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INTRODUCTION

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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).

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Oxide spinels have formula AB_2O_4 where the letter A and B represent either divalent and trivalent cations or, less frequently, tetravalent and divalent cations, respectively. The spinel structure is described, in the space group $Fd\bar{3}m$, 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 ${}^T(A_{1-i}B_i){}^M(A_iB_{2-i})O_4$, 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, Cr^{3+} , V^{3+} and Ti^{4+} strongly prefer the M site; Al and Cu^{2+} exhibit preference for M but are available to partly invert at the T site at high temperature; Fe^{3+} has no preference; Mg, Fe^{2+} , Mn^{2+} and Co^{2+} 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).

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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.

66 The temperature of apparent equilibration corresponding to the quenched-in ordering state,
67 that is, the temperature at which the rate of exchange slows to the point where the change is
68 no longer detectable, is defined as closure temperature T_c (Ganguly 1982). This process
69 implies that the cation ordering also relies on the rate at which spinel cooled, and is a track of
70 thermal history of host rock. A lot of studies focused on Mg-Al intracrystalline order-disorder
71 relationships, their dependence on equilibrium temperature, cooling history and composition,
72 with the aim of using Mg-Al rich-spinels for geothermometric purposes (e.g., Princivalle et al.
73 1989; Peterson et al. 1991; Millard et al. 1992; Della Giusta et al. 1996; Princivalle et al.
74 1999; Androzzzi et al. 2000; Androzzzi and Princivalle 2002). This intersite geothermometer
75 is analytically challenging, because requires the determination of the site distribution of Mg
76 and Al, which is (at least) temperature- and time-dependent. In fact, the higher the
77 temperature, the higher the disorder of Mg and Al over T and M; vice versa, during crystal
78 cooling Mg and Al progressively orders at T and M, respectively. As stated above, the
79 ordering process stops at T_c and depends on cooling rate: slow cooling allows a strong Mg-Al
80 intracrystalline ordering in spinel and the geothermometer calculates low T_c , whereas fast
81 cooling preserves the disordered state and consequently gives higher T_c (e.g., Princivalle et
82 al. 1989, 1999; Della Giusta et al. 1996; Lucchesi et al. 1998b, 2010).

83 Cr-bearing spinels represent 14% of all mineral inclusions in cratonic diamonds (e.g.,
84 Stachel and Harris 2008, Lenaz et al. 2009; Nestola et al. 2014), and are often among the first
85 phases that crystallize from a wide variety of mafic-ultramafic igneous rock types and tectonic
86 environments (e.g., Irvine 1965, 1967; Barnes and Roeder 2001; Lenaz et al. 2014a).
87 Therefore, they may preserve important records of the geological conditions in which they
88 formed in the crust and upper mantle, and understanding how to decipher those records is
89 extremely important. However, in Mg-Al-Cr-spinels, the marked preference of Cr for the
90 octahedral environment strongly influences both spinel crystal-chemistry and calculated T_c by
91 affecting the site distribution of Mg and Al (Lavina et al. 2003). Moreover, natural Mg-Al-Cr-
92 spinels often contain other chemical constituents such as Fe^{2+} and Fe^{3+} that may hinder the
93 influence of Cr on both cation ordering and T_c (Martignago et al. 2003). It is therefore crucial
94 to test geothermometric exchanges studying spinel samples along the Fe-free binary series
95 spinel *sensu stricto* (s.s.)-magnesiochromite (MgAl_2O_4 - MgCr_2O_4).

96 In the present study, the MgAl_2O_4 - MgCr_2O_4 spinel substitution series will be
97 investigated in order to reveal the crystal-chemical effects of Cr substitution for Al and their
98 influence on Mg-Al intracrystalline exchange. Flux-grown synthetic crystals, already studied
99 by optical absorption spectroscopy in Hålenius et al. (2010), will be structurally and

100 chemically characterized by single-crystal X-ray diffraction and electron microprobe, cation
101 distribution will be obtained with a tested optimization model for site populations, and T_c will
102 be finally calculated with the geothermometer equation of Princivalle et al. (1999). The
103 approach adopted will allow the definition of the compositional range where this
104 geothermometer applies when the $MgCr_2O_4$ component increases.

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EXPERIMENTAL METHODS

108 **Synthesis**

109 A flux-growth method with $Na_2B_4O_7$ used as flux compound was used to obtain single
110 crystals along the binary join spinel s.s.-magnesiochromite. Analytical grade MgO , $Al(OH)_3$
111 and Cr_2O_3 were dehydrated and dried at elevated temperatures before mixing with $Na_2B_4O_7$.
112 The starting materials were transferred to Pt/Au (5%) crucibles and covered by a Pt lid.
113 Thermal runs consisted of 24 h at 1200 °C followed by a slow decrease to 900 °C at a
114 controlled cooling rate of 4 °C/h. After shutting off the power to the heating elements and
115 removing crucibles from the furnace a rapid cooling to room temperature was obtained.
116 Successful runs consisted of octahedral spinel crystals, borate needles, and occasional
117 eskolaite (α - Cr_2O_3) embedded in a borate-rich glass. The glass phase and borate crystals were
118 dissolved in warm diluted HCl. The recovered spinel single crystal have typical size in the
119 range 200-300 μm . The largest, ruby-red, gem-quality crystals were obtained for Cr-poor
120 compositions, intermediate compositions yielded sub-regular crystals, but smaller, black
121 octahedra were also obtained close to magnesiochromite end member.

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123 **Single-crystal structural refinement**

124 The examined samples constitute a set of nine hand-picked spinel single crystals. For X-
125 ray data collection two single-crystal diffractometers were used (Siemens P4 and APEX-II).
126 In detail, six out of nine crystal-fragments were mounted on a Bruker Siemens P4 automated
127 four-circle diffractometer, equipped with a point detector. Unit-cell parameters were
128 measured, at 293 K, by centering 52 reflections (13 independent and their Friedel pairs, on
129 both sides of the direct beam), in the range 85-95° 2θ , with $Mo-K\alpha_1$ radiation (0.70930 Å).
130 Intensity data were collected, at 293 K, using $MoK\alpha$ radiation (0.71073 Å) monochromatized
131 by a flat graphite crystal in the 3-95° 2θ range with the ω -scan method and at a fixed scan
132 range (2.4°). One-eighth of the reciprocal space was examined. The scan speed was variable
133 (2.93-29.3°/min), depending on reflection intensity, as estimated through pre-scans. The

