The Meteoritical Society

Meteoritics & Planetary Science 48, Nr 2, 180–194 (2013)
doi: 10.1111/maps.12050

Large spinel grains in a CM chondrite (Acfer 331): Implications for reconstructions of ancient meteorite fluxes

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(Received 13 April 2012; revision accepted 29 October 2012)

Abstract–By dissolving 30–400 kg of marine limestone in HCl and HF acid, our group has previously recovered common relict chromite grains (approximately 63–250 μm) from ordinary chondritic micrometeorites that fell on ancient sea floors, up to 500 Myr old. Here, we evaluate if CM group carbonaceous chondritic material, which makes up an important fraction of the micrometeorite flux today, contains analogous grains that can be searched for in acid residues. We dissolved 8 g of CM2 meteorite Acfer 331 in HF, which yielded a characteristic assemblage of both transparent Mg-Al- and opaque Cr-spinels >28 μm. We find on average 4.6 and 130 Mg-Al-spinel grains per gram in the 63–250 and 28–63 μm size fractions, respectively. These grains are mostly pink or colorless, and often characterized by heterogeneous Cr-content. Black, opaque Cr-spinel grains are absent from the >63 μm fraction, but in the 28–63 μm fraction we find approximately 65 such grains per gram meteorite. The individual grains have a characteristic composition, with heterogeneous major element compositions (e.g., 44.4–61.7 wt% Cr_2O_3), but narrow ranges for maximum TiO_2 (0.6–1.6 wt%) and V_2O_3 (0.5–1.0 wt%) concentrations. The content of spinel grains in the 28–63 μm fraction of CM meteorites appears comparable at the order of magnitude level with the content of >63 μm sized chromite grains in fossil L-chondrites from Ordovician limestone. Our approach of recovering meteoritic spinel from sediment may thus be extended to include CM meteorites, but the smaller size fraction of the acid residues should be searched.

INTRODUCTION

An empirical approach has recently been developed in our group to reconstruct variations in the flux and types of ordinary chondritic, unmelted micrometeorites that fell on Earth through the last approximately 500 Myr (Schmitz et al. 2003; Cronholm and Schmitz 2007, 2010; Heck et al. 2008). We dissolve large samples, up to a few hundred kilograms, of slowly formed marine limestone in hydrochloric and hydrofluoric acid, and recover resistant, relict ordinary chondritic chromite grains ($FeCr_2O_4$; 63–250 μm) from the residues. Typically between a few up to a thousand of such chromite grains can be found in 100 kg of rock, depending on sedimentation rate and micrometeorite flux when the sediment formed (Schmitz and Häggström 2006; Cronholm and Schmitz 2007, 2010; Lindskog et al. 2012). Considering that the micrometeorite (<2 mm) flux to Earth today is dominated by carbonaceous chondritic material (e.g., Gounelle 2011) it would be valuable to develop a similar approach to reconstruct paleofluxes also of this material. As a first step, we here aim at quantifying the amounts and types of large (>28 μm) resistant spinel group minerals in a carbonaceous chondritic CM2 meteorite. By characterizing the full assemblage of large spinel grains in different meteorite groups, including the proportions of different types of spinel present, a tool for classifying fossil meteorites will also be established. Our studies of over 100 fossil L-chondrites (1–21 cm large) recovered from mid-Ordovician marine limestone show that the spinel grains are the only common meteoritic minerals that have survived weathering on the sea floor (e.g., Schmitz et al. 2001). The classification of a fossil meteorite is thus highly dependent on a thorough understanding of the abundances of large spinel grains in recent meteorite groups. We have shown that by leaching recent L-chondrites in strong hydrofluoric acid we can produce mineral residues that are similar to those found in the sea-floor weathered Ordovician L-chondrites (Alwmark et al. 2011).

Once a relict extraterrestrial spinel grain is recovered from an ancient sediment, a plethora of information can be obtained from the grain. Most of our previous studies of sediment-dispersed chromite relate to the break-up of the L-chondrite parent body in the asteroid belt 470 Ma, when the flux of L-chondritic micrometeorites and meteorites was enhanced by two to three orders of magnitude compared with today (Schmitz et al. 2001, 2003; Korochantseva et al. 2007; Lindskog et al. 2012). Judging from high concentrations of trapped solar gases the majority of the sediment-dispersed Ordovician chromite grains were once parts of micrometeorites (Heck et al. 2008). Major element and oxygen isotopic studies of the chromite grains as well as chemical analyses of original pyroxene and olivine inclusions in the chromite show an L-group affinity (Schmitz et al. 2001; Alwmark and Schmitz 2009; Heck et al. 2010). Quantification of sizes and abundances of the inclusions in chromite by 3-D X-ray microtomography can further be used to determine the petrologic type of the precursor micrometeorites (Alwmark et al. 2011).

