EQUILIBRIA INVOLVING Al–Cr SPINEL: Mg–Fe EXCHANGE WITH OLIVINE. EXPERIMENTS, THERMODYNAMIC ANALYSIS, AND CONSEQUENCES FOR GEOTHERMOMETRY

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ABSTRACT. The equilibrium
\[
\text{MgSi}_{0.5}\text{O}_2 + \text{Fe(Y)O}_4 = \text{FeSi}_{0.5}\text{O}_2 + \text{Mg(Y)O}_4
\]  

(1)

olivine spinel olivine spinel

(with Y = Al, Cr) was studied by means of bracketing exchange experiments. Fused Fe–Mg–chlorides provide suitable exchange media between 650° and 900°C, at 300 to 1000 bars. Products were analyzed by electron microprobe (solids) and AA (flux). Phase equilibrium data so obtained for eq (1) are combined with available thermochemical data from the literature to derive a consistent set of thermodynamic data, including solution models. The phase equilibria impose particularly tight constraints on \(\Delta_f G^0\) of hercynite and chromite.

Reciprocal spinel \((\text{MgAl}_2\text{O}_4,\text{FeAl}_2\text{O}_4,\text{FeCr}_2\text{O}_4,\text{MgCr}_2\text{O}_4)\) is modeled using a concise speciation formulation, which deviates from the classical reciprocal solution approach. In terms of the proposed speciation model, spinel is found to behave as a nearly ideal solution, requiring only a functionally simple, slightly negative excess enthalpy. By contrast, if the classical reciprocal salt model is used, excess terms required by the present data are both functionally more complex and substantially larger in magnitude. Term-by-term comparison of the two models indicates that this difference is primarily due to the inadequacies of classical (Temkin-type) formulation of the configurational entropy.

The internally consistent set of thermochemical data and derived solution models allow a recalibration of the spinel-olivine geothermometer. Compared to the widely used approach developed by Irvine (1965), the theoretical basis used here necessitates some modifications of that thermometer. These include the effects of composition on the distribution coefficient for eq (1) which, in turn, require some changes in the interpretation of temperatures derived for suites of natural mineral pairs. Approximate geothermometric equations are derived; remaining uncertainties and limitations are discussed.

INTRODUCTION

Chrome spinel is a common accessory constituent of many ultramafic rocks. Its apparently stable coexistence with a few ferromagnesian silicates over a wide range of conditions makes equilibria among these phases valuable targets for petrogenetic research in both igneous and metamorphic terranes. Irvine (1965) laid important theoretical groundwork on chromite-silicate equilibria, and most of the subsequent investigators
have drawn on his results. In recent years, particular emphasis has been placed on the temperature dependence of the Mg–Fe exchange equilibrium between spinel and olivine. No fewer than five distinct calibrations have been proposed for that geothermometer. These are based either entirely on thermochemical data (Jackson, 1969; Roeder, Campbell, and Jamieson, 1979), on natural assemblages (Evans and Frost, 1975; Fabriès, 1979), or on a combination of data from natural mineral pairs and a few phase equilibrium data at high temperatures (Fujii, 1977). However, despite the interest indicated by a large number of recent applications of the spinel-olivine geothermometer (for example, Irvine, 1967; Jackson, 1969; Irvine and Findlay, 1972; Medaris, 1975 and 1980; Evans and Frost, 1975; Stroh, 1976; Dick, 1977; Crawford, 1980; Tracy, 1980; Henry and Medaris, 1980), a comprehensive experimental calibration has so far been lacking.

The present work aims at filling that gap. Exchange equilibrium brackets are reported here for the equilibrium

\[
\text{MgSi}_{0.5} \text{O}_2 + \text{Fe(Y)}_2 \text{O}_4 = \text{FeSi}_{0.5} \text{O}_2 + \text{Mg(Y)}_2 \text{O}_4
\]

olivine spinel olivine spinel

where Y stands for Al and/or Cr. A thermodynamic analysis of these experimental data, collected between 650° and 900°C, provides a sound basis for reevaluation of some important theoretical concepts used in the literature, as well as a recalibration of the spinel-olivine geothermometer.

**NOTATION**

The following abbreviations are used throughout the paper:

1. For components and species:
   - \( \text{fa} = \) fayalite
   - \( \text{fo} = \) forsterite
   - \( \text{ch} = \) chromite
   - \( \text{hc} = \) hercynite
   - \( \text{mf} = \) magnesioferrite
   - \( \text{mt} = \) magnetite
   - \( \text{pc} = \) picrochromite
   - \( \text{sp} = \) spinel
   - \( \text{FeSi}_{0.5} \text{O}_2 \)
   - \( \text{MgSi}_{0.5} \text{O}_2 \)
   - \( \text{FeCr}_2 \text{O}_4 \)
   - \( \text{FeAl}_2 \text{O}_4 \)
   - \( \text{MgFe}_2 \text{O}_4 \)
   - \( \text{Fe}_2 \text{O}_4 \)
   - \( \text{MgCr}_2 \text{O}_4 \)
   - \( \text{MgAl}_2 \text{O}_4 \)

2. For phases:
   - \( \text{OL} = \) olivine (fo-fa)
   - \( \text{SP} = \) spinel (sp-hc-ch-pc)

**EXPERIMENTS**

*General approach.*—The primary aim was to equilibrate Mg–Fe–olivine and Mg–Fe–Al–Cr–spinel at conditions achievable in hydrothermal experiments using cold-seal pressure vessels. The available equipment set an upper temperature limit of about 900°C at pressures of a few hundred bars; kinetic factors determined the lower limit. The refractory nature of the solids involved, Cr-rich spinel in particular, required the use of a flux as exchange medium. Fused Fe–Mg chloride proved adequate in most respects for the present system. Not only do they effectively promote ion exchange at temperatures as low as 600° to 650°C, but the mineral products obtained are nearly always of a grain size sufficient for electron microprobe analysis (<1 to > 200 μm, typically 10-30 μm).
Equilibria involving Al-Cr spinel: Mg-Fe exchange with olivine

In order to bracket equilibrium (1), the starting compositions of olivine and spinel were selected so as to approach the final distribution coefficient \( K_{D,\text{ product}} \) from higher and lower values of \( K_{D,\text{ reactants}} \) where

\[
K_{D} = \left( \frac{X_{\text{Mg}}^{\text{sp}} X_{\text{Fe}}^{\text{ol}}}{X_{\text{Mg}}^{\text{ol}} X_{\text{Fe}}^{\text{sp}}} \right).
\]  

Clearly, equilibrium is demonstrated if a pair of such bracketing experiments, at constant bulk composition, yields final \( K_{D} \) values within analytical error of each other. For reasons specified below, however, such ideal conditions could not always be achieved here, and half-brackets were sometimes the best obtainable result.

**Experimental technique.**—The preparation of starting materials involved separate synthesis of three olivines, eight spinels, and two chloride fluxes. Synthesis temperatures for the spinels were chosen as low as possible in order to avoid non-stoichiometric products (Warshaw and Keith, 1954; Ulmer, 1964). Repeated heating and grinding cycles were often necessary to achieve \( \geq 98 \) percent yield and homogeneous products. All starting materials were ground to \( < 1 \mu m \) size under alcohol in an agate mortar prior to their further use. Olivine and spinel containing no Fe were prepared from dry reagent grade oxides in air, using Pt-crucibles as sample containers. The following conditions were successful:

- **Forsterite** \( \text{Mg}_2\text{SiO}_4 \) 3 cycles: 1000°C (20 hrs) + 1400°C (26 + 20 hrs)
- **Spinel** \( \text{MgAl}_2\text{O}_4 \) 2 cycles: 1000°C (1 hr) + 1200°C (24 hrs)
- **Picrochromite** \( \text{MgCr}_2\text{O}_4 \) 2 cycles: 900°C (8 days) + 1200°C (22 hrs)
- **sp50-pc50** \( \text{MgAlCr}_2\text{O}_4 \) 3 cycles: 1200°C (3 + 1 days) + 1300°C (2 days)

Fe-bearing solids were synthesized in vacuo from dry reagent-grade oxides (including \( \text{Fe}_2\text{O}_3 \)) and stabilized iron sponge (Turnock, Lindsey, and Grover, 1973) of analyzed oxygen content. Homogenized oxide-metal mixtures were wrapped in Pt- or Ag\(_{70}\)Pd\(_{30}\)-foil and heated in evacuated SiO\(_2\)-glass tubes. Where repeated synthesis cycles were required, the same foils were used in all runs of the same composition. Conditions used were as follows:

- **Fayalite** \( \text{Fe}_2\text{SiO}_4 \) 1 cycle: 850°C (\( \geq 5 \) days)
- **fo50-fa50** \( \text{MgFeSiO}_4 \) 2 cycles: 925°C (2 + 7 days)
- **Hercynite** \( \text{FeAl}_2\text{O}_4 \) 2 cycles: 760°C (8 hrs) + 900°C (7 days)
- **Chromite** \( \text{FeCr}_2\text{O}_4 \) 2 cycles: 900°C (3 + 2 days)
- **hc50-ch50** \( \text{FeAlCr}_2\text{O}_4 \) 2 cycles: 900°C (4 days) + 1050°C (3 days)
- **hc25-ch75** \( \text{FeAl}_{0.5}\text{Cr}_{1.5}\text{O}_4 \) 3 cycles: 900°C (8 days) + 1060°C (1 + 2 days)
- **sp50-ch50** \( \text{Mg}_{0.5}\text{Fe}_{0.5}\text{AlCr}_2\text{O}_4 \) 1 cycle: 1090°C (4 days)

Chloride fluxes were prepared from reagent grade FeCl\(_2\) • 4H\(_2\)O and MgCl\(_2\) • 6H\(_2\)O by slow dehydration in a stream of dry N\(_2\) or Ar. Temperature was increased stepwise up to just below the respective melting point. The products thus obtained still contain molecular H\(_2\)O (\( < 0.1 \) H\(_2\)O per FeCl\(_2\) and \( < 1.0 \) H\(_2\)O per MgCl\(_2\) and are strongly hygroscopic.

