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## Direct oxygen measurements of Cr-rich spinel: Implications for spinel stoichiometry

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### ABSTRACT

The availability of a synthetic multilayer crystal and accurately calibrated oxide and silicate standards make it possible to use the electron microprobe for precise O analysis of spinel. A requirement of the O measurement routine described is the use of repetitive statistical analyses of the O standards and subsequent corrections and recalibration. A representative set of O analyses for each spinel population studied is essential to obtain reliable data, and the danger of using single datum is emphasized. Magnesiochromite spinel grains, having broad compositional similarities but different petrogenetic and cooling histories, were analyzed for O and their stoichiometry was assessed. Diamond-indicator spinel from the Aries kimberlite and Argyle lamproite is stoichiometric. Spinel inclusions in olivine phenocrysts from Ti-poor tholeiite from the Hunter Fraction Zone and Ca-rich boninite from the Tonga Trench show a range of nonstoichiometry. High  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values calculated assuming stoichiometry for such spinel are invalid. Spinel samples from metamorphosed volcanics from the Peak Hill–Glengarry Basin and the Heazlewood River Ultramafic Complex are also nonstoichiometric, having significant  $\text{Fe}_{0.3}\text{O}_4\text{-Cr}_{0.3}\text{O}_4$  components. Our results demonstrate that nonstoichiometry is a common feature of Cr-rich spinel. This has important implications for the use of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  concentrations to estimate the oxidation state or temperature of formation.

### INTRODUCTION

Experimental studies of spinel within the Fe-Ti-O ternary have demonstrated substantial nonstoichiometry, which is a function of temperature, composition, and  $f_{\text{O}_2}$  (e.g., Aragon and McCallister 1982). The stoichiometry of natural Cr-Al-bearing spinel has also been a matter of recent debate (e.g., Wood and Virgo 1989; Ballhaus et al. 1991; Carmichael 1991). One important parameter of spinel composition dependent on stoichiometry is the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  value. From electron microprobe analytical data, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  value may be calculated by assuming that the spinel structure has a perfect stoichiometry with three cations per four O atoms. Stoichiometry calculations are based on the assumption of charge balance, with Fe as the only cation with a variable valency state (e.g., Finger 1972). It has been demonstrated that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  value is a potential  $f_{\text{O}_2}$  indicator, and several experimentally calibrated olivine-orthopyroxene-spinel  $\text{O}_2$  geobarometers have been developed on this basis (O'Neill and Wall 1987; Mattioli and Wood 1988; Ballhaus et al. 1991).

Ballhaus et al. (1990, 1991) and McGuire et al. (1989) demonstrated that for some samples of spinel,  $\text{Fe}^{3+}$  calculated from electron microprobe analyses assuming stoichiometry agrees well with  $\text{Fe}^{3+}$  independently measured by Mössbauer spectroscopy. On the other hand, Wood and Virgo (1989) and Carmichael (1991) showed that spinel from abyssal lherzolite assemblages is significantly nonstoichiometric according to  $\text{Fe}^{3+}$  analyses by Mössbauer spectroscopy. Because spinel often occurs as small grains and inclusions in other minerals, Mössbauer spectroscopy cannot be widely applied because it requires a relatively large sample size. To overcome this problem, we developed an O measurement technique, using an electron microprobe (e.g., Nash 1992), that allows an accurate assessment of stoichiometry and calculation of  $\text{Fe}^{3+}$  content in individual spinel grains.

In this paper we discuss results of O analyses of Cr-rich spinel having broad compositional similarities from both high- and low-pressure mantle-derived suites. Such spinels are widely used as petrogenetic indicators. Cr-rich xenocrystic spinel found in kimberlite and lamproite [magnesiochromite with  $\text{Cr}' = 100\text{Cr}/(\text{Cr} + \text{Al})$  of 70–95,  $\text{Mg}' = 100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  of 50–80 and  $\text{Fe}^{3+}/\Sigma \text{Fe} < 0.3$ ] is often used as diamond indicators (e.g., Haggerty 1979; Ramsay 1992; Kamperman et al. 1993). A typical feature of many diamond-indicator spinel compositions

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is that, when recalculated from metal-oxide analyses assuming stoichiometry, all Fe is present as  $\text{Fe}^{2+}$  and small amounts of Cr may also be present as  $\text{Cr}^{2+}$  (e.g., Haggerty 1979). Such compositional features are believed to be consistent with their formation in the upper mantle at the high-pressure reduced conditions of diamond stability (Haggerty 1986).

Cr-rich spinel from primitive subduction-related magmatic suites has  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values calculated according to stoichiometry that extend to very high values, particularly in some boninitic suites (e.g., Sigurdsson et al. 1993; Sobolev and Danyushevsky 1994). If valid, the observed range would imply reduced crystallization conditions for many subduction-related suites in contradiction of the generally accepted oxidized nature of magmas generated in subduction zones (e.g., Ballhaus et al. 1991).

We use our O measurement technique to demonstrate that nonstoichiometry is a common feature of Cr-rich spinel, and we argue that the possibility of spinel nonstoichiometry must be taken into account in petrologic applications.

## ANALYTICAL METHOD

### Design of analytical routine

The USNM 111989 gahnite from Brazil (Jarosewich et al. 1980) was used as a mineral standard for calibration of O. We chose this spinel standard because its mean atomic number ( $Z_{\text{calc}} = 16.10$ ) is comparable to that of Cr-rich spinel (e.g.,  $Z_{\text{calc}} = 16.29$  for USNM 117075 chromite standard; Jarosewich et al. 1980). The gahnite standard was analyzed for O by fast neutron activation analysis (FNAA, McGuire et al. 1992), and  $O_{\text{FNAA}}$  of 35.20 wt% ( $1\sigma$  0.57) compares well with  $O_{\text{calc}}$  (from electron microprobe metal-oxide analyses) of 34.92 wt%, suggesting that the spinel standard is stoichiometric (McGuire et al. 1992). The average value of 35.06 wt% is accepted here as the gahnite O content.

