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Stoichiometry of synthetic ulvöspinel single crystals

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ABSTRACT

Spinel single crystals (up to 4 mm in size) of eight compositions along the $FeFe_2O_4$-Fe_2TiO_4 solid-solution join, with more than 75 mol% ulvöspinel, were synthesized by use of a flux-growth method. The crystals were characterized by electron microprobe and Mössbauer spectroscopy. Results demonstrated that these ulvöspinels are statistically stoichiometric. The atomic proportions of Ti^{4+} and Fe^{2+} progressively increase from 0.75 to 0.94 and from 1.75 to 1.94 apfu, respectively. Concomitantly the Fe^{3+} content decreases from 0.49 to 0.13 apfu. Consequently, the cation substitutions are restricted to the ideal classic substitution $2Fe^{3+} \leftrightarrow Fe^{2+} + Ti^{4+}$.

An average equilibrium temperature from coexisting spinel-ilmenite pairs of about 950 °C was estimated using the QUILF95 and Ghiorso-Sack models.

In contrast to previous studies based on non-stoichiometric samples sintered at higher temperatures, the present stoichiometric ulvöspinel samples were grown from a melt under moderate temperatures. This fact indicates that the formation of vacancies is related to high-equilibration temperatures or growth mechanisms, whereas natural ulvöspinel may very well be stoichiometric under normal magmatic conditions.

Keywords: Ulvöspinel, ilmenite, Mössbauer spectroscopy

INTRODUCTION

Minerals belonging to the magnetite ($FeFe_2O_4$)-ulvöspinel (Fe_2TiO_4) series are commonly known as titanomagnetites ($Fe_{3-X}Ti_XO_4$). They have a spinel structure and represent important minerals in nature because they are essential carriers of the magnetic signals in rocks, such as ocean-floor basalts. The magnetic, electrical, and thermodynamic properties of these minerals depend on the concentration and distribution of Fe and Ti among sites of different symmetry in the structure.

In the Fe-Ti-O system, subsolidus exsolution processes occur. The Fe-Ti spinels are solid solutions that exhibit a miscibility gap: spinodal decomposition takes place at a consolute temperature of about 600 °C (Price 1981). Transformation of titanomagnetite to titanomaghemite occurs below 600 °C, involving oxidation of Fe^{2+} and production of cation vacancies, while at temperatures above 600 °C the oxidation (oxyexsolution) of primary titanomagnetite produces formation of titanohematite lamellae (Haggerty 1991). Reconstruction of pre-exsolution titanomagnetite compositions permits the calculation of temperature and the oxygen fugacity (Frost and Lindsley 1991; Herd et al. 2001). Therefore, an understanding of titanomagnetite crystal chemistry is essential for development and application of models for geothermometry and oxygen barometry.

Literature on titanomagnetite is extensive, and many papers report non-stoichiometric spinels for which the unit formulas deviate from 3 cations per 4 O atoms by the formation of cation vacancies. This is, in particular, common in studies on spinels in the ulvöspinel field (e.g., Wechsler et al. 1984; Senderov et al. 1993; Wanamaker and Moskowitz 1994; Lattard 1995). Some of these papers show the presence of cation vacancies in titanomagnetite samples synthesized by sintering of powders at relatively high temperatures (ca. 1000–1300 °C), using electron microprobe oxygen (EMPO) analysis. However, the work of Herd et al. (2001) discusses the uncertainty associated with EMPO measurements in spinel, and they conclude that the error in O measurements is large enough to raise doubts about the notion of a general non-stoichiometry in Ti-rich spinels. In addition, the uncertainties in absolute weight percent O measurements result in large uncertainties for the estimations of atomic Fe^{2+}/Fe^{3+} ratios, because the O atomic number is much lower than that of Fe (Kamperman et al. 1996). The Fe^{2+}/Fe^{3+} ratio is an important parameter that has significant effects on atomic proportions and estimates of oxygen fugacity during the formation of spinels and their host rocks (Wood 1991). Therefore, it is reasonable to explore further whether ulvöspinel may be stoichiometric or non-stoichiometric at the crystallization temperatures of common magmatic rocks.