Ordinary chondrites make up approximately 80 to 85% of the meteorite-sized fraction falling on Earth today, with carbonaceous chondrites representing only a few percent (Cassidy and Harvey 1991; Bevan et al. 1998). In the micrometeorite (10 μm–2 mm; see Rubin and Grossman 2010) fraction, however, the situation is reversed with carbonaceous chondritic material being the dominant component (Engrand and Maurette 1998; Parashar et al. 2010; Suavet et al. 2010; Cordier et al. 2011; Gounelle 2011). Early studies of large collections of micrometeorites from Antarctic ice indicated that the carbonaceous chondritic fraction is dominated by material related to hydrous CM and CR meteorites (Engrand and Maurette 1998), but oxygen isotopic analyses of large (>0.5 mm) Antarctic micrometeorites indicate instead a substantial (20–50%) fraction of CV/CO micrometeorites, and as much as 30% ordinary chondritic material (Suavet et al. 2010). It is likely that the amount of the more fragile, carbon-rich CM/CR material relative to the harder anhydrous carbonaceous and ordinary chondrites decreases with increasing size of the debris, reflecting how dust is created in the collision of the meteoritic debris with the upper atmosphere (Lal and Jull 2002; Flynn et al. 2009).

Most of the members of the spinel mineral group are very resistant to weathering in the terrestrial environment as well as to aggressive acid-leaching, and spinel grains are commonly found in placer deposits (Lumpkin 2001; Pownceby 2005). Spinel group minerals are oxides with the formula AB_2O_4. Based on the dominant A^{2+} and B^{3+} ions they can be divided into several endmember species, such as spinel ($MgAl_2O_4$), chromite ($FeCr_2O_4$), and magnetite (Fe_3O_4). The compositional variations in between these endmembers are large and therefore we use the terms Mg-Al-spinel when dominated by Mg and Al, and Cr-spinel when dominated by Fe and Cr. The term spinel is from here used for spinel group minerals in general. For different chondrite groups different oxide minerals have been reported. Chromite dominates the oxide fraction in ordinary chondrites, in enstatite chondrites oxides are rare, Cr-spinel dominates in R chondrites, whereas in carbonaceous chondrites a wide range of oxide minerals occur, e.g., magnetite, chromite, and different spinel group varieties (Rubin 1997).

Previous studies of spinel group minerals in the size range (>28 μm) of interest to us in CM2 meteorites have primarily dealt with freeze-thaw or acid residues of the Murchison meteorite (Simon et al. [1994], and references therein). This meteorite contains two distinctly different types of Mg-Al-spinel grains; one is ^{16}O-rich ($\delta^{18}O = -50‰$), small (10–30 μm) and probably resides in refractory inclusions, the other is coarse (63–325 μm), not ^{16}O-rich ($\delta^{18}O = 1.9 \pm 2.4‰$) with up to 37% Cr_2O_3 and up to 17% FeO. Simon et al. (1994) found about 100 grains of the second type from chips of an approximately 50–200 g sample used for freeze-thaw disaggregation. The larger type of Mg-Al-spinel grains has a wide range of Cr_2O_3 and FeO compositions; 0.3–36.9 wt% and 0.2–17 wt%, respectively, and the individual grains have heterogeneous Cr-contents showing itself as zoning patterns (chevron, gradual, patchy, core-rim, or homogeneous). Inclusions of aluminous diopside and forsteritic olivine are common in the grains, and Ca-, Al-, and Si-rich glass, FeS, and FeNi metal inclusions also occur. Many of these spinel grains have been considered to derive from chondrules, after comparison with similar spinel grains in chondrules from Allende CV3 meteorite (Simon et al. 2000). In addition to Mg-Al-spinel, from pure $MgAl_2O_4$ to compositions with considerable Fe and Cr, Murchison contains darker or black, opaque chromite or Cr-spinel, from pure $FeCr_2O_4$ to compositions with considerable Mg and Al (Fuchs et al. 1973; Johnson and Prinz 1991). Chromite is somewhat more common in Murchison than pure Mg-Al-spinel, according to Fuchs et al. (1973), and the magnetite content is quite variable, but generally lower than chromite. These authors also state that "the general low abundance of magnetite runs counter to many statements in the literature that it is a significant phase in all carbonaceous chondrites."

Here, we aim at a more detailed quantification of the different spinel group minerals (>28 μm) in an 8 g piece of the CM2 meteorite Acfer 331, to lay the basis for appropriate interpretations of spinel grains found in fossil meteorites and acid residues of ancient terrestrial sediments. In this study, we focus on Mg-Al-Cr-spinel grains. We evaluate the prospects of finding relict CM2 spinel grains in sediment acid residues, and discuss how one could distinguish the grains from terrestrial and other extraterrestrial spinel grains. A diagenetically altered 2.5 mm sized fossil meteorite was found by Kyte (1998) at the Cretaceous-Paleogene (K-Pg) boundary in a Pacific deep-sea core. The meteorite was interpreted as a fragment of the asteroid that hit Earth at that time. Kyte (1998) favors that the impactor was a CV, CO, CR, or possibly CM asteroid. Based on Cr-isotopic studies of whole-rock K-Pg boundary clays, Trinquier et al. (2006) favor a CM2 impactor. The data in the present study will also guide searches of relict material from the impactor in K-Pg boundary clays.