Exchange experiments were conducted by mixing spinel, olivine, and chloride(s) of suitable compositions and proportions (generally about 1:1:2 by weight) and sealing these powders in annealed Au-capsules (0.1
mm wall). For most experiments, standard cold-seal vessels were pressurized by methane; graphite filler rods were used. At run temperatures exceeding 820°C, a TZM pressure vessel (Williams, 1968) was employed, in which the pressure medium consisted of 90 volume-percent Ar and 10 volume-percent H₂. The latter had to be replenished periodically during runs to counterbalance the hydrogen loss through the vessel walls.

The experiments were quenched by cooling the pressure vessels in a stream of compressed air to below 350°C, where the chloride melts solidify.

Pressures were monitored periodically on a Heise Bourdon tube gauge or a calibrated Ashcroft gauge. Temperatures were measured at least once a day using inconel-sheathed chromel-alumel thermocouples positioned externally (8 mm from the charges). These had been calibrated previously in run configuration using a secondary standard thermocouple located inside the vessel. The secondary standard was known to read within ± 3K of the true thermodynamic temperature through repeated calibrations against a primary standard (Pt₅₀Rh₅₀) thermocouple, which in turn had been directly calibrated at the freezing points of pure Ag, Pb, and Zn.

Qualitative results.—Preliminary experiments involving fused chlorides revealed a number of characteristics that influenced both the approach to be taken in subsequent runs and the interpretation of the final data:

1. The Mg/Fe distribution between melt and solids is far from even, with (Mg/Fe)ₘₑₙₜ < (Mg/Fe)ₚₙₐₐ₅. Thus, the use of Mg-rich chlorides as starting material leads to strongly Fe-depleted solid products, which are of little use in constraining Kᵢₑ, because of the unfavorable propagation of analytical uncertainties. Therefore, chlorides with (Mg/Fe) << 1.0 were used in most further experiments.

2. The solvent power of fused chlorides for oxide components is much greater for MgO and FeO than for Al₂O₃, Cr₂O₃, and SiO₂. Owing to the resulting incongruent (partial) dissolution of olivine, the product assemblage typically included additional solids, in particular orthopyroxene and/or cordierite (fig. 1). As long as this dissolution process does not completely remove olivine, exchange equilibrium (I) is not affected by the presence of additional phases. However, the interpretation of a single experiment as a valid half-bracket may no longer be possible. A necessary condition for such an interpretation to be valid is the following: (ΔXₘ₉₉₉⁰/ΔXₘ₉₉₉⁰) < 1.0, where Δ refers to the difference between products and reactants.

3. There is clear evidence that the overall exchange reaction involves a dissolution/reprecipitation mechanism. Solid run products are nearly always single crystals of between ten and several hundred times the size of the starting materials.

4. Although no systematic study of the reaction path or reaction rate was attempted, a gradual, apparently continuous approach toward exchange equilibrium may be inferred from a series of four preliminary experiments at 700°C: Kᵢₑ changed from 0.0 (starting materials) to 1.22,
1.78, 1.82, and 1.83 in identical runs of 2, 7, 11, and 21 days duration (pure Al-system). These data would support the claim that each experiment can be regarded as a half-bracket to equilibrium (I), provided the condition stated under point (2) is satisfied.

Analytical procedures.—After quench, the run products were separated by boiling the charges in distilled water containing 0.4 volume-per-cent HCl, which dissolved the chloride flux. The aqueous solutions were analyzed for Mg and Fe by atomic absorption spectrophotometry.

The solid run products were washed, dried, mounted in epoxy, polished, and carbon-coated for analysis by electron microprobe (ARL-SEM with 6 wavelength-dispersive spectrometers, 15kV acceleration potential, 50nAmp sample current on brass). Standards included synthetic Al-spinels and olivines, natural chromites, olivines, orthopyroxene, and garnet. Full ZAF-matrix corrections were applied, except for olivines, for which working curves were established on the basis of seven well characterized olivines.

The fine grain size of the products and the occasionally abundant occurrence of sub-micron sized mutual inclusions required a special correction method (Engi, 1982). Neglecting these effects of grain overlap on probe analyses would have contributed unacceptable systematic errors to the final data, particularly for Cr-rich products. Due to the strong Mg/Fe fractionation between olivine and chromite, even a volumetrically small fraction of mutual inclusions affects the apparent element partitioning coefficient noticeably. The resulting error in $K_{D}$, for example, would commonly amount to more than 20 percent.

Experimental data.—Table 1 compiles the information on the final phase equilibrium experiments. Uncertainties quoted for compositional data represent two estimated standard deviations computed from replicate analyses and do not include uncertainties due to standards, counting statistics, and correction methods. Except for a few unusually homogeneous

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Fig. 1. Incongruent dissolution of olivine + spinel in fused chlorides causes the occurrence of more silicic solids in experimental products. Arrows schematically show the shift in composition toward the final mineral assemblage.
<table>
<thead>
<tr>
<th>Run#</th>
<th>Temp/K P/bar Time/days</th>
<th>Phases present</th>
<th>Init. X(Mg)</th>
<th>Final Composition X(Mg)</th>
<th>Y(Al)</th>
<th>Y(Fe)</th>
<th>Additional phases</th>
</tr>
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<td>106</td>
<td>1172(6) 300(40) 6</td>
<td>spinel olivine chloride</td>
<td>1.00 0.0 0.50</td>
<td>0.882(41) 0.992(4)</td>
<td>0.0 (0) 0.009(10)</td>
<td>+graphite?</td>
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<td>Time/days</td>
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<td>0.956(11)</td>
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</tbody>
</table>
product assemblages, these latter uncertainties are, however, negligible in comparison with the observed range of product compositions, that is, the chemical heterogeneity of the product phases.

Concentrations tabulated for Fe$^{3+}$ in spinel were computed from microprobe analyses by assuming ideal stoichiometry $\text{AB}_2\text{O}_4$. Uncertainties quoted for Fe$^{3+}$ were calculated by propagating the pertinent analytical uncertainties. It is evident that the ferric fractions thus obtained are generally very low. This result is consistent with the observed optical properties of product spinels and is supported, furthermore, by Mössbauer spectra (recorded at room temperature) of all Fe-bearing starting materials and several representative run products. In all cases, the observed isomer shift values indicated ferrous iron only.

It appears thus that the hydrogen fugacity imposed by graphite + CH$_4$ kept the experimental charges effectively reduced despite the use of Au-containers. It is possible that the corrosive effect of the fused chlorides on the Au-capsules facilitated rapid (grain boundary) diffusion of H$_2$.

The data listed in table 1 will be discussed further in the section entitled Data Analysis.

thermodynamic analysis

Phase equilibrium data in general and exchange equilibrium data in particular may serve to constrain the thermodynamic properties of any reaction investigated. The accuracy of reaction properties so derived commonly rivals even the best calorimetric results (Anderson, 1970; Gordon, 1973; Zen, 1977). Extracting thermodynamic properties for individual phases from these reaction properties requires careful consideration of their strong correlation (Anderson, 1977) and is not always unambiguous. Despite these reservations and the implicit danger of constructing a house of cards, the combined evaluation of independently gathered thermochemical and phase equilibrium data is much needed in order to achieve internal consistency in the thermodynamic data base (see, for example, Helgeson and others, 1978), which then permits the computation of phase equilibria at conditions not covered by experiment.

Coexisting solid solutions.—In theory (Kawasaki and Matsui, 1977), exchange equilibrium data permit the simultaneous extraction of solution properties for two (binary) solutions. In practice, however, results thus obtained are so highly correlated that independent data, such as activity coefficients for either phase, are desirable. Here, the results of a recent analysis (Engi, 1980a) of phase equilibrium and calorimetric data for olivine are used in combination with the present results on equilibrium (1) to derive a solution model for Al–Cr–spinel. The coexisting orthopyroxene and cordierite (table 1) have been treated in analogous ways; those results will be presented in a subsequent paper (in preparation).

Calorimetric reference values have been adopted from the compilation of Robie, Hemingway, and Fisher (1978) in preference to that of Helgeson and others (1978) because the latter does not include data on most of the spinels.
Solution behavior of olivine.—Many investigators have proposed various models to account for the thermodynamic solution behavior of the forsterite-fayalite series. Recent attempts include those of Williams (1972), Saxena (1972), Naiziger (1973), Obata, Banno, and Mori (1974), Matsui and Nishizawa (1974), Kawasaki and Matsui (1977), Sack (1980), Engi (1980a), Wood and Kieppl (1981), and Andersen and Lindsley (1981). In general, regular or sub-regular solution models have been found adequate to describe olivine, though few attempts have aimed at encompassing the entire temperature range covered by experimental data.

The model adopted here (Engi, 1980a) satisfies the following constraints:

1. Correct limiting behavior in temperature of the excess properties in the range $300^\circ$ to $1800^\circ$C.
2. Consistency with the high-temperature (800$^\circ$-1200$^\circ$C) phase equilibriurn data of Naiziger and Muan (1967), Larimer (1968), Medaris (1969), Matsui and Nishizawa (1974), Kawasaki and Matsui (1977), and O'Neill and Wood (1979). Orthopyroxene coexisting with olivine was assumed to behave as a two-site ideal solution (Obata, Banno, and Mori, 1974).
3. Consistency with the low-temperature (450$^\circ$-650$^\circ$C) phase equilibriurn data of Schulien, Friedrichsen, and Hellner (1972).
4. Consistency with the available calorimetric data listed in table 2, including specifically the heats of mixing measured by Wood and Kieppl (1981).

Within the confines of a Margules expansion of the excess properties, it was found that the simplest possible model to meet the above four conditions is the following asymmetric formulation:

$$\Psi = X_{Fe} X_{Mg}^2 W_{G,Fe} + X_{Fe}^2 X_{Mg} W_{G,Mg}$$

where $\Psi$ denotes the molar excess properties in free energy ($G_{xs}$), enthalpy ($H_{xs}$), and entropy ($S_{xs}$), and heat capacity ($C_{p,xs}$). The Margules parameters $W_{G}$ satisfy the usual thermodynamic relations, notably:

$$W_{H,T} = W_{H,ref} + (T - T_{ref}) W_{T,ref}$$

$$W_{S,T} = W_{S,ref} + \ln(T/T_{ref}) W_{C,T}$$

$$W_{G,T} = W_{H,T} - T W_{S,T}$$

Values for the required parameters were determined by non-linear regression analysis and are included in table 2; note that they pertain to the components MgSi$_{0.8}$O$_2$ and FeSi$_{0.5}$O$_{2.5}$.

