

Thermodynamics and stability of pseudobrookite-type MgTi_2O_5 (karrooite)

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ABSTRACT

Pseudobrookite-type MgTi_2O_5 (karrooite) is a synthetic crystalline phase with the *Bbmm* structure and a component in orthorhombic oxide solid solutions, $\text{R}^{2+}\text{Ti}_2\text{O}_5\text{-R}_2^{3+}\text{TiO}_5$, which are present as accessory minerals in lunar and terrestrial rocks. In this study, we present a model for the molar Gibbs free energy of MgTi_2O_5 as a function of T , P , and the order parameter $s = X_{\text{Mg}}^{\text{M1}} - 2X_{\text{Mg}}^{\text{M2}}$, ($-1 \leq s \leq 1$). We describe the molar Gibbs free energy, ($\bar{G}$), with the equation: $\bar{G} = \bar{g}_0 + \bar{g}_1 \cdot (1 - s) + 3/2 \bar{g}_2 \cdot (1 - s^2) - T \cdot \bar{S}_{\text{config}}$, and take parameter g_0 to represent the molar Gibbs free energy of ordered MgTi_2O_5 ($s = 1$), whereas parameters g_1 and g_2 may represent cation-disorder contributions. We used powder and single-crystal X-ray diffraction, and high-temperature relative enthalpy data, to calibrate the disorder contribution to the volume ($b_0 = 7.3822 \cdot 10^{-3}$ J/bar), and the model parameters g_1 (7370.8 J/mol) and g_2 (3576.1 J/mol), and heat capacity and volume equation coefficients. We also optimized standard state thermodynamic data from the elements for ordered MgTi_2O_5 , ($\Delta H^0 = -2498.51528$ J/mol, $S^0 = 149.55$ J/(mol·K), $\Delta G^0 = -2362.18172$ J/mol, $V^0 = 5.445$ J/bar) consistent with the model parameters and equations, the thermodynamic data in QUILF, and phase-equilibrium experiments involving MgTi_2O_5 , geikelite, rutile, orthoenstatite, and forsterite in the range 973 to 1673 K and 0.0001 to 2.0 GPa. Finally, we investigate theoretically the stability of MgTi_2O_5 (karrooite) with respect to geikelite, rutile, diopside, enstatite, and forsterite in the $\text{CaO-MgO-TiO}_2\text{-SiO}_2$ system. We find that diopside- and titanite-bearing reactions require extremely high temperatures, and are thus not stable with respect to liquid. The inferred phase relations can be of help in understanding the stability of MgTi_2O_5 with respect to rutile, geikelite, forsterite, and orthoenstatite, and by extrapolation that of armalcolite relative to rutile, ilmenite, olivine, and orthopyroxene in terrestrial mantle rocks and high-Ti lunar basalts.

INTRODUCTION

Pseudobrookite-type MgTi_2O_5 (karrooite), space group *Bbmm* (Pauling 1930), is a synthetic crystalline phase common in TiO_2 -bearing glass-ceramics (e.g., Bealle 1994). Additionally, MgTi_2O_5 is a component in the $\text{R}^{2+}\text{Ti}_2\text{O}_5\text{-R}_2^{3+}\text{TiO}_5$ solid solutions with the pseudobrookite structure where the divalent and trivalent cations are typically Fe^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , and Ti^{3+} (e.g., Bowles 1988; Hayob and Essene 1995). Knowledge of the thermodynamic parameters and conditions that affect the stability and phase relations between MgTi_2O_5 (karrooite) and other oxide and silicate phases can be of relevance to the design of Fe and Al-free glass-ceramics. Furthermore, in the more-complex terrestrial and lunar rocks that contain the orthorhombic $\text{R}^{2+}\text{Ti}_2\text{O}_5\text{-R}_2^{3+}\text{TiO}_5$ oxide solutions, the phase relations among ilmenite, spinel, orthorhombic oxide, and silicates can provide valuable information on the intensive parameters during crystallization of these rocks. Extrapolation beyond experimentally established phase relations among these phases requires a rigorous understanding of the thermodynamic

properties of the phases involved, something that may be particularly important in entropy-stabilized compounds such as the $\text{R}^{2+}\text{Ti}_2\text{O}_5\text{-R}_2^{3+}\text{TiO}_5$ oxide solid solutions (Navrotsky 1975, 1994). Finally, modeling of the thermodynamic properties and stability of the orthorhombic $\text{R}^{2+}\text{Ti}_2\text{O}_5\text{-R}_2^{3+}\text{TiO}_5$ oxide solid solutions can be facilitated by understanding first the behavior of end-members.

In this study, we calibrate a model for the molar Gibbs free energy of pseudobrookite-type MgTi_2O_5 as a function of T , P , and the $\text{Mg}^{2+}\text{-Ti}^{4+}$ distribution between the M1 and M2 sites based upon powder and single-crystal X-ray diffraction (XRD) at 1 bar and high pressures, high-temperature relative enthalpy measurements, and phase-equilibrium experiments. Also, we calibrate MgTi_2O_5 (karrooite)-bearing reactions and discuss their petrologic significance.

PREVIOUS WORK

MgTi_2O_5 (karrooite) has been studied by X-ray techniques (Yang and Hazen 1999, 1998; Brown and Navrotsky 1989; Wechsler and Navrotsky 1984; Wechsler and Von Dreele 1989; Lind and Housley 1972), calorimetry (Orr and Coughlin 1952; Todd 1952; Brown and Navrotsky 1989), and phase-equilib-

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rium experiments (MacGregor 1969; Lindsley et al. 1974; Pelton et al. 1998; this study).

In summary, the crystallographic studies have shown that the Mg^{2+} and Ti^{4+} cations occupy two non-equivalent octahedral sites, M1 and M2, with M1 larger than M2. The distribution of Mg^{2+} and Ti^{4+} between the two distinct M1 and M2 octahedral sites is thought to affect the structural and thermodynamic properties of this material (e.g., Lind and Housley 1972; Wechsler and Navrotsky 1984; Wechsler and Von Dreele 1989; Brown and Navrotsky 1989; Navrotsky 1994; Yang and Hazen 1999, 1998). The XRD experiments and, consequently, the derived cation disorder data differ in the way they were collected. One set consists of data collected in situ at high temperatures (Brown and Navrotsky 1989), whereas the second set consists of data collected at room temperature either at atmospheric or high-pressure conditions. In the latter case, the samples were annealed previously at high temperatures and subsequently fast quenched to room temperature (Yang and Hazen 1999, 1998; Brown and Navrotsky 1989; Wechsler and Navrotsky 1984; Wechsler and Von Dreele 1989; Lind and Housley 1972). The unit-cell volume and $\text{Mg}^{2+}\text{-Ti}^{4+}$ distribution data that were collected at room temperature from quenched samples are all very similar within their respective uncertainties, but also differ greatly from the data collected in situ at high temperatures (Figs. 1 and 2). This difference appears to hold regardless of whether single crystals (Yang and Hazen 1998; Lind and Housley 1972) or polycrystalline samples were used (Brown and Navrotsky 1989; Wechsler and Von Dreele 1989; Wechsler and Navrotsky 1984). Nonetheless, the data suggest that: (1) the high-temperature $\text{Mg}^{2+}\text{-Ti}^{4+}$ configuration probably can be quenched between 1000 to 1300 K (Fig. 3), whereas annealing in excess of 70 days is needed for temperatures below 1000 K and (2) cation disorder alone appears to contribute $0.7 \pm 0.1\%$ to the volume of MgTi_2O_5 (karrooite). Finally, the room-temperature and high-pressure Yang and Hazen (1999) data on two quenched MgTi_2O_5 samples indicate that the quantity $(\partial V/\partial P)_{T,s}$ is the same in both the quenched MgTi_2O_5 samples. Yet the degree of quenched cation disorder and the respective molar volumes are different because the MgTi_2O_5 crystals were annealed at different temperatures. Note that increasing pressure at room temperature did not modify the $\text{Mg}^{2+}\text{-Ti}^{4+}$ distribution between the M1 and M2 sites in those samples (Yang and Hazen 1999).

