the region of applicability of this system to oxygen-barometry/thermometry (Fig. 7).
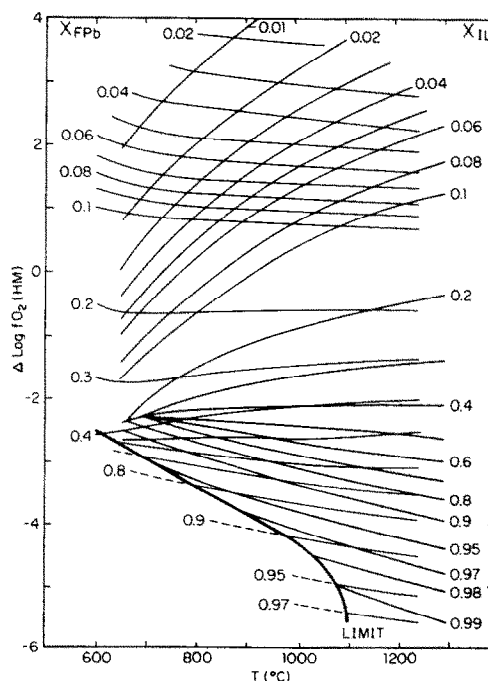

FIG. 7. Compositions of pseudobrookite$_{ss}$ in equilibrium with hematite$_{ss}$ contoured in $\Delta \log fO_2$-T space, showing the compositions and $\Delta \log fO_2$ values covered by this thermometer. Temperature and $\Delta \log fO_2$ values are obtained from the point of intersection of the curves representing the compositions of the coexisting pseudobrookite and hematite solid-solutions.
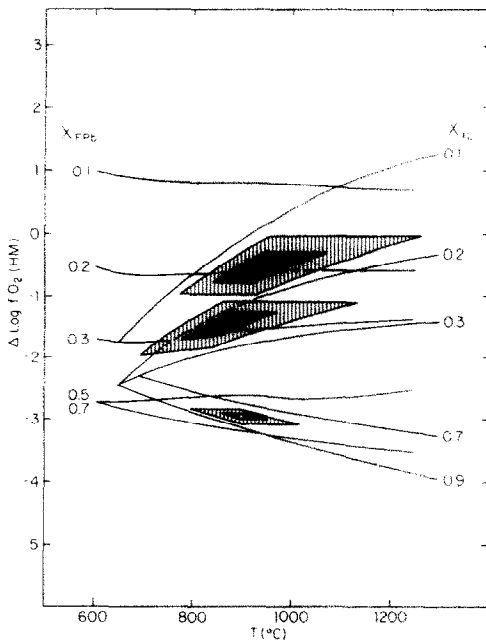
FIG. 8. Temperature and log $f\,O_2$ estimates for samples from Iceland and Hawaii reported by HAGGERTY (1971) and ANDERSON and WRIGHT (1972) respectively. Contours show the effects of ± 2 (solid field) and 4 mole percent (hachured field) errors in the estimated mole fractions of ilmenite and ferropseudobrookite.

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 oxybarometer/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 solution 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 (LINDSLEY, written commun., 1984) on the effects of solid-solution along the join ferropseudobrookite-pseudobrookite disagree somewhat with our calculation (Fig. 7). Three of four experiments in which the three-phase assemblage Fpb$_{ss}$-Ilm$_{ss}$-Ru is stable fall nicely within the three-phase field suggested by Fig. 7. A fourth experiment, however, at 750°C showed the three-phase assemblage stable at X_{Fpb} = 0.7, while our calculations would limit this assemblage to compositions between X_{Fpb} = 0.77 and X_{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 $a_{Fpb} = X_{Fpb}$ and $a_{Psb} = X_{Psb}$ and therefore $a_{Fpb} = 1 - X_{Psb}$. If pseudobrookite solid-solutions exhibit a positive deviation from ideality, $a_{Fpb} > X_{Fpb}$, $a_{Psb} > X_{Psb}$ and $a_{Fpb} > 1 - a_{Psb}$. This would stabilize the three-phase assemblage over the Fpb$_{ss}$ 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 Eqns. (24) and (25). For the pseudobrookite-hematite thermometer, temperature increases approximately 10°C/kbar and log $f\,O_2$ 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$_{ss}$ + hematite$_{ss}$. 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 ± 1–2 kbars should be obtainable.
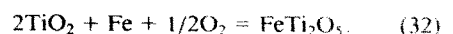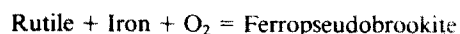
APPLICATIONS

The magnetite-ilmenite thermometer/oxygen-barometer 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 $f\,O_2$-T 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 6.

