

## The effects of recalculation on estimates of temperature and oxygen fugacity from analyses of multicomponent iron–titanium oxides

JOHN C. STORMER, JR.<sup>1</sup>

Department of Geology  
University of Georgia, Athens, Georgia 30605

### Abstract

Most analyses of natural iron–titanium oxides contain small but significant amounts of minor components. In order to determine the “mole” fractions of endmember ilmenite and ulvöspinel in coexisting oxides for geothermometry, a new recalculation scheme is proposed based on models of ionic substitution. This new scheme is consistent with a new thermodynamic model for the pure Fe–Ti system (Spencer and Lindsley, 1981). It should also provide a better basis for consideration of the actual effects of minor components on the geothermometer as the necessary data become available.

The temperatures and oxygen fugacities were calculated using several recalculation schemes for a large number of published analyses of coexisting Fe–Ti oxides from igneous rocks. Significantly different temperatures and oxygen fugacities were obtained with the Spencer and Lindsley geothermometer as opposed to the earlier Buddington and Lindsley version. Generally the differences between values using various recalculation schemes were less than 30°C and less than 0.5 units of  $\log f_{O_2}$ . The new scheme proposed here tends to give temperature and  $\log f_{O_2}$  values falling in the middle of the range of variation. Simply ignoring, or not analyzing for, minor components can lead to errors in excess of 150° and 4 units of  $\log f_{O_2}$ .

### Introduction

The iron–titanium oxide geothermometer of Buddington and Lindsley (1964) was recently reformulated by Spencer and Lindsley (1981). The temperature and oxygen fugacity of equilibrium between coexisting magnetite–ulvöspinel (spinel phase) and ilmenite–hematite solid solution (rhombohedral phase) can be obtained from the compositions of the two phases. Spencer and Lindsley fitted the experimental data to a thermodynamic model that included the solution properties of the  $Fe_3O_4$ – $Fe_2TiO_4$  (spinel phase) and  $Fe_2O_3$ – $FeTiO_3$  (rhombohedral phase) solid solutions. The mathematical relationships of S&L allow more precise interpolation and extrapolation within the pure Fe–Ti–O system. However, most natural specimens of the iron–titanium oxides contain minor constituents such as Mn, Mg, Al, Cr, and Si, which are not accounted for in the geothermometers.

Buddington and Lindsley (1964) recognized the need for a good recalculation scheme for analyses of natural specimens. They provided a scheme suggested by D. R. Wones. Lindsley and Spencer (1982) also suggested a scheme for recalculation. However, two other schemes, one suggested by Carmichael (1967, see also Ghiorso and

Carmichael, 1981) and the other by Anderson (1968), have been used (with minor variations) in most work. Whereas direct comparisons of the Anderson and Carmichael schemes (D’Arco and Maury, 1981; Fig. 2 here) show that in most cases the difference in temperature is quite small, certain samples show differences of 30°C or more between the two schemes. Although the statistical uncertainty in the fit of the Spencer and Lindsley model limits accuracy to 30° at best, the relative precision with good analyses could be better. Regardless of accuracy, values obtained using different recalculation schemes cannot be directly compared because the recalculation introduces a systematic bias.

A new scheme considering the effect of ionic substitution in Fe–Ti oxide solid solutions, consistent with the solution models of Spencer and Lindsley, is developed here. Then the effects of using the various schemes and geothermometers are assessed. Unfortunately, with the data that are presently available, it is not possible to show conclusively that any one scheme for recalculation is better than another.

### Solution models

#### Rhombohedral phase

The rhombohedral phase is the solid solution between hematite and ilmenite. (Refer to Lindsley, 1976a for a

<sup>1</sup> Present address: MS-959, U.S. Geological Survey, Reston, Virginia 22092.

more complete discussion of the crystal chemistry summarized here.) The structure is essentially a hexagonal close packed array of oxygen atoms with the metal cations in octahedral interstices. The metal cations can be viewed as lying in layers stacked along the [001] axis. In pure ilmenite there are two slightly different types of layers with sites designated A and B that alternate in the stacking sequence. In pure ilmenite (space group  $R\bar{3}$ ) the A sites contain  $\text{Fe}^{2+}$  and the B sites contain Ti. In pure hematite (space group  $R\bar{3}c$ ) the sites are indistinguishable containing only  $\text{Fe}^{3+}$ . The temperature of the  $R\bar{3}$  to  $R\bar{3}c$  transition is above the temperature of equilibration of most natural ilmenite solid solutions (Ishikawa, 1958; Lawson and others, 1981) so that only an ordered A-B model need be considered.

In their work, Spencer and Lindsley considered the consequences of a number of solution models and the configurational entropy contributions of various ordering schemes. They found that a relatively uncomplicated model of ionic substitution (Spencer and Lindsley, Equation 13) was adequate to represent their data. This model was equivalent to Equation 4, model B of Rumble (1977), which was derived from the well known expression for configurational entropy  $S_c$ .

$$\bar{S}_c = -R \sum_q \sum_s \alpha_q X_{sq} \ln X_{sq} \quad (1)$$

Here the subscript  $s$  refers to the ionic species,  $q$  to the type of crystallographic site,  $\alpha_q$  is the number of  $q$  sites per formula unit, and  $X_{sq}$  is the mole fraction of species  $s$  on site  $q$ . For this model Ti is assumed to be restricted to the B sites, as in pure ilmenite, where it mixes randomly with  $\text{Fe}^{3+}$ . Then  $\text{Fe}^{2+}$  is restricted to the A sites and mixes randomly with the remainder of the  $\text{Fe}^{3+}$ . The amount of  $\text{Fe}^{3+}$  on the A and B sites must be equal in order to maintain charge balance (for the pure Fe-Ti system). These constraints and Rumble's Equation 4 can then be written:

$$\bar{S}_c = -R (2n_{\text{Ti},\text{B}} \ln n_{\text{Ti},\text{B}} + 2n_{\text{Fe}^{3+},\text{B}} \ln n_{\text{Fe}^{3+},\text{B}}) \quad (2)$$

where  $n_{\text{Ti},\text{B}}$ , for instance, is the number of Ti ions on the B site per formula unit.  $X$  in Spencer and Lindsley's Equation 13 is equivalent to the number of moles of Ti on the B site, which in the pure Fe-Ti system is equivalent to the mole fraction of the ilmenite "molecule."  $1-X$ , then, is the number of moles of  $\text{Fe}^{3+}$  on the B site, which is equivalent to the number of moles of hematite.

