Geothermometry and oxygen barometry using coexisting iron–titanium oxides: a reappraisal

ROGER POWELL AND MARJORIE POWELL

Department of Earth Sciences, University of Leeds, Leeds LS2 9JT

SUMMARY. Equilibrium thermodynamic methods are used to develop an independent iron–titanium oxide geothermometer and oxygen barometer from the experimental data of Buddington and Lindsley (1964). The geothermometer and oxygen barometer are presented graphically for coexisting ilmenite solid solution and magnetite solid solution in the system $FeO-Fe_2O_3-TiO_2$. Equations are also given for calculating temperature and oxygen activity for natural coexisting iron–titanium oxides containing other components. Large departures in composition from the system $FeO-Fe_2O_3-TiO_2$ result in large uncertainties in the calculated temperature and activity of oxygen.

MINERALS that lie wholly or in part on the binary joins magnetite–ulvöspinel ($Fe_3O_4-Fe_2TiO_4$) and hematite–ilmenite ($Fe_2O_3-FeTiO_3$) are common in igneous and metamorphic rocks. Buddington and Lindsley (1964) proposed the use of the compositions of coexisting ilmenite–hematite and magnetite–ulvöspinel solid solutions in the system $FeO-Fe_2O_3-TiO_2$ as a geothermometer and oxygen barometer. Their data were presented graphically (Buddington and Lindsley, op. cit., fig. 5), intersections of contours of $x_{Fe_3O_4, mt}$ and $x_{FeTiO_3, ilm}$ giving temperature, T, and oxygen activity,[1] a_{O_2}. The use of such a method of intersecting contours inevitably results in uncertain determinations of both parameters, within the limitations of the method, particularly for coexisting $FeTiO_3$-rich ilmenites and Fe_2TiO_4-rich magnetites for which the two sets of contours are subparallel. Therefore the geothermometer and oxygen barometer have been reformulated on a thermodynamic basis using the experimental data of Buddington and Lindsley (1964) and are presented in a different way.

Geothermometer. A reaction can be written between coexisting Fe–Ti oxides that does not involve oxygen:

$$FeTiO_3(ilm) + Fe_3O_4(mt) \rightleftharpoons Fe_2O_3(ilm) + Fe_2TiO_4(mt). \tag{1}$$
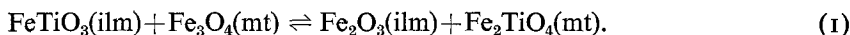
The equilibrium relation for this reaction is:

$$-\Delta G_1^0 = RT \ln (a_{Fe_2TiO_4, mt} \cdot a_{Fe_2O_3, ilm})/(a_{Fe_3O_4, mt} \cdot a_{FeTiO_3, ilm}). \tag{2}$$

Katsura *et al.* (1975) have shown that magnetite–ulvöspinel solid solutions are effectively ideal on a basis of molecular mixing at 1200° to 1300 °C and thus that $a_{Fe_3O_4} = x_{mt}$ and $a_{Fe_2TiO_4} = x_{ulv}$, where, for example, x_{ulv} is the proportion of ulvöspinel in the magnetite solid solution; this suggests that there are large short-range order effects (involving local charge or size balance) in magnetites (see also Kerrick and Darken, 1975).

Most natural ilmenites are rich in the $FeTiO_3$ component and therefore a reasonable approximation is to assume that the $FeTiO_3$ is in the Raoult's Law region and the Fe_2O_3 component is in the Henry's Law region. Assuming that short-range order effects are also important in ilmenite solid solutions, then: $a_{FeTiO_3} = x_{ilm}$ and $a_{Fe_2O_3} = hx_{hem}$, where h is the Henry's Law constant, which is independent of composition in a binary system, but is probably a function of temperature and pressure.

[1] For a standard state of pure O_2 at 1 bar and the temperature of interest this corresponds to the convention that $a = f_i x_i \gamma_i$ where f_i is the activity of *pure* O_2 at the pressure and temperature of interest. This a_i is equivalent to the f_i of, for example, Buddington and Lindsley (1964).

