

THERMODYNAMIC PROPERTIES OF Fe-Mg TITANIFEROUS MAGNETITE SPINELS

ROY L. HILL AND RICHARD O. SACK*

Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907, U.S.A.

ABSTRACT

Reversed Fe-Mg exchange experiments between olivine and Ti-rich magnetite [(Mg,Fe)₂TiO₄ - (Mg,Fe)Fe₂O₄] show that the distribution coefficient for the exchange reaction $\frac{1}{2} \text{Mg}_2\text{TiO}_4 + \frac{1}{2} \text{Fe}_2\text{SiO}_4 = \frac{1}{2} \text{Mg}_2\text{SiO}_4 + \frac{1}{2} \text{Fe}_2\text{TiO}_4$ varies from approximately 2.4 to 1.8 in the range 800-1400°C and suggest that Fe-Mg titanium-based spinel [(Mg,Fe)TiO_{0.5}O₂] exhibits small positive deviations from ideal mixing (≤ 170 cal/mol) in this temperature range. Comparison of these results with those for aluminum-based spinels suggests that the Gibbs energy of the reciprocal reaction $\text{MgAl}_2\text{O}_4 + \frac{1}{2}\text{Fe}_2\text{TiO}_4 = \text{FeAl}_2\text{O}_4 + \frac{1}{2}\text{Mg}_2\text{TiO}_4$ is about 6.2 and 5.2 kcal/gfw at 1400 and 800°C, respectively. A thermodynamic formulation for R₃O₄ FeO-MgO-Fe₂O₃-TiO₂ spinels based on a second-degree Taylor expansion in terms of composition and cation-ordering variables is calibrated. It uses the above data in combination with homogeneous and heterogeneous equilibria for the Fe₂TiO₄-Fe₃O₄, Mg₂TiO₄-MgFe₂O₄, and Fe₃O₄-MgFe₂O₄ spinel binary joins. The resulting calculated activity-composition relations and cation-ordering schemes are in accord with available experimental data and petrological constraints. This model indicates that Mg and Fe²⁺ are more strongly ordered between tetrahedral and octahedral sites in titanium-based spinels than in ferric-iron-based spinels (with Mg²⁺ showing a tetrahedral preference relative to Fe²⁺ in both spinels) and predicts an approximately symmetrical miscibility gap for *Fd3m* Mg₂TiO₄-MgFe₂O₄ spinels (T_c ~ 400°C). Calculated activity-composition relations indicate that the activities of both dilute and concentrated components that exhibit temperature-dependent cation distributions are typically underestimated by thermodynamic models that do not make explicit provisions for such cation ordering. A calibration for the olivine-spinel Fe-Mg exchange geothermometer is presented.

Keywords: titaniferous magnetite, Fe-Mg exchange experiments, thermodynamics, reciprocal reactions, cation ordering, activity-composition relations, miscibility gaps, olivine-spinel geothermometry.

SOMMAIRE

Des expériences (dans les deux sens) sur l'échange Fe-Mg entre olivine et magnétite titanifère [(Mg,Fe)₂TiO₄ - (Mg,Fe)Fe₂O₄] montrent que le coefficient de distribution pour la réaction $\frac{1}{2} \text{Mg}_2\text{TiO}_4 + \frac{1}{2} \text{Fe}_2\text{SiO}_4 = \frac{1}{2} \text{Mg}_2\text{SiO}_4 + \frac{1}{2} \text{Fe}_2\text{TiO}_4$ varie d'environ 2.4 à 1.8 entre 800 et 1400°C. Le spinelle Fe-Mg titanifère (Mg,Fe)Ti_{0.5}O₂ montrerait de légères déviations positives d'un modèle de mélange idéal (≤ 170 cal/mol) dans cet intervalle de température. Une comparaison avec les compositions alumi-

neuses fait penser que l'énergie de Gibbs pour la réaction réciproque $\text{MgAl}_2\text{O}_4 + \frac{1}{2}\text{Fe}_2\text{TiO}_4 = \text{FeAl}_2\text{O}_4 + \frac{1}{2}\text{Mg}_2\text{TiO}_4$ est d'environ 6.2 et 5.2 kcal/gfw à 1400 et 800°C, respectivement. Une expression thermodynamique est établie pour les spinelles R₃O₄ dans le système FeO-MgO-Fe₂O₃-TiO₂, par expansion de Taylor de deuxième degré en termes de composition et variables qui décrivent la mise en ordre des cations. Elle est fondée sur les données citées et les équilibres homogènes et hétérogènes pour les séries binaires Fe₂TiO₄ - Fe₃O₄, Mg₂TiO₄ - MgFe₂O₄, et Fe₃O₄ - MgFe₂O₄. Il en résulte des relations activité - composition calculées et des schémas de mise en ordre des cations qui concordent avec les données expérimentales disponibles et les contraintes pétrologiques. Ce modèle indique que Mg et Fe²⁺ sont plus effectivement ordonnés entre les sites tétraédriques et octaédriques dans les spinelles titanifères que dans les spinelles ferrifères (le Mg²⁺ préfère le site tétraédrique comparé au Fe²⁺ dans les deux spinelles); de plus, il prédit une lacune de miscibilité à peu près symétrique pour les spinelles *Fd3m* de la série Mg₂TiO₄ - MgFe₂O₄ (T_c environ 400°C). Les relations calculées entre activité et composition indiquent que l'activité des composants dilués aussi bien que des composants concentrés dont la distribution cationique dépend de la température est typiquement sous-estimée par les modèles thermodynamiques qui ne prennent pas compte de façon explicite du degré d'ordre parmi les cations. On présente un étalonnage du géothermomètre fondé sur la réaction d'échange Fe-Mg entre olivine et spinelle.

(Traduit par la Rédaction)

Mots-clés: magnétite titanifère, expériences d'échange Fe-Mg, approche thermodynamique, réactions réciproques, relations activité - composition, lacune de miscibilité, géothermométrie olivine - spinelle.

INTRODUCTION

The importance of oxide spinels as petrogenetic indicators of intensive variables operating during igneous and metamorphic processes in the crust and upper mantle has been emphasized in many contributions (e.g., Buddington & Lindsley 1964, Irvine 1965, Hill & Roeder 1974, Wood & Nicholls 1978, Sack 1980b, 1982a,b). [The oxide spinels of geochemical interest exhibit *Fd3m* symmetry (*Z* = 8) at high temperature, are composed predominantly of the cations Fe²⁺, Mg²⁺, Fe³⁺, Al³⁺, Cr³⁺ and Ti⁴⁺ (often with at least minor amounts of Zn²⁺, Mn²⁺, V³⁺, Ni²⁺ and Co²⁺), typically approximate the stoichiometry R₃O₄ in having one tetrahedral and two octahedral sites occupied per formula unit (equi-points 8a and 16d, respectively), and are composed

*To whom correspondence should be addressed.

of 2-3 and 2-4 components (e.g., $MgFe_2O_4$ and Mg_2TiO_4 , respectively) that exhibit variable degrees of cation ordering between tetrahedral and octahedral sites.] These and similar studies have shown that the diversity of spinel chemistry may be related to petrogenesis and bulk-rock chemistry through use of activity-composition relationships. However, such relationships are complicated because spinels show a wide range of substitution of cations and variation from R_3O_4 stoichiometry, particularly in ferric-iron-based spinels (e.g., Webster & Bright 1961, Taylor 1964, Aragon & McCallister 1982, Mattioli *et al.* 1987). Further complications result from the ordering of di- and trivalent cations between tetrahedral and octahedral sites (e.g., Barth & Posnjak 1932, Verwey & Heilmann 1947, Goodenough & Loeb 1955), and pronounced positive deviations from linearity in vibrational Gibbs energy along many compositional joins (e.g., Fe_2TiO_4 - $FeAl_2O_4$ and Mg_2TiO_4 - $MgAl_2O_4$; Muan *et al.* 1972; $FeAl_2O_4$ - Fe_3O_4 ; Turnock & Eugster 1962; Fe_2TiO_4 - Fe_3O_4 ; Lindsley 1981, Price 1981).

Development of a thermodynamic model that makes explicit provisions for all of the above-mentioned complexities is restricted owing to the lack of reliable data on homogeneous and heterogeneous equilibria (e.g., Sack 1982a, O'Neill & Navrotsky 1984). However, with the addition of recent high-temperature determinations of Fe^{2+} - Fe^{3+} ordering in the binary joins Fe_3O_4 - Fe_2TiO_4 and Fe_3O_4 - $MgFe_2O_4$ (e.g., Trestman-Matts *et al.* 1983, 1984) and the data supplied in this study, there are now sufficient data to develop a thermodynamic model relevant to the spinel system Fe_2TiO_4 - Mg_2TiO_4 - Fe_3O_4 - $MgFe_2O_4$ (FMFT) that

makes explicit provisions for cation ordering (assuming R_3O_4 stoichiometry and no short-range ordering). This system represents a model subsystem for many spinel-group minerals that occur in metamorphic rocks or in equilibrium with basic and more differentiated liquids (e.g., Sack & Carmichael 1984, Sack *et al.* 1987). Thus the intention of the present study is fourfold: (1) to supplement the available thermodynamic data-base for spinels, (2) to develop and test a thermodynamic model for the system Fe_2TiO_4 - Mg_2TiO_4 - Fe_3O_4 - $MgFe_2O_4$ that makes explicit provisions for cation ordering, (3) to use this thermodynamic model to predict activity-composition relations and Fe-Mg ordering in Fe_2TiO_4 - Mg_2TiO_4 spinels, and (4) to examine the petrogenetic significance of the activity-composition relations deduced from this model.

EXPERIMENTAL METHODS AND RESULTS

Mineral synthesis

Ulvöspinel, magnesium ulvöspinel, fayalite and forsterite were synthesized from Fe powder, Fe_2O_3 , TiO_2 , SiO_2 and MgO . The reagents Fe_2O_3 , TiO_2 , MgO and SiO_2 were dried for 24 hours before weighing, mixing, and grinding under acetone in an agate mortar. In the synthesis of ulvöspinel and fayalite, stoichiometric proportions of the appropriate reagents were annealed in Fe crucibles with friction-fitting lids at a temperature of 1150°C for three 48-hour periods in horizontal tube-furnaces under a stream of argon. Iron metal containers were employed to ensure that the spinels closely approximated R_3O_4 stoichiometry (e.g., Webster & Bright 1961, Taylor 1964). To aid homogenization, the contents were reground under acetone between cycles of annealing. Similar procedures were employed in the synthesis of forsterite and Mg_2TiO_4 , but they were annealed at 1350°C in Pt crucibles in air. The final products were examined by electron microprobe and powder X-ray-diffraction analysis. Microprobe analyses established that all end-member spinel and olivine compositions are homogeneous, stoichiometric phases. X-ray-diffraction patterns are characterized by sharp diffraction-maxima; cell edges deduced from these patterns are in the range established for these end members (e.g., Lindsley 1965, Wechsler *et al.* 1984).

Intermediate compositions along the Fe_2TiO_4 - Mg_2TiO_4 and Fe_2SiO_4 - Mg_2SiO_4 joins were synthesized by annealing appropriate proportions of end-member components in Fe crucibles with friction-fitting lids under a stream of argon in a vertical furnace. Olivine (Fe_{90} , Fe_{80} , Fe_{70} , Fe_{62} , Fe_{43} , and Fe_{22}) and titanium-based spinel compositions (Usp_{80} , Usp_{59} , Usp_{39} , and Usp_{21}) were produced by repeated annealing (1150-1350°C, 48 hr) and grind-

TABLE 1. RESULTS OF Fe^{2+} - Mg^{2+} EXCHANGE EXPERIMENTS INVOLVING OLIVINE AND TITANIUM-BASED SPINEL

Run #	T°C	Initial compositions			Final compositions			lnK _D
		O ₁ X _{Mg}	S _P X _{Mg}	2X _{OT} [†]	O ₁ X _{Mg}	S _P X _{Mg}	2X _{OT} [†]	
Ex-1	800	0.434	0.0	1.0	0.416(006)	0.051(003)	0.934	2.584(084)
Ex-2	800	0.434	0.204	1.0	0.423(006)	0.061(005)	0.935	2.423(112)
Ex-3	1000	0.216	0.204	1.0	0.193(003)	0.029(002)	0.959	2.130(086)
Ex-4	1000	0.216	0.0	1.0	0.204(005)	0.032(002)	0.975	2.046(096)
Ex-5	1000	0.216	0.0	1.0	0.276(004)	0.044(002)	0.959	2.121(064)
Ex-6	1000	0.434	0.204	1.0	0.451(004)	0.081(005)	0.958	2.224(097)
Ex-7	1200	0.434	0.204	1.0	0.458(005)	0.083(003)	0.979	2.228(060)
Ex-8	1000	0.620	0.204	1.0	0.629(005)	0.147(004)	0.969	2.287(060)
Ex-9	1000	0.620	0.204	1.0	0.633(003)	0.146(004)	0.971	2.315(050)
Ex-10	1200	0.216	0.0	1.0	0.203(005)	0.037(003)	0.879	1.896(116)
Ex-11	1200	0.216	0.0	1.0	0.220(005)	0.040(002)	0.946	1.921(080)
Ex-12	1200	0.216	0.204	1.0	0.243(007)	0.046(002)	0.856	1.892(076)
Ex-13	1200	0.216	0.204	1.0	0.283(006)	0.054(002)	0.958	1.931(083)
Ex-14	1200	0.434	0.0	1.0	0.401(005)	0.088(004)	0.903	1.975(072)
Ex-15	1200	0.434	0.204	1.0	0.444(003)	0.100(004)	0.922	1.971(045)
Ex-16	1200	0.434	0.412	0.983	0.493(009)	0.116(004)	0.906	1.998(080)
Ex-17	1200	0.620	0.0	1.0	0.577(006)	0.149(011)	0.983	2.057(112)
Ex-18	1200	0.701	0.0	1.0	0.679(005)	0.209(009)	0.944	2.078(079)
Ex-19	1200	0.701	0.412	0.983	0.732(005)	0.248(009)	0.935	2.115(078)
Ex-20	1200	0.799	0.204	1.0	0.786(004)	0.302(017)	0.948	2.137(110)
Ex-21	1200	0.799	0.412	0.983	0.807(003)	0.335(013)	0.934	2.115(077)
Ex-22	1200	0.898	0.412	0.983	0.886(006)	0.466(016)	0.951	2.190(123)
Ex-23	1200	0.898	0.615	0.982	0.903(004)	0.541(011)	0.957	2.073(084)
Ex-24	1400	0.701	0.615	0.982	0.778(003)	0.333(009)	0.974	1.952(051)
Ex-25	1400	0.799	0.412	0.983	0.823(005)	0.392(011)	0.982	1.974(083)
Ex-26	1400	0.799	0.615	0.982	0.865(003)	0.476(018)	0.960	1.961(088)
Ex-27	1400	0.898	0.412	0.983	0.871(003)	0.488(012)	0.956	1.952(079)
Ex-28	1400	0.898	0.615	0.982	0.908(005)	0.581(034)	0.951	1.961(197)

Results are based on the average of 15-20 microprobe analyses. Values of lnK_D as defined in the text, were calculated after correcting for the ferric-iron-bearing component in spinel assuming R_3O_4 stoichiometry.

ing under acetone until homogeneity could be established by electron-microprobe analysis (Table 1). Microprobe analyses of these materials and products of Fe-Mg exchange experiments were accomplished with a MAC 500 microprobe (Purdue Univ.) interfaced with a Digital Equipment Corporation PDP-11/05 computer. Operating conditions were 15 kV acceleration voltage and 0.25×10^{-6} A beam current. The raw analytical data were reduced by the ZAF correction procedure using MAGIC IV. Standards used were the end members Fe_2SiO_4 , Mg_2SiO_4 , Fe_2TiO_4 and Mg_2TiO_4 synthesized at the Lawrence Berkeley Laboratory and characterized at the University of California, Berkeley.

OLIVINE-SPINEL EXCHANGE EXPERIMENTS

Fe^{2+} - Mg^{2+} exchange experiments were conducted at 1400, 1200, 1000, and 800°C. Olivine and spinel were enclosed in Fe capsules with friction-

fitting lids. The capsules were machined from high-purity Fe rod (Johnson Matthey Chemicals, catalogue #40037), 5 mm in diameter, cut into 8-mm lengths. Capsules were loaded with 0.15–0.1 gram of material with a spinel:olivine weight ratio of about 30:70. All starting materials were stored in an evacuated desiccator and mixed under acetone to minimize water adsorption.

