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A Re-Evaluation of the Olivine-Spinel Geothermometer

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Abstract. The Irvine olivine-spinel geothermometer, as formulated by Jackson (1969), appears to yield magmatic temperatures when applied to plutonic rocks such as the Stillwater Complex but Evans and Wright (1972) have demonstrated that it gives temperatures in excess of 2,000° C when applied to volcanic assemblages. A re-evaluation of the geothermometer has shown that more realistic temperatures can be obtained for volcanic rocks by using a different free energy value of $FeCr_2O_4$ in the formulation. The revised geothermometer gives temperatures in the range 1,100–1,300° C for samples from Kilauea and 500–800° C for basic plutonic rocks from layered intrusions, indicating that Mg and Fe^{2+} have re-equilibrated at subsolidus temperatures in these intrusions as suggested by Irvine (1965). This theory was tested by heating uncrushed natural samples from layered intrusions to magmatic temperatures for periods ranging from two days to four weeks. The result was a marked increase in the Mg/Fe^{2+} ratio in the spinels and a decrease in the Mg/Fe^{2+} ratio in the olivines, confirming that considerable subsolidus re-equilibration had taken place in the unheated samples.

Introduction

Olivine and spinel coexist in a number of geological environments including alpine peridotites, layered intrusions, meteorites, metamorphic assemblages and basaltic flows. The equilibrium distribution of Fe^{2+} and Mg between these minerals can be expressed as follows:

$$\tfrac{1}{2}Fe_2SiO_4+Mg(Cr_\alpha Al_\beta Fe^{3+}_\gamma)_2O_4$$
$$=\tfrac{1}{2}Mg_2SiO_4+Fe(Cr_\alpha Al_\beta Fe^{3+}_\gamma)_2O_4 \qquad (1)$$

where α, β and, γ are the atomic fractions of the respective trivalent cations. This exchange is sensitive to temperature, especially for Cr-rich spinels, and Irvine (1965) described how it may be used as a geothermometer.

Jackson (1969) substituted what he considered to be the best available thermodynamic data into Eq. (1) and, assuming ideal solid solution, derived an expression which can be used to estimate the equilibrium temperature of coexisting olivine and chromite. Irvine used available thermodynamic data and coexisting olivine and spinel in some plutonic rocks to derive working values for equilibrium constants at temperatures of basaltic magmas. Both authors cautioned the reader that uncertainties in the thermodynamic data were such that the calculated temperatures should be applied only in a relative sense.

Jackson used his equation to calculate "*nominal temperatures*" for coexisting olivine and chromite in the G and H horizons of the Stillwater Complex, Montana. The average temperature he obtained for the H zone is 1,284° C (Standard deviation $\pm 82°$ C) and for the G zone is 1,036° C ($\sigma = \pm 158°$ C). The relative temperature changes up the layered Stillwater sequence, and the absolute values of the calculated temperatures, led Jackson to suggest that the iron-magnesium distribution between chromite and olivine represented a distribution dictated by magmatic processes. The temperatures he obtained are reasonable assuming crystallization from a basaltic liquid at temperatures between 1,000° C and 1,300° C.

Other workers have used Jackson's equation to calculate temperatures of a variety of igneous and metamorphic rocks. Sinton (1977), for example, calculated an average temperature of 1,060° C (range 930–1,140° C) for a series of ultrabasic rocks from the Red Mountain, New Zealand. Medaris (1972) used it to calculate temperatures between 1,200° C and 1,400° C for high-pressure peridotites from southwestern Oregon and these temperatures were slightly

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higher than those calculated from the O'Hara grid (1967) (1,075–1,175° C).

When Jackson's version of the geothermometer is applied to olivine-chromite pairs from Kilauean volcanic rocks (Evans and Wright, 1972), the calculated temperatures are 2,000–2,300° C. The liquidus temperatures of these rocks however are between 1,100° C and 1,300° C (Hill and Roeder, 1974).

Calculated temperatures of over 2,000° C were also found for volcanic rocks from Kilauea and Mt. Hood using unpublished experimental data of Potter (1975) and Roeder. Evans and Frost (1975) discussed some of the difficulties involved in using the olivine-chromite geothermometer and suggested a more empirical approach to the problem.

The present communication is an attempt to re-examine the equation used by Jackson in view of the thermodynamic data now available and to report experimental evidence that the compositions of coexisting olivine and spinel in layered intrusions represent equilibria established at subsolidus temperatures.

Olivine-Spinel Temperature Equation

Use of the olivine-spinel equilibrium as a geothermometer requires knowledge of the following: (1) the absolute value of the free energy of formation of the end-member spinels and olivines for the temperature range to which the thermometer will apply, and (2) the mixing behaviour of both olivine and spinel solid solutions over that temperature range. The free energies of formation of the end-member components is not known well enough at the present time to satisfy the first requirement. The free energy of formation of the end-member olivines and spinels shown in Table 1 can be used to calculate an equilibrium constant, K, over a range of temperatures. A distribution coefficient can be calculated by assuming ideal mixing of both the olivine solution and the spinel solid solution and multiplying the free energy of the end-member spinels by the mole fraction of that end-member.

$$K_d = \left(\frac{X_{Mg}}{X_{Fe^{2+}}}\right)_{olivine} \left(\frac{X_{Fe^{2+}}}{X_{Mg}}\right)_{spinel} \tag{2}$$

where X = mole fraction in solid solution ($Mg/Mg+Fe^{2+}$ and $Fe^{2+}/Mg+Fe^{2+}$). Wood and Nicholls (1978) have shown that this approach assumes ideal mixing within each of the two major cation structural positions in spinel but does not account for the interaction between the two positions.