134 background was measured with a stationary counter and crystal at the beginning and end of
135 each scan, in both cases for half the scan time. Three standard reflections were monitored
136 every 47 measurements. Data reduction was performed with the SHELXTL-PC program
137 package. Intensities were corrected for polarization and Lorentz effects. Absorption correction
138 was accomplished with a semi-empirical method (North et al. 1968). Three out of nine
139 crystal-fragments were mounted on a Bruker KAPPA APEX-II diffractometer, equipped with
140 a CCD area detector ($6.2 \times 6.2 \text{ cm}^2$ active detection area, 512×512 pixels) and a graphite
141 crystal monochromator, using $\text{MoK}\alpha$ radiation from a fine-focus sealed X-ray tube. The
142 sample-to-detector distance was 4 cm. More than 5000 exposures per sample were measured
143 (step = 0.2° , time/step = 10 s) covering the full reciprocal sphere with an average redundancy
144 of about 20. Final unit-cell parameters were refined by using the Bruker AXS SAINT
145 program from about 2000 (about 1200 for sample MgCr5c) recorded reflections with $I > 10$
146 σ_I in the range $8^\circ < 2\theta < 90^\circ$ (72° for sample MgCr5c). The intensity data were processed and
147 corrected for Lorentz, polarization and background effects with the APEX2 software program
148 of Bruker AXS. The data were corrected for absorption using multi-scan method (SADABS),
149 leading to a significant improvement in R_{int} . No violation of $Fd\bar{3}m$ symmetry was noted.

150 Structure refinement was done with the SHELXL-2013 program (Sheldrick 2013). All
151 reflections were used in the refinement. Variable parameters during the structural refinement
152 were: overall scale factor, oxygen coordinate, site-scattering values, atomic-displacement
153 parameters, and extinction parameter. In the final stage of the refinement, the extinction
154 parameter was removed from the variables of sample MgCr5c, because its value refined to
155 zero. Setting the origin at $\bar{3}m$, initial atomic positions for oxygen atoms were taken from
156 Hålenius and Bosi (2014). The T site was modeled with Mg and the M site with Al vs. Cr
157 (except for crystal MC02bb, which was modeled considering only ^MAl due to the small Cr
158 concentrations). Convergence was attained when the shifts in all refined parameters were less
159 than their estimated standard deviation. A further refinement with chemical constraints was
160 done for CIF (on deposit¹) by modelling the T site cation occupancy of crystals MC02bb and
161 MC02de with the ^TMg and ^TAl fixed to the value obtained from the structural formula. The
162 results are statistically equal to those reported in Table 1, which summarizes structural
163 parameters and refinement details.

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165 **Electron microprobe analysis**

166 The same crystals as used for X-ray data collection were mounted on a glass slide and
167 polished for electron microprobe analysis on a Cameca SX50 instrument equipped with four
168 wavelength dispersive spectrometers (WDS mode) and operated at an accelerating potential of
169 15 kV and a sample current of 15 nA, with an incident beam diameter of ca. 1 μm . No less
170 than 10 spot analyses for each sample were performed to obtain the average chemical
171 compositions and to estimate compositional homogeneity. Synthetic standards used were
172 periclase (Mg), corundum (Al) and metallic Cr. For raw data reduction, the PAP computer
173 program was applied (Pouchou and Pichoir 1984). Spinel formulae were calculated on the
174 basis of 4 oxygen atoms and 3 cations per formula unit. The resulting atomic fractions (atoms
175 per formula unit, apfu) are well supported by the match between number of electrons per
176 formula unit derived from chemical and structural analysis (Table 2).

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178 **Cation distribution**

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

$$182 \quad F(X_i) = \frac{1}{n} \sum_{j=1}^n \left(\frac{O_j - C_j(X_i)}{\sigma_j} \right)^2$$

183 where O_j is the observed quantity, σ_j its standard error, X_i the variables, i.e., cation fractions at
184 the T and M sites, and $C_j(X_i)$ the same quantity as O_j calculated by means of X_i parameters.
185 The nO_j quantities taken into account were: a - and u -parameter, T-O and M-O bond distances,
186 mean atomic number of T and M sites, total atomic fractions derived from electron-
187 microprobe analyses, constraints relative to the formula electroneutrality (8 positive and 8
188 negative charges) and site population (T = 1.000 and M = 2.000). The M-O and T-O bond
189 distances were calculated as the linear contribution of each cation multiplied by its ideal bond
190 distance reported by Lavina et al. (2002): ${}^T\text{Mg-O} = 1.966 \text{ \AA}$, ${}^M\text{Mg-O} = 2.082 \text{ \AA}$, ${}^T\text{Al-O} =$
191 1.774 \AA , ${}^M\text{Al-O} = 1.908 \text{ \AA}$, ${}^M\text{Cr}^{3+}\text{-O} = 1.995 \text{ \AA}$. More details about the minimization
192 procedure may be found in Lavina et al. (2002). Due to crystal-field stabilization energy, a
193 marked octahedrally coordinated site preference is expected for Cr^{3+} , thus it was constrained
194 to occur at the M site. The calculated parameters fit the observed ones within 2σ in 95% of
195 cases (Table 3, on deposit). The results of optimized cation distributions are reported as
196 structural formulae in Table 4.

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RESULTS AND DISCUSSION

200 **Crystal structure**

201 Crystal structure of Cr-bearing spinels at environmental conditions is commonly
202 described on the basis of $Fd\bar{3}m$ space group. The end member $MgCr_2O_4$ exhibits a first-order
203 phase transition at 12.5 K with a pronounced peak in heat capacity coinciding with the phase
204 transition from cubic to tetragonal symmetry ($I4_1/amd$ space group; Ehrenberg et al. 2002).
205 Moreover, a post-spinel $MgCr_2O_4$ orthorhombic phase, $Bbmm$ space group, was recently
206 synthesized at 23 GPa and 1600 °C (Bindi et al. 2014) and found in ultrahigh-pressure
207 chromitites (Ishii et al. 2015).

208 Previously studies also stated that the structure of Cr-rich spinels at environmental
209 conditions may be better described by the space group $F\bar{4}3m$ (Grimes 1971; Sickafus et al.
210 1999) due to the displacement of Cr at the M site along the direction [111] from a
211 centrosymmetric position to a non-centrosymmetric position, which causes a reduction in
212 point symmetry of the M site from $\bar{3}m$ to $3m$. In addition, Lutz et al. (2000) suggested that the
213 occurrence of a less symmetric space group in Cr-rich spinels is due to the strength of the
214 metal-metal bonds.

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

218

219 **Crystal chemistry**

220 The flux-grown spinel crystals investigated are characterized by $Cr \leftrightarrow Al$ substitution
221 along the whole substitution series and are representative of the entire $MgAl_2O_4$ - $MgCr_2O_4$
222 series. The Cr_2O_3 contents vary from 4.9(5) to 76.1(1) wt% (Table 2) and the corresponding
223 magnesiochromite component from 3% to 96% (Table 4). To attain a complete picture of the
224 structural relations along the whole series, we included crystal-chemical data of the synthetic
225 end-member magnesiochromite $T(Mg)^M(Cr)_2O_4$, grown in the same conditions (Nestola et al.
226 2014).