For the 1400 and 1200°C exchange runs, the Fe capsules were placed in an outer capsule of Fe metal crimped at both ends, hung by platinum wire in a vertical alumina-tube furnace, and annealed under a stream of argon. The experiments were quenched by dropping the sample through the furnace tube into a water bath introduced immediately prior to quench. In the 1000 and 800°C exchange experiments, the iron capsules were sealed in evacuated silica tubes and annealed in horizontal tube furnaces. Temperatures were measured periodically during each experiment with a Pt-Pt₉₀Rh₁₀ thermocouple calibrated

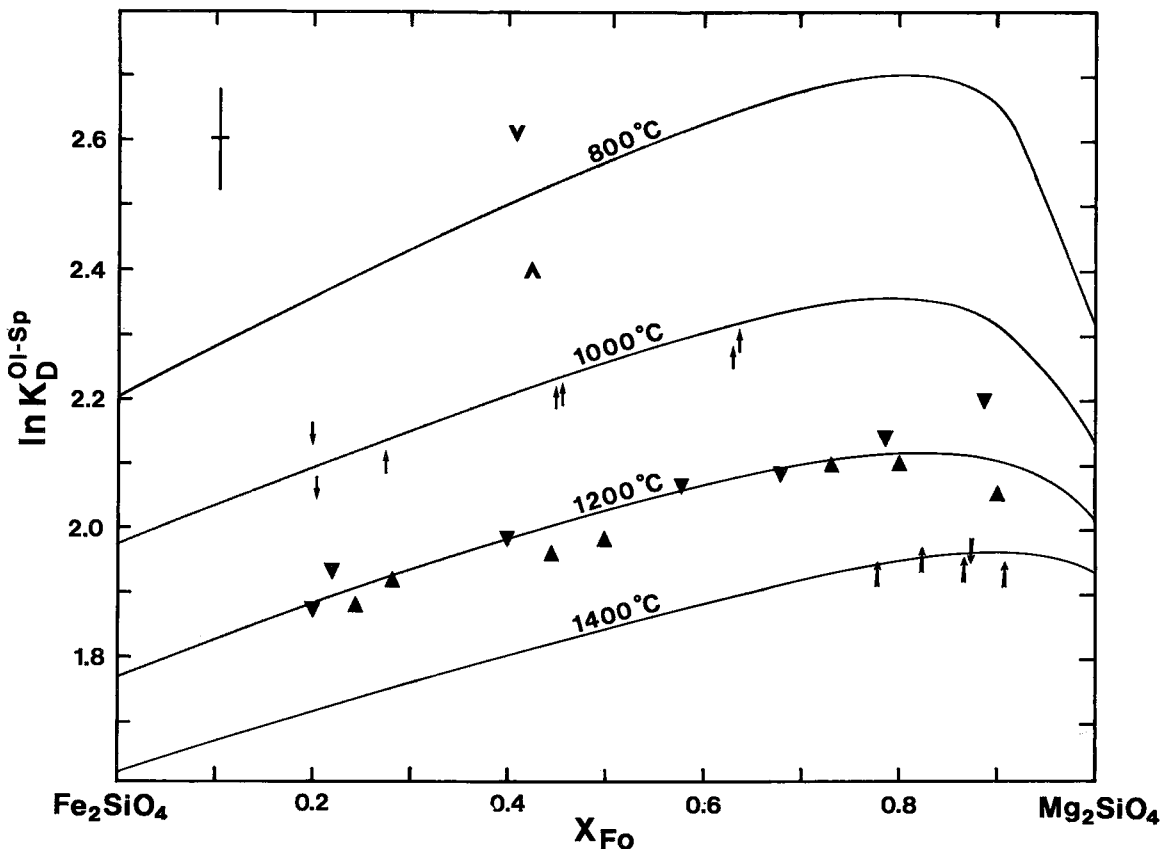


FIG. 1. Experimental determinations of the Fe^{2+} - Mg exchange distribution coefficients for coexisting olivine and Ti^{4+} -rich spinels, where $K_D^{\text{Ol-Sp}} = (X_{\text{Mg}}/X_{\text{Fe}^{2+}})^{\text{Ol}}(X_{\text{Fe}^{2+}}/X_{\text{Mg}})^{\text{Sp}}$. Solid lines are calculated distribution-isotherms using the expressions of Davidson & Mukhopadhyay (1984) for the mixing properties of olivine, and the appropriate expressions and parameters of the model presented herein. Arrows indicate directions of change of $\ln K_D^{\text{Ol-Sp}}$ during Fe-Mg exchange experiments. Error bar shown in upper left corner represents typical uncertainty.

against the melting point of gold (1064°C), with an accuracy of $\pm 5^\circ\text{C}$. Demonstration of Fe^{2+} - Mg^{2+} exchange equilibrium was achieved through use of reversals, *i.e.*, for each olivine composition, appropriate spinel compositions were loaded such that the equilibrium Fe^{2+} - Mg^{2+} distribution coefficient ($K_D^{\text{Ol-Sp}}$) was approached from opposite directions. In general, the 1400°C and 1200°C experiments exhibited convergence of the Fe^{2+} - Mg^{2+} distribution coefficient within 1 to 2 weeks. Such convergence of the 1000 and 800°C experiments occurred within 2 to 4 and approximately 10 months, respectively.

EXPERIMENTAL RESULTS

The Fe-Mg exchange experiments demonstrate that $\ln K_D^{\text{Ol-Sp}}$ (where $K_D^{\text{Ol-Sp}} = [X_{\text{Mg}}^{\text{Ol}}/X_{\text{Fe}^{2+}}^{\text{Ol}}]^{\text{Ol}} [X_{\text{Fe}^{2+}}^{\text{Sp}}/X_{\text{Mg}}^{\text{Sp}}]^{\text{Sp}}$) is both temperature- and composition-dependent (Fig. 1; see Table 1 for experimental data). For the spinels defining the Fe-Mg exchange isotherms, molar concentrations of $(\text{Fe},\text{Mg})\text{Fe}_2\text{O}_4$ between 2 and 15 mole % are calculated from microprobe data, assuming charge balance and

R_3O_4 stoichiometry for spinels in equilibrium with Fe metal (Webster & Bright 1961, Taylor 1964). As will be noted from Figure 1, the 1200°C experiments establish the composition dependence of $\ln K_D^{\text{Ol-Sp}}$ over most of the range of $\text{Mg}/(\text{Mg} + \text{Fe})$ values of olivine. At 1400°C, data collection was restricted to the most Mg-rich compositions of the Fe-Mg exchange isotherm, owing to melting of Fe-rich products. At 1000 and 800°C, the long-term experiments produced useful data only for the more Fe-rich compositions. Collectively, the experimental results suggest that the compositional dependence on $\ln K_D^{\text{Ol-Sp}}$ is approximately a linear function of $X_{\text{Fe}^{2+}}^{\text{Ol}}$ in the fayalite-rich portion of Figure 1 (Fo_{10} - Fo_{60}). In general, the compositional dependence in this range can be accounted for by considering the nonideal properties of olivine (*e.g.*, Davidson & Mukhopadhyay 1984), because changes in $X_{\text{Mg}_2\text{TiO}_4}^{\text{Ol}}$ are small compared to changes in $X_{\text{Fe}^{2+}}^{\text{Ol}}$. Beyond Fo_{60} the compositional dependence of $\ln K_D^{\text{Ol-Sp}}$ on $X_{\text{Fe}^{2+}}^{\text{Ol}}$ may be nonlinear owing to nonideal effects of the Fe-Mg substitution in spinel solid-solutions.

THERMODYNAMIC MODELING

Formulation of a thermodynamic model

As a compromise between feasibility and exactitude it will be assumed that a second-degree Taylor expansion in terms of composition and ordering variables will adequately describe the vibrational (*i.e.*, nonconfigurational) Gibbs energy of R_3O_4 spinels in the composition space $\text{FeO-MgO-Fe}_2\text{O}_3\text{-TiO}_2$, *i.e.*, FMFT spinels. This assumption is equivalent to assuming that spinels exhibit symmetrical regular-solution-type behavior (*e.g.*, Thompson 1967, 1969, Sack 1982a) along the joins of the space defined by composition and ordering variables. It is the simplest one that makes explicit provision for dependence of the energetics of cation ordering on degree of inversion in unary spinels. It is also the most complicated one that can be supported by currently available phase-equilibrium and site-population constraints (*e.g.*, Sack 1982a, Trestman-Matts *et al.* 1983, 1984).

It will be assumed that Ti^{4+} occupies octahedral sites only (Ishikawa *et al.* 1964, 1971, O'Reilly & Banerjee 1965, Stephenson 1969, Wechsler *et al.* 1984) and that no short-range or long-range ordering of cations occurs on octahedral sites. Making explicit provision for long-range ordering of di- and trivalent cations between octahedral and tetrahedral sites, the following composition (r_1 and r_2) and ordering (s_1 and s_2) variables may be chosen to describe a R_3O_4 -FMFT spinel: $r_1 = 1 - (X_{\text{Mg}}^{\text{TET}} + 2X_{\text{Mg}}^{\text{OCT}})$; $r_2 = (X_{\text{Fe}^{2+}}^{\text{TET}} + 2X_{\text{Fe}^{3+}}^{\text{OCT}}) - 1$; $s_1 = X_{\text{Fe}^{2+}}^{\text{TET}} - 2X_{\text{Fe}^{3+}}^{\text{OCT}}$; $s_2 = (X_{\text{Fe}^{2+}}^{\text{TET}} - 2X_{\text{Fe}^{3+}}^{\text{OCT}}) + 1$. These variables assume values of either +1, 0, or -1 for the vertices (*i.e.*, end-member components) of composition -

TABLE 2. RELATIONSHIPS BETWEEN THE THERMODYNAMIC PARAMETERS AND EXPANSION COEFFICIENTS

g_0	$= 1/16(3W_{14} + W_{13} - \Delta\delta_{34}^*) + 1/8(W_{78} - W_{56} + W_{15} - W_{27})$ $+ \Delta\delta_{1s_1}^* + 5\Delta\delta_{r_1r_2}^* + 1/4(W_{16} + 1/2(\delta_{27}^* + \delta_{56}^* - \Delta\delta_{78}^*))$
g_{r_1}	$= 1/8(\Delta\delta_{1s_1}^* - \Delta\delta_{34}^*) + 1/4(W_{27} - W_{15} + W_{56} - W_{78} + W_{14})$ $- 3\Delta\delta_{r_1r_2}^* + 1/2(\delta_{27}^* - \delta_{56}^* - \Delta\delta_{56}^* + \Delta\delta_{78}^*)$
g_{r_2}	$= 1/8(\Delta\delta_{34}^* - \Delta\delta_{r_1r_2}^* + W_{56} + W_{78}) + 1/4(W_{27} - W_{14} - W_{16} + \Delta\delta_{r_1r_2}^*)$ $+ 1/2(\delta_{27}^* - \delta_{56}^*)$
g_{s_1}	$= 1/8(3\Delta\delta_{34}^* - \Delta\delta_{r_1s_1}^*) + 1/4(W_{78} - W_{56} + W_{14} + W_{15} - W_{27} + \Delta\delta_{r_1r_2}^*)$
g_{s_2}	$= 1/2\Delta\delta_{78}^* - 1/8(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\delta_{34}^*)$ $- 1/4(W_{16} - W_{27} + \Delta\delta_{r_1r_2}^*)$
$g_{r_1s_1}$	$= 1/2(W_{13} - W_{14})$
$g_{r_1r_2}$	$= 1/8(\Delta\delta_{34}^* + \Delta\delta_{r_1s_1}^*) + 1/4(W_{15} - W_{27} + W_{13} - \Delta\delta_{r_1r_2}^*)$
$g_{r_1s_2}$	$= 1/4(\Delta\delta_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + 1/2(\Delta\delta_{56}^* - \Delta\delta_{78}^*)$ $+ W_{15} - W_{27} + \Delta\delta_{r_1r_2}^*$
$g_{r_2s_1}$	$= 1/8(\Delta\delta_{r_1s_1}^* - \Delta\delta_{34}^*) + 1/4(W_{15} - W_{27} - W_{13} + \Delta\delta_{r_1r_2}^*)$
$g_{r_2s_2}$	$= 1/8(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\delta_{34}^*) + 1/4(W_{16} - W_{27} + \Delta\delta_{r_1r_2}^*)$
$g_{s_1s_2}$	$= 1/4(\Delta\delta_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})$
$g_{r_1r_1}$	$= -1/4(\delta_{r_1s_1}^* + W_{14} + W_{13})$
$g_{r_2r_2}$	$= 1/16(W_{14} - W_{13} - \Delta\delta_{34}^*) + 1/8(\Delta\delta_{r_1r_2}^* - W_{27} - W_{15})$
$g_{s_1s_1}$	$= 1/4(\Delta\delta_{r_1s_1}^* - W_{14} - W_{13})$
$g_{s_2s_2}$	$= -1/4 W_{78}$

Vertices of composition-ordering space are as follows:

- 1) Fe_2TiO_4 [101]; 2) Mg_2TiO_4 [101]; 3) $\text{Fe}(\text{Mg},\text{Ti})_2\text{O}_4$ [011];
- 4) $\text{Mg}(\text{Fe},\text{Ti})_2\text{O}_4$ [011]; 5) $\text{Fe}^{3+}(\text{Fe}^{2+},\text{Fe}^{3+})_2\text{O}_4$ [111]; 6) $\text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ [111]; 7) $\text{Fe}^{3+}(\text{Mg},\text{Fe}^{3+})_2\text{O}_4$ [010]; 8) $\text{Mg}(\text{Fe}^{3+})_2\text{O}_4$ [010], where parentheses indicate cations in octahedral co-ordination. Enclosed in square brackets is the numerical representation of each component in terms of the composition and ordering variables (r_1, r_2, s_1, s_2), respectively. By convention, the second vertex (subscript) is subtracted from the first in defining appropriate parameters.

ordering space (see caption to Table 2) and are independent only for mixed FMFT spinels (see Appendix). A second-degree Taylor expansion in terms of these variables results in the following expression for the vibrational Gibbs energy of a FMFT spinel solid-solution:

$$\bar{G}^* = g_0 + g_{r_1}(r_1) + g_{r_2}(r_2) + g_{s_1}(s_1) + g_{s_2}(s_2) + g_{r_1r_2}(r_1)(r_2) + g_{r_1s_1}(r_1)(s_1) + g_{r_1s_2}(r_1)(s_2) + g_{r_2s_1}(r_2)(s_1) + g_{r_2s_2}(r_2)(s_2) + g_{s_1s_2}(s_1)(s_2) + g_{r_1r_1}(r_1)^2 + g_{r_2r_2}(r_2)^2 + g_{s_1s_1}(s_1)^2 + g_{s_2s_2}(s_2)^2.$$

The coefficients of the above expansion may be identified with five types of linearly independent thermodynamic parameters by setting the values of r_1 , r_2 , s_1 and s_2 to those they assume at the vertices and along the joins of composition-ordering space (e.g., Thompson 1969, Sack 1982a). The parameters chosen here are as follows:

- A. Vibrational Gibbs energies of the vertices Fe_2TiO_4 [\bar{G}_1^*], Mg_2TiO_4 [\bar{G}_2^*], and $\text{Fe}^{3+}(\text{Fe}^{3+}, \text{Fe}^{2+})_2\text{O}_4$ [\bar{G}_3^*].
- B. Vibrational Gibbs energies of cation-ordering reactions between the following vertices: $\text{Fe}(\text{Mg}, \text{Ti})_2\text{O}_4$ [3] and $\text{Mg}(\text{Fe}, \text{Ti})_2\text{O}_4$ [4] [$\Delta\bar{G}_{34}^* = \bar{G}_3^* - \bar{G}_4^*$], $\text{Fe}^{3+}(\text{Fe}^{3+}, \text{Fe}^{2+})_2\text{O}_4$ [5] and $\text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ [6] [$\Delta\bar{G}_{56}^* = [\bar{G}_5^* - \bar{G}_6^*]$], and $\text{Fe}^{3+}(\text{Mg}^{2+}, \text{Fe}^{3+})_2\text{O}_4$ [7] and $\text{Mg}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ [8] [$\Delta\bar{G}_{78}^* = \bar{G}_7^* - \bar{G}_8^*$].
- C. Vibrational Gibbs energies of the reciprocal reactions $\text{Fe}_2\text{TiO}_4 + \text{Mg}_2\text{TiO}_4 = \text{Fe}(\text{Mg}, \text{Ti})_2\text{O}_4 + \text{Mg}(\text{Fe}, \text{Ti})_2\text{O}_4$ [$\Delta\bar{G}_{r1s1}^*$] and $\frac{1}{2}\text{Mg}_2\text{TiO}_4 + \text{Fe}^{3+}(\text{Fe}^{3+}, \text{Fe}^{2+})_2\text{O}_4 = \text{Fe}^{3+}(\text{Fe}^{3+}, \text{Mg}^{2+})_2\text{O}_4 + \frac{1}{2}\text{Fe}_2\text{TiO}_4$ [$\Delta\bar{G}_{r1r2}^*$].
- D. Symmetrical regular-solution-type parameters describing departures from linearity in the vibrational Gibbs energy along joins between vertices differing in composition, $\text{Fe}_2\text{TiO}_4 - \text{Fe}(\text{Mg}, \text{Ti})_2\text{O}_4$ [W_{13}], $\text{Fe}_2\text{TiO}_4 - \text{Mg}(\text{Fe}, \text{Ti})_2\text{O}_4$ [W_{14}], $\text{Fe}_2\text{TiO}_4 - \text{Fe}^{3+}(\text{Fe}^{3+}, \text{Fe}^{2+})_2\text{O}_4$ [W_{15}], $\text{Fe}_2\text{TiO}_4 - \text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ [W_{16}], and $\text{Mg}_2\text{TiO}_4 - \text{Fe}^{3+}(\text{Mg}^{2+}, \text{Fe}^{3+})_2\text{O}_4$ [W_{27}] (e.g., Thompson 1967, Sack 1982a).
- E. Symmetrical regular-solution-type parameters describing departures from linearity in vibrational Gibbs energy along joins between vertices differing only in degree of order, $\text{Fe}^{3+}(\text{Fe}^{3+}, \text{Fe}^{2+})_2\text{O}_4 - \text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ [W_{56}] and $\text{Fe}^{3+}(\text{Fe}^{3+}, \text{Mg}^{2+})_2\text{O}_4 - \text{Mg}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ [W_{78}] (e.g., Sack 1982a, p. 178-181, O'Neill & Navrotsky 1983).

The relationships between the parameters given above and the coefficients of the Taylor's series expansion are given in Table 2. It is important to note that the parameters chosen do not define a unique set of such types of thermodynamic

TABLE 3. ESTIMATED VALUES OF THERMODYNAMIC PARAMETERS

$\Delta\bar{G}_{56}^*$	= -2.845 + 0.0027*T
$\Delta\bar{G}_{78}^*$	= -3.437 + 0.000955*T
$\Delta\bar{G}_{34}^*$	= 5.97 - 0.001745*T
$\Delta\bar{G}_{r_1s_1}^*$	= 5.795 - 0.003255*T
$\Delta\bar{G}_{r_1r_2}^*$	= -0.8626 + 0.000755*T
W_{56}	= 0.003255*T
W_{78}	= 0.00
W_{15}	= 6.2
W_{16}	= 2.0
W_{27}	= 5.4
W_{14}	= 0.5
W_{13}	= 0.5

All parameter values and temperatures are expressed in kcal/gfw and degrees kelvin. Uncertainties in parameter values are difficult to estimate owing to the varied data sets employed in their calibration. However, sufficient data are available for the Fe_2TiO_4 - Fe_3O_4 binary to constrain values of $\Delta\bar{G}_{56}^*$, W_{56} , W_{15} , and W_{16} to within ± 1 kcal.

With the exception of W_{13} and W_{14} , all remaining parameter values are considered to have associated with them an uncertainty of at least ± 1 kcal owing to a high degree of covariance between many of them. The uniqueness of the values of these parameters may be tested only as more data relevant to FMFT spinels become available.

parameters. For example, W_{27} might equally well be replaced by a regular-solution-type parameter for the join Mg_2TiO_4 - $\text{Mg}(\text{Fe}^{3+})_2\text{O}_4$ (i.e., W_{28}). This non-uniqueness of the chosen thermodynamic parameters requires that there are relationships between these parameters and all other such parameters relevant to $R_3\text{O}_4$, FMFT spinels. These relationships are the consequence of the assumption that a Taylor expansion of only second degree is adequate to describe the vibrational Gibbs energy of $R_3\text{O}_4$, FMFT spinels. They are developed in the Appendix and will be utilized subsequently.

Given the above relation for \bar{G}^* and an expression for the molar configuration entropy, an expression for the Gibbs energy of $R_3\text{O}_4$, FMFT spinels may be obtained from the relation

$$\bar{G} = \bar{G}^* - T\bar{S}^{\text{IC}} \quad (2)$$

Given the site-population constraints for $R_3\text{O}_4$, FMFT spinels,

$$(X_{\text{Fe}^{2+}}^{\text{TET}} + X_{\text{Mg}^{2+}}^{\text{TET}} + X_{\text{Fe}^{3+}}^{\text{TET}}) = 1, \quad (X_{\text{Fe}^{2+}}^{\text{OCT}} + X_{\text{Mg}^{2+}}^{\text{OCT}} + X_{\text{Fe}^{3+}}^{\text{OCT}} + X_{\text{Ti}^{4+}}^{\text{OCT}}) = 1, \quad \text{and} \quad (2X_{\text{Fe}^{3+}}^{\text{OCT}} + X_{\text{Fe}^{3+}}^{\text{OCT}} + \frac{1}{2}X_{\text{Fe}^{3+}}^{\text{TET}}) = 1, \quad \text{an expression for } \bar{S}^{\text{IC}} \text{ is readily derived from the relation}$$

$$\bar{S}^{\text{IC}} = -R \sum_s \sum_i b_s n_{i,s} \ln n_{i,s} \quad (3)$$

where b_s is the number of sites b per formula unit and $n_{i,s}$ is the fraction of species i on site s . It is

expressed here in terms of the composition and ordering variables r_1 , r_2 , s_1 and s_2 :

$$\begin{aligned} \bar{S}^{\text{IC}} = & -R \left\{ \left[\frac{1}{4}(3-r_2) - \frac{1}{2}(r_1 + s_1 + s_2) \right] \cdot \ln \left[\frac{1}{4}(3-r_2) \right. \right. \\ & \left. \left. - \frac{1}{2}(r_1 + s_1 + s_2) \right] \right\} + \left\{ \left[\frac{1}{4}(1-r_2) + \frac{1}{2}(r_1 + s_1) \right] \cdot \right. \\ & \left. \ln \left[\frac{1}{4}(1-r_2) + \frac{1}{2}(r_1 + s_1) \right] \right\} + \left\{ \left[\frac{1}{2}(s_2 + r_2) \right] \cdot \right. \\ & \left. \ln \left[\frac{1}{2}(s_2 + r_2) \right] \right\} + \left\{ \left[\frac{1}{4}(1+r_2) + \frac{1}{2}(s_1 + s_2 - r_1) \right] \cdot \right. \\ & \left. \ln \left[\frac{1}{4}(1+r_2) + \frac{1}{2}(s_1 + s_2 - r_1) \right] \right\} + \left\{ \left[\frac{1}{4}(1-r_2) + \right. \right. \\ & \left. \left. \frac{1}{2}(r_1 - s_1) \right] \cdot \ln \left[\frac{1}{4}(1-r_2) + \frac{1}{2}(r_1 - s_1) \right] \right\} + \left\{ \left[1 + \right. \right. \\ & \left. \left. \frac{1}{2}(r_2 - s_2) \right] \cdot \ln \left[\frac{1}{2} + \frac{1}{4}(r_2 - s_2) \right] \right\} + \left\{ \left[\frac{1}{2}(1-r_2) \right] \cdot \right. \\ & \left. \ln \left[\frac{1}{4}(1-r_2) \right] \right\}. \quad (4) \end{aligned}$$

From the resulting expression for \bar{G} , expressions for the conditions of homogeneous equilibrium, $(\partial \bar{G} / \partial s_1)_{T,P,r_2,r_1,s_2} = (\partial \bar{G} / \partial s_2)_{T,P,r_2,r_1,s_1} = 0$, may be readily derived. Expressions for the chemical potentials of the vertices of composition-order space may be derived from the relation

$$\begin{aligned} \mu_{ijkl} = & \bar{G} + (i-r_1)(\partial \bar{G} / \partial r_1)_{T,P,r_2,s_1,s_2} + (j-r_2) \\ & (\partial \bar{G} / \partial r_2)_{T,P,r_1,s_1,s_2} + (k-s_1)(\partial \bar{G} / \partial s_1)_{T,P,r_1,r_2,s_2} + \\ & (\ell-s_2)(\partial \bar{G} / \partial s_2)_{T,P,r_1,r_2,s_1} \quad (5) \end{aligned}$$

where i , j , k , and ℓ represent the respective values r_1 , r_2 , s_1 , and s_2 have in the vertex of interest (e.g., $i = +1$, $j = -1$, $k = 0$, and $\ell = +1$ for Fe_2TiO_4 component). Such expressions are given in Table A of the appendix.

Calibration

In principle, calibration of the energetic parameters may be achieved from analysis of the three types of data presently available: 1) site occupancies for unary and binary spinels, 2) activity-composition determinations and miscibility-gap data for binary spinels, and 3) Fe^{2+} - Mg^{2+} exchange data for coexisting olivine and spinels. Any calibration, however, will be *ad hoc* to some extent owing to the large number of parameters relative to the data sets available. In order to decrease the number of adjustable parameters we assume the following: 1) all regular-solution-type parameters describing joins between vertices with different composition are constants greater than zero, and 2) $W_{13} = W_{14} = 0.5$ - 1.0 kcal, based on the similar volumes of Mg^{2+} - versus Fe^{2+} -bearing end members (Lawson 1947, Sack 1980a, Ganguly & Saxena 1984). Given these assumptions, provisional model thermodynamic parameters are calibrated by first developing constraints on relationships between subsets of parameters from data relevant to homogeneous equilibrium for Fe_3O_4 and MgFe_2O_4 . Values for parameters relevant to the Fe_2TiO_4 - Fe_3O_4 binary join may then be constrained from analysis of homogeneous equilibrium, miscibility gap, activity-composition, and volume-composition data. Internally consistent values for the remaining parameters may then be established by analysis of appropriate homogeneous and heterogeneous constraints for the binary systems Mg_2TiO_4 - MgFe_2O_4 , Fe_2TiO_4 - Mg_2TiO_4 and Fe_3O_4 - MgFe_2O_4 , and application of relationships (A-15), (A-16) and (A-18).

The energetic parameters of Fe_2TiO_4 - Fe_3O_4 spinels are constrained best by the current data. We may use the site-occupancy data of Wu & Mason (1981) and relationship (A-4) to calculate possible relationships among $\Delta \bar{H}_{56}^*$, $\Delta \bar{S}_{56}^*$, and W_{56} for Fe_3O_4 . These constraints and site-occupancy data

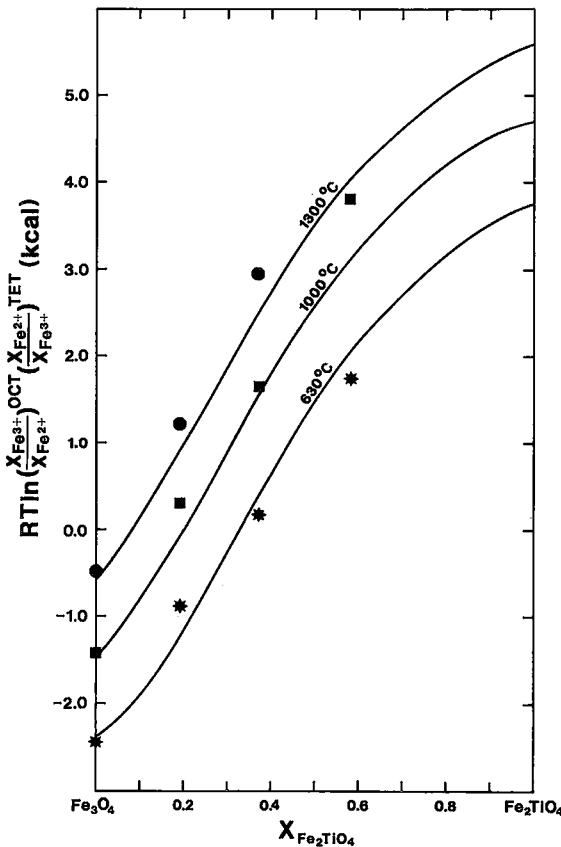


FIG. 2. Calculated $RT \ln K_D$ -composition relationships for the Fe_3O_4 - Fe_2TiO_4 binary join, where $K_D = (X_{\text{Fe}^{2+}}/X_{\text{Fe}^{3+}})^{\text{TET}}(X_{\text{Fe}^{3+}}/X_{\text{Fe}^{2+}})^{\text{OCT}}$. Dots, squares and stars are experimental determinations of Trestman-Matts *et al.* (1984) at 1300, 1000 and 630°C, respectively. Not considered are the data of Trestman-Matts *et al.* (1984) for samples with $X_{\text{Usp}} = 0.69$ and $X_{\text{Usp}} = 0.58$ at 1300°C. Samples prepared to have $X_{\text{Usp}} = 0.69$ contain minor amounts of hematite and ilmenite (Trestman-Matts *et al.* 1984). The value of $RT \ln K_D$ for the sample with $X_{\text{Usp}} = 0.58$ at 1300°C deviates significantly from the trend defined by the samples with X_{Usp} less than 0.5.

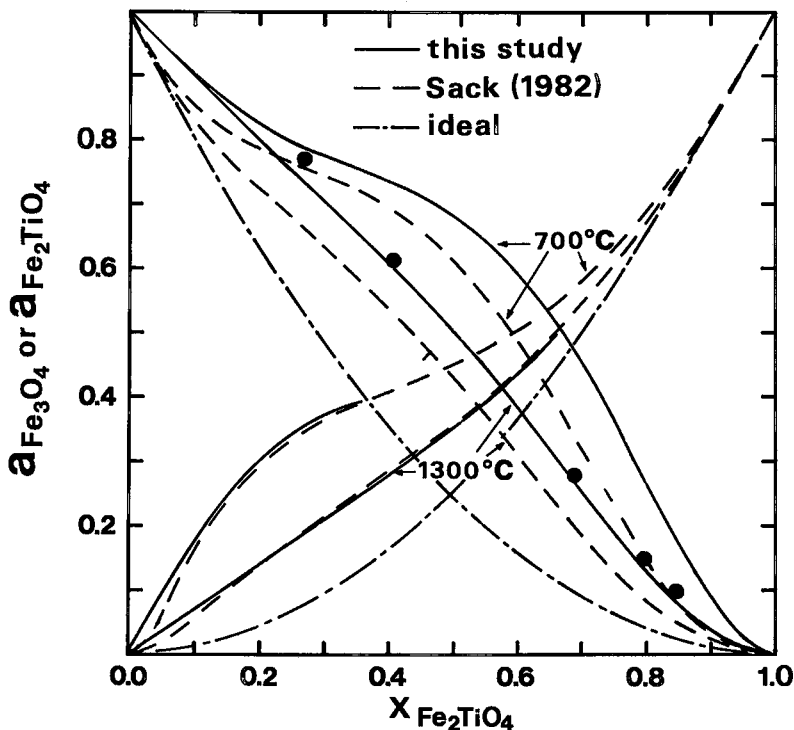


FIG. 3. Activity-composition relations for the $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{TiO}_4$ binary join predicted by the model presented herein, the model of Sack (1982a), and for a statistically ideal $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{TiO}_4$ spinel ($a = X^2$). Dots are experimental determinations of Katsura *et al.* (1975) at 1300°C . Calculated activities of Fe_2TiO_4 beyond $X_{\text{Fe}_2\text{TiO}_4}$ greater or equal to 0.5 are equivalent for both models.

