Nonstoichiometry of magnetite-ulvöspinel solid solutions quenched from 1300 °C

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ABSTRACT

Magnetite-ulvöspinel (Fe₅O₈·Fe₃TiO₄) solutions were synthesized in CO₂ + H₂ atmospheres and quenched from 1300 °C to liquid N₂. The fₒ₂ during synthesis was monitored by a solid electrolyte cell (ZrO₂ with 9% Y₂O₃). There are noticeable differences in unit-cell parameters, a₀, of samples synthesized with the same Ti/Fe ratio but under different fₒ₂ conditions. The samples obtained under relatively reducing conditions at the boundary with fields containing wüstite or metallic Fe have systematically higher a₀ values than ulvöspinel coexisting with rhombohedral solid solutions or synthesized near this boundary under relatively oxidizing conditions. The change in a₀ across the solid-solution field at a fixed Ti/Fe ratio becomes more pronounced and approaches 0.01 Å for high Ti compositions. The unit-cell parameter variation at a constant Ti/Fe ratio is related to the deviation from stoichiometry [Fe + Ti]/3 < 1 for the solution Feₓ₋₁₋ₓ·TiₓO₄₋ₓ₋₊. Trends were obtained in the cation to O ratio with increasing fₒ₂ at fixed Ti/Fe by direct O analysis using the electron microprobe. A gain of approximately 2 mol% O (y = 0.08) for quenched samples with x ≥ 0.7 under the most oxidizing conditions is seen relative to samples quenched under reducing conditions and assumed to be stoichiometric (y = 0). A phase diagram in x - fₒ₂ space at 1300 °C is presented.

INTRODUCTION

The study of magnetite-ulvöspinel (Fe₅O₈·Fe₃TiO₄) solutions is stimulated by their interest to the materials science community (Fe metallurgy, ferrites) and Earth science community (indicators of magnetic, redox, and thermal history of rocks). Important features of these solid solutions, though complete in terms of continuous Fe-Ti variation, are not really pseudobinary because they depart from stoichiometry, (Fe + Ti)/3 < 1/3, because of oxidation (Webster and Bright, 1961; Taylor, 1964; Katsumi et al., 1976; Simon and Woermann, 1978).

When synthesized at low fₒ₂, in equilibrium with wüstite, magnetite-ulvöspinel solutions contain little cation excess (Dieckmann, 1982; Aragon and McCallister, 1982), and their composition varies essentially along the stoichiometric magnetite-ulvöspinel join, Feₓ₋₁₋ₓ·TiₓO₄₋ₓ₋₊. As oxidation proceeds with increasing fₒ₂, the reactions at constant cation composition produce phases enriched in O relative to cations, Ti + Fe. Keeping the total number of cations equal to 3, the magnetite-ulvöspinel solution composition could be expressed by the formula Feₓ₋₁₋ₓ·TiₓO₄₋ₓ₋₊, with y a convenient indicator of nonstoichiometry. However, oxidation occurs with an increase in the Fe³⁺/Fe²⁺ ratio and with the formation of cation vacancies while the O sublattice remains intact (Dieckmann, 1982; Aragon and McCallister, 1982).

Deviations from stoichiometric compositions although noticeable, are generally small at high temperatures. Estimations of this rather narrow nonstoichiometric range are scarce and fragmentary. Taylor (1964), from gravimetric experiments at 1300 °C, suggested that the maximum amount of vacancies did not depend on the Ti content and could probably approach about 2 mol%. Similar values were obtained for magnetite from in situ high-temperature measurements (Dieckmann, 1982) and for a sample, Feₓ₋₁₋ₓ·TiₓO₄₋ₓ₋₊, weighed after quenching from 1275 °C (Hauptman, 1974).

Magnetite-ulvöspinel solutions can be oxidized to Ti-bearing maghemite (γ-phase) spinel at low temperatures (<400 °C). Its range of nonstoichiometry is much greater than that seen at high temperatures and includes the fully oxidized composition with no Fe²⁺ present. In the Ti-free end-member that is γ-Fe₂O₃, Feₓ₋₁₋ₓ·O_y with y = 0.08. However, this oxidized Ti-bearing maghemite is generally poorly crystalline and metastable. The degree of oxidation and the compositional variation in these samples correlate with the observed unit-cell parameter change (Readman and O'Reilly, 1972; Nishitani and Kono, 1983; Goss, 1988).

