Chromium influence on Mg-Al intracrystalline exchange in spinels and geothermometric implications

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ABSTRACT

Flux-grown spinel crystals belonging to the MgAl_2O_4-MgCr_2O_4 spinel series were investigated in order to reveal the effects of Cr substituting for Al on cation distribution and their influence on Mg-Al intracrystalline exchange. Samples were structurally and chemically characterized by single-crystal X-ray diffraction and electron microprobe, and cation distribution was obtained with a tested optimization model for site populations. The results evidenced that the contribution of the tetrahedral bond distance to the unit-cell parameter is smaller than that of the octahedral bond distance, which is driven by the substitution of Cr for Al. Moreover, the influence that Cr exerts on Mg-Al order-disorder intersite exchange is non-linear along the whole series.

The comparison between the cation distributions derived from crystal-chemical data and the O’Neill-Navrotsky thermodynamic model (with $\alpha_{\text{Mg-Al}} = 23 \text{ kJ mol}^{-1}$ and $\beta_{\text{Mg-Al}} = 13 \text{ kJ mol}^{-1}$) shows large discrepancies, which can be reconciled assuming $\alpha_{\text{Mg-Al}}$ values variable from 23 kJ mol$^{-1}$ to 100 kJ mol$^{-1}$ as a function of Cr. This suggests that, irrespective of temperature, the Al ordering at the octahedrally-coordinated site increases with increasing Cr substitution for Al. The geothermometric implications of the present study point out that closure temperatures, calculated from a well-tested intersite geothermometer, are reliable for spinels with magnesiochromite component smaller than 85%, i.e., $\text{Cr/(Cr+Al)} < 0.85$, whereas spinels with larger magnesiochromite component yield unreliable closure temperature.
MINERAL SPECIES WITH SPINEL-TYPE STRUCTURE ARE DIFFUSE IN A WIDE RANGE OF GEOLOGICAL ENVIRONMENTS, FROM UPPER MANTLE TO CRUST, CRYSTALLIZING IN various PHYSICO-CHEMICAL CONDITIONS. THEIR IMPORTANCE AS PETROGENETIC INDICATORS AND FOR OXYGEN THERMOBAROMETRY HAS BEEN WIDELY RECOGNIZED AND HAS PROMPTED EXTENSIVE STUDIES (e.g., Ghiorso and Sack 1991; Righter et al. 2006; Papike et al. 2015).

OXIDE SPINELS HAVE FORMULA AB₂O₄ WHERE THE LETTER A AND B REPRESENT EITHER DIVALENT AND TRIVALENT CATIONS OR, LESS FREQUENTLY, TETRAVALEN'T AND DIVALENT CATIONS, RESPECTIVELY. THE SPINEL STRUCTURE IS DESCRIBED, IN THE SPACE GROUP Fd̅3m, AS A SLIGHTLY DISTORTED CUBIC close-packed ARRAY OF OXYGEN ATOMS, IN WHICH A AND B CATIONS ARE DISTRIBUTED OVER 1/8 OF THE TETRAHEDRAL (T) AND 1/2 OF THE OCTAHEDRAL (M) COORDINATED SITES: (8a and 16d Wyckoff notation, respectively). THE UNIT CELL (a) CONTAINS 32 OXYGEN ATOMS (AT FRACTIONAL COORDINATES u, u, u).

Two extreme cation distributions are possible in spinel: normal (i = 0) and inverse (i = 1), resulting in the formula T⁵(A₁₋ᵢBᵢ)M(AᵢB₂₋ᵢ)O₄, WHERE THE LETTER i REPRESENTS THE INVERSION PARAMETER, THAT IS THE NUMBER OF B CATIONS AT THE T SITE. THIS i PARAMETER IS TEMPERATURE-DEPENDENT AND INCREASES IN NORMAL SPINELS FROM CA. 0 TO CA. 0.35, WHEREAS IT DECREASES IN INVERSE SPINELS FROM CA. 1 TO CA. 0.70 (Nell et al. 1989; O’Neill et al. 1992; Redfern et al. 1999; Andreozzi et al. 2000). THE i VALUE IS ALSO DEPENDENT ON SPINEL COMPOSITION, OXYGEN FUGACITY AND CRYSTALLIZATION KINETICS (e.g., Andreozzi et al. 2001a,b; Andreozzi and Princivalle 2002; Nestola et al. 2007, 2009; Perinelli et al. 2014; Papike et al. 2015). IN ADDITION, CATION SITE PREFERENCE HAS TO BE TAKEN INTO ACCOUNT WHEN ANALYZING CATION DISTRIBUTION IN SPINELS. FOR EXAMPLE, CR³⁺, V³⁺ AND Ti⁴⁺ STRONGLY PREFER THE M SITE; AL AND Cu²⁺ EXHIBIT PREFERENCE FOR M BUT ARE AVAILABLE TO PARTLY INVERT AT THE T SITE AT HIGH TEMPERATURE; Fe³⁺ HAS NO PREFERENCE; Mg, Fe²⁺, Mn²⁺ AND Co²⁺ EXHIBIT PREFERENCE FOR THE T SITE BUT CAN ALSO PARTLY INVERT AT THE M SITE AT HIGH TEMPERATURE; Zn ONLY OCCUPIES THE T SITE (e.g., Lucchesi et al. 1998a; Andreozzi et al. 2001a; Andreozzi and Lucchesi 2002; Bosi et al. 2008, 2010, 2012; 2016; Hålenius et al. 2007; Fregola et al. 2012; D’Ippolito et al. 2012).