Comparison with previous models shows that the derived excess functions are generally similar in magnitude, at least where such a direct comparison is possible. Notable discrepancies are (1) the more complex functional form adopted here and (2) the behavior at temperatures below about 700$^\circ$C. The first point is a direct consequence of the required limiting behavior and merely expresses analytically the generally accepted increase in non-ideality with decreasing temperature: Whereas near-
<table>
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<tr>
<th>Compound</th>
<th>Property*</th>
<th>Adopted value (/mole)</th>
<th>Source</th>
<th>Remarks</th>
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<tr>
<td>MgSi_{0.6}O_{2}</td>
<td>S°</td>
<td>48.02 J/K</td>
<td>Robie, Hemingway, and Fisher (1978)</td>
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<td>(forsterite)</td>
<td>all others:</td>
<td>face values given by</td>
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<td>Δ_r G°, V:</td>
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<td>Δ_r G°, V:</td>
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<tr>
<td>FeSi_{0.6}O_{2}</td>
<td>S°</td>
<td>76.17 J/K</td>
<td>Essene, Wall, and Westrum (1980)</td>
<td>Adjusted by − 2σ (see text)</td>
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<td>(fayalite)</td>
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<td>C_p**</td>
<td>78.420 J/K</td>
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<td>W_h(Fe)</td>
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<td>Wood and Kleppa (1981)</td>
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<td>W_c_p(Fe)</td>
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* The reference state is (298 K, 1 bar), except where stated otherwise. Subscript f implies "formation from elements."

** Maier-Kelley coefficients were generated by least squares regression of the drop colorimetry data to $C_p = a + bT + cT^{-2}$ (present study).
ideality (or a slight positive deviation from ideal behavior) is observed above 1000° to 1100°C, a distinct positive deviation is indicated by calormetry and phase equilibria below 800°C. Attempts by Saxena (1972) and Obata, Banno, and Mori (1974) at determining the actual amount of this deviation are based on the ion-exchange data by Schulien, Friedrichsen, and Hellner (1972). Because these involve aqueous Mg–Fe–chloride fluids, the solution properties of which we are only beginning to understand, some simplifying assumptions made by the earlier investigators are now untenable. Explicit provision for the dissociation of aqueous MgCl₂ (Frantz and Popp, 1979, 1981; Frantz and Marshall, 1982) and FeCl₂ (Boctor, Popp, and Frantz, 1980) in the model for aqueous chloride solutions has a profound effect (Engi, 1980b; Bartholomew, 1982) on the solution properties derived from coexisting olivine. Further improvements in the data base on aqueous chlorides, particularly FeCl₂, will thus undoubtedly modify again the low temperature solution properties derived for olivine. It is chiefly for this reason that the proposed excess parameters (especially in the derivative properties W₈ and Wₑₚ) should be interpreted with caution.

Solution behavior of Al–Cr–spinel.—The compositional variation of spinel in the experiments presented here and, to a first approximation, in many spinel peridotites, can be described by (MgₓFe₁₋ₓ) (CrₗAlₜ₋ₗ)₂O₄, with 0 ≤ x ≤ 1, 0 ≤ y ≤ 1. The system is thus of a reciprocal salt type: x and y are not coupled by any charge balance constraints, and the entire composition space is physically accessible; in fact, all four endmembers of this three component system are known to have considerable stability fields. Structurally, all four endmembers are predominantly normal spinels (divalent cations in tetrahedral coordination, trivalent ones occupying octahedra), although at high temperatures the aluminates may be partially disordered. There are no site occupancy data available for intermediate ternary spinels of the system (Mg,Fe) (Al,Cr)₂O₄ but, on the basis of site preference energies (Dunitz and Orgel, 1957; Navrotsky and Kleppa, 1967), the local ordering characteristics may be expected to resemble those of the endmembers.

The thermodynamic solution behavior of these ternary spinels has been modelled by Irvine (1965), Nicholls (1977), and Wood and Nicholls (1978). The latter two studies follow the classical work on reciprocal salt systems (for example, Blander, 1964; Lumsden, 1966). The approach taken here uses the theoretical framework developed by Brown and Greenwood (in preparation), which differs conceptually from those above. The data of the present study provide for an instructive comparison of these formulations. The total molar free energy of the spinel solid solution in question can be described as

\[ \mathcal{G}_{\text{total}} = \mathcal{G}_{\text{mechanical}} + \mathcal{G}_{\text{excess}} \]  

\[ = \mathcal{G}_{\text{mechanical}} - T \Delta S_{\text{configurational}} + \mathcal{G}_{\text{excess}} \]  

\[ = \sum_{i} X_{i} \mu_{0}^{i} - T \left( -R \sum_{i} n_{i} X_{i} \ln X_{i} \right) + \mathcal{G}_{\text{excess}} \]
where $T$ is the absolute temperature (K), $R$ is the gas constant (8.3143 J K$^{-1}$mole$^{-1}$), subscript $i$ refers to the pertinent species $i$ or component $i$, $x_i$ is the mole fraction, and $\mu^o_i$ its chemical potential at $x_i = 1$ and at the conditions of interest; $n_i$ stands for the multiplicity of the site shared by species $i$. $\Gamma_{\text{excess}}$ may thus be viewed as a correction term relating $\Gamma_{\text{ideal}}$ to the true (observed) $\Gamma_{\text{total}}$ of the solution. Regarding the predictive power of a particular model, a small or vanishing $\Gamma_{\text{excess}}$ would, of course, be desirable. One may expect substantial differences in the required $\Gamma_{\text{excess}}$ for ternary (Mg,Fe$^{2+}$,Al,Cr)-spinel as a result of the three different formulations proposed for $\Gamma_{\text{ideal}}$.

1. Irvine’s (1965) approach implies formulation of the ideal part in terms of any three of the four limiting endmember components, for example:

$$\begin{align*}
i = 1 & \quad \text{sp} & (\text{MgAl}_2\text{O}_4) & \quad X_1 = X_{\text{Mg}}(1-Y_{\text{Cr}}) f \\
i = 2 & \quad \text{hc} & (\text{FeAl}_2\text{O}_4) & \quad X_2 = (1-X_{\text{Mg}})(1-Y_{\text{Cr}}) f \\
i = 3 & \quad \text{pc} & (\text{MgCr}_2\text{O}_4) & \quad X_3 = X_{\text{Mg}} Y_{\text{Cr}} f
\end{align*}$$

(10)

where $f = 1/(1-(1-X_{\text{Mg}})Y_{\text{Cr}})$

and $X_{\text{Mg}} = Mg/(Mg + Fe)$ in spinel

and $Y_{\text{Cr}} = Cr/(Cr + Al)$ in spinel.

Wood and Nicholls (1978) show that Irvine’s model fails to consider the constraint of the internal equilibrium:

$$\text{MgAl}_2\text{O}_4 + \text{FeCr}_2\text{O}_4 = \text{FeAl}_2\text{O}_4 + \text{MgCr}_2\text{O}_4$$

(11)

except if $\Delta_{11}G^o$ happens to be zero. In fact, however, $\Delta_{11}G^o$ is of the order of 10 kJ mole$^{-1}$ at geologically accessible conditions.

2. In an effort to circumvent these undesirable implications, Nicholls (1977), Wood and Nicholls (1978), and, in a recent extension, Sack (1982) adopt the classical reciprocal salt approach, which again involves the arbitrary selection of three endmembers as components. To preserve invariance of the solution’s properties to this selection and to satisfy equilibrium (11), a new term has to be introduced. Maintaining the above set of components, this cross term takes the form:

$$\Gamma_{\text{cross}} = (1-X_{\text{Mg}}) Y_{\text{Cr}} (\mu^o_{\text{ch}} + \mu^o_{\text{sp}} - \mu^o_{\text{pc}} - \mu^o_{\text{hc}})$$

(12)

Using eqs (2), (3), and (4) of Wood and Nicholls, we get

$$\Gamma_{\text{ideal}} = (X_{\text{Mg}} - Y_{\text{Cr}}) \mu^o_{\text{sp}} + (1-X_{\text{Mg}}) \mu^o_{\text{hc}} + Y_{\text{Cr}} \mu^o_{\text{pc}} + \Gamma_{\text{cross}}$$

$$+ R T (X_{\text{Mg}} \ln X_{\text{Mg}} + (1-X_{\text{Mg}}) \ln (1-X_{\text{Mg}})$$

$$+ 2 (1-Y_{\text{Cr}}) \ln (1-Y_{\text{Cr}}) + Y_{\text{Cr}} \ln Y_{\text{Cr}})$$

(13)

3. By contrast to Wood and Nicholls’ stoichiometric approach, the condition of homogeneous equilibrium is formulated in the present study.