MATERIALS AND METHODS

Two approximately 4 g samples (3.9 and 4.1 g) of chondrite Acfer 331 were prepared for the study. This meteorite, fragments totaling 750 g, was found in Algeria in the end of 2001 by F. Beroud and C. Boucher. The fragments were insignificantly weathered (W0) and are classified as a CM2 meteorite (Russell et al. 2003). After cutting and weighing, the samples were gently broken down with the thumb into smaller pieces in a teflon beaker and then placed in an ultrasonic bath for further disaggregation. Samples were then treated with 17 M hydrofluoric acid at room temperature for approximately 24 h with occasional stirring, to dissolve the silicates. After careful neutralization and washing, remaining grains were separated using 63 and 28 μm mesh sieves. Between different samples, sieves were treated in an ultrasonic bath, rinsed out, and examined for cleanliness under the microscope to prevent cross-contamination. The residues were dried and the spinel grains were picked with a fine brush under an optical microscope. The >63 μm fraction was studied from both subsamples, whereas the fraction 28–63 μm was only studied in one subsample. Aggregates with individual grains smaller than the respective fraction size were not considered. Spinel grains were divided into two groups, the transparent to translucent, colorless to red grains, termed Mg-Al-spinel grains, and the mainly opaque, dark colored to black grains, termed Cr-spinel grains.

Grains were analyzed for major and minor elements with an INCA Oxford systems energy dispersive X-ray device (EDS) attached to a Hitachi S-3400N scanning electron microscope (SEM) at the Department of Geology, Lund University, Sweden. All grains picked were mounted on carbon tape and analyzed semiquantitatively to certify that they were spinel grains. Thereafter, all confirmed spinel grains >63 μm and 10% of the Mg-Al-spinel grains and Cr-spinel grains from the 28–63 μm fraction, which were randomly chosen, were prepared for further element analyses. The grains were mounted in epoxy, polished flat with 6 and 1 μm diamond paste, and coated with carbon. For the SEM analyses, electron voltage was set to 15 keV and working distance to 10 mm. For analyses and imaging (BSE, i.e., back scattered electrons) of the polished sections pressure was set to <1 Pa, and for the preceding semiquantitative analyses to approximately 80 Pa. For standardization of the instrument a cobalt standard was used. For standardization of the spectrum peaks the following standards were chosen: synthetic pure spinel for Mg and Al, chromite for Cr, hematite for Fe, titanite for Ti, and quartz for Si. The compositions of the grains are assumed to fall on the spinel-chromite series; therefore Fe is analyzed as Fe^{2+}. Counting time was set to 60–80 s per analysis. Analysis spots were chosen to represent as much as possible of the surface and heterogeneities. Cracks and heterogeneities have affected some analyses, and therefore analyses within a total 95–105 wt% are considered in this article, except for grains which only had total wt% outside this range (see the Results section and tables). Concentrations equal to or below two sigma uncertainties (2σ, i.e., standard deviations) are considered as b.d. (below detection limit). Spinel grains with Cr-content variations less or equal to the 2σ uncertainties are considered homogeneous, otherwise they are heterogeneous.

We have assessed the quality of our SEM-EDS chemical analyses by comparing analyses for three homogeneous Mg-Al-spinel grains and one heterogeneous Mg-Al-spinel grain with higher Cr-content, using a Cameca SX-50 electron probe microanalyzer (EPMA) at the Department of Geophysical Sciences, University of Chicago (Table 1). The probe was operated at 15 kV and 50 nA, using wavelength dispersive spectrometers. Counting time was 60 s per analysis spot; each grain was analyzed at four spots. Pure synthetic oxides, anorthite glass, natural olivine (Mn-hortonolite), and Ni metal standards were used.

Table 1. Spinel grains analyzed with both SEM-EDS and EPMA (mean wt% ± 2σ).

	FeO	TiO_2	MgO	Al_2O_3	SiO_2	Cr_2O_3	V_2O_3
Acfer 331:2 grain 15							
SEM-EDS	<0.20	0.40 ± 0.16	28.64 ± 0.3	70.82 ± 0.44	0.33 ± 0.1	<0.18	0.65 ± 0.18
EPMA	0.04 ± 0.02	0.44 ± 0.03	27.94 ± 0.25	71.03 ± 0.39	0.19 ± 0.04	0.22 ± 0.03	0.61 ± 0.02
Acfer 331:2 grain 8							
SEM-EDS	3.75 ± 0.48	<0.20	24.68 ± 0.42	59.57 ± 0.58	<0.14	10.90 ± 0.54	<0.24
EPMA	3.71 ± 0.02	0.17 ± 0.03	24.27 ± 0.25	59.58 ± 0.39	0.30 ± 0.04	10.45 ± 0.03	0.20 ± 0.02
Acfer 331:3 grain 5							
SEM-EDS	0.16 ± 0.12	0.18 ± 0.08	28.30 ± 0.18	70.74 ± 0.22	0.25 ± 0.08	0.18 ± 0.1	0.18 ± 0.1
EPMA	0.15 ± 0.02	0.07 ± 0.03	27.98 ± 0.25	69.85 ± 0.39	0.16 ± 0.04	0.21 ± 0.03	0.12 ± 0.02
Acfer 331:3 grain 8							
SEM-EDS	0.48 ± 0.12	0.21 ± 0.08	27.06 ± 0.16	67.54 ± 0.22	0.25 ± 0.08	0.23 ± 0.1	0.23 ± 0.08
EPMA	0.52 ± 0.02	0.15 ± 0.03	27.57 ± 0.25	69.44 ± 0.39	0.36 ± 0.04	0.94 ± 0.03	0.23 ± 0.02

SEM-EDS = scanning electron microscope-energy dispersive X-ray device. EPMA = electron probe microanalyzer.
wt% sums for SEM-EDS analyses are 95–105 wt%, for EPMA wt% sums are 97–102 wt%.