A survey of the literature reveals that there is a range of free energy values for all of the end-member spinels involved in Eq. (1). Table 1 show values of the free energy of formation of spinels from oxides at 1,000° K and 1,273° K calculated from data in the various sources listed. The discrepancies between $\Delta G°$ values for particular spinels are 2 Kcal/mol or less at these temperatures, with the exception of $FeCr_2O_4$. Thermodynamic information for olivines is less problematic; data from other sources are within 0.5 Kcal/mol of the values used (Schwerdtfeger and Muan, 1966; King et al., 1967).

The assumed linear variation in the logarithm of the equilibrium constant, as a function of reciprocal temperature, is shown in Fig. 1 for three different olivine-spinel reactions. These three reactions involve the Fe^{2+}-Mg exchange equilibrium between olivine and the chrome, alumina and ferric spinels. All of the lines in Fig. 1 were calculated with the same free energy values for fayalite and forsterite, and with several different sets of free energy data, arbitrarily chosen, for the spinels as indicated in Table 1.

The alumina spinel-olivine equilibria has the lowest ln K values and three different solid-dot lines (4, 5, 6) are shown, representing three different choices of free energy values. The ln K values of the ferrite-olivine equilibria (dashed lines 7, 8, 9) are significantly higher than for the alumina spinels. This means that for a particular olivine composition the higher the ferric content of the spinel the greater the ferrous relative to magnesium in the spinel. This is one of the reasons why aluminous spinels associated with basic igneous rocks are high in magnesium whereas Fe^{3+}-rich spinels are high in ferrous iron.

The greater the slope of the lines in Fig. 1 the greater the change in composition of coexisting olivine and spinel as a function of temperature and the more useful the geothermometer. Thus the very low slope of line 8 would suggest that the olivine-ferrite spinel equilibria is not very sensitive to temperature. This is supported by experimental data of Speidel and Osborn (1967).

There are significant discrepancies in the free energy data for $FeCr_2O_4$ and this is reflected by the separation of the light solid lines 1, 2, and 3 in Fig. 1.

In order to demonstrate how differences in the free energy of formation will affect the temperatures calculated from coexisting olivine and spinel found in nature, we have calculated equilibrium temperatures using differing values for the free energy of formation of $FeCr_2O_4$. The free energy of $FeCr_2O_4$ was chosen as a variable because the published free energies of formation for this compound show the greatest range in values of the spinel end-members (see Table 1), and because $FeCr_2O_4$ is an important component of most natural spinel solutions.

Table 2 lists a number of representative olivine-spinel pairs from a variety of sources. The tempera-

Table 1. Gibb's free energy of formation for end-member spinels

Spinel	ΔG_f° from oxides (kcal/mol^{-1})		Lines in Fig. 1 constructed with these data	Reference[c]
	1,000 K	1,273 K		
$MgCr_2O_4$	− 8.60	− 8.16	1, 2, 3	[12] emf measurement[a]
	− 8.67	− 8.01		[13] ΔH_f° measured calorimetrically ΔS_f° calculated from [12]
$FeCr_2O_4$	−13.25	−12.54	1	[14] gas-crystal equilibria[b]
	− 9.85	− 8.75	3	[12] emf measurement[a]
	−11.14	−10.12		[15] emf measurement
	−10.72	−10.24	2	[16] emf measurement
$MgAl_2O_4$	− 8.00	− 8.30	6	[12] calculated from other equilibria[b]
	− 7.03	− 7.33	5, 4	[17] ΔH° measured calorimetrically ΔS° calculated from [12]
	− 9.21	− 9.39		[18]
	− 7.74	− 7.91		[19]
$FeAl_2O_4$	− 6.46	− 6.06	6	[20] liquidus phase equilibria[a]
	− 6.71	− 5.60	4	[21] emf measurement
	− 5.88	− 5.67	5	[22] emf measurement
$MgFe_2O_4$	− 5.45	− 5.37	8	[12] calculated from other equilibria[a]
	− 5.45	− 6.50	7, 9	[17] ΔH_f° measured calorimetrically ΔS_f° calculated from [12]
	− 3.04	− 3.38		[18]
$FeFe_2O_4$	− 6.79	− 7.54	7, 8	[12] calculated from other equilibria[a]
	− 5.69	− 6.21	9	[19]
	− 6.62	− 7.56		[18]

Where ΔG_f° was measured electrochemically, it was found to be a linear function of temperature over the temperature range shown in Fig. 1. Where ΔH_f° was measured calorimetrically, ΔS_f° was calculated from free energy values, and both ΔH_f and ΔS_f were assumed to be constant with respect to temperature

