First crystal-structure determination of chromites from an acapulcoite and ordinary chondrites

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ABSTRACT – We report the first crystal structure determinations of chromites from an acapulcoite and from ordinary chondrites. Cell edges range from 8.3212 (3) to 8.3501 (1) Å, while the oxygen positional parameters are in the range 0.2624 (3) to 0.26298 (9). Their compositions show they are very close to the chromite end-member FeCr$_2$O$_4$ with limited Al and Mg content. Titanium oxide content exceeds 1%, whereas the amount of Fe$^{3+}$ is negligible. Extraterrestrial chromite is readily distinguished from terrestrial analogues on the basis of cell edge and oxygen positional parameter. These distinctions will facilitate ongoing attempts to reconstruct the paleoflux of meteorites to Earth from resistant extraterrestrial spinel grains recovered from ancient sediments.

Keywords: chromite; acapulcoite; ordinary chondrite; X-ray single crystal diffraction; meteorite flux

1. INTRODUCTION

Chromite is a minor but regular constituent of ordinary chondrites and its chemistry in meteorites has been studied since the 1960's. Bunch et al. (1967) were the first to give a survey of the chemical composition of chondritic chromites. They suggested that there is a relationship between chromite Fe-Mg contents and olivine Fe-Mg contents in the H, L and LL groups of equilibrated chondrites. Besides the main components FeO and Cr$_2$O$_3$, chromite contains minor amounts of MgO and Al$_2$O$_3$. The increase in Fe$^{2+}$(Fe$^{2+}$+Mg) from H to LL chondrites is evident. Nonetheless, Wlotzka (2005) argued it was not possible to distinguish between the H and L groups from the chromite composition alone, as has been attempted for fossil chondrites (Bridges et al., 2007), because of the overlapping Fe$^{2+}$(Fe$^{2+}$+Mg) ratios of chromites. Besides Al and Mg, Ti is a major element in the chromite. Although there is overlap in the composition of
chromites from H, L and LL chondrites, the average element composition of a larger set
of chromite grains from fossil meteorite gives an indication of the dominant origin of
the grains (Schmitz, 2013). This relation has been confirmed by oxygen isotopic
analyses of chromites from fossil Ordovician meteorites showing that these indeed are
dominantly pseudomorphosed L chondrites, as indicated by their chromite chemical
composition (Heck et al., 2010). Acapulcoites are coarsely crystalline, unshocked
objects of chondritic composition and igneous texture (Palme et al., 1981; Folco et al.,
2006; Rubin, 2007). Equilibration temperatures for acapulcoites are much higher than
those estimated for the most equilibrated ordinary chondrites (950-1250 K; Dodd,
1969). Oxygen-three isotopes indicate possible aqueous alteration of acapulcoites prior
to the onset of thermal metamorphism (Greenwood et al., 2012), and a comparison of
chromite from acapulcoites and ordinary chondrites is thus of interest.

It is well known that terrestrial Cr-bearing spinel can be considered as a petrogenetic
indicator because chromite composition is a rich source of information on the origin and
evolution of its parent magmas (Irvine, 1967; Dick and Bullen, 1984). The relationships
between composition, structural parameters and genetic environment of Cr-bearing
spinels from different terrestrial occurrences have been considered by several authors
for a better understanding of their genesis and/or oxidation mechanisms (Della Giusta et
al., 1986; Princivalle et al., 1989; Carbonin et al., 1999; Carraro, 2003; Bosi et al.,
2004; Uchida et al., 2005; Lenaz et al., 2010, 2011; Derbyshire et al., 2013; Princivalle
et al., 2014).

This study presents the first structural and chemical data of meteoritic chromite. Data
are given for a total of nine chromite grains, including one from an acapulcoite (labeled
ACAP), and four each from the Kernouvé H6 ordinary chondrite (H6) and from an ~
470 Ma old fossil meteorite, Gol 001 (GOL), found in Ordovician limestone at
Kinnekulle in Sweden and originating from the coeval disruption of the L-chondrite
parent body (Schmitz et al., 2001; Heck et al., 2010; Schmitz, 2013). Recently, Alwmark and Schmitz (2009) and Heck et al. (2010) distinguished terrestrial and extraterrestrial chromite using relict silicate inclusions and high-precision oxygen three-isotopes SIMS analyses, respectively. As these analyses are time-consuming and necessitate a lot of material, our study aims to determine whether structural parameters, such as cell edge and oxygen positional parameter, can be used to distinguish extraterrestrial from terrestrial chromite. Since structure refinement requires much less material, this will facilitate ongoing attempts to reconstruct the paleoflux of meteorites to Earth from resistant extraterrestrial spinel grains recovered from ancient sediments.