Orr and Coughlin (1952) and Brown and Navrotsky (1989) presented relative enthalpy data from transposed-temperature-drop calorimetry (Fig. 4). In addition, Todd (1952) measured the heat capacity of the Orr and Coughlin (1952) MgTi_2O_5 sample in the range 50–300 K, and estimated the entropy at 298 K to be equal to 127.19 J/mol. More recently, Berman and Brown (1985) presented a heat capacity equation for MgTi_2O_5 (karrooite) based on the Orr and Coughlin (1952) and Todd (1952) data, without an explicit treatment of cation disorder contributions. The ordering state of the samples in the Todd (1952) and Orr and Coughlin (1952) studies is unknown. However, the MgTi_2O_5 crystals in those studies probably retained a high-temperature cation configuration, because they were originally synthesized between 1573 and 1773 K and then quenched from these temperatures (Orr and Coughlin 1952). However, it

is permissible that at temperatures above 1000 K, the MgTi_2O_5 crystals in the studies of Orr and Coughlin (1952) and Brown and Navrotsky (1989) either approached or achieved the high-temperature equilibrium $\text{Mg}^{2+}\text{-Ti}^{4+}$ configuration during the transposed-temperature-drop calorimetry experiments (see Fig. 3). Thus, at temperatures higher than 1000 K, each enthalpy measurement may be taken to represent the sum of both ideal and excess enthalpy due to equilibrium cation disorder.

The stability of MgTi_2O_5 (karrooite) with respect to magnesium titanates and silicates, and titanium oxides has been studied experimentally in the systems $\text{MgO-TiO}_2\text{-Ti}_2\text{O}_3$ (Pelton et al. 1998), MgO-TiO_2 (Lindsley et al. 1974; this study), and $\text{MgO-TiO}_2\text{-SiO}_2$ (MacGregor 1969; Winter 1988; this study) within a fairly large range of temperature, pressure, and oxygen fugacity conditions. In addition, the effect of the $\text{Mg}^{2+}\text{-Ti}^{4+}$ distribution between the M1 and M2 sites to the thermodynamic properties of MgTi_2O_5 (karrooite) was examined theoretically by Ghiorso et al. (1999) and Brown and Navrotsky (1989). Last, Pelton et al. (1998), Hayob and Essene (1995), and Eriksson and Pelton (1993) either optimized or estimated standard state thermodynamic data for MgTi_2O_5 .

THERMODYNAMIC MODEL

The molar Gibbs free energy, $(\bar{G})$, of MgTi_2O_5 (karrooite) in terms of configurational and lattice vibrational contributions can be written as

$$\bar{G} = \bar{G}_{\text{vib}}^* - T\bar{S}_{\text{config}} \quad (1)$$

(Thompson 1969, 1970; Sack 1982). The configurational entropy $(\bar{S}_{\text{config}})$ as a function of cation site fractions is expressed as:

$$\bar{S}_{\text{config}} = -R(X_{\text{Mg}}^{\text{M1}} \ln X_{\text{Mg}}^{\text{M1}} + X_{\text{Ti}}^{\text{M1}} \ln X_{\text{Ti}}^{\text{M1}} + 2X_{\text{Mg}}^{\text{M2}} \ln X_{\text{Mg}}^{\text{M2}} + 2X_{\text{Ti}}^{\text{M2}} \ln X_{\text{Ti}}^{\text{M2}}) \quad (2)$$

Cation site fractions as a function of an order parameter s , where $-1 \leq s \leq 1$ and $s = X_{\text{Mg}}^{\text{M1}} - 2X_{\text{Mg}}^{\text{M2}}$ (Ghiorso and Sack 1991; Ghiorso et al. 1999), are given by:

$$X_{\text{Mg}}^{\text{M1}} = \frac{1+s}{2} \quad (3a)$$

$$X_{\text{Mg}}^{\text{M2}} = \frac{1-s}{4} \quad (3b)$$

$$X_{\text{Ti}}^{\text{M1}} = \frac{1-s}{2} \quad (3c)$$

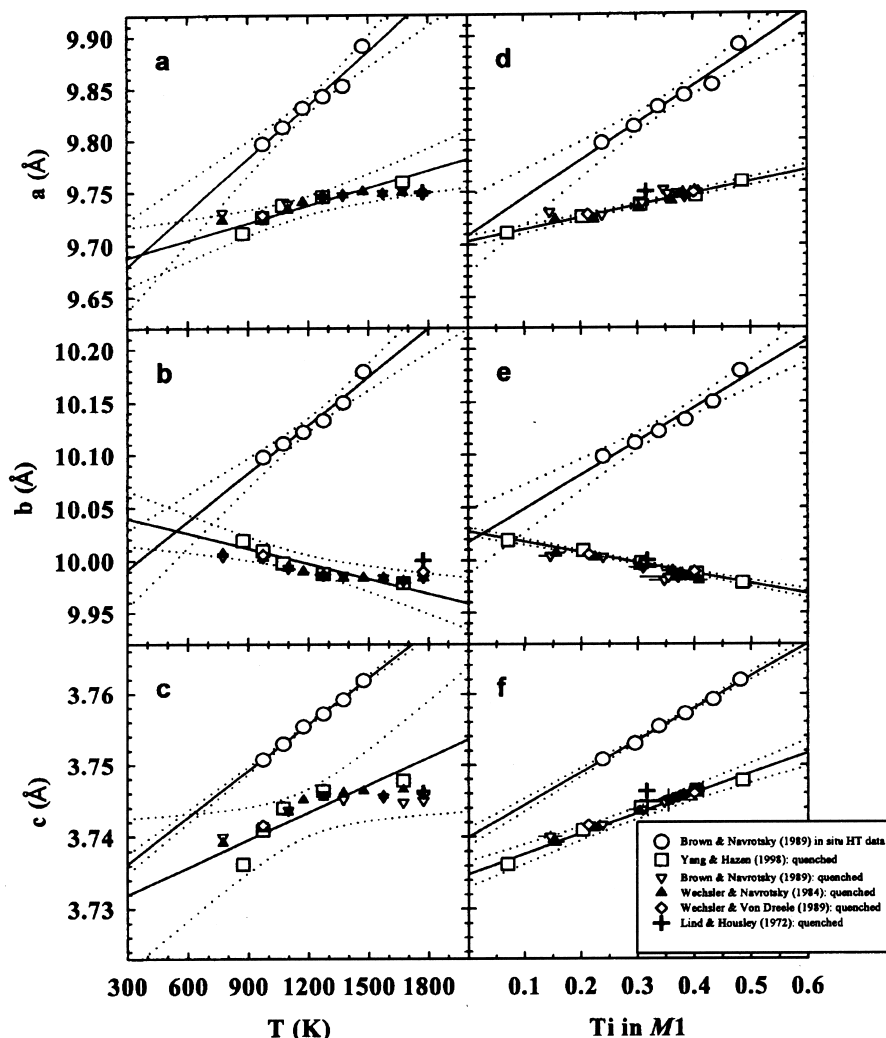
$$X_{\text{Ti}}^{\text{M2}} = \frac{3+s}{4} \quad (3d)$$