The aim of this study was to refine the limits of compositional variation in magnetite-ulvöspinel solutions, synthesized and quenched from 1300 °C, and to determine the variation of O content with fₒ₂ and with the Fe/Ti ratio. These samples will then be used for further structural and thermochemical studies. In this paper we report the synthesis procedures, unit-cell measurements, a phase diagram in x - fₒ₂ space, and compositions, both Ti/Fe ratios and O contents, based on electron microprobe analyses.
Starting materials and synthesis procedure

Dried Fe₂O₃ and TiO₂ (both 99.999% purity, Johnson Mathey Inc.) were used for mixture preparation. The reagents were ground together in an agate mortar under methanol, dried, pressed into pellets of 120–150 mg, and sintered in air at 1200 °C. The sintered pellets were wrapped in 0.1-mm Pt wire, suspended at the level of the hot spot in a Deltech vertical tube furnace, and annealed for 1–2 d at 1300 °C. This period significantly exceeds the estimates of time needed by 3–6 h, for Fe-Ti oxide equilibration with gas atmospheres at 1300 °C, based on weight loss and gain (Taylor, 1964; Hauptman, 1974). Microprobe analysis (see below) showed the samples to be homogeneous in Fe/Ti ratio and O content (except for oxidized quench rims, discussed below). Thus we considered it unnecessary to do several cycles of grinding and annealing. The reproducibility of temperature between experiments was ±5 °C.

A H₂–CO₂ gas mixture at total pressure of 1 atm was used to create various fO₂ values (Deines et al., 1974). A CO₂–O₂ atmosphere was also used to maintain higher fO₂ values (log fO₂ > -3). Gas flowed from the top to the bottom of the furnace tube.

The fO₂ was monitored using a solid electrolyte cell of ZrO₂ with 9 wt% Y₂O₃. Total gas flow was 100 cc/min. Values of log fO₂ were calculated from emf measurements, with air as a reference. More details of gas flow regulation and emf measurement are in Brown et al. (in preparation). The cell was calibrated at 1300 °C against the Ni + NiO and wustite + magnetite buffers. Equilibrium log fO₂ values of these reactions at 1300 °C, estimated from equations summarized by Chou (1987) vary in a range of about 0.1 in log fO₂ for both buffers. Our measurements fall into the cited ranges. The uncertainty in calculated log fO₂ values is ±0.05.

At the end of an experiment, a special bottom plug on the furnace tube was opened, the Pt wire which held the pellet was burned and the pellet fell into liquid N₂.

A potential problem is Fe loss to any Pt container or wire holding the samples. Our Pt wires were not presaturated with Fe (that would have made them too brittle to bend). However, the length of the wire, 0.1 mm in diameter, in contact with a pellet of 120–150 mg, was <30 mm, and its weight <5 mg. Even if the Pt absorbed its own weight in Fe (a worst case), the change in Fe/(Ti + Fe) in a typical sample would be on the order of 2 mol%.

The microprobe analyses (see below) indeed confirmed that the analyzed ratios were within 2% or better of the stoichiometries, and the analyzed compositions were used in further calculations. Thus we believe that Fe loss is not a serious complication in these experiments.

X-ray diffraction

Quenched samples were studied by X-ray diffraction at room temperature with a Scintag PAD V powder automated diffractometer equipped with a solid-state detec-

The lattice parameter was refined using the least-squares procedure of Appleman and Evans (1973). Some 8–15 reflections (25° < 2θ < 100°) were used in each refinement.

The 2 σd error of the a₀ value refined for one X-ray pattern usually exceeds the deviation from the mean of the a₀ value for several patterns of the same sample. We show the standard deviation of the mean value, or 2 σd of the individual fit if a sample was scanned only once. In most cases the error is better than ±0.002 Å.

Electron microprobe analysis

Part of each quenched sample was polished and used for optical microscopy and electron microprobe analysis. Reflected light microscopy was used for preliminary characterization of samples to determine phase homogeneity, distribution of pores, and other features.

The Jeol JXA-8600 Superprobe at Rutgers University was used with 15-KeV accelerating voltage, and 20-nA specimen current. The beam diameter was about 1 μm. The crystals used were PET for Ti, LiF for Fe, and LDEI for O.

Special care was taken during sample preparation. Polishing and coating of specimens in each group analyzed were performed simultaneously under the same conditions and calibrated against the same reference sample. To improve counting statistics, the counting time was increased to 100 s, which gave a standard deviation of 0.3% for O. A further increase in analysis time was not desirable because of deterioration in the O count rate due to sample damage under the electron beam. Another factor limiting count time was contamination by a precipitate, probably formed from traces of hydrocarbons polymerized by the beam.

Natural pure magnetite and ilmenite (Anderson, 1968) were used for calibration of Fe, Ti, and O. Fe was calibrated against magnetite and Ti against ilmenite. When analyzing spinel solid solution with x < 0.5, Ti(Ti + Fe) < 0.166, O was calibrated against magnetite. If Ti(Ti + Fe) was >0.166, the O was calibrated against ilmenite.