In spinel, at high temperature most of the cations are partially disordered between the T and M sites due to role of entropy in controlling order-disorder in these systems and as the structure is somewhat more accommodating of the different-sized cations than at low temperature. During the cooling path, on the other hand, there is a continuous cation ordering, which firstly follows an equilibrium path and then progressively deviates from it.
The temperature of apparent equilibration corresponding to the quenched-in ordering state, that is, the temperature at which the rate of exchange slows to the point where the change is no longer detectable, is defined as closure temperature $T_c$ (Ganguly 1982). This process implies that the cation ordering also relies on the rate at which spinel cooled, and is a track of thermal history of host rock. A lot of studies focused on Mg-Al intracrystalline order-disorder relationships, their dependence on equilibrium temperature, cooling history and composition, with the aim of using Mg-Al rich-spinels for geothermometric purposes (e.g., Princivalle et al. 1989; Peterson et al. 1991; Millard et al. 1992; Della Giusta et al. 1996; Princivalle et al. 1999; Andreozzi et al. 2000; Andreozzi and Princivalle 2002). This intersite geothermometer is analytically challenging, because requires the determination of the site distribution of Mg and Al, which is (at least) temperature- and time-dependent. In fact, the higher the temperature, the higher the disorder of Mg and Al over T and M; vice versa, during crystal cooling Mg and Al progressively orders at T and M, respectively. As stated above, the ordering process stops at $T_c$ and depends on cooling rate: slow cooling allows a strong Mg-Al intracrystalline ordering in spinel and the geothermometer calculates low $T_c$, whereas fast cooling preserves the disordered state and consequently gives higher $T_c$ (e.g., Princivalle et al. 1989, 1999; Della Giusta et al. 1996; Lucchesi et al. 1998b, 2010).

Cr-bearing spinels represent 14% of all mineral inclusions in cratonic diamonds (e.g., Stachel and Harris 2008, Lenaz et al. 2009; Nestola et al. 2014), and are often among the first phases that crystallize from a wide variety of mafic-ultramafic igneous rock types and tectonic environments (e.g., Irvine 1965, 1967; Barnes and Roeder 2001; Lenaz et al. 2014a). Therefore, they may preserve important records of the geological conditions in which they formed in the crust and upper mantle, and understanding how to decipher those records is extremely important. However, in Mg-Al-Cr-spinels, the marked preference of Cr for the octahedral environment strongly influences both spinel crystal-chemistry and calculated $T_c$ by affecting the site distribution of Mg and Al (Lavina et al. 2003). Moreover, natural Mg-Al-Cr-spinels often contain other chemical constituents such as Fe$^{2+}$ and Fe$^{3+}$ that may hinder the influence of Cr on both cation ordering and $T_c$ (Martignago et al. 2003). It is therefore crucial to test geothermometric exchanges studying spinel samples along the Fe-free binary series spinel sensu stricto (s.s.)-magnesiochromite ($\text{MgAl}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$).

In the present study, the $\text{MgAl}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ spinel substitution series will be investigated in order to reveal the crystal-chemical effects of Cr substitution for Al and their influence on Mg-Al intracrystalline exchange. Flux-grown synthetic crystals, already studied by optical absorption spectroscopy in Hålenius et al. (2010), will be structurally and
chemically characterized by single-crystal X-ray diffraction and electron microprobe, cation distribution will be obtained with a tested optimization model for site populations, and $T_c$ will be finally calculated with the geothermometer equation of Princivalle et al. (1999). The approach adopted will allow the definition of the compositional range where this geothermometer applies when the MgCr$_2$O$_4$ component increases.