All analyses were performed on a Cameca SX-50 electron probe microanalyzer (EPMA) at the University of Tasmania in Hobart. A PC1 W/Si (2d = 6 nm) multilayer crystal in an inclined spectrometer was used for measurement of O. The remaining spectrometers were set with TAP and LiF analyzing crystals. A multipurpose analytical routine designed to analyze the O content of minerals was programmed to include Mg (TAP crystal, USNM 117075 chromite standard), Al (TAP crystal, USNM 111989 gahnite standard), Si (TAP crystal, USNM R17701 quartz standard), Ti (LiF crystal, Astimex MIMN 25–53 rutile standard), Cr (LiF crystal, USNM 117075 chromite standard), Mn (LiF crystal, Astimex MIMN 25–53 rhodonite standard), Fe (LiF crystal, USNM 96189 ilmenite standard), Ni (LiF crystal, Astimex MIMN 25–53 nickel silicide standard), V (LiF crystal, pure vanadium), and Zn (LiF crystal, USNM 111989 gahnite standard). Metal-oxide concentrations of spinel inclusions in olivines from modern subduction-related suites were analyzed using a separate analytical routine, which differed

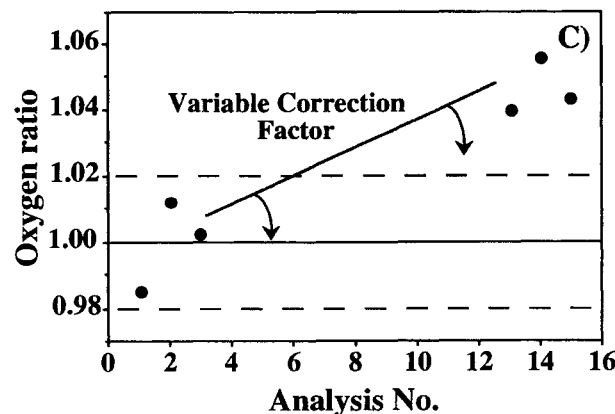
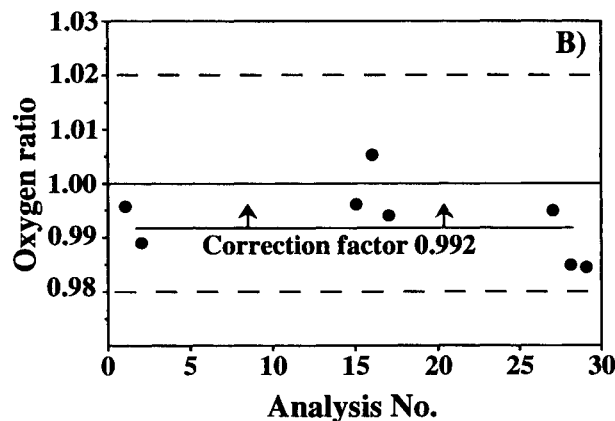
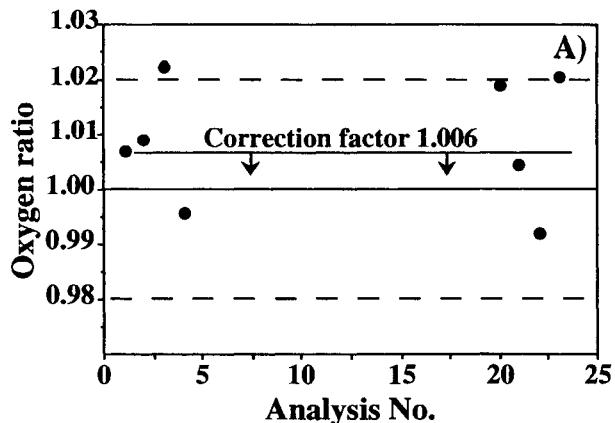
in that Cr and Ti were analyzed on a PET crystal, and the results were combined with O contents analyzed using the first routine. For both routines, analyses were performed at 15 keV accelerating voltage, an electrical beam current of 20 nA, and a beam diameter varying from 1 to 10  $\mu\text{m}$  at a 10000 $\times$  magnification. O was analyzed at the beginning of each analysis; counting time was 40 s on the peak and 20 s on the background measured on both sides of the analytical peak. All other elements were analyzed at 10 s on the peak and 5 s on the background. For these counting times the calculated tolerance, which is the detection limit (at  $2\sigma$ ) divided by the weight percent concentration, for the major cations is <1% (relative), which is within the quoted total precision of 2% (relative) of the analytical system. Concentrations were calculated from relative peak intensities using the PAP matrix correction procedure (Pouchou and Pichoir 1991). On the gahnite standard containing 35.06 wt% O, the analytical conditions yielded a peak-to-background ratio for O of 93, comparable to that of Al (82) and better than Zn (62).

Probe mounts of mineral grain composites under investigation were made using cold-set epoxy. Care was taken to obtain a high-quality polish, using various grades of diamond-polishing paste. Sample probe mounts and the standard probe mount were coated at the same time with a thin film of ultra-high-purity carbon, ensuring uniformity of coating of standards and samples.

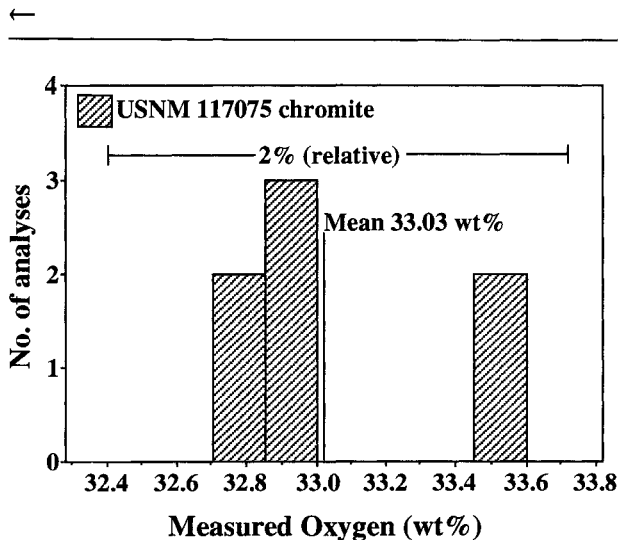
### Analytical procedure

The O standards were recalibrated at the beginning of each analytical session. The gahnite O standard was checked at regular intervals (after every 5–10 analyses) during each analytical session, and crystal reverifications or recalibrations were made when the value of  $O_{\text{analyzed}}$ :  $O_{\text{accepted}}$  was <0.98 or >1.02. Each analysis represents an average of two or three analytical points, always taken from the same area of the standard grain to avoid any possibility of incorporating standard nonhomogeneity. The unknown grains were analyzed over very small areas (generally  $\sim 10 \mu\text{m}$  apart) and did not involve core-to-rim analyses, thus avoiding the possibility of grain nonhomogeneity. Analytical values quoted for unknown grains also represent an average of two or three analytical points, and for O and the major cations these values demonstrate a precision better than 2% (relative).

