THERMOMETRY OF DIOGENITES

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Abstract: Mg-Fe^{2+} exchange reaction between orthopyroxene and spinel has been calibrated thermodynamically and empirically and applied to the thermometry of diogenites. Based on regression of the orthopyroxene-spinel Mg-Fe^{2+} distribution coefficients against the Cr–mole fractions of the spinel of a number of naturally and experimentally equilibrated samples, the empirical calibration is more successful, gives internally consistent results and agrees well with independent temperature estimates of a wide range of terrestrial test samples. Uncertainty of the empirically determined temperatures, however, increases with decreasing Mg-Fe^{2+} distribution coefficient between orthopyroxene and spinel and increasing Cr-content of the spinel. Applied to a number of diogenites, the empirical calibration gives moderately high temperatures (687 and 885°C) for the Johnstown and Yamato-75032 diogenites and very high temperatures (between 1512 and 1941°C) for Y-692, -74013 and -74136 diogenites. The Johnstown and Y-75032 diogenites possibly represent thermally equilibrated orthopyroxene-spinel assemblages comparable to slowly cooled terrestrial ultramafic plutonic bodies broadly in the 700–900°C temperature regime. The higher temperature Yamato group on the other hand appears to be disequilibrium assemblages, affected by shock-reheating, partial melting and recrystallization.

1. Introduction

The model of a layered HED (howardite, eucrite and diogenite) parent body with the layer-sequence, from the surface downwards, somewhat like: (1) surface-type unequilibrated eucrite with Fe-Mg-zoned pyroxene, (2) shallow level, cumulate eucrites, with inverted pigeonite and pyroxenes showing exsolution lamellae, (3) polymict eucrite with dispersed, minor diogenites at intermediate levels, (4) howardites at deeper levels and (5) diogenites at the deepest level has been put forward in recent years (TAKEDA *et al.*, 1976, 1979, 1983). One of the tests for the validity of this model is quantitative thermobarometry–aiming to establish a reasonable and realistic *P-T* profile across the presumed layer sequence. In principle, however, it would be difficult, and of dubious validity, to apply equilibrium thermodynamic methods to rocks, the large majority of which are of a mixed, polymict nature and clearly unequilibrated. Textural and chemical indications of homogeneity and equilibration are therefore important prerequisites for a study of this nature. Also, it is an advantage in such studies if the expected order of the pressure and temperature is much larger in magnitude than the ranges of uncertainty in the *P-T* estimates inherent in the applied methods. In this paper, we present new methods of estimating the temperature of equilibration of diogenites, the rocks supposedly located at the deepest level and, therefore, possibly at

the highest P-T regime of the HED parent body, and apply these methods to some terrestrial and meteoritic orthopyroxene-chrome spinel rocks.

2. Thermometry

Diogenites are relatively coarse-grained achondrites with dominant orthopyroxene, some chromite, metal and troilite and a little plagioclase and silica mineral.   The orthopyroxenes have generally low Ca (recalculated Fe percentage between 23 and 28). The chromite compositions may be represented by the formula (Mg, Fe^{2+}) (Cr, Al, Fe^{3+})$_2$ O_4, ignoring small amounts of Ti, V, Si, Mn, etc.   A *normal* spinel configuration is assumed.   The small amount of Fe^{3+} is placed wholly in the octahedral B site on the basis of ideal stoichiometry.   The Mg-Fe^{2+} exchange equilibrium between the orthopyroxene and the chromite of the diogenites is an obvious choice for thermometric application.   IRVINE (1965) recognized the thermometric potential of the Mg-Fe^{2+} exchange equilibrium between chrome spinel and an Mg-Fe^{2+} silicate, and developed the thermodynamic theory.   Since then a fairly large number of investigations on olivine-spinel thermometry have been carried out and several calibrations are in existence (JACKSON, 1969; EVANS and FROST, 1975; FUJII, 1978; FABRIÈS, 1979).   In comparison, little attention has been paid to the thermometric significance of orthopyroxene-spinel equilibrium, although the temperature sensitivity of the Mg-Fe^{2+} distribution between coexisting orthopyroxene and a spinel should be higher than the same between olivine and spinel, because the reaction enthalpy of the Mg-Fe^{2+} exchange reaction between orthopyroxene and spinel is larger than that between olivine and spinel.   MEDARIS (1975) discussed the regularity of the Mg-Fe^{2+} distribution between coexistent orthopyroxene and chromite without deriving a thermometric expression.   WILSON (1982) modelled some isotherms based on estimated Mg-Fe^{2+} diffusion coefficients for adjacent orthopyroxene and chromite grains in the Great 'Dyke' ultramafics.   These investigations will be referred to in greater detail later.   We adopt here two different courses of calibration of an orthopyroxene-spinel thermometer. First, we make an attempt of a direct thermodynamic calibration, using available standard state thermodynamic data for the orthopyroxene and the spinel end members and generally accepted activity-composition relations.   Next, we also attempt an empirical calibration based on several sets of terrestrial parageneses, where independent temperature estimates are available.