(Trestman-Matts *et al.* 1983), activity-composition determinations (Katsura *et al.* 1975), approximate miscibility-gap constraints (Kawai *et al.* 1954, Kawai 1956, Vincent *et al.* 1957, Price 1981, Lindsley 1981), and composition-volume relationships (*e.g.*, Lindsley 1965, Wechsler *et al.* 1984) for $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{TiO}_4$ spinels allow determination of plausible values for the energetic parameters $\Delta\bar{H}_{56}^*$, $\Delta\bar{S}_{56}^*$, W_{56} , W_{15} and W_{16} employing relations (A-7), (A-19) and (A-21). In a first approximation, the site-population data of Trestman-Matts *et al.* (1983) for titaniferous magnetite with $X_{\text{Fe}_3\text{O}_4} \geq 0.5$ provide a direct estimate for the quantity $(W_{16} - W_{15} - W_{56})$ in equation (A-7), because they indicate that the ordering variable s_2 is effectively constant at 630, 1000, and 1300°C (see caption to Fig. 2). These data require that $\partial W_{56}/\partial T$ be marginally negative, given the ground rule that W_{15} and W_{16} are constants. With these constraints and the previous constraints on relationships among $\Delta\bar{H}_{56}^*$, $\Delta\bar{S}_{56}^*$, and W_{56} , all $\text{Fe}_2\text{TiO}_4 - \text{Fe}_3\text{O}_4$ parameters may be estimated from the remaining data. In particular, room-temperature volume-composition relations (Lindsley 1965, Wechsler *et al.* 1984) suggest

that $(W_{16} - W_{15})$ is approximately equal to -4.2 kcal based on (A-7), the cation radii of O'Neill & Navrotsky (1983), and the expressions of Hill *et al.* (1979), whereas high-temperature activity-composition determinations and miscibility-gap features suggest that W_{15} is approximately 6.0 kcal if $(W_{16} - W_{15})$ is equal to -4.2 kcal. Less negative values of $W_{16} - W_{15}$ appear to be unrealistic because such values result in dramatic changes in s_2 (ordering) with composition at low temperatures. Such features are inconsistent with the measured composition-volume relationship, assuming that the $\text{Fe}^{2+} - \text{Fe}^{3+}$ electron exchange between tetrahedral and octahedral sites cannot be quenched at high temperature (*i.e.*, composition-volume measurements reflect ordering schemes closer to room temperature) (*e.g.*, O'Donovan & O'Reilly 1980, Diekmann 1982, Wechsler *et al.* 1984, Mattioli *et al.* 1987). Substantially more negative values of $W_{16} - W_{15}$ are unsatisfactory because they would be inconsistent with values predicted by empirical size-mismatch considerations (*e.g.*, Lawson 1947, Davies & Navrotsky 1983, O'Neill & Navrotsky 1984) and would also require

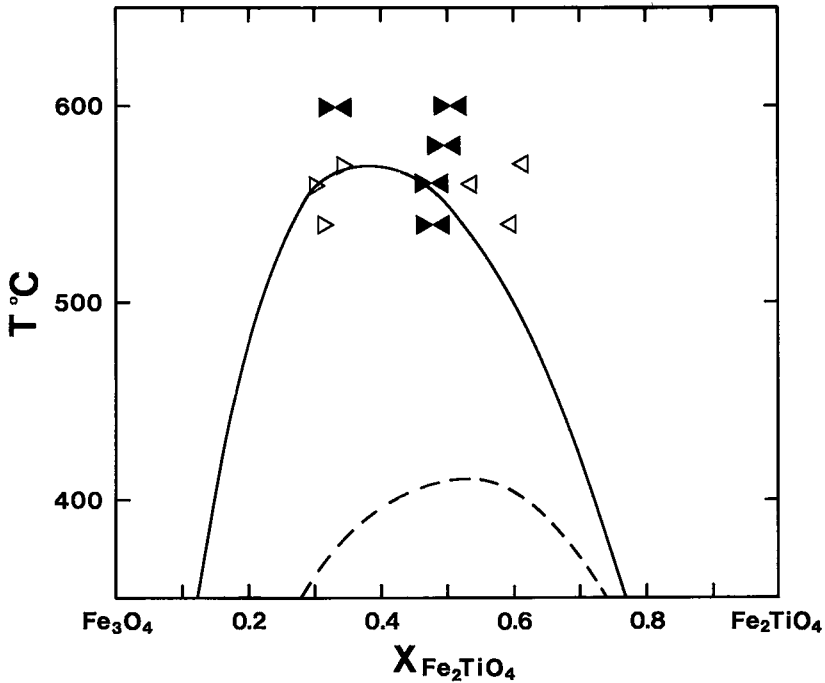


FIG. 4. Calculated position of the solvus in the $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{TiO}_4$ binary system (solid line) compared with the results of the homogenization experiments of Lindsley (1981). Arrow pairs at each temperature indicate the extent of homogenization; closed symbols indicate that an essentially homogeneous product was obtained. Dashed line is the solvus for the $\text{MgFe}_2\text{O}_4 - \text{Mg}_2\text{TiO}_4$ binary given by the model presented herein.

negative values of W_{56} at lower temperatures. Larger values of W_{15} result in a consolute temperature greater than that determined experimentally, whereas lower values result in poor fits to high-temperature activity-composition determinations. Accordingly, parameter values consistent with the above constraints have been used to calculate cation ordering - composition relationships, activity-composition relationships, and miscibility-gap features. Such calculations are compared with experimental determinations in Figures 2, 3 and 4.

In contrast to the $\text{Fe}_2\text{TiO}_4 - \text{Fe}_3\text{O}_4$ binary system, only site-occupancy data are available to constrain the energetic parameters relevant to the $\text{Mg}_2\text{TiO}_4 - \text{MgFe}_2\text{O}_4$ join, $\Delta\bar{H}_{78}^*$, $\Delta\bar{S}_{78}^*$, W_{78} , W_{27} and W_{28} . In analogous fashion as for Fe_3O_4 , relations among the parameters $\Delta\bar{H}_{78}^*$, $\Delta\bar{S}_{78}^*$, and W_{78} may be constrained from analysis of the site-occupancy data of Kriessman & Harrison (1956), Epstein & Frackiewicz (1958), Pauthenet & Bochirol (1951), Mozzi & Paladino (1963), and Pucher (1971) for MgFe_2O_4 employing (A-5). For $\text{Mg}_2\text{TiO}_4 - \text{MgFe}_2\text{O}_4$ spinels, relations between the values of $(W_{27} - W_{28} - W_{78})$ and W_{78} were obtained from the site-occupancy data of DeGrave *et al.* (1975) at 1100°C by employing (A-8).

With the above relations, values for W_{27} may then be calculated from (A-18) given a value for $\Delta\bar{G}_{r_1, r_2}^*$. Employing values of $\Delta\bar{G}_{r_1, r_2}^*$ that will be determined subsequently, considerations of (A-8) and (A-18) suggest that all possible values of $(W_{28} - W_{27} - W_{78})$ and W_{78} consistent with the data of DeGrave *et al.* (1975) are also consistent with a value of W_{27} of approximately 5.4 kcal, a value consistent with size-mismatch considerations (*i.e.*, $W_{27} < W_{15}$). Using similar size-mismatch constraints to define W_{28} , final values for W_{78} , $\Delta\bar{H}_{78}^*$ and $\Delta\bar{S}_{78}^*$ may then be determined. Comparison of the calculated site-occupancies (Fig. 5) and miscibility gap (Fig. 4) with experimental determinations and petrological constraints (*e.g.*, Price 1981) suggests that the energetic parameters selected are consistent with them.

Olivine - "ulvöspinel" $\text{Fe}^{2+} - \text{Mg}^{2+}$ exchange data reported in this study are the only data available to develop constraints on energetic parameters relevant to $\text{Fe}_2\text{TiO}_4 - \text{Mg}_2\text{TiO}_4$ spinels. Analysis of the condition of Fe-Mg exchange equilibrium

$$\frac{1}{2}\mu_{\text{Mg}_2\text{TiO}_4}^{\text{SP}} + \frac{1}{2}\mu_{\text{Fe}_2\text{SiO}_4}^{\text{OL}} = \frac{1}{2}\mu_{\text{Fe}_2\text{TiO}_4}^{\text{SP}} + \frac{1}{2}\mu_{\text{Mg}_2\text{SiO}_4}^{\text{OL}} \quad (6)$$

by employing (A-6), (A-19), (A-20) and the calibration of Davidson & Mukhopadhyay (1984) yields only relationships between possible values of $\Delta\bar{G}_{34}^*$ and $\Delta\bar{G}_{r1s1}^*$, for assumed values of W_{14} and W_{13} . However, probable bounds on these parameters and the parameters $\Delta\bar{G}_{r1r2}^*$ may be developed by simultaneous consideration of the data collected in this study and the following data relevant to the Fe_3O_4 - MgFe_2O_4 binary: 1) site-occupancy data (Trestman-Matts *et al.* 1983), 2) activity-composition relations (Tret'yakov 1967, Shishkov *et al.* 1980), and 3) exchange data for the pair Fe^{2+} - Mg^{2+} olivine-ferric-iron-based spinel (Jamieson & Roeder 1984). This is achieved by employing expressions (A-6), (A-9), (A-10), (A-11), (A-19-A-22), and three relationships that may be derived from (A-15), (A-16), and (A-18) for the ground rule that all regular-solution-type compositional parameters are constants,

$$\Delta\bar{S}_{r1s1}^* = \partial W_{56}/\partial T \quad (7)$$

$$\Delta\bar{S}_{34}^* = 2(\Delta\bar{S}_{78}^* - \Delta\bar{S}_{56}^*) - \Delta\bar{S}_{r1r2}^* + \partial W_{56}/\partial T, \quad (8)$$

$$\text{and } \Delta\bar{S}_{r1r2}^* = \frac{1}{2}(\Delta\bar{S}_{78}^* - \Delta\bar{S}_{56}^* + \partial W_{56}/\partial T) \quad (9)$$

Accordingly, a final set of these parameters was determined by testing values of $\Delta\bar{G}_{34}^*$ and $\Delta\bar{G}_{r1s1}^*$ consistent with expressions (7), (8), (9) and the data for Fe_2TiO_4 - Mg_2TiO_4 spinels, against the data for Fe_3O_4 - MgFe_2O_4 spinels, to achieve a fit that satisfies all of the available data. A value of $\Delta\bar{G}_{r1r2}^*$ was determined by considering expression (9), the data collected in this study and the data of Jamieson & Roeder (1984). Comparison of calculated results and available experimental determinations for Fe_3O_4 - MgFe_2O_4 and Fe_2TiO_4 - Mg_2TiO_4 spinels are given in Figures 6, 7, 8, and Figure 1, respectively.

A listing of a FORTRAN computer program that calculates cation ordering states and activities of components in $R_3\text{O}_4$, FMFT spinels based on the expression given in Table A is available from the authors on request.

DISCUSSION

Several aspects of the thermodynamic model and experimental data merit further discussion. It is of interest to examine the predictions about titanium-based and ferric-iron-based spinels that follow from this model, compare them with those given by other models (Sack 1982a, Urosov 1983, O'Neill & Navrotsky 1983, 1984) and use the results of this study to refine a calibration of the olivine-spinel Fe-Mg exchange geothermometer (*e.g.*, Irvine 1967, Jackson 1968, Evans & Frost 1975, Roeder *et al.*

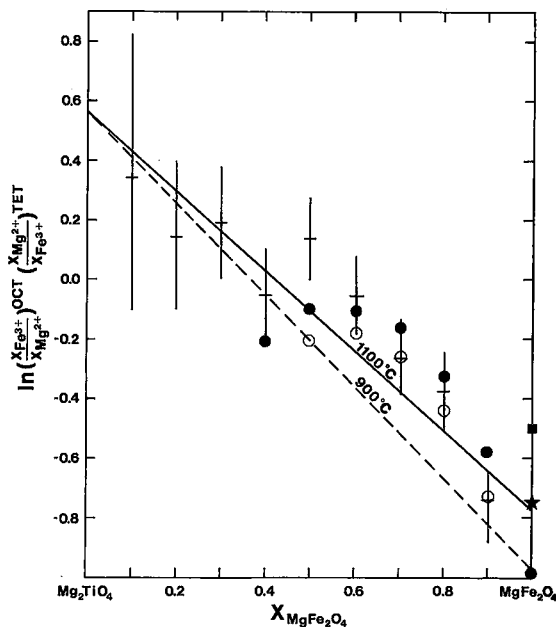


FIG. 5. Comparison of calculated values of $\ln K_D$ (solid and dashed lines) with experimental determinations for the Mg_2TiO_4 - MgFe_2O_4 binary join. Error bars represent the data of DeGrave *et al.* (1975) at 1100°C, circles represent the data of Tellier (1967) at 1100°C (filled) and 900°C (open), and the star and square represent the 1100°C data of Pauthenet & Bochirol (1951) and Epstein & Frackiewicz (1958), respectively.

1979, Sack 1982a, Engi 1983). Firstly, the calculations are in accord with predicted site-preferences of cations for 2-4 and 2-3 spinels (*e.g.*, O'Neill & Navrotsky 1983): Mg shows a greater preference for tetrahedral co-ordination in titanium-based than in ferric-iron-based spinels (Fig. 9). These calculations also indicate that the titanium-based spinels exhibit slight positive deviations from ideality between 800 and 1400°C (see Figs. 10, 11). To an excellent approximation, the excess Gibbs energy is symmetrical with respect to composition and decreases regularly with increasing temperature. A similar scenario for ferric-iron-based spinels is predicted by this model and is in accord with experimental determinations (*e.g.*, Tret'yakov 1967, Shishkov *et al.* 1980). Secondly, it may be noted that the calculations suggest a critical temperature of approximately 400°C for Mg_2TiO_4 - MgFe_2O_4 , $Fd3m$ spinels as opposed to about 570°C for Fe_2TiO_4 - Fe_3O_4 , $Fd3m$ spinels (Fig. 4). Although the latter temperature and calculated binodal curves are in agreement with the experimental constraints of Lindsley (1981), the former suggests that the discrepancy between critical temperatures determined by Lindsley (1981) and

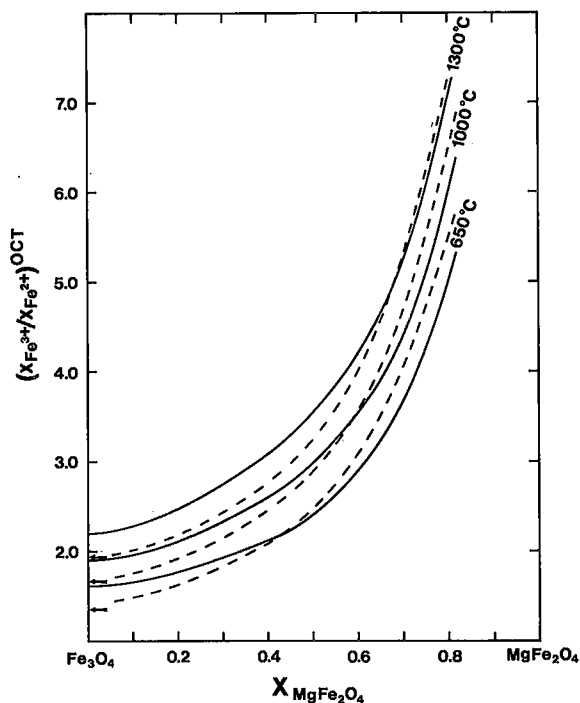


FIG. 6. Calculated values of the ratio of ferric to ferrous iron in octahedral co-ordination (dashed lines) compared with an interpolation (solid lines) through the experimental determinations of Trestman-Matts *et al.* (1984) for the Fe_3O_4 - MgFe_2O_4 binary system. Arrows indicate experimental determinations for end-member Fe_3O_4 by Wu & Mason (1981) at 1300°C, 1000°C and 650°C, from top to bottom, respectively.