$^1$Wood and Nicholls refer to this term variably as “excess free energy”, “cross-site” or “reciprocal” term. The first choice seems unfortunate because of the usual connotation of the phrase, that is, its association with non-ideal (ionic) interaction. “Cross-site term” or simply “cross term” appear preferable and are used here. Accordingly, $\Gamma_{\text{cross}}$ here corresponds to $\Gamma_{\text{ex}}$ of Wood and Nicholls.
as a distribution-of-species problem (Brown and Greenwood, in preparation). In a solid solution, the species in question may be identified with elementary structural units (Thompson, 1969), the mixing of which is regarded as functionally analogous to discrete species in gaseous or liquid (non-electrolyte) solutions. There are, of course, limits to the adequacy of such an analogy. For example, any particular selection of species may imply long range order or cluster formation. Where available, crystal-chemical data should support such assumed ordering characteristics for an adequate selection of species. Appendix A derives and justifies the set of species adopted for spinel in the present study. The model developed in appendix A allows the computation of the molar total free energy of the ideal solution as

$$\bar{G}_{\text{ideal}} = \sum_{i=1}^{4} X_i \mu^2 + R T \sum_{i=1}^{4} X_i \ln X_i$$  \hspace{1cm} (14)$$

where

\begin{align*}
  i = 1 & : \text{sp (MgAl}_2\text{O}_4) \\
  i = 2 & : \text{hc (FeAl}_2\text{O}_4) \\
  i = 3 & : \text{pc (MgCr}_2\text{O}_4) \\
  i = 4 & : \text{ch (FeCr}_2\text{O}_4)
\end{align*}

In the speciation approach, these four mole fractions are not determined solely by the composition of the system but depend on the standard chemical potentials of the pertinent species as well. Consequently, the equilibrium distribution of species needs to be computed at any given composition, temperature, and pressure, for example by minimizing the Gibbs function (14) (Thompson, 1969). For the system at hand, this is equivalent to solving the following system of simultaneous equations:

\begin{align*}
  X_1 + X_3 &= X_{\text{Mg}} \\
  X_3 + X_4 &= X_{\text{Cr}} \\
  \sum_{i=1}^{4} X_i &= 1 \\
  (X_2 X_3)/(X_1 X_4) &= K_{11}
\end{align*}  \hspace{1cm} (15)

Solutions to (15) turn out to be simple quadratic equations, for example

$$X_{\text{hc}} = \frac{C + (C^2 + 4 K_{11} (1-K_{11}) (1-Y_{\text{Cr}}) (1-X_{\text{Mg}}))^{1/2}}{2 (1-K_{11})}$$

with

$$C = (1-K_{11}) (1-Y_{\text{Cr}} - X_{\text{Mg}}) - K_{11}$$

Excess properties for spinel, if required by phase equilibrium data, are easily incorporated into the present model. A functionally simple
approach describes the excess free energy as a function of the bulk composition of the solution. For example, using a regular solution approach, binary interaction terms $W_G^{MgMg}$, $W_G^{Fe}$ may be introduced, yielding the following contribution to the excess free energy:

$$\bar{C}_{xs}^{Mg} = X_{Mg}^2 (1-X_{Mg}) W_G^{Mg} + X_{Mg} (1-X_{Mg})^2 W_G^{Fe}$$

(16)

Analogous contributions could be written for $\bar{C}_{xs}^{Cr}$ and, if needed, for the ternary ($\bar{C}_{xs}^{MgCr}$), with the total excess free energy being the sum of these parts.

**DATA ANALYSIS**

*Evaluation of available thermochemical data.*—The data base for the two magnesian endmember spinels, spinel and picrochromite, is complete and fairly well established, although largely untested by phase equilibrium work. Uncertainties in $\Delta_r H^o$ and $\Delta_r G^o$ are of the order of ± 800 J (Robie, Hemingway, and Fisher, 1978). This situation contrasts sharply with the large uncertainties and gaps in the data base on the ferroan endmembers, hercynite and chromite. For hercynite, Robie, Hemingway, and Fisher indicate ± 8.5 kJ in the above properties, although several sets of electrochemical data, the results of which are evaluated by Chan, Alcock, and Jacob (1973), suggest smaller uncertainties in $\Delta_r G^o_{he}$ and $\Delta_r H^o_{he}$, perhaps ± 3 kJ. I have found no measurements of the high-temperature heat capacity for hercynite. Noting that $\Delta_n V < 0.06$ J bar$^{-1}$ mole$^{-1}$, $C_p^{he}$ may be estimated by assuming $\Delta_{11} C_p$ to be zero and using values (table 3) from Robie, Hemingway, and Fisher (1978):

$$C_p^{he} = C_p^{sp} + C_p^{ch} - C_p^{se}$$

(17)

**Table 3**

**Thermochemical data for Mg$^{2+}$–Al–Cr–spinel**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Property**</th>
<th>Adopted value (J/mole)</th>
<th>Comparison, uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl$_2$O$_4$ (sp)</td>
<td>$S^*$</td>
<td>80.21 J/K</td>
<td>(= Robie – 2$\sigma$)</td>
</tr>
<tr>
<td></td>
<td>$\Delta_r G^*$</td>
<td>-1842.95 J/K</td>
<td>uncertainty &lt; ± 0.4 kJ</td>
</tr>
<tr>
<td></td>
<td>$S^*$</td>
<td>107.99 J/K</td>
<td>Robie: -1850.795 ± 8.5 kJ</td>
</tr>
<tr>
<td></td>
<td>$C_p$</td>
<td>135.34</td>
<td>Robie: 106.27 ± 0.4 J/K</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>0.06474</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>-2894815.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>-0.000014657</td>
<td></td>
</tr>
<tr>
<td>MgCr$_2$O$_4$ (pc)</td>
<td>$S^*$</td>
<td>106.86</td>
<td>(= Robie + 2$\sigma$)</td>
</tr>
<tr>
<td>FeCr$_2$O$_4$ (ch)</td>
<td>$\Delta_r G^*$</td>
<td>-1331.90 J/K</td>
<td>uncertainty &lt; ± 1.25 kJ</td>
</tr>
<tr>
<td>Solid solution (sp–hc–ch–pc)</td>
<td>$W_H^{Fe}$</td>
<td>-1.65 J/K</td>
<td>(Robie – 2$\sigma$)</td>
</tr>
<tr>
<td></td>
<td>$W_H^{Mg}$</td>
<td>-2.09 J/K</td>
<td>see equations 14-16</td>
</tr>
</tbody>
</table>

* The table contains only values that were not taken directly from Robie, Hemingway, and Fisher (1978) at face value.

** Entropy values modified in the present study were used in combination with Robie, Hemingway, and Fisher's $\Delta_r G^o$. The label "Robie – 2$\sigma$" indicates that the value for $S^*$ given in column 3 corresponds to the lower error bracket allowed by Robie, Hemingway, and Fisher (1978); similarly for "Robie + 2$\sigma$".
Calorimetric enthalpy data are lacking for chromite, presumably owing to its refractory nature. A large number of e.m.f. studies have appeared (see Jacob and Alcock, 1975) which unfortunately yield an extraordinary scatter of free energies of formation, spanning some 36 kJ. Although several of the more recent investigators are in much better agreement than this (Dellien, Hall, and Hepler, 1976), the remaining uncertainty is probably ± 3 kJ, as for hercynite. Further comparison of this estimate based on electrochemical work is afforded by a number of high temperature phase equilibrium studies (Richardson and Jeffes, 1949; Schmahl and Dillenburg, 1969; Snethlage and Klemm, 1975). It is clear from these that the above uncertainty is, if anything, somewhat optimistic.

In view of these substantial uncertainties, which currently preclude any reliable prediction of exchange equilibrium (11), the data in table 1 will be used not only to derive solution properties for spinel but also to refine the free energies of hercynite and chromite. Furthermore, phase equilibrium data may be expected to test the consistency and adequacy of the remainder of the data base, in particular the entropies of the four endmembers (Kleppa, 1981). Owing to the partially disordered state of high-temperature aluminates, this test is of special significance, because it is not clear what configurational contribution may be due to a metastably high degree of inversion in the Al-spinels employed in calorimetric studies.

Computing and fitting techniques.—Given a complete thermochemical data base, including excess parameters, equilibrium (1) is readily calculated by minimizing the total free energy of the system subject to the mass balance constraints. Owing to the non-linear dependence of both $\mathcal{G}_{\text{total}}^{OL}$ and $\mathcal{G}_{\text{total}}^{SP}$ on composition, such a minimization necessarily requires an iterative root-finding method (Van Zeggeren and Storey, 1970). A modified version of White's RAND method (Oliver, Stephanou, and Baier, 1962) has proven fast and stable in the current application. One particularly appealing characteristic of the G-minimization approach is its generality, which permits simple extension of the computation to include, for example, further ferromagnesian phases such as pyroxenes, or further spinel species such as ferrites.

In order to determine a set of thermodynamic data consistent with the phase equilibria studied, non-linear least squares regression analysis was used. It may be worth reminding ourselves, however, that this choice does not suit the inherent structure of phase equilibrium brackets very well. The implicit assumption in using any regression technique is that these brackets represent actual equilibrium points in composition-temperature-pressure space or that they are, at least, distributed randomly around the equilibrium surface in that space (for example, Lindsley, Grover, and Davidson, 1981). Reference to table 1 and figures 2 to 4 shows the above assumption to be quite untenable in some cases, particularly for the Cr-rich spinel systems investigated.

Methods in fundamentally better accord with such data have been developed (Gordon, 1973, 1977) to retrieve thermodynamic reaction prop-
Fig. 2. Mg-Fe exchange equilibrium data (table 1) for olivine and spinel at 700°C and 1 kbar; error boxes correspond to 2 e.s.d. in replicate probe analyses (see text); arrows indicate the direction of approach toward equilibrium (from reactant to product compositions); adjacent numbers are the Al/(Cr + Al) values of spinel. The data may be compared with the computed isopleths in $Y_{Al}$, which are based on the present models (text) and data in tables 2 and 3 and in Robie, Hemingway, and Fisher (1978).

Fig. 3. As figure 2, but for 800°C and 1 kbar.
Fig. 4. As figure 2, but for 930 °C and 390 bar.

...erties from experimental studies. So far, however, these methods rely on linear programming techniques, whereas the present problem would require non-linear optimization. Keeping the above in mind, a satisfactory compromise may be reached by selecting from table 1 only those data that appear to approximate equilibrium conditions. The results of the regression analysis performed on the basis of this selected data set then have to be checked for their compatibility with all the data, including those not used in the fitting.

In detail, the problem solved here by regression analysis may be stated as follows: Find the set A of fit parameters that minimizes the sum of squares of residuals

$$
\Sigma_i (\hat{X}_{fo,i} - X_{fo,i})^2
$$

subject to the mass balance constraints

$$
X_{fo,i} = \frac{r_{modal,i}^1}{1 + r_{modal,i}^1} \hat{X}_{fo,i} + \frac{1}{1 + r_{modal,i}^1} (\hat{X}_{Mg^{i,SP}} - X_{Mg^{i,SP}})
$$

$$
0 \leq X_{fo,i} \leq 1 \quad \text{and} \quad Y_{cr,i} = \hat{Y}_{cr,i}.
$$

Here, $\hat{X}_{fo,i}$ and $\hat{X}_{Mg^{i,SP}}$ denote the mole fractions $\text{Mg}/(\text{Mg+Fe})$ measured in olivine and spinel of products $i$; $X_{fo,i}$ and $X_{Mg^{i,SP}}$ are the computed equilibrium values pertinent to bulk composition $i$;
is the modal abundance ratio olivine/spinel used in experiment $i$;

\[ \hat{Y}_{Cr} \] and \[ Y_{Cr} \] are the measured and computed mole fractions \[ Cr/(Cr+Al) \] in spinel $i$.