One of the major problems in the literature on titanomagnetite is the incomplete chemical characterization of the samples. In fact, the presence of transition metals with variable valence-states (e.g., Fe^{2+} and Fe^{3+}) often needs to be studied by a combination of complementary methods. These include electron microprobe analysis (EMPA) to measure the elemental composition and methods such as Mössbauer spectroscopy (MS), to determine the valence state distribution of Fe. Thus, to explore whether titanomagnetites may be stoichiometric at magmatic formation temperatures, a detailed chemical study on synthetic magnetite-ulvöspinel solid-solution crystals has been undertaken.

EXPERIMENTAL METHODS

Synthesis

Spinel single crystals (up to 4 mm in size) of eight different compositions along the $FeFe_2O_4$-Fe_2TiO_4 solid-solution join were synthesized by use of a flux-

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growth method. Nutrient components were weighed out in oxide form (analytical grade) in proportions to the desired compositions, but with an excess of Fe_2O_3, which has a considerably higher solubility than TiO_2 in the fluxed melt. In the initial runs $Na_2B_4O_7$ was used as flux compound, but due to problems with melt migration and small spinel yields a mixture of BaO + B_2O_3 was used as flux in most of the runs. Details regarding mixing proportions are listed in Table 1. The experimental charges were homogenized under acetone in an agate mortar, and ~4 g of the mixtures were placed in 8 mL yttria-stabilized Pt/Au(5%) crucibles. These were covered by lids and placed in a vertical furnace equipped with Tylan CO_2:H_2 flow controllers. A continuous flow of the two gases in the ratios reported in Table 1 was adopted to obtain oxygen fugacities ranging from 10^{-9} to 10^{-17} bars when the temperature was varied from 1200 to 900 °C. Thermal runs consisted of an initial increase to 1200 °C where the temperature was kept constant for 24 h to allow for complete dissolution of the oxides and melt homogenization. Subsequently, the temperature was decreased by 4 °C/h to 900 °C, followed by a fast cooling down to ambient temperature. To reach a composition close to the ulvöspinel end-member, the nutrient composition (TiO_2/FeO ratio), flux/nutrient ratio and CO_2:H_2 ratio was changed between experiments (Table 1). X-ray diffraction (XRD) experiments were performed to identify the products. Within the resolution of XRD, the synthesis products consisted of spinel, ilmenite, rutile, metallic iron (Table 1), plates of a Ba-Fe-Ti-O compound, and prismatic borate crystals dispersed in borate glass. The metallic iron, borate crystals and glass were dissolved in a cold dilute HCl solution.

Electron microprobe analysis

Prior to chemical analysis, the investigated single crystals were checked by reflected light and by scanning electron microscope (SEM) back-scattered electron imaging to explore the potential presence of exsolution structures. However, no exsolution features were observed at this spatial resolution (ca. 0.1 μm).

Electron microprobe analyses (WDS method) of spinel and ilmenite crystals were obtained with a Cameca SX50 instrument at the University of Uppsala operating at an accelerating potential of 20 kV and a sample current of 15 nA. Standard samples used were synthetic $MnTiO_3$ (for Ti) and Fe_2O_3 (for Fe). For raw data reduction, the PAP matrix correction procedure was applied (Pouchou and Pichoir 1991). The results, which are summarized in Table 2, represent mean values of a minimum of 10 spot analyses per analyzed crystal and their standard errors (below 1%) substantiate crystal homogeneity.

Al_2O_3 was checked as possible contaminant from the furnace tube, but it was not detected in the samples.

Mössbauer spectroscopy

For the purpose of determining $Fe^{3+}/\Sigma Fe$ ratios, ^{57}Fe Mössbauer spectra were obtained on absorbers prepared by placing finely ground crystals between mylar windows in a ca. 2.5 mm circular aperture of a Pb disk. Spectra were collected at room temperature using a conventional spectrometer system operated in constant acceleration mode with a nominal 10 mCi ^{57}Co/Rh point source. Spectral data for the solid-solution samples with an ulvöspinel component of >80 mol% were recorded for the velocity range –4.5 to +4.5 mm/s in a multichannel analyser using 1024 channels. Spectra of Ti-poorer solid-solution samples and a sample of the magnetite end-member were recorded in the velocity range –10 to +10 mm/s. After velocity calibration against room temperature α-iron foil spectra, raw spectrum data were folded and fitted using a least-square fitting program (Jernberg and Sundqvist 1983). Lorentzian line shapes, equal recoil-free fractions, and equal intensities of the quadrupole components were assumed in the fitting procedure. For the magnetic spectra, the intensity ratios among the individual sets were constrained to a 3:2:1 relationship. For the spectra of the non-magnetic spinel samples, a fitting model using four quadrupole doublets due to ferrous iron and one caused by ferric iron was adopted. Using models with fewer doublets resulted in considerably poorer fits.