**EXPERIMENTAL METHODS**

**Synthesis**

A flux-growth method with Na$_2$B$_4$O$_7$ used as flux compound was used to obtain single crystals along the binary join spinel s.s.-magnesiochromite. Analytical grade MgO, Al(OH)$_3$ and Cr$_2$O$_3$ were dehydrated and dried at elevated temperatures before mixing with Na$_2$B$_4$O$_7$. The starting materials were transferred to Pt/Au (5%) crucibles and covered by a Pt lid. Thermal runs consisted of 24 h at 1200 °C followed by a slow decrease to 900 °C at a controlled cooling rate of 4 °C/h. After shutting off the power to the heating elements and removing crucibles from the furnace a rapid cooling to room temperature was obtained. Successful runs consisted of octahedral spinel crystals, borate needles, and occasional eskolaite ($\alpha$-Cr$_2$O$_3$) embedded in a borate-rich glass. The glass phase and borate crystals were dissolved in warm diluted HCl. The recovered spinel single crystal have typical size in the range 200-300 μm. The largest, ruby-red, gem-quality crystals were obtained for Cr-poor compositions, intermediate compositions yielded sub-regular crystals, but smaller, black octahedra were also obtained close to magnesiochromite end member.

**Single-crystal structural refinement**

The examined samples constitute a set of nine hand-picked spinel single crystals. For X-ray data collection two single-crystal diffractometers were used (Siemens P4 and APEX-II). In detail, six out of nine crystal-fragments were mounted on a Bruker Siemens P4 automated four-circle diffractometer, equipped with a point detector. Unit-cell parameters were measured, at 293 K, by centering 52 reflections (13 independent and their Friedel pairs, on both sides of the direct beam), in the range 85-95° 2θ, with Mo-$K\alpha_1$ radiation (0.70930 Å). Intensity data were collected, at 293 K, using MoK$\alpha$ radiation (0.71073 Å) monochromatized by a flat graphite crystal in the 3-95° 2θ range with the $\omega$-scan method and at a fixed scan range (2.4°). One-eighth of the reciprocal space was examined. The scan speed was variable (2.93-29.3°/min), depending on reflection intensity, as estimated through pre-scans. The
background was measured with a stationary counter and crystal at the beginning and end of each scan, in both cases for half the scan time. Three standard reflections were monitored every 47 measurements. Data reduction was performed with the SHELXTL-PC program package. Intensities were corrected for polarization and Lorentz effects. Absorption correction was accomplished with a semi-empirical method (North et al. 1968). Three out of nine crystal-fragments were mounted on a Bruker KAPPA APEX-II diffractometer, equipped with a CCD area detector (6.2 × 6.2 cm² active detection area, 512 × 512 pixels) and a graphite crystal monochromator, using MoKα radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. More than 5000 exposures per sample were measured (step = 0.2°, time/step = 10 s) covering the full reciprocal sphere with an average redundancy of about 20. Final unit-cell parameters were refined by using the Bruker AXS SAINT program from about 2000 (about 1200 for sample MgCr5c) recorded reflections with \( I > 10 \sigma_I \) in the range \( 8^\circ < 2\theta < 90^\circ \) (72° for sample MgCr5c). The intensity data were processed and corrected for Lorentz, polarization and background effects with the APEX2 software program of Bruker AXS. The data were corrected for absorption using multi-scan method (SADABS), leading to a significant improvement in \( R_{int} \). No violation of \( Fd \overline{3}m \) symmetry was noted.

Structure refinement was done with the SHELXL-2013 program (Sheldrick 2013). All reflections were used in the refinement. Variable parameters during the structural refinement were: overall scale factor, oxygen coordinate, site-scattering values, atomic-displacement parameters, and extinction parameter. In the final stage of the refinement, the extinction parameter was removed from the variables of sample MgCr5c, because its value refined to zero. Setting the origin at \( \overline{3}m \), initial atomic positions for oxygen atoms were taken from Hålenius and Bosi (2014). The T site was modeled with Mg and the M site with Al vs. Cr (except for crystal MC02bb, which was modeled considering only \( ^{\text{M}}\text{Al} \) due to the small Cr concentrations). Convergence was attained when the shifts in all refined parameters were less than their estimated standard deviation. A further refinement with chemical constraints was done for CIF (on deposit\(^1\)) by modelling the T site cation occupancy of crystals MC02bb and MC02de with the \(^{\text{T}}\text{Mg} \) and \(^{\text{T}}\text{Al} \) fixed to the value obtained from the structural formula. The results are statistically equal to those reported in Table 1, which summarizes structural parameters and refinement details.

**Electron microprobe analysis**
The same crystals as used for X-ray data collection were mounted on a glass slide and polished for electron microprobe analysis on a Cameca SX50 instrument equipped with four wavelength dispersive spectrometers (WDS mode) and operated at an accelerating potential of 15 kV and a sample current of 15 nA, with an incident beam diameter of ca. 1 µm. No less than 10 spot analyses for each sample were performed to obtain the average chemical compositions and to estimate compositional homogeneity. Synthetic standards used were periclase (Mg), corundum (Al) and metallic Cr. For raw data reduction, the PAP computer program was applied (Pouchou and Pichoir 1984). Spinel formulae were calculated on the basis of 4 oxygen atoms and 3 cations per formula unit. The resulting atomic fractions (atoms per formula unit, apfu) are well supported by the match between number of electrons per formula unit derived from chemical and structural analysis (Table 2).