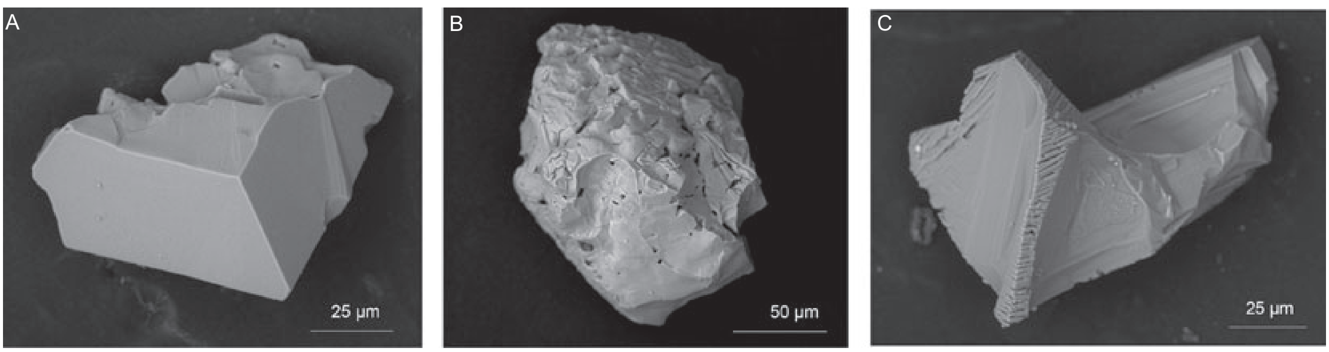

Fig. 1. The Mg-Al-spinel grains >63 µm are commonly around 100 µm and show a wide variety of morphologies. Here SEM-BSE images of three spinel grains from Acfer 331:2 are presented: A) angular grain 3:10; B) Grain 2:4 has an irregular surface with several cavities; C) Angular and flat grain 2:13 with linear striations in its grain surface.

To compare abundances of durable spinel grains in CM carbonaceous chondrites with ordinary chondrites we counted the number of chromite grains >63 µm in small (approximately 0.1–0.7 g) samples of nine fossil L-chondrites recovered from mid-Ordovician marine limestone at Kinnekulle in Sweden (Schmitz et al. 2001). The informal names of the meteorites are Gla3/001, Gla3/002, Gla2/004, Gla2/006, Gla1/002, Gla1/003, Gla1/004, God 002, and Tre 004 (for formal names see Table 5). The meteorites originate from five different beds in the Thorsberg quarry (Schmitz et al. 2001). The samples were treated with 6 M HCl at room temperature to remove and disaggregate secondary calcite and clay minerals. The residues were washed, placed in an ultrasonic bath for approximately 60 s, then sieved at 63 µm, and thereafter a count of the number of chromite grains was performed under an optical microscope. Samples (approximately 0.5–5 g) of two recently fallen meteorites, Ghubara (L4-6 breccia) and Lundsgård (L6), were gently crushed in an agate mortar into millimeter-sized pieces, and then leached in 11 M (Ghubara) or 17 M (Lundsgård) hydrofluoric acid. The resistant >63 µm fraction was recovered, and chromite grains picked and counted. The identification of chromite grains from fossil and recent L-chondrites was confirmed by semiquantitative SEM-EDS analyses, see above.

RESULTS

Transparent to Translucent Mg-Al-Spinel Grains in Acfer 331

From the >63 µm size fraction of Acfer 331 one of the samples contained 17 large Mg-Al-spinel grains and the other 20, i.e., on average 4.6 grains per gram of meteorite. Most grains in this fraction are 63–150 µm but a few reach approximately 250 µm (Table 2, Fig. 1). In the 28–63 µm residue from one of the approximately 4 g splits 530 Mg-Al-spinel grains were found, i.e., approximately 130 grains per gram meteorite. The Mg-Al-spinel grains are mostly subhedral and angular, transparent to translucent, and commonly colorless or

Table 2. Physical properties and chemical composition (wt%) of the transparent Mg-Al-spinel grains larger than 63 μm.