RESULTS AND DISCUSSION

The purity of the present spinel single crystals is shown by their diffraction pattern (Bosi et al. 2007), in which neither extra peaks corresponding to additional phases nor development of satellite intensity around the base of each peak were observed. The chemical homogeneity of the crystals was demonstrated by analytical traverses from crystal core to rim. Furthermore, even under the assumption that all iron is present as FeO, the calculated cation sums for each point analysis was never less than three. This indicates that any contribution of FeO associated with fine lamella of ilmenite, which could be too small to be observed by SEM, is absent or occurs in insignificant amounts (Herd at al. 2001). Consequently, the present spinels have not been subject to exsolution processes and can be considered homogeneous.

The Mössbauer spectra of all presently investigated spinel and ilmenite samples show the presence of Fe^{3+}, although $Fe^{3+}/\Sigma Fe$ ratios approach very low values (ca. 0.03) in the most Ti-rich spinel samples. Spectra of Ti-rich samples (Usp ≥80 mol%) are characterized by a relatively broad "quasidoublet" that is well reproduced by fitting several Fe^{2+}-related Lorentzian shaped doublets with center shifts (CS) of ca. 1.0 mm/s and one Fe^{3+} doublet with a CS of 0.35 mm/s (Fig. 1). The broadness and deviation from Lorentzian line shape of the "quasidoublet" is a general feature of spectra of Fe^{2+}-bearing oxide spinels. For instance, reasonable fits of Mössbauer spectra of hercynite require four to five Lorenzian quadrupole doublets (Larsson et al. 1994) with hyperfine parameters comparable to those obtained in the present fits, or alternatively, fitting procedures that apply quadrupole splitting distributions. This is generally attributed to variable next-nearest cation distribution at the resonance nuclei. Although the hyperfine parameters obtained by different fitting strategies may vary, the obtained $Fe^{3+}/\Sigma Fe$ ratios, which are directly related to the area asymmetry of the two components of the broad "quasidoublet," remain nearly constant. Mössbauer spectra of solid-solution samples with less than ca. 80 mol% Usp reveal magnetic interactions and additional spectral broadening at room temperature. This precluded accurate determinations of the $Fe^{3+}/\Sigma Fe$ ratios from spectra of these Fe-rich and Ti-poor solid-solution samples. The Mössbauer spectrum of the ilmenite sample is dominated by a strong Fe^{2+} quadrupole doublet, but a weak Fe^{3+} doublet corresponding to 10 wt% of the total iron in this phase is also obvious (Fig. 2). The estimated intensity

TABLE 1. Synthesis conditions and products

Sample	*T* (˚C) of synthesis	CO_2:H_2	Oxygen fugacity	TiO_2/FeO	Flux/nutrient	Crystal phases*
FeTib1	1200–900	1:1	10^{-11}–10^{-16}	0.30	1.20	Spinel
FeTib2	1200–900	1:1	10^{-11}–10^{-16}	0.25	1.05	Spinel, rutile
FeTib3	1200–900	1:1	10^{-11}–10^{-16}	0.19	1.05	Spinel, rutile
FeTib4	1200–900	1:2	10^{-12}–10^{-17}	0.28	1.05	Spinel, metallic iron, Ba-Ti-Fe phase†
FeTib5	1200–900	1:1	10^{-11}–10^{-16}	0.28	1.05	Spinel, Ba-Ti-Fe phase†
FeTib6	1200–900	1:1	10^{-11}–10^{-16}	0.28	1.15	Spinel
FeTib7	1200–900	1:2	10^{-12}–10^{-17}	0.28	1.15	Spinel, rutile, metallic iron, Ba-Ti-Fe phase†
FeTi80‡	1200–900	10:1	10^{-9}–10^{-14}	0.36	0.90	Spinel, ilmenite

* Ba (or Na)-borate crystals are present in all synthesis experiments.

† Average composition (wt%): BaO = 14.4(1), FeO = 41.1(5), TiO_2 = 44.1(2).