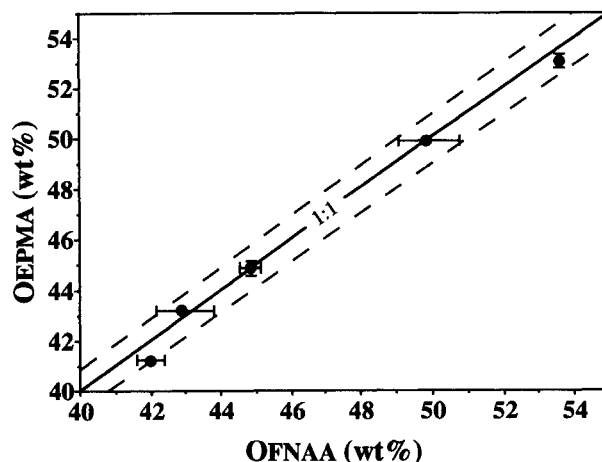
O data corrections (in terms of O by weight percent) were made by adjusting the analytical results when a systematic shift (Figs. 1A and 1B) or consistent regular drift occurred (Fig. 1C) between two adjacent sets of standard analyses. To check the reliability of the corrected data obtained during intervals when the standard drift occurred, analyses of some grains were repeated after verification and compared with the corrected value. Table 1 illustrates the results of this procedure from analyses on the same spinel grain (an inclusion in olivine from a Tongan boninite) during an analytical session before and after verification. The results demonstrate a precision better than 2% (relative).



**FIGURE 1.** (A and B) Correction method used for adjusting O analytical results if a systematic standard shift occurred upward (A) or downward (B) during an analytical session. O data for a session were adjusted by an average correction factor calculated from the ratio (= O ratio) of the measured O content to the accepted O content of 35.06 wt% for the gahnite standard. (C) Correction method used for adjusting O analytical results if standard drift occurred during an analytical session. O data for a session were adjusted by a variable correction factor calculated from the O ratio. The O ratio between 0.98 and 1.02 indicates the range of acceptable measured O values from the gahnite standard. See text for recalibration and reverification procedure used if the ratio was  $<0.98$  or  $>1.02$ .



**FIGURE 2.** Frequency histogram of repetitive O analyses of the USNM 117075 chromite during an analytical session. The chromite has an average O content of 33.03 wt%. The error bar indicates 2% (relative) of the mean.



**FIGURE 3.** Comparison of O of secondary standards (see Table 2 for details) measured by electron microprobe vs. O measured using the fast neutron activation technique (McGuire et al. 1992). The dashed lines indicate 2% (relative) of the mean. Error bars (shown only if error is larger than the size of the symbol) represent standard deviations.

**TABLE 1.** Procedure for correcting O data following standard drift during an analytical session

No. Analyses Sample	1 1-3 Gahnite	2 11-12 5-28/OL10-SP	3 13-15 Gahnite	4 5-28/OL10-SP (corrected)	5 16-18 Gahnite (recalibrated)	6 19-20 5-28/OL10-SP (new)	7 21 Gahnite
O (wt%)	34.99(0.39)	33.02(0.08)	36.62(0.25)	31.61	34.98(0.27)	31.53(0.26)	34.96
O <sub>ratio</sub>	0.9980		1.0445		0.9977		0.9971

Note: The O analyses were obtained in one continuous session. The row labeled "Analyses" indicates the order of samples analyzed during the session. Data shown are average values of corresponding points, with data in parentheses representing standard deviations. O<sub>ratio</sub> values were obtained by O<sub>meas</sub>/O<sub>accepted</sub> for the gahnite standard of McGuire et al. (1992). See text for discussion.

The cation standards were checked at the beginning of each analytical session, and recalibrations were made when the value of  $\text{cation}_{\text{analyzed}}:\text{cation}_{\text{standard}}$  was  $<0.98$  or  $>1.02$ . The USNM 117075 chromite standard was checked at the beginning and the end of each analytical session, and for the duration of a given analytical session cation drift did not exceed 1% (relative). Only analyses with totals (which equal the sum of cations plus O<sub>meas</sub>) between 98.5 and 101.0 wt% were accepted.

#### Accuracy of O measurements

Repetitive analyses of the same grain performed during one analytical session (Fig. 2) show deviations  $<2\%$  (relative). To enable comparison of the data analyzed during different analytical sessions, we analyzed several grains during different sessions. For example, data for sample 5-28/OL5-SPA are 31.02 and 31.16 wt% O. An average of 31.09 wt% was accepted as the O content. Data for sample 5-28/OL8-SPB are 32.62 and 32.82 wt% O. An average of 32.72 was accepted as the O content. Finally, analyses of secondary standards with known O content analyzed by FNAAs (Table 2 and Fig. 3) all imply that there is no systematic error in the analytical routine introduced by PAP matrix corrections, and that the precision is 2% (relative).

#### RESULTS

The following parameters are used in this paper: (1)  $\Sigma_{\text{cations}}$  is the sum of cations calculated on the basis of 4 O atoms, assuming all Fe is present as Fe<sup>2+</sup> and all Cr is present as Cr<sup>3+</sup>. (2) O<sub>calc</sub> is weight percent O calculated from metal-oxide compositions assuming stoichiometry. If our analyses indicated a possible presence of Cr<sup>2+</sup> (i.e.,  $\Sigma_{\text{cations}}$  was  $<3$ ), we did not incorporate this effect into our calculations because our analyses did not result in a  $\Sigma_{\text{cations}}$  deficiency beyond the accuracy of the electron microprobe analyses. (3)  $\Delta\text{O} = \text{O}_{\text{meas}} - \text{O}_{\text{calc}}$  is the deviation from stoichiometry. (4) O<sub>max</sub> is the calculated O content assuming that all Fe is present as Fe<sup>3+</sup>, all Cr as Cr<sup>3+</sup>, all Mn as Mn<sup>2+</sup>; O<sub>min</sub> is the calculated O content assuming all Fe is present as Fe<sup>2+</sup>.