2.1. Thermodynamic calibration

Mg-Fe^{2+} exchange equilibrium between the major orthopyroxene and spinel components is governed by the reactions (combined in eq. (d) of IRVINE (1965) and eq. (1) of FABRIÈS (1979)):

$$FeSiO_3 + MgCr_2O_4 = MgSiO_3 + FeCr_2O_4 , \qquad (1)$$

$$FeSiO_3 + MgAl_2O_4 = MgSiO_3 + FeAl_2O_4 , \qquad (2)$$

$$FeSiO_3 + MgFe_2O_4 = MgSiO_3 + Fe_3O_4 . \qquad (3)$$
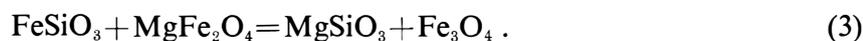
In working only with the Mg-Fe^{2+} exchange reactions between orthopyroxene and chrome spinel, we implicitly accept that the equilibrium temperature for these re-

actions may not be the same as that for other, for instance, the 'net-transfer' reactions between the two phases. Reactions (1), (2) and (3) may be combined to give the following equilibrium equation:

$$\frac{a^{opx}_{MgSiO_3} \cdot (a^{Sp}_{FeCr_2O_4})^{Y^{Sp}_{Cr}} \cdot (a^{Sp}_{FeAl_2O_4})^{Y^{Sp}_{Al}} \cdot (a^{Sp}_{Fe_3O_4})^{Y^{Sp}_{Fe^{3+}}}}{a^{opx}_{FeSiO_3} \cdot (a^{Sp}_{MgCr_2O_4})^{Y^{Sp}_{Cr}} \cdot (a^{Sp}_{MgAl_2O_4})^{Y^{Sp}_{Al}} \cdot (a^{Sp}_{MgFe_2O_4})^{Y^{Sp}_{Fe^{3+}}}}$$

$$= \exp \left[-\{ Y^{Sp}_{Cr}(\varDelta G^0_1 - \varDelta S^0_1(T-298.15)) \right.$$

$$+ Y^{Sp}_{Al}(\varDelta G^0_2 - \varDelta S^0_2(T-298.15))$$

$$+ Y^{Sp}_{Fe^{3+}}(\varDelta G^0_3 - \varDelta S^0_3(T-298.15))\}/RT] ,$$ (4)