Shorter counting times (up to 1% sd) were used when routine analyses were aimed only at Ti/Fe ratio calculations.

Despite the care taken, we were not satisfied with the absolute values of O contents. Totals (Fe + Ti + O) ranged from 99 to 101%. The O contents determined depended too much on which standard (magnetite or ilmenite) was used. These problems were not surprising and are caused by the high absorption of O X-rays by other elements (which render standard correction procedures inadequate), by the lack of well-analyzed O standards, and by the high degree of accuracy and precision needed to determine small degrees of nonstoichiometry.
Realizing that we needed highly precise measurements of the change in the O content with \( f_{O_2} \), we decided to adopt a relative procedure, which provided trends in O content for samples with similar Ti/Fe ratios by using, as a standard for each group, a sample produced under low \( f_{O_2} \), a relative procedure, which provided trends in O content for samples with similar Ti/Fe ratios by using, as a standard for each group, a sample produced under low \( f_{O_2} \), a relative procedure, which provided trends in O content for samples with similar Ti/Fe ratios by using, as a standard for each group, a sample produced under low \( f_{O_2} \), a relative procedure, which provided trends in O content for samples with similar Ti/Fe ratios by using, as a standard for each group, a sample produced under low \( f_{O_2} \). This procedure is described further below. With this procedure, the relative error in O to cation ratio determination did not exceed 1%. The error in Ti/(Ti + Fe) ratio determination was several thousandths, and the absolute error in \( x \) (mole fraction of ulvöspinel) did not exceed ±0.01. This study represents the determination of much smaller deviations from stoichiometry than the microprobe analyses of Furuta et al. (1985) on more oxidized low-temperature samples.

**RESULTS**

**Phase boundaries**

The results of synthesis are shown in Table 1 and Figure 1. Magnetite-ulvöspinel solutions synthesized as single phases with a constant Ti/(Ti + Fe) ratio lie along vertical lines crossing the field in Figure 1. Only a gain or loss of O can be involved in change of composition along these O reaction lines. The \( f_{O_2} \) range for constant Ti/Fe composition is terminated from above by the boundary with the two-phase field of spinel + rhombohedral phase (hematite-ilmenite) and from below by spinel + wüstite or metallic Fe associations. The log \( f_{O_2} \) values indicate that the phase assemblages in Fe-Ti-O at 1300 ± 5 °C are limited by a large number of phase boundaries shown in Figure 1. Only a gain or loss of O can be involved in change of composition along these O reaction lines. The \( f_{O_2} \) range for constant Ti/Fe composition is terminated from above by the boundary with the two-phase field of spinel + rhombohedral phase (hematite-ilmenite) and from below by spinel + wüstite or metallic Fe associations. The log \( f_{O_2} \) values indicate that the phase assemblages in Fe-Ti-O at 1300 ± 5 °C are limited by a large number of phase boundaries shown in Figure 1.
as a single phase (sample 78) bracketed the wüstite + magnetite equilibrium, located at $f_{O_2} = -7.50$. The magnetite-hematite boundary is located at $f_{O_2} = -1.59$ by this two-phase synthesis product (sample 87). Both these equilibria confirm earlier evaluations of these buffer reaction parameters (Chou, 1987).

At low $f_{O_2}$ (Fig. 1) an invariant equilibrium, spinel + wüstite + metallic Fe, separates the wüstite + spinel from the Fe + spinel regions. The $f_{O_2}$ values of this equilibrium must be between $f_{O_2} = -10.07$ (spinel + wüstite, sample 36) and $f_{O_2} = -11.03$ (spinel + metallic Fe, sample 51). This is in agreement with the estimation of the invariant equilibrium at $f_{O_2} = -10.65$ (Simons and Woermann, 1978). The equilibrium marks a break on the lower boundary of the spinel field because the boundary curve must change slope when transferring from the association of wüstite + spinel to the Fe + spinel. Spinel equilibrated with wüstite is assumed to have virtually stoichiometric O content. The change of slope then means a departure from magnetite-ulvöspinel stoichiometry. The limiting point of stoichiometric phase stability is at approximately 90 mol% ulvöspinel. Spinels with $x > 0.9$ can have only nonstoichiometric compositions.

High-Ti specimens can have a noticeable excess of Ti over the ideal ratio in ulvöspinel of $Ti/(Fe + Ti) = 0.333$, for example, spinel no. 83, Tables 1, 2. This spinel, with $Ti/(Fe + Ti) = 0.355$ was produced at $f_{O_2} = -11.00$ with ilmenite, which was nonstoichiometric too, under conditions approaching those of invariant equilibrium spinel + ilmenite + Fe, which defines the lowest $f_{O_2}$ of the ulvöspinel stability range.