If Cr<sup>2+</sup> is not present, O<sub>meas</sub> is expected to be between O<sub>max</sub> and O<sub>min</sub>; if O<sub>meas</sub> is less than O<sub>min</sub>, this may indicate that Cr<sup>2+</sup> is present. Assuming that no other elements but Fe and Cr can be present in variable oxidation states (+2 or +3), O<sub>meas</sub> is not expected to be larger than O<sub>max</sub>.

Because O has a low atomic number in comparison with Fe, the established 2% (relative) accuracy of our O analyses corresponds to very large differences in calculated Fe<sup>2+</sup> and Fe<sup>3+</sup>. For example, 2% (relative) O for a typical Cr-rich spinel is  $\sim 0.65$  wt%, which corresponds

**TABLE 2.** O analyses of O standards (values in wt%)

Sample USNM no.	Gahnite 111989	Quartz 122838	Kaersutite 131928	Albite 131705	Olivine 131929	Almandine 112140
O <sub>EPMA</sub>	34.99(0.39)	53.05(0.31)	43.22(0.14)	49.95(0.16)	44.93(0.27)	41.25(0.08)
O <sub>FNAAs</sub>	35.20(0.57)	53.55(0.07)	42.87(0.83)	49.83(0.87)	44.8(0.30)	41.94(0.39)
O <sub>calc</sub>	34.92	53.25	43.05	48.65	43.98	41.87
Si		46.74	18.51	31.82	19.58	17.95
Al	29.28		7.82	10.47		11.91
Fe <sup>2+</sup>	1.53		0.56		6.86	19.78
Fe <sup>3+</sup>			8.63	0.06		0.83
Mg			7.49		29.76	5.03
Mn	0.29		0.09		0.10	1.69
Ti			3.11			0.03
Cr						0.03
Ca			7.45	0.17	0.02	1.24
Na			2.09	8.49	0.01	0.09
K			1.19	0.22		
Ni					0.34	
Zn	34.14					
H			0.01			

Note: O<sub>EPMA</sub> values determined in this work using an electron microprobe analyzer. O<sub>FNAAs</sub> values determined by McGuire et al. (1992) using fast neutron activation analysis. O<sub>calc</sub> values calculated by McGuire et al. (1992) assuming perfect charge balance and using measured H contents and Fe<sup>3+</sup>/Σ Fe values where applicable. Values in parentheses represent standard deviations. Major elements determined by Jarosewich et al. (1980).

**TABLE 3.** Representative analyses of diamond-indicator spinel (values in wt%)

No.	1	2	3	4	5	6
Locality	Argyle	Aries	Aries	Aries	Aries	Aries
Grain no.		13	8	12	11	5
Type	Lmp	Kmb	Kmb	Kmb	Kmb	Kmb
Si	0.04 ( $\pm 0.01$ )	0.02	0.02	0.05	0.02	0.02
Ti	0.02 ( $\pm 0.00$ )	0.03	0.00	0.14	0.23	0.02
Al	2.15 ( $\pm 0.47$ )	5.81	4.89	3.41	5.99	6.17
Cr	47.01 ( $\pm 0.87$ )	42.20	43.74	45.71	40.65	41.75
V	0.09 ( $\pm 0.01$ )	0.12	0.10	0.16	0.12	0.12
Fe	10.61 ( $\pm 0.21$ )	10.63	10.94	9.77	11.52	10.42
Mg	7.37 ( $\pm 0.04$ )	7.63	7.25	7.25	7.29	7.78
Mn	0.22 ( $\pm 0.04$ )	0.22	0.20	0.22	0.26	0.22
Ni	0.05 ( $\pm 0.02$ )	0.06	0.08	0.04	0.06	0.07
Zn	0.05 ( $\pm 0.04$ )	0.10	0.11	0.09	0.07	0.11
O	31.83 ( $\pm 0.35$ )	32.59	32.53	31.94	32.77	33.44
Total	99.43 ( $\pm 0.56$ )	99.40	99.86	98.77	98.98	100.12
O <sub>calc</sub>	31.70 ( $\pm 0.12$ )	32.91	32.62	32.02	32.53	33.06
$\Delta O$	0.13 ( $\pm 0.21$ )	-0.32	-0.09	-0.08	0.24	0.38
$\Sigma_{\text{cations}}$	3.001	2.997	2.994	2.983	3.000	2.997
O <sub>min</sub>	31.69	32.91	32.62	32.02	32.53	33.06
O <sub>max</sub>	33.21	34.44	34.19	33.42	34.18	34.55
FeO (corr.)	13.65	13.68	14.08	12.57	14.82	13.41
Fe <sub>2</sub> O <sub>3</sub> (corr.)	0	0	0	0	0	0

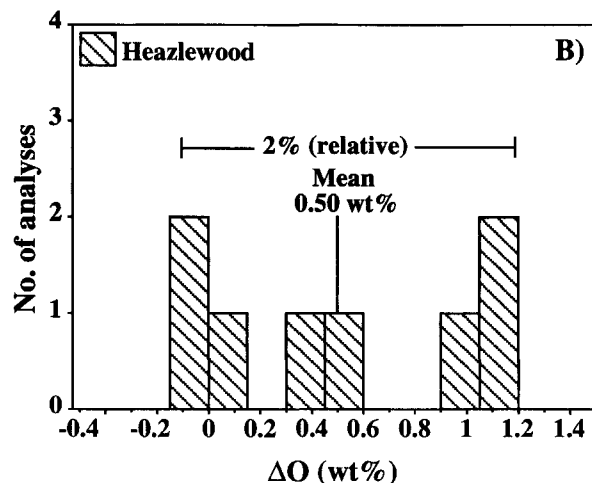
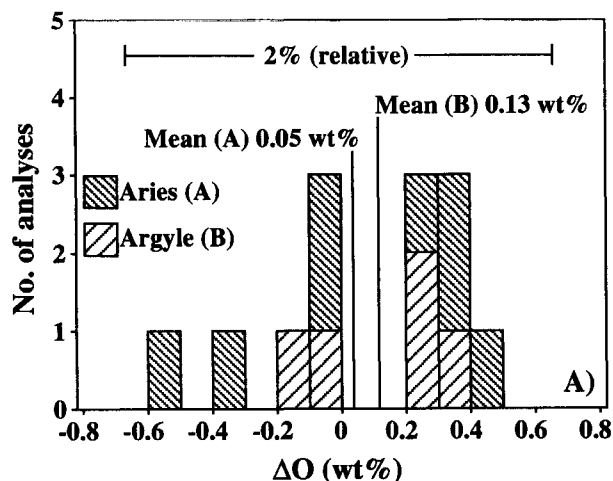
Note: Kmb = kimberlite, Lmp = lamproite. Analysis no. 1 is an average of five analyses of individual grains; numbers in parentheses give the range of individual analyses. See the beginning of the Results section for the definition of parameters of spinel compositions used in this table. FeO (corr.) = wt% of FeO present in spinel as calculated from O measurements. Fe<sub>2</sub>O<sub>3</sub> (corr.) = wt% of Fe<sub>2</sub>O<sub>3</sub> present in spinel as calculated from O measurements.