[a] data used in equation B, and equations A for $FeCr_2O_4$

[b] data used for $FeCr_2O_4$ in equation B

[c] see reference list on page 10

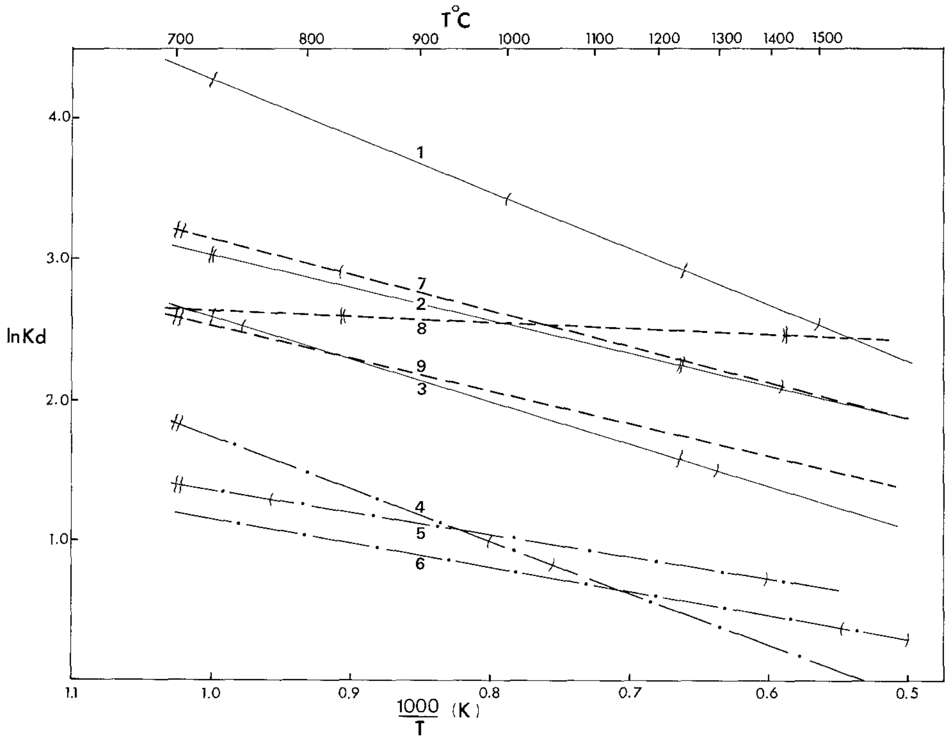

Fig. 1. The relation of olivine-spinel equilibria to temperature. *Solid lines:* $FeSi_{1/2}O_2 + MgCr_2O_4 = MgSi_{1/2}O_2 + FeCr_2O_4$, *solid-dot lines:* $FeSi_{1/2}O_2 + MgAl_2O_4 = MgSi_{1/2}O_2 + FeAl_2O_4$, *dashed lines:* $FeSi_{1/2}O_4 + MgFe_2O_4 = MgSi_{1/2}O_2 + FeFe_2O_4$. *Data sources* listed in Table 1. The braces refer to the limits of applicability of the Mg-spinel thermodynamic data, and the parentheses to the limits of the Fe^{2+}-spinel data. The temperature range of the olivine data used is 1,000–1,150° C for fayalite and 950–1,300° C for forsterite

Table 2. Calculated temperatures for olivine-spinel pairs from selected geological environments

No.	Geological Environment	Calculated temp. °C		Spinel				Oliv.	Ref.[a]
		A	B	Cr(α)	Al(β)	Fe^{+3}(γ)	Mg	Mg	
1	Mt. Albert (Alp.)	762	1,034	0.271	0.686	0.044	0.697	0.915	*
2	Mt. Albert	697	928	0.248	0.684	0.068	0.679	0.919	*
3	Mt. Albert	615	1,050	0.610	0.348	0.042	0.505	0.918	*
4	Mt. Albert	658	1,105	0.580	0.383	0.037	0.559	0.921	*
5	Vulcan Peak Harzburgite (Alp.)	735	1,240	0.59	0.40	0.01	0.57	0.907	[24]
6	Vulcan Peak Dunite	580	1,036	0.70	0.26	0.04	0.50	0.934	[24]
7	Vulcan Peak Dunite	670	1,059	0.47	0.47	0.06	0.48	0.878	[24]
8	Vulcan Peak Chromitite	715	1,190	0.56	0.41	0.03	0.65	0.934	[24]
9	Vulcan Peak Chromitite	679	1,043	0.42	0.50	0.08	0.55	0.899	[24]
10	Lizard Primary Peridotite (H.P.)	1,087	1,385	0.191	0.756	0.051	0.771	0.903	[25]
11	Lizard Primary Peridotite	1,018	1,298	0.194	0.750	0.054	0.771	0.910	[25]
12	Stillwater G. Zone (L.I.)	433	743	0.460	0.199	0.341	0.177	0.823	[3]
13	Stillwater G. Zone	554	956	0.550	0.253	0.197	0.413	0.911	[3]
14	Ave Stillwater G. Zone	614	1,036						
15	Stillwater H. Zone	751	1,274	0.559	0.353	0.088	0.533	0.897	[3]
16	Stillwater H. Zone	867	1,425	0.477	0.395	0.128	0.529	0.868	[3]
17	Ave Stillwater H. Zone	764	1,284						
18	Stillwater Sep. Chr. & Ol. G. Zone	912	1,611	0.542	0.267	0.191	0.415	0.823	[3]
19	Stillwater Sep. Chr. & Ol. G. Zone	1,094	2,022	0.587	0.265	0.148	0.496	0.831	[3]
20	Stillwater Sep. Chr. & Ol. H. Zone	1,077	1,936	0.600	0.348	0.052	0.561	0.848	[3]
21	Seiad Alpine Peridotite (Alp.)	580	1,081	0.704	0.280	0.015	0.441	0.916	[26]
22	Seiad Alpine Peridotite	549	905	0.547	0.405	0.048	0.384	0.885	[26]
23	Finero Alpine Peridotite (Alp.)	707	956	0.268	0.682	0.050	0.663	0.912	[26]
24	Finero Alpine Peridotite	679	858	0.194	0.739	0.067	0.570	0.872	[26]
25	Red Mt. (NZ) Harzburgite – C (Alp.)	809	1,126	0.304	0.672	0.023	0.690	0.907	[4]
26	Red Mt. (NZ) Harzburgite – R	663	905	0.289	0.696	0.015	0.631	0.907	[4]
27	Red Mt. (NZ) Olivine Chromitite – C	662	1,249	0.810	0.159	0.031	0.661	0.961	[4]
28	Red Mt. (NZ) Olivine Chromitite – R	694	1,308	0.796	0.164	0.041	0.683	0.961	[4]
29	Red Mt. (NZ) Dunite	1,662	3,894	0.475	0.000	0.525	0.560	0.889	[4]
30	Peridotite in SW Oregon (Alp.)	157	1,378	0.132	0.837	0.030	0.794	0.900	[5]
31	Peridotite in SW Oregon	982	1,232	0.186	0.794	0.020	0.757	0.901	[5]
32	Peridotite in SW Oregon	877	1,251	0.322	0.630	0.047	0.696	0.905	[5]
33	Ave Gobabeb Meteorite	520	982	0.835	0.139	0.024	0.169	0.817	[27]
34	Odessa Meteorite	613	1,220	0.975	0.025	–	0.591	0.964	[28]
35	Netschaevo Meteorite	488	894	0.783	0.217	–	0.212	0.859	[28]
36	Lherz. Incl. Alkali Basalt	350	1,586	0.116	0.860	0.023	0.819	0.898	[29]
37	Harz. Xeno. Kimberlite	807	1,520	0.768	0.199	0.032	0.641	0.936	[29]
38	Flow top komatiite	964	1,807	0.695	0.241	0.062	0.640	0.912	[30]
39	Kilauea Lava	1,137	2,134	0.615	0.267	0.119	0.606	0.877	[1]
40	Kilauea Lava	1,102	2,020	0.564	0.269	0.167	0.525	0.847	[1]
41	Kilauea Lava	1,196	2,256	0.602	0.274	0.124	0.629	0.880	[1]
42	Kilauea Lava	1,163	2,158	0.564	0.273	0.164	0.557	0.854	[1]