Cation distribution

The intersite cation distribution was obtained by minimizing the residuals between calculated and observed chemical-structural data by using a least-squares approach. The minimized function is:

$$F(X_i) = \frac{1}{n} \sum_{j=1}^{n} \left( \frac{O_j - C_j(X_i)}{\sigma_j} \right)^2$$

where $O_j$ is the observed quantity, $\sigma_j$ its standard error, $X_i$ the variables, i.e., cation fractions at the T and M sites, and $C_j(X_i)$ the same quantity as $O_j$ calculated by means of $X_i$ parameters. The $nO_j$ quantities taken into account were: $a$- and $u$-parameter, T-O and M-O bond distances, mean atomic number of T and M sites, total atomic fractions derived from electron-microprobe analyses, constraints relative to the formula electroneutrality (8 positive and 8 negative charges) and site population (T = 1.000 and M = 2.000). The M-O and T-O bond distances were calculated as the linear contribution of each cation multiplied by its ideal bond distance reported by Lavina et al. (2002): $^{\text{T}}$Mg-O = 1.966 Å, $^{\text{M}}$Mg-O = 2.082 Å, $^{\text{T}}$Al-O = 1.774 Å, $^{\text{M}}$Al-O = 1.908 Å, $^{\text{M}}$Cr$^{3+}$-O = 1.995 Å. More details about the minimization procedure may be found in Lavina et al. (2002). Due to crystal-field stabilization energy, a marked octahedrally coordinated site preference is expected for Cr$^{3+}$, thus it was constrained to occur at the M site. The calculated parameters fit the observed ones within 2$\sigma$ in 95% of cases (Table 3, on deposit). The results of optimized cation distributions are reported as structural formulae in Table 4.
RESULTS AND DISCUSSION

Crystal structure

Crystal structure of Cr-bearing spinels at environmental conditions is commonly described on the basis of $Fd\bar{3}m$ space group. The end member MgCr$_2$O$_4$ exhibits a first-order phase transition at 12.5 K with a pronounced peak in heat capacity coinciding with the phase transition from cubic to tetragonal symmetry ($I4_1/amd$ space group; Ehrenberg et al. 2002). Moreover, a post-spinel MgCr$_2$O$_4$ orthorhombic phase, $Bbmm$ space group, was recently synthesized at 23 GPa and 1600 °C (Bindi et al. 2014) and found in ultrahigh-pressure chromitites (Ishii et al. 2015).

Previously studies also stated that the structure of Cr-rich spinels at environmental conditions may be better described by the space group $F\bar{4}3m$ (Grimes 1971; Sickafus et al. 1999) due to the displacement of Cr at the M site along the direction [111] from a centrosymmetric position to a non-centrosymmetric position, which causes a reduction in point symmetry of the M site from $\bar{3}m$ to $3m$. In addition, Lutz et al. (2000) suggested that the occurrence of a less symmetric space group in Cr-rich spinels is due to the strength of the metal-metal bonds.

However, structure refinements of the present study, along with the results of O’Neill and Dollase (1994), Lenaz et al. (2004) and Nestola et al. (2014), fully support the occurrence of $Fd\bar{3}m$ space group for both Cr-bearing spinels and the magnesiocromite end member.

Crystal chemistry

The flux-grown spinel crystals investigated are characterized by Cr ↔ Al substitution along the whole substitution series and are representative of the entire MgAl$_2$O$_4$-MgCr$_2$O$_4$ series. The Cr$_2$O$_3$ contents vary from 4.9(5) to 76.1(1) wt% (Table 2) and the corresponding magnesiocromite component from 3% to 96% (Table 4). To attain a complete picture of the structural relations along the whole series, we included crystal-chemical data of the synthetic end-member magnesiocromite $T(Mg)M(Cr)_2O_4$, grown in the same conditions (Nestola et al. 2014).

Site distribution of Mg, Al and Cr shows that the T site is mainly populated by Mg and by small amounts of Al which decrease with increasing Cr content. The M site is dominated by the substitution Cr ↔ Al and also shows small amounts of Mg which decrease with increasing Cr. Accordingly, the degree of inversion decreases from 0.23 to 0.00 with
increasing Cr content (Table 4). As a consequence, the distribution of Mg and Al over the T and M sites is well explained by the order-disorder reaction $^{M}\text{Al} + ^{\text{T}}\text{Mg} \leftrightarrow ^{\text{T}}\text{Al} + ^{M}\text{Mg}$.