Thus for binary ilmenite solid solutions and binary magnetite solid solutions in the system $FeO–Fe_2O_3–TiO_2$: $-\Delta G_1^0 = RT \ln [x_{ulv}(1-x_{ilm})]/[(1-x_{ulv})x_{ilm}]+RT \ln h$. As both $RT \ln h$ and the Gibbs energy of reaction are likely to be linear functions of temperature they can be combined to give: $A/T+B = \ln K_D = \ln [x_{ulv}(1-x_{ilm})]/[(1-x_{ulv})x_{ilm}]$. $\ln K_D$ is plotted against $1/T$ for the NNO and QFM buffered data of Buddington and Lindsley (1964), Table 1, in

TABLE I. *Calibration data from Buddington and Lindsley (1964). NNO buffer equation from Huebner and Sato (1970), QFM buffer equation from Wones and Gilbert (1969). Mole fractions are for the centres of the experimental brackets.*

T(K)	$10^4/T$	x_{mt}	x_{ilm}	$\ln a_{O_2}$	$\ln K_D$	$\ln K_D'$
NNO buffer						
1273	7.86	0.495	0.871	−23.38	−1.93	−25.40
1173	8.53	0.440	0.895	−27.21	−2.83	−30.31
1073	9.32	0.340	0.914	−31.75	−3.03	−36.85
973	10.28	0.217	0.927	−37.23	−3.83	−45.23
873	11.45	0.110	0.935	−43.97	−4.76	−56.58

| T(K)	$10^4/T$	x_{mt}	x_{ilm}	$\ln a_{O_2}$	$\ln K_D$	$\ln K_D'$
QFM buffer						
1273	7.86	0.617	0.908	−25.50	−1.81	−25.90
1173	8.53	0.544	0.922	−29.44	−2.29	−31.10
1073	9.32	0.413	0.931	−34.12	−2.96	−37.95
973	10.28	0.255	0.940	−39.76	−3.83	−47.00
873	11.45	0.134	0.945	−46.68	−4.71	−58.11

fig. 1. The MW data were not used because of large relative uncertainties in the composition of the ilmenite. The error brackets drawn for the NNO data points represent the experimental uncertainty. Within the limits of the experimental data $\ln K_D$ is a linear function of reciprocal temperature, and can be represented by the equation:

$$\ln K_D = -8155/T+4\cdot59 \quad \text{(with } T \text{ in K)} \tag{3}$$

This equation reproduces the experimental data within the experimental uncertainties, and predicts that $\Delta G_1^0 = 1\cdot8$ kcals at 1300 °C. The calculated value using data from Stull and Prophet (1971) and Johnson et al. (1971) is 2·9 kcal, with an uncertainty of about ±2·5 kcal. The Gibbs energy of reaction predicted if mixing on sites in ilmenite is assumed is 7·8 kcal, so that a model of molecular mixing in ilmenite is more consistent with the thermodynamic data within the other assumptions in this development.

Equation (3) is an Fe–Ti oxide geothermometer that is independent of oxygen activity. The geothermometer is presented graphically in terms of x_{ulv} versus x_{ilm} contoured for temperature in fig. 2, Table II. It is important to note that fig. 2 is only strictly applicable to Fe–Ti oxides in the system $FeO–Fe_2O_3–TiO_2$. Application of the geothermometer to coexisting Fe–Ti oxides involving other components is considered in a later section. From fig. 2 it is apparent that temperature estimates are very sensitive to small changes in x_{ilm}.

Oxygen barometer. The reaction

$$6FeTiO_3+2Fe_3O_4 = 6Fe_2TiO_4+O_2(g) \tag{4}$$
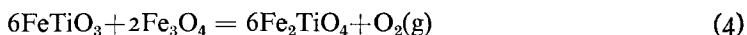
can be calibrated as an oxygen barometer. The equilibrium relation for this reaction is:

$$-\Delta G_6^0 = RT \ln (a_{Fe_2TiO_4, mt}^6)/(a_{FeTiO_3, ilm}^6 \cdot a_{Fe_3O_4, mt}^2)+RT \ln a_{O_2}. \tag{5}$$

Making the same assumption about the activity-composition relations of the coexisting Fe–Ti oxides as above, this becomes: $A'+B'/T = \ln [x_{ulv}^6/(1-x_{ulv})^2 \cdot x_{ilm}^6]+\ln a_{O_2} = \ln K_D'$ for binary ilmenite solid solutions and binary magnetite solid solutions.