227 Site distribution of Mg, Al and Cr shows that the T site is mainly populated by Mg and
228 by small amounts of Al which decrease with increasing Cr content. The M site is dominated
229 by the substitution $Cr \leftrightarrow Al$ and also shows small amounts of Mg which decrease with
230 increasing Cr. Accordingly, the degree of inversion decreases from 0.23 to 0.00 with

231 increasing Cr content (Table 4). As a consequence, the distribution of Mg and Al over the T
232 and M sites is well explained by the order-disorder reaction ${}^M\text{Al} + {}^T\text{Mg} \leftrightarrow {}^T\text{Al} + {}^M\text{Mg}$.

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

235
$$\text{T-O} = 0.1926 \cdot {}^T\text{Mg} + 1.7733, (r^2 = 0.9998);$$

236
$$\text{M-O} = 0.0327 \cdot {}^M\text{Cr} + 1.9266, (r^2 = 0.996).$$

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

239
$$\text{M-O} = 1.991 - 0.521 \cdot i + 1.146 \cdot i^2, (r^2 = 0.985),$$

240 and T-O shows a non-linear relation with Cr content ($r^2 = 0.995$).

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

259

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

261 The intracrystalline cation distribution of the present spinel s.s.-magnesiochromite series was
262 tentatively modeled by the general thermodynamic model for spinel binary substitution series
263 proposed by O'Neill and Navrotsky (1984), which was proved to be adequate for modeling
264 cation distribution as a function of temperature in spinels of different composition (e.g.,

265 Waerenborgh et al. 1994a,b; Andreozzi et al. 2001a; Andreozzi and Lucchesi 2002;
266 Martignago et al. 2006; Princivalle et al. 2012). Applying this model to MgAl_2O_4 - MgCr_2O_4
267 and disregarding the Cr inversion at T, due to its strong octahedral preference, the Mg-Al
268 intersite exchange can be modeled as a function of temperature by the order-disorder reaction
269 ${}^{\text{M}}\text{Al} + {}^{\text{T}}\text{Mg} \leftrightarrow {}^{\text{T}}\text{Al} + {}^{\text{M}}\text{Mg}$. Accordingly, the system of two equations, required for the general
270 case, may be simplified as follows:

$$271 \quad -RT\ln\left[\frac{i^2}{(1-i)(2-i-2z)}\right] = \alpha_{\text{Mg-Al}} + 2\beta_{\text{Mg-Al}} i \quad (3)$$

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

281 The O'Neill-Navrotsky model assumes that cation ordering behavior in a substitution
282 series can be entirely predicted on the basis of the energetics of the two end members (or one
283 end member in this case, as the other is constrained to be perfectly normal). This is seen in
284 equation (3), where the ordering is controlled by the parameters α and β , which are entirely
285 constrained by the equilibrium ordering behavior in end member MgAl_2O_4 . This approach,
286 however, ignores the important energetic contributions from Al-Cr pairwise interactions, that
287 are only present along the substitution series, and whose effects cannot possibly be predicted
288 from the end member behavior alone. Actually, in the present case the deviation between the
289 model and observations is maximum for intermediate Cr contents because this is where the
290 maximum number of Al-Cr interactions occur (Fig. 4a). This issue was discussed extensively
291 for the magnesioferrite-qandilite series in Palin and Harrison (2007) and Harrison et al.
292 (2013), who found that the total energy of such a series can formally be expressed as a sum of
293 pairwise cation-cation interaction parameters and chemical potentials. The atomistic approach
294 used by Harrison et al. (2013) is rigorous and effectively describes the underlying physics of
295 spinel order-disorder with temperature along a substitution series. However, it is complex and
296 lacks of an analytical solution, having rather limited practical use. On the other hand, the
297 O'Neill-Navrotsky model is relatively simple and has been successfully used in many cases.

298 Nevertheless, it has been proved unsuccessful for the magnesioferrite-qandilite series
299 (Harrison et al. 2013) as well as for the studied spinel s.s.-magnesiochromite series as it led to
300 cation distribution inconsistent with experimental data. In the present study, for example, for
301 an intermediate composition such as crystal MC15ad the T-O and M-O bond distances
302 derived from thermodynamic data were 1.9341 and 1.9681 Å, respectively, which are
303 significantly smaller than the corresponding observed values 1.9538(9) and 1.9588(5) Å
304 (Table 1).

305 The unique way to apply the O'Neill-Navrotsky model to the present series is varying
306 $\alpha_{\text{Mg-Al}}$ and $\beta_{\text{Mg-Al}}$ values in equation (3) as both T and i are known parameters. Using the
307 inversion values of Table 4 and assuming a constant value of $\beta_{\text{Mg-Al}} = 13 \text{ kJmol}^{-1}$ (Andreozzi
308 et al. 2000), $\alpha_{\text{Mg-Al}}$ values spanning from 23 to 100 kJmol^{-1} along the whole series were
309 determined (Table 4). A strong correlation was observed between $\alpha_{\text{Mg-Al}}$ and Cr, as well as
310 between $\alpha_{\text{Mg-Al}}$ and $^{\text{T}}\text{Al}/\text{Al}_{\text{tot}}$. The latter can be described by the equation $\alpha_{\text{Mg-Al}} = 125 - 1560$
311 $\cdot (^{\text{T}}\text{Al}/\text{Al}_{\text{tot}}) + 5960 \cdot (^{\text{T}}\text{Al}/\text{Al}_{\text{tot}})^2$, ($r^2 = 0.995$). As $\alpha_{\text{Mg-Al}}$ represents the difference in the site
312 preference energies of Mg and Al, the progressively higher values here retrieved would
313 account for an increasing preference of Al for the octahedral coordination as a function of Cr,
314 which may be ascribed to the pairwise Al-Cr interaction.

315

316 **Geothermometry**

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

324 Due to common occurrence and high relevance of Cr-bearing spinels in geosciences,
325 after Princivalle et al. (1999) the geothermometer was applied to natural Cr-bearing spinels by
326 Lavina et al. (2003), Uchida et al. (2005), Lucchesi et al. (2010), Lenaz et al. (2010; 2014b,c;
327 2015) and Perinelli et al. (2014). All these studies validated the successful application of this
328 single-phase geothermometer on geological evidences or against other geothermometers
329 based on coexisting phases. None validation, however, has been done against synthetic spinel
330 samples with increasing Cr contents under controlled temperature. The present samples were

331 grown by controlled, slow-cooling thermal runs ending at 900 °C, after that they were not
332 quenched, but carefully removed from the vertical furnace. Due to this procedure, crystals
333 remained in the furnace for several minutes after switching off heating elements. Due to fast
334 Mg-Al intersite exchange kinetics between 900 and 800 °C (Andreozzi and Princivalle 2002),
335 their closure temperature is therefore expected to be about 800 °C.