‡ $Na_2B_4O_7$ was used as flux compound in this experiment.

errors for Mössbauer analyses are normally ±1%, but as the Fe^{3+}-component in the present spectra of the non-magnetic spinel samples is not resolved we have estimated this intensity error to be considerably larger (σ_{MS} = 2%) although the statistical spread in the non-resonant part of the spectrum indicates smaller errors.

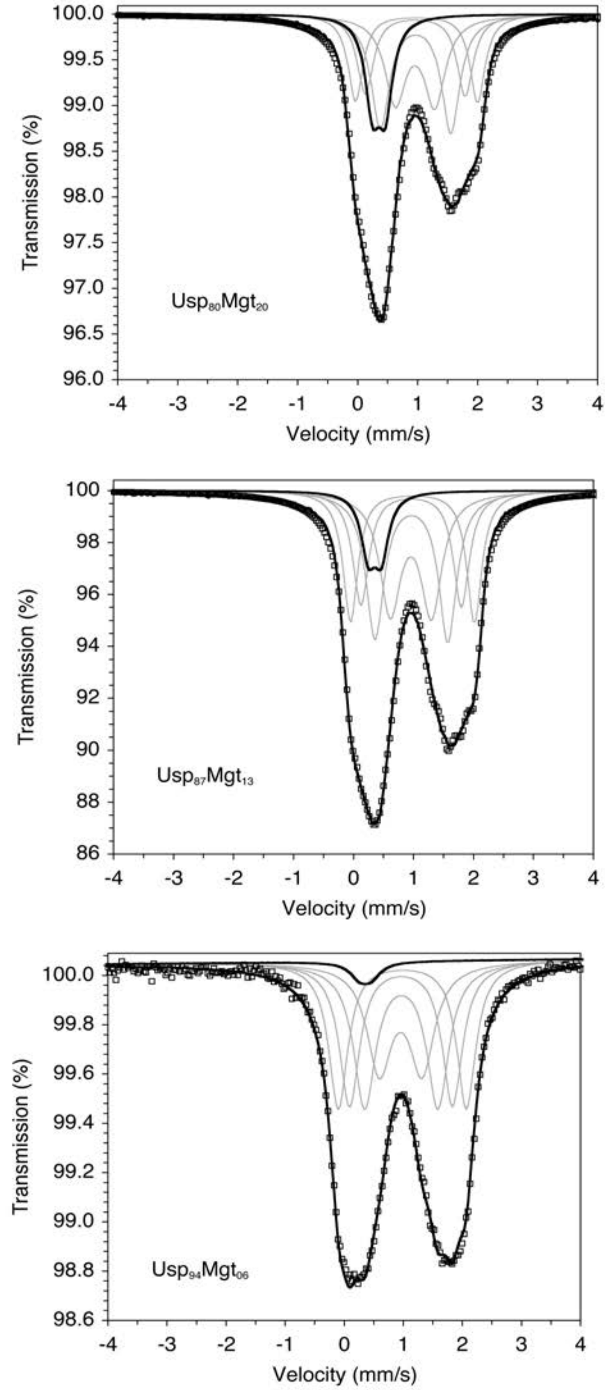

FIGURE 1. Room-temperature Mössbauer spectra of samples FeTib3 (top), FeTib6, and FeTib1 (bottom). Squares show experimental data. The bold line along the experimental data point shows the spectrum fits summing up the intensities of one fitted Fe^{3+} quadrupole doublet (black) and four fitted Fe^{2+} quadrupole doublets (dark gray).

In accordance with redox potential arguments, the simultaneous presence of Fe^{3+} and Ti in spinel and ilmenite indicate that the valence state of Ti is 4+ or higher. The spinel atomic proportions calculated on the basis of the EMPA element analyses and the $Fe^{3+}/\Sigma Fe$ ratios obtained from MS (i.e., without taking into account its error) reveal slightly more than 3 cations per 4 O atoms. This minor deviation could be explained if a small fraction of the titanium occurs in the pentavalent state. However, the extraordinary stability of the Ti^{4+} configuration does not support this hypothesis. In fact, the energy needed to remove an electron from the Ti^{4+} cation (ca. 56 eV) is so large that it appears to be unrealistic in multiple oxides.