where $a^{opx}_{MgSiO_3}$ and $a^{Sp}_{FeCr_2O_4}$ and similar expressions represent the activity of an orthopyroxene (opx) end member, e.g. $MgSiO_3$, and a spinel (sp) end member, e.g. $FeCr_2O_4$, respectively. Y^{Sp}_{Cr} and the similar expressions stand for the mole fractions of the trivalent ions in B sites, e.g. $Y^{Sp}_{Cr}=X_{Cr}/(X_{Cr}+X_{Al}+X_{Fe^{3+}})$. $\varDelta G^0_1$, $\varDelta G^0_2$, $\varDelta G^0_3$ and $\varDelta S^0_1$, $\varDelta S^0_2$, $\varDelta S^0_3$ stand for the standard state (298.15 K and 1 bar) Gibbs free energy and entropy of the reactions (1), (2) and (3). R is the gas constant. Volume change being extremely small was neglected. For pyroxene activity the relationship used is: $a^{opx}_{MgSiO_3}=X_{Mg,M1} \cdot X_{Mg,M2}$ (and a similar expression for $FeSiO_3$), where M1 and M2 stand for the M1 and M2 sites. For calculating the spinel activities, both the ideal Temkin-type relationship, e.g. $a^{Sp}_{FeCr_2O_4}=(X_{Fe^{2+}}) \cdot (X_{Cr})^2$ etc. and the nonideal formulation of SACK (1982) were used for comparison. The thermodynamic parameters used in the calculations are given in Table 1. Temperatures were calculated by solving eq. (4). Results of application and evaluation of this calibration are given under Section 2.3. Generally speaking, however, a thermodynamic calibration of this nature suffers form a great deal of uncertainty, connected mainly with the chosen set of standard set thermodynamic parameters. JACKSON's (1969) olivine-spinel thermometer faced similar problems. These problems can be overcome by extracting thermodynamic relationships, e.g. equilibrium constants, from a regression of natural or experimental parageneses having independently established temperature estimates (e.g. FABRIÈS, 1979). An attempt of this nature is made in the next section. Our aim in attempting the thermody-

Table 1. Thermodynamic data used in the equilibrium calculations.

Phase	Molar volume cal. bar^{-1}	Gibbs energy of formation from elements at 298.15 K 1 bar; kcal. mol^{-1}	Entropy of formation from elements at 298.15 K, 1 bar; Gibbs mol^{-1}
$MgSiO_3$	0.7522 (1)	−349.1594 (1)	− 69.6355 (1)
$FeSiO_3$	0.7876 (2)	−267.1600 (2)	− 61.9638 (2)
$FeCr_2O_4$	1.0519 (1)	−326.2001 (3)	− 80.9847 (1)
$MgCr_2O_4$	1.0411 (1)	−398.9196 (1)	− 91.8356 (1)
$FeAl_2O_4$	0.9740 (1)	−442.351 (1)	− 92.7366 (1)
$MgAl_2O_4$	0.9491 (1)	−519.8040 (1)	−100.1554 (1)
$MgFe_2O_4$	1.0652 (1)	−314.772 (1)	− 89.3141 (1)
Fe_3O_4	1.0641 (1)	−242.009 (1)	− 82.6960 (1)

Numbers in parentheses give the source of the data: (1) ROBIE et al. (1978), (2) HELGESON et al. (1978), (3) ENGI (1978).

namic calirbration has been to get a comparative temperature estimate based on currently available standard state thermodynamic parameters and an ideal mixing model, that can be judged against independently estimated natural and experimental parageneses.

2.2. Empirical calibration

The reactions (1), (2) and (3) can be written together as:

$$FeSiO_3 + Y_{Cr}^{Sp} \cdot MgCr_2O_4 + Y_{Al}^{Sp} \cdot MgAl_2O_4 + Y_{Fe^{3+}}^{Sp} \cdot MgFe_2O_4$$

$$= MgSiO_3 + Y_{Cr}^{Sp} \cdot FeCr_2O_4 + Y_{Al}^{Sp} \cdot FeAl_2O_4 + Y_{Fe^{3+}}^{Sp} \cdot Fe_3O_4 \ . \tag{5}$$
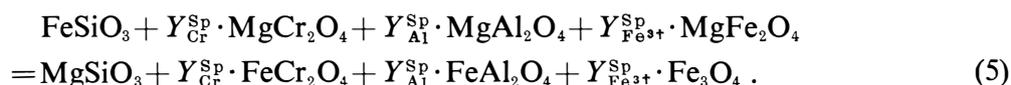
Following Irvine (1965) and Fabriès (1979), for ideal solutions at constant temperature the following relation can be written:

$$\ln K_D = \ln \frac{X_{Mg}^{opx} \cdot X_{Fe}^{Sp}}{X_{Fe}^{opx} \cdot X_{Mg}^{Sp}} = \ln K_7 + Y_{Cr}^{Sp} \cdot \ln K_8 + Y_{Fe^{3+}}^{Sp} \cdot \ln K_9 \ , \tag{6}$$