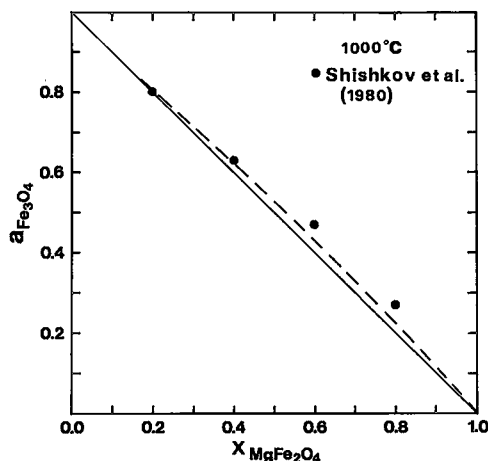


FIG. 7. Predicted activity-composition relations (dashed line) compared with the experimental determinations of Shishkov *et al.* (1980) at 1000°C for the Fe_3O_4 - MgFe_2O_4 binary system. Solid line indicates ideal mixing, which closely approximates the data of Tret'yakov (1967) at 1100°C.

Price (1981), 540–570°C and ~490°C, respectively, cannot be attributed to the small amount of Mg in the natural samples of titaniferous magnetite annealed by Price (1981), even if one does not consider that such spinel compositions probably undergo octahedral site splitting at these temperatures (*e.g.*, Preudhomme & Tarte 1980, Wechler & Navrotsky 1984).

To outline the requirements for a thermodynamic model that will accurately predict activity-composition relations in complex spinels of geochemical and petrological interest, it is appropriate to compare the general features of the model presented here with those that result from other formulations of thermodynamic mixing properties (*e.g.*, Sack 1982a, Urosov 1983, O'Neill & Navrotsky 1983, 1984, Lehmann & Roux 1984). Firstly, because Fe^{3+} - Fe^{2+} and Fe^{3+} - Mg^{2+} cation distributions exhibit substantial dependence on temperature and composition, calibrations of macroscopic formulations for thermodynamic mixing properties will not allow adequate description of activity-composition relations in ferric-iron-based spinels (*e.g.*, Sack 1982a, p. 178-181). The inadequacy of macroscopic models in this regard may be illustrated by comparing activity-composition relations for Fe_2TiO_4 - Fe_3O_4 spinels calculated from the microscopic model given here with those calculated from the macroscopic model of Sack (1982a) or Spencer & Lindsley (1981) (Fig. 3, see also Mattioli & Wood 1986b). Sack (1982a) used primarily miscibility-gap features and olivine-spinel Fe-Mg exchange data to calibrate the thermodynamic coefficients of a third-degree Taylor expansion for the $R_3\text{O}_4$, FeO-MgO- Fe_2O_3 - Al_2O_3 - Cr_2O_3 - TiO_2 (FMFACT) spinels in terms of macroscopic (composition) variables only; in calculating the configurational entropy, Sack made the following limiting approximation for cation distributions in FMFT spinels:

$$X_{\text{Cr}^{3+}}^{\text{TET}} = X_{\text{Al}^{3+}}^{\text{TET}} = X_{\text{Ti}^{4+}}^{\text{TET}} = 0,$$

$$(X_{\text{Fe}^{2+}}^{\text{TET}}/X_{\text{Mg}^{2+}}^{\text{TET}}) = (X_{\text{Fe}^{2+}}^{\text{OCT}}/X_{\text{Mg}^{2+}}^{\text{OCT}}), \text{ and}$$

$(X_{\text{Fe}^{3+}}^{\text{TET}}/X_{\text{Fe}^{3+}}^{\text{OCT}}) = 2$. Although this calibration adequately describes the activity of the Fe_2TiO_4 component over most of the composition range, it underestimates its activity in the dilute range, and it underestimates the activity of Fe_3O_4 throughout most of the compositional range. A similar conclusion was reached by Sack (1982a, p. 178-181) for activities of Fe_3O_4 and MgFe_2O_4 in binary spinels in the subsystems FFA, FFT, MFA, MFC, and MFT; this conclusion has also been substantiated for Fe_3O_4 - MgAl_2O_4 spinels (Mattioli & Wood 1986b). The consistent underestimation of Fe_3O_4 indicated above would suggest, for example, that the discrepancies between oxygen fugacities calculated from mantle xenoliths bearing the assemblage spinel -

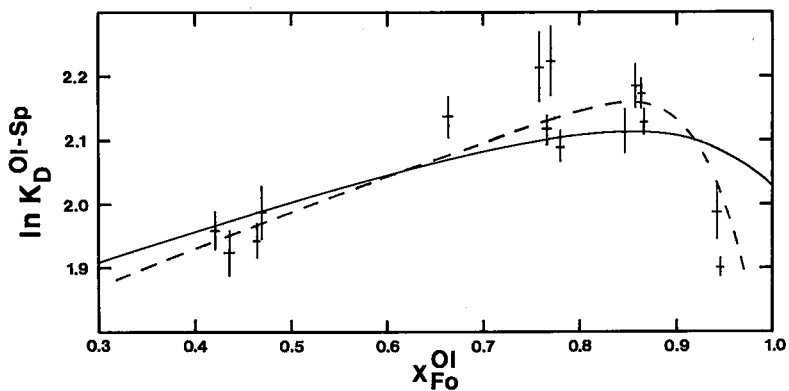


FIG. 8. Calculated values of the Fe^{2+} -Mg exchange distribution-coefficients (solid line) for coexisting olivine and ferric-iron-based spinel at 1300°C compared with the experimental determinations of Jamieson & Roeder (1984), where $K_D^{OI-Sp} = (X_{Mg}/X_{Fe^{2+}})^{OI}(X_{Fe^{2+}}/X_{Mg})^{Sp}$. Dashed line is the calculated fit of Jamieson & Roeder. Calculations were achieved through use of the expressions of Davidson & Mukhopadhyay (1984) for the mixing properties of Fe^{2+} -Mg olivine and the appropriate equations of the model presented herein.

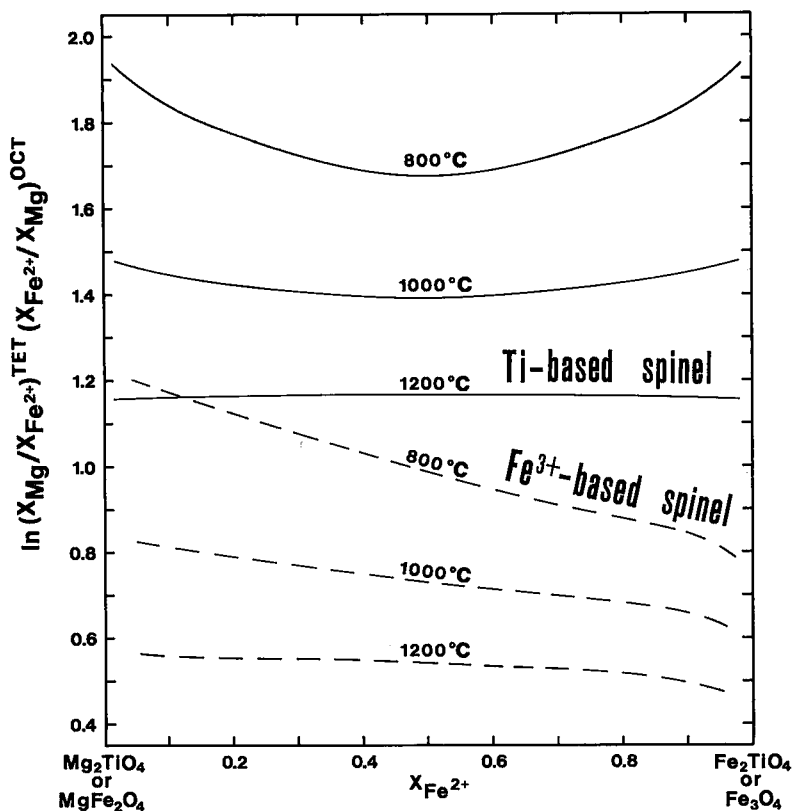


FIG. 9. Values of $\ln K_D$ for the Fe^{2+} -Mg ordering reaction for titanium-based spinels (solid lines) and ferric-iron-based spinels (dashed lines).

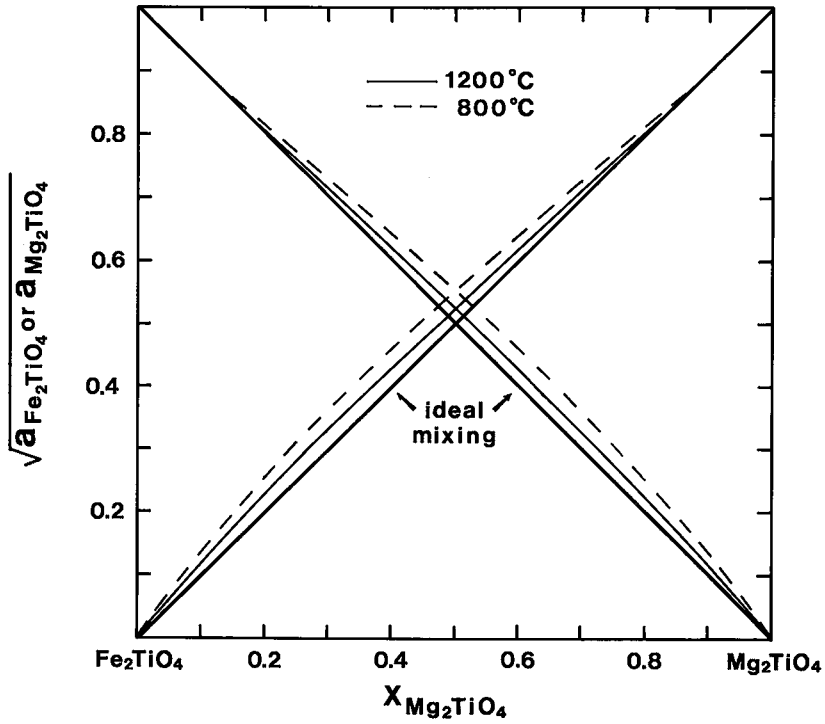


FIG. 10. Predicted activity-composition relations for the $\text{Fe}_2\text{TiO}_4 - \text{Mg}_2\text{TiO}_4$ binary join.

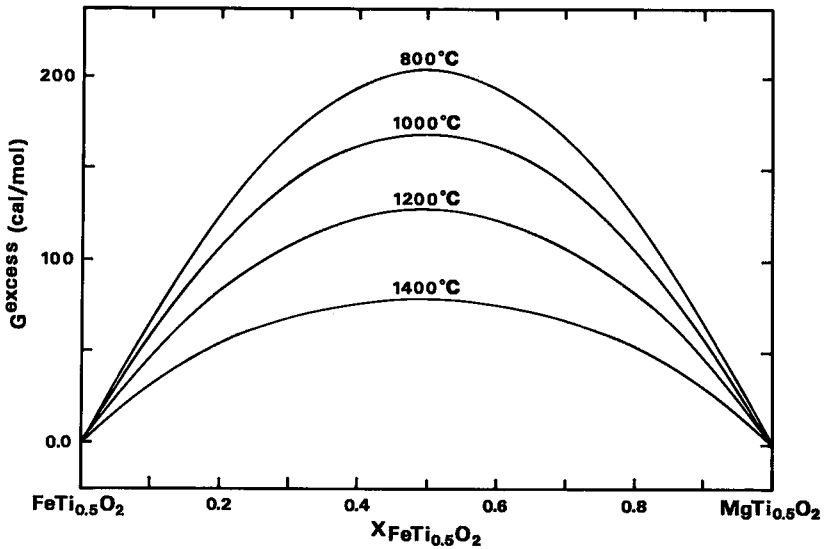


FIG. 11. Calculated excess Gibbs energy of mixing for the $\text{FeTi}_{0.5}\text{O}_2 - \text{MgTi}_{0.5}\text{O}_2$ binary join.

olivine - orthopyroxene (e.g., Mo *et al.* 1982, Mattioli & Wood, 1986a) and those obtained from determinations of intrinsic oxygen fugacity on individual minerals (e.g., Arculus & Delano 1981) may be even larger than the several orders of magnitude differences noted by Mo *et al.* (1982). The above observations suggest that a macroscopic model is incapable of adequately describing simultaneously activities of dilute and concentrated components unless a polynomial expansion of greater than third degree is used to describe the excess Gibbs energy. Such an approach would be strictly empirical. It would require that activity-composition relations be well known over the temperature and composition range of interest, because the coefficients of the expansion would not be simple functions of temperature, and many of them would not be related simply to measurable thermodynamic quantities. Accordingly, it is appropriate to examine various microscopic formulations of thermodynamic properties.

Although the formulations given here and by Sack (1982a, p. 178-181) for Fe₃O₄ - FeCr₂O₄ spinels are identical to those of Urosov (1983) and O'Neill & Navrotsky (1983) for unary spinels, they differ in several respects for binary and more complex spinels. The formulations of O'Neill & Navrotsky (1983) and Urosov (1983) both assume that, in unary spinels, the vibrational Gibbs energy is a quadratic function of the degree of disorder or that, for example, the conditions of homogeneous equilibrium for Fe₃O₄ and MgFe₂O₄ are:

$$RT \ln \left(\frac{X_{Fe^{2+}}^{TET}}{X_{Fe^{2+}}^{OCT}} \right) \left(\frac{X_{Fe^{3+}}^{OCT}}{X_{Fe^{3+}}^{TET}} \right) = \Delta \bar{G}_{56}^* - W_{56}(s_2) \quad (10)$$

and

$$RT \ln \left(\frac{X_{Mg^{2+}}^{TET}}{X_{Mg^{2+}}^{OCT}} \right) \left(\frac{X_{Fe^{3+}}^{OCT}}{X_{Fe^{3+}}^{TET}} \right) = \Delta \bar{G}_{78}^* - W_{78}(s_2), \quad (11)$$

respectively. However, they consider that the W_{ij} terms are identical constants for spinels of a given type (e.g., 2-3 spinels). In their extensions to binary spinels, O'Neill & Navrotsky (1984) and Navrotsky (1986) assumed that (10) and (11) apply directly, and that the equation defined by their difference describes Fe²⁺-Mg²⁺ ordering in Fe₃O₄ - MgF₂O₄ and Fe₂TiO₄ - Mg₂TiO₄ spinels. They also include a size-mismatch (regular-solution type) term in their formulation for the vibrational Gibbs energy of mixing.

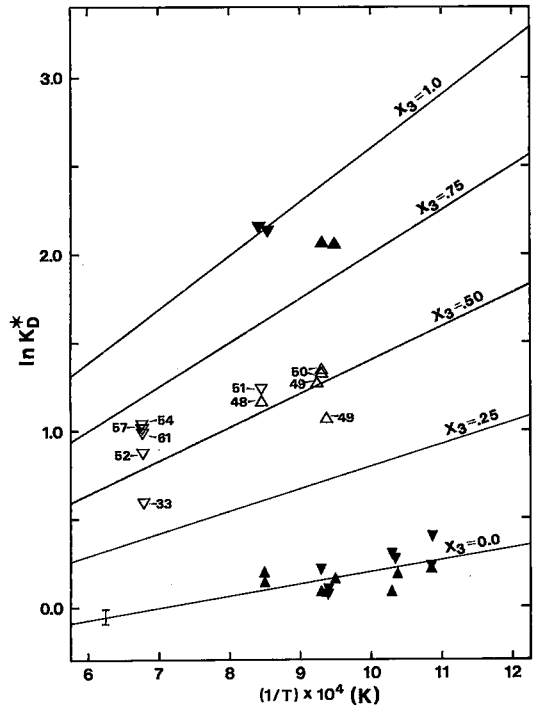


FIG. 12. A plot of $\ln K_D^*$ versus reciprocal temperature for experimental olivine-FMFAC spinel assemblages where $\ln K_D^*$ is defined by the expression

$$\begin{aligned} \ln K_D^* &= \ln K_D - \frac{\Delta \mu_{25}^0}{RT} (X_3) - \frac{\Delta \bar{G}_x^0}{2RT} (1 - 2X_{Fa}^{OL}) \\ &= - \frac{\Delta \bar{G}_{EX}^0}{RT} + \frac{\Delta \mu_{23}^0}{RT} (X_3). \end{aligned}$$

Dot with associated error bar represents experimental data of Jamieson & Roeder (1984) for 1300°C. Open arrows pointing downward at 1200°C represent heating experiments of Roeder *et al.* (1979) on natural olivine-spinel assemblages. Remaining arrows represent tightest reversal brackets of Fe-Mg exchange experiments of Engi (1983) for olivine - aluminum-based spinel (small solid arrows), olivine - aluminum- and chromium-based spinel (open arrows), and olivine - chromium-based spinel (large solid arrows) assemblages with $X_{Fe}^{OL} < 0.95$. Tips of arrows represent data points, direction of arrows (up or down) indicates direction of change of $\ln K_D$ during experiment, numbers associated with open arrows indicate the molar ratio $Cr^{3+}/(Cr^{3+} + Fe^{3+} + Al^{3+})$ of spinels. Lines represent calibration of $\ln K_D$ for aluminium- and chromium-based spinels with $X_3 = 0.0, 0.25, 0.50, 0.75, 1.0$ employing the following values for $-\Delta \bar{G}_{EX}^0, \Delta \mu_{23}^0, \Delta \mu_{25}^0$, and $\Delta \bar{G}_x^0$: 1.33795 - (0.0009539) T(K), 4.80, 6.39, and 1.68 kcal/gfw, respectively.