As stated earlier, the fit parameters included

\[ \Delta_t G^o_{he}, \Delta_t G^o_{eh}, W_G^{Mg}, W_G^{Fe}, W_G^{Cr}, \text{ and } W_G^{Al} \]

where all the $W_G$ denote Margules parameters for spinel (compare eq 16). It was not clear at the outset of the regression analysis which of these would be required by the data and whether they might have to be formulated as temperature dependent.

Results of the regression analysis.—Preliminary fitting involved the pure Al-subsystem only and yielded values for $W_G^{Mg}$ and $W_G^{Fe}$ which are independent of temperature (650°C-900°C) but do require a slight asymmetry. Very tight constraints on $\Delta_t G^o_{he}$ leave a maximum uncertainty of less than ± 400 J mole$^{-1}$. In order to satisfy the temperature dependence of $\Delta_t G$ indicated by the exchange data, $\Delta_t S$ has to be slightly more negative than implied by the adopted data base of thermochemical data. Although this discrepancy might be attributed in part to the estimated value for $C_{p,he}$, that value was maintained. Instead, all the entropies in the data base were allowed to be adjusted within published uncertainties while attempting to satisfy the constraints from the exchange data on $\Delta_t S$. This procedure reduced the discrepancy to 0.88 J K$^{-1}$mole$^{-1}$, which was the value added to $S^o_{he}$.

Having achieved internal consistency for the pure aluminate system, all subsequent fits included the data on Cr-bearing spinel systems. Values derived for $W_G^{Mg}$ and $W_G^{Fe}$ show little change when compared to pure aluminates. Inclusion of $W_G^{Al}$ and $W_G^{Cr}$ did not appear to improve the quality of the fit, and these parameters were set zero in the final spinel model. The value of $\Delta_t G^o_{eh}$ cannot, on the basis of present data, be constrained quite as effectively as $\Delta_t G^o_{he}$; the remaining uncertainty for chromite is about ± 1250 J mole$^{-1}$. Again, as for the pure Al-system, a slight adjustment of the entropy greatly improves the fit. In the case of chromite and picrochromite, the changes required are within the uncertainties (Robie, Hemingway, and Fisher, 1978).

Table 3 lists the accepted final values of thermochemical data for the spinels considered. Estimated uncertainties are included for the actual fit parameters only; they are intended merely as indications of the remaining relative error. Owing to their high correlation, they cannot be used as independent variables, for example, in error propagation schemes, without violating the internal consistency established here. Figures 2 to 4 display $Y_{Cr}$-isopleths of spinel in equilibrium with olivine. These compositions were computed using thermochemical data from tables 2 and 3. Also shown in these figures are all the pertinent experimental data from table 1, some of which had not been used in the regression analysis. The relat-

\[ ^2 \text{ The modal abundance is introduced merely as a link between Mg/(Mg+Fe) values in olivine, spinel, and the bulk experimental charge.} \]
Equilibria involving Al–Cr spinel: Mg–Fe exchange with olivine

tively small data sets collected at 650°C and 750°C are not shown, although
they were used in the fitting and are consistent with the final model. True
compositional uncertainties are slightly larger than indicated by the error
boxes (figs. 2-4), because the latter were computed solely from replicate
microprobe analyses and do not include other analytical uncertainties
(p. 33).

Implications.—The Margules parameters derived above for spinel
require no temperature dependence between 650°C and 900°C. Hence, \(W_Q\)
may be identified with \(W_H\), and the molar excess free energy corresponds
to the molar excess enthalpy. The small (negative) deviation from ideality
observed for the Mg–Fe\(^{2+}\)–Al–Cr spinel solution virtually rules out the
possibility of unmixing. This conclusion agrees with the continuous solu-
tion behavior established by Warshaw and Keith (1954) along the join
spinel–picrochromite and by Chassagneux and Rouset (1976) along hercynite–chromite. The latter work challenged earlier results by Cremers
(1969), but in both studies the respective claims were based on synthesis
data only, hence they were inconclusive. The well established solvus along
the join magnetite–hercynite, which has been invoked as an analog (for
example, Cremers. 1969), may not be very adequate as such, since magnetite
has an inverse spinel structure, whereas both hercynite and chromite are
normal spinels.

THERMODYNAMIC CONSEQUENCES

The thermochemical data base derived (tables 2 and 3) is not only
internally consistent within the constraints of the experimental data
(table 1) but is also compatible with standard thermodynamic data from
the literature, with the exception of a slight discrepancy in the entropy
of hercynite. This broad agreement provides a basis for extrapolation to
somewhat lower and, perhaps with more confidence, to higher tempera-
tures than those covered by experiment. Limiting quantities in either
direction are (1) the free energy of chromite, (2) the entropies of the
aluminates, especially at high temperature, and (3) the small non-ideality
of spinel which may not persist to temperatures above 1000°C and is likely
to increase in magnitude below 600°C.

Before attempting to recalibrate the olivine-spinel geothermometer
on the basis of the models developed above, it may be of interest to com-
pare quantitatively some of the implications of the different solution
models proposed for spinel. This can be done most instructively by sepa-
rating the various terms involved and depicting them graphically in free
energy-composition (hc–sp–pc–ch) space.

Comparison of models.—Figures 5 to 12 compare the distribution-of-
species (DS) model proposed here with the classical reciprocal salt (RS)
model adopted by Wood and Nicholls (1978) and extended by Sack (1982)
to include further components. Note that the vertical (molar free energy)
scale varies from figure to figure.

1. Comparison of the first term in eq (14) with the first three terms
in eq (13) shows the crucial difference between \(\Omega_{\text{mechanical}}^{DS}\) and the corre-
responding \(\Omega_{\text{endmember}}^{RS}\): while the DS quantity satisfies the equation of a
Fig. 5. Difference between the Gibbs free energy of mechanical mixing expressed by models DS (distribution of species) and RS (reciprocal salt solution model) for ternary spinel; compare with figure 6.

Fig. 6. The Gibbs free energy due to reciprocal interaction of components as expressed by model RS; compare with figure 5.
Equilibria involving Al–Cr spinel: Mg–Fe exchange with olivine

plane in $G - X_{Mg} - Y_{Cr}$ space, this is not true for RS unless $\Delta_{11}G^\circ$ is zero. Figure 5 depicts the difference between these two terms only. Comparison with figure 6 shows, however, that the cross term (eq 12) proposed by Wood and Nicholls yields a surface similar in magnitude and shape to that difference. For the sake of the present comparison, at least, one may thus be justified in regarding $\mathcal{C}_{\text{endmember}}^{\text{RS}} + \mathcal{C}_{\text{cross}}^{\text{RS}}$ as analogous to $\mathcal{C}_{\text{mechanical}}^{\text{DS}}$. That they are not identical, however, can be seen in figure 7.

2. The respective configurational contributions may be compared in figures 8 and 9. The marked difference here is due entirely to the octahedral site-multiplicity factor of 2 in Wood and Nicholls’ formulation (compare eqs 8, 9, 13, and 14).

3. Finally, figures 10 and 11 allow the direct comparison of the excess free energy required by the data presented in this study. Clearly $\mathcal{C}_{\text{excess}}$ is both smaller and simpler for the DS model than for RS. A satisfactory analytical representation of $\mathcal{C}_{\text{excess}}$ using site activity coefficients as proposed by Wood and Nicholls would, in fact, be rather complex. It may be noted, however, that the major contribution to both the magnitude and shape of the surface shown in figure 11 is a consequence of the functional form proposed to describe the configurational entropy of mixing. If, instead of adopting an ionic (Temkin) model, one formulates a molecular model, the site-multiplicity factor is $n = 1$. Designating the so modified reciprocal salt model by “RS(mod)”, it follows that $\mathcal{C}_{\text{configurational}}^{\text{RS (mod)}} = \mathcal{C}_{\text{configurational}}^{\text{DS}}$ (fig. 9), which leaves a much smaller excess free energy for model “RS(mod)” (fig. 12) than for “RS”. Still, its magnitude is about eight times higher than that required for the speciation model, and, more importantly, it varies considerably with $Y_{Cr}$, which complicates its analytical representation.

---

Fig. 7. Difference in the Gibbs free energy surface represented in figures 5 and 6. The surface shown here dips gently toward the minimum at [0.5, 0.5, −3.3 kJ].
APPLICATIONS TO GEOTHERMOMETRY

The temperature dependence of the distribution coefficient

$$K_D^{1} = \frac{X_{Mg}^{sp} X_{Fe}^{ol}}{X_{Mg}^{ol} X_{Fe}^{sp}}$$

(2)

has received considerable attention as a geothermometer, specifically with application to chromite-bearing ultramafic rocks. Irvine (1965, p. 660) was

Fig. 8. The ideal configurational part of the Gibbs free energy as expressed by the speciation model DS. Minimum at [0.5, 0.5, -10.9 kJ]. Compare with figure 9 (same scale).

Fig. 9. The ideal configurational part of the Gibbs free energy as expressed by the reciprocal solution model RS. Minimum at [0.5, 0.5, -18.6 kJ]. Compare with figure 8 (same scale).
the first to suggest the now widely used graphical portrayal of isotherms in $Y_{Cr}$-$lnK^*_D$ space, and it seems fitting to refer to such diagrams as Irvine diagrams (for example, fig. 13). If one adopts Irvine's formulation of the spinel solid solution and assumes ideality (or cancelling non-idealities) for spinel and olivine, a number of simple properties are readily deduced for this type of diagram (see also Evans and Frost, 1975). (A) Isotherms plot as straight lines; (B) their spacing (in 1/T) is proportional to $\Delta_H$; and (C) the position of the isotherms varies linearly with the ferrite-fraction ($Y_{Fe}$) of spinel and is notably independent of $X_{Mg}$ of the system.