where K_7, K_8 and K_9 are respectively the equilibrium constants of the following reactions:

$$FeSiO_3 + MgAl_2O_4 = MgSiO_3 + FeAl_2O_4 \ , \tag{7}$$

$$MgCr_2O_4 + FeAl_2O_4 = MgAl_2O_4 + FeCr_2O_4 \ , \tag{8}$$

$$MgFe_2O_4 + FeAl_2O_4 = MgAl_2O_4 + Fe_3O_4 \ . \tag{9}$$
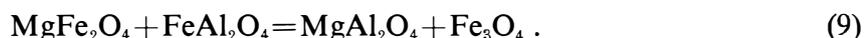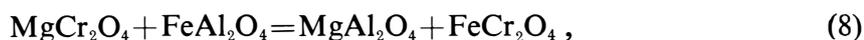
In diogenites and bronzite achondrites (Bunch and Keil, 1971), Fe^{3+} in the spinel is commonly very low with $Y_{Fe^{3+}}^{Sp} < 0.04$. We may write eq. (6) as:

$$\ln K_D^0 = \ln K_7 + Y_{Cr}^{Sp} \cdot \ln K_8 \ , \tag{10}$$

where $\ln K_D^0$ is the distribution coefficient normalized to a ferric-free basis, so that

$$\ln K_D^0 = \ln K_D - Y_{Fe^{3+}}^{Sp} \cdot \ln K_9 \ . \tag{11}$$

Fabriès (1979) showed that for olivine-spinel equilibrium eq. (10) can be derived also after incorporating the reciprocal or cross-site exchange terms for the spinel, as formulated by Wood and Nicholls (1978). The same conclusion can be readily extended to our orthopyroxene–spinel formulation also. For $\ln K_9$, the value of 4 was used by Irvine (1965), Fabriès (1979) and also Fujii (1978), although it was regarded to be somewhat too high.

Thus we may use eq. (10) as the basic linear relationship between the Mg-Fe^{2+} distribution coefficient between orthopyroxene and chromite (normalized to a ferric-free basis) and Y_{Cr}^{Sp}. For the ferric-free normalization we have used the relation:

$$\ln K_D^0 = \ln K_D - 4 Y_{Fe^{3+}}^{Sp} \ . \tag{12}$$

The two 'unknowns' of eq. (10), $\ln K_7$ and $\ln K_8$, can now be determined from a linear regression of data sets, for which independent temperature estimates are available.

For olivine-spinel equilibrium, Fabriès (1979) computed a 700°C isotherm from a linear regression of 32 data points of Medaris (1975) from the metaperidotites of the Seiad and Finero complexes. We have used 16 data points out of these, for which orthopyroxene compositions are also given by Medaris (1975) along with spinel and

olivine. Our linear regression of the orthopyroxene-spinel $\ln K_D^0$ and Y_{Cr}^{Sp} for these points gives the equation:

$$\ln K_D^0 = 0.88 + 2.37 Y_{Cr}^{Sp} \,. \tag{13}$$

WILSON (1982) has shown that in the Great 'Dyke' ultramafics the $Mg\text{-}Fe^{2+}$ diffusion coefficient between orthopyroxene and chromite is lower than that between olivine and chromite, resulting in a higher blocking temperature for the orthopyroxene-chromite equilibrium. However, the $\ln K_D$ vs. Y_{Cr}^{Sp} plots of the orthopyroxene-chromite pairs from the Great 'Dyke' rocks show a wide scatter (WILSON, 1982, Fig. 19) and the agreement between WILSON's (1982) measured and modelled diffusion profiles is not entirely satisfactory. Even so, the difference between WILSON's 700°C isotherm for orthopyroxene-spinel, modelled on diffusion estimates, and the same isotherm based on the Seiad and Finero olivine-spinel pairs of Medaris is less than 50°C. This difference is within the limits of uncertainty due to the analytical errors in the determination of the orthopyroxene and spinel compositions (FABRIÈS, 1979; JACKSON, 1969). We believe therefore that basing our orthopyroxene-spinel 700°C isotherm on the same isotherm for olivine-spinel in the same rocks is not seriously in error.