2. MATERIALS AND BACKGROUND

Acapulcoites belong to the class of acapulcoite-lodranite (A-L) meteorites (McCoy et al., 1993). A high degree of recrystallization and mineral chemical data indicate formation of acapulcoites under redox conditions intermediate between those of H- and E-chondrites, at about 1100°C, from which it cooled at a rate > 10°C/Ma (Dodd, 1969). The major element composition is within the range of H-chondrites. Troilite and metal are heterogeneously distributed. Associated trace elements are heterogeneously distributed whereas chromium content is a factor of two higher than in H-chondrites. Acapulcoites consist of an assemblage of orthopyroxene, olivine and feldspar associated with comparatively large amounts of metallic nickel-iron, and minor amounts of diopside, troilite, chromite and phosphate. The chromite is rather constant in composition from grain to grain and appears to be distinct from chromite in ordinary chondrites (Bunch et al., 1967), silicate inclusions of iron meteorites (Bunch et al., 1970), pallasites, mesosiderites, and eucrites (Bunch and Keil, 1971). The distribution of divalent cations fits into the correlation observed for equilibrated meteorites. The
high concentrations of Cr, Mn and Zn in chromites are also observed in chromite from silicate inclusions of iron meteorites. ZnO concentrations in acapulcoite chromites range from 0.9 to 1.3%; these relatively high contents reflect the unusually high bulk Zn content of acapulcoite (Palme et al., 1981).

Kernouvé is an ordinary chondrite of the H group from an observed fall in France in 1869. It is texturally metamorphosed and of petrologic type 6. It contains abundant metals, was heated for a significant period of time before the onset of partial melting, and is minimally shocked (Ford et al., 2008). It contains relict chondrules set in a coarse-grained, recrystallized matrix of olivine (Fo80), orthopyroxene (Fs15.7-18.1), plagioclase, Fe-Ni metal, troilite, chromite and phosphate (Ford et al., 2008). Chromite grains from this chondrite are chemically homogeneous and have the typical equilibrated H-chondritic composition with generally somewhat lower TiO₂ (~2.5 wt%) and higher Al₂O₃ (~6.0 wt%) contents than equilibrated L chondrites (typically TiO₂ ~3.0 wt% and Al₂O₃ ~ 5.2 wt%) (Bunch et al., 1967; Schmitz et al., 2001).

Meteorite Gol 001 (formal name Österplana 029) is a relatively large (6 x 9 x 2 cm) mid-Ordovician fossil meteorite found in the Golvsten bed in the Thorsberg quarry in southern Sweden (Schmitz et al., 2001). The meteorite contains abundant, large and well-preserved chromite grains. Chromite grains are homogeneous in chemical composition throughout the meteorite, and the average composition of several of the grains plots with equilibrated L chondrites (Schmitz et al., 2001). Based on these data and the maximum chromite grain diameter, Bridges et al. (2007) assigned it to the L6 group and type. Oxygen-three isotopic analyses of the chromite grains confirm an L or LL chondritic origin (Greenwood et al., 2007; Heck et al., 2010). The cosmic-ray exposure age of meteorite Gol 001 is ca. 300 kyr based on noble (neon) gas isotopic measurements of chromite grains from the meteorite (Heck et al., 2004). This age concurs very well with the estimated timing of the break-up of the L chondrite parent-
body based on the stratigraphic first appearance of abundant sediment-dispersed chromite grains from L-chondritic micrometeorites (Schmitz, 2013). Altogether the isotopic and chemical data show that the chromite grains from this meteorite are excellently preserved despite having been buried in marine limestone for 470 Ma.

3. METHODS

X-ray diffraction data for the nine chromite grains analyzed were recorded on an automated KUMA-KM4 (K-geometry) diffractometer at the Department of Mathematics and Geosciences (University of Trieste), using MoKα radiation, monochromatized by a flat graphite crystal. Chromites from the studied meteorites are usually rather small. The longer axis in these chromite grains is up to about 120 μm, but usually below 100 μm, the other axis is between 20 and 50 μm so that in some cases the grain is nearly "two-dimensional" with a thickness of only 20 μm. Given that, for the largest grains, twenty-four equivalent reflections of (12 8 4) peak, at about 80° of 2θ, were accurately centered at both sides of 2θ, and the α1 peak barycenter was used for cell parameter determination. For the smallest grains, forty-eight reflections of (8 4 0) and (8 4 4) peaks, at about 45-50° of 2θ, have been used. Data collection was made, according to Della Giusta et al. (1996), up to 50° of θ in the ω-2θ scan mode, scan width 1.8°2θ, counting time from 20 to 50 seconds depending on the peak standard deviation. Corrections for absorption and background were performed according to North et al. (1968). Structural refinement using the SHELX-97 program (Sheldrick, 2008) was carried out against $F_0^2$ in the Fd-3m space group (with origin at -3m), since no evidence of different symmetry appeared. Scattering factors were taken from Prince (2004) and Tokonami (1965). Neutral scattering curves, Mg vs. Fe in T site and Cr vs. Al in M site, were assigned, with the constraints of full site occupancy and equal displacement parameters. Oxygen ionization was varied from one grain to another in
order to reach the best fit between structural refinement and chemical analyses and to obtain the best value for all conventional agreement factors. Results are in Table 1.