Trestman-Matts *et al.* (1983, 1984) have demonstrated that, to a first approximation, the above formulation adequately accounts for site-occupancy constraints, activity-composition relations, and volume-composition data for $\text{Fe}_2\text{TiO}_4 - \text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4 - \text{MgFe}_2\text{O}_4$ spinels, provided W_{56} is not equal to W_{78} , W_{56} is temperature-dependent, and the regular-solution formulation for the mixing term in $\text{Fe}_2\text{TiO}_4 - \text{Fe}_3\text{O}_4$ spinels is replaced by a subregular (asymmetrical) solution formulation. Owing to the different formulations employed [see equations (A-7), (A-8), (A-9), and (A-10)], the regular-solution-type parameters deduced here (*e.g.*, W_{15} , W_{16} , W_{27}) are systematically larger than those deduced from application of the formulation of O'Neill & Navrotsky (1984). Extension of their formulation to compositionally more complex spinels is problematical, however, owing to the need to develop expressions for the vibrational Gibbs energy that 1) allow for differences in tetrahedral-octahedral site-preference energies for Fe^{2+} and Mg^{2+} in 2-3 versus 2-4 spinels, 2) are based on a consistent set

of mathematical assumptions, 3) incorporate reciprocal energy-terms, and 4) make explicit provision for size-mismatch contributions to cation distributions through incorporation of cross-terms in composition-ordering variables.

In principle, the approach outlined here may be readily extended to complex spinels of general petrological and geochemical interest. Such an extension would require additional composition and ordering variables. Specifically, it would be necessary to consider additional composition variables for Cr and Al, and at least one additional ordering variable specifying the distribution of Al between octahedral and tetrahedral sites (*e.g.*, Wood *et al.* 1986). It would also require inclusion of a provision for cation vacancies, at least at temperatures above 1000°C, if it were extended to treat $T-f(\text{O}_2)$ relations in assemblages of titaniferous magnetite and rhombohedral oxide (*e.g.*, Webster & Bright 1961, Taylor 1964, Aragon & McCallister 1982, Mattioli *et al.* 1987).

Lastly, it is of interest to apply the results obtained here to the development of an olivine-spinel Fe-Mg

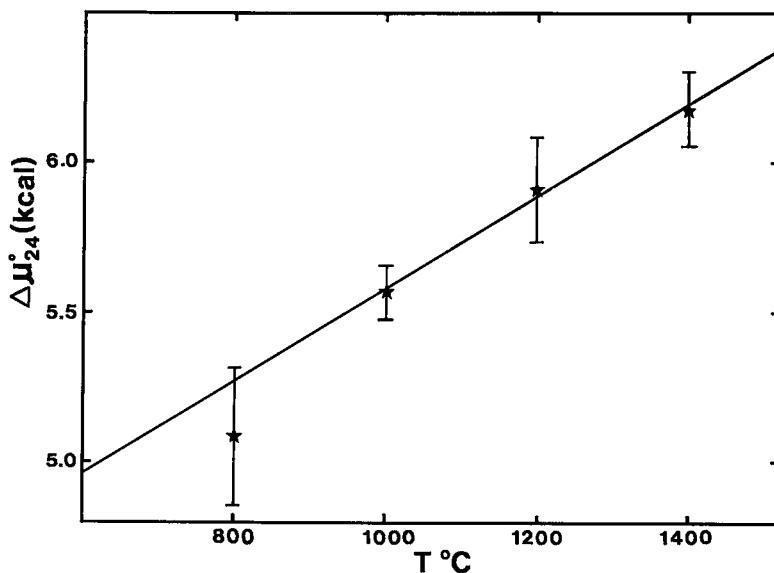


FIG. 13. The Gibbs energy of the reciprocal reaction $\text{MgAl}_2\text{O}_4 + \frac{1}{2}\text{Fe}_2\text{TiO}_4 = \text{FeAl}_2\text{O}_4 + \frac{1}{2}\text{Mg}_2\text{TiO}_4$, $\Delta\mu_{24}^0$, as a function of temperature. Values of $\Delta\mu_{24}^0$ computed from the experimental data given in Table 1 employing the parameter values given in the caption to the figure and the following expression:

$$\Delta\mu_{24}^0 = 1/X_4[(RT \ln K_D^{\text{OL-SP}} - \Delta\mu_{25}^0(1-X_4) + \Delta G_{\text{EX}}^* - \frac{1}{2}\Delta G_{\text{X}}^{\text{OL}}(1-2X_{\text{Fe}}^{\text{OL}})].$$

Errors bars indicate standard deviations defined by the data sets at each temperature. Least-squares fit to the 1000-1400°C exchange data is given by the following expression:

$$\Delta\mu_{24}^0 = 3.5561 + (0.0015698) T(\text{K}) \quad (r=0.9998).$$

exchange geothermometer. Unfortunately, such a development for FMFACT spinels must be based on a macroscopic formulation for thermodynamic properties, as a calibration of a microscopic formulation for such spinels is beyond the scope of this study. In the simplest plausible macroscopic formulation for the Fe–Mg exchange reaction between olivine and FMFACT spinel, it is considered that spinel is an “ideal” reciprocal solution (e.g., Irvine 1965, Wood & Nicholls 1978, Rawson & Irvine 1980) and that olivine is a symmetrical regular solution (e.g., Sack 1980a, Davidson & Mukhopadhyay 1984). For these assumptions, the condition of Fe–Mg exchange equilibrium between olivine and FMFACT spinel may be written as follows:

$$\ln K_D^{\text{OL-SP}} = -\frac{\Delta\bar{G}_{\text{EX}}^0}{RT} + \frac{\Delta\mu_{23}^0}{RT}(X_3) + \frac{\Delta\mu_{24}^0}{RT}(X_4) + \frac{\Delta\mu_{25}^0}{RT}(X_5) + \frac{\text{OL}\Delta\bar{G}_x^0}{2RT}(1-2X_{\text{Fa}}^{\text{OL}}) \quad (10)$$

where

$$*\Delta\bar{G}_{\text{EX}}^0 = \frac{1}{2}(\bar{G}_{\text{Mg}_2\text{SiO}_4}^{\text{OL}} - \bar{G}_{\text{Fe}_2\text{SiO}_4}^{\text{OL}}) + (\bar{G}_{\text{FeAl}_2\text{O}_4}^{\text{SP}} - \bar{G}_{\text{MgAl}_2\text{O}_4}^{\text{SP}}),$$

$$\Delta\mu_{23}^0 = (\bar{G}_{\text{MgCr}_2\text{O}_4}^{\text{SP}} + \bar{G}_{\text{FeAl}_2\text{O}_4}^{\text{SP}}) - (\bar{G}_{\text{FeCr}_2\text{O}_4}^{\text{SP}} + \bar{G}_{\text{MgAl}_2\text{O}_4}^{\text{SP}}),$$

$$\Delta\mu_{24}^0 =$$

$$(\frac{1}{2}\bar{G}_{\text{Mg}_2\text{TiO}_4}^{\text{SP}} + \bar{G}_{\text{FeAl}_2\text{O}_4}^{\text{SP}}) - (\frac{1}{2}\bar{G}_{\text{Fe}_2\text{TiO}_4}^{\text{SP}} + \bar{G}_{\text{MgAl}_2\text{O}_4}^{\text{SP}}),$$

$$\Delta\mu_{25}^0 = (\bar{G}_{\text{MgFe}_2\text{O}_4}^0 + \bar{G}_{\text{FeAl}_2\text{O}_4}^0) - (\bar{G}_{\text{Fe}_3\text{O}_4}^0 + \bar{G}_{\text{MgAl}_2\text{O}_4}^0),$$

$$\Delta\bar{G}_x^{\text{GL}} = (\bar{G}_{(\text{Fe})\text{M}_2(\text{Mg})\text{M}_1\text{SiO}_4}^0 + \bar{G}_{(\text{Mg})\text{M}_2(\text{Fe})\text{M}_1\text{SiO}_4}^0) - (\bar{G}_{\text{Fe}_2\text{SiO}_4}^0 - \bar{G}_{\text{Mg}_2\text{SiO}_4}^0),$$

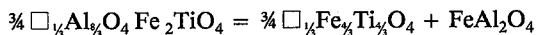
$$X_2 = n_{\text{Mg}^{2+}}^{\text{SP}}, \quad X_3 = \frac{1}{2}n_{\text{Cr}^{3+}}^{\text{SP}}, \quad X_4 = n_{\text{Ti}^{4+}}^{\text{SP}}, \quad X_5 = \frac{1}{2}n_{\text{Fe}^{3+}}^{\text{SP}},$$

the n_i terms are the number of the i cations in a formula unit based on three cations, and $\text{OL}\Delta\bar{G}_x^0 = 1.68$ kcal/gfw (Davidson & Mukhopadhyay 1984).

Analysis of the Fe–Mg exchange experiments of Engi (1983), Roeder *et al.* (1979) and Jamieson & Roeder (1984) permits estimates for the quantities $\Delta\mu_{23}^0$ and $\Delta\bar{G}_{\text{EX}}^0$ and demonstrates that this formulation is consistent with all of the current experimental data for FMAC spinels to an excellent approxi-

mation (see Fig. 12). The data of Jamieson & Roeder (1984) permit an estimate of 6.39 kcal/gfw for $\Delta\mu_{25}^0$ at 1300°C; in combination with the above result for $-\Delta\bar{G}_{\text{EX}}^0$, this estimate is in accord with those obtained from low-temperature (greenschist-facies) magnetite–olivine assemblages (e.g., Hoffman & Walker 1978; 420°C). In combination with these results for $-\Delta\bar{G}_{\text{EX}}^0$ and $\Delta\mu_{25}^0$, the experimental constraints presented herein are consistent with the calibration for $\Delta\mu_{24}^0$ given in Figure 13.

Although the calibration given above appears adequate for FMFAC and FMT spinels, it may not be adequate for many high-temperature FMFACT and FMFT spinels. In particular, the experimental results of Sack (1982a) and Rawson & Irvine (1980) for FMFACT and FMFT spinel–olivine assemblages, respectively, give values of $\ln K_D^{\text{OL-SP}}$ systematically greater than those predicted by this calibration. A similar finding is suggested by comparing values of $\ln K_D^{\text{OL-SP}}$ with temperatures for ilmenite – titaniferous magnetite assemblages in basaltic lavas (e.g., Nicholls *et al.* 1982) obtained by employing the calibration of Buddington & Lindsley (1964). Such discrepancies may well be due to non-negligible deviations from R_3O_4 stoichiometry in the synthetic spinels of Sack (1982a) and Rawson & Irvine (1980) (e.g., Webster & Bright 1961, Taylor 1964) and preferential retrograde exchange of Mg^{2+} and Fe^{2+} between olivine and spinel relative to $\text{Fe}^{2+}\text{Ti} \rightleftharpoons \text{Fe}_2^+\text{exchange}$ between ilmenite and spinel in the natural assemblages. Two observations favor cation vacancies as the cause for the discrepancy between the calibration given here and the experimental data of Sack (1982a) and Rawson & Irvine (1980). Firstly, higher-than-actual values of $\ln K_D^{\text{OL-SP}}$ are calculated for FMFT and FMFACT spinels exhibiting non-negligible cation-vacancy substitution, if R_3O_4 stoichiometry is assumed. Secondly, the calibration of the olivine–spinel exchange reaction given here yields temperatures for assemblages of olivine and titaniferous magnetite virtually identical with those obtained from the Buddington–Lindsley calibration for coexisting iron–titanium oxides for lower-temperature (granulite-facies) cumberlandites from the Adirondack Mountains (Sack 1979: $670 \pm 30^\circ\text{C}$). Assuming that cation vacancies are the cause of the observed discrepancies at high temperatures, it would be necessary to make explicit provision for non-zero Gibbs energies of reciprocal reactions involving vacancy-bearing components such as



in the formulation of the olivine–spinel Fe–Mg exchange geothermometer (e.g., Diekmann 1982). Although it would result in slight modifications of

the values of parameters in the calibration for olivine-FMFACT spinel assemblages, inclusion of such a provision for slight departures from ideality due to mixing of Fe^{2+} and Mg^{2+} would not ameliorate the discrepancy noted above and would be problematical, as such information is not well known for aluminum- and chromium-based spinels (e.g., Mattioli *et al.* 1987).

ACKNOWLEDGEMENTS

We thank C. Sandberg, the late H. Harrison, and J. Stebbins for assistance with the preparation of starting materials, D.H. Anderson, F.C. Hill, R.F. Martin, G.S. Mattioli and A. Navrotsky for helpful reviews, and V.G. Ewing for typing. The support of NSF grants EAR82-18286 and EAR84-19158 (R.O.S.) and U.S. Bureau of Mines grant G114411 is gratefully acknowledged.

REFERENCES

- ARAGON, R. & MCCALLISTER, R.H. (1982): Phase and point defect equilibria in the titanomagnetite solid solution. *Phys. Chem. Minerals* **8**, 112-120.
- ARCULUS, R.J. & DELANO, J.W. (1981): Intrinsic oxygen fugacity measurements: techniques and results for spinels from the upper mantle peridotites and megacryst assemblages. *Geochim. Cosmochim. Acta* **45**, 899-913.
- BARTH, T.F.W. & POSNJAK, E. (1932): Spinel structures: with and without variate atom equipoints. *Z. Krist.* **A82**, 325-341.
- BUDDINGTON, A.F. & LINDSLEY, D.H. (1964): Iron-titanium oxide minerals and synthetic equivalents. *J. Petrology* **5**, 310-357.
- DAVIDSON, P.M. & MUKHOPADHYAY, D.K. (1984): Ca-Fe-Mg olivines: phase relations and a solution model. *Contr. Mineral. Petrology* **86**, 256-263.
- DAVIES, P.K. & NAVROTSKY, A. (1983). Quantitative correlations of deviations from ideality in binary and pseudobinary solid solutions. *J. Solid State Chem.* **46**, 1-22.
- DEGRAVE, E., DESITTER, J. & VANDENBERGHE, R. (1975): On the cation distribution in the spinel system Mg_2TiO_4 -(1-y) MgFe_2O_4 . *Appl. Phys.* **7**, 77-80.
- DIEKMANN, R. (1982): Defects and cation diffusion in magnetite. IV. Nonstoichiometry and point defect structure of magnetite ($\text{Fe}_{3-x}\text{O}_4$). *Ber. Bunsenges. Phys. Chem.* **86**, 112-118.
- ENGI, M. (1983): Equilibria involving Al-Cr spinel: Mg-Fe exchange with olivine. Experiments, thermodynamic analysis, and consequences of geothermometry. *Amer. J. Sci.* **283A**, 29-71.
- EPSTEIN, D.J. & FRACKIEWICZ, B. (1958): Some properties of quenched magnesium ferrites. *J. Appl. Phys.* **29**, 376-377.
- EVANS, B.W. & FROST, B.R. (1975): Chrome-spinel in progressive metamorphism: a preliminary analysis. *Geochim. Cosmochim. Acta* **39**, 959-972.
- GANGULY, J. & SAXENA, S.K. (1984): Mixing properties of aluminosilicate garnets: constraints from natural and experimental data, and applications to geothermo-barometry. *Amer. Mineral.* **69**, 88-97.
- GOODENOUGH, J.B. & LOEB, A.L. (1955): Theory of ionic ordering, crystal distortion, and magnetic exchange due to covalent forces in spinels. *Phys. Rev.* **98**, 391-408.
- HILL, R.J., CRAIG, J.R. & GIBBS, G.V. (1979): Systematics of the spinel structure type. *Phys. Chem. Minerals* **4**, 317-340.
- HILL, R. & ROEDER, P. (1974): The crystallization of spinels from basaltic liquids as a function of oxygen fugacity. *J. Geol.* **2**, 709-729.
- HOFFMAN, M.A. & WALKER, D. (1978): Textural and chemical variations of olivine and chrome spinel in the East Dover ultramafic bodies, south-central Vermont. *Geol. Soc. Amer. Bull.* **89**, 699-710.
- IRVINE, T.N. (1965): Chromian spinel as a petrogenetic indicator. 1. Theory. *Can. J. Earth Sci.* **2**, 648-672.
- (1967): Chromian spinel as a petrogenetic indicator. 2. Petrologic applications. *Can. J. Earth Sci.* **4**, 71-103.
- ISHIKAWA, Y., SATO, S. & SYONO, Y. (1971): Neutron and magnetic studies of a single crystal of Fe_2TiO_4 . *Tech. Rep. Inst. Solid State Phys., Univ. Tokyo, Tokyo, Ser. A*, 455.
- , SYONO, Y. & AKIMOTO, S. (1964): Neutron diffraction study of Fe_3O_4 - Fe_2TiO_4 series. *Annual Progress Rep., Rock Magnetism Research Group, Inst. Solid State Phys., Univ. Tokyo, Tokyo*, 14-20.
- JACKSON, E.D. (1968): Chemical variation in co-existing chromitite and olivine in chromite zones of the Stillwater complex. *Econ. Geol., Mon.* **4**, 41-75.
- JAMIESON, H.E. & ROEDER, P.L. (1984): The distribution of Mg and Fe^{2+} between olivine and spinel at 1300°C. *Amer. Mineral.* **69**, 283-297.
- KATSURA, T., WAKIHARA, M., HARA, S.I. & SUGIHARA, T. (1975): Some thermodynamic properties of spinel solid solutions with the Fe_3O_4 component. *J. Solid State Chem.* **13**, 107-113.
- KAWAI, N. (1956): Exsolution of titanomagnetites and its effect on rock-magnetism. III. *Proc. Japan. Acad.* **32**, 464-468.