During the replacement of Al by Cr, the bond distances T-O and M-O linearly increase with increasing $^{\text{T}}\text{Mg}$ and $^{M}\text{Cr}$, respectively, according to the equations:

- \[ T\text{-O} = 0.1926 \cdot ^{\text{T}}\text{Mg} + 1.7733, \quad (r^2 = 0.9998); \]
- \[ M\text{-O} = 0.0327 \cdot ^{M}\text{Cr} + 1.9266, \quad (r^2 = 0.996). \]

Moreover, M-O decreases with increasing inversion degree ($i = ^{\text{T}}\text{Al}$) according to a non-linear trend:

- \[ M\text{-O} = 1.991 - 0.521 \cdot i + 1.146 \cdot i^2, \quad (r^2 = 0.985), \]
- and T-O shows a non-linear relation with Cr content ($r^2 = 0.995$).

The unit-cell parameter increases from 8.092 Å to 8.332 Å with increasing Cr (Fig. 1) and is positively correlated with both T-O and M-O, which vary from 1.922 Å to 1.967 Å and from 1.930 Å to 1.994 Å, respectively. Therefore, the contribution of T-O to the unit-cell parameter variation is smaller than that of M-O, which is driven by the Cr variation in the spinel structure. The correlation between $a$-parameter and T-O and M-O bond distances is better described by a non-linear regression (Fig. 2), which non-linearity can be ascribed to the occurrence of a non-linear relation between $i$ and Cr content (see below). These non-linear trends can be better explained by using the parameter $^{\text{T}}\text{Al}/\text{Al}_{\text{tot}} = (1 + ^{\text{T}}\text{Al}/^{M}\text{Al})$ that represents the availability of Al to be inverted with Mg, when Cr increases. Far from being constant, the parameter $^{\text{T}}\text{Al}/\text{Al}_{\text{tot}}$ shows a decreasing trend along the studied series, with a further drop for magnesiochromite component higher than 80% (Fig. 3). Notably, a constant value of $^{\text{T}}\text{Al}/\text{Al}_{\text{tot}}$ would account for a constant T-site preference of Al along the whole series, whereas decreasing values at increasing Cr contents suggest a minor tetrahedral affinity of Al. Hence, the trend observed in Figure 3 represents the influence of Cr on Mg-Al intersite exchange at any given equilibration temperature or thermal pathway, that is, irrespective of temperature. Moreover, the Cr influence on Mg-Al intersite exchange may also be invoked to explain the inconsistencies observed by Lavina et al. (2003) in modelling cation distribution and cooling rates of natural Cr-bearing spinels.

**Thermodynamics of Mg-Al intersite exchange in presence of Cr**

The intracrystalline cation distribution of the present spinel s.s.-magnesiochromite series was tentatively modeled by the general thermodynamic model for spinel binary substitution series proposed by O’Neill and Navrotsky (1984), which was proved to be adequate for modeling cation distribution as a function of temperature in spinels of different composition (e.g.,
Waerenborgh et al. 1994a,b; Andreozzi et al. 2001a; Andreozzi and Lucchesi 2002; Martignago et al. 2006; Princivalle et al. 2012). Applying this model to MgAl₂O₄-MgCr₂O₄ and disregarding the Cr inversion at T, due to its strong octahedral preference, the Mg-Al intersite exchange can be modeled as a function of temperature by the order-disorder reaction 

\[ ^{\text{M}}\text{Al} + ^{\text{T}}\text{Mg} \leftrightarrow ^{\text{T}}\text{Al} + ^{\text{M}}\text{Mg} \]  

Accordingly, the system of two equations, required for the general case, may be simplified as follows:

\[-RT\ln\left(\frac{i}{1-i} \right) = \alpha_{\text{Mg-Al}} + 2\beta_{\text{Mg-Al}} i \]  

where \( i = ^{\text{T}}\text{Al} \) in apfu, \( 2z = \) magnesiochromite molar content (i.e., Cr₉₀ in apfu), \( \alpha_{\text{Mg-Al}} = 23 \) kJmol⁻¹, and \( \beta_{\text{Mg-Al}} = 13 \) kJmol⁻¹ (Andreozzi et al. 2000). Equation (3) was solved for a range of temperatures, but \( T = 800 \) °C was eventually fixed (see below), and for \( 2z \) corresponding to the Cr contents of Table 4. The resulting values of \( i \), however, show a large deviation from \( i \) values derived from the crystal-chemical data (Fig. 4a). This deviation is maximum for intermediate Cr contents. The values calculated from the thermodynamic model would also suggest that, as a consequence of the influence of Cr on Mg-Al intersite exchange, the T-site preference of Al is non-linearly enhanced along the series. However, this is opposite to what observed (Fig. 4b).