to 2.9 wt% FeO or 2.16 wt% Fe<sub>2</sub>O<sub>3</sub>. This demonstrates the danger of using individual O analyses for estimations of real spinel Fe<sup>2+</sup>/Fe<sup>3+</sup> values and for assessing the existence of nonstoichiometry. Because of this, we employed a statistical approach to the O data. We considered average  $\Delta O$  when the difference between individual  $\Delta O$  values did not exceed 2% (relative) of O<sub>meas</sub> and either analyzed spinels showed similar cation contents (inside the microprobe accuracy) or no correlation existed between  $\Delta O$  and cation concentrations. Where a good correlation existed between  $\Delta O$  and cation concentrations [standard deviations < 2% (relative) of O concentrations], a line of best fit illustrating  $\Delta O$  as a function of cation

composition was selected to represent a sample population, rather than a single average composition.

#### Diamond-indicator spinel

We analyzed five spinel grains from the Middle Proterozoic diamond-bearing Argyle olivine lamproite diatreme in the East Kimberley region of Western Australia (Jaques et al. 1986). These grains occur as ~1 mm xenocrysts in the lamproite matrix. They are characterized by a very constant composition, including O, and the average of the analyses is shown in Table 3 (no. 1). According to our cation analyses, these spinel grains are stoichiometric with all Fe present as Fe<sup>2+</sup>. O contents (in



**FIGURE 4.** (A) Frequency histogram of  $\Delta O$  for spinel from the Aries kimberlite and Argyle lamproite. The error bar indicates 2% (relative) of the mean. (B) Frequency histogram of  $\Delta O$

for spinel from the metamorphosed Heazlewood River Ultramafic Complex. The error bar indicates 2% (relative) of the mean.

**TABLE 4.** Representative analyses of spinel inclusions in olivine phenocrysts from primitive subduction-related magmas (values in wt%)

No.	1	2	3	4	5	6	7	8	9	10
Grain no.	115-4/H1 OL80-SP	115-4/H1 OL15E-SP	115-4/H1 OL88-SP	115-4/H1 OL77A-SP	115-4/H1 OL19-SPA	5-24/ OL3-SP	5-24/ OL3A-SPC	5-24/ OL27-SP	5-24/ OL4-SPA	5-24/ OL4-SPB
Type	Thol	Thol	Thol	Thol	Thol	Bon	Bon	Bon	Bon	Bon
Si	0.04	0.05	0.05	0.04	0.03	0.03	0.03	0.03	0.04	0.05
Ti	0.13	0.07	0.05	0.06	0.10	0.07	0.06	0.02	0.05	0.04
Al	6.57	5.20	5.21	5.22	5.57	3.29	3.45	3.47	3.28	3.23
Cr	34.59	38.29	36.78	37.07	36.89	41.97	41.24	40.94	44.21	43.03
Fe	18.14	15.97	17.26	16.86	16.57	15.44	15.54	16.01	10.72	11.13
Mg	6.98	7.35	6.80	6.98	7.04	7.07	7.07	6.88	8.43	8.25
Mn	0.22	0.28	0.21	0.22	0.20	0.20	0.23	0.24	0.16	0.17
Ni	0.07	0.09	0.05	0.06	0.08	0.06	0.06	0.06	0.04	0.09
Zn	0.09	0.03	0.06	0.02	0.05	0.06	0.03	0.08	0.09	0.04
O	32.67	32.62	32.64	32.85	33.14	32.06	32.08	32.20	33.15	32.71
Total	99.49	99.96	99.10	99.37	99.68	100.26	99.79	99.93	100.17	98.73
O <sub>calc</sub>	32.71	32.64	31.99	32.11	32.29	32.14	32.00	31.91	32.42	31.90
$\Delta O$	-0.04	-0.02	0.65	0.74	0.85	-0.08	0.08	0.29	0.73	0.81
$\Sigma_{\text{cations}}$	3.079	3.062	3.071	3.070	3.065	3.053	3.056	3.059	3.027	3.033
O <sub>min</sub>	31.88	31.98	31.26	31.99	31.61	31.60	31.42	31.30	32.15	31.56
O <sub>max</sub>	34.48	34.27	33.73	33.81	33.98	33.81	33.65	33.59	33.68	33.15
FeO (st)	15.90	14.64	15.64	15.23	15.25	14.95	14.78	15.13	11.30	11.22
Fe <sub>2</sub> O <sub>3</sub> (st)	8.26	6.56	7.30	7.17	6.74	5.46	5.79	6.08	2.77	3.44
Fe <sup>2+</sup> /Fe <sup>3+</sup> (st)	2.138	2.479	2.382	2.359	2.513	3.041	2.835	2.765	4.532	3.622
FeO (corr.)	16.25	14.82	9.77	8.60	7.55	15.70	14.08	12.48	4.78	3.97
Fe <sub>2</sub> O <sub>3</sub> (corr.)	7.88	6.37	13.83	14.54	15.30	4.64	6.58	9.02	10.02	11.50
Fe <sup>2+</sup> /Fe <sup>3+</sup> (corr.)	2.292	2.585	0.785	0.659	0.549	3.763	2.377	1.537	0.530	0.384
Fo	88.00	89.44	88.21	88.55	89.04	88.70	88.70	88.62	93.26	93.26