336 Applied to the present crystals with Cr content up to 1.66 apfu the geothermometer of
337 Princivalle et al. (1999) yields T_c spanning from 768 to 824 °C, with an average value of
338 796 ± 20 °C that is consistent with the expected value of 800 °C (Fig. 5). For larger Cr
339 contents, such as that of crystal MC50b (Cr = 1.92 apfu), the geothermometer yields
340 unreliable T_c (637 °C), significantly lower than 800 °C. This large deviation can be ascribed
341 to the non-linear behavior of the Mg-Al order-disorder reaction caused by Cr.

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IMPLICATIONS

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

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587 dashed lines represent inversion of a constant percentage of Al along the series. The
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590 Navrotsky thermodynamic model with $\alpha_{\text{Mg-Al}} = 23 \text{ kJmol}^{-1}$ and $\beta_{\text{Mg-Al}} = 13 \text{ kJmol}^{-1}$
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592 guide for the eye. Dashed line represents inversion of a constant percentage of Al
593 along the series. See text for details on the thermodynamic model.

594 **FIGURE 5.** Plot of closure temperature (*T_c*) against Cr content for the MgAl₂O₄-MgCr₂O₄
595 spinel series studied. Dashed line represents the expected *T_c*.

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

Crystal	MC02bb	MC02de	MgCr5c	MC10db	MC15ad	MC15aa	MgCr20	MgCr25	MC50b
Instrument	Siemens P4	Siemens P4	APEX-II	Siemens P4	Siemens P4	Siemens P4	APEX-II	APEX-II	Siemens P4
Crystal size (mm)	0.20×0.22×0.23	0.20×0.23×0.23	0.08×0.09×0.10	0.22×0.25×0.29	0.18×0.22×0.26	0.20×0.21×0.24	0.09×0.09×0.10	0.09×0.10×0.10	0.22×0.25×0.27
<i>a</i> (Å)	8.0924(6)	8.1044(4)	8.1539(4)	8.2085(5)	8.2176(5)	8.2376(6)	8.2808(3)	8.2933(3)	8.3244(4)
<i>u</i>	0.26214(4)	0.26232(4)	0.26212(6)	0.26223(8)	0.26227(6)	0.26208(7)	0.26171(6)	0.26164(7)	0.26134(8)
T-O (Å)	1.9222(5)	1.9276(6)	1.9366(8)	1.9511(12)	1.9538(9)	1.9559(10)	1.9609(7)	1.9627(10)	1.9658(11)
M-O (Å)	1.9299(3)	1.9314(3)	1.9447(4)	1.9569(6)	1.9588(5)	1.9649(5)	1.9780(4)	1.9815(5)	1.9912(6)
T-m.a.n.	12.23(5)	12.23(6)	12.07(6)	11.95(12)	12.00(10)	12.10(10)	12.00(7)	12 ^a	12.10(15)
M-m.a.n.	12.99(4)	13.57(4)	15.82(6)	18.21(16)	18.78(13)	19.64(16)	21.67(17)	22.26(22)	23.52(19)
T- <i>U</i> ¹¹ (Å ²)	0.0050(1)	0.0043(1)	0.0058(2)	0.0072(2)	0.0059(2)	0.0055(2)	0.0055(2)	0.0056(2)	0.0046(2)
M- <i>U</i> ¹¹ (Å ²)	0.00449(9)	0.00322(9)	0.0052(1)	0.0061(1)	0.00478(9)	0.00432(9)	0.00419(7)	0.0042(1)	0.00313(9)
M- <i>U</i> ¹² (Å ²)	-0.00019(4)	-0.00022(5)	-0.00014(6)	-0.00031(4)	-0.00024(4)	-0.00023(5)	-0.00021(3)	-0.00022(3)	-0.00016(4)
O- <i>U</i> ¹¹ (Å ²)	0.0081(1)	0.0070(1)	0.0083(2)	0.0091(2)	0.0073(2)	0.0068(2)	0.0058(2)	0.0057(2)	0.0042(2)
O- <i>U</i> ¹² (Å ²)	0.00019(7)	-0.00012(9)	-0.0002(1)	-0.0003(1)	-0.0006(1)	-0.0006(1)	-0.00040(9)	-0.0002(1)	-0.0002(1)
Reciprocal range <i>hkl</i>	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 16	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 16	-12 ≤ <i>h</i> ≤ 13 -9 ≤ <i>k</i> ≤ 13 -12 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 16	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 16	0 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 17 0 ≤ <i>l</i> ≤ 17	-16 ≤ <i>h</i> ≤ 16 -15 ≤ <i>k</i> ≤ 10 -12 ≤ <i>l</i> ≤ 16	-16 ≤ <i>h</i> ≤ 16 -15 ≤ <i>k</i> ≤ 15 -9 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 17 0 ≤ <i>l</i> ≤ 17
No. reflections	624	624	1814	639	639	653	2685	2276	672
No. unique reflections	147	147	84	151	151	155	140	140	158
No. refined parameters	10	10	9	10	10	10	10	9	10
EXTI	0.0053(4)	0.0039(9)	0 ^a	0.006(2)	0.0040(8)	0.0044(8)	0.0024(4)	0.0025(6)	0.0095(9)
<i>R</i> int. (%)	2.27	2.52	2.00	1.82	1.89	2.77	1.46	1.15	3.37
<i>R</i> 1 (%) all reflections	1.36	1.86	0.99	2.40	1.70	1.94	1.17	1.48	1.76
<i>wR</i> 2 (%)	2.60	3.30	2.23	6.04	4.28	3.96	2.79	4.13	3.99
Goof	1.248	1.189	1.263	1.203	1.135	1.136	1.201	1.188	1.122
Diff. Peaks (± <i>e</i> /Å ³)	-0.20; 0.26	-0.58; 0.24	-0.12; 0.15	-0.45; 0.76	-0.53; 0.48	-0.52; 0.46	-0.41; 0.34	-0.73; 0.48	-0.82; 0.58

Notes: *a* = unit-cell parameter; *u* = oxygen fractional coordinate; T-O and M-O = tetrahedral and octahedral bond lengths, respectively; T- and M-m.a.n. = T- and M-mean atomic number; *U*¹¹ = atomic displacement parameter; *U*¹¹ = *U*²² = *U*³³ and *U*¹² = *U*¹³ = *U*²³ (= 0 for T-site due to symmetry reasons); EXTI = extinction parameter; *R* int. = merging residual value; *R*1 = discrepancy index, calculated from *F*-data; *wR*2 = weighted discrepancy index, calculated from *F*²-data; GooF = goodness of fit; Diff. Peaks = maximum and minimum residual electron density. Radiation, Mo-*K*α = 0.71073 Å. Data collection temperature = 293 K. Range for data collection 8° < 2θ < 91° (< 72° for sample MgCr5c). Origin fixed at $\bar{3}m$. Space group *Fd* $\bar{3}m$. *Z* = 8. Spinel structure has cations at Wyckoff positions 8a ≡ T (1/8, 1/8, 1/8) 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 2. Chemical composition of the MgAl₂O₄-MgCr₂O₄ spinels series studied