The O'Neill-Navrotsky model assumes that cation ordering behavior in a substitution series can be entirely predicted on the basis of the energetics of the two end members (or one end member in this case, as the other is constrained to be perfectly normal). This is seen in equation (3), where the ordering is controlled by the parameters \( \alpha \) and \( \beta \) which are entirely constrained by the equilibrium ordering behavior in end member MgAl₂O₄. This approach, however, ignores the important energetic contributions from Al-Cr pairwise interactions, that are only present along the substitution series, and who’s effects cannot possibly be predicted from the end member behavior alone. Actually, in the present case the deviation between the model and observations is maximum for intermediate Cr contents because this is where the maximum number of Al-Cr interactions occur (Fig. 4a). This issue was discussed extensively for the magnesioferrite-qandilite series in Palin and Harrison (2007) and Harrison et al. (2013), who found that the total energy of such a series can formally be expressed as a sum of pairwise cation-cation interaction parameters and chemical potentials. The atomistic approach used by Harrison et al. (2013) is rigorous and effectively describes the underlying physics of spinel order-disorder with temperature along a substitution series. However, it is complex and lacks of an analytical solution, having rather limited practical use. On the other hand, the O'Neill-Navrotsky model is relatively simple and has been successfully used in many cases.
Nevertheless, it has been proved unsuccessful for the magnesioferrite-qandilite series (Harrison et al. 2013) as well as for the studied spinel s.s.-magnesiochromite series as it led to cation distribution inconsistent with experimental data. In the present study, for example, for an intermediate composition such as crystal MC15ad the T-O and M-O bond distances derived from thermodynamic data were 1.9341 and 1.9681 Å, respectively, which are significantly smaller than the corresponding observed values 1.9538(9) and 1.9588(5) Å (Table 1).

The unique way to apply the O’Neill-Navrotsky model to the present series is varying $\alpha_{\text{Mg-Al}}$ and $\beta_{\text{Mg-Al}}$ values in equation (3) as both $T$ and $i$ are known parameters. Using the inversion values of Table 4 and assuming a constant value of $\beta_{\text{Mg-Al}} = 13$ kJmol$^{-1}$ (Andreozzi et al. 2000), $\alpha_{\text{Mg-Al}}$ values spanning from 23 to 100 kJmol$^{-1}$ along the whole series were determined (Table 4). A strong correlation was observed between $\alpha_{\text{Mg-Al}}$ and Cr, as well as between $\alpha_{\text{Mg-Al}}$ and $^T\text{Al}/\text{Al}_{\text{tot}}$. The latter can be described by the equation $\alpha_{\text{Mg-Al}} = 125 - 1560 \cdot (^T\text{Al}/\text{Al}_{\text{tot}}) + 5960 \cdot (^T\text{Al}/\text{Al}_{\text{tot}})^2$, ($r^2 = 0.995$). As $\alpha_{\text{Mg-Al}}$ represents the difference in the site preference energies of Mg and Al, the progressively higher values here retrieved would account for an increasing preference of Al for the octahedral coordination as a function of Cr, which may be ascribed to the pairwise Al-Cr interaction.

**Geothermometry**

Della Giusta et al. (1996) and Princivalle et al. (1999) defined a geothermometric relation that allows calculation of the closure temperature for a spinel from its cation distribution. The geothermometer is based on the temperature-dependent intracrystalline exchange reaction $^M\text{Al} + ^T\text{Mg} = ^T\text{Al} + ^M\text{Mg}$. The closure temperature is obtained by the equation: $T_c = 6640 \cdot (^T\text{Al}/\text{Al}_{\text{tot}} + 0.101(1 - ^T\text{Mg} - ^T\text{Al}) + 0.041(2 - ^M\text{Al} - ^M\text{Mg}))$, where the coefficients should take into account the compositional influence of the other cations such as Cr. The estimated error associated with this geothermometer is $\pm 20$ °C.

Due to common occurrence and high relevance of Cr-bearing spinels in geosciences, after Princivalle et al. (1999) the geothermometer was applied to natural Cr-bearing spinels by Lavina et al. (2003), Uchida et al. (2005), Lucchesi et al. (2010), Lenaz et al. (2010; 2014b,c; 2015) and Perinelli et al. (2014). All these studies validated the successful application of this single-phase geothermometer on geological evidences or against other geothermometers based on coexisting phases. None validation, however, has been done against synthetic spinel samples with increasing Cr contents under controlled temperature. The present samples were
grown by controlled, slow-cooling thermal runs ending at 900 °C, after that they were not quenched, but carefully removed from the vertical furnace. Due to this procedure, crystals remained in the furnace for several minutes after switching off heating elements. Due to fast Mg-Al intersite exchange kinetics between 900 and 800 °C (Andreozzi and Princivalle 2002), their closure temperature is therefore expected to be about 800 °C.