Our 1200°C isotherm for orthopyroxene-spinel equilibrium is based on a regression of only 3 data points: lunar basalt reequilibrated at 1230°C and 5 kbar (GREEN et al., 1972), spinel lherzolite (2L) experimentally equilibrated at 1200°C and 16 kbar (MORI, 1977) and synthetic olivine-orthopyroxene-spinel mixture experimentally equilibrated at 1200°C and 15 kbar (FUJII, 1978). The Y_{Cr}^{Sp} range of our 1200°C isotherm is rather low, 0.10 to 0.27 only and the orthopyroxene composition taken from FUJII's (1978) experiment is estimated from the 1200°C olivine-orthopyroxene $K_D^{Mg\text{-}Fe}$. The location of the 1200°C isotherm therefore should be considered as less precise than that of the 700°C isotherm. This lack of precision may be significant for orthopyroxene-spinel pairs with $\ln K_D^0$ much less than 2 and Y_{Cr}^{Sp} in the region of 0.5 and above. We will come back to this point later. The regression equation of the 1200°C isotherm is:

$$\ln K_D^0 = 0.30 + 2.37 Y_{Cr}^{Sp} \,. \tag{14}$$

The regression lines for the 700 and 1200°C isotherms are shown in Fig. 1.

The values of $\ln K_7$ and $\ln K_8$ were calculated from eqs. (13) and (14) as:

$$\ln K_7 = \frac{1662.97}{T} - 0.829 \,, \tag{15}$$

$$\ln K_8 = 2.37 \,. \tag{16}$$

Combining eqs. (10), (15) and (16) we get the final thermometric expression:

$$T(K) = \frac{1662.97}{\ln K_D^0 - 2.37 Y_{Cr}^{Sp} + 0.829} \,. \tag{17}$$

2.3. Application and evaluation

We have calculated the orthopyroxene-spinel equilibrium temperature of several terrestrial and meteoritic parageneses, employing both the thermodynamic and the
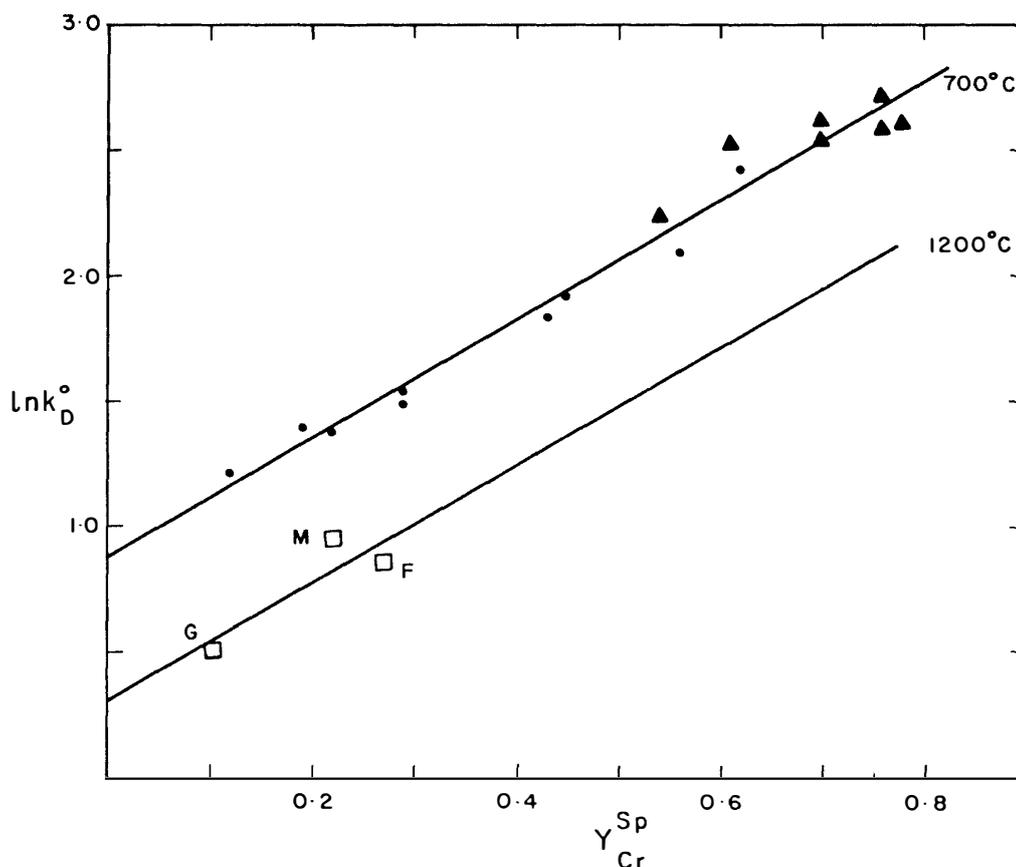
Fig. 1. Mg-Fe distribution coefficient between orthopyroxene and spinel as a function of Y^{Sp}_{Cr} and isotherms drawn by regression. Symbols: solid circles–Finero Complex, solid triangles–Seiad Complex (MEDARIS, 1975); open squares–G (lunar basalt 4310 (GREEN et al., 1972)), M (spinel lherzolite 2L equilibrated at 1200°C and 16 kbar (MORI, 1977)), F (olivine-orthopyroxene-spinel mixture equilibrated at 1200°C and 15 kbar (FUJII, 1978)).