Crystal	MC02bb	MC02de	MgCr5c	MC10db	MC15ad	MC15aa	MgCr20	MgCr25	MC50b
Cr ₂ O ₃ (wt%)	4.90(46)	10.33(1.10)	26.20(9)	47.68(1.33)	50.34(1.05)	53.75(1.32)	66.04(2)	68.86(17)	76.09(14)
Al ₂ O ₃	67.43(36)	60.91(1.02)	48.26(23)	29.25(1.40)	25.78(1.03)	22.26(1.20)	11.73(13)	9.44(40)	2.00(3)
MgO	27.89(5)	26.85(29)	26.03(1)	24.47(46)	24.05(42)	23.66(22)	22.06(10)	22.09(1)	21.34(9)
Total	100.21	98.10	100.49	101.40	100.17	99.67	99.83	100.38	99.43
Cr ³⁺ (apfu)	0.093(8)	0.204(20)	0.534(2)	1.042(26)	1.128(21)	1.228(25)	1.583(3)	1.660(10)	1.916(3)
Al	1.908(7)	1.795(19)	1.466(4)	0.953(33)	0.861(26)	0.758(32)	0.419(4)	0.340(12)	0.075(1)
Mg	0.998(5)	1.001(14)	1.000(2)	1.008(22)	1.016(18)	1.020(18)	0.997(3)	1.004(5)	1.013(3)
Total	2.999	3.000	3.000	3.003	3.005	3.007	2.999	3.004	3.004
# epfu from EMPA	39.02	40.25	43.89	49.49	50.46	51.58	55.40	56.31	59.12
# epfu from SREF	38.20	39.37	43.70	48.38	49.55	51.29	55.34	56.52	59.14

Notes : Cations on the basis of 4 oxygen atoms per formula unit (apfu). Digits in parentheses are estimated uncertainties (1 σ): 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 (on deposit). Observed and calculated crystal-chemical parameters for the MgAl₂O₄-MgCr₂O₄ spinels series studied

Crystal	Al (apfu)	Mg (apfu)	Cr (apfu)	<i>a</i> (Å)	<i>u</i>	T-O (Å)	M-O (Å)	T-man	M-man
MC02bb	1.908(7)	0.998(5)	0.093(8)	8.0924(6)	0.26214(4)	1.9222(5)	1.9299(3)	12.23(5)	12.99(4)
	1.942	0.999	0.059	8.0933	0.26213	1.9223	1.9301	12.23	13.21
MC02de	1.795(19)	1.001(14)	0.204(20)	8.1044(4)	0.26232(4)	1.9276(6)	1.9314(3)	12.23(6)	13.57(4)
	1.861	1.000	0.139	8.1044	0.26232	1.9276	1.9314	12.20	13.66
MgCr05	1.466(4)	1.000(2)	0.534(2)	8.1539(4)	0.26212(6)	1.9366(8)	1.9447(4)	12.07(6)	15.82(6)
	1.466	1.000	0.534	8.1538	0.26217	1.9372	1.9443	12.15	15.86
MC10db	0.953(33)	1.008(22)	1.042(26)	8.2085(5)	0.26223(8)	1.9511(12)	1.9569(6)	11.95(12)	18.21(16)
	1.027	1.000	0.973	8.2088	0.26222	1.9511	1.9570	12.08	18.31
MC15ad	0.861(26)	1.016(18)	1.128(21)	8.2176(5)	0.26227(6)	1.9538(9)	1.9588(5)	12.00(10)	18.78(13)
	0.951	1.000	1.049	8.2182	0.26226	1.9538	1.9590	12.06	18.74
MC15aa	0.758(32)	1.020(18)	1.228(25)	8.2376(6)	0.26208(7)	1.9559(10)	1.9649(5)	12.00(10)	19.64(16)
	0.794	1.000	1.206	8.2378	0.26208	1.9559	1.9650	12.05	19.61
MgCr20	0.419(4)	0.997(4)	1.583(3)	8.2808(3)	0.26171(5)	1.9609(7)	1.9780(4)	12.00(7)	21.67(17)
	0.425	0.998	1.576	8.2816	0.26169	1.9608	1.9783	12.02	21.66
MgCr25	0.340(12)	1.004(5)	1.660(10)	8.2933(3)	0.26164(7)	1.9627(10)	1.9815(5)	12	22.26(22)
	0.344	1.000	1.656	8.2934	0.26164	1.9627	1.9815	12.02	22.10
MC50b	0.075(1)	1.013(3)	1.916(3)	8.3244(4)	0.26134(8)	1.9658(11)	1.9912(6)	12.10(15)	23.52(19)
	0.077	0.999	1.924	8.3253	0.26131	1.9656	1.9916	12.00	23.58

Note: Standard errors in brackets

TABLE 4. Empirical structural formulae (apfu), thermodynamic data (kJmol^{-1}) and closure temperatures ($^{\circ}\text{C}$) of the MgAl_2O_4 - MgCr_2O_4 spinels series studied

Crystal	Structural formula	$\alpha_{\text{Mg-Al}}$	T_c
MC02bb	$^{\text{T}}(\text{Mg}_{0.773}\text{Al}_{0.227})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.226}\text{Al}_{1.715}\text{Cr}_{0.059})_{\Sigma 2.000} \text{O}_4$	23	805
MC02de	$^{\text{T}}(\text{Mg}_{0.800}\text{Al}_{0.200})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.200}\text{Al}_{1.661}\text{Cr}_{0.139})_{\Sigma 2.000} \text{O}_4$	26	778
MgCr5c	$^{\text{T}}(\text{Mg}_{0.850}\text{Al}_{0.150})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.150}\text{Al}_{1.316}\text{Cr}_{0.534})_{\Sigma 2.000} \text{O}_4$	31	824
MC10db	$^{\text{T}}(\text{Mg}_{0.923}\text{Al}_{0.077})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.077}\text{Al}_{0.950}\text{Cr}_{0.973})_{\Sigma 2.000} \text{O}_4$	43	805
MC15ad	$^{\text{T}}(\text{Mg}_{0.937}\text{Al}_{0.063})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.062}\text{Al}_{0.889}\text{Cr}_{1.049})_{\Sigma 2.000} \text{O}_4$	46	768
MC15aa	$^{\text{T}}(\text{Mg}_{0.948}\text{Al}_{0.052})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.052}\text{Al}_{0.742}\text{Cr}_{1.206})_{\Sigma 2.000} \text{O}_4$	48	786
MgCr20	$^{\text{T}}(\text{Mg}_{0.975}\text{Al}_{0.025})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.023}\text{Al}_{0.400}\text{Cr}_{1.577})_{\Sigma 2.000} \text{O}_4$	57	819
MgCr25	$^{\text{T}}(\text{Mg}_{0.983}\text{Al}_{0.017})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.017}\text{Al}_{0.327}\text{Cr}_{1.656})_{\Sigma 2.000} \text{O}_4$	62	785
MC50b	$^{\text{T}}(\text{Mg}_{0.999}\text{Al}_{0.001})_{\Sigma 1.000} \text{M}(\text{Mg}_{0.001}\text{Al}_{0.075}\text{Cr}_{1.924})_{\Sigma 2.000} \text{O}_4$	100	637