The configurational entropy model can be extended to include the minor elements if they can be assigned to the proper sites. At present, these site preferences are speculative. At least Mg shows complete solid solution with  $\text{Fe}^{2+}$  (geikielite-ilmenite) and probably has a similar ordered structure. The oxides of the common minor trivalent ions are isostructural with hematite ( $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ ; Bloss 1971, p. 252).  $\text{Cr}_2\text{O}_3$  enters an apparently ideal solution with hematite and has a significant solu-

bility in geikielite ( $\text{MgTiO}_4$ ) (Muan, 1975). In the  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  system there is a solvus and an intermediate compound ( $\text{FeAlO}_3$ , monoclinic) at high temperatures, but there is about 10% solubility of  $\text{Al}_2\text{O}_3$  in hematite (Levin and others, 1964). Although little else is known, simple ionic radius is not likely to be a good predictor of site preference, because the A and B sites are essentially the same in size. Charge (or charge/radius) does seem to be important, however. It will be assumed here that the divalent ions ( $\text{M}^{2+}$ ) will be confined to the A site with  $\text{Fe}^{2+}$ , that the 4+ ions ( $\text{M}^{4+}$ ) are on the B sites with Ti and that the trivalent ions ( $\text{M}^{3+}$ ) and  $\text{Fe}^{3+}$  are randomly mixed in equal proportions on both sites. In other words, free substitution is allowed among ions of like charge. Following Equation 1 the ideal configurational entropy becomes:

$$\begin{aligned} \bar{S}_c = -R & \left( n_{\text{Fe}^{2+},\text{A}} \ln n_{\text{Fe}^{2+},\text{A}} + n_{\text{Ti},\text{B}} \right. \\ & \cdot \ln n_{\text{Ti},\text{B}} + 2 n_{\text{Fe}^{3+},\text{B}} \ln n_{\text{Fe}^{3+},\text{B}} \\ & \left. + \left[ \sum_i n_{\text{M}_i,\text{A}} \ln n_{\text{M}_i,\text{A}} + \sum_j n_{\text{M}_j,\text{B}} \ln n_{\text{M}_j,\text{B}} \right] \right) \quad (3) \end{aligned}$$

(the terms in square brackets are the contribution of the "minor" elements to the configurational entropy of the solution.) Note that  $n_{\text{Fe}^{2+},\text{A}}$  does not have to equal  $n_{\text{Ti},\text{B}}$ . Also,  $n_{\text{Fe}^{3+},\text{A}}$  and  $n_{\text{Fe}^{3+},\text{B}}$  must be equal (to combine in the third term of Equation 3), but they do not have to equal  $(1 - n_{\text{Ti},\text{B}})$ . The minor elements make up any difference in charge balance and site occupancy.

The contribution of the ideal configurational entropy to the free energy of the solution is simply Equation 3 multiplied by  $-T$ . The contribution to the chemical potential of a given component (natural logarithm of ideal activity) is obtained by differentiating equation 3 with respect to the number of moles of the component in question (ilmenite for example).

$$\begin{aligned} -\frac{1}{R} \left( \frac{\partial \bar{S}_c}{\partial n_{\text{FeTiO}_3}} \right) &= \ln a_{\text{FeTiO}_3} \\ &= \frac{d(n_{\text{Fe}^{2+}} \ln n_{\text{Fe}^{2+},\text{A}})}{d n_{\text{FeTiO}_3}} + \frac{d(n_{\text{Ti},\text{B}} \ln n_{\text{Ti},\text{B}})}{d n_{\text{FeTiO}_3}} \\ &+ \frac{d(2(n_{\text{Fe}^{3+},\text{B}} \ln n_{\text{Fe}^{3+}}))}{d n_{\text{FeTiO}_3}} + \frac{d(n \text{M}_i \ln n \text{M}_i)}{d n_{\text{FeTiO}_3}} \quad (4) \end{aligned}$$

The stoichiometry of endmember ilmenite requires that any change in  $n_{\text{FeTiO}_3}$  result in an equal change in both  $n_{\text{Fe}^{2+},\text{A}}$  and  $n_{\text{Ti},\text{B}}$ , even though  $n_{\text{Fe}^{2+},\text{A}}$  does not equal  $n_{\text{Ti},\text{B}}$ .

$$d n_{\text{Fe}^{2+},\text{A}} = d n_{\text{Ti},\text{B}} = d n_{\text{FeTiO}_3} \quad (5)$$

But elements other than  $\text{Fe}^{2+}$  and Ti are unchanged by a change in the ilmenite component.

$$0 = \frac{d n_{\text{Fe}^{3+},\text{B}}}{d n_{\text{FeTiO}_3}} = \frac{d n_{\text{M}_i}}{d n_{\text{FeTiO}_3}} = \dots \quad (6)$$

Equation 4 then reduces to:

$$\ln a_{\text{FeTiO}_3} = \ln n_{\text{Fe}^{2+},\text{A}} + \ln n_{\text{Ti},\text{B}} \quad (7)$$

Since all  $\text{Fe}^{2+}$  is on site A and all Ti on site B we can combine and take the antilogarithms to obtain:

$$a_{\text{FeTiO}_3} = (n_{\text{Fe}^{2+},\text{F}}) (n_{\text{Ti},\text{F}}) \quad (8)$$

where  $n_{\text{Fe}^{2+},\text{F}}$  indicates the total number of  $\text{Fe}^{2+}$  ions per formula unit. It should be noted at this point that this model is really independent of the way the minor elements are distributed. All Cr might be on the A site and Al on the B site so long as all  $\text{Fe}^{2+}$  is on A, all Ti is on B, and  $\text{Fe}^{3+}$  is equally divided between the two.