After X-ray data collection, the same crystals used for X-ray data collection were mounted on glass slides, polished and carbon coated for electron microprobe analyses on a CAMECA-CAMEBAX microprobe at IGG-CNR, Padua, operating at 15kV and 15nA. A 20-s counting time was used for both peak and total background. Synthetic oxide standards (MgO, Fe₂O₃, MnO, ZnO, NiO, Al₂O₃, Cr₂O₃, TiO₂ and SiO₂; purity 99.99 %) and synthetic chromite and Mg-chromite (Lenaz et al., 2004b) were used. Raw data were reduced by PAP-type correction software provided by CAMECA. Results are in Table 2.

Several different procedures may be adopted to determine cation distribution, and very satisfactory results have recently been obtained by combining data from single-crystal X-ray structural refinements and electron microprobe analyses. This approach simultaneously takes into account both structural and chemical data and reproduces the observed parameters by optimizing cation distributions. Differences between measured and calculated parameters are minimized by a function F(X) taking in consideration different parameters as the observed quantity and their standard deviations, cation fractions in T and M sites, unit cell and oxygen parameter, mean atomic numbers of T and M sites, atomic proportions given by microprobe analyses, and constraints imposed by crystal chemistry (total charges and occupancies of T and M sites) (see Appendix). Several minimization cycles of the equation containing these parameters were performed until convergence according to the procedures described in Carbonin et al. (1996) and Lavina et al. (2002) (Table 2 and Table 3). We should note that the program operates in order that the number of cations totals 3. As a result, the GOL samples have large F(X) values and errors because the number of cations never exceeds 2.985. A similar situation arose with the Franz1 chromite analyzed by Carbonin et al. (1999).
Considering the possible valence state partitioning (Papike et al., 2005) we tested the effects of V$_2$O$_5$ instead of V$_2$O$_3$ without improvement. In Table 3 it is possible to observe the observed and calculated values of parameters involved in the minimization process.

4. RESULTS AND DISCUSSION

The cell edge of chromites in H6 ranges from 8.3480 (2) to 8.3501 (1) Å, while in GOL it varies from 8.3212 (3) to 8.3463 (3) Å (Table 1). The oxygen positional parameter ranges from 0.2627 (2) to 0.26298 (9) in H6 and from 0.2624 (3) and 0.26267 (9) in GOL (Table 1). These values show that there are minor differences in chromite composition and structure from the two types of chondrites. The ACAP chromite shows a cell edge equal to 8.3384 (1) Å and an oxygen positional parameter of 0.26251 (9) (Table 1).

The chemical composition of H6 and ACAP samples is rather homogeneous while GOL chromites present different compositions from one point to the other. This feature creates patch-like surfaces with local enrichment/depletion in major oxides. The analyzed chromites point to a nearly pure end-member composition with limited Al$\leftrightarrow$Cr (Al $<$ 0.26 apfu) and Mg$\leftrightarrow$Fe$^{2+}$ (Mg $\leq$ 0.15 apfu, except for the ACAP sample) substitutions. Ferric iron is negligible in all the analyzed chromites (Table 2), a feature characteristic of other phases too, in extraterrestrial materials (Papike et al., 1998). All the GOL chromites here analyzed have been assigned to the L-chondrite group (TiO$_2$ in the range 2.9 – 3.3 wt.%)(Table 2).

The large excess octahedral crystal field stabilization energy of Cr$^{3+}$ ($\Delta$ CFSE$_{\text{oct-tet}}$) is about 160 kJ mol$^{-1}$; O’Neill and Navrotsky, 1984) should ensure that Cr-bearing spinels have an almost completely normal cation distribution (Urusov, 1983), meaning that about $\frac{3}{4}$ of the M site is filled by Cr. Titanium and vanadium can also be assumed to...
occupy this site, consequently only about 0.3 cation could be filled by other cations. Cation assignment, taking in account structural and chemical parameters, shows an ordered distribution where Al almost completely fills the balance of the M site (Table 2).