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 1

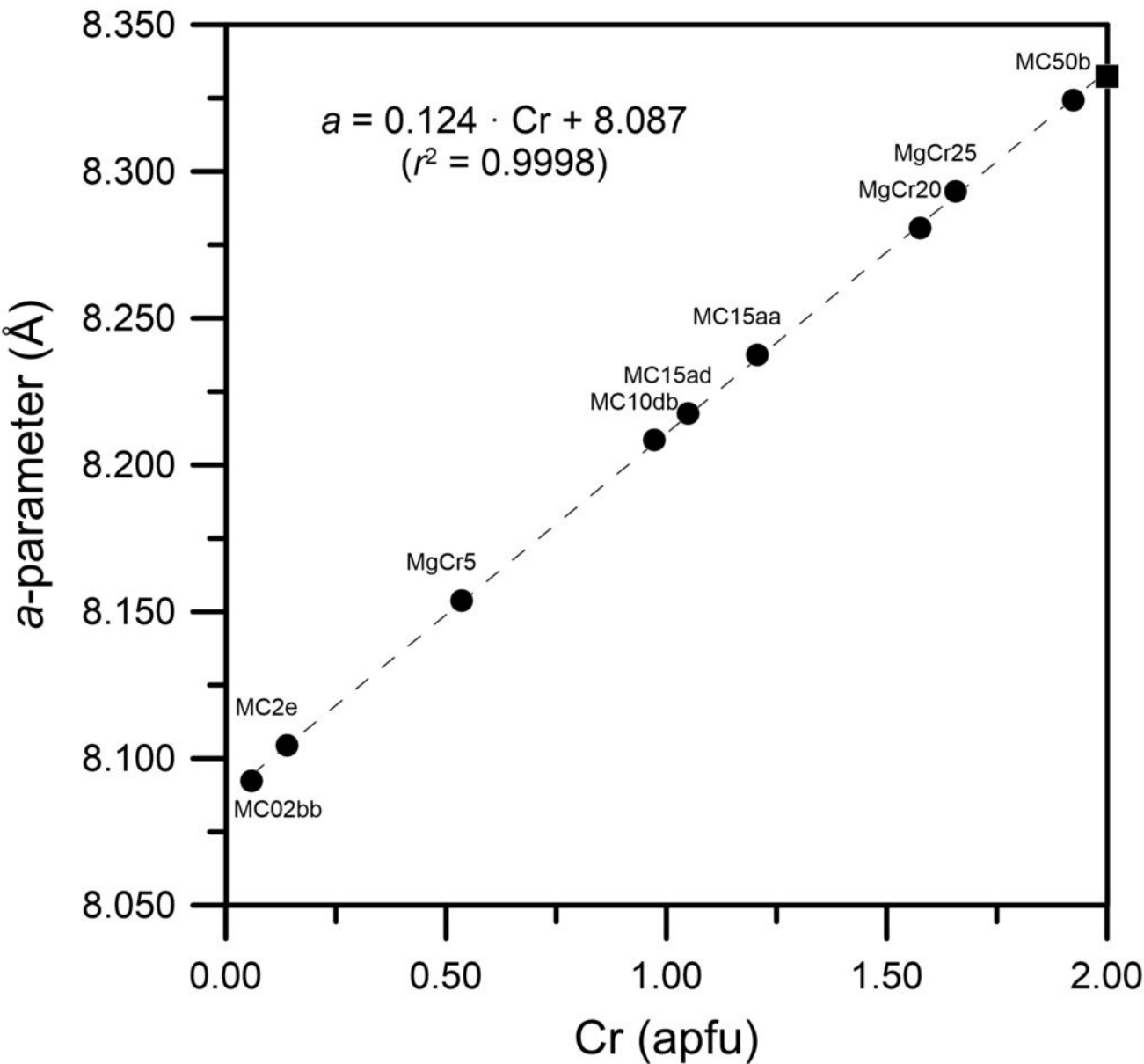


Figure 2