In a similar way we can obtain the ideal activity of hematite in such a solution.

$$a_{\text{Fe}_2\text{O}_3} = n_{\text{Fe}^{3+},\text{A}}^2 = (0.5 n_{\text{Fe}^{3+},\text{F}})^2 \quad (9)$$

The factor 2 in the logarithmic expression used by Spencer and Lindsley (their Equation 13) leads to a squared relationship between Spencer and Lindsley's  $X_{\text{Ilm}}$  and the ideal activity defined above. For pure  $\text{FeTiO}_3$ - $\text{Fe}_2\text{O}_3$  binary solutions this leads to:

$$X_{\text{Ilm}} = n_{\text{Ti,tot}} = \sqrt{(n_{\text{Fe}^{2+},\text{F}})(n_{\text{Ti},\text{F}})} \quad (10)$$

and

$$1 - X_{\text{Ilm}} = n_{\text{Fe}^{3+},\text{A}} = 0.5 n_{\text{Fe}^{3+},\text{F}} \quad (11)$$

The activities of ilmenite and hematite appear as a ratio in the equilibrium constant of the exchange reaction,  $K_{\text{exch}}$ . (Spencer and Lindsley, Equation 18). Extrapolating the activities in the multicomponent solution to the binary  $\text{Fe}_2\text{O}_3$ - $\text{FeTiO}_3$  join, keeping a constant ratio of the ideal activities, gives an apparent mole fraction of ilmenite,  $X'_{\text{Ilm}}$ , at the binary.

$$X'_{\text{Ilm}} = \frac{\sqrt{(n_{\text{Fe}^{2+},\text{F}})(n_{\text{Ti},\text{F}})}}{(0.5 n_{\text{Fe}^{3+},\text{F}}) + \sqrt{(n_{\text{Fe}^{2+},\text{F}})(n_{\text{Ti},\text{F}})}} \quad (12)$$

Perhaps the most critical unknown factor in the model above is the possibility that a strong site preference of the minor trivalent cations could displace  $\text{Fe}^{3+}$  from the A or B site preferentially. If this could be demonstrated,  $n_{\text{Fe}^{3+},\text{A}}$  and  $n_{\text{Fe}^{3+},\text{B}}$  would be different, and Equation 9 would become:

$$a_{\text{Fe}_2\text{O}_3} = (n_{\text{Fe}^{3+},\text{A}}) (n_{\text{Fe}^{3+},\text{B}}) \quad (9A)$$

The square root of this activity would replace  $0.5 n_{\text{Fe}^{3+},\text{F}}$  in Equations 10 and 11. Fortunately Al, Cr, and V are not abundant in ilmenite solid solutions in equilibrium with a spinel phase, and the maximum possible shift in  $X'$  for any natural ilmenite is probably less than 1 mole percent.

### Spinel phase

The crystallography of the Fe-Ti spinels is discussed in detail by Lindsley (1976a and 1976b). All spinel structures are based on an arrangement of oxygens approximating a cubic close packed arrangement. The metal cations occupy certain octahedral (d) and tetrahedral (a) interstices between the oxygens. The oxygens and metal cations can be viewed as a stacking of layers along the [111] axis in the sequence O-d-O-ada-O-. The importance of this "layering" in controlling crystal properties is reflected in the predominant occurrence of octahedral (111) habit in all spinels and the fact that oxidation in Fe-Ti spinels produces hematite lamellae parallel to the (111) plane. There are two octahedral cations and one tetrahedral cation per formula unit. The structure is extremely flexible and a large number of elements can combine to form spinels. Given the general formula  $\text{AB}_2\text{O}_4$ , spinel structures are "normal" when A cations occupy the tetrahedral sites and B cations occupy only octahedral sites. "Inverse" spinels, however, have one half of the B cations on the tetrahedral sites and the other half of the B cations and the A cations on octahedral sites. With increasing temperature the cations can become disordered on all sites (see Navrotsky and Kleppa, 1967). Magnetite and ulvöspinel are "inverse spinels" and their structural formulae could be written  $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$  and  $\text{Fe}^{2+}[\text{Fe}^{2+}\text{Ti}]\text{O}_4$  ([ ] indicate the octahedral positions).

There is an extensive body of literature on the site preferences of cations in pure stoichiometric spinels leading to predictions of normal vs. inverse structure (Price *et al.*, 1982). However, only a small part of this literature has application to spinels of geological interest. Recently, Sack (1982) developed a model for the activities of endmember spinel components by taking into consideration the available data of this type and the limited phase equilibrium data that exists for spinel systems. For ulvöspinel and magnetite, the configurational entropy terms in Sack's activity expressions are equivalent to expressions independently derived here from a consideration of ulvöspinel-magnetite solutions only.

There are several models which have been proposed for the distribution of ions in magnetite-ulvöspinel solutions. (Lindsley (1976a) discusses these in detail and his Figure L-8 is a particularly clear presentation.) Recent data (Wechsler, 1981) suggests that an Akimoto distribution model "with a hint of ordering" is appropriate for the magnetite ulvöspinel solid solution. Only the Akimoto distribution (Akimoto, 1954) will be considered here. For this distribution model the two octahedral sites always contain one  $\text{Fe}^{2+}$  per formula unit. Ti and  $\text{Fe}^{3+}$  substitute on another octahedral site and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  substitute on the tetrahedral sites in ratios equal to the molar ratio of ulvöspinel to magnetite.

Spencer and Lindsley (1981) found that their data could be fitted to a molecular model of solution. The molecular

model and the Akimoto model with complete disorder on each site were considered by Rumble (1977, Fig. 4, curves A and D). Even if the configurational entropy of disorder on the octahedral site of the pure endmembers is removed (as it would be in Spencer and Lindsley's model for the free energy of solution), the Akimoto distribution predicts entropies which are twice as high as those of the molecular model. In order to reconcile apparent molecular solution with the Akimoto distribution there must be considerable short range ordering of octahedral Ti with tetrahedral  $\text{Fe}^{2+}$  and octahedral  $\text{Fe}^{3+}$  with tetrahedral  $\text{Fe}^{3+}$ . If we assume that local charge balance effects exert a major control on the apparently "molecular" ordering, then we could assume an Akimoto type distribution with all the 4+ cations substituting for Ti, the 2+ cations substituting for  $\text{Fe}^{2+}$ , and all 3+ cations substituting for  $\text{Fe}^{3+}$ . Local charge balance does seem to be an important effect in spinels (Bloss, 1971, p. 279). For an "ionic" model with charge balance ordering, the activity would be given by

$$a_{\text{Fe}_2\text{TiO}_4} = \left( \frac{n_{\text{Ti,d}}}{n_{\text{M}^{4+},\text{d}} + n_{\text{Ti,d}} + n_{\text{M}^{3+},\text{d}}} \right) \left( \frac{n_{\text{Fe}^{2+},\text{d}}}{n_{\text{Fe}^{2+},\text{d}} + n_{\text{M}^{2+},\text{d}}} \right) \cdot \left( \frac{n_{\text{Fe}^{2+},\text{a}}}{n_{\text{Fe}^{2+},\text{a}} + n_{\text{M}^{2+},\text{a}}} \right) \quad (13)$$