Consequently, the configurational entropy as a function of the order parameter s can be written as

$$\bar{S}_{\text{config}} = -R\left(\frac{1+s}{2} \ln \frac{1+s}{2} + \frac{1-s}{2} \ln \frac{1-s}{2} + \frac{1-s}{2} \ln \frac{1-s}{4} + \frac{3+s}{2} \ln \frac{3+s}{4}\right) \quad (4)$$

Random cation distribution between the M1 and M2 sites is described by $s = -1/3$ and $X_{\text{Mg}}^{\text{M2}} = 1/3$ whereas ordered MgTi_2O_5 (karrooite) will have all of Ti in M2, thus, $s = 1$ and $X_{\text{Mg}}^{\text{M2}} = 0$,

FIGURE 1. MgTi_2O_5 (karrooite) unit-cell parameters as a function of temperature (a through c), and Ti in M1 (d through f). For quenched samples, the temperature represents the annealing temperature, because the XRD data were collected at ambient conditions. Straight solid lines are linear least-squares fits to the data with their respective 95% confidence envelopes (dotted lines).



and anti-ordered MgTi_2O_5 (karrooite) will have all of Ti in M1, $s = -1$ and $X_{\text{Mg}}^{\text{M1}} = 0$.

The vibrational component $\bar{G}_{\text{vib}}^*$ of the molar Gibbs free energy is expanded in terms of Legendre polynomials (e.g., Sansone 1991; Bale and Pelton 1974), and subsequently truncated at the third term. This group of orthogonal polynomials is valid for real numbers that take values between -1 and 1 (e.g., Sansone 1991).¹ After expansion and truncation, the molar Gibbs free energy of MgTi_2O_5 (karrooite) transforms to

$$\bar{G} = \bar{g}_0^* + \bar{g}_1^*s + 1/2 \cdot \bar{g}_2^*[3 \cdot s^2 - 1] - T \cdot \bar{S}_{\text{config}}^* \quad (5)$$

In order to express the molar Gibbs free energy more conveniently in terms of ideal and excess terms, we rearrange Equation 5 to

$$\bar{G} = \bar{g}_0 + \bar{g}_1 \cdot (1 - s) + 3/2 \cdot \bar{g}_2 \cdot (1 - s^2) - T \cdot \bar{S}_{\text{config}}^* \quad (6)$$

The relationship among parameters g_i^* in Equation 5 and g_i in Equation 6 ($g_0 = g_0^* + g_1^* + g_2^*$, $g_1 = -g_1^*$, and $g_2 = -g_2^*$) can be derived by successively setting the order parameter s to 1 , 0 ,

and -1 . Equations 5 and 6 resemble the Ghiorso et al. (1999) Equations 6 and 8 that were derived from a Taylor series expansion truncated at the second term.

We take g_0 to represent the molar Gibbs of an ordered MgTi_2O_5 (karrooite) ($s = 1$), and parameters g_1 and g_2 to represent excess contributions due to cation disorder. We subsequently adopt, slightly modified, the Haas and Hemingway (1992) heat capacity and volume equations:

$$C_p = \frac{a_1}{T^3} + \frac{a_2}{T^2} + \frac{a_3}{T} + \frac{a_4}{\sqrt{T}} + a_5 + a_6 \cdot T + a_7 \cdot T^2 + a_8 \cdot T^3 + C_p^{\text{excess}} \quad (7)$$

$$V = [b_0 \cdot (1 - s) + b_1 + b_2 \cdot T + b_3 \cdot e^{-T/300}] \cdot [1 + b_4 \cdot P + b_5 \cdot e^{-P/35000}] \quad (8)$$

The excess heat capacity C_p^{excess} is given by the relation $T(\partial \bar{G}^2 / \partial s \partial T)^2 / (\partial \bar{G}^2 / \partial s^2)$ (see also Ghiorso et al. 1999), and the term $b_0 \cdot (1 - s)$ was found adequate in fitting the volume data (Yang and Hazen 1999, 1998; Brown and Navrotsky 1989). The standard state Gibbs free energy, enthalpy, and entropy of fully

¹ Parenthetically, Bale and Pelton (1974) first used Legendre and other orthogonal polynomials to model the properties of solutions on the basis of their intrinsic characteristics, namely: (1) functional form consistent with observations regarding behavior of solutions and (2) the small degree of correlation among the coefficients that consequently change little or not at all when their number is increased. They pointed out that the latter feature does not hold for the coefficients of a Taylor series expansion.

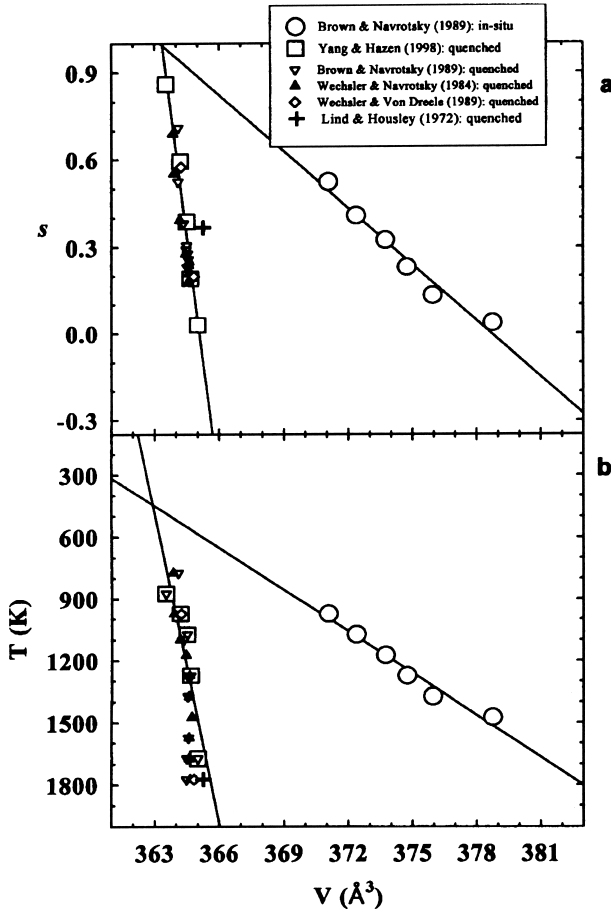


FIGURE 2. Plots of (a) the unit-cell volume vs. the order parameter s , and (b) the unit-cell volume vs. temperature. For quenched samples, the temperature represents the annealing temperature, as the XRD data were collected at ambient conditions. Straight solid lines are linear least-squares fits to the data.

ordered MgTi_2O_5 ($s = 1$) are given by the fundamental relations:

$$\Delta G^{P,T} = \Delta H^{P,T} - T \cdot \Delta S^{P,T} \quad (9a)$$

$$\Delta H^{P,T} = \Delta H^{P_r, T_r} + \int_{T_r}^T C_p dT + \int_{P_r}^P \left[V^{P_r, T_r} - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (9b)$$

$$S^{P,T} = S^{P_r, T_r} + \int_{T_r}^T \frac{C_p}{T} dT - \int_{P_r}^P \left(\frac{\partial V}{\partial T} \right)_P dP \quad (9c)$$

Model calibration

The model energy parameters can be calibrated from cation disorder data, providing that equilibrium $\text{Mg}^{2+}\text{--Ti}^{4+}$ distribution was achieved, and once the latter is known from high-temperature enthalpy data, and phase-equilibrium experiments.