Calculation of the formulae for the chromites in the GOL samples from Kinnekulle gives a total number of cations less than 3 and a total number of electrons per formula unit significantly higher than that derived from structural refinement. In terrestrial samples this fact, coupled with a low oxygen parameter value (< 0.2620), suggested the presence of vacancies (Carbonin et al., 1999; Bosi et al., 2004; Lenaz et al., 2014a, 2014c). The low oxygen positional parameter in terrestrial samples (in the range 0.2608-0.2620) is a product of the $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{vacancies}$ transformation under oxidizing conditions. This causes the development of a magnetite component as seen from a combined X-ray single crystal diffraction and Mössbauer (MS) approach (Lenaz et al., 2014a, 2014c) and exemplified by Lenaz et al. (2013) by comparing the results of structural refinement (SREF), microprobe analyses, point-MS and powder-MS collected on several chromite samples. They showed that in some cases there was a large discrepancy between SREF and powder-MS because commonly used powder-MS needs a lot of grains where oxidation degree could be very different among the grains, while SREF and point-MS have been performed on the same single crystal yielding a good comparison. These phenomena in the terrestrial environment are considered as the result of oxidation processes that happened after primary chromite formation at temperatures between 600-700°C. It is unlikely this oxidation processes in the present case took place on the sea floor or during diagenesis, consequently we think that this non-stoichiometry should be primary. Alwmark and Schmitz (2007) noticed in some extraterrestrial chromites from the Lockne crater in central Sweden, Zn enrichment and oxidation that they suggested to be a result of the hydrothermal system induced by the
impact. In the present case there is undoubtedly a non-stoichiometry, but the absence
of Zn enrichment as well as the oxygen parameters higher than 0.2624 suggest that the
non-stoichiometry is not due to oxidation. Moreover, this feature has been already
noticed in other extraterrestrial mineral phases (Weill et al., 1971; Herd and Papike,
1998; Yurimoto et al., 2001; Abreu et al., 2014). Yurimoto et al. (2001) suggested a
rapid crystallization to explain the non-stoichiometry of some spinels from a CO
chondrite, while Abreu et al. (2014) suggested shock metamorphism for non-
stoichiometry in CR chondrite grains of several unknown ferromagnesian silicates
(Fe₅MgSi₂O₁₀, Fe₄MgSi₃O₁₁ and other similar compounds). We suggest that the spinels
studied here present a non-stoichiometry for similar reasons.

By comparison with the structural parameters of chromites from terrestrial occurrences,
in an oxygen positional parameter vs. cell edge diagram (Fig. 1) the extraterrestrial
chromites fall in a field close to that of chromites from komatiites (Lenaz et al., 2004a),
kimberlites and included in diamonds (Lenaz et al., 2009), and not far from that of
layered intrusions (Lenaz et al., 2007, 2012) and the synthetic MgCr₂O₄-FeCr₂O₄ series
(Lenaz et al., 2004b). When comparing the meteoritic spinels studied by us with the
mantle occurrences from a structural point of view we can see that they fall in a field
more or less parallel to that of the MgCr₂O₄-FeCr₂O₄ binary synthetic series (Lenaz et
al., 2004b). Considering that the MgAl₂O₄ and FeAl₂O₄ spinels have cell edges equal to
8.0855 and 8.1646 Å and oxygen positional parameter equal to 0.2613 and 0.2642,
respectively, changes along the x-axis roughly suggest a Cr↔Al substitution (see also
Lenaz and Skogby, 2013, for the hercynite-chromite synthetic series) while changes
along the y-axis roughly suggest a Mg↔Fe²⁺ (Fig. 2). Our data suggest a limited
Cr↔Al substitution (Al₂O₃ is close to 6.5 wt. % for H6 and to 5.8 wt. % for GOL) and a
larger Mg↔Fe²⁺ (MgO ranges from 2 to 7 wt. %). Therefore the chromites in our
meteorites (excluding the non-stoichiometric ones), those included in diamonds (Lenaz
et al., 2009) and those from komatiites (Lenaz et al., 2004a) are on a trend (R²=0.92). As all of these occurrences are mantle related, it is possible that this is a consequence of the degree of differentiation of the liquid from which they originated.

Hazen and Ferry (2010) defined three eras and ten stages of mineral evolution in our solar system. During the first era, the so-called Era of Planetary Accretion (>4.55 Ga), perhaps 60 different mineral species appeared as primary condensates. These planet-forming materials developed as planetesimals. As asteroids grew and began to experience modest heating by the decay of short-lived radionuclides such as ²⁶Al, the melting of ice and the subsequent alteration at low temperatures increased mineral diversity to 250 (McCoy, 2010). In fact, one of the many mechanisms that drove mineral diversification is increase in the ranges of intensive variables such as pressure, temperature and the activities of H₂O, CO₂ and O₂ (Hazen and Eldredge, 2010). Even while this aqueous alteration and thermal metamorphism were occurring in asteroids, an era of intense bombardment began. These impacts formed new minerals as chondritic asteroids were subjected to intense heat and pressure (McCoy, 2010). As heating continued, the solidus temperature of about 950°C was exceeded and melting began. The earliest partial melts formed from FeNi metal and the iron sulfide troilite, but they also incorporated minerals like chromite and phosphates (McCoy, 2010). By using the geothermometer proposed by Princivalle et al. (1999) an intracrystalline equilibration temperature equal or higher than about 1250°C (Table 2) has been found for H6 and ACAP chromite grains, showing that the temperature reached after heating was very high. Calculated temperatures for GOL chromites are unreliable (> 1700°C). This happened also for some terrestrial occurrences (Derbyshire et al. 2013) where zoning is present, so that it is possible to assume that where well-defined core-rim zoning or patches are present, as in the GOL chromites, it is not possible to use the thermometer.
5. CONCLUSIONS