The first term is simply the mole fraction relative to Ti and substituting cations on one octahedral site. Given the stoichiometry of the Akimoto distribution, all Ti must be on the octahedral site and the sum in the denominator must be equal to 1. If  $\text{Fe}^{2+}$  does not show a site preference relative to the other 2+ cations, then the next two terms are equal to the mole fraction of  $\text{Fe}^{2+}$  relative to the sum of all 2+ cations ( $X_{\text{Fe}^{2+},\text{S}2+}$ ), and Equation 13 becomes

$$a_{\text{Fe}_2\text{TiO}_4} = n_{\text{Ti,F}} (X_{\text{Fe}^{2+},\text{S}2+})^2 \quad (14)$$

where  $n_{\text{Ti,F}}$  is the total Ti cations per formula unit. The first term could be viewed as the "molecular" activity of titanium spinel which is modified for 2+ cation substitution by the squared term. (The Carmichael scheme simply takes the first term as  $X_{\text{Usp}}$ .) In a similar way the ideal activity of magnetite can be written:

$$a_{\text{Fe}_3\text{O}_4} = 0.5 n_{\text{Fe}^{3+},\text{F}} (X_{\text{Fe}^{2+},\text{S}2+}) (X_{\text{Fe}^{3+},\text{S}3+}) \quad (15)$$

where  $\text{Fe}^{3+}$  is assumed not to have a significant preference for tetrahedral or octahedral sites, and  $X_{\text{Fe}^{3+},\text{S}3+}$  is the mole fraction of  $\text{Fe}^{3+}$  vs. all other 3+ cations.

The apparent mole fraction of ulvöspinel ( $X'_{\text{Usp}}$ ) to be used in the Spencer and Lindsley formulas is again obtained by extrapolation to the binary  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$  join maintaining the ratio of ideal activities.

$$X'_{\text{Usp}} = \frac{(n_{\text{Ti,F}})(X_{\text{Fe}^{2+},\text{S}2+})}{(0.5 n_{\text{Fe}^{3+},\text{F}})(X_{\text{Fe}^{3+},\text{S}3+}) + (n_{\text{Ti,F}})(X_{\text{Fe}^{2+},\text{S}2+})} \quad (16)$$

The alternative to this scheme is to assume that the ions

are perfectly ordered to form spinel "molecules", *i.e.*,  $\text{MgAl}_2\text{O}_4$ ,  $\text{FeCr}_2\text{O}_4$ , *etc.* Recalculation schemes based on sequential calculation of a set of "molecules" (such as Anderson, 1968; Buddington and Lindsley, 1964; Lindsley, 1982) assume, in effect, that there is a very high degree of ordering, even for  $\text{Fe}^{2+}$  and Mg. Lindsley and Spencer (1982) presented data suggesting a coupling of Mn and Ti, but there is little evidence to justify a particular scheme for other elements. The simple sequential schemes also imply ideal molecular solution which is probably inappropriate for a multi-site, multi-element reciprocal solution. Assumption of molecular solution would lead to unnecessarily complex models for the nonideal contribution when the necessary data become available. If the consequences of the site occupancies and ideal configurational entropy for mixtures of "molecules" are considered, as done by Sack (1982), the resulting activity expressions are equivalent to those presented here, and in either case the nonideal component of activity or excess free energy of solution can be expressed by some function of composition.

Sack (1982) presents complete expressions for the activity of spinel components including ulvöspinel and magnetite. Ideally it would be preferable to utilize Sack's expressions (perhaps with modified parameters) in the Spencer and Lindsley equations. However, we cannot simply replace the activity terms in Spencer and Lindsley with those from Sack (1982). As Spencer and Lindsley clearly state, their activity coefficients are internally consistent, but the refined values of the parameters for one solution are affected by the inaccuracy in assumptions about the other solution and in assumptions about the standard state exchange reaction. Spencer and Lindsley's models assume a linear temperature dependence of the Margules parameters. Sack's models are very different (*i.e.*, constant Margules parameters and temperature dependent "reciprocal bonding terms"). Although both models are internally consistent and useful for their intended purposes, they cannot be simply combined without refitting of the data and adjustment of the parameters.

Ultimately, the effects of the minor components may be fitted to an expression modeling the excess free energies of multicomponent solutions. There is no uniquely correct model. As pointed out by Sack *et al.* (1980, p. 373) even a relatively simple regular solution model for multicomponent solutions may require evaluation of an impossibly large number of regression coefficients. As a practical matter, a simpler empirical equation may be a better choice. In either case the expressions given above, or the equivalent from Sack (1982), provide a more appropriate expression for the ideal configuration entropy contribution to solution properties.

#### Recalculation procedure

Although it may not be explicitly stated, virtually all recalculations (including Anderson, 1968; Carmichael,

1967; and Ghiorso and Carmichael, 1981) have the effect of normalizing the cations to a stoichiometric formula and of balancing the number of cation charges by varying the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio. (See the justification of this procedure in Spencer and Lindsley, 1981, p. 1192–3).

A flow sheet for the recalculation procedure recommended here is as follows:

(1) Calculate the molar proportions of all cations in the analyses for both the rhombohedral and spinel phases.

(2) Normalize the cations in the spinel phase to a formula unit of 3 sites, and the cations in the rhombohedral phase to a formula unit of 2 sites.

(3) Calculate the sum of the cationic charges per formula unit and subtract 8 for the spinel phase. For the rhombohedral phase subtract 6. The resulting numbers are the cation charge deficiency (or excess).

(4) Convert  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  to eliminate the charge deficiency. (Do the reverse to eliminate an excess.) If it is not possible to balance the charges, the analysis cannot represent a stoichiometric oxide phase.