As the calculated cation excess is very small, it is highly relevant to explore the uncertainties related to the calculated formulas. The $Fe^{3+}/\Sigma Fe$ ratios, which have been obtained experimentally by Mössbauer spectroscopy, can also be calculated from EMPA results assuming charge balance and stoichiometry (Table 2). This calculated ratio is subject to standard errors (σ_{EMPA}) derived from the experimental EMPA measurements of the oxide components.

To understand if the $Fe^{3+}/\Sigma Fe$ ratios obtained from MS are consistent with stoichiometry, they have to be compared with those calculated from EMPA. The difference (Δ_{Fe}) between $Fe^{3+}/\Sigma Fe$ ratios derived from EMPA and those obtained from MS spectroscopy are summarized in Table 2. The standard errors related to the residual Δ_{Fe} were calculated by summing the respective errors of EMPA and MS in quadrate: $\sigma_{\Delta Fe} = (\sigma_{EMPA}^2 + \sigma_{MS}^2)^{1/2}$. Assuming Δ_{Fe} to be distributed around zero according to a normal distribution, the uncertainty in Δ_{Fe} at the 95% confidence level is given by ±2 standard errors. In line with this statistical criterion, Δ_{Fe} values deviate within experimental error from zero (i.e., stoichiometry), away from the cation vacancy field (Fig. 3). As a consequence, the present spinel and ilmenite samples can be considered stoichiometric, and the existence of cation vacancies appears extremely unlikely. Oxidation of the

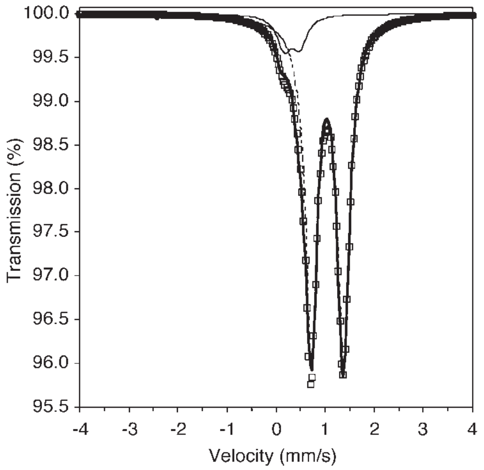

FIGURE 2. Room-temperature Mössbauer spectrum of ilmenite-80A showing the experimental data (squares), the fitted spectrum (dashed line), the fitted Fe^{2+} and Fe^{3+} (solid line) quadrupole doublets.

TABLE 2. Chemical composition by EMPA and $Fe^{3+}/\Sigma Fe$ ratios by MS of the studied Fe-Ti oxides

	FeTib1	FeTib5	FeTib4	FeTib7	FeTib6	FeTib2	FeTib3	FeTi80A	Ilmenite-80A
TiO_2 (wt%)	33.12(48)	32.54(66)	31.88(21)	32.28(26)	30.77(38)	29.69(33)	28.10(19)	26.63(13)	49.84(43)
FeOtotal	65.54(30)	67.25(48)	66.07(38)	67.35(42)	68.33(44)	68.10(40)	69.46(55)	71.42(22)	49.67(46)
Fe_2O_3*	4.41	6.46	6.46	6.88	9.62	10.89	14.01	17.43	5.38
FeO*	61.57	61.43	60.25	61.16	59.67	58.30	56.86	55.74	44.83
Total	99.10	100.43	98.59	100.32	100.06	98.88	98.97	99.80	100.05
$Fe^{3+}/\Sigma Fe$ (EMPA)*	0.06(1)	0.09(2)	0.09(1)	0.09(1)	0.13(1)	0.14(1)	0.18(1)	0.22(1)	0.10(2)
$Fe^{3+}/\Sigma Fe$ (MS)	0.03(2)	0.08(2)	0.07(2)	0.06(2)	0.09(2)	0.11(2)	0.17(2)	0.21†	0.10(1)
ΔFe‡	0.03(2)	0.01(3)	0.02(2)	0.03(2)	0.04(2)	0.03(2)	0.01(2)	0.01	0.00(2)
Cations on basis of 4 O atoms (spinel) and 3 O atoms (ilmenite)									
Ti^{4+} (apfu)	0.938(10)	0.910(14)	0.908(6)	0.904(7)	0.865(9)	0.845(8)	0.800(7)	0.753(4)	0.949(8)
Fe^{3+}	0.125(14)	0.181(21)	0.184(9)	0.193(9)	0.270(13)	0.310(12)	0.399(10)	0.493(5)	0.102(12)
Fe^{2+}	1.937(10)	1.910(14)	1.908(6)	1.904(7)	1.865(9)	1.845(8)	1.800(6)	1.753(4)	0.949(9)
Total cations	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	2.000