Under strongly reducing conditions, Fe becomes significantly volatile. Ti-rich spinels formed under these conditions have a Ti/Fe ratio that differs from that of the starting material because of Fe loss, especially after longer experiments (sample 42 in Table 1). This is also the region where the Fe loss to Pt is greatest.

Unit-cell parameters

Variation in the unit-cell parameter, $a_0$, along the O-reaction lines may indicate stoichiometric change at a constant $Ti/(Ti + Fe)$ ratio (see Fig. 3). The unit-cell parameter decreases as $f_{O_2}$ increases. When $x < 0.7$, the range of $a_0$ variation becomes as great as approximately 0.01 Å.

In the Fe-rich part of the system, the changes in $a_0$ are not so pronounced, despite the wider range of $f_{O_2}$ variation. A decrease of $a_0$ near the high $f_{O_2}$ boundary can be detected, however, even for magnetite-rich compositions.

Electron microprobe analysis

To avoid problems of incompatibility of O determinations when samples had different Ti/Fe ratios, we divided analyses into groups with narrow ranges in composition (Table 2, Fig. 1).

Within each group, we chose a reference sample that was essentially stoichiometric with respect to O. These were samples 78, 74, and 32, which were synthesized at
conditions near the stability of wüstite + spinel, and sample 51, which was equilibrated at conditions near the wüstite + Fe + spinel invariant equilibrium (Fig. 1). The assumption that these samples are essentially stoichiometric (three cations to four O atoms) relies on the work of Dieckmann (1982) for magnetite and Simons and Woermann (1978) for magnetite-ulvöspinel solutions. Instead of cation vacancies and a full O sublattice [corresponding to $(\text{Fe} + \text{Ti})/\text{O} < \frac{3}{4}$], under strongly reducing conditions there is a slight metal excess (O deficiency), accommodated by cation interstitials, and resulting in $(\text{Fe} + \text{Ti})/\text{O} > \frac{3}{4}$. However, the extent of this O loss is at least an order of magnitude less than that of the O gain under oxidizing conditions, and, thus, from the point of view of the analysis here, these samples can be assumed stoichiometric in metal to O ratio (though some Ti$^{3+}$ may be present).

Averaged values for several analyses of each sample are given in Table 2. Standard deviation for each set is given in parentheses. The amounts of Fe, Ti, and O were used to calculate cation to cation and O to cation ratios. To eliminate probable systematic uncertainties in O results, the O to cation ratios were corrected on the basis of the assumption that, in the reference sample, this ratio must be $\frac{\text{O}}{(\text{Ti} + \text{Fe})} = \frac{7}{9}$.

Taking into account that the systematic error for all samples within the same group is the same, we found a group correction factor, $C$, common to each group. For the assumed stoichiometric reference sample, with $r = \frac{\text{O}}{(\text{Ti} + \text{Fe})}$,

$$C = r(\text{stoich})/r(\text{obs}) = 1.333/r(\text{obs}).$$

(1)

For other analyzed samples in the same group [with similar $\frac{\text{Ti}}{(\text{Ti} + \text{Fe})}$]

$$r(\text{corr}) = C \cdot r(\text{obs}).$$

(2)

These corrected O to cation ratios are also given in Table 2.

Figure 1 shows that the O increase became more significant in more Ti-rich spinels, when $x \geq 0.7$. The spinels in this region have $y$ for samples synthesized at the boundary with ilmenite in the range of 0.06–0.10, which corresponds to the gain of 1.5–2.5 mol% O relative to reference samples. In Fe-rich spinels, the O gain does not exceed the error of its determination. This correlates with the less pronounced variation of unit-cell parameters for those compositions.

**DISCUSSION**

Figure 4 shows $a_0$ values for spinels from two-phase boundary associations (spinel + rhombohedral phase, spinel + wüstite, spinel + Fe) or produced at $f_{O_2}$ near the boundaries. The samples synthesized and quenched under most reducing conditions have systematically higher $a_0$ values for a given $\frac{\text{Ti}}{(\text{Fe} + \text{Ti})}$. These spinels, which are presumed to be stoichiometric and associated with wüstite, lie along the upper curve, which almost coincides with the unit-cell parameter curve from Wechsler et al. (1984) for compositions with $x < 0.7$.

For compositions with $x > 0.9$, the boundary ulvöspinel coexists with metallic Fe. The unit-cell parameter of this spinel does not vary strongly with composition.