(5) You now have the number of moles of each cation per formula unit for both phases. For the spinel phase only, calculate the mole fraction of  $\text{Fe}^{2+}$  relative to the sum of all 2+ cations, and the mole fraction of  $\text{Fe}^{3+}$  relative to all 3+ cations.

(6) Calculate  $X'_{\text{Usp}}$  using equation 15, and calculate  $X'_{\text{Ilm}}$  using equation 11.

(7) Determine  $T$  and  $f_{\text{O}_2}$  using  $X'_{\text{Usp}}$  and  $X'_{\text{Ilm}}$  with the relationships in Spencer and Lindsley (1981).

A BASIC computer program which calculates  $T$  and  $f_{\text{O}_2}$  using these procedures as well as those of Carmichael (1967), Anderson (1968) and Lindsley and Spencer (1982) is available from the author.

### Applications

A computer program was written to calculate temperature and oxygen fugacities from analyses of coexisting spinel and rhombohedral phase oxides. This program uses the model of Spencer and Lindsley (1981) and calculates the mole fractions of ilmenite and ulvöspinel using the Anderson (1968), Carmichael (1967), and Lindsley and Spencer (1982) schemes recommended here. The output contains the  $X'$ ,  $T$ , and  $\log f_{\text{O}_2}$  data for all three methods. Using this program,  $T$  and  $\log f_{\text{O}_2}$  data were calculated for the 51 analyses of "Representative Coexisting Oxides" compiled by Haggerty (1976, Table Hg-20, p. Hg-259) as well as several suites of analyses from Stormer (1972) and Whitney and Stormer (1976). Examples of these results are shown in Figure 1 and Table 1. Haggerty's (1976) compilation covers the spectrum of compositions found in igneous rocks. Naturally, such a sample will overemphasize some unusual compositions, but the results do cover the range of composition, temperature and oxygen fugacity expected in igneous rocks.

The results of the temperature and oxygen fugacity calculations show a considerable difference from the

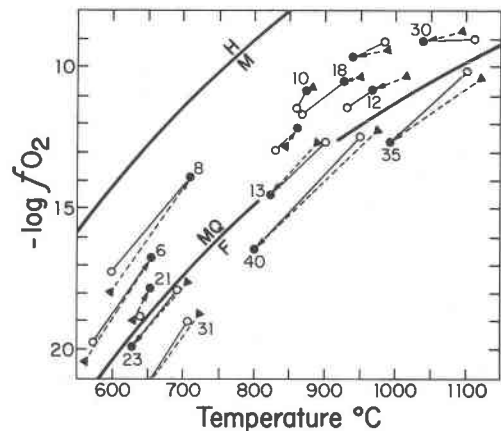


Fig. 1. Temperature and oxygen fugacity of equilibration for selected coexisting Fe-Ti oxide analyses compiled by Haggerty (1976, Table Hg-20). The numbers of the points refer to the number of the analyses in Haggerty's table. Solid circle—as calculated using the scheme recommended in this paper and the model of Spencer and Lindsley (1981). Open circle—as given in Haggerty (1976). Solid triangle—as calculated using the scheme recommended in this paper and Fig. 5 of Buddington and Lindsley (1964). The dashed line represents the shift in temperature and oxygen fugacity due to the difference between the Spencer and Lindsley (1981) and the Buddington and Lindsley (1964) geothermometers. The temperatures and oxygen-fugacities of the hematite-magnetite buffer and the fayalite-magnetite-quartz buffer are shown by the heavy lines labeled HM and FMQ. These selected data are representative of the shifts in all data so far analyzed.

values reported by Haggerty (1976). The major part of the shift is due to the differences between the Spencer and Lindsley (1981) formulation and Buddington and Lindsley's (1964) formulation of the geothermometer. The large magnitude of the shifts due to the new Spencer and Lindsley model was not expected. Although Spencer and Lindsley (1981, p. 1196) state "Readers will note only negligible differences between the old and the new curves in the vicinity of NNO and FMQ buffers. . .", the temperature and oxygen fugacity obtained in this vicinity is extremely sensitive to model (or analytical) variation because the two sets of isopleth curves intersect at a very low angle. Samples at temperatures over 800°C and at lower temperatures near the FMQ buffer are shifted to lower  $T$  and  $f_{\text{O}_2}$ . Samples plotting at low temperature and high  $f_{\text{O}_2}$  are shifted to higher  $T$  and  $f_{\text{O}_2}$ . Samples plotting near or below FMQ are shifted by as much as 150° in temperature and 4 orders of magnitude in oxygen fugacity. The shifts are generally parallel to the FMQ and HM buffer curves.

Undoubtedly such large shifts will force a reevaluation of the interpretation of much Fe-Ti oxide data, and, perhaps, raise some questions as to the validity of the Spencer and Lindsley model. The data presented here do not in themselves suggest which formulation is more

Table 1. Examples of recalculated oxide analyses

Oxide Weight Percents								
	1. SP	1. RH	2. SP	2. RH	3. SP	3. RH	4. SP	4. RH
SiO <sub>2</sub>	0.1	0.1	-	-	0.09	0.06	-	-
TiO <sub>2</sub>	7.1	44.9	3.4	42.3	28.80	50.32	28.80	50.32
Al <sub>2</sub> O <sub>3</sub>	-	-	5.7	1.5	1.18	0.02	-	-
V <sub>2</sub> O <sub>3</sub>	-	-	0.4	0.1	0.97	0.11	-	-
Cr <sub>2</sub> O <sub>3</sub>	-	-	4.0	0.5	0.02	-	-	-
Fe <sub>2</sub> O <sub>3</sub> *	52.96	7.86	52.67	22.41	10.74	4.34	10.32	2.81
FeO*	36.35	40.43	27.33	18.37	56.06	43.85	56.44	45.23
MnO	0.5	2.2	0.7	1.3	0.82	0.50	-	-
MgO	-	-	4.4	10.3	0.50	0.49	-	-
CaO	-	-	-	-	0.14	0.07	-	-
ZnO	-	-	-	-	0.12	-	-	-
Nb <sub>2</sub> O <sub>5</sub>	0.02	4.0	-	-	-	-	-	-
Total	97.03	99.49	98.60	96.78	99.44	99.76	95.56	98.34