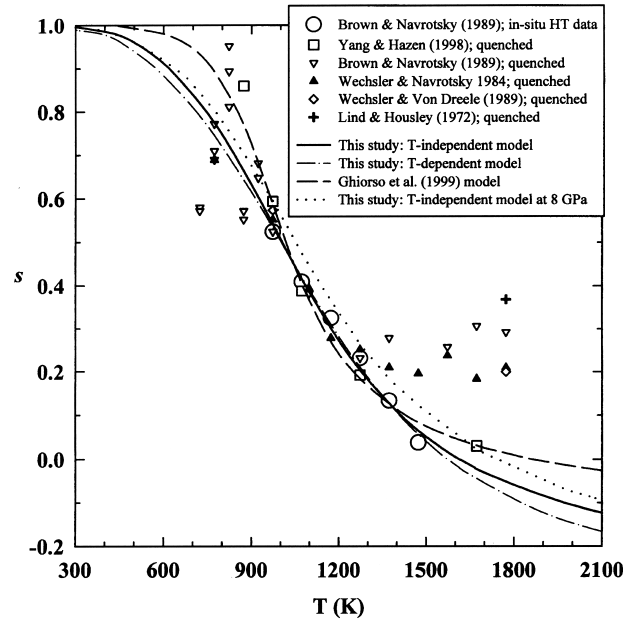


FIGURE 3. Order parameter s as a function of temperature at 1 bar and 8 GPa. Except for the Ghiorso et al. (1999) model curve at 1 bar, the rest of the model curves were calculated with the parameters derived in this study (Table 1). The latter were based solely on the in situ Brown and Navrotsky (1989) data; in contrast, Ghiorso et al. based their model on the quenched samples of Yang and Hazen (1999, 1998). Note that MgTi_2O_5 (karrooite) melts at 1963 ± 20 K apparently before achieving random cation distribution ($s = -1/3$), and that an isothermal increase in pressure may cause MgTi_2O_5 (karrooite) to become less disordered.

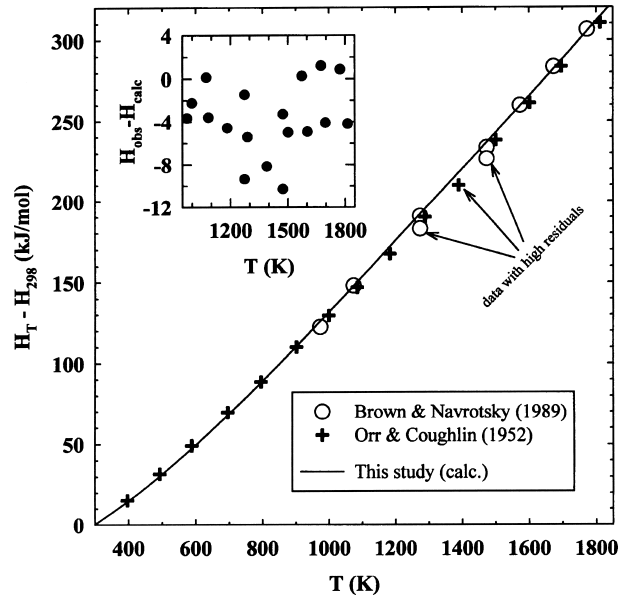


FIGURE 4. Relative enthalpy of MgTi_2O_5 (karrooite) as a function of temperature. The Orr and Coughlin (1952) and Brown and Navrotsky (1989) data were measured with transposed-temperature-drop calorimetry. The model curve was calculated with the heat-capacity and temperature-independent g_1 and g_2 parameters in Table 1, assuming equilibrium cation configuration. The residuals range between +2 to -5 kJ/mol, except for the three points shown with the arrows (-8 to -12 kJ).

The equilibrium $\text{Mg}^{2+}\text{-Ti}^{4+}$ distribution can be described with the relation:

$$\left(\frac{\partial \bar{G}}{\partial s}\right)_{P,T} = -\bar{b}_0 \cdot (P-1) - (\bar{g}_1 + 3 \cdot \bar{g}_2 \cdot s) + \frac{1}{2} R \cdot T \cdot \left[\ln \frac{(1+s) \cdot (3+s)}{(1-s)^2} \right] = 0 \quad (10)$$

In order to calibrate the energy parameters g_1 and g_2 in Equation 10, we fitted the in situ high-temperature data of Brown and Navrotsky (1989), first, using temperature-independent, and second, temperature-dependent g_1 and g_2 parameters (Table 1; Fig. 3). [The order parameter s in Equation 10 can be easily transformed to any particular cation site fraction using the appropriate relation, e.g., $s = 1 - 2 \cdot X_{\text{Ti}}^{\text{Mg}}$. $X_{\text{Ti}}^{\text{Mg}}$ is most commonly used as the order parameter in MgTi_2O_5 (e.g., Brown and Navrotsky 1989; Lennie et al. 1999, 2000)]. At 1 bar and in the range 1000 to 1300 K, both models reproduce the Brown and Navrotsky (1989) data and also compare well with the Yang and Hazen (1998) data. However, as anticipated, the models do not agree with the Yang and Hazen (1998) data at 973 and 1673 K (Fig. 3). The difference between our two models is small (Fig. 3); hence, we adopt the temperature-independent model in the rest of the discussion. Because parameters g_1 and g_2 are treated as independent of temperature, the excess entropy is equal to $\bar{S}_{\text{config}}$ and the excess enthalpy is given by the equation

$$\bar{H}^{\text{excess}} = \bar{g}_1 \cdot (1-s) + 3/2 \cdot \bar{g}_2 \cdot (1-s^2) \quad (11)$$

As noted above, the Yang and Hazen (1999) high-pressure data do not indicate that the order parameter s changes with increasing pressure at room temperature. Furthermore, the evolution of molar volume as a function of pressure at room temperature (Fig. 5a) suggests that change of the volume as a function of pressure is probably the same although the respective compressibilities ($-1/V^0 \cdot \partial V / \partial P$) differ, simply because of differences in the initial sample molar volumes, i.e., 5.473 J/bar at “873” K vs. 5.496 J/bar at “1673” K. Hence, we fitted the high-pressure molar volume data with the equation $V^0 \cdot [1 + b_4 \cdot P + b_5 \cdot e^{-P/35000}]$, where V^0 was the molar volume at “873” and “1673” K, respectively. The high-temperature data of Brown