Fig. 10. The excess Gibbs free energy as required by the present data (table 1) on the basis of the speciation model DS. Compare with figure 11 (same scale).

Fig. 11. The excess Gibbs free energy as required by the present data (table 1) on the basis of the classical model RS. Compare with figure 10 (same scale).
The simplicity of these relations is of obvious appeal and may be responsible, to a large part, for the popularity of Irvine diagrams evident in the literature. Most investigators (implicitly or explicitly) rely on the above consequences of Irvine's theoretical approach; this is true for the repeated recalibrations, as well as for many applications that make interpretive use of Irvine diagrams.

The results of the present study ask for several modifications in the calibration, application, and interpretation of Irvine diagrams. In particular, one may anticipate implications (B) and (C) to change: The non-ideality of olivine and spinel renders $K_{P}^{i}$ dependent on the bulk $X_{Mg}$; and the relation between $\ln K_{P}^{i}$ and $Y_{Cr}$ is, in the light of species interaction, likely to be more complex than implied by Irvine's theoretical treatment. These expectations are borne out by actual calculations. The consequences of non-ideality can be monitored effectively on Irvine diagrams (figs. 13-15). The isotherms shown were computed from the models and thermochemical data presented in the previous sections. The particular choice of bulk composition parameters ($X_{Mg}^{bulk}$ and $r_{modal}$) used for these calculations is justified below and in appendix B. It is evident from figures 13 to 15 that the computed isotherms in an Irvine diagram are not straight lines. The deviation from linearity is primarily a consequence of the speciation in spinel and only fractionally due to the Mg-Fe non-idealities.

In addition to being non-linear, the isotherms depend in shape and position on the bulk composition of the system. Upon first consideration, only a simple dependence of $\ln K_{P}^{i}$ on $X_{Mg}$ may be obvious, that is, one might anticipate a more-or-less parallel displacement of the isotherms, attributable to the Mg-Fe non-idealities of olivine and spinel. The observed additional change in shape is the result of a fairly complex inter-

---

**Fig. 12.** The excess Gibbs free energy as required by the present data (table 1) on the basis of the modified reciprocal salt solution model RS(mod), see text. Minimum at [0.5, 0.5, -3.7 kJ].
Fig. 13. Irvine diagram: logarithm of partition coefficient of Mg–Fe exchange equilibrium (1) as a function of Cr/(Cr + Al + Fe\textsuperscript{3+}). Isotherms between 600\degree C and 1400\degree C computed from data in tables 2 and 3 and from Robie, Hemingway, and Fisher (1978). They pertain to compositions of type "AT" (see text, table 4, and fig. 17).

Fig. 14. Irvine diagram for type "LI", compare to figure 18 and caption to figure 13.
play of the effects of speciation and non-idealities. Consider equilibrium (1) in a series of (isothermal, isobaric) systems, for example, a suite of rocks, in which the principal compositional variation occurs in Cr/(Cr + Al). At Al-rich compositions, the available Mg and Fe will be distributed fairly evenly among olivine and spinel; at more Cr-rich compositions, spinel will incorporate increasing proportions of total available Fe. The fractional change in spinel composition obviously depends on the relative abundance $r_{\text{modal}}$ of the two phases, hence on the bulk ratio Si/(Al + Cr). Recasting this line of reasoning in terms of equilibrium calculations (by G-minimization), one observes that the relative influence of $T_{\text{total}}^{SP}$ and $T_{\text{total}}^{\text{OD}}$ on $T_{\text{total}}^{\text{SYSTEM}}$ evidently changes with $Y_{\text{Cr}}$.

These complications of the geometric aspect of Irvine diagrams might be taken as a general challenge to the usefulness of such representations. Such a pessimistic conclusion, however, is not warranted, provided the following constraints are kept in mind:

1. Any (series of) isotherm(s) in an Irvine diagram represent(s) a specific choice of bulk composition parameters and vice versa.

2. A given suite of systems or mineral assemblages may not correspond to any one set of such parameters, that is, these may well vary within a suite.

The latter point suggests a strategy to define the required bulk composition parameters, which should ensure adequacy of the Irvine diagram (and of derived versions of the olivine-spinel geothermometer) for many common applications: The aim is to define the composition of the system in terms of a set of mineralogic/geochemical variables that vary little

---

**Fig. 15.** Irvine diagram for type "CO", compare figure 19 and caption to figure 13.
Equilibria involving Al–Cr spinel: Mg–Fe exchange with olivine

within typical rock suites. Appendix B offers one set of such variables and develops approximate geothermometric equations based on them.

Comparison with previous studies.—Figure 16 compares several earlier attempts to calibrate the spinel-olivine geothermometer with the one developed here by depicting the respective isotherms at 700°C and 1200°C. Where necessary, the literature versions were reduced to \( Y_{Fe} = 0.0 \) by means of the correction suggested in the referenced original papers. Results of the present study (see app B) are represented by the isotherms (bold curves) for classes “AT” and “CO” only.

At 700°C one observes fair agreement between the pertinent curve (“AT”) and the linear isotherms proposed on the basis of metamorphic assemblages (Evans and Frost, 1975; Fujii, 1977; Fabriès, 1979). There is, however, serious conflict between all of these and the versions proposed on the basis of thermochemical data alone (Jackson, 1969; Roeder, Campbell, and Jamieson, 1979), which serves to emphasize again that independently gathered data of this kind generally do not predict phase relations reliably.

At 1200°C the picture is less clear, but close examination of the original natural data (used by Evans and Frost, Fujii, and Fabriès) shows that the agreement with the present version is considerably better than would appear from figure 16. The reason lies again in the fact that bulk compositional effects are not represented in Irvine diagrams. Differences in the treatment of the ferrite component, for example, contribute almost

![Graph showing isotherms for spinel-olivine geothermometer comparison.](image)

**Fig. 16.** Comparison of proposed isotherms for the spinel-olivine geothermometer normalized to 1 bar pressure and \( Y_{Fe} = 0.0 \). Bold curves correspond to the isotherms derived in the present work: Top = class “AT”; bottom = class “CO”. Discussion in text.
50 percent to the apparent discrepancy between Evans and Frost's 1200\textdegree C isotherm and the one proposed here (type "LI", which would be more representative than "AT"). The substantially different slope of Fujii's (1977) experimentally determined curve, however, remains difficult to explain (compare Fabriès, 1979, p. 331). Clearly, a well reversed experimental isotherm at or above 1200\textdegree C would be very valuable in order to test the reliability of the current model at very high temperatures, particularly since few of the data presented here exceed 900\textdegree C.

**Uncertainties in and interpretation of derived temperatures.**—Uncertainties introduced into the thermometer by use of the approximate corrections (app. B: eqs B-2, B-3, B-6, and B-7) are of the order of 2\textdegree to 6\textdegree C. (This value does not include the far more substantial systematic uncertainty due to the inadequate model for ferrite-components in spinel!) The total uncertainty remaining in the composition range of the present calibration is estimated to be about ± 25\textdegree C between 600\textdegree and 950\textdegree C; at temperatures above 1200\textdegree C, however, it may well exceed ± 50\textdegree C. These estimates of calibration error pertain to the absolute temperature value derived from a single measurement of lnK^\text{IP} (assuming no analytical error and a spinel devoid of Fe^{3+}). Relative uncertainties are much lower: Assemblages equilibrated at temperatures as little as 10\textdegree apart should be discernable. Such resolution, however, is only possible on the basis of accurate mineral analyses spanning a range of Y\text{Cr} at nearly constant, low Y\text{Fe}. As discussed by Fabriès (1979, p. 332), the precise computation of Fe^{3+} from microprobe analyses demands complete\textsuperscript{a} spinel analyses (see also Osborne, Fleet, and Bancroft, 1981, p. 255).

A wide range of Y\text{Cr} is most crucial and, fortunately, often available if samples are strategically taken. For example, dunite and harzburgite and/or lherzolite commonly occur in close association and typically contain spinels of distinct Al/Cr ratios. Whether one may assume (local) equilibration of an entire suite of such samples at one specific temperature depends, of course, on the particular geologic situation. Application of the spinel-olivine geothermometer to samples of variable Y\text{Cr} may be helpful in testing such a hypothesis. If substantiated, the indicated temperature-range typically covers a spread of less than 30\textdegree C. If negated, that is, if highly variable temperatures are obtained, the possibility of sub-solidus reequilibration should be considered.

A number of investigators have reported evidence of fairly low blocking temperatures for the Mg–Fe exchange between olivine and spinel (Irvine, 1967; Smith and Levy, 1976; Fabriès, 1979; Roeder, Campbell, and Jamieson, 1979; Henry and Medaris, 1980; Smith and Roden, 1981). While some of these indications were based on inadequate thermometric calibrations (Engi and Evans, 1980) and thus need major modification in the light of the present work, such kinetic constraints certainly apply. At present these may limit our ability to interpret temperatures derived from slowly cooled spinel-olivine pairs. Comparison with other, possibly more "stable" thermometers applied to suitable samples offers oppor-

\textsuperscript{a} For ultramafic samples these should include Mg, Al, Ti, V, Cr, Mn, Fe, Ni, and Zn.
tunities for much fruitful research. The situation is, after all, very much akin to the thermal re-setting of certain isotope systems or of fission tracks. In those cases it is the very existence of these kinetic limits that has provided powerful new tools, for example, for thermal modelling. It seems unlikely that the intercrystalline exchange kinetics between spinel and olivine could be explored adequately by experimental or purely theoretical methods. Natural assemblages from terranes with well characterized thermal and kinematic histories, on the other hand, may contain the record needed for a kinetic interpretation of partially reset temperatures.

CONCLUSIONS

A set of thermochemical data was derived, which is consistent with olivine-spinel exchange equilibrium results (650°-900°C) presented here and which conforms, furthermore, with calorimetric data from the literature. The solution properties of olivine were described by an asymmetric Margules model, whereas the reciprocal spinel system (Mg,Fe) (Al,Cr)\textsubscript{2}O\textsubscript{4} was found to behave nearly ideally, provided the internal equilibrium constraints are formulated suitably. By adopting the distribution-of-species approach of Brown and Greenwood (in preparation), all constraints imposed by the present data are satisfied by a small, negative excess enthalpy term, which involves terms in \(X_{\text{Mg}}\) only.