Applied to the present crystals with Cr content up to 1.66 apfu the geothermometer of Princivalle et al. (1999) yields $T_c$ spanning from 768 to 824 °C, with an average value of 796±20 °C that is consistent with the expected value of 800 °C (Fig. 5). For larger Cr contents, such as that of crystal MC50b (Cr = 1.92 apfu), the geothermometer yields unreliable $T_c$ (637 °C), significantly lower than 800 °C. This large deviation can be ascribed to the non-linear behavior of the Mg-Al order-disorder reaction caused by Cr.

**IMPLICATIONS**

Chromium influence on Mg-Al intracrystalline exchange in spinels implies that the geothermometer of Princivalle et al. (1999) yields reliable $T_c$ values for spinel compositions with $\text{Cr/(Cr+Al)} < 0.85$, whereas $T_c$ values calculated for spinels with $\text{Cr/(Cr+Al)} > 0.85$ should be treated with caution. This finding, along with the unreliable $T_c$ estimated for non-stoichiometric Cr-bearing spinels (Perinelli et al. 2014; Lenaz et al. 2015) put some limitations on the compositional field where this spinel geothermometer can be used, i.e., Cr contents lower than 1.70 apfu and absence of cation vacancies. The geological implications may be relevant: for example, spinels with very high Cr contents, $\text{Cr/(Cr+Al)} > 0.85$, are typically found as inclusions in diamonds or contained in kimberlites, komatiites, boninites and ophiolitic chromitites (e.g., Barnes and Roeder 2001). An improper use of the geothermometer of Princivalle et al. (1999) on such spinels would lead to incorrect interpretations such as lower closure temperature indicating slow cooling rate due to a slow cooling path experienced by their host rock or, alternatively, long exposure to low-to-medium-grade metamorphic conditions, which are characterized by sluggish kinetics.

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TABLE 1. Selected X-ray diffraction data for the MgAl₂O₄-MgCr₂O₄ spinels series studied

TABLE 2. Chemical composition of the MgAl₂O₄-MgCr₂O₄ spinels series studied

TABLE 3. Observed and calculated crystal-chemical parameters for the MgAl₂O₄-MgCr₂O₄ spinels series studied (on deposit)

TABLE 4. Empirical structural formulae (apfu), thermodynamic data (kJmol⁻¹) and closure temperatures (°C) for the MgAl₂O₄-MgCr₂O₄ spinels series studied

LIST OF FIGURES AND FIGURE CAPTIONS

FIGURE 1. Variations in the unit cell $a$-parameter versus Cr content in the MgAl₂O₄-MgCr₂O₄ spinel series studied. Filled circles: samples from this study; filled square: Nestola et al. (2014). The symbol size is proportional to the analytical error. Dashed line is linear regressions.

FIGURE 2. Variations in the unit cell $a$-parameter versus bond distances (T-O and M-O) in the MgAl₂O₄-MgCr₂O₄ spinel series studied. Circles: samples from this study; squares: Nestola et al. (2014). The symbol size is proportional to the analytical error. The dashed line are non-linear regressions.

FIGURE 3. Plot of the T-site preference of Al in the MgAl₂O₄-MgCr₂O₄ spinel series studied expressed as $^{T}\text{Al}/\text{Al}_{\text{tot}}$ against Cr. Filled circles: samples from this study; filled square: Nestola et al. (2014); filled triangles: Lavina et al. (2003). The horizontal dashed lines represent inversion of a constant percentage of Al along the series. The solid lines are linear regression.

FIGURE 4. Plot of the inversion (a) and $^{T}\text{Al}/\text{Al}_{\text{tot}}$ (b) values derived from the O’Neill-Navrotsky thermodynamic model with $\alpha_{\text{Mg-Al}} = 23$ kJmol⁻¹ and $\beta_{\text{Mg-Al}} = 13$ kJmol⁻¹ (crosses) and from crystal-chemical data (filled circles) against Cr. Solid line is a guide for the eye. Dashed line represents inversion of a constant percentage of Al along the series. See text for details on the thermodynamic model.