Cations Per Formula Unit (SP.=3, RH.=2)								
Si	.0039	.0026	- - -	- - -	.0034	.0015	- - -	- - -
Ti	.2104	.8740	.0932	.7691	.8078	.9560	.8480	.9728
Al	- - -	- - -	.2448	.0428	.0519	.0006	- - -	- - -
V	- - -	- - -	.0096	.0016	.0239	.0018	- - -	- - -
Cr	- - -	- - -	.1152	.0096	.0006	- - -	- - -	- - -
Fe <sup>+3</sup>	1.5705	.1531	1.4440	.4078	.3014	.0825	.3041	.0543
Fe <sup>+2</sup>	1.1980	.8752	.8327	.3714	1.7485	.9265	1.8480	.9728
Mn	.0167	.0482	.0216	.0266	.0259	.0107	- - -	- - -
Mg	- - -	- - -	.2389	.3711	.0278	.0184	- - -	- - -
Ca	- - -	- - -	- - -	- - -	.0056	.0019	- - -	- - -
Zn	- - -	- - -	- - -	- - -	.0033	- - -	- - -	- - -
Nb <sup>+4</sup>	.0004	.0468	- - -	- - -	- - -	- - -	- - -	- - -

Recalculated Mole Fractions								
Scheme	X <sub>Usp</sub>	X <sub>I1m</sub>	X <sub>Usp</sub>	X <sub>I1m</sub>	X <sub>Usp</sub>	X <sub>I1m</sub>	X <sub>Usp</sub>	X <sub>I1m</sub>
Stormer	.209	.920	.110	.724	.866	.958	.848	.973
Anderson	.208	.919	.037	.646	.840	.957	"	"
Carmichael	.215	.923	.093	.769	.811	.958	"	"
Lindsley	.205	.915	.102	.789	.841	.958	"	"

	T°C	log fO <sub>2</sub>	T°C	log fO <sub>2</sub>	T°C	log fO <sub>2</sub>	T°C	log fO <sub>2</sub>
Stormer	710	-15.88	794	-11.40	990	-12.69	824	-16.45
Anderson	709	-15.89	724	-12.05	955	-13.21	"	"
Carmichael	704	-16.14	768	-12.12	917	-13.85	"	"
Lindsley	715	-15.61	764	-12.31	949	-13.34	"	"

1. Conway Granite analyses 12 and 17 from Whitney and Stormer, (1976).

2. Nephelinite, 855-380 from Stormer (1972).

3. Tholeiite, analysis 35 from Haggerty (1976) table Hg-20.

4. Same as 3. ignoring minor components.

\* FeO and Fe<sub>2</sub>O<sub>3</sub> as calculated from charge balance on given number of sites.

\*\* Stormer - scheme recommended in this paper.

Anderson - refer to Anderson (1968).

Carmichael - refer to Carmichael (1967).

Lindsley - refer to Lindsley and Spencer (1982).

accurate. On philosophical grounds an objective mathematical fit is preferred, but such a fit then depends upon the adequacy of the assumptions in the model.

The different effects of using each of the three recalculation schemes are shown in Table 1 and Figure 2. Analyses 1 and 2 were selected because they included

large amounts of some unusual elements. Analysis 1 contains 4 percent of Nb<sub>2</sub>O<sub>5</sub> in the rhombohedral phase. Nb and Ti commonly exhibit isomorphous substitution in a variety of oxide and silicate structures (Vlasov, 1966). The valence of Nb varies from 3+ to 5+ and it has an ionic radius in the 4+ and 5+ state that is similar to Ti.

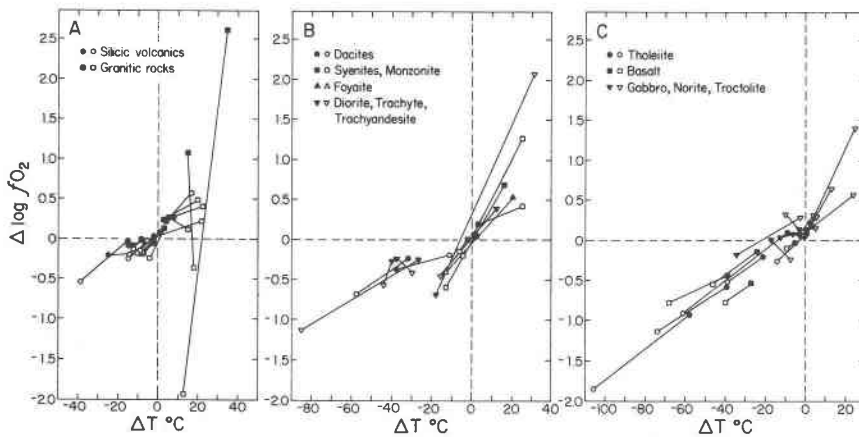


Fig. 2. The differences in temperature and oxygen fugacity between the scheme recommended in this paper and Anderson (1968)—solid symbols—and Carmichael (1967)—open symbols. All of the analyses of coexisting Fe-Ti oxides are from the compilation by Haggerty (1976, Table Hg-20) are plotted.  $T$  and  $\log f_{O_2}$  calculations are based on the model of Spencer and Lindsley (1981).

Most discussion in the geological literature (including Vlasov, 1966) assumes a valence of 5+ for Nb in all minerals. The analyses do not always show a stoichiometry requiring a 5+ valence, and in view of the ubiquitous substitution for  $Ti_{4+}$ , it seems possible that  $Nb_{4+}$  may be the ionic species in many Ti minerals. The equilibrium  $\log f_{O_2}$  calculated for the reduction of pure  $Nb_2O_5$  to  $NbO_2$  is only a few units below FMQ (data from Robie *et al.*, 1977), so that the solution of  $Nb^{4+}$  in oxide minerals is probably not unreasonable. Presence of  $Nb^{3+}$  (as assumed by Whitney and Stormer, 1976) probably does require unreasonably low oxygen fugacities. Calculation as  $Nb^{5+}$  affects the  $Fe^{3+}/Fe^{2+}$  ratio and requires either vacancies or an imbalance of  $Fe^{3+}$  on A and B sites in ilmenite. Trial calculations with analysis 1 sp show that calculation with  $Nb^{4+}$  (substituting simply for Ti) gives a more consistent  $T$  and  $f_{O_2}$ . Because rather different assumptions are made in the different schemes, it is surprising that the large amount of  $Nb^{4+}$  produces very little difference between the schemes in calculated  $T$  and  $f_{O_2}$ .