TABLE II. x_{ilm} coordinates as a function of $T(K)$ and x_{ulv}

$T(K)$	x_{ulv}										
	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95
773	0.953	0.977	0.990	0.994	0.996	0.997	0.998	0.999	0.999	0.999	0.999
823	0.915	0.958	0.981	0.989	0.993	0.995	0.997	0.998	0.999	0.999	0.999
873	0.859	0.930	0.967	0.980	0.987	0.991	0.994	0.996	0.998	0.999	0.999
923	0.786	0.886	0.946	0.968	0.979	0.986	0.991	0.994	0.996	0.998	0.999
973	0.700	0.831	0.917	0.950	0.967	0.978	0.985	0.990	0.994	0.997	0.999
1023	0.608	0.766	0.880	0.927	0.951	0.967	0.978	0.986	0.992	0.996	0.998
1073	0.516	0.694	0.835	0.897	0.931	0.953	0.968	0.979	0.988	0.995	0.997
1123	0.432	0.616	0.783	0.861	0.906	0.935	0.956	0.971	0.984	0.992	0.996
1173	0.358	0.541	0.726	0.820	0.876	0.914	0.941	0.961	0.977	0.990	0.995
1223	0.296	0.470	0.666	0.774	0.842	0.889	0.923	0.949	0.970	0.986	0.993
1273	0.244	0.406	0.606	0.725	0.804	0.860	0.902	0.935	0.961	0.982	0.992

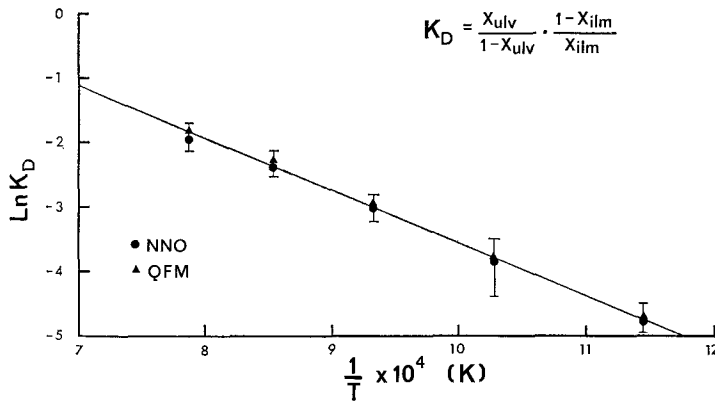$$K_D = \frac{X_{ulv}}{1-X_{ulv}} \cdot \frac{1-X_{ilm}}{X_{ilm}}$$

FIG. 1. Ln K_D versus $1/T$ for the NNO and QFM buffered data of Buddington and Lindsley (1964). Error brackets give the uncertainty in ln K_D for the NNO data points.

$$LnK_D' = Ln \frac{X_{ulv}^6}{[1-X_{ulv}]^2 X_{ilm}^6} + Ln a_{O_2}$$

FIG. 2   FIG. 3

FIG. 2. Geothermometer: x_{ulv} versus x_{ilm} contoured for temperature in °C.