Because meteoritic material on the Earth surface is rapidly altered or weathered away with the exception of chromite, similarly to what happens for terrestrial mafic – ultramafic material (Lenaz et al., 2009, 2014b), different methodologies have been recently developed to recognize the extraterrestrial detrital chromitic material such as relict silicate inclusions (Alwmark and Schmitz, 2009) and high-precision oxygen three-isotopes SIMS analyses (Heck et al., 2010). This work demonstrates that a structural study can, as well, distinguish extraterrestrial from terrestrial material and also that different chondritic (H and L) origins can be recognized. This will facilitate ongoing attempts to reconstruct the paleoflux of meteorites to Earth from resistant extraterrestrial spinel grains recovered from ancient sediments.

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APPENDIX

I) Cation distribution

The cation distribution for the present samples has been achieved by using the Lavina et al. (2002) model. This model yields cation distribution by minimizing the weighted differences between observed crystal chemical data and data calculated from site atomic
fractions. This cation distribution in the tetrahedral (T) and octahedral (M) sites must be consistent with the assumptions that:

1 – The mean atomic number (m.a.n.) corresponds to:

\[
\text{m.a.n. T} = \sum_i X_i \text{IV}_i N_i \quad \text{(A1)}
\]

\[
\text{m.a.n. M} = \sum_i X_i \text{VI}_i N_i \quad \text{(A2)}
\]

where \( \text{IV}_i \) and \( \text{VI}_i \) are chemical species in T and M respectively and \( N \) is their atomic number

2 – The site bond length arises from a linear contribution of each species to the tetrahedral (T-O) and octahedral (M-O) coordination distances so that:

\[
\text{T-O} = \sum_i \text{IV}_i X_i \text{IV}_i D_i \quad \text{(A3)}
\]

\[
\text{M-O} = \sum_i \text{VI}_i X_i \text{VI}_i D_i \quad \text{(A4)}
\]

where \( \text{IV}_i D_i \) and \( \text{VI}_i D_i \) are the cation-to-oxygen bond distances of each cation in tetrahedral and octahedral coordination, respectively.

To summarize, site atomic fractions \( \text{IV}_i X_i \) and \( \text{VI}_i X_i \) must not only satisfy the above equations, but also correspond to the atomic proportions from the chemical analyses and obey three crystal-chemical constrains: occupancies of T and M sites and formal valence. Consequently, \( \text{IV}_i X_i \) and \( \text{VI}_i X_i \) may be calculated by minimizing the following sum of residuals:

\[
F(X_i) = \frac{1}{n} \sum_{j=1}^{n} \left( \frac{O_j - C_j(X_i)}{\sigma_j} \right)^2 \quad \text{(A5)}
\]

Where \( O_j \) are the observed quantities with their standard deviation \( \sigma_j \), \( O_j \) are the four observed crystallographic parameters (a, u and m.a.n. of T and M sites) and the chemical proportions for a total of \( n \). \( C_j(X_i) \) are the corresponding quantities calculated by means of variable cation fractions \( X_i \).

II) Temperature calculation
Della Giusta et al. (1996) fitted the data of their heating experiments on spinels with the following empirical equation

$$T(°C) = C_1 - C_2 B + C_3 B^2$$  

(A6)

where

$$B = \frac{Al(T)}{Al_{tot}} + C_4 (1-Mg(T) - Al(T) + C_5 (2 - (Al(M) - Mg(M))$$  

(A7)

and C1 to C5 are the fitting coefficients. The second term of A7 takes into account the compositional influence of \((Fe^{2+} + Fe^{3+} + Si + Mn + Zn)\) in the T site, and the third term \((Cr + Fe^{2+} + Fe^{3+} + Ti + Ni)\) in the M site. Princivalle et al. (1999) revised the above equations obtaining the linear equation

$$T(°C) = 6640 B$$  

(A8)

with new coefficients C4 and C5 being 0.101 and 0.041, respectively. Obtained temperatures for the chromites studied by us are in Table 2. As happened for severely altered terrestrial chromites (Derbyshire et al., 2013), the temperatures of non-stoichiometric chromites are unreliable and, consequently, not reported.

REFERENCES


Fig. 1: Oxygen positional parameter, $u$ vs. cell edge, a. Red circles: H6, this study; red squares: GOL, this study; black diamond: ACAP chromite, this study; blue diamonds: chromite in kimberlites and included in diamonds (Lenaz et al., 2009); purple squares: chromites in komatiites (Lenaz et al., 2004a); yellow circles: chromites in layered intrusions (Lenaz et al., 2007; 2012); green circles: MgCr$_2$O$_4$-FeCr$_2$O$_4$ synthetic spinels (Lenaz et al., 2004b).