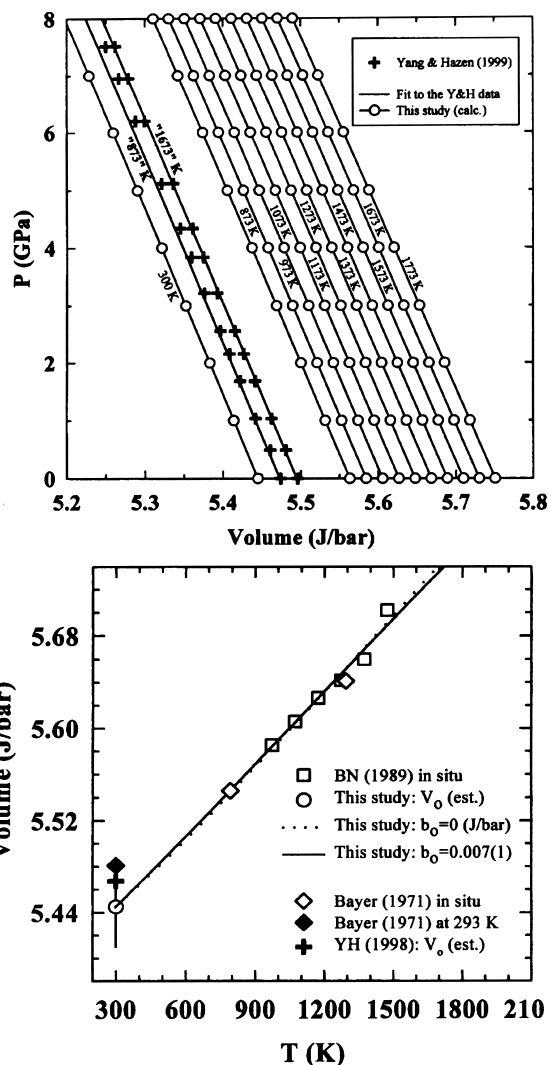


FIGURE 5. (a) Plot of molar volume as a function of pressure. The Yang and Hazen (1998) high-pressure data were collected at room temperature. The “873” and “1673” K labels denote the temperature of annealing. The rest of the curves were calculated with the s -dependent volume equation, and represent P - V data at different temperatures and for an equilibrium cation configuration. (b) Plot of molar volume vs. temperature at 1 atm. BN stand for Brown and Navrotsky, and YH (est.) denotes the Yang and Hazen (1998) estimate for the volume of MgTi_2O_5 at 298 K.

TABLE 1. Optimized thermodynamic data for pseudobrookite-type MgTi_2O_5

ΔH° (J/mol)	S° (J/mol K)	ΔG° (J/mol)	g_1 (J/mol)	g_2 (J/mol)	Comment
-2,498,515.28	149.55	-2,362,181.72	7370.8	3576.1	* Preferred
-2,499,685.41	148.80	-2,363,128.06	7370.8	3576.1	†
-2,504,887.40	137.34	-2,364,913.43			‡
		137.65			§
b_0	b_1	b_2	b_3	b_4	b_5
7.3822 10^{-3}	5.3848	2.0284 10^{-4}	1.6802 10^{-3}	-5.6930 10^{-7}	-2.2410 10^{-4}
0.00	5.3670	2.2097 10^{-4}	3.6749 10^{-2}	-5.6930 10^{-7}	-2.2410 10^{-4}

* Data consistent with preferred volume equation ($b_5 \neq 0$).

† Data consistent with s -independent volume equation ($b_5 = 0$). Both sets of standard state data were calculated with the heat capacity equation:

$C_p = \frac{5.8214 \cdot 10^8}{T^3} + \frac{(-5.6391 \cdot 10^6)}{T^2} + \frac{(2.3344 \cdot 10^3)}{T} + \frac{2.5128 \cdot 10^2}{\sqrt{T}} + 1.4301 \cdot 10^2 + 6.8666 \cdot 10^{-2} \cdot T + (-1.2569 \cdot 10^{-5}) \cdot T^2 + C_p^{\text{excess}}$, and the T-independent parameters g_1 and g_2 . Parenthetically, the T-dependent excess energy parameters g_1 and g_2 are described by the expressions $7033 \cdot T \cdot 0.0415$ and $1202.8 + T \cdot 2.5319$, respectively.

‡ Eriksson and Pelton (1993) and Pelton et al. (1998).

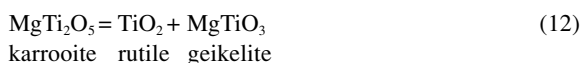
§ Hayob and Essene (1995).

and Navrotsky (1989) can be fitted equally well with the expressions: $[b_1 + b_2 \cdot T + b_3 \cdot e^{-T/300}]$ or $[b_0 \cdot (1 - s) + b_1 + b_2 \cdot T + b_3 \cdot e^{-T/300}]$ (Fig. 5b, Table 1). Because s appears to contribute to the volume, we adopt the latter expression in all of our subsequent calculations. Based upon the volume data of the quenched samples, our best estimate for the parameter b_0 is $7.3822\text{E-}003$ (J/bar). The 793 and 1293 K data points of Bayer (1971) in Figure 5b were not included in our fitting of the data. Nonetheless, they are in good agreement with the Brown and Navrotsky (1989) in situ measurements and the calculated curves. We also estimate the volume of nearly ordered MgTi_2O_5 ($s = 0.9981$) at 300 K to be equal to 5.445 ± 0.034 J/bar ($361.69 \pm 2.23 \text{ \AA}^3$). This value is constrained from the crystallographic data shown in Figure 1 whereas the parameter s is calculated with the temperature-independent model. Additionally, the estimated unit-cell parameters for MgTi_2O_5 (karrooite) at 300 K are: $a = 9.6781 \pm 0.0370 \text{ \AA}$, $b = 10.0110 \pm 0.0462 \text{ \AA}$, and $c = 3.7331 \pm 0.0053 \text{ \AA}$. At 298 K, the Yang and Hazen (1998) unit-cell parameters and volume for ordered MgTi_2O_5 (karrooite) are: $a = 9.7031 \text{ \AA}$, $b = 10.0262 \text{ \AA}$, $c = 3.7329 \text{ \AA}$, and $V^0 = 363.17 \text{ \AA}^3$. Nominally at 293 K, Bayer (1971) reports $a = 9.7363 \text{ \AA}$, $b = 9.9870 \text{ \AA}$, $c = 3.7442 \text{ \AA}$, and $V^0 = 364.0726 \text{ \AA}^3$.

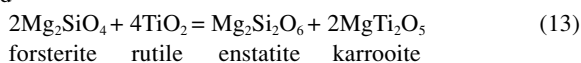
To derive parameters a_1 through a_7 of Equation 7 (a_8 was set equal to 0), we fitted the Orr and Coughlin (1952) and Brown and Navrotsky (1989) enthalpy measurements with Equations 9b and 11 ($\Delta H^{\text{ideal}} + \Delta H^{\text{excess}}$), but only above 1000 K where the samples probably either achieved or approached equilibrium cation configuration. The Berman and Brown (1985) empirically estimated heat-capacity coefficients were used as starting points, and the heat capacity was constrained to approach the limit of $C_p = 3nR + (a^2 V_0 T/b)$ at high temperatures, practically at >2000 K. The derived heat-capacity parameters are presented in Table 1, and the calculated and observed enthalpy data are compared in Figure 4. The average deviation between the calculated and observed relative enthalpy data is -3800 kJ/mol with a standard error of 800 kJ/mol. Below 1000 K, we calculated the relative enthalpy assuming equilibrium cation disorder, which may not be correct as the samples probably carry over a high-temperature cation configuration. The latter is probably lower than that of their synthesis conditions, i.e., s may correspond to that at 1000 or 1200 K instead of 1500 K. The calculated excess heat capacity, entropy, enthalpy, and Gibbs free energy due to cation disorder are shown in Figure 6.