Alp. = alpine, L.I. = layered intrusion, H.P. = high temperature peridotite

* (I. MacGregor, personal communication)

[a] see reference list on page 10

tures calculated using Jackson's equation are listed in column B. Jackson used the free energies of formation from the oxides of $MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$ and $FeFe_2O_4$ which are all taken from the same source, Tretjakow and Schmalzied (1965). The data for $FeAl_2O_4$ were from McLean and Ward (1966) and the data for $FeCr_2O_4$ were from Novokhatskii and Lenev (1966). If Jackson had chosen the free energy values for $FeCr_2O_4$ from the same source (Tretjakow and Schmalzried, 1965) as he used for the four other spinel end-members, the calculated temperatures would have been considerably lower, as shown in column A (Table 2). Changing only the free energy values for $FeCr_2O_4$ makes a difference in the calculated temperatures of up to 1,000° C. The free energy values for $FeCr_2O_4$ used to calculate the temperatures in columns A and B of Table 2 are those used for the lines 3 and 1, respectively, shown in Fig. 1. If a third value for the ΔG of $FeCr_2O_4$ is chosen, that determined by Jacob and Alcock (1975), the calculated temperatures would be intermediate between those of columns A and B. Choosing different thermodynamic data for other spinels produces less significant changes in the calculated temperatures. The equations used to calculate temperatures in columns A and B represent two of many possible choices of thermodynamic data.

The discrepancies between the free energy values for particular spinels can probably be explained by the complex internal chemistry of spinel. The possibility of nonstoichiometry, or order-disorder phenomena, and the difficulty in controlling the oxidation state of iron and chromium, suggest that the differing free energy values reported represent the thermodynamic characteristics of different spinels.

It is apparent that the discrepancies among the free energy values of the end-member spinels have a significant effect on the calculated equilibrium temperatures. There is no simple way to judge the relative merits of the thermodynamic data. Furthermore, although the departure from ideality of the olivine solid solution is known to be small (Nafziger and Muan, 1967), there is little evidence to justify the assumption of ideal mixing in the spinel solid solution, particularly at lower temperatures.

Recently Fujii (1978) published experimental data for fifteen olivine-spinel pairs run at temperatures of 1,200–1,350° C and pressures of 1 atm to 15 Kbar. Fujii used the experimental data together with chemical data from the Finero and Seiad complexes to calculate, by least squares, an equation which can be used as an olivine-spinel geothermometer. Many of the temperatures calculated with Fujii's equation are similar to those in column A but his temperatures are unreasonable for volcanic samples from Kilauea (1,600–2,000° C). We believe that this is because Fujii used a value of 4 for the ln K for the Mg-Fe^{2+} exchange equation between ferrites and aluminates. Fujii took this value from Irvine (1967) and assumed it did not vary with temperature. Our calculations indicate that ln K is close to 2.0 at 1,200° C and decreases as the temperature is lowered. However Fujii's equation works quite well whenever iron is low (γ less than 0.05).

Experiments are currently underway to measure the distribution of iron and magnesium between olivine and spinels.

Petrologic Application

Many authors (Jackson, 1969; Evans and Frost, 1975; Wood and Fraser, 1976) have suggested that, because of all the uncertainties in the thermodynamic data, any calculated absolute temperature using olivine and spinel are suspect but the relative scale of temperatures may be correct. For example, the calculated temperatures for volcanic samples (Nos. 38–42 in Table 2) and high temperature experiments are always higher than the calculated temperatures for metamorphic samples (Evans and Frost, 1975). Jackson (1969) calculated temperatures of 900–1,400° C for coexisting olivine and chromite in Stillwater samples but the same equation gives unreasonable temperatures of 1,800–2,200° C for coexisting olivine and chromite in Kilauea lavas (Evans and Wright, 1972). The temperatures in columns A and B of Table 2 and those derived from Fujii's equation for the coexisting olivine and chromite in the Stillwater samples (Nos. 12–16) all show a much lower temperature than the volcanic samples (Nos. 38–42). On the basis of the calculated temperatures of 900–1,400° C, Jackson concluded that the iron-magnesium distribution between olivine and chromite in the Stillwater samples was due to magmatic processes. We believe however that the iron-magnesium distribution between coexisting olivine and chromite in the Stillwater samples reflects temperatures well below the solidus and the temperatures as given in column A (400–800° C) are more reasonable.