					MgO		Al_2O_3		Cr_2O_3		FeO		TiO_2	V_2O_3	SiO_2
Grain	Color	Size (μm)	Cr-zoning	n*	Min	Max	Min	Max	Min	Max	Min	Max	Max	Max	Max
Spinel grains from Acfer 331:2															
1	Red	91 × 121	het	9	25.9	27.3	59.5	66.6	5.4	10.6	0.9	1.6	0.3	0.2	0.2
2	Pink	81 × 95	het	5	25.7	26.8	58.2	63.8	6.3	11.9	0.6	1.1	0.4	0.4	b.d
3	Pink	114 × 135	het	9	27.1	27.8	61.6	67.2	5.1	9.7	0.8	1.2	0.4	0.5	0.4
4	Pink	131 × 169	het	5	26.5	28.0	64.6	68.6	1.9	6.4	b.d	1.3	0.4	0.4	b.d
5	Pink	85 × 93	hom	4	21.1	28.4	68.2	70.4	b.d	b.d	b.d	12.0	0.5	0.6	b.d
6	Pink	142 × 177	het	6	26.8	28.8	64.4	70.8	1.7	5.3	b.d	0.5	0.3	0.3	0.3
7	Pink	77 × 97	het	3	26.0	26.2	63.6	65.0	4.7	7.7	2.2	2.5	b.d	b.d	0.3
8	Pink	89 × 94	het	5	24.1	25.1	57.1	60.9	10.5	12.2	3.5	3.9	b.d	b.d	b.d
9	Pink	75 × 104	het	9	27.0	29.2	64.8	71.0	2.6	8.2	b.d	0.6	0.4	0.4	0.4
10	Pink	84 × 111	het	10	26.3	28.1	63.9	68.7	4.0	5.1	0.6	1.0	0.5	0.3	0.3
11	C.less	87 × 111	hom	6	28.2	29.6	69.6	73.0	0.9	1.0	b.d	0.4	0.4	b.d	b.d
12	C.less	116 × 172	het	5	27.2	28.9	68.0	73.0	b.d	0.5[d]	b.d	0.5	b.d	0.3	b.d
13	C.less	78 × 123	hom	8	27.7	29.1	69.3	71.6	0.6	1.0	b.d	0.4	0.4	0.4	0.3
14	C.less	69 × 69	hom	5	27.7	29.5	68.8	73.2	0.8	1.0	b.d	0.3	0.3	b.d	0.4
15	Blue	124 × 141	hom	6	27.9	29.5	68.9	73.0	b.d	0.2	b.d	b.d	0.5	0.7	0.3
16	Pink	129 × 137	-	2[a]	24.4	24.6	60.1	60.2	7.4	8.1	3.8	4.2	b.d	b.d	b.d
17	Pink	140 × 190	het	3	23.8	25.3	60.9	63.9	5.5	7.4	3.6	3.9	b.d	b.d	b.d
Spinel grains fromAcfer 331:3															
1	Red	80 × 132	het	3	22.0	22.8	48.5	52.6	17.5	20.4	4.6	4.9	0.3	0.6	0.3
2	Red	141 × 149	het	6	21.8	23.2	53.9	60.9	7.0	13.7	4.9	6.0	0.6	b.d	0.4
3	Pink	149 × 290	het	7	25.6	26.9	60.2	68.3	1.0	9.0	0.9	1.2	0.4	0.4	b.d
4	C.less	82 × 113	het	3	25.6	26.3	61.0	65.7	1.9	6.7	0.7	0.9	0.2	0.2	0.4
5	C.less	73 × 119	hom	6	27.2	29.6	68.0	73.7	b.d	0.3	b.d	0.2	0.2	0.3	0.3
6	C.less	83 × 89	hom	3	28.4	28.8	70.7	71.5	0.5	0.7	0.2	0.4	0.3	0.2	0.4
7	C.less	85 × 111	het	3	26.4	28.3	66.9	69.8	1.0	1.6	0.4	0.7	0.3	b.d	0.4
8	C.less	69 × 70	hom	3	26.8	27.4	66.9	68.5	0.8	0.9	0.5	0.5	0.2	0.3	0.3
9	C.less	132 × 167	het	3	26.6	26.8	65.4	66.8	1.2	3.2	0.6	0.7	0.3	b.d	0.4
10	C.less	78 × 90	het	5	26.3	27.3	60.8	66.7	1.1	7.6	0.3	0.6	0.3	0.5	0.5
11	C.less	75 × 88	-	1[b]	-	26.2	-	66.4	-	0.7	-	b.d	b.d	b.d	b.d
12	C.less	106 × 113	het	4	28.3	29.0	70.4	71.3	0.7	1.1	0.2	0.4	0.3	0.2	0.5
13	C.less	71 × 101	hom	4	27.4	27.9	68.8	70.6	0.2	0.4	b.d	b.d	0.4	0.4	0.3
14	C.less	73 × 145	het	4	26.8	27.6	65.8	68.5	1.0	3.1	0.2	0.5	0.4	b.d	0.3
15	C.less	74 × 111	het	3	26.9	27.1	67.8	68.3	0.8	1.5	0.3	0.5	0.4	0.2	0.2
16	C.less	94 × 155	het	7	27.8	28.6	68.7	70.6	0.8	2.6	b.d	0.5	0.3	b.d	0.4
17	C.less	122 × 131	het	4	26.4	27.1	63.2	68.7	0.5	5.2	b.d	0.5	0.5	b.d	0.4
18	C.less	219 × 247	-	2[c]	27.6	28.3	67.1	69.7	1.2	1.4	0.4	0.7	b.d	b.d	1.5
19	C.less	84 × 96	hom	4	27.0	27.7	66.9	69.5	0.4	0.6	b.d	0.3	0.5	0.3	0.3
20	C.less	79 × 114	het	4	27.1	27.4	68.0	68.3	0.5	0.8	b.d	0.4	0.3	b.d	0.4