Note: Thol = tholeiite, Bon = boninite. Analyses 1–5 = spinel inclusions from Ti-poor tholeiite from the Hunter Fracture Zone. Analyses 6–10 = spinel inclusions from Ca-rich boninite from the northern Tonga Trench. See the beginning of the Results section for the definition of parameters of spinel compositions used in this table. Abbreviation st = values calculated assuming stoichiometry from cation analyses; corr. = values calculated on the basis of O data. During cation analyses of these spinels, V was not included in the analytical label. V<sub>2</sub>O<sub>5</sub> of 0.15 wt% assumed in all recalculations. This assumption is based on the results obtained by Sobolev and Danyushevsky (1994) and Danyushevsky (unpublished data), who analyzed many spinel inclusions from the same samples. Results indicated a value for V<sub>2</sub>O<sub>5</sub> of 0.15 ± 0.07 wt%, with no correlation to other element concentrations.

terms of  $\Delta O$ ) of the individual spinels are shown in Figure 4A. The variations between individual analyses are well inside the precision, and an average of 31.83 wt% was accepted as the O content of these spinels. Thus, our results lead to  $\Delta O$  of +0.13 wt%. Although this may indicate a low degree of nonstoichiometry with some Fe present as Fe<sup>3+</sup>, we believe that the existing data are insufficient for such a conclusion and rather show a good agreement between cation and O data, which indicate that Argyle spinel is stoichiometric with all Fe present as Fe<sup>2+</sup>.

We also conclude that spinel from the Lower Proterozoic diamond-bearing Aries kimberlite diatreme in the Kimberley region, Western Australia (Edwards et al. 1992) is stoichiometric on the basis of analyses of eight grains from a spinel concentrate. Like the Argyle spinel, these spinel grains occur as ~1 mm xenocrysts in the matrix. Despite the fact that they are characterized by some significant variations in cation contents (Table 3, nos. 2–6), the cation data indicate that, within error, all Fe is present as Fe<sup>2+</sup>, and the average spinel has  $\Delta O$  of +0.05 wt% (Fig. 4A).

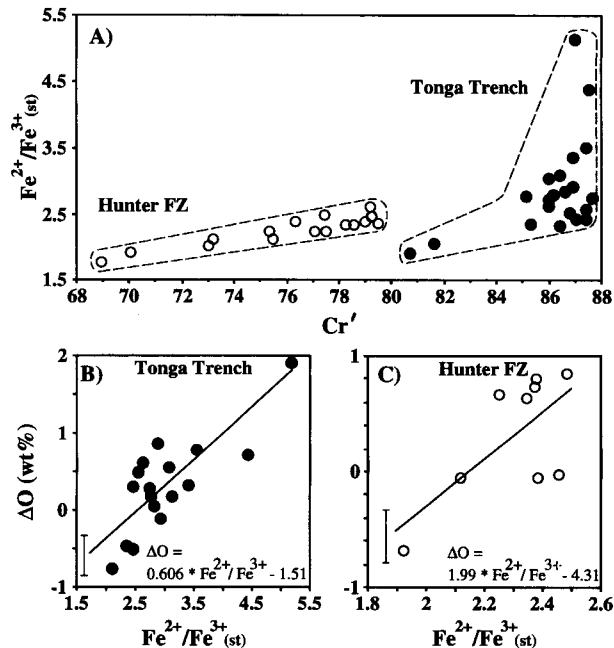
#### Spinel inclusions in olivine from primitive subduction-related magmas

Cr-rich spinel is a common liquidus mineral in primitive subduction-related suites. Usually it is found as inclusions (up to 50  $\mu\text{m}$  in diameter but more often 15–20  $\mu\text{m}$  in diameter) in olivine phenocrysts. Two suites de-

scribed here, Ti-poor tholeiite from the Hunter Fracture Zone, North Fiji Basin (Sigurdsson et al. 1993) (Table 4, nos. 1–5), and Tongan Ca-rich boninite (Sobolev and Danyushevsky 1994) (Table 4, nos. 6–10) are characterized by a large range of olivine compositions and subsequent variations in the compositions of spinel inclusions (Table 4, Fig. 5). Unlike the diamond-indicator spinel, all analyzed spinel grains have  $\Sigma_{\text{cations}} > 3$ , implying the presence of Fe<sup>3+</sup> if this spinel is to be stoichiometric. Both suites demonstrate a positive correlation between Cr' and Fe<sup>2+</sup>/Fe<sup>3+</sup> values calculated assuming stoichiometry (Fig. 5A). Spinel from the Hunter Fracture Zone shows a range of Fe<sup>2+</sup>/Fe<sup>3+</sup> values from 1.9 to 2.5, and spinel from Tongan boninite shows a range from 2.1 to 5.2.

Unlike the diamond-indicator spinel, O data for spinel inclusions in olivine phenocrysts from subduction-related suites show wide deviations from stoichiometry ( $-0.75 < \Delta O < +1.9$ ), which cannot be accounted for by the precision of the technique. Also, unlike the diamond-indicator spinel, these spinel grains show a good correlation between nonstoichiometry and spinel composition (Figs. 5B and 5C). Spinel Fe<sup>2+</sup>/Fe<sup>3+</sup> values calculated according to stoichiometry correlate with  $\Delta O$ . This leads to corrected (i.e., actual) Fe<sup>2+</sup>/Fe<sup>3+</sup> values (Table 4) that are significantly lower for spinel with high Fe<sup>2+</sup>/Fe<sup>3+</sup>.

Results obtained are of particular importance for estimating MgO contents (and consequently liquidus temperatures) of primitive subduction-related melts that were in equilibrium with Cr-rich spinels and their olivine hosts.



**FIGURE 5.** (A)  $\text{Fe}^{2+}/\text{Fe}^{3+}$  vs.  $\text{Cr}'$  for spinel inclusions in olivine from Ti-poor tholeiite from the Hunter Fraction Zone and Tongan Ca-rich boninite.  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is calculated assuming spinel stoichiometry. (B and C) Plot of  $\Delta\text{O}$  vs.  $\text{Fe}^{2+}/\text{Fe}^{3+}$  for spinel inclusions from the Tongan boninite and the Hunter Fraction Zone tholeiite, respectively. The equations for  $\Delta\text{O}$  as a function of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  represent lines of best fit. Calculated regression coefficients for the lines of best fit in B and C are 0.78 and 0.68, respectively. The error bars indicate 2% (relative) of the mean.