Irvine (1967) suggested that there is evidence, from some layered intrusions, of subsolidus re-equilibration between olivine and chromite and that the amount of composition change increases for each mineral as its percentage in the rock decreases. Thus temperatures closer to the liquidus temperature are obtained if the composition of an olivine from an olivine-rich layer is used together with a chromite from an adjacent chromite-rich layer in preference to coexisting olivines and chromites from the same sample. The temperatures calculated using this method for three Stillwater samples give much higher temperatures in column A (Nos. 18–20, 900–1,100° C) than the temperatures calculated using coexisting olivine and chromite from the same sample (Nos. 12–17, 400–800° C). The temperatures calculated using Jackson's equation (column B) are unreasonably high for olivine and chromite from separate layers but those in column A are more reasonable. Thus, the composition of olivines from olivine-rich layers and chromites from chromite-rich layers are probably a closer reflection of magmatic temperatures in the Stillwater Complex and the coexisting olivine and chromite within the same sample show an element distribution controlled by diffusion at subsolidus temperatures.

In order to test whether there was redistribution of iron and magnesium between olivine and chromite at subsolidus temperatures, high-temperature experiments were conducted on samples from Bushveld, Bay of Islands, Rhum and the Jimberlana Intrusion

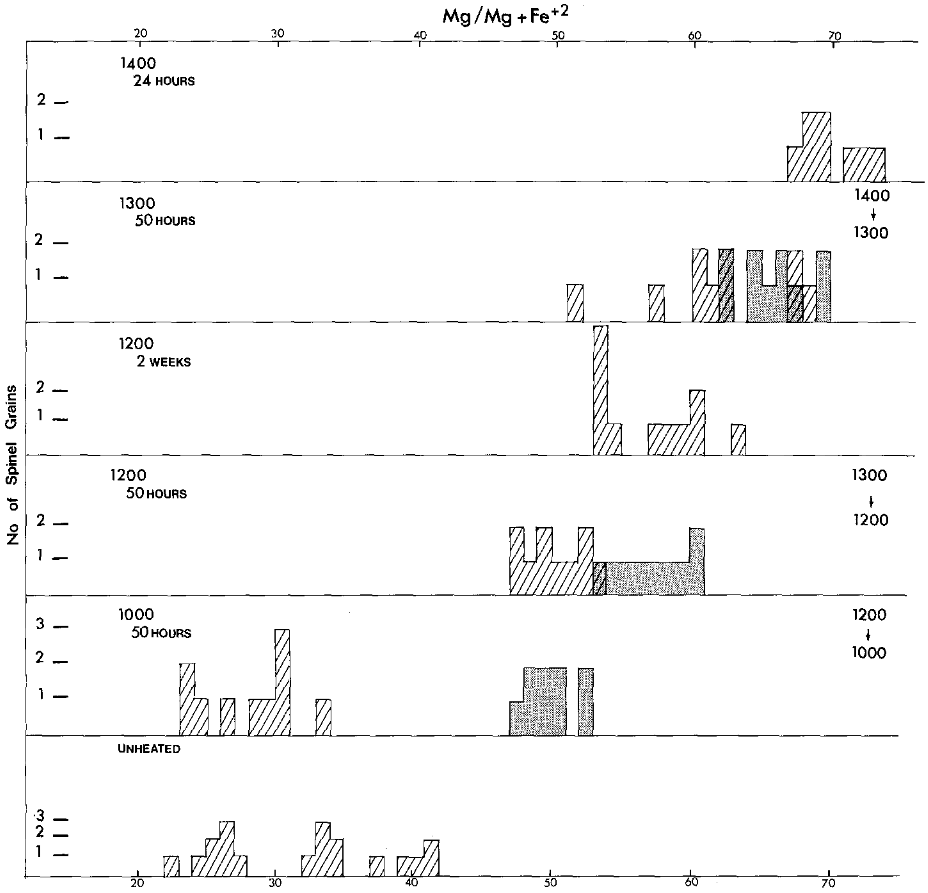

Fig. 2. The change in the Mg/Mg+Fe^{2+} ratio of spinels produced by heating an olivine orthocumulate (ND 1.68) from the upper layered series of the Jimberlana Intrusion. The results of the normal heating experiments are shown by ruling and the run times and temperatures are indicated on the left of the diagram. The reversed runs are indicated by shading. These runs were held at the higher of the temperatures, given at the right of the diagram, for 50 h and then at the lower temperature, again for 50 h

of Western Australia (Campbell, 1977). Uncrushed samples were hung by a thin platinum wire in a furnace with an oxygen fugacity which was controlled near the fayalite-magnetite-quartz buffer by mixing CO_2 and H_2. Samples were run for times ranging from two days to four weeks and then quenched. The olivines and chromites in each sample were analyzed before and after heating with the electron probe equipped with an energy dispersive spectrometer. The chromite analyses were checked by analyzing a series of chemically analyzed chromites kindly supplied by Beeson of the U.S.G.S. and the mineral formulae were calculated assuming the chromites were stoichiometric.

Heating the samples resulted in considerable redistribution of magnesium and ferrous iron between olivine and chromite. Chromite, since it was a minor phase in all specimens, was most affected but a small change in olivine composition was also noted. Two types of experiments were carried out.