The lower curve (Fig. 4) is for spinels coexisting with the rhombohedral phase. The decrease in $a_0$ of these samples is further evidence for nonstoichiometry. The direction of the unit-cell parameter change is the same as in the case of low-temperature spinel oxidation and the formation of Ti-bearing maghemite (Readman and O'Reilly, 1972; Nishitani and Kono, 1983).

The $a_0$ value of quenched spinels correlates with composition (Fig. 4), confirming the s-shaped dependence of $a_0$ on the $\frac{\text{Ti}}{(\text{Fe} + \text{Ti})}$ ratio in both the stoichiometric and nonstoichiometric series (Lindsley, 1965; Banerjee et al., 1967; Wechsler et al., 1984). However, their studies did not consider the nonstoichiometry, $y$. The dependence of the $a_0$ decrease on a change in $y$ is shown in Figure 5. Data for spinel pairs of the same $\frac{\text{Ti}}{(\text{Fe} + \text{Ti})}$
### Table 2. Microprobe analyses and phase compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (wt%)</th>
<th>Ti (wt%)</th>
<th>O (wt%)</th>
<th>Total (wt%)</th>
<th>Fe (at%)</th>
<th>Ti (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78* (n = 9)</td>
<td>72.599 (182)</td>
<td>0.000</td>
<td>27.590 (177)</td>
<td>100.189</td>
<td>42.982 (107)</td>
<td>0.000</td>
<td>57.018 (365)</td>
</tr>
<tr>
<td>87 (n = 5)</td>
<td>72.594 (252)</td>
<td>0.008 (7)</td>
<td>27.750 (155)</td>
<td>100.352</td>
<td>42.836 (149)</td>
<td>0.006 (5)</td>
<td>57.158 (319)</td>
</tr>
<tr>
<td>34 (n = 5)</td>
<td>70.366 (181)</td>
<td>1.856 (25)</td>
<td>27.600 (62)</td>
<td>99.852</td>
<td>41.668 (95)</td>
<td>1.281 (17)</td>
<td>57.050 (126)</td>
</tr>
<tr>
<td>62 (n = 6)</td>
<td>70.303 (137)</td>
<td>1.880 (8)</td>
<td>27.582 (94)</td>
<td>99.765</td>
<td>41.655 (81)</td>
<td>1.299 (6)</td>
<td>57.046 (194)</td>
</tr>
<tr>
<td>78 (n = 7)</td>
<td>70.935 (146)</td>
<td>1.363 (48)</td>
<td>27.618 (35)</td>
<td>99.916</td>
<td>41.991 (86)</td>
<td>0.941 (33)</td>
<td>57.068 (72)</td>
</tr>
<tr>
<td>74* (n = 6)</td>
<td>61.063 (267)</td>
<td>10.465 (114)</td>
<td>28.638 (216)</td>
<td>100.166</td>
<td>35.250 (154)</td>
<td>7.043 (77)</td>
<td>57.707 (435)</td>
</tr>
<tr>
<td>10 (n = 5)</td>
<td>61.452 (269)</td>
<td>10.370 (92)</td>
<td>28.996 (117)</td>
<td>100.818</td>
<td>35.164 (154)</td>
<td>6.918 (61)</td>
<td>57.917 (234)</td>
</tr>
<tr>
<td>32* (n = 5)</td>
<td>57.456 (116)</td>
<td>14.966 (38)</td>
<td>27.276 (63)</td>
<td>99.669</td>
<td>33.744 (68)</td>
<td>10.258 (26)</td>
<td>55.968 (129)</td>
</tr>
<tr>
<td>28 (n = 5)</td>
<td>57.356 (77)</td>
<td>14.996 (44)</td>
<td>27.734 (131)</td>
<td>100.086</td>
<td>33.415 (45)</td>
<td>10.186 (30)</td>
<td>56.400 (266)</td>
</tr>
<tr>
<td>47 Sp (n = 5)</td>
<td>56.769 (104)</td>
<td>15.396 (44)</td>
<td>27.633 (65)</td>
<td>99.798</td>
<td>33.164 (61)</td>
<td>10.478 (30)</td>
<td>56.349 (133)</td>
</tr>
<tr>
<td>51* (n = 19)</td>
<td>51.257 (282)</td>
<td>19.837 (163)</td>
<td>29.450 (171)</td>
<td>100.544</td>
<td>28.929 (159)</td>
<td>13.053 (107)</td>
<td>58.018 (337)</td>
</tr>
<tr>
<td>42 (n = 10)</td>
<td>50.056 (157)</td>
<td>20.934 (39)</td>
<td>28.678 (175)</td>
<td>100.127</td>
<td>28.211 (88)</td>
<td>12.579 (65)</td>
<td>58.387 (344)</td>
</tr>
<tr>
<td>43 (n = 14)</td>
<td>51.521 (180)</td>
<td>19.294 (100)</td>
<td>30.025 (239)</td>
<td>100.840</td>
<td>28.811 (68)</td>
<td>12.579 (65)</td>
<td>58.609 (467)</td>
</tr>
<tr>
<td>73 Sp (n = 5)</td>
<td>49.792 (85)</td>
<td>20.150 (19)</td>
<td>29.640 (93)</td>
<td>99.402</td>
<td>27.922 (47)</td>
<td>13.339 (13)</td>
<td>58.389 (383)</td>
</tr>
<tr>
<td>75 Sp (n = 3)</td>
<td>49.297 (158)</td>
<td>20.597 (42)</td>
<td>29.450 (131)</td>
<td>99.344</td>
<td>27.992 (90)</td>
<td>13.636 (28)</td>
<td>58.372 (260)</td>
</tr>
<tr>
<td>54 (n = 7)</td>
<td>48.717 (116)</td>
<td>21.356 (50)</td>
<td>27.934 (326)</td>
<td>99.807</td>
<td>27.461 (65)</td>
<td>14.035 (32)</td>
<td>58.504 (641)</td>
</tr>
<tr>
<td>83 Sp (n = 5)</td>
<td>47.722 (174)</td>
<td>22.538 (97)</td>
<td>25.752 (134)</td>
<td>100.012</td>
<td>28.832 (98)</td>
<td>14.775 (84)</td>
<td>58.393 (263)</td>
</tr>
</tbody>
</table>