Notes: Digits in parentheses are estimated errors (1σ). Standard errors for oxides are derived from repeated analyses on individual crystals, whereas the standard errors for cations were calculated according to Wood and Virgo (1989).
* From stoichiometry.
† Estimated from the regression equation (Fig. 4).
‡ Difference between $Fe^{3+}/\Sigma Fe$ (EMPA) and $Fe^{3+}/\Sigma Fe$ (MS).

spinel crystal surfaces due to grinding and polishing during the preparation of sections for EMPA (Elfström and Olefjord 1977) may be an additional reason (systematic error) for the higher $Fe^{3+}/\Sigma Fe$ ratios recorded in EMP analyses as compared to the Mössbauer spectra. Although it was not possible to obtain a reliable $Fe^{3+}/\Sigma Fe$ ratio from the magnetic room temperature Mössbauer spectrum of the FeTi80A spinel it is highly likely that it is, consistent with the samples with higher Ti-concentrations, stoichiometric. In addition, the regression analysis of the $Fe^{3+}/\Sigma Fe$ ratios for the high Ti-spinels and the magnetite end-member underline this assumption (Fig. 4). This is also in accordance with the results of a structure-refinement study on spinels along the magnetite-ulvöspinel series, in which the partition of Fe and Ti over tetrahedral and octahedral sites, obtained by stoichiometric formulas and effective ionic radii, is in agreement with the observed bond lengths (Bosi et al. 2007).

In conclusion, the observed data strongly support that stoichiometry, rather than cation vacancy, characterize the Fe- and Ti-distribution in the present spinels. In detail, the atomic proportions of Ti^{4+} and Fe^{2+} progressively increase from 0.75 to 0.94 and from 1.75 to 1.94 atoms per formula unit (apfu), respectively. Concomitantly the Fe^{3+} content decreases from 0.49 to 0.13 apfu. Consequently, the cation substitutions in these ulvöspinels are restricted to the ideal classic substitution $2Fe^{3+} \leftrightarrow Fe^{2+} + Ti^{4+}$.

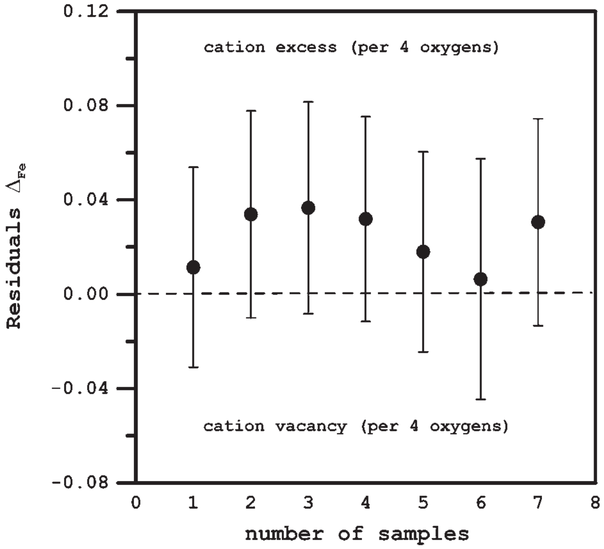

FIGURE 3. Plot of residuals (Δ_{Fe}) between the $Fe^{3+}/\Sigma Fe$ ratio calculated from EMPA and that obtained from Mössbauer spectroscopy for samples with ulvöspinel component >80 mol%. The vertical bars represent the estimated uncertainty ($2\sigma_{\Delta_{Fe}}$). The solid dashed line represents the stoichiometry.