C.less = colorless; Cr-content is either hom = homogeneous or het = heterogeneous.
Analyses are presented with maximum and minimum wt% oxide of the main components measured in each grain; out of n* analyses and maximum wt% oxide for the minor but common elements (TiO_2, V_2O_3, SiO_2).
b.d = below detection (analyze $\leq 2\sigma$).
Grain 2:16, 3:16, and 3:18 were lost during sample preparation and only preliminary analyses on unpolished surfaces were available.
[a]Preliminary analyses with sum <80 wt%, standardized to 100%.
[b]Analyses with sum of 93–105 wt%.
[c]Preliminary analyses, within sum 95–105 wt%.
[d]Up to 3 wt% Cr_2O_3 has been measured, however with a sum of 108.9 wt%.

with a weak tint of pink. Some grains are strongly pink, red, or blue-green.

Major elements are Mg and Al with MgO in the range 21.1–29.6 wt% and Al_2O_3 in the range 41.9–73.7 wt% (Tables 2 and 3). Cr and Fe are important constituents of most grains, but in smaller amounts. Cr_2O_3 contents reach maximum up to 28 wt%, FeO reaches up to 12 wt%. More than 80% of the grains have Cr_2O_3 content less than 10 wt% for grains >63 μm and less than 5 wt% for grains 28–63 μm (Fig. 2). For

Table 3. Physical properties and chemical composition (wt%) of the transparent Mg-Al-spinel grains sizes 28–63 μm.