* Reference sample.
** Number of analyses.
† On the base of Ti + Fe = 3.

ratio are used to find Δa and Δy values. These pairs are samples 34-62, 78-87, 72-54, 71-10, 51-43, 32-38, and 42-73 (Table 2). A correlation between the Δy increase and the Δa decrease appears to exist independent of Ti/(Fe + Ti), and a 0.01 Å decrease in Δa corresponds, on average, to a Δy = 0.08 O gain. The unit-cell parameter, therefore, does serve as an indicator of nonstoichiometry. We suggest that part of the decrease in the data of Wechsler et al. (1984) for Δa of magnetite-ulvöspinel solutions with x > 0.7 can be attributed to deviation from stoichiometry, which, though it was not characterized by Wechsler et al., was also not excluded.

Figure 6 shows proposed phase relations. The nonstoichiometry range of quenched spinels decreases as the magnetite content increases.

Transformation from a stoichiometric phase Fe₃₋₂Ti₂O₄ to a nonstoichiometric phase Fe₃₋₂Ti₂O₄₋ₓ, resulting from oxidation, can be described as

\[
(1 + x)\text{Fe}^{2+} + [(1 + x)\frac{z}{4}]\text{O}_2 \\
\rightarrow (1 + x)(1 - z)\text{Fe}^{3+} + [(1 + x)z]\text{Fe}^{3+} \\
+ [(1 + x)z/2]\text{O}^{2-} + [3(1 + x)z/8] \square. \quad (3)
\]

Here z is the atomic fraction of oxidized Fe²⁺ ions in the total number (1 + x) of Fe²⁺ in an unoxidized initial specimen. Then \( y = \frac{1}{2}(1 + x)z \). This expression permits us to calculate z from O gain data, y, and estimate the Fe²⁺/Fe³⁺ ratio in spinels (Table 2).

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![Fig. 4. Unit-cell parameter variation along high and low fO₂ boundaries of the spinel field.](image_url)

![Fig. 5. Correlation of y with Δa change.](image_url)
Oxidation (Reaction 3) is accompanied by a vacancy formation. Vacancies can also result from an Fe-Ti substitution:

$$2\text{Fe}^{2+} \rightarrow \square + \text{Ti}^{4+}.$$ (4)

This mechanism must be the only one effective for the formation of nonstoichiometric spinel on the FeO-TiO$_2$ join (Fig. 6). This is probably the case for sample 83 (Table 2). It is a nonstoichiometric spinel formed, with ilmenite, near the low $f_{O2}$ limit of the spinel field. It is reasonable to assume that, for this very Ti-rich sample synthesized under strongly reducing conditions, Fe$^{2+}$ is absent, and Ti$^{3+}$ can probably be neglected. Although a small amount of Ti$^{3+}$ was proposed as a component in the ultraspinel solid solution in equilibrium with ilmenite and Fe at this temperature (Simons and Woernmann, 1978), direct evidence of its existence is lacking, and in any case, the Ti$^{3+}$ fraction in the spinel must be very small.