FIG. 3. Ln K_D' versus $1/T$ for the NNO and QFM buffered data of Buddington and Lindsley (1964). Error brackets give the uncertainty in ln K_D' for the NNO data points. .
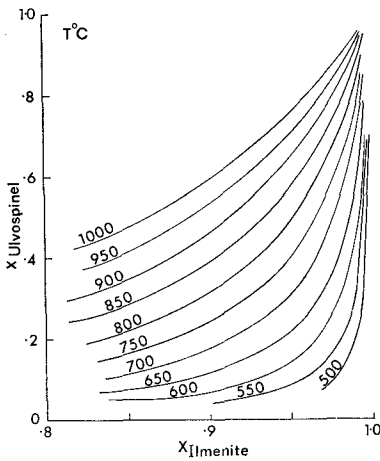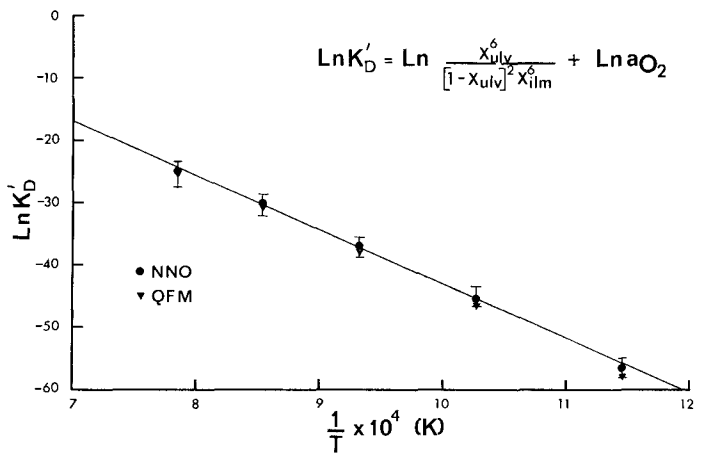
TABLE III. x_{ilm} coordinates as a function of $\ln a_{O_2}$ and x_{ulv}

x_{ulv}	$\ln a_{O_2}$							
	−20	−25	−30	−35	−40	−45	−50	−55
0.1	0.532	0.674	0.782	0.858	0.909	0.942	0.963	0.977
0.2	0.656	0.769	0.849	0.903	0.938	0.961	0.975	0.984
0.3	0.729	0.821	0.884	0.926	0.953	0.970	0.981	0.988
0.4	0.783	0.858	0.909	0.942	0.963	0.977	0.985	0.991
0.5	0.826	0.888	0.928	0.954	0.971	0.982	0.989	0.993
0.6	0.864	0.912	0.944	0.965	0.978	0.986	0.991	0.994
0.7	0.897	0.935	0.959	0.974	0.984	0.990	0.993	0.996
0.8	0.929	0.955	0.972	0.982	0.989	0.993	0.996	0.997
0.9	0.961	0.976	0.985	0.990	0.994	0.996	0.998	0.999
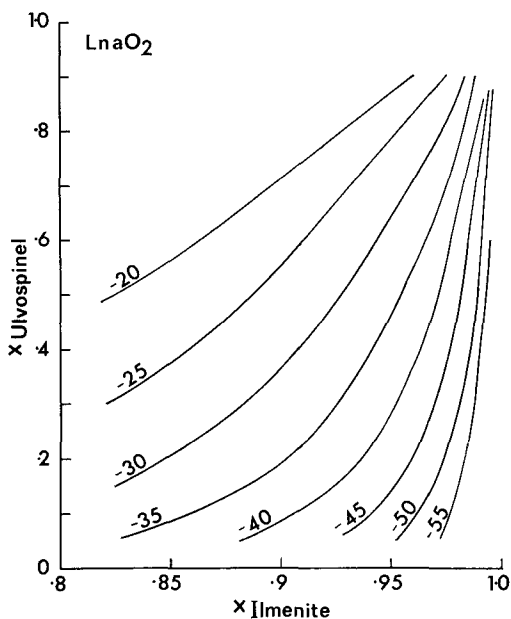
FIG. 4. Oxygen barometer: x_{ulv} versus x_{ilm} contoured for $\ln a_{O_2}$.

Ln K'_D has been plotted against $1/T$ for the NNO and QFM data of Buddington and Lindsley (1964) in fig. 3. Error brackets drawn for the NNO data represent the experimental uncertainty. The data define a straight line that can be represented by the equation:

$$\ln K'_D = -87270/T + 44 \cdot 18 \quad (T \text{ in K}) \tag{6}$$

This equation reproduces the experimental data within the experimental uncertainties. Equations 3 and 6 can be combined to eliminate temperature thus:

$$\ln a_{O_2} = \ln [(x_{ilm}^6[1-x_{ulv}]^2/x_{ulv}^6) \cdot (x_{ulv}[1-x_{ilm}]/[1-x_{ulv}]x_{ilm})^{10.702}] - 4 \cdot 94 \tag{7}$$

Equation (7) thus gives the activity of oxygen in terms of the compositions of the ilmenite and magnetite independently of temperature; it is only strictly applicable to binary solid solutions. The oxygen barometer is presented graphically in fig. 4 in terms of x_{ulv} and x_{ilm} contoured for $\ln a_{O_2}$. The data required to plot this graph are given in Table III. The geobarometer is more sensitive to the composition of the ilmenite than it is to the composition of the magnetite.