Fig. 2: Oxygen positional parameter, $u$ vs. cell edge, a for synthetic series and the meteoritic chromites studied here. Blue squares: MgAl$_2$O$_4$-FeAl$_2$O$_4$ (Andreozzi and Lucchesi, 2002); orange diamonds: FeAl$_2$O$_4$-FeCr$_2$O$_4$ (Lenaz and Skogby, 2013); green circles: MgCr$_2$O$_4$-FeCr$_2$O$_4$ spinels (Lenaz et al., 2004b). The meteorite chromites of this study are represented by red circles.
Table 1: Results of crystal structure refinements of chromite

<table>
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<tr>
<th>Sample</th>
<th>H6-1</th>
<th>H6-2</th>
<th>H6-C</th>
<th>H6-D</th>
<th>ACAP</th>
<th>GOL-A</th>
<th>GOL-B</th>
<th>GOL-C</th>
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<td>a (Å)</td>
<td>8.3488 (1)</td>
<td>8.3501 (1)</td>
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<td>8.3384 (1)</td>
<td>8.3463 (3)</td>
<td>8.3349 (3)</td>
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<td>u</td>
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<td>0.26291 (7)</td>
<td>0.26298 (9)</td>
<td>0.2627 (2)</td>
<td>0.26251 (9)</td>
<td>0.26267 (9)</td>
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<td>0.2624 (3)</td>
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<td>1.9856 (5)</td>
<td>1.9845 (7)</td>
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<td>22.5 (6)</td>
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<td>0.0039 (1)</td>
<td>0.0045 (1)</td>
<td>0.0039 (2)</td>
<td>0.0045 (1)</td>
<td>0.0046 (1)</td>
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<td>0.0075 (2)</td>
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<td>0.0060 (3)</td>
<td>0.0070 (5)</td>
<td>0.0063 (2)</td>
<td>0.0068 (2)</td>
<td>0.0084 (3)</td>
<td>0.0072 (4)</td>
<td>0.0085 (9)</td>
</tr>
<tr>
<td>N. refl.</td>
<td>155</td>
<td>152</td>
<td>122</td>
<td>117</td>
<td>177</td>
<td>155</td>
<td>127</td>
<td>118</td>
<td>85</td>
</tr>
<tr>
<td>R1</td>
<td>2.01</td>
<td>1.86</td>
<td>1.80</td>
<td>3.01</td>
<td>1.67</td>
<td>2.04</td>
<td>2.23</td>
<td>2.43</td>
<td>3.55</td>
</tr>
<tr>
<td>wR2</td>
<td>2.77</td>
<td>3.11</td>
<td>2.67</td>
<td>6.65</td>
<td>3.31</td>
<td>3.62</td>
<td>3.34</td>
<td>4.64</td>
<td>5.50</td>
</tr>
<tr>
<td>GooF</td>
<td>1.241</td>
<td>1.088</td>
<td>1.119</td>
<td>1.173</td>
<td>1.154</td>
<td>1.258</td>
<td>1.145</td>
<td>1.137</td>
<td>1.296</td>
</tr>
<tr>
<td>Diff. peaks</td>
<td>2.91; -0.99</td>
<td>1.63; -0.64</td>
<td>1.12; -0.89</td>
<td>2.26; -1.53</td>
<td>1.74; -0.84</td>
<td>2.33; -1.29</td>
<td>1.62; -0.61</td>
<td>2.28; -0.63</td>
<td>1.75; -1.21</td>
</tr>
</tbody>
</table>

a: cell parameter (Å); u: oxygen positional parameter; T-O and M-O: tetrahedral and octahedral bond lengths (Å), respectively; m.a.n.T and M: mean atomic number; U(M), U(T), U(O): displacement parameters for M site, T site and O; N. Refl.: number of unique reflections; R1 all (%), wR2 (%), GooF as defined in Sheldrick (2008). Diff. peaks: maximum and minimum residual electron density (± e/Å³). Space Group: Fd-3m. Origin fixed at –3m. Z=8. Reciprocal space range: -19 ≤ h ≤ 19; 0 ≤ k ≤ 19; 0 ≤ l ≤ 19. Estimated standard deviations in brackets.
Table 2. Mean chemical analyses and cation distribution of chromite