Analysis 2 was selected because of the large amounts of Mg in the rhombohedral phase and Mg and Al in the spinel phase. If the rhombohedral phase were calculated as "molecules", the amount of geikelite ( $MgTiO_3$ ) would be almost double the amount of hematite and equal to the ilmenite component. But, the greatest effect on  $T$  and  $f_{O_2}$  calculations is seen in the spinel phase (see Pinckney and Lindsley, 1976). In the Anderson scheme  $Mg_2TiO_4$  is calculated before  $Fe_2TiO_4$ . Therefore, in analyses with large amounts of Mg (not compensated by enough Al for  $MgAl_2O_4$ ) the activity of ulvöspinel is probably underestimated. The Carmichael scheme also probably underestimates  $X'_{Usp}$ . It effectively ratios Ti to all other tetrahedral cations, not just the  $Fe^{3+}$  of magnetite. There is, unfortunately, no way of determining which temperature is most correct, but the scheme presented here does give

the highest temperature (though all of the temperatures seem somewhat low for a mafic volcanic rock).

Analysis 3 shows the effect of the calculations on coexisting oxides which contain a large number of minor components, none of which is very abundant (only  $Al_2O_3$  reaches 1 wt.%). Analysis 4 shows the effect of simply ignoring these minor elements (or not analyzing for them). The important thing to note here is that the temperature changes by more than  $150^\circ$  and oxygen fugacity by almost four orders of magnitude. This difference is due largely to the difference in  $X'_{ilm}$  and it is magnified by the near parallelism of the isopleths at low oxygen fugacities as discussed above.

Figure 2 shows the difference in temperature and in  $\log f_{O_2}$  between the scheme recommended here (always plotting at 0.0) and the Anderson and Carmichael schemes. The scales of Figure 2 are greatly expanded, but the ratio of the  $T$  and  $\log f_{O_2}$  scales is the same as in Figure 1; hence  $\log f_{O_2}$  vs.  $T$  slopes are the same. Much of the scatter is very roughly parallel to the FMQ and other "buffer" curves. The values for the scheme recommended in this paper, the Anderson scheme, and the Carmichael scheme lie approximately on a line (except for a few unusual samples). This line is also parallel to the "buffer" curves. This parallelism makes it difficult to select the "best" scheme on the basis of natural data alone.

The data presented in Figure 1 show that the difference between recalculation schemes is less than  $30^\circ$  and 0.5 log unit for most samples. (This has also been the case for much data that has been calculated but not used here due to space limitations.) In a majority of cases the choice of a particular recalculation scheme could result in a shift about equal to the uncertainty in the Spencer and Lindsley model (1981, p. 1198). However, under some  $T$  and  $f_{O_2}$  conditions, the oxide equilibria are extremely sensitive with respect to compositional variation. As noted above, this sensitivity is due to the near parallelism of the

ilmenite and ulvöspinel isopleths at and below FMQ. The basalts, which show considerable scatter in Figure 2c, fall in this region.

The temperatures and oxygen fugacities calculated using the scheme presented here are in many cases intermediate between those calculated by the Anderson and Carmichael schemes (see Analysis 1, Table 1 for an example with unusual composition). Considering all cases, there is a tendency for the variation due to the Anderson or Carmichael calculation scheme to scatter equally to values higher and lower than the scheme presented here. (Interestingly, the scheme presented here is generally closer to the Anderson scheme than the Carmichael scheme.) The scheme proposed by Lindsley and Spencer (1982) also produces variations similar to those shown. Temperature and  $\log f_{\text{O}_2}$  are usually within the range of the Anderson or Carmichael schemes but do not consistently follow either.

### Conclusions

The minor components in the Fe-Ti oxides can have a significant effect on the temperatures and oxygen fugacities calculated using the Spencer and Lindsley (1981) or Buddington and Lindsley (1964) geothermometers. The calculation of the proper apparent mole fractions of ulvöspinel and ilmenite to use in these geothermometers is important. Unfortunately, there are not sufficient experimental data to adequately determine the effects of the minor components and to properly account for them in recalculation for geothermometry. Alumina, in particular, is often present in significant amounts and is likely to have a highly non-ideal relationship. The experimental determination of its effect on the activity of magnetite and ulvöspinel in Fe-Ti oxide spinel phases would be very important work.

The Anderson (1968) and Carmichael (1967) schemes for the recalculation of multicomponent Fe-Ti oxides are typical of previous attempts to account for the minor components. These schemes depend upon the calculation of mineral "molecules" in a specified sequence. The scheme recommended here is derived from a consideration of a simple ideal model of substitution in the Fe-Ti oxide minerals. This scheme is more consistent with the model used by Spencer and Lindsley for fitting the experimental data (at least for the rhombohedral phase). This scheme or some similar model should be more useful as a basis for consideration of the real effects of the substitution of the various minor constituents.

For the majority of coexisting Fe-Ti oxide samples, the difference between recalculation schemes will be of the same magnitude as the uncertainty in the model for the pure system. However, in some cases there will be a significant difference, and for all cases precise comparisons between suites of samples will require the use of a consistent recalculation scheme. The scheme recommended here gives temperature and oxygen fugacity

values that are generally intermediate with respect to the Anderson and Carmichael schemes.

The position of the ilmenite and ulvöspinel isopleth curves shown by Spencer and Lindsley (1981) are only slightly shifted with respect to temperature and oxygen fugacity, from those of Buddington and Lindsley (1964). However, the changes in temperature and oxygen fugacity obtained for many samples will be very significantly different. Values obtained with the Buddington and Lindsley (1964) geothermometer cannot be directly compared with values obtained using the Spencer and Lindsley geothermometer. Older data *must* be reevaluated using the Spencer and Lindsley calibration before comparisons can be made.

*Note added in proof*

It has recently become apparent that the discrepancy between the Buddington and Lindsley (1964) and the Spencer and Lindsley (1981) geothermometers could be due to the assumption of constant  $\Delta H$  and  $\Delta S$  over a very large temperature range for the exchange reaction (equations 1 and 11 in Spencer and Lindsley, 1981). There may be a significant temperature coefficient as seen in a  $\Delta C_p$  about 10 Joules/deg.K. Recent rock melting experiments (R. Helz, pers. comm.) suggest that temperatures obtained using the Buddington and Lindsley (1964) curves *may* be more accurate, at least for basaltic rocks near and below the QFM oxygen buffer curve. This does not affect the major conclusions of this paper, and the recalculation procedure presented here is applicable to either geothermometer.