The derived base of internally consistent thermodynamic data and models permits the computation of a number of equilibria of petrologic importance, among them a recalibration of the spinel-olivine geothermometer. A direct comparison with earlier versions of that thermometer on the basis of the traditional Irvine diagram (\(Y_{\text{Cr}}\) versus \(\ln K'_{\text{Mg}}\)) is possible only in part, owing to the compositional dependence of \(\ln K'_{\text{Mg}}\). For similar compositions and for temperatures between 600° and 800°C, the new calibration resembles those proposed on the basis of metamorphic assemblages. At 1200°C, however, one observes considerable disparity, which cannot be fully rationalized at present. A major portion of the conflict likely stems from uncertainties regarding Fe\textsuperscript{3+}. The current data base available for ferrite equilibria does not allow formulation of an adequate solution model.

Other limits to the (meaningful) application of the spinel-olivine geothermometer include the possibility of partial resetting upon slow cooling. The extent of that problem, however, may have to be re-evaluated on the basis of the present calibration.

ADDENDUM

At a late stage in the preparation of the present paper, I received from Heather E. Jamieson a copy of her dissertation entitled "The Distribution of Magnesium and Iron Between Olivine and Spinel at 1300°C" (Ph.D. thesis, Queens University, September 1981). A thorough integration of her as yet unpublished results has not been attempted here, but a few points of interest are noted:

Jamieson established a 1300°C isotherm (1 atm) for the exchange equilibria between olivine and aluminates (Mg,Fe)Al\textsubscript{2}O\textsubscript{4} and between olivine and ferrites (Mg,Fe)Fe\textsubscript{2}O\textsubscript{4}. Her data on the former compare favorably with the extrapolation attempted here and thus lend very welcome support to the present model, at least for the Al-rich part of the system. Furthermore, Jamieson's data on the ferrite equilibrium are in good accord with the correction for Fe\textsuperscript{3+} adopted here (app. B, eqs B-6 and B-7).
ACKNOWLEDGMENTS

Work presented here is contained, to a large part, in my doctoral thesis (ETH Zurich). I was fortunate to be able to extend and finally complete this study while holding two postdoctoral positions, first at State University of New York at Stony Brook and then at The University of British Columbia, Vancouver. During all this time I have benefitted greatly from stimulating colleagues and received generous help from many friends. Don Lindsley, Hugh Greenwood, and Tom Brown have decisively influenced my work in various aspects, in particular the approach to complex solutions. Ernie Perkins’ interactive graphics system was invaluable in the development and comprehensive testing of the models presented. Gordon Hodge, JoAnne Nelson, and Jill Kaplan gave generously of their time and skills in the preparation of figures and manuscript. The presentation has been markedly improved by perceptive reviewers: Rob Berman, Bernard Evans, Ron Frost, Hugh Greenwood, and Bernard Wood. Any remaining confusion is entirely my own.

Support for my work has come, at various stages, from the Schweizerrischer Nationalfonds (grant 5.615-0.76 to V. Trommsdorff), the Zentenarfonds ETH, the Canada Council, the N.S.F. (grant to D. H. Lindsley), and N.S.E.R.C. (grant A-4222 to H. J. Greenwood). I am grateful to all these individuals and institutions for their generous support.

APPENDIX A

Selection of species for (Mg,Fe) (Al,Cr)_{2}O_{4} spinels

Following Brown and Greenwood (in preparation), the most general formulation requires 24 species: 3 configurations for each of 4 compositional endmembers (for example, MgAl_{2}O_{4}, AlMgAlO_{4}, AlAlMgO_{4}), plus 6 species for each of the intermediate compositions MgAlCrO_{4} and FeAlCrO_{4}. On this basis, the ideal Gibbs free energy involves 24 chemical potentials:

$$
\mathcal{G}_{\text{ideal}}^{\text{sp}} = \sum_{i=1}^{24} X_i (\mu_i^* + R T \ln X_i)
$$

(A-1)

To use this general model in practice would require values for all 24 potentials \( \mu_i^* \). Substantial simplification is possible a priori on the basis of available crystal chemical information. It is well documented that chrome spinels assume a completely normal cation distribution (McClure, 1957; Robbins and others, 1971; Paul and Basu, 1974; Osborne, Fleet, and Bancroft, 1981), as do aluminates, except possibly at very high temperatures, where partial disordering may occur (MgAl_{2}O_{4}; Brun and Hafner, 1962; Stoll and others, 1964; Navrotsky and Kleppa, 1967, 1968; Schmocker, Boesch, and Waldner, 1972; Schmocker and Waldner, 1976; FeAl_{2}O_{4}; Roth, 1964; Yagnik and Mathur, 1968; Chassagneux and Rousset, 1976; Osborne, Fleet, and Bancroft, 1981). Incorporating this information in the speciation model reduces the number of configurations from 24 to 8, thereby ignoring all those implying inverse cation distribution (square brackets designate octahedral cations):

- Mg[AlAl]O_{4}, Mg[AlCr]O_{4}, Mg[CrCr]O_{4},
- Mg[AlAl]O_{4}, Mg[CrAl]O_{4}, MgAlCrO_{4}, Fe[CrAl]O_{4}, FeAlCrO_{4}, Fe[CrCr]O_{4}

Data on the ordering among trivalent cations in normal spinels are very scanty, but Osborne, Fleet, and Bancroft (1982) report on a Mössbauer spectroscopic investigation of Fe(Al,Cr)_{2}O_{4} powders. Second-nearest neighbor effects reveal substantial clustering,
that is, non-random distribution of Al and Cr around \( \text{FeO}_4 \) tetrahedra. The extent of such ordering has not yet been determined quantitatively, and the exact effect on the configurational entropy is thus not known. Following the principle of minimization of the number of fit parameters, a limiting approximation is adopted here, which assumes that the entropy contribution due to the mixing of octahedral cations may be negligible. In other words, Al-Al and Cr-Cr pairs are assumed much more likely than mixed couples. This amounts to ignoring all intermediate configurations in the present DS-model, that is, only the four fully ordered compositional endmembers are retained as species.

Appendix B

Development of approximate geothermometric equations for spinel-olivine pairs from typical ultramafic rocks

A set of parameters is sought that describes the observed compositional variation within any typical ultramafic suite. On the basis of the extensive documentation available on the petrology of ultramafic rocks, it appears that three classes may suffice to approximate a majority of natural occurrences of spinel-olivine pairs (table 4). The following couple of variables appears to be especially stable within each class: (1) the modal abundance ratio \( r_{\text{modal}} \) of olivine/spinel and (2) the bulk mole fraction \( X_{\text{Mg}_{\text{bulk}}} \) of the olivine-spinel assemblage. The three classes defined on the basis of published compilations (in particular, Jackson, 1969; Irvine and Findlay, 1972; Arai, 1980) are labelled according to typical associations ("AT": alpine-type peridotites; "LI": layered intrusions; "CO": chromite-olivine cumulates; table 4). These labels are not meant to have genetic connotation. In terms of common applications, the first two classes should represent nearly all the pertinent rock types including, for example, most ultramafic nodules. Owing to the wide variation of \( r_{\text{modal}} \) values observed in cumulates, even within one sequence, type "CO" may not be so representative of certain extreme cases. Complete equilibrium calculations would be indicated for such cases.

Figures 14 to 16 depict three series of isotherms computed for the three classes introduced above. The variations in actual phase compositions, as opposed to their distribution coefficient, are shown in figures 17 to 19. These graphs should be used to assess which of the three classes, if any, may represent a suitable model for a particular suite of samples. In order to facilitate applications to geothermometry, a set of analytical representations seems desirable, which express temperature as a function of composition (and pressure). For this purpose, a set of polynomial expressions was derived, one for each of the above classes. The following functional form proved adequate to reproduce computed equilibrium temperatures at 1 bar:

\[
T = \sum_{j=0}^{3} \sum_{i=0}^{3} A_{ij} \left( \ln K'_{i,j} \right)^{i} \left( Y_{cr} \right)^{j}
\]  

(B-1)

The coefficients \( A_{ij} \) were obtained by non-linear least-squares regression of an array of computed equilibrium values (spanning \( 600^\circ \text{C} \leq T \leq 1400^\circ \text{C}, 0 \leq Y_{cr} \leq 1, \) and \(-0.3 \leq \ln K'_{b} \leq 3.3 \)). \( Y_{cr} \) is the mole fraction \( \text{Cr}/(\text{Cr} + \text{Al}) \); \( \ln K'_{i,j} \) is equal to \( \ln K_{i,j}^{\text{eq}} \) only at 1 bar pressure and in the absence of \( \text{Fe}^{3+} \) from spinel (below). Table 5 contains the regression coefficient matrices \( A \) for the three classes "AT", "LI", and "CO"; figures 20 to 22 display the resulting isopleths in \( Y_{cr} \). Residuals due to the regression for B-1 are typically 1° to 3° in and never exceed 6°.