<table>
<thead>
<tr>
<th>Sample</th>
<th>H6-1</th>
<th>H6-2</th>
<th>H6-C</th>
<th>H6-D</th>
<th>ACAP</th>
<th>GOL-A</th>
<th>GOL-B</th>
<th>GOL-C</th>
<th>GOL-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>3.35 (8)</td>
<td>3.3 (1)</td>
<td>3.2 (1)</td>
<td>3.0 (1)</td>
<td>6.9 (3)</td>
<td>2.3 (2)</td>
<td>2.9 (3)</td>
<td>2.0 (1)</td>
<td>2.67 (9)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.5 (2)</td>
<td>6.4 (1)</td>
<td>6.46 (8)</td>
<td>6.7 (1)</td>
<td>6.1 (1)</td>
<td>5.9 (1)</td>
<td>5.8 (1)</td>
<td>5.8 (3)</td>
<td>5.78 (4)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.3 (2)</td>
<td>2.32 (7)</td>
<td>2.29 (4)</td>
<td>2.10 (7)</td>
<td>1.18 (4)</td>
<td>3.08 (4)</td>
<td>3.2 (1)</td>
<td>2.9 (1)</td>
<td>3.32 (3)</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>0.74 (6)</td>
<td>0.67 (5)</td>
<td>0.66 (3)</td>
<td>0.71 (6)</td>
<td>0.57 (3)</td>
<td>0.67 (1)</td>
<td>0.73 (5)</td>
<td>0.65 (5)</td>
<td>0.69 (1)</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>56.9 (4)</td>
<td>56.9 (5)</td>
<td>57.2 (1)</td>
<td>56.4 (5)</td>
<td>61.7 (5)</td>
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<td>57.0 (8)</td>
<td>56.62 (6)</td>
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<tr>
<td>MnO</td>
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<td>0.87 (6)</td>
<td>0.95 (7)</td>
<td>0.84 (4)</td>
<td>1.6 (5)</td>
<td>0.68 (7)</td>
<td>0.71 (6)</td>
<td>0.57 (6)</td>
<td>0.93 (6)</td>
</tr>
<tr>
<td>FeO</td>
<td>28.7 (3)</td>
<td>29.1 (3)</td>
<td>29.0 (2)</td>
<td>29.2 (2)</td>
<td>21.1 (4)</td>
<td>29.5 (1.0)</td>
<td>29.0 (1.0)</td>
<td>28.9 (1.5)</td>
<td>28.6 (3)</td>
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<tr>
<td>NiO*</td>
<td>0.03 (3)</td>
<td>0.02 (3)</td>
<td>0.00 (0)</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
</tr>
<tr>
<td>ZnO*</td>
<td>0.37 (2)</td>
<td>0.36 (5)</td>
<td>0.31 (3)</td>
<td>0.33 (4)</td>
<td>1.0 (1)</td>
<td>0.30 (3)</td>
<td>0.33 (6)</td>
<td>0.7 (1)</td>
<td></td>
</tr>
<tr>
<td>Sum</td>
<td>99.74</td>
<td>99.92</td>
<td>100.00</td>
<td>99.19</td>
<td>100.13</td>
<td>99.39</td>
<td>99.23</td>
<td>98.8</td>
<td>99.3</td>
</tr>
</tbody>
</table>

T Site

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Mn</th>
<th>Fe²⁺</th>
<th>Zn</th>
<th>Vac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.152 (4)</td>
<td>0.107 (6)</td>
<td>0.110 (4)</td>
<td>0.101 (6)</td>
<td>0.32 (1)</td>
<td>0.105 (9)</td>
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<tr>
<td>Al</td>
<td>0.009 (1)</td>
<td>0.013 (1)</td>
<td>0.0090 (4)</td>
<td>0.020 (1)</td>
<td>0.017 (1)</td>
<td>0.027 (2)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.027 (2)</td>
<td>0.026 (2)</td>
<td>0.027 (2)</td>
<td>0.025 (1)</td>
<td>0.05 (1)</td>
<td>0.020 (2)</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.803 (6)</td>
<td>0.843 (8)</td>
<td>0.845 (5)</td>
<td>0.844 (7)</td>
<td>0.59 (1)</td>
<td>0.82 (2)</td>
</tr>
<tr>
<td>Zn</td>
<td>0.009 (1)</td>
<td>0.009 (1)</td>
<td>0.009 (1)</td>
<td>0.009 (1)</td>
<td>0.025 (3)</td>
<td>0.0079 (8)</td>
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<tr>
<td>Vac.</td>
<td>0.0184 (5)</td>
<td>0.13 (1)</td>
<td>0.0114 (8)</td>
<td>0.0104 (8)</td>
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</tr>
</tbody>
</table>

M Site

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Fe²⁺</th>
<th>Vac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.027 (2)</td>
<td>0.067 (5)</td>
<td>0.058 (3)</td>
<td>0.057 (4)</td>
<td>0.033 (4)</td>
<td>0.022 (4)</td>
<td>0.040 (7)</td>
</tr>
<tr>
<td>Al</td>
<td>0.260 (5)</td>
<td>0.252 (5)</td>
<td>0.260 (2)</td>
<td>0.262 (4)</td>
<td>0.231 (4)</td>
<td>0.225 (6)</td>
<td>0.230 (6)</td>
</tr>
<tr>
<td>Ti</td>
<td>0.060 (3)</td>
<td>0.062 (2)</td>
<td>0.061 (1)</td>
<td>0.056 (2)</td>
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<td>0.082 (2)</td>
<td>0.082 (3)</td>
</tr>
<tr>
<td>V</td>
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<td>0.019 (1)</td>
<td>0.0187 (8)</td>
<td>0.020 (2)</td>
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<td>0.0191 (4)</td>
<td>0.020 (1)</td>
</tr>
<tr>
<td>Cr</td>
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<td>1.588 (9)</td>
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<td>1.584 (9)</td>
<td>1.68 (1)</td>
<td>1.61 (2)</td>
<td>1.52 (2)</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.038 (1)</td>
<td>0.0076 (1)</td>
<td>0.0090 (5)</td>
<td>0.018 (1)</td>
<td>0.012 (1)</td>
<td>0.044 (5)</td>
<td>0.020 (5)</td>
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<tr>
<td>Vac.</td>
<td>0.006 (2)</td>
<td>0.0086 (7)</td>
<td>0.0050 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