Indeed, the  $\text{Mg}'$  of such melts can be inferred using well-known parameters of olivine-melt equilibria (e.g., Ford et al. 1983). Thus,  $\text{MgO}$  contents are a function of  $\text{Fe}^{2+}$  concentrations, which, in turn, are dependent on  $f_{\text{O}_2}$  (e.g., Kress and Carmichael 1988). The high  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values calculated in the most primitive Cr-rich spinel according to stoichiometry would lead to erroneously low  $f_{\text{O}_2}$  values when calculated using a spinel O geosensor. This, in turn, would lead to erroneously high  $\text{Fe}^{2+}$  and, as a result, high  $\text{MgO}$  in primitive subduction-related melts.

Our results indicate that  $f_{\text{O}_2}$  cannot be correctly estimated assuming stoichiometry and using the cation compositions of Cr-rich spinel from primitive subduction-related magmas. Correct estimations of  $f_{\text{O}_2}$  for these suites remain a problem, as even known accurate cation compositions of nonstoichiometric spinel are not sufficient for  $f_{\text{O}_2}$  calculation, because the effect of cation deficiency (or excess) on the activity of elements in Cr-rich spinel is unknown.

#### Spinel from metamorphosed volcanic rocks

We also analyzed two populations of Cr-rich spinel from old volcanic complexes of boninitic affinity, the weakly metamorphosed Upper-Middle Cambrian Heazlewood River Ultramafic Complex, Western Tasmania (Peck 1990), and the Middle Proterozoic graywackes and volcanic rocks from the greenschist facies Glengarry Group in the Peak Hill area, central Western Australia (Hynes and Gee 1986). Although a magmatic origin has been suggested for both spinel populations, these spinels, un-

**TABLE 5.** Representative analyses of spinel from metamorphosed volcanic rocks (values in wt%)

No.	1	2	3	4	5	6	7	8	9
Locality	Peak Hill	Peak Hill	Peak Hill	Peak Hill	Peak Hill	Peak Hill	Peak Hill	Peak Hill	Heazlewood
Grain no.	507	405	202	304	204	806	708	203	
Si	0.04	0.01	0.03	0.02	0.03	0.03	0.04	0.03	0.03 ( $\pm 0.01$ )
Ti	0.01	0.09	0.07	0.01	0.02	0.01	0.05	0.02	0.03 ( $\pm 0.00$ )
Al	1.46	2.76	1.69	1.67	1.54	1.46	1.79	1.85	3.20 ( $\pm 0.26$ )
Cr	48.31	42.00	47.73	47.40	46.76	47.39	44.72	45.89	42.56 ( $\pm 0.67$ )
V	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04 ( $\pm 0.00$ )
Fe	9.39	19.20	8.16	9.87	11.49	10.67	14.91	12.29	17.28 ( $\pm 1.11$ )
Mg	7.08	2.05	7.52	6.50	5.66	5.52	3.46	5.20	5.26 ( $\pm 0.23$ )
Mn	0.53	1.41	0.90	0.99	0.81	1.04	0.83	0.60	0.24 ( $\pm 0.05$ )
Ni	0.12	0.01	0.10	0.06	0.05	0.10	0.05	0.00	0.04 ( $\pm 0.04$ )
Zn	0.06	0.56	0.43	0.27	0.36	0.77	0.95	1.37	0.07 ( $\pm 0.03$ )
O	33.04	31.33	33.37	33.06	32.76	32.88	32.07	33.33	31.88 ( $\pm 0.62$ )
Total	100.04	99.42	99.99	99.84	99.48	99.87	98.87	100.57	100.61 ( $\pm 0.68$ )
$\text{O}_{\text{calc}}$	31.25	29.36	31.34	30.91	30.40	30.47	29.39	30.37	31.38 ( $\pm 0.28$ )
$\Delta\text{O}$	1.79	1.97	2.03	2.15	2.36	2.41	2.68	2.96	0.50 ( $\pm 0.65$ )
$\Sigma_{\text{cations}}$	2.988	3.002	2.992	2.989	2.989	2.982	2.985	2.994	3.030
$\text{O}_{\text{min}}$	31.25	29.36	31.34	30.91	30.40	30.47	29.39	30.37	31.06
$\text{O}_{\text{max}}$	32.59	32.11	32.50	32.33	32.04	32.00	31.53	32.13	33.53
FeO (st)	12.08	24.57	10.50	12.69	14.78	13.73	19.19	15.81	19.34
$\text{Fe}_2\text{O}_3$ (st)	—	—	—	—	—	—	—	—	3.21
$\text{Fe}^{2+}/\text{Fe}^{3+}$ (st)	—	—	—	—	—	—	—	—	6.703
FeO (corr.)	—	7.00	—	—	—	—	—	—	14.89
$\text{Fe}_2\text{O}_3$ (corr.)	13.43	19.67	11.66	14.11	16.42	15.26	21.32	17.57	8.16
$\text{Fe}^{2+}/\text{Fe}^{3+}$ (corr.)	—	0.395	—	—	—	—	—	—	2.029
% maghemite	52.4	56.2	57.2	61.7	68.3	71.2	79.6	81.8	—

Note: Analysis 9 is an average of eight analyses of individual grains; numbers in parentheses show the range of individual analyses. See the beginning of the Results section for the definition of parameters of spinel compositions used in this table. Abbreviation st = values calculated assuming stoichiometry from cation analyses; corr. = values calculated on the basis of O data; % maghemite = % of  $\square_{1/3}\text{Me}_{2/3}\text{O}_4$  in spinel structure calculated on the basis of O data.