The pressure dependence of \( \ln K'_{b} \).—The volume change associated with reaction 1 is small, about \( 35 \) \( T \) \( \text{kb}^{-3} \), based on volume data at 298K and 1 bar (Robie, Hemingway, and Fisher, 1978). The effect of pressure on \( \ln K'_{b} \) is thus not expected to be very large, though it may be worth considering that some interesting applications of the geothermometer, for example, to ultramafic xenoliths, typically involve pressures of the order of 10 to 20 \( \text{kb} \) and as high as 50 \( \text{kb} \) for nodules from kimberlites. For that reason a pressure correction term for \( \ln K'_{b} \) is included here. It is based on equilibrium isotherms computed for elevated pressures, using models and data discussed earlier. Figure 23 shows the effect of 20 \( \text{kb} \) pressure on \( \ln K'_{b} \). For Cr-rich spinel at 1000°C (\( \partial T/\partial P \)) is found to be about 4 degrees per \( \text{kb} \). In order to facilitate thermometric applications, the following equation was devised:

\[
\Delta_{P} \ln K'_{b} = P \left( C_{1} T^{\alpha} + C_{2} Y_{cr} + C_{3} (1 - T/1420) (Y_{cr} - 0.35)^{2} \right)
\]  

(B-2)

with pressure \( P \) in \( \text{kb} \), temperature \( T \) in \( \text{K} \), and where
<table>
<thead>
<tr>
<th>Type</th>
<th>Designation and definition</th>
<th>Reported typical range of $X_{Mg}^{OL}$</th>
<th>$X_{Mg}^{SP}(Y_{Al}^{SP})$</th>
<th>$r_{modal}$</th>
<th>Adopted characteristic values</th>
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<tbody>
<tr>
<td>&quot;AT&quot;</td>
<td>Alpine-type peridotite, including dunite, lherzolite and harzburgite; high-grade metamorphic ultramafics in general</td>
<td>0.86-0.95</td>
<td>0.86-0.92(1.0)</td>
<td>18-30</td>
<td>0.88</td>
</tr>
<tr>
<td>&quot;LI&quot;</td>
<td>Layered intrusive type peridotite; less magnesian than &quot;AT&quot;.</td>
<td>0.83-0.93</td>
<td>0.82-0.88(1.0)</td>
<td>10-25</td>
<td>0.80</td>
</tr>
<tr>
<td>&quot;CO&quot;</td>
<td>Chromite-olivine cumulate type; quite variable in relative abundance of olivine and spinel. Not included are varieties rich in Fe$^{3+}$.</td>
<td>0.80-0.91</td>
<td>0.25-0.48(0.0)</td>
<td>0.02-20</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Note: $X_{Mg}^{bulk}$ is the abundance-weighted average of $X_{Mg}^{olivine}$ and $X_{Mg}^{spinel}$.

$r_{modal}$ is the modal ratio olivine/spinel (volume-percent = mol-percent).
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\[ C_1 = 0.017904 \]
\[ C_2 = -0.292880 \]
\[ C_3 = 0.004468 \]
\[ C_4 = 0.018530 \]

Before applying eq (B-1) to any measured value of \( \ln K_p' \), the pressure correction (B-2) should thus be subtracted to obtain \( \ln K_p' \). Moreover, if the particular spinel analysis indicates significant deviations from (Mg,Fe)(Al,Cr)\_2O\_4 stoichiometry, additional correction terms are required.

The effects of other components on \( \ln K_p' \).

Natural spinels display a very wide chemical variability by incorporating notably many transition metals. The most commonly observed extensive substitution in chrome spinels involves ferric iron. Evans and Frost (1975) documented and discussed the compositional evolution of spinel in ultramafic rocks during prograde metamorphism. At conditions of the upper amphibolite facies or higher, the ferrite (mole) fraction \( Y_F = Fe^{++}/(Fe^{++} + Cr + Al) \) is typically between 0.0 and 0.1.

There is, at present, no entirely satisfactory basis to account for the effect of Fe\(^{3+}\) on \( \ln K_p' \). Although the solution model presented above for spinel can easily be extended to incorporate ferrite species, the experimental data base for calibration is entirely insufficient. Phase equilibrium data are available for the binary joins magnetite–hercynite (Turnock and Eugster, 1962), magnetite–chromite (Snethlage and Klemm, 1975), and on the Mg–Fe exchange between olivine and ferriian ulvöspinel (Rawson and Irvine, 1980). While the latter study constrains the solution properties of spinel along the join magnetite–magnesioferrite, there are notably no such constraints for the ternary or quaternary spinnels. This is particularly unfortunate because the available crystal chemical information indicates a very complex and temperature-dependent ordering behavior of Fe\(^{3+}\)-bearing spinels (Allen, 1966, 1968; Robbins and others, 1971). Therefore, the assumption of ideal mixing cannot be expected to approximate their actual solution behavior satisfactorily (see also Snethlage and Schroecke, 1976).

![Equilibrium compositions of olivine and spinel](image)

**Fig. 17.** Equilibrium compositions of olivine and spinel for bulk compositions corresponding to class “AT” (table 4) and temperatures between 600° and 1400°C. Owing to the high modal abundance ratio olivine/spinel, the effect of equilibria (1) and (11) is reflected almost exclusively in \( X_{Mg} \) of spinel.
Fig. 18. As in figure 17, but for the more Fe-rich class "LI" (table 4).

Fig. 19. As in figure 17, but for the chromite-rich class "CO" (table 4). By contrast to "AT" and "LI", the forsterite contents varies markedly with temperature and Cr/(Cr + Al).
Equilibria involving Al–Cr spinel: Mg–Fe exchange with olivine

Table 5
Regression coefficients \( A_{ij} \) for eq (B-1)

<table>
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<th>( \text{Type &quot;AT&quot;} )</th>
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<th>( 2 )</th>
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<td>2419.561</td>
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<td></td>
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<td>886.513</td>
<td>-354.403</td>
<td>63.247</td>
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</tr>
</tbody>
</table>

Despite these reservations a series of equilibrium calculations has been performed (assuming ideality for spinel), primarily with the aim of comparing the results of such a treatment with the classical correction method developed by Irvine (1965). As discussed previously, Irvine’s solution model treats complex spinels as a series of linearly independent, binary Mg–Fe-subsystems, the properties of which contribute to those of the phase in the proportions of the respective trivalent cation. Thus, Irvine derived the following relation for the exchange equilibrium with olivine:

\[
\ln K_{b} = \ln \left( \frac{X_{r0}/(1-X_{r0})}{X_{a0}} \right) + Y_{A1} \ln \left( X_{r0}/X_{a0} \right) + Y_{Cr} \ln \left( X_{b0}/X_{a0} \right) + Y_{Fe} \ln \left( X_{mt}/X_{mt} \right)
\]  

(B-4)

Equivalently (using Irvine’s notation for equilibrium constants):

\[
\ln K_{b} = \ln K_{b} + Y_{Cr} \ln K_{s} + Y_{Fe} \ln K_{t}
\]  

(B-5)

where the constants refer to the following exchange equilibria

\[
K_{b} : 0.5\text{Fe}_{2}\text{SiO}_{4} + 0.5\text{MgAl}_{2}\text{O}_{4} = 0.5\text{MgSiO}_{4} + \text{FeAl}_{2}\text{O}_{4}
\]

\[
K_{s} : \text{MgCr}_{2}\text{O}_{4} = \text{FeCr}_{2}\text{O}_{4} + \text{MgFe}_{2}\text{O}_{4}
\]

\[
K_{t} : \text{FeAl}_{2}\text{O}_{4} + \text{MgFe}_{2}\text{O}_{4} = \text{MgAl}_{2}\text{O}_{4} + \text{FeO}_{4}
\]

In applications of the spinel-olivine geothermometer in the literature, eq (B-5) has been used to obtain normalized values of \( \ln K^{*}_{b} = \ln K_{b} - (Y_{Fe}-Y_{Fe}) \ln K_{Fe} \), with \( Y_{Fe} = 0.0 \) or 0.05. The latter choice has been adopted by Evans and Frost (1975) in order to minimize error propagation from \( \ln K_{Fe} \) into \( \ln K^{*}_{b} \). Irvine (1965) computed a value of \( \ln K_{Fe} = 4.0 \) from thermochemical data available at the time; this value appears to have been favored until recently (for example, Evans and Frost, 1975; Fujita, 1977). An alternative calibration by Jackson (1969) yielded considerably lower values and indicated a temperature dependence: \( \ln K_{Fe} = 2.82 - 350 \text{Kelvin/T} \) (yielding 1.90 and 1.56 at 1200°C and 800°C, respectively). Recent phase equilibrium data by Rawson and Irvine (1980) for the (Al–Cr-free) ferrite-olivine system indicate a value of \( \ln K_{Fe} = 2.5 \) to 2.6 at 1167°C.

Independent support of a fairly low value of \( \ln K_{Fe} \) comes from the present equilibrium calculations: The (admittedly crude) ideal speciation model for Fe⁺⁺-bearing spinels yields equilibrium relations at 800°C, which can be approximated by \( \ln K_{Fe} = 2.1 \) (for \( 0 < Y_{Fe} < 0.15 \), \( Y_{A1} = 1-Y_{Fe} \)) and by \( \ln K_{Fe} = 2.3 \) (for \( 0 < Y_{Fe} < 0.15 \), \( Y_{Cr} = 1-Y_{Fe} \)).
Fig. 20. Equilibrium temperature as a function of the logarithm of the distribution coefficient (2). Isopleths in Cr/(Cr + Al) were computed using eq (B-1) with coefficients from table 5. The approximation afforded by that polynomial can be seen by comparison to the triangular symbols which represent complete equilibrium calculations (by G-minimization). The computations pertain to the compositional class "AT"; see also figure 17.

Fig. 21. As in figure 20, but for class "LI"; see also figure 18.
Fig. 22. As in figure 20, but for class "CO"; see also figure 19.

Fig. 23. Pressure correction for the distribution coefficient (2) as a function of Cr/(Cr + Al) and (estimated) temperature. Isotherms represent approximation (B-2) with coefficients from (B-3); triangles depict the results of full equilibrium calculations for class "CO" at 600°C, 1000°C, and 1400°C. Although eq (B-2) was derived on the basis of equilibrium calculations for classes "AT" and "L1", it approximates other compositions satisfactorily.
In these calculations, the data of Rawson and Irvine have been used to refine the free energy value for MgFeO$_3$; hence, the results computed here for low Y$_P$ are consistent with Rawson and Irvine's phase equilibrium data.

On the basis of these computations, the following ferrite-correction is tentatively proposed:

$$\Delta Y_P \ln K'_P = 2.2 Y_P$$  \hfill (B-6)

The temperature-dependence of this correction cannot be established with any confidence based on present data, and the approximation should not be used for ferrite-rich spinels ($Y_P > 0.15$).

In summary, approximate values of lnK$^*$ required for eq (B-1) may be computed from measured values of lnK'_P by computing

$$\ln K'^* = \ln K'_P - \Delta_P \ln K'_P - \Delta_P \ln K'_P.$$  \hfill (B-7)

Similar corrections for further components, for example, Ti$^{4+}$, may be derived and appended if required. The currently available data base, however, is too scanty to allow reliable calibration.

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