T °C: 1245 1374 1265 1512 1377

T °C is the intracrystalline temperature calculated by using the thermometer of Princivalle et al. (1999). *Ni and, occasionally, Zn not present in cation distribution because of the deviation higher than 2σ. Estimated standard deviations are in brackets. High F(X) values are caused by the not-stoichiometry of the spinels with a number of cations in the range 2.980-2.984. Temperatures for non-stoichiometric chromites are unreliable and, consequently, not reported (see Appendix for details).
Table 3. Comparison of observed number of electrons, cell edge a and oxygen positional parameter u with corresponding values calculated with the MINUIT program.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H6-1</th>
<th>H6-2</th>
<th>H6-C</th>
<th>H6-D</th>
<th>ACAP</th>
<th>GOL-A</th>
<th>GOL-B</th>
<th>GOL-C</th>
<th>GOL-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^T_{\text{obs}}$</td>
<td>23.7 (4)</td>
<td>24.0 (6)</td>
<td>24.2 (5)</td>
<td>24.5 (6)</td>
<td>21.3 (2)</td>
<td>23.3 (3)</td>
<td>21.9 (4)</td>
<td>24.0 (5)</td>
<td>22.1 (5)</td>
</tr>
<tr>
<td>$e^T_{\text{calc}}$</td>
<td>23.7</td>
<td>24.3</td>
<td>24.3</td>
<td>24.3</td>
<td>21.3</td>
<td>23.7</td>
<td>20.5</td>
<td>24.2</td>
<td>23.6</td>
</tr>
<tr>
<td>$e^M_{\text{obs}}$</td>
<td>22.1 (5)</td>
<td>22.1 (7)</td>
<td>22.5 (5)</td>
<td>22.0 (5)</td>
<td>22.5 (3)</td>
<td>22.4 (3)</td>
<td>21.9 (6)</td>
<td>22.6 (6)</td>
<td>22.3 (5)</td>
</tr>
<tr>
<td>$e^M_{\text{calc}}$</td>
<td>22.4</td>
<td>22.1</td>
<td>22.1</td>
<td>22.2</td>
<td>22.5</td>
<td>22.5</td>
<td>22.8</td>
<td>22.4</td>
<td>22.6</td>
</tr>
<tr>
<td>$a_{\text{obs}}$</td>
<td>8.3488 (1)</td>
<td>8.3501 (1)</td>
<td>8.3480 (2)</td>
<td>8.3485 (2)</td>
<td>8.3384 (1)</td>
<td>8.3463 (3)</td>
<td>8.3349 (3)</td>
<td>8.3439 (3)</td>
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<td>$a_{\text{calc}}$</td>
<td>8.3488</td>
<td>8.3501</td>
<td>8.3480</td>
<td>8.3485</td>
<td>8.3384</td>
<td>8.3463</td>
<td>8.3348</td>
<td>8.3439</td>
<td>8.3215</td>
</tr>
<tr>
<td>$u_{\text{obs}}$</td>
<td>0.26286 (7)</td>
<td>0.26291 (7)</td>
<td>0.26298 (9)</td>
<td>0.2627 (2)</td>
<td>0.26251 (9)</td>
<td>0.26267 (9)</td>
<td>0.2625 (1)</td>
<td>0.2626 (1)</td>
<td>0.2624 (2)</td>
</tr>
<tr>
<td>$u_{\text{calc}}$</td>
<td>0.26284</td>
<td>0.26287</td>
<td>0.26294</td>
<td>0.2627</td>
<td>0.26248</td>
<td>0.26266</td>
<td>0.2620</td>
<td>0.2626</td>
<td>0.2622</td>
</tr>
<tr>
<td>$F(X)$</td>
<td>0.16</td>
<td>0.14</td>
<td>0.22</td>
<td>0.72</td>
<td>0.09</td>
<td>0.54</td>
<td>4.08</td>
<td>0.51</td>
<td>8.94</td>
</tr>
</tbody>
</table>

$F(x)$: minimisation factor, which takes into account the mean of square differences between calculated and observed parameters, divided by their standard deviations.
The graph shows a scatter plot of oxygen positional parameter, $u$, versus cell edge, $a$ (Å). The correlation coefficient $R^2$ is 0.92, indicating a strong linear relationship between the two variables.