Application to natural Fe–Ti *oxides*

The graphical geothermometer and oxygen barometer, figs. 2 and 4, should only be used for natural coexisting Fe–Ti oxides that depart little from the system $FeO-Fe_2O_3-TiO_2$. In this case uncertainties in the calculated temperature of ± 30 °C and in $\ln a_{O_2}$ of $\pm 2 \cdot 0$, as suggested by Buddington and Lindsley (1964), should also be appropriate here. Uncertainties may be larger for reducing systems if any of the assumptions in the above analysis are incorrect because the calibrations could not include the MW data.

However, most natural coexisting Fe–Ti oxides deviate in composition, in some cases substantially, from the system $FeO-Fe_2O_3-TiO_2$ (for example, Carmichael, 1967; Wass, 1973). This has always provided a problem in the application of the Buddington and Lindsley geothermometer and various recalculation methods have been devised to minimize the uncertainties involved (for example, Carmichael, 1967; Anderson, 1968).

Equation (3) can still be used as a geothermometer if the thermodynamics of magnetite and ilmenite solid solutions can be adequately represented by a model of ideal mixing of molecular species:

$$\ln K_D = \ln (x_{ulv} x_{hem}/x_{mt} x_{ilm}) = -8155/T + 4 \cdot 59 \qquad (8)$$

The equation for the oxygen barometer can be rewritten similarly:

$$\ln a_{O_2} = \ln [(x_{mt}^2 x_{ilm}^6/x_{ulv}^6) \cdot (x_{ulv} x_{hem}/x_{mt} x_{ilm})^{10.702}] - 4 \cdot 94 \qquad (9)$$

To use (8) and (9) it is necessary to recast analyses of coexisting ilmenite and magnetite solid solutions in terms of end-members. There is no mathematically unique method of doing this for multicomponent phases. However, it is possible to calculate the maximum and minimum values of x_{mt}, x_{ulv}, x_{ilm}, and x_{hem} for a particular pair of analyses. These can then be combined in the most unfavourable way to get the maximum uncertainty when the values are substituted in (8) or (9). If the magnetite solid solution is recalculated on 4 oxygens, and n_i is the amount of i in the recalculated analysis, and n_{M^2} is the amount of divalent cations other than Fe^{2+}, then:

maximum $x_{ulv} = n_{Ti}$ gives a minimum $x_{mt} = \frac{1}{2}n_{Fe^{3+}} - n_{M^2}$

maximum $x_{mt} = \frac{1}{2}n_{Fe^{3+}}$ gives a minimum $x_{ulv} = n_{Ti} - \frac{1}{2}n_{M^2}$

If the ilmenite is recalculated on 3 oxygens, and n_i is the amount of i in the recalculated analysis, and n_{M^2} and n_{M^3} are the amounts of divalent and trivalent cations other than Fe^{2+} and Fe^{3+}, then:

maximum $x_{hem} = \frac{1}{2}n_{Fe^{3+}}$ gives a minimum $x_{ilm} = n_{Ti} - n_{M^2}$

maximum $x_{ilm} = n_{Ti} - n_{M^2}$ gives a minimum $x_{hem} = \frac{1}{2}(n_{Fe^{3+}} - n_{M^3})$.