(1) Two samples from Jimberlana, an adcumulate from the No. 4 olivine cumulate layer in the lower layered series and an orthocumulate from the No. 2 olivine cumulate layer of the upper layered series were heated to various temperatures for differing lengths of time (normally 50 h). A minimum of ten chromites were analyzed in each sample and the range in the Mg/Mg+Fe^{2+} ratio as a function of temperature is shown for the orthocumulate in Fig. 2 and the adcumulate in Fig. 3. Samples heated to 1,000° C and 1,100° C (not shown) showed no significant change but those heated to 1,200° C and above showed a marked change in the Mg and Fe^{2+} of the chromite. Many of the experimental runs at higher temperatures developed a liquid phase which helped to equilibrate olivine and chromite. The calculated temperatures for the higher temperature runs in column A are reasonably close to the actual furnace temperature. An attempt to reverse the experiments by heating first to a higher temperature for 50 h and then to the indicated temperature was partially successful. These experiments are shown by the stipled areas and the higher and lower temperatures are indicated on the right hand side of Figs. 2 and 3. The range in spinel composition for runs at 1,300° C is the same whether the runs were heated directly to 1,300° C (ruled area) or heated first to 1,400° C and then to 1,300° C (shaded area). Since the starting material was uncrushed rock the degree of equilibrium between different olivine and chromite grains was variable and

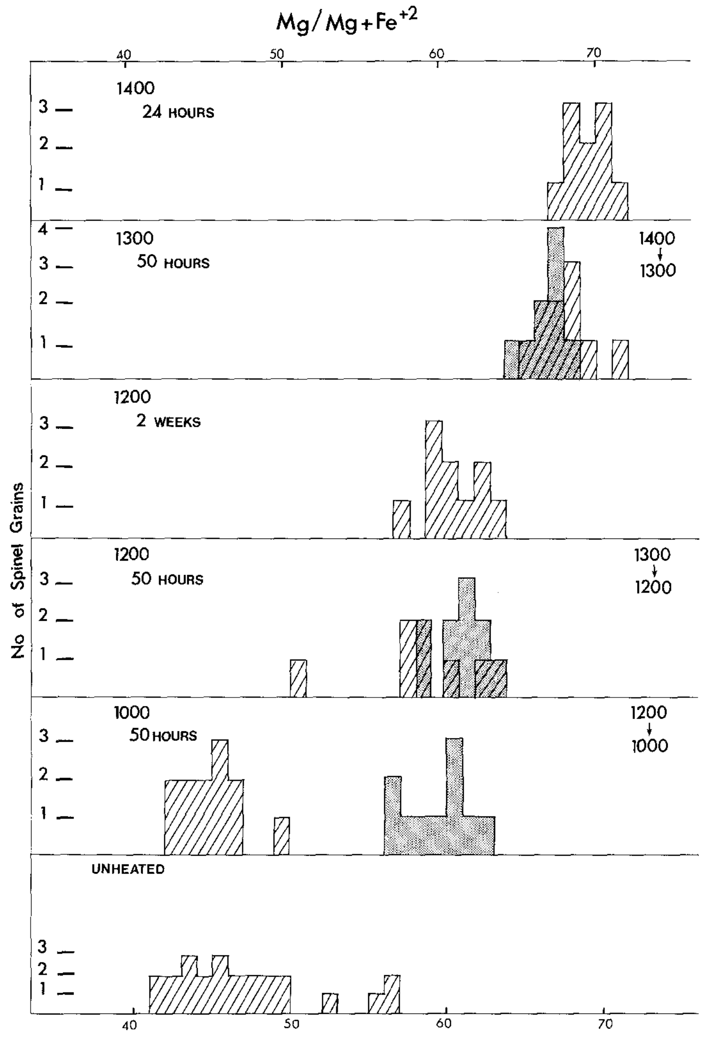

Fig. 3. The change in the Mg/Mg+Fe^{2+} ratio of spinel from an olivine adcumulate (BRD 11.1001) from the lower layered series of the Jimberlana Intrusion. The conventions used in Fig. 2 have also been adopted in this diagram

depended on the size, distribution and proximity of other grains or liquid.

(2) Samples from the Bushveld, Bay of Islands, Rhum and Jimberlana were heated for one month in a controlled atmosphere at approximately 1,200° C. The results are tabulated in Table 3 and illustrated in Fig. 4. Each tie-line in Fig. 4 represents an average of five analyses per sample. All the samples show a significant increase in the magnesium content of spinel heated to 1,200° C (solid line) relative to unheated spinel (dashed line). Some of the heated spinels are zoned indicating that complete equilibrium between olivine and spinel was not achieved.

The temperatures calculated using the Jackson equation (column B in Table 3) are 800–1,300° C for the unheated samples and are 1,800–2,200° C for samples heated at 1,200° C. The temperatures calculated in column A are close to the actual temperature of heating (1,200° C) except for the high alumina spinel from the Bay of Islands. Temperatures calculated using Fujii's equation are all high because of the ferric iron problem mentioned earlier. The large change in spinel composition between unheated samples and the samples heated above 1,200° C is interpreted to mean that the Mg and Fe^{2+} in the unheated samples represent a distribution established at temperatures well below 1,200° C and probably well below the basalt solidus. The calculated temperatures of the unheated samples shown in column A (500–800° C) are much more reasonable than those shown in column B. In nature the very slow cooling rate of layered intrusions allows considerable Mg and Fe^{2+} mobility at temperatures well below the dry solidus of basalts (1,000° C).