empirical calibrations.   The results are given in Table 2.   On the whole, the empirical orthopyroxene-spinel calibration gives temperatures which agree well with the olivine-spinel thermometer of FABRIÈS (1979).   This is to be expected, because both calibrations are based on similar reference samples.   In the 10 comparative estimates (Table 2), the temperature differences between the two calibrations are 8, 9, 13, 15, 27, 38, 39, 40, 55 and 135°C.   The single case of the large difference of 135°C is the spinel-facies peridotite (sample No. R196) of the Ronda ultramafic complex (OBATA, 1980), in which the $Y^{spinel}_{Fe^{3+}}$ value of OBATA is nearly 178% larger than for the spinels in the other three Ronda samples used in our calculations.   It is also to be noted that the orthopyroxene-spinel empirical calibration is able to distinguish between the significantly higher temperature (1078°C in average) of the Lizard intrusive (GREEN, 1964), the moderately high equilibration temperature of the ultramafic nodules of Tasmania (919°C in average, MORI, 1977) and the lower temperature of the alpine peridotites (average temperature of the Ronda samples, excluding R196, is 854°C and the average temperature of the Red Mt. samples is 736°C).   Among the other geothermometers

Table 2. *Mineral compositions and calculated temperatures of some orthopyroxene-spinel parageneses.*

Sample	Ortho-pyroxene X_{Mg}	Olivine X_{Mg}	Spinel X_{Mg}	Spinel Y_{Cr}	Spinel Y_{Fe}^{3+}	$T°C$ Empirical calibration	$T°C$ Thermodynamic calibration	$T°C$ Other geothermometers
Alpine peridotites								
Lizard, Cornwall (GREEN, 1964):								
No. 90683	0.81	0.90	0.77	0.19	0.052	1039	584	999[1]
No. 90681	0.81	0.89	0.77	0.19	0.056	1116	632	1101[1]
Ronda, Spain (OBATA, 1980):								
No. A501 (m)	0.87	0.90	0.72	0.26	0.01	838	625	811[1]
No. R196	0.86	0.91	0.81	0.12	0.025	1055	597	920[1], 943[2]
No. R243	0.88	0.90	0.78	0.10	0.01	857	560	802[1], 830[2]
No. R123	0.85	0.88	0.75	0.10	0.01	868	540	855[1], 842[2]
Red Mt., New Zealand (SINTON, 1977):								
No. 37010 (orthopyroxenite, mineral rims)	0.91	—	0.46	0.61	0.052	688	619	980[3]
No. 37014 (harzburgite, mineral rims)	0.91	0.91	0.70	0.29	0.015	746	567	754[1]
No. 37140 (harzburgite, mineral rims)	0.91	0.91	0.68	0.32	0.012	775	547	736[1], 1020[4], 880[3]
Ultramafic nodules								
Tasmania (MORI, 1977):								
LJ7 (spinel lherzolite)	0.85	0.90	0.80	0.12	0.021	942	595	904[1]
SC4 (spinel lherzolite)	0.86	0.89	0.78	0.10	0.012	895	538	886[1] For both LJ7 and SC4 between 1100–1200°C approximately[5]
Diogenites								
Johnstown diogenite (FLORAN et al., 1981)	0.72	—	0.15	0.75	0.029	687	1146 (1137)	
Y-74013 diogenite (MUKHERJEE and VISWANATH, 1986):								
Core composition	0.69	—	0.27	0.82	0.021	2004	2142	
Rim composition	0.70	—	0.26	0.73	0.024	1512	1828	
Y-692 diogenite (TAKEDA et al., 1975)	0.73	—	0.30	0.81	0.028	1941	1982	
Y-74136 diogenite (TAKEDA et al., 1978)	0.73(L)	—	0.31	0.70	0.035	1579	1723	
—	0.72(M)	—	0.31	0.70	0.035	1607	1743	
—	0.71(H)	—	0.31	0.70	0.035	1642	1786	
Y-75032 diogenite (TAKEDA et al., 1978)	0.65	—	0.10	0.77	0.077	885	1455	