### Acknowledgments

The assistance of Dr. Jim Whitney in discussing early ideas and reviewing various versions of this paper was essential as were reviews by D. H. Lindsley and W. P. Leeman. This work was partially supported by National Science Foundation Grants EAR-7818127 and 8204568 and the U.S. Geological Survey. Jane, Karen, and Eric Stormer helped provide the funds for the purchase of the computer system (APPLE II+) used for this work.

### References

- Anderson, A. T. (1968) Oxidation of the LaBlache Lake titaniferous magnetite deposit, Quebec. *Journal of Geology*, 76, 528-547.
- Akimoto, S. (1954) Thermo-magnetic study of ferromagnetic minerals contained in igneous rocks. *Journal of Geomagnetism and Geoelectricity*, 6, 1-14.
- Bloss, F. D. (1971) *Crystallography and Crystal Chemistry*. Holt, New York.
- Buddington, A. F. and Lindsley, D. H. (1964) Iron-titanium oxide minerals and synthetic equivalents. *Journal of Petrology*, 5, 310-357.
- Carmichael, I. S. E. (1967) The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contributions to Mineralogy and Petrology*, 14, 36-64.
- D'Arco, Phillippe and Maury, R. C. (1981) Comparative geothermometry of some magnetite-ilmenite-orthopyroxene-clino-



- pyroxene associations from volcanic rocks. *Canadian Mineralogist*, 19, 461-467.
- Ghiorso, M. S. and Carmichael, I. S. E. (1981) A FORTRAN IV computer program for evaluating temperatures and oxygen fugacities from the compositions of coexisting iron-titanium oxides. *Computers and Geosciences*, 7, 123-129.
- Haggerty, S. E. (1976) Opaque mineral oxides in igneous rocks. In D. Rumble III, Ed., *Oxide Minerals*, p. Hg-101-300. Mineralogical Society of America Short Course Notes.
- Ishikawa, Y. (1958) An order-disorder transformation phenomenon in the  $\text{FeTi}_3\text{-Fe}_2\text{O}_3$  solid solution series. *Journal of the Physical Society of Japan*, 13, 828-813.
- Lawson, C. A., Nord, G. L., Jr., Dowty, E., and Hargraves, R. B. (1981) Antiphase domains and reverse thermoremanent magnetism in ilmenite-hematite minerals. *Science*, 213, 1372-1374.
- Levin, E. M., Robbins, C. R., and McMurdie, H. F. (1964) Phase Diagrams for Ceramists, Supplement (1969). The American Ceramic Society.
- Lindsley, D. H. (1976a) The crystal chemistry and structure of oxide minerals as exemplified by the Fe-Ti oxides. In D. Rumble III, Ed., *Oxide Minerals*, p. Hg-101-300. Mineralogical Society of America Short Course Notes.
- Lindsley, D. H. (1976b) Experimental studies of oxide minerals. In D. Rumble III, Ed., *Oxide Minerals*, p. Hg-101-300. Mineralogical Society of America Short Course Notes.
- Lindsley, D. H., and Spencer, K. J. (1982) Fe-Ti oxide geothermometry: Reducing analyses of coexisting Ti-Magnetite (Mt) and Ilmenite (Ilm). *Transactions, American Geophysical Union*, 63, 471.
- Muan, Arnulf (1975) Phase relations in chromium oxide-containing systems at elevated temperatures. *Geochimica et Cosmochimica Acta*, 39, 791-802.
- Navrotsky, Alexandra and Kleppa, O. J. (1967) The thermodynamics of cation distributions in simple spinels. *Journal of Inorganic and Nuclear Chemistry*, 29, 2701-2714.
- Pinckney, L. R. and Lindsley, D. H. (1976) Effects of magnesium on iron-titanium oxides. *Geological Society of America, Abstracts with Programs*, 1976 Annual Meetings, 8, 1051.
- Price, G. D., Price, S. L., and Burdett, J. K. (1982) The factors influencing cation site preferences in spinels, a new mendeleevian approach. *Physics and Chemistry of Minerals* 8, 69-76.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978) *Thermodynamic Properties of Minerals and Related Substances*. U.S. Geological Survey Bulletin 1452, U.S. Government Printing Office, Washington, D.C.
- Rumble III, D. (1977) Configurational entropy of magnetite-ulvospinel<sub>ss</sub> and hematite-ilmenite<sub>ss</sub>. *Carnegie Institution of Washington Yearbook*, 76, 581-584.
- Sack, R. O. (1982) Spinels as petrogenetic indicators: activity composition relations at low pressures. *Contributions to Mineralogy and Petrology*, 79, 169-186.
- Sack, R. O., Carmichael, I. S. E., Rivers, M., and M. S. Ghiorso (1980) Ferric-ferrous equilibria in natural silicate liquids at 1 bar. *Contributions to Mineralogy and Petrology*, 75, 369-376.
- Spencer, K. J. and Lindsley, D. H. (1981) A solution model for coexisting iron-titanium oxides. *American Mineralogist*, 66, 1189-1201.
- Stormer, J. C., Jr. (1972) Mineralogy and petrology of the Raton-Clayton volcanic field, northeastern New Mexico. *Geological Society of America Bulletin*, 83, 3299-3322.
- Vlasov, K. A. (1964) *Geochemistry and Mineralogy of Rare Elements and Genetic Types of Their Deposits, Volume II Mineralogy of Rare Elements*. Academy of Sciences of the USSR, Moscow (transl. Israel Program for Scientific Translations, Cat. No. 2123, 1966).
- Wechsler, B. A. (1981) *Crystallographic Studies of Titanomagnetite and Ilmenite*. Ph.D. Thesis, State University of New York at Stony Brook, New York (not seen: extracted from Spencer and Lindsley, 1981).
- Whitney, J. A. and Stormer, J. C., Jr. (1976) Geothermometry and Geobarometry in epizonal granitic intrusions: a comparison of iron-titanium oxides and coexisting feldspars. *American Mineralogist*, 61, 751-761.

*Manuscript received, April 23, 1982;  
accepted for publication, December 21, 1982.*