Experimental constraints

To calculate the standard-state enthalpy, entropy, and Gibbs free energy of ordered MgTi_2O_5 (karrooite) at 298 K and 1 bar we used phase equilibrium constraints for the reactions (Fig. 7):



and



in the range 973 to 1673 and 0.01 to 2.0 GPa (MacGregor 1969; Lindsley et al. 1974; this study). Each half-bracket in the phase-

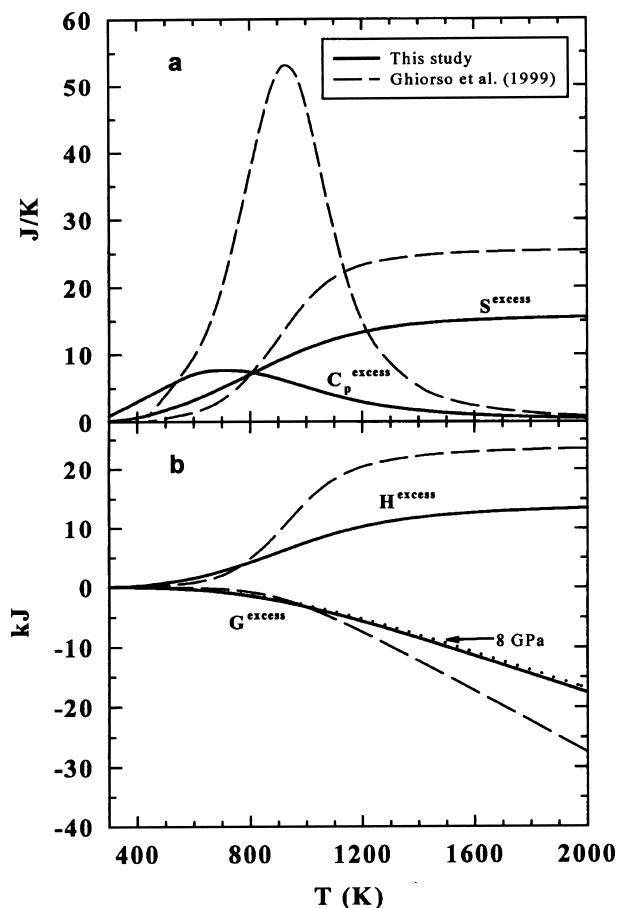


FIGURE 6. Calculated temperature dependence of (a) the heat capacity and entropy associated with cation disorder, and (b) the enthalpy and Gibbs free energy associated with cation disorder at 1 bar and 8 GPa (G^{excess} only).

equilibrium experiments constrains the Gibbs free energy of MgTi_2O_5 (karrooite) via the inequalities:

$$\mu_{\text{MgTi}_2\text{O}_5}^{\text{Kar}} - \mu_{\text{TiO}_2}^{\text{Rt}} - \mu_{\text{MgTiO}_3}^{\text{Gk}} >, \text{ or } < 0,$$

$$\text{and } 2\mu_{\text{Mg}_2\text{SiO}_4}^{\text{Fo}} + 4\mu_{\text{TiO}_2}^{\text{Rt}} - \mu_{\text{MgTi}_2\text{O}_5}^{\text{Kar}} - \mu_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{En}} <, \text{ or } > 0.$$

To better constrain reactions 12 and 13, which were originally constrained by only one half-bracket at 0.1 GPa and 700 °C (Lindsley et al. 1974), we performed new experiments at 600–1100 °C and 0.0001–0.4 GPa (Table 2). The MgTi_2O_5 starting material in this study was synthesized using a portion of the original Lindsley et al. (1974) $\text{MgTiO}_3 + \text{TiO}_2$ mixture. This mixture was reacted in a Pt crucible at 1 atm and 1190 °C for four days, plus one day of cooling at a rate of 1 °C/min to induce ordering. The final product had a barely detectable rutile peak as well. Thus, either the final mixture also has MgO , MgTiO_3 , and Mg_2TiO_4 —all below the detectability of XRD—or the MgTi_2O_5 (karrooite) is slightly non-stoichiometric. Phase pure forsterite and enstatite were synthesized from the respec-

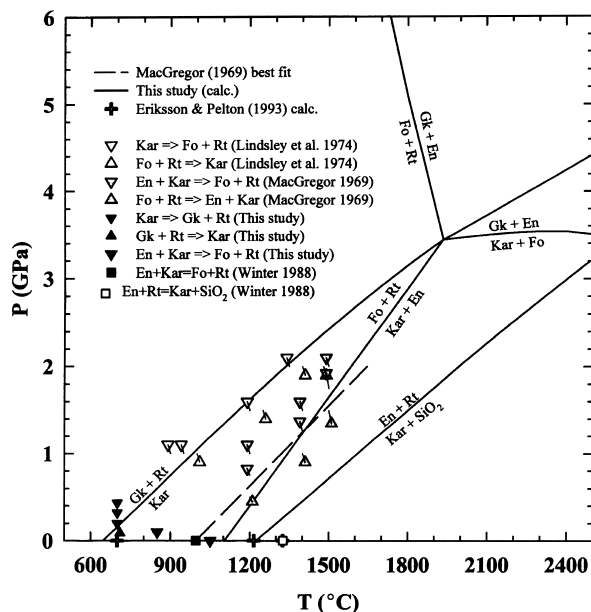


FIGURE 7. Calculated phase relations and experimental data for reactions among orthorhombic oxide, olivine, orthopyroxene, ilmenite, rutile, and silica in the $\text{MgO-TiO}_2\text{-SiO}_2$ system. Above 1500 °C, these reactions must be partly metastable with respect to liquid in this system (MacGregor 1969). (See text for discussion regarding the experimental results and calculations at 1 bar).

tive oxides at 1 atm and 1400 °C, and 940 °C and 2.0 GPa, respectively.

To bracket reaction 12 we performed hydrothermal experiments in the range 600–700 °C and 0.2–0.4 GPa (Table 2). Portions of MgTi_2O_5 and $\text{MgTiO}_3 + \text{TiO}_2$ mechanical mixtures with 8 mg of de-ionized H_2O were loaded into $\text{Ag}_{80}\text{Pd}_{20}$ capsules and welded shut. The capsules were then mounted into externally heated, cold-seal pressure vessels. The temperature and pressure were measured by type-K thermocouples and by a Bourdon-tube gauge, respectively. After each experiment was terminated, the capsules were extracted and checked for H_2O leaks. Then the pinkish-gray polycrystalline samples were re-

moved and ground in an agate mortar under acetone by hand, and finally examined by means of XRD using a Scintag diffractometer ($2\theta = 10$ to 90° , step size = 0.02° , scan rate = 2° per min).

For reaction 13, we performed constraining experiments at 850–1050 °C and 0.0001–0.1 GPa using seeded mechanical mixtures of $\text{MgSiO}_3 + \text{MgTi}_2\text{O}_5$ and $\text{Mg}_2\text{SiO}_4 + 2\text{TiO}_2$. The 1 atm anhydrous experiments were performed in a fast-quench (vertical) Pt-wound furnace. The temperature was recorded with a Pt-Pt₉₀Rh₁₀ thermocouple calibrated against the melting point of Au at room pressure. The mixtures were loaded in Pt capsules that were welded shut and subsequently placed in the hot spot of the furnace. The experiments were terminated by dropping the Pt capsules into a glass beaker filled with water. The details of the hydrothermal experiments were the same as above, except that this time we used Pt instead of $\text{Ag}_{80}\text{Pd}_{20}$ capsules. All reaction products were first ground in an agate mortar and then examined with powder XRD.