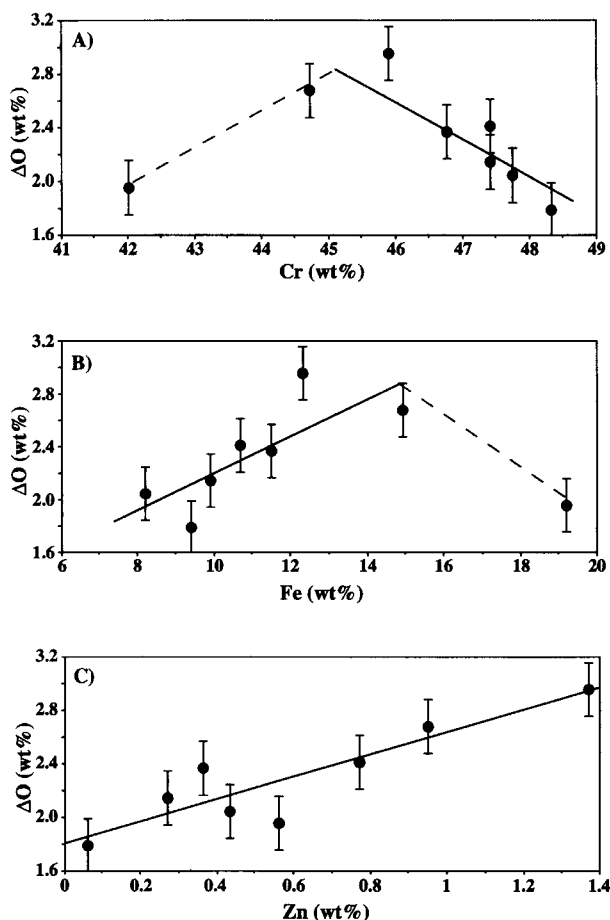


FIGURE 6. Plot of (A)  $\Delta O$  vs. Cr, (B)  $\Delta O$  vs. Fe, and (C)  $\Delta O$  vs. Zn for spinel grains from the Glengarry Group in the Peak Hill area. The error bars indicate 2% (relative) of the mean.

like spinels described in the previous sections, have undergone metamorphic reequilibration.

We analyzed eight spinel grains from a spinel concentrate from the Peak Hill area. The grains are characterized by very high  $Cr_2O_3$  contents (61–71 wt%), variably high Mn and Zn, and generally low Fe contents (Table 5) in comparison with the previously discussed spinel samples. According to cation analyses, they are stoichiometric with all Fe present as  $Fe^{2+}$ . Unlike diamond-indicator and boninitic spinel, these spinel grains have very high  $\Delta O$  (+1.8 to +3 wt%), and a good correlation exists between  $\Delta O$  and Zn, Fe, and Cr content (Fig. 6). With the exception of one spinel grain (Table 5, no. 2), the  $O_{meas}$  is significantly higher than  $O_{max}$ , which requires that all Mn is present as  $Mn^{3+}$  and that some Cr is present as  $Cr^{4+}$  to achieve electric neutrality. Although the presence of  $Cr^{4+}$  implies a very high oxidation state, minor amounts of  $Cr^{4+}$  have been reported in other minerals (e.g., rutile, Ishida et al. 1990). The relationships between O and cations indicate that these spinel grains deviate greatly from spinel stoichiometry and have compositions that lie between the  $Me_3O_4$  and  $\square_{1/3}Fe_8O_4$ - $\square_{1/3}Cr_8O_4$  (magnetite-

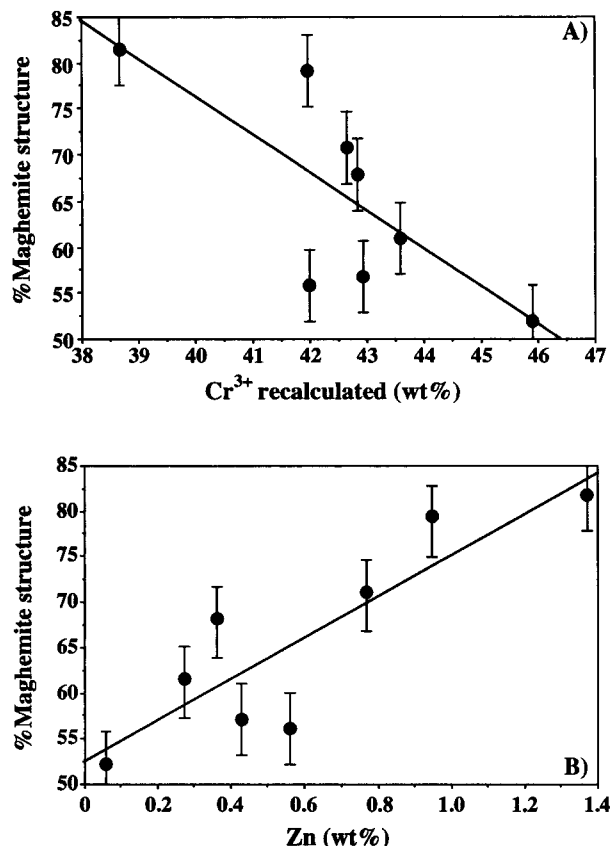


FIGURE 7. (A) Percent maghemite vs.  $Cr^{3+}_{recalc}$  and (B) percent maghemite vs. Zn for spinel grains from the Glengarry Group in the Peak Hill area. Percent maghemite represents the amount of  $\square_{1/3}Me_8O_4$  end-member and is calculated from the O data.  $Cr^{3+}_{recalc}$  is calculated from the O data assuming all Fe is  $Fe^{3+}$ , all Mn is  $Mn^{3+}$ , and some Cr is  $Cr^{4+}$  to achieve electric neutrality. The error bars indicate 2% (relative) of the mean.

Cr equivalent of magnetite) end-members. To estimate the degree of nonstoichiometry of each analysis, we calculated the percent of  $\square_{1/3}Me_8O_4$ , which varies between 50 and 80% (Fig. 7).

Spinel from the Heazlewood Complex probably occurred originally as inclusions in mafic silicate phenocrysts. Eight analyzed grains have very similar cation compositions, and an average of the analyses is shown in Table 5 (no. 9). O data show variations inside 2% (relative) of  $O_{meas}$ , with a mean of  $\Delta O = +0.5$  wt% (Fig. 4B), and because no correlation was observed between cation compositions and  $\Delta O$  variations, an average of 31.88 wt% O was accepted as the O content of this spinel.

Our O data indicate that Heazlewood spinel is significantly nonstoichiometric, having an excess of 4.95 wt%  $\square_{1/3}Fe_8O_4$  in comparison with stoichiometry.

## CONCLUSIONS

Our results indicate that spinel nonstoichiometry may be a common occurrence in Cr-rich spinels. This has serious consequences when using  $Fe^{3+}$  in spinels to calcu-

late the  $f_{O_2}$  from heterogeneous mineral redox equilibria, or  $Fe^{2+}$  to calculate the temperature of formation from mineral exchange reactions.

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