				MgO		Al_2O_3		Cr_2O_3		FeO		TiO_2	V_2O_3	SiO_2
Grain	Color	Cr-zoning	n*	Min	Max	Min	Max	Min	Max	Min	Max	Max	Max	Max
1	C.less	hom	3	26.3	29.0	66.2	71.5	1.4	1.7	b.d	0.2	0.4	b.d	0.3
2	Pink	het	3	21.5	23.0	41.9	46.3	26.2	28.1	3.2	4.2	0.6	0.4	b.d
3	C.less	hom	3	26.9	28.3	67.3	70.7	0.9	1.1	b.d	0.2	0.3	0.2	0.3
4	W.pink	het	3	26.2	27.5	63.2	65.4	4.2	8.3	0.2	0.7	0.2	b.d	0.3
5	C.less	het	3	27.0	27.0	67.8	69.1	0.6	0.8	0.4	0.5	0.3	b.d	0.3
6	C.less	hom	3	27.3	28.0	67.5	69.0	0.9	0.9	0.4	0.5	0.3	0.2	0.3
7	C.less	het	3	27.5	27.8	68.1	69.2	0.9	1.2	b.d	0.2	0.4	b.d	0.2
8	C.less	het	3	27.1	27.8	66.8	69.0	1.3	2.6	0.4	0.5	0.4	b.d	0.3
9	C.less	het	3	27.0	27.4	66.3	69.0	1.3	3.2	0.3	0.4	0.3	b.d	b.d
10	Blue	hom	3	27.8	28.7	68.8	72.2	b.d	0.3	b.d	b.d	0.3	0.8	0.2
11	W.blue	het	3	26.9	28.4	67.3	70.7	0.7	1.1	0.2	0.4	0.5	0.4	0.5
12	Pink	het	3	24.3	24.5	61.2	63.8	6.1	7.7	3.8	4.1	0.2	0.3	b.d
13	C.less	hom	3	27.6	28.1	67.8	69.8	1.5	1.6	0.2	0.3	0.3	0.3	0.2
14	C.less	hom	3	27.5	27.7	67.8	69.4	0.7	0.7	0.2	0.3	0.4	b.d	0.9
15	C.less	het	3	27.1	28.0	67.2	69.5	1.4	1.6	0.3	0.3	0.4	b.d	0.3
16	C.less	hom	3	27.2	28.3	67.6	70.2	0.7	0.8	0.3	0.4	0.3	0.4	0.3
17	C.less	hom	3	27.1	27.5	68.4	69.0	0.9	1.0	b.d	0.3	0.3	0.2	0.3
18	C.less	hom	3	27.2	28.3	67.6	70.4	0.6	0.7	0.3	0.5	0.3	0.2	0.2
19	C.less	het	3	26.2	27.1	66.5	69.0	0.4	1.4	1.4	1.6	1.0	b.d	0.3
20	C.less	het	3	27.1	27.3	67.3	67.8	0.9	1.6	0.4	0.5	0.2	0.2	0.3
21	Blue	hom	3	27.0	27.9	67.8	69.5	0.3	0.4	b.d	0.3	0.4	0.5	0.2
22	C.less	hom	3	26.4	27.1	68.0	69.1	1.2	1.3	1.2	2.5	0.4	0.3	0.3
23	C.less	hom	3	27.2	28.4	68.5	71.7	0.4	0.5	b.d	b.d	b.d	b.d	0.3
24	C.less	het	3	26.3	27.4	62.0	65.7	4.9	7.8	0.6	0.7	0.4	0.3	0.2
25	C.less	het	3	25.2	26.5	64.6	67.8	3.0	4.3	0.6	0.7	0.2	0.4	0.3
26	C.less	hom	3	27.3	27.9	67.3	69.6	0.9	1.0	0.3	0.4	0.4	0.2	0.2
27	C.less	hom	3	27.1	27.7	68.0	68.7	0.7	0.8	b.d	0.2	b.d	0.4	0.2
28	C.less	het	3	27.5	28.3	68.2	70.2	0.8	1.0	0.4	0.4	0.2	0.3	0.4
29	W.blue	het	3	26.6	27.6	67.1	69.6	0.2	0.5	1.1	1.2	0.3	0.4	0.3
30	C.less	hom	3	27.3	28.0	67.2	69.5	0.8	0.9	0.4	0.5	b.d	0.2	0.4
31	C.less	het	3	27.2	28.2	65.9	68.8	2.6	3.0	0.5	0.6	0.4	0.2	0.3
32	C.less	het	3	27.1	27.7	66.8	68.6	2.6	3.7	0.4	0.5	0.4	0.2	0.3
33	C.less	het	3	27.5	28.1	67.5	68.7	2.0	2.4	0.4	0.4	0.4	b.d	0.3
34	C.less	het	3	27.6	27.9	67.0	68.0	3.0	3.3	0.4	0.6	0.3	0.2	0.3
35	Pink	het	3	27.7	28.0	66.9	67.5	2.2	2.6	b.d	0.2	0.4	0.4	0.4
36	Pink	hom	2	27.7	27.5	67.6	67.1	4.0	3.8	0.8	0.7	0.2	0.2	0.3
37	Pink	het	3	27.5	28.6	68.5	70.5	1.1	1.3	0.2	0.3	0.2	0.2	0.5
38	C.less	het	3	27.7	28.0	68.2	69.9	0.8	1.0	0.3	0.3	0.3	0.2	0.4
39	C.less	hom	3	28.1	28.4	69.1	70.1	0.6	0.7	b.d	b.d	0.4	b.d	0.4
40	C.less	het	3	27.6	27.9	68.0	68.9	1.4	1.5	0.5	0.5	0.4	0.2	0.4
41	C.less	het	3	27.5	28.3	67.0	69.1	2.3	3.3	0.3	0.4	0.2	b.d	0.4
42	C.less	hom	3	27.6	28.7	68.5	70.6	0.3	0.4	b.d	b.d	0.4	b.d	0.4
43	W.blue	het	3	27.4	28.5	67.6	69.8	b.d	0.3	0.3	0.4	0.9	b.d	0.2
44	C.less	hom	3	27.7	28.2	68.3	69.5	0.7	0.8	0.4	0.5	0.2	0.2	0.4
45	Pink	het	3	27.1	27.5	65.4	66.4	3.3	4.2	0.6	0.7	0.2	0.2	0.4
46	C.less	het	3	26.6	28.3	66.1	69.7	1.6	3.3	0.5	1.4	0.2	0.3	0.5
47	C.less	het	3	27.4	27.6	65.2	66.7	3.9	5.2	0.5	0.6	0.3	b.d	0.5
48	C.less	het	3	26.9	28.2	66.8	69.7	0.8	1.0	0.5	0.5	0.3	0.3	0.4
49	Pink	het	3	27.5	28.6	67.7	70.6	0.8	1.3	0.2	0.3	0.3	0.2	0.4

C.less = colorless; w.pink = weakly pink; w.blue = weakly blue; het = heterogeneous Cr-content; hom = homogeneous Cr-contents.
Analyses of the grains have sums 95–102 wt%. See Table 2 for further information.

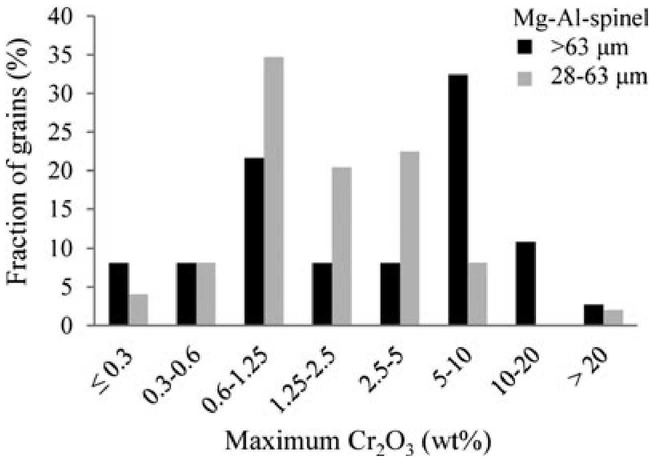

Fig. 2. The Mg-Al-spinel grains >63 μm are overall richer in Cr_2O_3 than the 28–63 μm grains. This is illustrated by separating the grains into groups based on maximum Cr_2O_3 content, in relation to size range.