Figure 6 shows that coexisting spinel and ilmenite compositions (Table 1) are linked by connode lines. It follows that the mechanism for the ilmenite solid solution within the low $f_{O2}$ limit of the spinel field is the only one effective for the formation of nonstoichiometric spinel on the FeO-TiO$_2$ join. Evidently, Ti$^{3+}$ can probably be neglected. Although a small amount of Ti$^{3+}$ was proposed as a component in the ultraspinel solid solution in equilibrium with ilmenite and Fe at this temperature (Simons and Woernmann, 1978), direct evidence of its existence is lacking, and in any case, the Ti$^{3+}$ fraction in the spinel must be very small.

Figure 6 shows that coexisting spinel and ilmenite compositions (Table 1) are linked by connode lines. It follows that the ilmenite solid solution that would preferentially accommodate Ti$^{3+}$ in equilibrium with ultraspinel. The composition of a nonstoichiometric spinel may be expressed as (Fe$_{m}$Ti$_{n}$O$_{2m+2n}$). From electron microprobe analysis (Tables 1, 2), $n/(m + n)$ is known. Together with electroneutrality ($2m + 4n = 8$) and cation site number ($m + n + q = 3$), we have enough constraints to find $m$, $n$, and $q$. The calculations for the spinel phase from sample 83 give (Fe$_{1.90}$Ti$_{0.04}$O$_{2.04}$) or (Fe$_{1.93}$Ti$_{0.06}$)O$_{4.06}$. The estimated value of $y = 0.065$ is very close to the analytical data for this sample ($y = 0.062$, Table 2). This consistency supports both the above assumptions and the electron microprobe analysis for O.

The data on spinel oxidation obtained here for quenched samples contradict Taylor’s (1964) suggestion that O gain does not depend on Ti/(Fe + Ti). The present data also are at variance with Dieckmann’s (1982) estimations of O increase in oxidized magnetite up to 2 mol% at 1300 °C. We observe such O contents only in the high Ti part of the system. Dieckmann’s values were obtained directly at high temperature, whereas ours are from quenched samples. It is reasonable to presume that this may account for the difference, and that quenching the fully oxidized state becomes more difficult with increasing Fe content because of the ease of electron transfer through Fe$^{2+}$-Fe$^{3+}$ hopping mechanisms.

The ability to lose and gain O may be further related to the Fe$^{2+}$/Fe$^{3+}$ ratio in the spinel and the cation distrib...
bution. Fe\textsuperscript{3+} has an apparent energetic preference for tetrahedral sites (Blasse, 1964; Navrotsky and Kleppa, 1967; O'Neill and Navrotsky, 1983). Therefore, Fe\textsuperscript{2+} in these sites may be energetically somewhat easier to oxidize. Oxidized Fe tends to be tetrahedrally surrounded, even in excess of the number of normally occupied tetrahedral sites, and can occupy, after oxidation, some tetrahedral interstitial sites to preserve fourfold coordination for Fe\textsuperscript{3+} (Goss, 1988).

The Fe\textsuperscript{3+} preference for tetrahedral sites may be another reason for preferential loss of O by Fe-rich spinels during quenching. Above 1200°C, differently charged cations in magnetite are almost randomly distributed over tetrahedral and octahedral sites (Wu and Mason, 1981; Schmalzried, 1983a, 1983b) (if indeed one can distinguish Fe\textsuperscript{2+} and Fe\textsuperscript{3+} at all). At low temperatures, magnetite is an inverse spinel. An oxidized spinel at low temperatures would have to contain excess Fe\textsuperscript{3+} and vacancies on octahedral sites. The rapid process of cation ordering upon quench may conceivably expel the excess Fe\textsuperscript{3+} together with O loss.

Fe-rich and Ti-rich compositions differ also in the extent of the stability range along the f\textsubscript{O2} axis. The defect chemistry is not similar at low and high f\textsubscript{O2}, as shown in magnetite by a tracer diffusion study (Dieckmann, 1982). Although under more oxidizing conditions magnetite has a certain cation deficit and vacancies represent the defects, at low f\textsubscript{O2} some small cation excess can take place and Fe interstitials are predominant point defects. The position of the crossover from one regime to the other is approximately in the middle of the log f\textsubscript{O2} interval for magnetite. The concentration of interstitial Fe (b in Fe\textsubscript{3+}O\textsubscript{4}) equilibrated at 1300°C at low f\textsubscript{O2} is \(10^{-3}\). It is less by an order of magnitude than the cation deficit, \(10^{-2}\), caused by vacancy formation in the high O region. The concentration of interstitial defects is much less than the precision of our analytical method. From a chemical viewpoint, the concentration of interstitials can, therefore, be taken as virtually zero for samples in equilibrium with wüstite. This is just as we have assumed when choosing reference samples for electron microprobe analysis. We have further assumed that cation excess is insignificant across the entire composition range from Fe\textsubscript{3+}O\textsubscript{4} to Fe\textsubscript{2+}TiO\textsubscript{4}, which appears reasonable in view of the above.