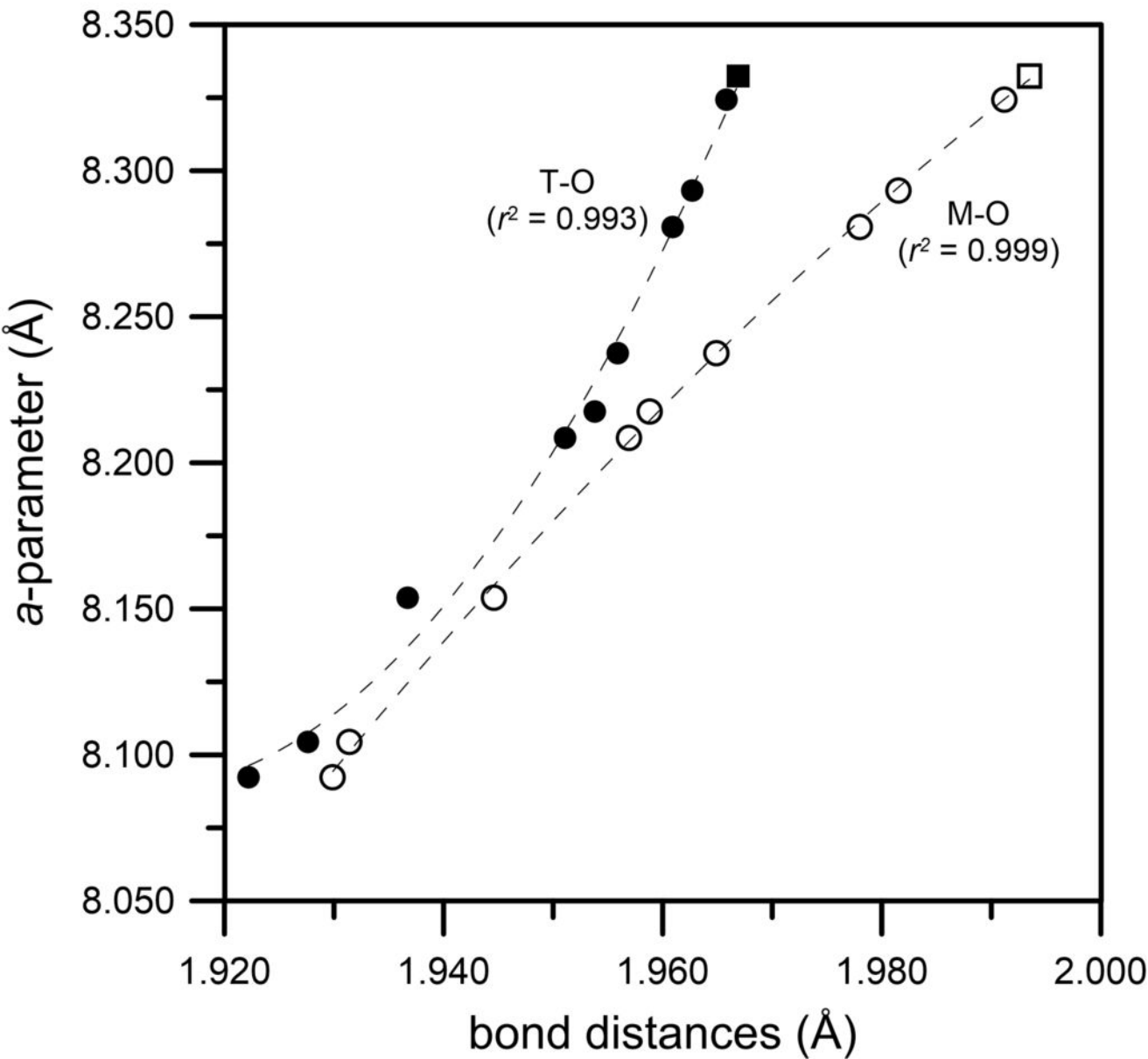


Figure 3

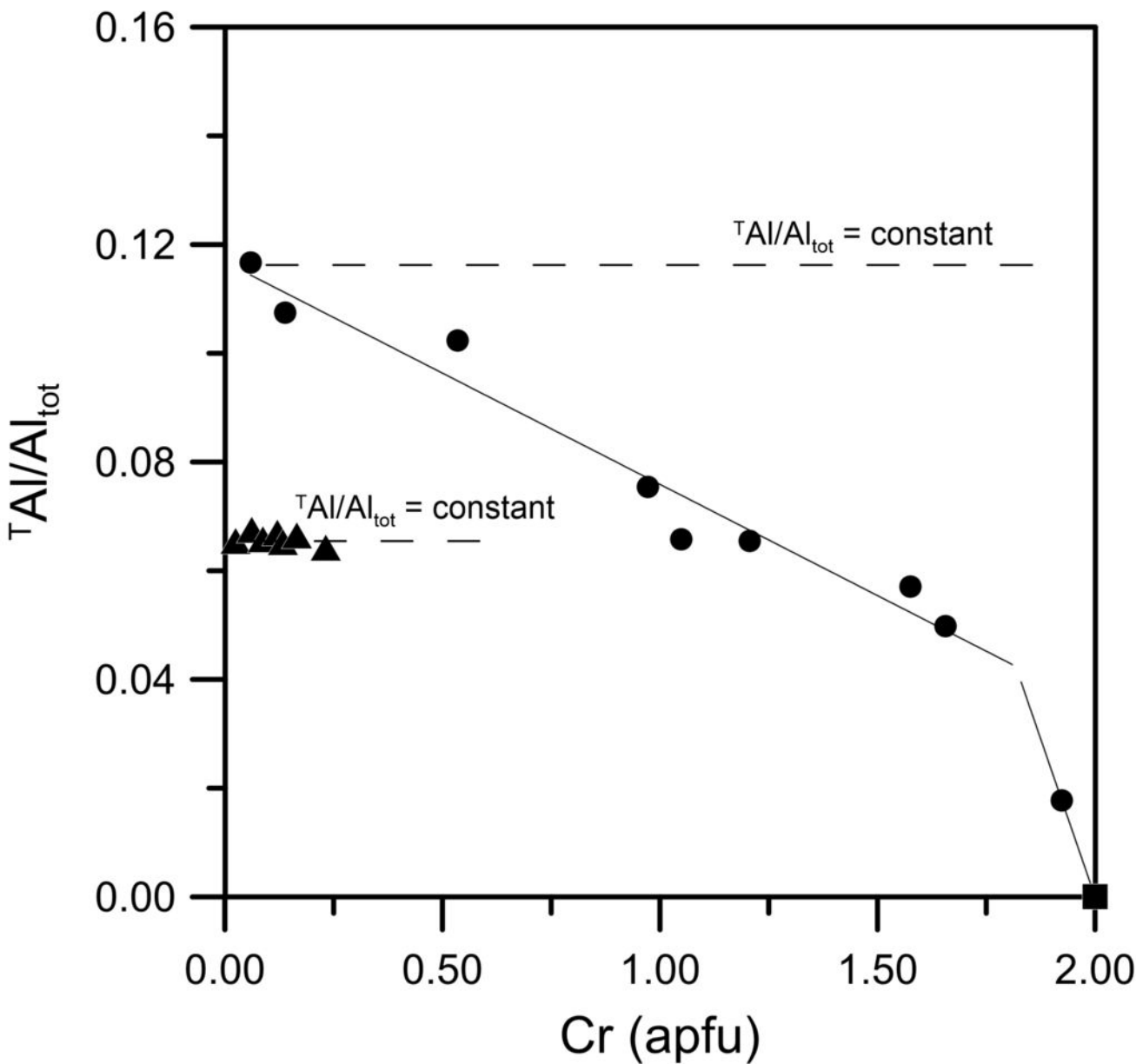


Figure 4