[1] FABRIÈS (1979): olivine-spinel; [2] GASPARIK and NEWTON (1984): olivine-orthopyroxene-spinel; [3] WOOD and BANNO (1973): orthopyroxene-clinopyroxene; [4] JACKSON (1969): olivine-spinel; [5] MORI (1977): orthopyroxene-clinopyroxene; olivine-clinopyroxene-spinel; olivine-orthopyroxene-spinel. L, M and H indicate relatively low, intermediate and high Ca contents of the orthopyroxene. Temperature within parentheses is calculated using SACK's (1982) formulations for spinel activity.

applied to these same assemblages, the Wood-Banno calibration is believed to give at least a hundred degree too high temperatures (BOHLEN and ESSENE, 1979); and the JACKSON calibration of the olivine-spinel thermometer (JACKSON, 1969) has an uncertainty of about $\pm 300°C$. At least one important reason why thermometers based on net-transfer reactions, e.g. $Mg_2Si_2O_6$ (orthopyroxene)$=Mg_2Si_2O_6$ (clinopyroxene), or $Mg_2Si_2O_6$ (orthopyroxene)$+MgAl_2O_4$ (spinel)$=MgAl_2SiO_6$ (orthopyroxene)$+Mg_2SiO_4$ (olivine) (MORI, 1977), should give higher temperatures than Mg-Fe^{2+} exchange thermometers is that the exchange reactions possibly continue down-temperature significantly further than the net-transfer reactions because of kinetic reasons (FABRIÈS, 1979; NEWTON, 1983). We believe that the empirical calibration of the orthopyroxene-spinel thermometer, as applied to terrestrial rocks, is successful and dependable. The thermodynamic calibration, on the other hand, gives temperatures which are too low and which do not register temperature differences between different thermal regimes.

Application of the orthopyroxene-spinel calibrations gives very high temperatures, between 1500 and 2100°C approximately, for the Yamato-74013, -74136 and -692 diogenites. The empirical and the thermodynamic temperature estimates are roughly of similar orders of magnitudes for the diogenites. Only the Johnstown and the Y-75032 diogenites give empirical temperature estimates, 687 and 885°C respectively, that are comparable to slowly cooled, deep-seated, terrestrial plutonic bodies. Of these two, the Johnstown meteorite shows a uniform, equilibrated orthopyroxene composition in both the brecciated and unbrecciated portions (FLORAN et al., 1981). Also, the crystallographic study of a Johnstown bronzite shows a highly ordered Mg-Fe distribution between the M1 and the M2 sites, indicating slow cooling and equlibration in the 500–700°C range (MIYAMOTO et al., 1975). Y-75032 is an unrecrystallized, monomict meteorite with fragments of orthopyroxene hosting blebby augite inclusions. Many of these pyroxenes may represent inverted low-calcium pigeonites (TAKEDA et al., 1978). The published description of Y-75032 (TAKEDA et al., 1978) suggests that it is a slowly cooled, possibly equilibrated and a uniformly iron-rich (compared to all other diogenites) diogenite of eucritic affinity. Using SACK's (1982) activity formulations for spinel in our thermodynamic calibration, we got for the Johnstown diogenite equilibrium temperature within 9°C of the estimate obtained using ideal Temkin-type spinel activities.