However, rigorous thermodynamic and structural consideration may require taking both types of defects into account (Aragon and McCallister, 1982). True stoichiometric compositions may lie at some distance in f\textsubscript{O2} from the boundary with wüstite, and for magnetite they are stable near the middle of the log f\textsubscript{O2} region (Dieckmann, 1982).

In more Ti-rich spinels, unit-cell parameters (Fig. 3) tend to decrease with increasing f\textsubscript{O2} in the whole interval of accessible f\textsubscript{O2}. This decrease is probably an indication of oxidation and vacancy formation in the whole f\textsubscript{O2} range. One might further hypothesize that the shrinking f\textsubscript{O2} extent of the spinel field with increasing Ti/(Ti + Fe) reflects a decrease in the (already very small) amount of interstitial Fe under reducing conditions.

An attempt was also made to analyze O content in the spinels by another technique. Daniele Cherniak from Rensselaer Polytechnic Institute investigated our samples by Rutherford backscattering (RBS) with H ions. The data (see Table 3) show a trend similar to that of the microprobe results. Samples that were identified as unoxidized in microprobe analyses have the lowest extent of oxidation in the Rutherford data (samples 78 and 32). However, oxidized nonstoichiometric spinels show by RBS significantly greater O contents, approaching values corresponding to complete oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+}. That probably means that the surface, which contributes significantly to RBS, may be much more oxidized than the bulk. That could occur during quench, or during subsequent sample handling in air.

Table 3. Comparison of O content determination by electron microprobe and Rutherford backscattering methods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula</th>
<th>Microprobe</th>
<th>Rutherford backscattering</th>
<th>Complete oxidation calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>Fe\textsubscript{2,0}Ti\textsubscript{0,9}O\textsubscript{1,0}</td>
<td>0.07(03)</td>
<td>0.57(10)</td>
<td>0.85</td>
</tr>
<tr>
<td>32</td>
<td>Fe\textsubscript{2,0}Ti\textsubscript{0,9}O\textsubscript{1,0}</td>
<td>0.00(01)</td>
<td>0.09(09)</td>
<td>0.85</td>
</tr>
<tr>
<td>42</td>
<td>Fe\textsubscript{2,0}Ti\textsubscript{0,9}O\textsubscript{1,0}</td>
<td>0.06(03)</td>
<td>0.13(08)</td>
<td>0.98</td>
</tr>
<tr>
<td>43</td>
<td>Fe\textsubscript{2,0}Ti\textsubscript{0,9}O\textsubscript{1,0}</td>
<td>0.10(04)</td>
<td>0.29(10)</td>
<td>0.96</td>
</tr>
<tr>
<td>78</td>
<td>Fe\textsubscript{0,9}O\textsubscript{0,9}</td>
<td>0.00(03)</td>
<td>0.03(09)</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Our analyzed samples are now ready for a high-temperature solution calorimetric study of mixing properties in the Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}TiO\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{4} system to detail the effects of both the Fe/Ti ratio and nonstoichiometry on thermodynamic properties. We defer discussion of thermodynamic consequences for activity-composition relations and oxide geothermometry-geobarometry till such studies are completed. Before destroying the samples by calorimetry, we are making Mössbauer measurements on them.

**Conclusions**

High and low f\textsubscript{O2} boundaries of the magnetite-ulvöspinel solution stability region are refined at 1300°C, 1 atm.

The composition of magnetite-ulvöspinel solutions in equilibrium with wüstite at 1300°C cannot exceed approximately 90 mol% Fe\textsubscript{2}TiO\textsubscript{4}. More Ti-rich spinels are formed at low f\textsubscript{O2} in equilibrium with metallic Fe and are nonstoichiometric.

Spinel solid solutions synthesized and quenched at higher f\textsubscript{O2} and equilibrated with the rhombohedral phase or produced near the boundary with it show an increase in O to cation ratio relative to samples synthesized at low f\textsubscript{O2}. O gain is greatest (2 mol%) in Ti-rich spinels (x \(\geq\) 0.7), corresponding to compositions (Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{4}. In high-Fe compositions (x \(\geq\) 0.5) the observed nonstoichiometry range in analyzed quenched species is two or more times less than in high-Ti samples.

The unit-cell parameter variation is a sensitive indi-
cator, not only of composition \([\text{Ti}/(\text{Ti} + \text{Fe})]\), but of high-temperature nonstoichiometric \([\text{O}/(\text{Ti} + \text{Fe})]\) ulvöspinel solid solutions.

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REFERENCES CITED


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