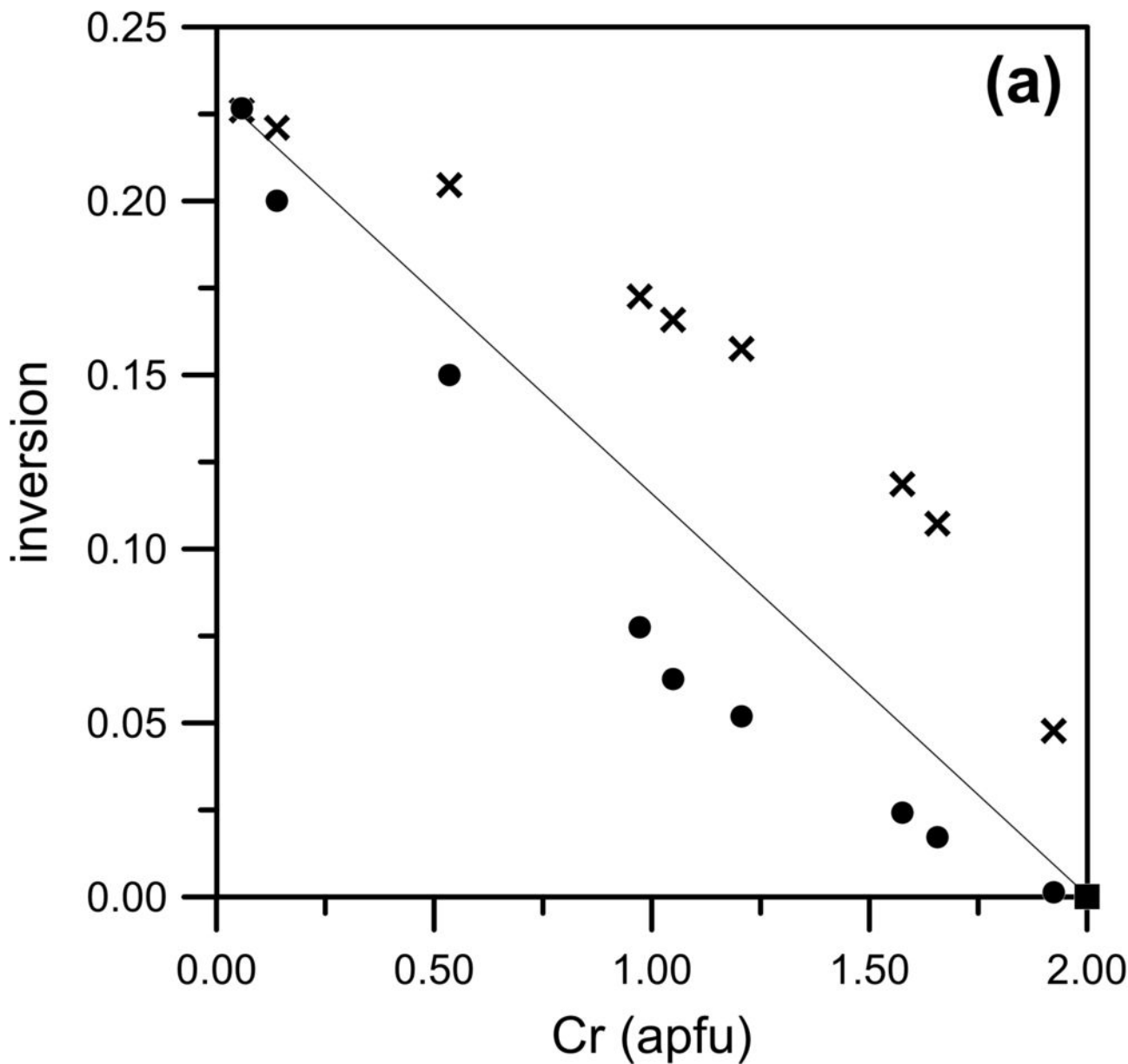


Figure 4

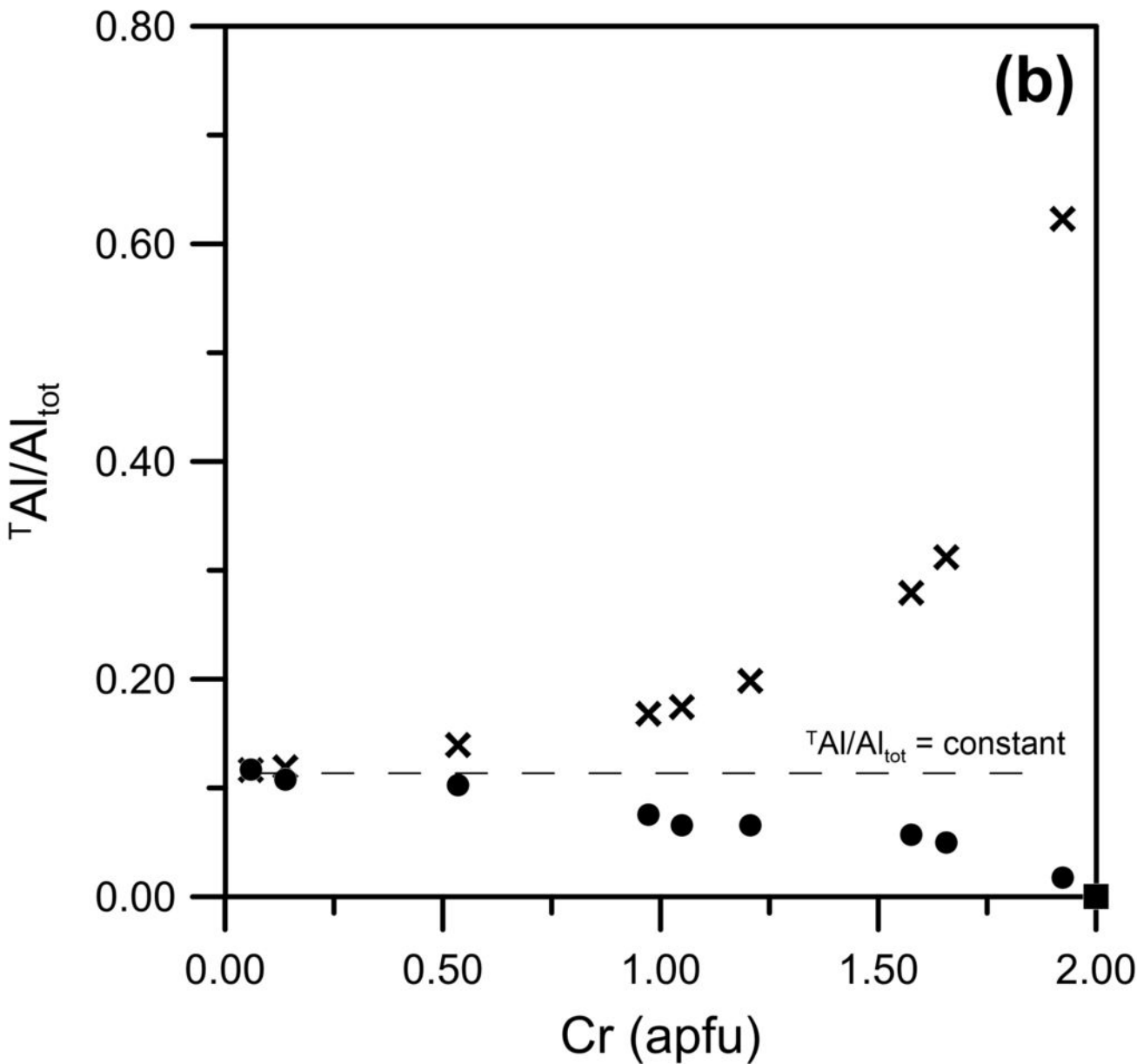


Figure 5