FIGURE 5. Plot of closure temperature ($T_c$) against Cr content for the MgAl₂O₄-MgCr₂O₄ spinel series studied. Dashed line represents the expected $T_c$. 
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<thead>
<tr>
<th>Crystal</th>
<th>MC02bb</th>
<th>MC02dc</th>
<th>MgCr5c</th>
<th>MC10db</th>
<th>MC15ad</th>
<th>MC15aa</th>
<th>MgCr20</th>
<th>MgCr25</th>
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<td>u</td>
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<td>0.26232(4)</td>
<td>0.26212(6)</td>
<td>0.26223(8)</td>
<td>0.26220(7)</td>
<td>0.26217(6)</td>
<td>0.26171(6)</td>
<td>0.26164(7)</td>
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<td>1.9366(8)</td>
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<td>1.9609(7)</td>
<td>1.9627(10)</td>
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<td>M-O (Å)</td>
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<td>M-m.a.n.</td>
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<td>21.67(17)</td>
<td>22.26(22)</td>
<td>23.52(19)</td>
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<td>0.0072(2)</td>
<td>0.0059(2)</td>
<td>0.0055(2)</td>
<td>0.0055(2)</td>
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<td>-0.00024(4)</td>
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<td>0 ≤ h ≤ 16</td>
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<td>0 ≤ h ≤ 16</td>
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<td>-16 ≤ h ≤ 16</td>
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<td>2685</td>
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<td>Diff. Peaks (±e/Å³)</td>
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<td>-0.58; 0.24</td>
<td>-0.12; 0.15</td>
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<td>-0.53; 0.48</td>
<td>-0.52; 0.46</td>
<td>-0.41; 0.34</td>
<td>-0.73; 0.48</td>
<td>-0.82; 0.58</td>
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Notes: a = unit-cell parameter; u = oxygen fractional coordinate; T- and M-O = tetrahedral and octahedral bond lengths, respectively; T- and M-m.a.n.. = T- and M-mean atomic number; U11 = atomic displacement parameter; U11 = U22 = U33 and U12 = U13 = U23 = 0 for T-site due to symmetry reasons; EXT1 = extinction parameter; R int. = merging residual value; R1 = discrepancy index, calculated from F-data; wR2 = weighted discrepancy index, calculated from F²-data; Goof = goodness of fit; Diff. Peaks = maximum and minimum residual electron density. Radiation, Mo-Kα = 0.71073 Å. Data collection temperature = 293 K. Range for data collection 8° < 2θ < 91° (< 72° for sample MgCr5c). Origin fixed at 3m. Space group 3m. Z = 8. Spinel structure has cations at Wyckoff positions 8a = T (1/2, 1/2, 1/2) and 16d = M (1/2, 1/2, 1/2), and oxygen anions at 32e (u, u, u).

*a Fixed in the final stages of refinement.
<table>
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<tr>
<th>Crystal</th>
<th>MC02bb</th>
<th>MC02de</th>
<th>MgCr5c</th>
<th>MC10db</th>
<th>MC15ad</th>
<th>MC15aa</th>
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<th>MgCr25</th>
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<tr>
<td>Cr₂O₃ (wt%)</td>
<td>4.90(46)</td>
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<td>Al₂O₃</td>
<td>67.43(36)</td>
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<td>25.78(1.03)</td>
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<td>9.44(40)</td>
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<td>24.05(42)</td>
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<td>22.06(10)</td>
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<td>21.34(9)</td>
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<td>98.10</td>
<td>100.49</td>
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<td>99.67</td>
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**Notes:** Cations on the basis of 4 oxygen atoms per formula unit (apfu). Digits in parentheses are estimated uncertainties (1σ); for reported oxide concentrations, they represent standard deviations of several analyses on individual crystals, whereas, for cations, they were calculated according to error propagation theory; epfu = electrons per formula unit.
### Table 3

Observed and calculated crystal-chemical parameters for the MgAl$_2$O$_4$-MgCr$_2$O$_4$ spinels series studied.

<table>
<thead>
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<th>Crystal</th>
<th>Al (apfu)</th>
<th>Mg (apfu)</th>
<th>Cr (apfu)</th>
<th>a (Å)</th>
<th>u</th>
<th>T-O (Å)</th>
<th>M-O (Å)</th>
<th>T-man</th>
<th>M-man</th>
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<td>0.998(5)</td>
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<td>13.66</td>
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<td>MC50b</td>
<td>0.075(1)</td>
<td>1.013(3)</td>
<td>1.916(3)</td>
<td>8.3244(4)</td>
<td>0.26134(8)</td>
<td>1.9658(11)</td>
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Note: Standard errors in brackets.
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Notes: $T =$ tetrahedrally-coordinated site; $M =$ octahedrally-coordinated site; $\alpha_{\text{Mg-Al}} =$ coefficient of the O’Neill & Navrotsky (1983) thermodynamic model; $T_c =$ closure temperature.
Figure 2

The diagram shows a plot of $a$-parameter ($\text{Å}$) against bond distances ($\text{Å}$). The plot includes two sets of data points:

- **T-O** line with an $r^2$ value of 0.993, indicated by filled circles.
- **M-O** line with an $r^2$ value of 0.999, indicated by open circles.

The graph visually represents the relationship between the $a$-parameter and bond distances for the two types of bonds.
Figure 4

![Graph showing the relationship between inversion and Cr (apfu).](image-url)
Figure 5

The graph shows the relationship between Cr (apfu) and $T_c$ ($^\circ$C). The data points are plotted with error bars, indicating the variability in the measurements. The horizontal dashed line at $T_c = 800$ $^\circ$C is included as a reference. The x-axis represents the Cr concentration in atomic per formula unit (apfu), while the y-axis represents $T_c$ in degrees Celsius.