Maximum and minimum values of x_{ulv}, x_{mt}, x_{ilm}, and x_{hem} have been calculated for six ilmenite–magnetite pairs from Carmichael (1967) see Table IV. The analyses used are all microprobe analyses for which Fe_2O_3 contents have been estimated using charge balance criteria[1] (Carmichael, 1967). Maximum and minimum temperatures calculated using the above are also shown in Table IV. The large uncertainty in the calculated temperature for specimen 25 is due to large amounts of MgO and Al_2O_3 in the magnetite solid solution and MgO in the

---

[1] If the magnetite grain being analysed has exsolution lamellae of ilmenite then an average analysis of the grain will not permit an adequate estimate of the Fe_2O_3 content of the original unexsolved grain because the ilmenite lamellae form as a result of an oxidation mechanism (Buddington and Lindsley, 1964). The total FeO content (all Fe as FeO) determined by an average microprobe analysis of the grain will be too low due to oxidation of some of the original Fe^{2+} to Fe^{3+}. In such cases an estimate of x_{ulv} can be obtained using $x_{ulv} = $ wt. % $TiO_2/35 \cdot 73$. Temperatures and oxygen activities can then be obtained approximately using figs. 2 and 4.

TABLE IV. *Comparison of T and ln a_{O_2} calculated from (8) and (9) with those determined from Buddington and Lindsley (1964), for several coexisting Fe–Ti oxide pairs from Carmichael (1967). The number of decimal places in the mole fractions does not imply this accuracy.*

Rock no.	2	5	9	12	25	28
$x_{ulv,max}$	0.6256	0.4319	0.7615	0.3898	0.3298	0.1540
$x_{mt,min}$	0.3111	0.5044	0.1555	0.4453	0.4001	0.7172
$x_{mt,max}$	0.3555	0.5452	0.2269	0.5448	0.5919	0.8043
$x_{ulv,min}$	0.6034	0.4115	0.7258	0.3401	0.2339	0.1105
$x_{ilm,max}$	0.9201	0.8970	0.9097	0.7733	0.6070	0.6491
$x_{hem,min}$	0.0473	0.0526	0.0380	0.1077	0.2236	0.2478
$x_{hem,max}$	0.0477	0.0532	0.0380	0.1127	0.2296	0.2508
$x_{ilm,min}$	0.9201	0.8970	0.9097	0.7733	0.6070	0.6491
T_{max}	917	804	1047	953	1144	878
T_{min}	887	785	962	887	978	809
Av.T,°C	902±15	795±10	1005±42	920±33	1061±83	844±35
$T_{Car.}$*	915	810	1025	880	1010	865
ln a_{O_2} { Max.	−28.7	−33.4	−23.5	−23.3	−12.7	−21.4
Min.	−31.1	−35.3	−29.1	−28.6	−23.7	−28.5
Ave.	−29.9	−34.3	−26.3	−25.9	−18.2	−25.0
	±1.2	±1.0	±2.8	±2.7	±5.5	±3.5
Car.*	−29.7	−33.8	−25.8	−28.1	−21.2	−25.1

* Carmichael

ilmenite. Thus the greater the compositional deviation of the coexisting phases from the system $FeO-Fe_2O_3-TiO_2$ the greater the uncertainty in the calculated temperature. Such uncertainties are not apparent in Carmichael's analysis of the data. Maximum and minimum values of $\ln a_{O_2}$ calculated from (9) are also given in Table IV. As above, the uncertainties are related to compositional deviations from the system $FeO-Fe_2O_3-TiO_2$.

REFERENCES

Anderson (A. T.), 1968. *Am. J. Sci.* **266**, 704–27.
Buddington (A. F.) and Lindsley (D. H.), 1964. *J. Petrol.* **5**, 310–57.
Carmichael (I. S. E.), 1967. *Contrib. Mineral. Petrol.* **14**, 36–64.
Huebner (J. S.) and Sato (M.), 1970. *Am. Mineral.* **55**, 934–53.
Johnson (R. E.), Woermann (E.), and Muan (A.), 1971. *Am. J. Sci.* **271**, 278–92.
Katsura (T.), Wakihara (M.), Hara (D.), and Sugihara (T.) 1975. *J. Solid State Chem.* **13**, 107–13.
Kerrick (D. M.) and Darken (L. S.), 1975. *Geochim. cosmochim. Acta*, **39**, 1431–42.
Stull (D. R.) and Prophet (J.), 1971. *JANAF Thermochemical Tables, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.)*, **37**, 1141p.
Wass (S. Y.), 1973. *J. Geol. Soc. Austr.* **20**, 427–47.
Wones (D. R.) and Gilbert (M. C.), 1969. *Am. J. Sci.* **276A**, 480–8.