We believe that the temperatures above 1500°C for the Y-74013, -74136 and -692 diogenites are indicative of chemical disequilibrium. Y-692, -74013 and -74136 are believed to be parts of the same fall (TAKEDA et al., 1978). TAKEDA et al. (1981) have described from Y-74013, -74097 and -74136 evidences of shock-heating and remelting, followed by recrystallization. Their observations on the chemical zoning preserved in the clear coarse orthopyroxene, distribution of the coarse and small orthopyroxene grains, and the compositional differences between the coarse and the small chromite grains suggest localized melting at the orthopyroxene-chromite grain boundaries, followed by recrystallization. It is likely that this shock-induced melting triggered element-transport between different parts of the shocked and partly melted grains resulting in a chemical disequlibrium, which was preserved by a relatively fast cooling. MUKHERJEE and VISWANATH (1986) have shown that in Y-74013 the large chromite

euhedra have distinctly pallasitic compositional characteristics and the chromite zoning pattern has features of a very high temperature, pre-silicate crystallization. The orthopyroxene, on the other hand, has normal diogenite chemistry and, apparently, the orthopyroxene and the chromite of the Y-74013 group of diogenites are products of quite dissimilar thermal regimes and their unequilibrated juxtaposition in a coarse, xenomorphic, granular texture remains an intriguing problem.

The Johnstown and the Y-75032 diogenites possibly represent thermally equilibrated meteoritic pyroxene-spinel parageneses broadly within a 700–900°C temperature regime. The $\ln K_D^0$ and Y_{Cr}^{Sp} parameters of both these meteorites are relatively high and sufficiently close to our reference samples setting up the 700°C isotherm. The empirical orthopyroxene spinel Mg-Fe^{2+} exchange equilibrium temperatures of these two meteorites are therefore unlikely to be affected by any possible inaccuracy of our 1200°C isotherm. The same is, however, not true for the Y-74013 group of diogenites, which have relatively low $\ln K_D^0$ values in the region between 1.5 and 1.8 coupled with the Y_{Cr}^{Sp} parameters above 0.70. The uncertainty of the empirical equilibrium temperatures of this group is therefore to be considered as relatively higher.

3. Summary and Conclusions

The emerging picture of a differentiated and layered HED parent body with the probable location of diogenites—an essentially orthopyroxene-spinel paragenesis—at the deepest level has focused on the need of independent estimates of the condition of equilibration of these meteorites. We have made an attempt to calibrate both thermodynamically and empirically the Mg-Fe^{2+} exchange reaction between orthopyroxene and spinel as a thermometer. The empirical calibration is based on the regression of two sets of $\ln K_D^0$-Y_{Cr}^{Sp} data from both naturally and experimentally equilibrated olivine-orthopyroxene-spinel rocks, for which independent temperature estimates are available. The results of application of the empirical calibration to a wide range of terrestrial rocks are internally consistent and agree well with the temperature estimates from an independent thermometer, e.g. the olivine-spinel thermometer of FABRIÈS (1979). Applied to several diogenites, the empirical calibration gives two widely separated temperature regimes: a moderately high temperature (687 and 885°C) regime for the Johnstown and the Y-75032 diogenites and a very high temperature range between 1455 and 2142°C for the Y-692 and its probable 'split-parts', Y-74013 and -74136. While the lower temperature group may represent slowly cooled, relatively deep-seated materials, comparable to terrestrial, mantle-derived ultramafic bodies, the *anomalously* high temperatures of the second group indicate strong thermal disequilibrium. The thermodynamic calibration gives rather low temperatures and cannot distinguish between the test parageneses from different thermal regimes.

Acknowledgments

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