An Evaluation of the Revised Geothermometer

If the free energy data for $FeCr_2O_4$ of Tretjakow and Schmalzried (1965) is used in preference to the data of Novokhatskii and Lenev (1966), the equation

Table 3. Calculated temperatures for unheated and heated olivine-spinel pairs from layered intrusions

	Run time (days)	Run temp.	Calculated temp. °C		Spinel				Olivine
			A	B	Cr(α)	Al(β)	Fe^{+3}(γ)	Mg[a]	Mg[a]
Bushveld Harzburgite (Eastern Bushveld)									
C*	unheated		531	901	54.3 (3.6)[a]	29.7 (4.3)	16.1 (2.1)	32.0 (2.2)	
R*	unheated		530	897	53.8 (3.7)	30.0 (4.2)	16.1 (1.1)	32.1 (3.2)	87.5
C	30	1,200	1,217	2,187	52.8 (2.5)	33.8 (7.0)	13.2 (5.5)	63.4 (3.1)	
R	30	1,200	1,260	2,240	52.1 (2.8)	38.1 (2.9)	9.6 (2.1)	66.1 (1.3)	87.4
Rhum Olivine Cumulate 2882									
C	unheated		516	889	51.8 (1.0)	22.7 (1.3)	25.3 (1.1)	30.1 (1.2)	
R	unheated		533	921	53.0 (2.0)	22.8 (1.1)	24.0 (2.2)	31.1 (1.1)	87.7
C	30	1,200	1,183	2,157	52.8 (2.3)	29.4 (4.4)	17.7 (5.6)	56.7 (2.9)	
R	30	1,200	1,128	2,019	54.0 (2.5)	32.0 (2.6)	13.8 (2.6)	56.7 (2.5)	85.5
Bay of Islands Dunite 72–71 (North Arm Mountain)									
C	unheated		844	1,221	32.8 (1.4)	57.8 (1.4)	9.3 (1.4)	65.5 (1.7)	
R	unheated		797	1,146	32.4 (1.5)	57.8 (0.8)	9.7 (1.2)	63.4 (0.7)	90.0
C	30	1,200	1,386	2,125	34.0 (1.4)	58.0 (1.6)	7.8 (1.1)	74.9 (1.4)	
R	30	1,200	1,417	2,294	33.9 (2.6)	58.0 (3.5)	7.9 (1.5)	75.4 (1.6)	88.6
Jimberlana Olivine Adcumulate BRD 11.1001									
C	unheated		750	1,312	61.2 (2.0)	30.2 (3.1)	8.6 (1.2)	47.0 (4.5)	87.9
C	30	1,200	1,234	2,308	60.9 (1.0)	32.5 (0.9)	6.4 (1.8)	65.2 (1.0)	87.5
Jimberlana Olivine Orthocumulate ND 1.68									
C	unheated		720	1,250	56.0 (3.6)	27.1 (4.3)	16.8 (3.3)	32.1 (6.2)	81.3
C	30	1,200	1,187	2,163	57.2 (3.4)	33.3 (4.5)	9.6 (2.0)	57.2 (4.4)	84.3

C*: cores of spinel grains; R*: rims of spinel grains

[a] Mg/Mg+Fe^{+2}

[b] numbers in parentheses are standard deviations on a minimum of five samples

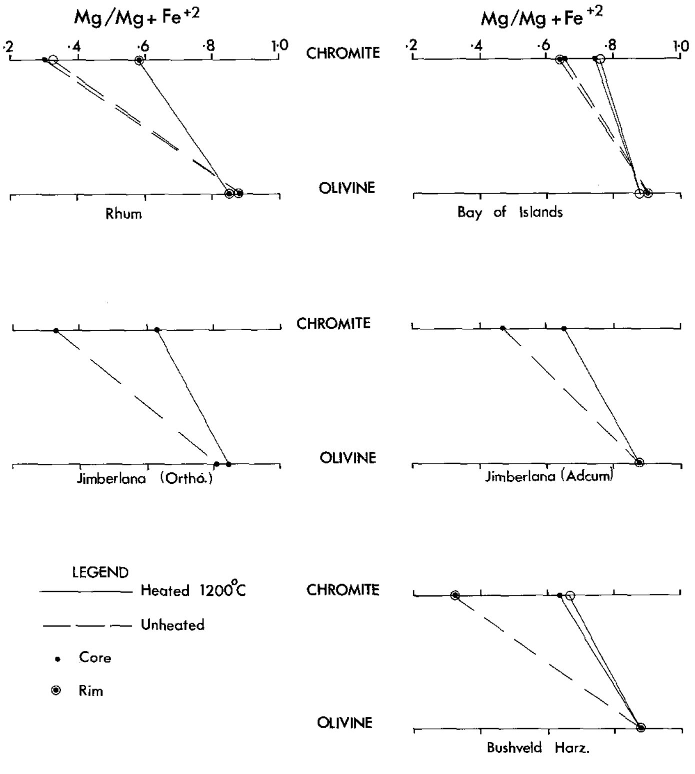

Fig. 4. The Mg/Mg+Fe^{2+} ratio in coexisting olivines and spinels from a number of plutonic igneous bodies before heating and after heating for 4 weeks. Each point represents the mean of five analyses