Thermodynamic data for all the phases but MgTi_2O_5 (karrooite) were taken from Andersen et al. (1993) and the optimization procedures were similar to Xirouchakis and Lindsley (1998) and Berman (1988). Each half-bracket was expanded to included pressure and temperature uncertainties: $\pm 10^\circ\text{C}$ and ± 0.1 GPa to the Lindsley et al. (1974) data, and $\pm 10^\circ\text{C}$ and $\pm 10\%$ relative in pressure to the MacGregor (1969) data. Except for the experiments reported here (Table 2), all other pertinent information can be found in the original studies.

The degree of cation disorder in the MgTi_2O_5 crystals either produced or used as reactants in the of MacGregor (1969) and Lindsley et al. (1974) experiments is not known. But in the latter study, the unit-cell volume of the MgTi_2O_5 starting material is equal to $364.4453 \text{ \AA}^3$ (5.4876 J/bar), which, utilizing Figure 2, indicates a value for s of ~ 0.35 that corresponds to a quenched configuration of ~ 1130 K. Because the Lindsley et al. (1974) experiments were performed between 1173 and 1673 K, it is probable that the reactant MgTi_2O_5 crystals in their experiments may have had time to re-equilibrate and approach or even achieve the equilibrium cation configuration prior to reacting. We assume that the MgTi_2O_5 crystals in the experiments of MacGregor (1969) behaved similarly, although the uncertainty in that case is much greater as MacGregor does not pro-

TABLE 2. List of new phase equilibrium experiments

Run no.	T (°C)	P (GPa)	Time (h)	Reactants	Products
karrooite 9	700	0.43	493.5	Gk + Rt (+1wt% Kar)	Gk + Rt
Karrooite 10	700	0.43	493.5	Kar (+1wt% Gk + Rt)	Gk + Rt
karrooite 11	600	0.43	670	Gk + Rt (+1wt% Kar)	Gk + Rt
karrooite 12	600	0.43	670	Kar (+1wt% Gk + Rt)	Gk + Rt
karrooite 13	700	0.32	493.5	Gk + Rt (+1wt% Kar)	Gk + Rt
karrooite 14	700	0.32	493.5	Kar (+1wt% Gk + Rt)	Gk + Rt
karrooite 15	698.5	0.2	665.75	Gk + Rt (+1wt% Kar)	Gk + Rt
karrooite 16	698.5	0.2	665.75	Kar (+1wt% Gk + Rt)	Gk + Rt (+Kar)
Fo + 2Rt 1	1052	0.0001	120	Fo + 2Rt (+traces of En + Kar)	no change
En + Kar 1	1052	0.0001	120	En + Kar (+traces of Fo + 2Rt)	no change
Fo + 2Rt 1	1049	0.0001	336	Fo + 2Rt (+traces of En + Kar)	no change
En + Kar 1	1049	0.0001	336	En + Kar (+traces of Fo + 2Rt)	Fo + Rt growth
Fo + 2Rt 3	850	0.1	244	Fo + 2Rt (+traces of En + Kar)	no change
Kar + En 3	850	0.1	244	Kar + En (+traces of Fo + 2Rt)	Fo + Rt growth

Notes: Uncertainties are: $\pm 5^\circ\text{C}$ and ± 0.005 GPa for the hydrothermal experiments, and $\pm 2^\circ\text{C}$ for the 1 atm anhydrous experiments. Traces means that the added amounts of either En + Kar or Fo + 2Rt were just below powder XRD detectability.

vide any pertinent data. In all cases, we assumed that the product MgTi₂O₅ crystalline material crystallized with an equilibrium cation configuration. Certainly, most of the Lindsley et al. (1974) and the new experiments reported here were run long enough to make the assumption of equilibrium cation configuration reasonable. The derived standard-state thermodynamic data are presented in Table 1 along with the corresponding $C_p(T)$, $V(T, P)$, and excess parameters.

Model predictions

Our preferred model and that of Ghiorso et al. (1999) for the Gibbs free energy of MgTi₂O₅ as a function of pressure, temperature, and cation disorder exhibit many broad similarities. For instance, both show similar sympathetic variations in excess entropy, enthalpy, heat capacity, and Gibbs free energy with increasing temperature (Fig. 6). The specific differences are the result of the different data sets used in their calibration.

At 1 bar, both models predict nearly identical s values in the range 1000 to 1400 K, where the order parameter increases linearly with temperature (Fig. 3). However, the differences become greater below 1000 K and above 1400 K, where s as a function of temperature shows curvature. Interestingly, it is in these curved segments that the equilibrium cation configuration of MgTi₂O₅ either cannot be quenched or requires periods of long annealing. Our model predicts that MgTi₂O₅ (karrooite) is still somewhat disordered at <450 K; in contrast, the Ghiorso et al. (1999) model predicts essentially ordered MgTi₂O₅ below 450 K. At the melting temperature (1663 ± 20 K), our value for the cation disorder parameter s is -0.098 [cf., -0.0087 (Ghiorso et al. 1999) and 0.10 (Brown and Navrotsky 1989)]. Obviously, MgTi₂O₅ (karrooite) melts before achieving random cation distribution between the M1 and M2 sites, i.e., $s = -1/3$ and $X_{Mg}^{M2} = 1/3$. From Figures 3 and 6, we also infer that at constant pressure, higher temperatures will always stabilize MgTi₂O₅ (karrooite) (i.e., $S^{\text{total}} >> 0$, $G^{\text{total}} << 0$); in contrast, MgTi₂O₅ (karrooite) becomes thermodynamically less stable for isothermal increases in pressure, as this will result in a more-ordered MgTi₂O₅ (karrooite) and a less-negative Gibbs free energy of disorder. Although there are no experimental data regarding cation disorder in MgTi₂O₅ at high pressures and temperatures, in light of the data regarding Ni-Mg disorder in olivine (Chen et al. 1996; Henderson et al. 2001) and predictions (Hazen and Navrotsky 1994), it is not unreasonable to expect that pressure may affect the order parameter s .

The predicted temperature dependence of the equilibrium constant

$$\left(K_D = \frac{(X_{Ti}^{M1})^2}{(1 - X_{Ti}^{M1}) \cdot (2 - X_{Ti}^{M1})} = \frac{(1 - s)^2}{(1 + s) \cdot (3 + s)} \right)$$

of the interchange reaction $Ti(M1) + Mg(M2) = Ti(M2) + Mg(M1)$ is in good agreement with the in situ neutron diffraction data of Lennie et al. (1999, 2000). We find that K_D increases linearly between 1000–1600 K and changes slope between 1000 and 900 K becoming nearly flat below 900 K. From fitting an equation of the form, $\ln K_D = -\Delta G_D/RT = \Delta S_D/R - \Delta H_D/RT$, to our model K_D values, we estimate that the en-

thalpy (ΔH_D) and entropy (ΔS_D) associated with cation disorder may range between 42–46 kJ/mol and 15–21 J/(mol·K), respectively. Brown and Navrotsky (1989) calculated the ΔH_D and ΔS_D to be 47.34 kJ/mol and 2.65 J/(mol·K). The latter value, however, seems to be a typographical error and it is perhaps closer to 20.65 for the $\Delta H_D - T \cdot \Delta S_D$ and ΔG_D terms to be equal. Lennie et al. (1999, 2000) obtained a site exchange energy of 40–43 kJ/mol from measurements between 1073 and 1873 K.