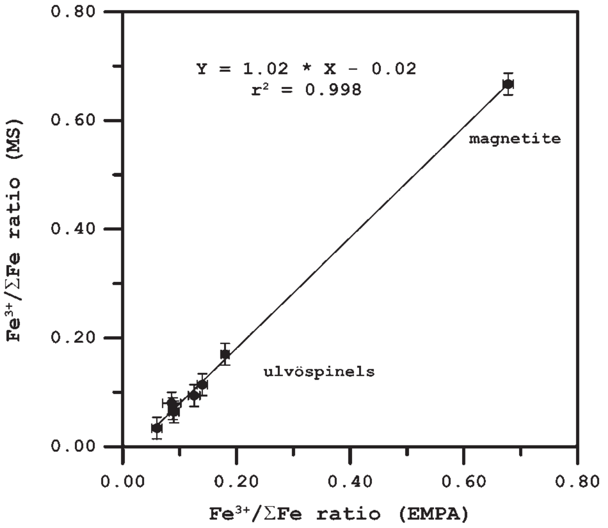

FIGURE 4. $Fe^{3+}/\Sigma Fe$ ratios obtained from Mössbauer spectroscopy vs. those calculated from EMPA suggest that the stoichiometry of titanomagnetites covers the whole $FeFe_2O_4$-Fe_2TiO_4 compositional range. The Mössbauer spectrum of the magnetite is reported in Bosi et al. (2007), and its $Fe^{3+}/\Sigma Fe$ ratio is 0.68(2). In the regression equation (solid line), the intercept value represents the systematic error, while the deviation of slope from 1 represents the random errors. Vertical and horizontal bars represent the estimated errors (σ_{MS} and σ_{EMPA}, respectively).

Equilibrium temperature

It has been suggested that vacancy formation in synthetic, specifically sintered, spinels and ilmenites is related to high temperatures of formation (e.g., O'Neill et al. 1992; Lattard 1995). Large proportions of vacancies are also known to occur in spinel crystals grown at very high temperatures by the Verneuil method (e.g., Lucchesi and Della Giusta 1994). As we have not observed any indication of vacancies in the flux-grown spinels, which are formed by very different nucleation and growth processes, it is of some importance to define and document the equilibrium temperature of the present ulvöspinels.

In our flux growth experiments, the crystals nucleate and grow somewhere along the main cooling path from 1200 to 900 °C, at a cooling rate of 4°/h. After 900 °C, the cooling rate is considerably faster, initially a few hundred degrees per hour, and any substantial crystal growth during this stage is unlikely. Absence of indications for subsolvus unmixing (spinodal decomposition) suggests that our spinels have been equilibrated above the consolute temperature of the system (ca. 600 °C). However, our samples were not quenched during the synthesis process and a continuous exchange of Fe and Ti between titanomagnetite and ilmenite in the subsolidus cannot be ruled out. Consequently, we need to evaluate their subsolidus equilibration temperature. To do this, we have applied the titanomagnetite-ilmenite thermo-oxybarometer with the software QUILF95 (most recent version of the QUILF program of Anderson et al. 1993) and the geothermometer of Ghiorso and Sack (1991). These models provide tools to determine equilibration temperature (T) and oxygen fugacity (f_{O_2}) by using the chemical composition of coexisting oxides, such as titanomagnetite and ilmenite pairs. Using the spinel FeTi80A and ilmenite-80A, the following T and f_{O_2} were estimated:

$T = 1000$ °C and $f_{O_2} = 10^{-12}$ (QUILF95 model)
$T = 909$ °C and $f_{O_2} = 10^{-14}$ (Ghiorso-Sack model)

The two models provide reasonable and comparable results, and indicate that the two phases were growing under equilibrium conditions at the end of the main cooling stage, and that this equilibrium was maintained during the continued cooling. It should also be noted that the calculated oxygen fugacity is in excellent agreement with the experimental range adopted during the thermal run (Table 1). In conclusion, the temperature at which the spinel FeTi80A and ilmenite-80A phases were last in equilibrium is in the range 1000–900 °C. Since the thermal runs are the same in all synthesis experiments, an average temperature of about 950 °C may be assumed for our additional Fe-Ti-spinels.

The present ulvöspinel samples grown from a melt under moderate temperatures are stoichiometric, within the accuracy of the analytical methods, in contrast to previous studies (e.g., Senderov et al. 1993; Lattard 1995) based on potentially non-stoichiometric samples sintered at higher temperatures. This observation indicates that the formation of vacancies is related to high equilibration temperatures and other experimental conditions or growth mechanisms, whereas natural ulvöspinel may very well be stoichiometric under normal magmatic conditions. However, subsolidus cooling, especially in the presence of aqueous fluids, will lead to oxidation and transfer to maghemite-bearing solid solutions with cation vacancies (Xu et al. 1997).

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