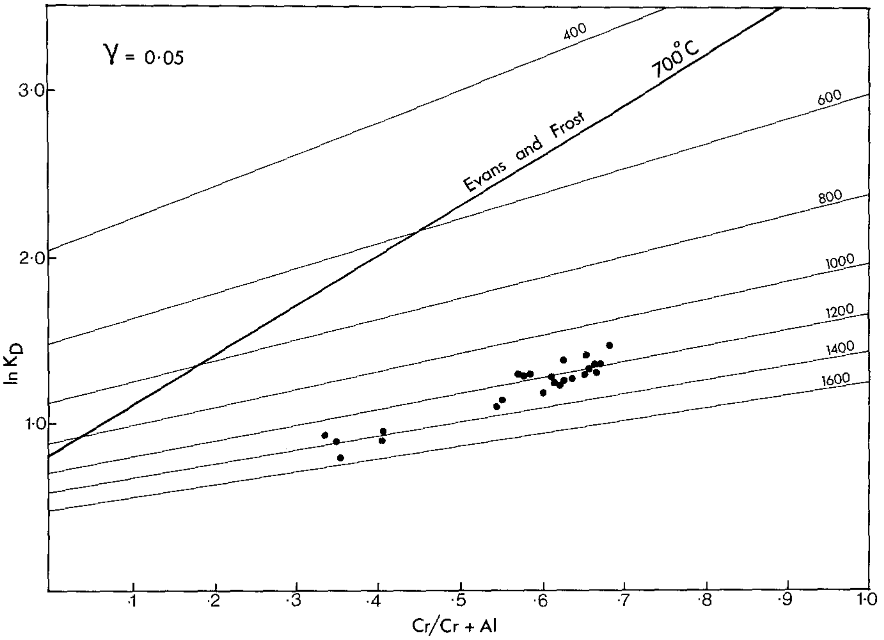

Fig. 5. A plot of ln K_D against Cr/Cr+Al at γ ($Fe^{3+}/Fe^{3+}+Cr+Al)=0.05$. The diagram was contoured for temperature using Eq. (3). The rims of all chromite grains from the 30 day heating experiments with γ's between 0.0 and 0.1 have been plotted on the diagram after making the necessary correction to ln K_D for γ (Evans and Frost, 1975; Fuji, 1978). The Evans and Frost 700° C natural contour is also shown

for the olivine-spinel geothermometer used to calculate the values in column A of Tables 2 and 3 is:

$$t(°K)=\frac{\alpha 3480+\beta 1018-\gamma 1720+2400}{\alpha 2.23+\beta 2.56-\gamma 3.08-1.47+1.987 \ln K_D} \quad (3)$$

where

$$\alpha=\frac{Cr}{Cr+Al+Fe^{3+}}, \quad \beta=\frac{Al}{Cr+Al+Fe^{3+}}$$

and

$$\gamma=\frac{Fe^{3+}}{Cr+Al+Fe^{3+}}$$

This equation has been used to construct temperature contours on Fig. 5, a plot of ln K_D against the Cr/Cr+Al ratio at $\gamma=0.05$. The results of the four week experiments at 1,200° C with γ between 0.0 and 0.10 have been projected onto this diagram after making the necessary correction for the different γ's in the various spinels. An approximate 700° C isotherm of Evans and Frost (1975), constructed from coexisting olivines and spinels in metamorphic rocks of similar grade, is also plotted. Both the experimental data and the 700° C 'natural isotherm' are discordant with the calculated isotherm and it is apparent that although there is good agreement between the experiments and the calculations at high Cr/Cr+Al ratios, at low Cr/Cr+Al ratios the calculated temperatures (isotherms of Fig. 5) may be too high.

Conclusions

The distribution of Mg and Fe^{2+} between olivine and spinel may be a useful guide to the thermal history of various basic igneous and metamorphic rocks. The formulation by Jackson for calculating temperatures of olivine and spinel equilibration does not give reasonable temperatures, particularly for samples formed at temperatures between 1,100° C and 1,300° C. The range in published free energy data for the end-member spinels is such that any formulation for calculating the temperature of equilibration of olivine and spinel is suspect until these values are known more accurately. Calculated temperatures using other published free energy values for $FeCr_2O_4$ give temperatures which are geologically more reasonable than temperatures calculated from Jackson's equation. We believe that the temperatures calculated in column A, Eq. (3) are geologically the most reasonable. The calculated temperatures for alumina-rich spinels tend to give high temperatures using any combination of the available free energy data. The calculated temperatures for spinels high in ferric-iron give a large and unreasonable range of temperatures. We conclude that the Mg and Fe^{2+} distribution between olivine and ferric-rich spinel is relatively insensitive to temperature and is not useful as a geothermometer. Thus small analytical errors in the spinel or olivine analyses may lead to very large errors in calculated temperature for ferric-rich spinels. No attempt was made to evaluate the effect of Ti in the spinel on the olivine-spinel geothermometer. The chrome-rich spinels are potentially the most valuable as a geothermometer but alumina-rich spinels should also be useful when the free energy values for the alumina end-member spinels are better known. Experiments on natural samples show the relative ease with which Fe^{2+} and Mg re-equilibrate at temperatures above 1,200° C. We suggest that the experimental data and the temperature calculations using differing free energy values for $FeCr_2O_4$ are evidence that Mg and Fe^{2+} re-equilibrate on the scale of a thin section to temperatures well below the solidus in most plutonic rocks.

The agreement reported by some workers (Sinton, 1977; Medaris, 1972) for the temperatures calculated from olivine and spinel using Jackson's equation and temperatures calculated from other geothermometers, such as the two-pyroxene geothermometer, is misleading. When the olivine-spinel geothermometer is calibrated at lower temperatures at some future date we believe that most plutonic olivine-spinel assemblages will be found to have re-equilibrated at temperatures well below 1,000° C. Considering the amount of movement of Mg and Fe^{2+} that we recorded in a few days at 1,200° C, it is not surprising that these elements can redistribute at subsolidus temperatures in layered intrusions which take thousands of years to cool to below 800° C.

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