Ferropseudobrookite-ilmenite

The assemblage ferropseudobrookite + ilmenite + iron $\pm$ 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:

Ferropseudobrookite + Iron + O_2 = Ilmenite

$$FeTi_2O_5 + Fe + 1/2O_2 = 2FeTiO_3 \qquad (31)$$
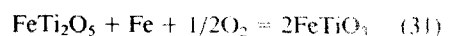
and on reactions (12) and (32):

Rutile + Iron + O_2 = Ferropseudobrookite

$$2TiO_2 + Fe + 1/2O_2 = FeTi_2O_5 \qquad (32)$$

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

Table 6. Formulae of Iron-Titanium Oxides from the Literature

Anal.	1	2	3	4	5	6	7	8	9
Phase	Fpb	Il	Uv	Il	Il	Fpb	Mt	Il	Il
Si_{4+}	0.002	0.004	-	-	-	-	-	-	-
Ti_{4+}	1.870	0.965	0.924	0.980	0.995	1.883	0.648	0.882	0.931
Ti_{3+}	0.116	-	-	0.014	0.002	0.178	-	-	-
Al	0.086	0.002	0.038	0.004	0.005	0.052	0.143	0.055	-
V	0.001	-	-	-	-	-	-	-	-
Cr_{3+}	0.056	0.009	0.002	-	0.003	0.004	0.006	-	-
Fe_{3+}	-	0.087	0.112	-	-	-	0.555	0.182	0.139
Fe_{2+}	0.445	0.808	1.907	0.984	0.772	0.595	1.394	0.686	0.680
Mn	0.004	0.013	0.011	0.008	0.013	0.007	0.012	0.008	-
Mg	0.418	0.107	0.004	0.004	0.210	0.281	0.242	0.187	0.250
Ca	0.001	0.005	-	-	-	-	-	-	-
Zr	-	-	0.002	0.006	-	-	-	-	-
	3.0	2.0	3.0	2.0	2.0	3.0	3.0	2.0	2.0

Anal.	10	11	12	13	14	15	16	17
Phase	Fpb	Mt	Il	Fpb	Psb	Psb	Il	Il
Si_{4+}	-	-	-	-	-	-	-	-
Ti_{4+}	1.746	0.545	0.838	1.684	1.290	1.196	0.223	0.168
Ti_{3+}	-	-	-	-	-	-	-	-
Al	0.068	0.146	0.023	0.065	-	-	-	-
V	-	-	-	-	-	-	-	-
Cr_{3+}	-	0.011	-	-	-	-	-	-
Fe_{3+}	0.440	0.753	0.300	0.568	1.420	1.608	1.554	1.664
Fe_{2+}	0.430	1.297	0.655	0.375	0.290	0.196	0.223	0.168
Mn	-	0.014	0.006	-	-	-	-	-
Mg	0.316	0.234	0.177	0.308	-	-	-	-
Ca	-	-	-	-	-	-	-	-
Zr	-	-	-	-	-	-	-	-
	3.0	3.0	2.0	3.0	3.0	3.0	3.0	2.0

(1-2) El Goresy et al. (1974); (3-4) Meyer and Boctor (1974); (5-6) Pederson (1981); (7-13) Anderson and Wright (1972); (14-17) Haggerty (1971). Analyses have been renormalized to integral cation totals. Spinels and orthorhombic oxides are normalized to three cations, and rhombohedral oxides to two cations. Dashed elements were not analyzed.

imately 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 Ti_3O_5 component in the ferropseudobrookite used in SATO et al.'s experiments. Indeed, SIMONS and WOERMANN (1978) suggest that at these temperatures equilibrium ferropseudobrookite contains significant Ti_3O_5. 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 fO_2 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 ferropseudobrookite 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, $\log fO_2 = -14.7$, 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 fO_2 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 Al^{3+}, Cr^{3+} and Ti^{3+} solid-solutions. This temperature is well below what Pederson infers from co-existing pyroxenes, and suggests that this assemblage equilibrated during subsolidus cooling. Assuming ideal mixing as before, $\log fO_2 = -17.5$, 10.7 log units below hematite-magnetite.

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

Ulvöspinel = Ilmenite + Iron + O_2

$$Fe_2TiO_4 = FeTiO_3 + Fe + 1/2O_2. \quad (33)$$
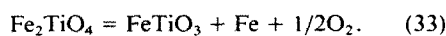
While this reaction does not permit temperatures to be calibrated, it fixes fO_2 for this rock as a function of temperature. Reaction (33) yields:

$$\log K(33) = \log (a_{Il} \cdot a_{Fe}/a_{Uv}) + \log fO_2. \quad (34)$$

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

$$\log (a_{Il} \cdot a_{Fe}/a_{Uv}) = 0.03 \quad (35)$$

assuming ideal mixing. This implies that the rock equilibrated at fO_2 conditions nearly identical to those calculated from reaction (33) (Fig. 5).

Pseudobrookite-hematite

HAGGERTY (1971) graphically reports analyses for two pseudobrookite$_{ss}$-hematite$_{ss}$ 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 fO_2 1.5 log units below hematite-magnetite for the more ferrous pair, and $T = 880°C$, fO_2 0.8 log units below HM for the more ferric pair.

ANDERSON and WRIGHT (1972) report the assemblage ilmenite$_{ss}$ + pseudobrookite$_{ss}$ + magnetite$_{ss}$ in a basalt from Kilauea, Hawaii. While this cannot be an equilibrium 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 $\Delta \log fO_2 = -5.0$, while the pseudobrookite$_{ss}$-hematite$_{ss}$ pairs yield 900°C and $\Delta \log fO_2 = -3.0$. 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 calibrations used.

Small analytical errors may lead to large errors in the temperatures calculated from pseudobrookite$_{ss}$-hematite$_{ss}$ or ferropseudobrookite$_{ss}$-ilmenite$_{ss}$ pairs. 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 $\Delta \log fO_2$. While $\Delta \log fO_2$ varies by less than ±0.5 log units, temperature may vary by several hundred degrees. A typical magnetite/ilmenite pair (sample SR-31, BOHLEN and ESSENE, 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 $\Delta \log fO_2$ with a ±2 mole percent error in the measured ilmenite and magnetite 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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