We used the preferred thermodynamic data for MgTi₂O₅ (karrooite) in Table 1 to calculate the equilibrium location of MgTi₂O₅ (karrooite)-bearing reactions by minimizing the quantities $|\Delta G_{\text{reaction}}|$ and $|\partial G/\partial s|_{P,T}^{\text{Kar}}$, simultaneously (Fig. 7). Although both sets of the optimized standard state thermodynamic data and corresponding volume equations in Table 1 satisfy the phase-equilibrium constraints, we only show the calculated curves based on the preferred model. At 1 bar, we predict that MgTi₂O₅ (karrooite) breaks down to geikielite plus rutile below 919 K (646 °C), whereas MgTi₂O₅ (karrooite) and enstatite reacts to form forsterite and rutile below 1377 K (1104 °C). For the same reactions, Eriksson and Pelton (1993) report 973 ± 20 K (700 °C) and 1489 ± 20 K (1216 °C), respectively. These authors also cite the work of Winter (1988), who determined experimentally that MgTi₂O₅ (karrooite) plus enstatite reacts to form forsterite and rutile below 1269 K (996 °C), and MgTi₂O₅ (karrooite) + silica breaks down to enstatite + rutile below 1599 K (1326 °C). We do not have any experimental data for the latter reaction, but we predict a breakdown temperature of 1499 K (1226 °C) whereas the 1269 K (996 °C) datum is clearly in disagreement with our 1322 K (1049 °C) datum (Fig. 7 and Table 2). Eriksson and Pelton (1993) also noted that they could not satisfy the Lindsley et al. (1974) constraints and both the Winter (1988) results. Clearly, there are inconsistencies between our data and those of Winter that we cannot resolve at present.

In Figure 7, we also present inferred reactions among solid phases for which we presently have no constraining experimental data. Moreover, they must be partly metastable with respect to liquid in the MgO-TiO₂-SiO₂ system above 1500 °C (MacGregor 1969). Our calculations also suggest that diopside- and titanite-bearing reactions are not stable relative to liquid in the Ca-Mg-Ti-Si-O system, because the required temperatures are extremely high (>2000 °C), regardless of pressure. Nonetheless, the inferred reactions shown in Figure 7 may be helpful in understanding the relations among armalcolite, ilmenite, rutile, olivine, and orthopyroxene in terrestrial mantle rocks and xenoliths, and high-Ti lunar basalts (e.g., Haggerty 1991; Papike et al. 1998, and references therein). For instance, from the calculated topology and in conjunction with pertinent experimental data in Fe-bearing systems, we argue that silica-enriched melt from the breakdown of orthopyroxene in the oceanic mantle xenoliths described by Gregoire et al. (2000) is not essential to the formation of armalcolite, as these authors proposed. Instead, we anticipate armalcolite to react with silica or silica-enriched melt or fluid and to produce more orthopyroxene or olivine. Alternatively, reactions between olivine, orthopyroxene and ilmenite or rutile, or a TiO₂-rich melt/fluid with olivine and orthopyroxene, appear more plausible mechanisms. It is also reasonable to argue that in general, de-

compression at nearly constant (but also high) temperature seems to favor armalcolite over rutile and/or ilmenite; in contrast, cooling at low pressure conditions will favor ilmenite over armalcolite.

The reactions in Figure 7 may also partially explain why armalcolite is observed to coexist with olivine, orthopyroxene, and liquid, or olivine and liquid, in high-temperature experiments at low and high pressures, and for either Fe-rich or Mg-rich bulk compositions (e.g., Grove and Beaty 1980; Delano 1980; Xirouchakis et al. 2001). Interestingly, Cazzaniga and Hess (1995) report armalcolite replacing ilmenite in the presence of olivine and pyroxene with increasing temperature (1265–1275 °C) at 1.0 GPa (Fig. 8). Moreover, in many of the crystallization experiments using lunar basaltic compositions (see Papike et al. 1998 for a recent compilation), the initial high-temperature $\text{Ol} + \text{Arm} + \text{Liq}$ assemblage changes to $\text{Ol} + \text{Ilm} + \text{Liq} \pm \text{Px}$ with decreasing temperature. In light of the experimental data in the $\text{MgO-FeO-Fe}_2\text{O}_3\text{-TiO}_2$ and $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ systems (Fig. 8), (Haggerty and Lindsley 1969; Friel et al. 1977), we argue that the Cazzaniga and Hess (1995) datum is perhaps the only experimental evidence for the displacement of the reaction MgTi_2O_5 (karrooite) + forsterite = orthopyroxene + geikelite—either its metastable or stable extension—due to addition of Fe.

The addition of Fe, Ca, and Al will cause the high pressure and temperature invariant point in Figure 7 to become a divariant field or an univariant curve (depending upon the number of phases) that has to extend to lower pressures and temperatures suitable for lunar petrogenesis. However, along this curve or within this field, olivine and orthopyroxene can coexist with liquid, armalcolite, and ilmenite (i.e., $\text{Ol} + \text{Opx}$ cotectic).

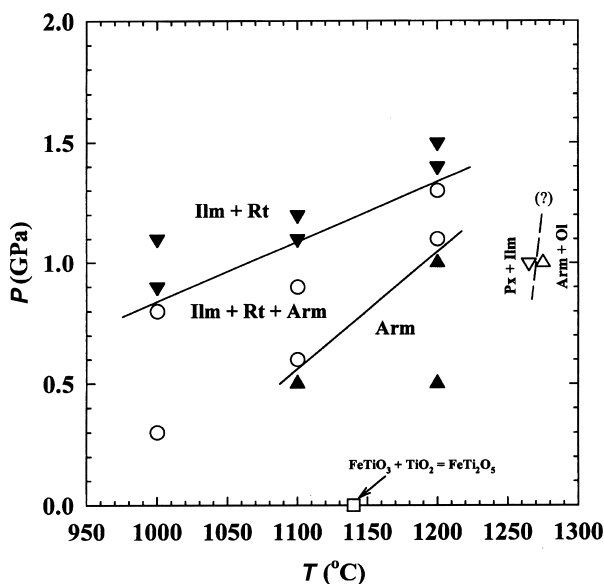


FIGURE 8. Experimental data for the reactions $\text{Arm} = \text{Ilm} + \text{Rt}$ (Friel et al. 1977), $\text{FeTi}_2\text{O}_5 = \text{FeTiO}_3 + \text{TiO}_2$ (Haggerty and Lindsley 1969), and possibly $\text{Ol} + \text{Arm} = \text{Ilm} + \text{Opx}$ (Cazzaniga and Hess 1995) in the $\text{FeO-MgO-TiO}_2\text{-SiO}_2$ system. Lines were drawn by hand.

Although the Ti-rich phase responsible for the enrichment in TiO_2 in lunar basalts is generally thought to be ilmenite (e.g., Hubbard and Minear 1975; Wagner and Grove 1997), because Fe^{2+} -rich armalcolite is richer in Ti than ilmenite, and high temperature seems to favor armalcolite relative to ilmenite and/or rutile over the range of pressures and oxygen fugacities appropriate for lunar basalt petrogenesis, it is conceivable that armalcolite may be a more or equally significant mineral in the Ti-enriched portions of the lunar mantle.

In summary, we have calibrated a thermodynamic model for the Gibbs free energy of pseudobrookite-type MgTi_2O_5 (karrooite) that accounts for cation disorder. The model can be used in computations of mineral equilibria in FeO-free compositions, and it can serve as basis for examining the thermodynamics of Fe-bearing orthorhombic oxide solutions with the pseudobrookite structure. To facilitate calculations the MgTi_2O_5 (karrooite) model will be incorporated into the Win-dows and JAVA versions of the QUILF program (<http://www.geo.sunysb.edu/GEO/general/faculty/lindsley.html>).

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