- _____, KUME, S. & SASAJIMA, S. (1954): Magnetism of rocks and solid phase transformations in ferromagnetic minerals. *Proc. Imp. Acad. Japan* **30**, 538-593.
- KRIESSMAN, C.J. & HARRISON, S.E. (1956): Cation distributions in ferros spinels. Magnesium-manganese ferrite. *Phys. Rev.* **103**, 857-860.
- LAWSON, A.W. (1947): On simple binary solid solutions. *J. Chem. Phys.* **15**, 831-842.
- LEHMANN, J. & ROUX, J. (1984): Calculations of activity-composition relations in multi-site solid solutions: the example of AB_2O_4 spinels. *Contr. Mineral. Petrology* **87**, 328-336.
- LINDSLEY, D.H. (1965): Iron-titanium oxides. *Carnegie Inst. Wash. Year Book* **64**, 144-148.
- _____. (1981): Some experiments pertaining to the magnetite-ulvospinel miscibility gap. *Amer. Mineral.* **66**, 759-762.
- MATTIOLI, G.S. & WOOD, B.J. (1986a): Upper mantle oxygen fugacity recorded by spinel-lherzolites. *Nature* **322**, 626-628.
- _____. & _____. (1986b): Experimental determination of Fe_3O_4 activity in complex spinels: implications for upper mantle fO_2 . *Int. Mineral. Assoc. Abstr. Programs* **14**, 168.
- _____, _____. & CARMICHAEL, I.S.E. (1987): Ternary spinel volumes in the system $MgAl_2O_4$ - Fe_3O_4 - Fe_2O_3 : implications for the effect of pressure on intrinsic oxygen fugacity measurements on mantle xenolith spinels. *Amer. Mineral.* **72**, 468-480.
- MO, XUANKUE, CARMICHAEL, I.S.E., RIVERS, M. & STEBBINS, J. (1982): The partial molar volume of Fe_2O_3 in multicomponent silicate liquids and the pressure dependence of oxygen fugacity in magmas. *Mineral. Mag.* **45**, 237-245.
- MOZZI, R.L. & PALADINO, A.E. (1963): Cation distributions in magnesium ferrites. *J. Chem. Phys.* **39**, 435-439.
- MUAN, A., HAUCK, J. & LOFALL, T. (1972): Equilibrium studies with a bearing on lunar rocks. *Proc. Third Lunar Sci. Conf. (suppl. 3)*, *Geochim. Cosmochim. Acta* **1**, 185-196.
- NAVROTSKY, A. (1986): Cation distribution energetics and heats of mixing in $MgFe_2O_4$ - $MgAl_2O_4$, $ZnFe_2O_4$ - $ZnAl_2O_4$, and $NiAl_2O_4$ - $ZnAl_2O_4$ spinels: study by high temperature calorimetry. *Amer. Mineral.* **71**, 1160-1169.
- NICHOLLS, J., STOUT, M.Z. & FIESINGER, D.W. (1982): Petrologic variations in Quaternary volcanic rocks, British Columbia, and the nature of the underlying upper mantle. *Contr. Mineral. Petrology* **79**, 201-218.
- O'DONOVAN, J.B. & O'REILLY, W. (1980): The temperature dependent cation distribution in titanomagnetites: an experimental test. *Phys. Chem. Minerals* **5**, 235-243.
- O'NEILL, H. St.C. & NAVROTSKY, A. (1983): Simple spinels: crystallographic parameters, cation radii, lattice energies, and cation distributions. *Amer. Mineral.* **68**, 181-194.
- _____. & _____. (1984): Cation distributions and thermodynamic properties of binary spinel solid solutions. *Amer. Mineral.* **69**, 733-753.
- O'REILLY, W. & BANERJEE, S.K. (1965): Cation distribution in titanomagnetites $(1-X)Fe_3O_4$ - XFe_2TiO_4 . *Phys. Letters* **17**, 237-238.
- PAUTHENET, R. & BOCHIROU, L. (1951): Spontaneous magnetization of ferrites. *J. Phys. Radium* **12**, 249-251.
- PREUDHOMME, J. & TARTE, P. (1980): Studies of spinels. VII. Order-disorder transition in the inverse germanate spinels. *J. Solid State Chem.* **35**, 272-277.
- PRICE, G.D. (1981): Subsolidus phase relations in the titanomagnetite solid solution series. *Amer. Mineral.* **66**, 751-758.
- PUCHER, R. (1971): Magnetic and X-ray diffraction measurements of the synthetic spinel system $FeFe_2O_4$ - $MgFe_2O_4$ - $NiFe_2O_4$. *Z. Geophys.* **37**, 349-356.
- RAWSON, S.A. & IRVINE, T.N. (1980): Mg- Fe^{2+} partitioning between olivine and ferrian ulvospinel. *Carnegie Inst. Wash. Year Book* **79**, 332-337.
- ROEDER, P.L., CAMPBELL, I.H. & JAMIESON, H.E. (1979): A re-evaluation of the olivine-spinel geothermometer. *Contr. Mineral. Petrology* **68**, 325-334.
- SACK, R.O. (1979): *Studies of Mafic Granulites*. Ph.D. thesis, Harvard Univ., Cambridge, Massachusetts.
- _____. (1980a): Some constraints on the thermodynamic mixing properties of Fe-Mg orthopyroxenes and olivines. *Contr. Mineral. Petrology* **71**, 257-269.
- _____. (1980b): Adirondack mafic granulites and a model lower crust. *Geol. Soc. Amer. Bull.* **91** (Part I), 89-93, (Part II), 349-442.
- _____. (1982a): Spinels as petrogenetic indicators: activity-composition relations at low pressures. *Contr. Mineral. Petrology* **79**, 169-186.
- _____. (1982b): Reaction skarns between quartz-bearing and olivine-bearing rocks. *Amer. J. Sci.* **282**, 970-1011, 1342.

- ____ & CARMICHAEL, I.S.E. (1984): $\text{Fe}^{2+} \rightleftharpoons \text{Mg}^{2+}$ and $\text{TiAl}_2 \rightleftharpoons \text{MgSi}_2$ exchange reactions between clinopyroxenes and silicate melts. *Contr. Mineral. Petrology* **85**, 103-115.
- ____, WALKER, D. & CARMICHAEL, I.S.E. (1987): Experimental petrology of alkalic lavas: constraints on cotectics of multiple saturation in natural basic liquids. *Contr. Mineral. Petrology* **96**, 1-23.
- SHISHKOV, V.I., LYKASOV, A.A. & IL'INA, A.F. (1980): Activity of the components of iron-magnesium spinel. *Russ. J. Phys. Chem.* **54**, 440-441.
- SPENCER, K.J. & LINDSLEY, D.H. (1981): A solution model for coexisting iron-titanium oxides. *Amer. Mineral.* **66**, 1189-1201.
- STEPHENSON, A. (1969): The temperature dependent cation distribution in titanomagnetites. *Geophys. J. Roy. Astron. Soc.* **18**, 199-210.
- TAYLOR, R.W. (1964): Phase equilibria in the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ at 1300°C . *Amer. Mineral.* **49**, 1016-1030.
- TELLIER, J.-C. (1967): Sur la substitution dans le ferri-rite de magnésium des ions ferriques par les ions trivalents, tétravalents et pentavalents. *Rev. Chimie Minérale* **4**, 325-365.
- THOMPSON, J.B., JR. (1967): Thermodynamic properties of simple solutions. In *Researches in Geochemistry 2* (P.H. Abelson, ed.). J. Wiley & Sons, New York.
- ____ (1969): Chemical reactions in crystals. *Amer. Mineral.* **54**, 341-375.
- TRESTMAN-MATTS, A., DORRIS, S.E., KUMARAKRISHNAN, S. & MASON, T.O. (1983): Thermoelectric determination of cation distributions in $\text{Fe}_3\text{O}_4-\text{Fe}_2\text{TiO}_4$. *J. Amer. Ceram. Soc.* **66**, 829-834.
- ____, ____ & MASON, T.O. (1984): Thermoelectric determination of cation distributions in $\text{Fe}_3\text{O}_4-\text{MgFe}_2\text{O}_4$. *J. Amer. Ceram. Soc.* **67**, 69-74.
- TRETYAKOV, YU. D. (1967): *Thermodynamics of Ferrites*. Izd. Khimiya, Moscow (in Russ.).
- TURNOCK, A.C. & EUGSTER, H.P. (1962): Fe-Al oxides: phase relationships below 1000°C . *J. Petrology* **3**, 533-565.
- UROSOV, V.S. (1983): Interactions of cations on octahedral and tetrahedral sites in simple spinels. *Phys. Chem. Minerals* **9**, 1-5.
- VERWEY, E.J.W. & HEILMANN, E.L. (1947): Physical properties and cation arrangement of oxides with spinel structures. I. Cation arrangement in spinels. *J. Chem. Phys.* **15**, 174-187.
- VINCENT, E.A., WRIGHT, J.B., CHEVALLIER, R. & MATHIEU, S. (1957): Heating experiments on some natural titaniferous magnetites. *Mineral. Mag.* **31**, 624-655.
- WEBSTER, A.H. & BRIGHT, N.F.H. (1961): The system iron-titanium-oxygen at 1200°C and oxygen partial pressures between 1 atm and 2×10^{-14} atm. *J. Amer. Ceram. Soc.* **44**, 110-116.
- WECHSLER, B.A., LINDSLEY, D.H. & PREWITT, C.T. (1984): Crystal structure and cation distribution in titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$). *Amer. Mineral.* **69**, 754-770.
- ____ & NAVROTSKY, A. (1984): Thermodynamics and structural chemistry of compounds in the system $\text{MgO}-\text{TiO}_2$. *J. Solid State Chem.* **55**, 165-180.
- WOOD, B.J., KIRKPATRICK, R.J. & MONTEZ, B. (1986): Order-disorder phenomena in MgAl_2O_4 spinel. *Amer. Mineral.* **71**, 999-1006.
- ____ & NICHOLLS, J. (1978): The thermodynamic properties of reciprocal solid solutions. *Contr. Mineral. Petrology* **66**, 389-400.
- WU, C.C. & MASON, T.O. (1981): Thermopower measurement of cation distribution in magnetite. *J. Amer. Ceram. Soc.* **64**, 520-522.

Received January 3, 1986, revised manuscript accepted September 7, 1986.

APPENDIX.

EXPRESSION FOR CHEMICAL POTENTIALS
AND THE CONDITIONS OF HOMOGENEOUS EQUILIBRIA
IN R_3O_4 , FMFT SPINELS

In Table A, expressions for the conditions of homogeneous equilibrium (A-1, A-2 and A-3) and chemical potentials of four vertices of composition-order space (A-19, A-20, A-21 and A-22) are given for R_3O_4 , FMFT spinels. These expressions are based on the choice of a set of thermodynamic parameters given in the text. As noted in the text, this set of parameters is not a unique set of such parameters. Accordingly, the expressions given for homogeneous equilibrium in FMFT spinels are simplified to those that apply in the constituent binary and unary systems to identify relations between the parameters chosen and those appropriate to the constituent subsystems. These relations are given in expressions (A-15), (A-16) and (A-18). An example of the derivation of one of these relations, (A-18), is outlined for further clarification.

Consider binary spinels on the join $Mg_2TiO_4 - MgFe_2O_4$. For such spinels we have the following relationships between the composition-ordering variables used to describe FMFT spinels: $r_1 = r_2$ and $s_1 = 0$. Taking into account these simplifications, relation (A-2) for FMFT

spinels may be reduced to relation (A-8) for $Mg_2TiO_4 - MgFe_2O_4$ spinels. However, relation (A-8) is expressed in terms of the thermodynamic coefficients chosen for FMFT spinels. For such spinels an appropriate set of thermodynamic parameters would be \bar{G}_2^* , \bar{G}_7^* , $\Delta\bar{G}_{78}^*$, W_{27} , W_{28} , and W_{78} . Identifying these parameters with the coefficients in a second-degree Taylor expansion in r_2 and s_2

$$\begin{aligned} \bar{G}^* = & g_0 + g_{r_2}(r_2) + g_{s_2}(s_2) + g_{r_2r_2}(r_2)^2 \\ & + g_{s_2s_2}(s_2)^2 + g_{r_2s_2}(r_2s_2) \end{aligned}$$

and combining this result with an expression for \bar{S}^{IC} through the relation $\bar{G} = \bar{G}^* - T\bar{S}^{IC}$, leads to relation (A-17) for the condition of homogeneous equilibrium ($[\partial\bar{G}/\partial s_2]_{r_2} = 0$) in $Mg_2TiO_4 - MgFe_2O_4$ spinels. Comparing (A-17) with (A-8), it is concluded that the parameter W_{28} must be related to the set of thermodynamic parameters chosen for FMFT spinels by relation (A-18) for the assumption that a second-degree Taylor's series expansion in r_1 , r_2 , s_1 , and s_2 is adequate to describe the vibrational Gibbs energy of R_3O_4 , FMFT spinels. Following a similar procedure for $Fe_3O_4 - MgFe_2O_4$ spinels, relations (A-15) and (A-16) may be readily derived.

TABLE A. EXPRESSIONS USED FOR CALCULATION OF CATION SITE OCCUPANCIES AND CHEMICAL POTENTIALS

Conditions of Homogeneous Equilibrium for a FMFT Spinel.

$$\begin{aligned} \frac{\partial \bar{G}}{\partial S_1} = 0 &= 1/4(3\Delta\bar{G}_{34}^* - \Delta\bar{G}_{r_1s_1}^*) + 1/2(W_{78} - W_{56} + W_{14} + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*) + r_1(W_{13} - W_{14}) \\ &+ r_2[1/4(\Delta\bar{G}_{r_1s_1}^* - \Delta\bar{G}_{34}^*) + 1/2(W_{15} - W_{27} - W_{13} + \Delta\bar{G}_{r_1r_2}^*)] + s_1(\Delta\bar{G}_{r_1s_1}^* - W_{14} - W_{13}) \\ &+ s_2[1/2(\Delta\bar{G}_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})] - RT \ln[(X_{Mg}/X_{Fe^{2+}})^{TET}(X_{Fe^{2+}}/X_{Mg})^{OCT}] \end{aligned} \quad (A-1)$$

$$\begin{aligned} \frac{\partial \bar{G}}{\partial S_2} = 0 &= \Delta\bar{G}_{78}^* - 1/4(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{34}^*) - 1/2(W_{16} - W_{27} + \Delta\bar{G}_{r_1r_2}^*) \\ &+ r_1[1/2(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*] \\ &+ r_2[1/4(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{34}^*) + 1/2(W_{16} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)] \\ &+ s_1[1/2(\Delta\bar{G}_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})] - s_2(W_{78}) - RT \ln[(X_{Mg}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Mg})^{OCT}] \end{aligned} \quad (A-2)$$

$$\begin{aligned} \left(\frac{\partial \bar{G}}{\partial S_2}\right) - \left(\frac{\partial \bar{G}}{\partial S_1}\right) = 0 &= \Delta\bar{G}_{78}^* + W_{27} - \Delta\bar{G}_{r_1r_2}^* - 1/2(\Delta\bar{G}_{34}^* + W_{16} + W_{15}) + 1/4(W_{13} - 3W_{14} + 3W_{56} - W_{78} + \Delta\bar{G}_{r_1s_1}^*) \\ &+ r_1[1/2(W_{14} - W_{13} + \Delta\bar{G}_{34}^* - W_{56} + W_{78}) + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*] \\ &+ r_2[1/4(W_{14} + W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{r_1s_1}^*) + 1/2(W_{16} - W_{15})] \\ &+ s_1[1/2(W_{56} - W_{78} + W_{14} + W_{13} - \Delta\bar{G}_{r_1s_1}^*)] - s_2[1/2(W_{78} + W_{56} - W_{14} - W_{13} + \Delta\bar{G}_{r_1s_1}^*)] \\ &- RT \ln[(X_{Fe^{2+}}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Fe^{2+}})^{OCT}] \end{aligned} \quad (A-3)$$

Conditions of Homogeneous Equilibrium for Unary Spinel of the FMFT Spinel System.

$$\begin{aligned} Fe^{2+}(Fe^{3+})_2O_4 - Fe^{3+}(Fe^{3+}, Fe^{2+})_2O_4 \\ RT \ln[(X_{Fe^{2+}}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Fe^{2+}})^{OCT}] = \Delta\bar{G}_{56}^* - s_2(W_{56}) \end{aligned} \quad (A-4)$$

$$\begin{aligned} Mg(Fe^{3+})_2O_4 - Fe^{3+}(Mg, Fe^{3+})_2O_4 \\ RT \ln[(X_{Mg}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Mg})^{OCT}] = \Delta\bar{G}_{78}^* - s_2(W_{78}) \end{aligned} \quad (A-5)$$

Conditions of Homogeneous Equilibrium for Binary Spinel of the FMFT Spinel System.

$$\begin{aligned} Fe_2TiO_4 - Mg_2TiO_4 \\ RT \ln[(X_{Mg}/X_{Fe^{2+}})^{TET}(X_{Fe^{2+}}/X_{Mg})^{OCT}] = \Delta\bar{G}_{34}^* + r_1(W_{13} - W_{14}) + s_1(\Delta\bar{G}_{r_1s_1}^* - W_{14} - W_{13}) \end{aligned} \quad (A-6)$$

$$\begin{aligned} Fe_3O_4 - Fe_2TiO_4 \\ RT \ln[(X_{Fe^{2+}}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Fe^{2+}})^{OCT}] = \Delta\bar{G}_{56}^* + 1/2(W_{15} - W_{16} + W_{56}) + r_2[1/2(W_{16} - W_{15} - W_{56})] \\ - s_2(W_{56}) \end{aligned} \quad (A-7)$$

TABLE A cont.

MgFe₂O₄-Mg₂TiO₄

$$RT \ln[(X_{Mg}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Mg})^{OCT}] = 1.5\Delta\bar{G}_{78}^* - \Delta\bar{G}_{r_1 r_2}^* + W_{27} + 1/2(W_{56} - \Delta\bar{G}_{56}^* - W_{15} - W_{16}) \\ + r_2[\Delta\bar{G}_{r_1 r_2}^* - W_{27} + 1/2(W_{16} - W_{56} + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15})] - s_2(W_{78}) \quad (A-8)$$

Fe₃O₄-MgFe₂O₄

$$RT \ln[(X_{Mg}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Mg})^{OCT}] = \Delta\bar{G}_{78}^* \\ + r_1[1/2(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1 r_2}^*] \\ + s_1[1/2(\Delta\bar{G}_{r_1 s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})] - s_2(W_{78}) \quad (A-9)$$

$$RT \ln[(X_{Fe^{2+}}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Fe^{2+}})^{OCT}] = \Delta\bar{G}_{78}^* - \Delta\bar{G}_{r_1 r_2}^* + W_{27} - W_{15} + 1/2(W_{56} - W_{78} + W_{13} - W_{14} - \Delta\bar{G}_{34}^*) \\ + r_1[1/2(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{13} + W_{14}) + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1 r_2}^*] \\ + s_1[1/2(W_{56} - W_{78} + W_{14} + W_{13} - \Delta\bar{G}_{r_1 s_1}^*)] - s_2[1/2(W_{78} + W_{56} + \Delta\bar{G}_{r_1 s_1}^* - W_{14} - W_{13})] \quad (A-10)$$

$$RT \ln[(X_{Mg}/X_{Fe^{2+}})^{TET}(X_{Fe^{2+}}/X_{Mg})^{OCT}] = W_{15} - W_{27} + \Delta\bar{G}_{r_1 r_2}^* + 1/2(\Delta\bar{G}_{34}^* + W_{78} - W_{56} + W_{14} - W_{13}) \\ + r_1(W_{13} - W_{14}) + s_1(\Delta\bar{G}_{r_1 s_1}^* - W_{14} - W_{13}) + s_2[1/2(W_{56} - W_{78} + \Delta\bar{G}_{r_1 s_1}^* - W_{14} - W_{13})] \quad (A-11)$$

Conditions of Homogeneous Equilibrium in Terms of the Subsystem Parameters W₅₈, W₆₇ and W₂₈

Fe₃O₄-MgFe₂O₄

$$RT \ln[(X_{Mg}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Mg})^{OCT}] = \Delta\bar{G}_{78}^* + r_1[1/2(W_{67} - W_{58} + W_{13} - W_{14})] \\ + s_1[1/2(W_{58} + W_{67} - 2W_{78} - W_{14} - W_{13})] - s_2(W_{78}) \quad (A-12)$$

$$RT \ln[(X_{Fe^{2+}}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Fe^{2+}})^{OCT}] = \Delta\bar{G}_{56}^* + 1/2(W_{58} - W_{67} + W_{13} - W_{14}) \\ + r_1[1/2(W_{67} - W_{58} - W_{13} + W_{14})] + s_1[1/2(W_{13} + W_{14} - W_{58} - W_{67}) + W_{56}] \\ - s_2[1/2(W_{56} + W_{67} - W_{14} - W_{13})] \quad (A-13)$$

$$RT \ln[(X_{Mg}/X_{Fe^{2+}})^{TET}(X_{Fe^{2+}}/X_{Mg})^{OCT}] = \Delta\bar{G}_{78}^* - \Delta\bar{G}_{56}^* + 1/2(W_{67} - W_{58} + W_{14} - W_{13}) + r_1(W_{13} - W_{14}) \\ + s_1(W_{58} + W_{67} - W_{56} - W_{78} - W_{13} - W_{14}) + s_2[1/2(W_{58} + W_{67} - 2W_{78} - W_{14} - W_{13})] \quad (A-14)$$

$$\text{where} \quad W_{67} = \Delta\bar{G}_{r_1 r_2}^* + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{78} + W_{15} - W_{27} + 1/2(\Delta\bar{G}_{r_1 s_1}^* + \Delta\bar{G}_{34}^*) \quad (A-15)$$

$$\text{and} \quad W_{58} = \Delta\bar{G}_{78}^* - \Delta\bar{G}_{56}^* - \Delta\bar{G}_{r_1 r_2}^* + W_{56} - W_{15} + W_{27} + 1/2(\Delta\bar{G}_{r_1 s_1}^* - \Delta\bar{G}_{34}^*) \quad (A-16)$$

Mg₂TiO₄-MgFe₂O₄

$$RT \ln[(X_{Mg}/X_{Fe^{3+}})^{TET}(X_{Fe^{3+}}/X_{Mg})^{OCT}] = \Delta\bar{G}_{78}^* + 1/2(W_{27} - W_{28} - W_{78}) + r_2[1/2(W_{28} - W_{27} - W_{78})] \\ - s_2(W_{78}) \quad (A-17)$$

$$\text{where} \quad W_{28} = 2\Delta\bar{G}_{r_1 r_2}^* + \Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* - W_{56} + W_{16} + W_{15} - W_{27} + W_{78} \quad (A-18)$$

Expressions for the Chemical Potentials of FMFT Spinel Components Used in the Text.

$$\begin{aligned} \mu_{\text{Fe}_2\text{TiO}_4} = & \bar{G}_{\text{Fe}_2\text{TiO}_4}^* + RT \ln[(X_{\text{Fe}^{2+}})^{\text{TET}}(X_{\text{Fe}^{2+}})^{\text{OCT}}(X_{\text{Ti}})^{\text{OCT}}] \\ & + [1/8(\Delta\bar{G}_{34}^* + \Delta\bar{G}_{r_1s_1}^*) + 1/4(W_{15} - W_{27} + W_{13} - \Delta\bar{G}_{r_1r_2}^*)][(1+r_2)(1-r_1)] \\ & - [1/4(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + 1/2(\Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1-r_1)(1-s_2)] \\ & + [1/8(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{34}^*) + 1/4(W_{16} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1+r_2)(1-s_2)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{14} + W_{13})][1-r_1]^2 - [1/16(W_{14} - W_{13} - \Delta\bar{G}_{34}^*) + 1/8(\Delta\bar{G}_{r_1r_2}^* - W_{27} - W_{15})][1+r_2]^2 \\ & + [1/2(W_{13} - W_{14})][(1-r_1)(s_1)] - [1/8(\Delta\bar{G}_{r_1s_1}^* - \Delta\bar{G}_{34}^*) + 1/4(W_{15} - W_{27} - W_{13} + \Delta\bar{G}_{r_1r_2}^*)][(1+r_2)(s_1)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})][(1-s_2)(s_1)] - [1/4(\Delta\bar{G}_{r_1s_1}^* - W_{14} - W_{13})](s_1)^2 \\ & + 1/4 W_{78} (1-s_2)^2 \end{aligned} \quad (\text{A-19})$$

$$\begin{aligned} \mu_{\text{Mg}_2\text{TiO}_4} = & \bar{G}_{\text{Mg}_2\text{TiO}_4}^* + RT \ln[(X_{\text{Mg}})^{\text{TET}}(X_{\text{Mg}})^{\text{OCT}}(X_{\text{Ti}})^{\text{OCT}}] \\ & - [1/8(\Delta\bar{G}_{34}^* + \Delta\bar{G}_{r_1s_1}^*) + 1/4(W_{15} - W_{27} + W_{13} - \Delta\bar{G}_{r_1r_2}^*)][(1+r_2)(1+r_1)] \\ & + [1/4(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + 1/2(\Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1+r_1)(1-s_2)] \\ & + [1/8(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{34}^*) + 1/4(W_{16} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1+r_2)(1-s_2)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{14} + W_{13})][(1+r_1)^2 - [1/16(W_{14} - W_{13} - \Delta\bar{G}_{34}^*) + 1/8(\Delta\bar{G}_{r_1r_2}^* - W_{27} - W_{15})][(1+r_2)^2 \\ & + 1/4(W_{78})(1-s_2)^2 - [1/2(W_{13} - W_{14})][(r_1+1)(s_1)] \\ & - [1/8(\Delta\bar{G}_{r_1s_1}^* - \Delta\bar{G}_{34}^*) + 1/4(W_{15} - W_{27} - W_{13} + \Delta\bar{G}_{r_1r_2}^*)][(r_2+1)(s_1)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})][(1-s_2)(s_1)] - [1/4(\Delta\bar{G}_{r_1s_1}^* - W_{14} - W_{13})](s_1)^2 \end{aligned} \quad (\text{A-20})$$

$$\begin{aligned} \mu_{\text{Fe}^{3+}(\text{Fe}^{2+}, \text{Fe}^{3+})_2\text{O}_4} = & \bar{G}_{\text{Fe}^{3+}(\text{Fe}^{2+}, \text{Fe}^{3+})_2\text{O}_4}^* + RT \ln[(X_{\text{Fe}^{2+}})^{\text{OCT}}(X_{\text{Fe}^{3+}})^{\text{TET}}(X_{\text{Fe}^{3+}})^{\text{OCT}}] \\ & - [1/8(\Delta\bar{G}_{34}^* + \Delta\bar{G}_{r_1s_1}^*) + 1/4(W_{15} - W_{27} + W_{13} - \Delta\bar{G}_{r_1r_2}^*)][(1-r_1)(1-r_2)] \\ & + [1/2(W_{13} - W_{14})][(1-r_1)(1+s_1)] \\ & - [1/4(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + 1/2(\Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1-r_1)(1-s_2)] \\ & + [1/8(\Delta\bar{G}_{r_1s_1}^* - \Delta\bar{G}_{34}^*) + 1/4(W_{15} - W_{27} - W_{13} + \Delta\bar{G}_{r_1r_2}^*)][(1-r_2)(1+s_1)] \\ & - [1/8(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{34}^*) + 1/4(W_{16} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1-r_2)(1-s_2)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})][(1+s_1)(1-s_2)] + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{14} + W_{13})][(1-r_1)^2 \\ & - [1/16(W_{14} - W_{13} - \Delta\bar{G}_{34}^*) + 1/8(\Delta\bar{G}_{r_1r_2}^* - W_{27} - W_{15})][(1-r_2)^2 \\ & - [1/4(\Delta\bar{G}_{r_1s_1}^* - W_{14} - W_{13})][(1+s_1)^2 + 1/4 W_{78}(1-s_2)^2 \end{aligned} \quad (\text{A-21})$$

$$\begin{aligned} \mu_{\text{Fe}^{3+}(\text{Mg}, \text{Fe}^{3+})_2\text{O}_4} = & \bar{G}_{\text{Fe}^{3+}(\text{Mg}, \text{Fe}^{3+})_2\text{O}_4}^* + RT \ln[(X_{\text{Fe}^{3+}})^{\text{OCT}}(X_{\text{Fe}^{3+}})^{\text{TET}}(X_{\text{Mg}})^{\text{OCT}}] \\ & - [1/8(W_{14} - W_{13} - W_{56} - W_{78} - \Delta\bar{G}_{34}^*) + 1/4(W_{16} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(1-r_2)(1-s_2)] \\ & + [1/8(\Delta\bar{G}_{34}^* + \Delta\bar{G}_{r_1s_1}^*) + 1/4(W_{15} - W_{27} + W_{13} - \Delta\bar{G}_{r_1r_2}^*)][(r_1)(1-r_2)] - [1/2(W_{13} - W_{14})][(r_1)(s_1)] \\ & + [1/8(\Delta\bar{G}_{r_1s_1}^* - \Delta\bar{G}_{34}^*) + 1/4(W_{15} - W_{27} - W_{13} + \Delta\bar{G}_{r_1r_2}^*)][(s_1)(1-r_2)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{56} - W_{78} - W_{14} - W_{13})][(s_1)(1-s_2)] \\ & + [1/4(\Delta\bar{G}_{34}^* - W_{56} + W_{78} - W_{14} + W_{13}) + 1/2(\Delta\bar{G}_{56}^* - \Delta\bar{G}_{78}^* + W_{15} - W_{27} + \Delta\bar{G}_{r_1r_2}^*)][(r_1)(1-s_2)] \\ & + [1/4(\Delta\bar{G}_{r_1s_1}^* + W_{14} + W_{13})(r_1)^2 - [1/4(\Delta\bar{G}_{r_1s_1}^* - W_{14} - W_{13})](s_1)^2 \\ & - [1/16(W_{14} - W_{13} - \Delta\bar{G}_{34}^*) + 1/8(\Delta\bar{G}_{r_1r_2}^* - W_{27} - W_{15})][(1-r_2)^2 + 1/4 W_{78}(1-s_2)^2 \end{aligned} \quad (\text{A-22})$$