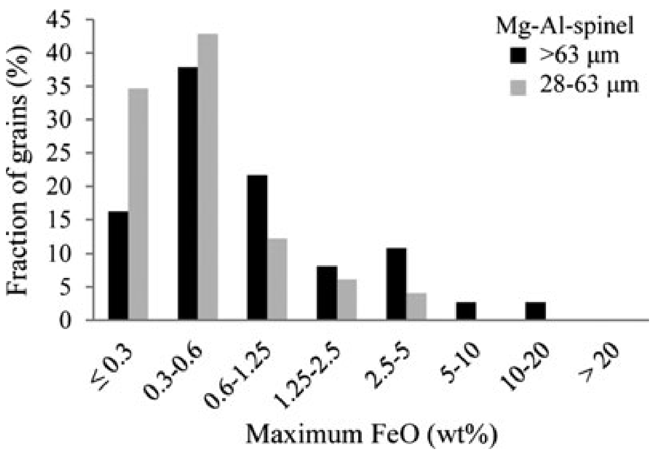

Fig. 3. The Mg-Al-spinel grains >63 μm are generally richer in FeO than the grains in the 28–63 μm size range. The grains are grouped based on maximum FeO content, in relation to size range.

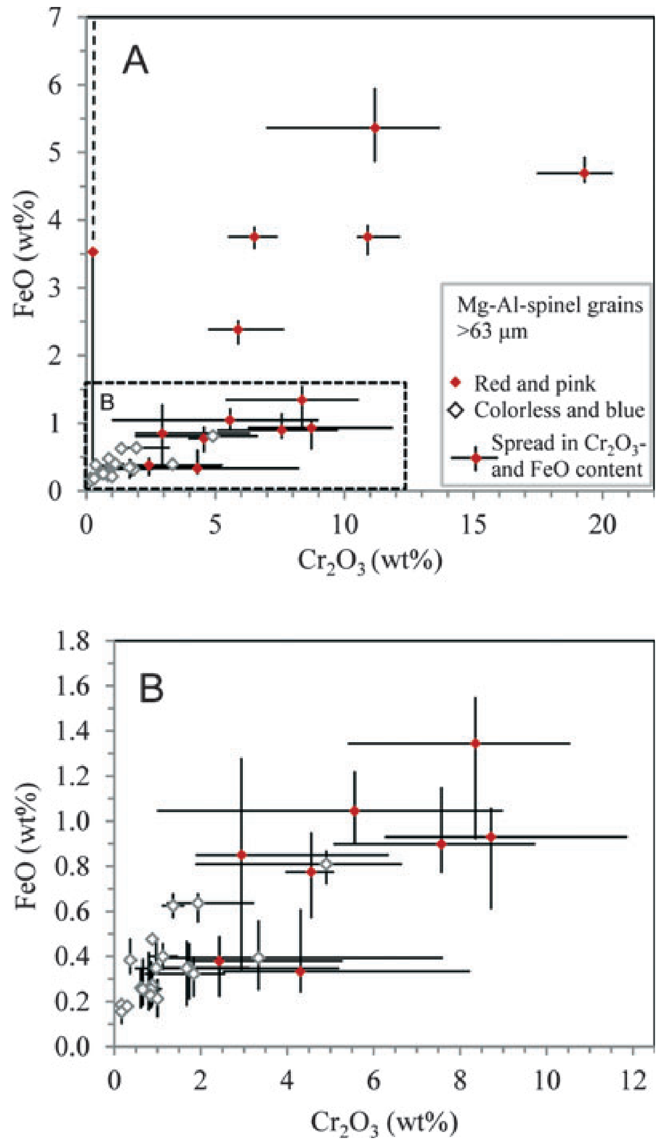

Fig. 4. A) The pink and red Mg-Al-spinel grains have generally a higher content of Cr and Fe than colorless grains. The plot shows wt% FeO versus wt% Cr_2O_3 for the separate grains >63 μm, according to observed color (red and pink, colorless and blue). The spot indicates the mean content whereas the vertical and horizontal lines show the spread in content measured within the grain (see Table 2). The vertical line of grain 2:15 continues above the maximum FeO value of the plot. B) Enlargement of area B showing the grains with lower Cr_2O_3 and FeO contents.

the FeO content the corresponding amount is less than 2.5 wt% for grains >63 μm and less than 1.25 wt% for grains 28–63 μm (Fig. 3). High Cr_2O_3 and FeO typically correlate with red or pink colors of the grains, whereas colorless and blue grains are mostly low in these oxides (Fig. 4). Generally, the higher the Cr_2O_3, the higher is the FeO content. Ti and V occur in minor amounts; TiO_2 up to 1.0 wt%, V_2O_3 up to 0.8 wt%, but for many grains the concentrations of these elements lie below or close to the detection limits (approximately 0.2–0.3 wt%).

Backscattered electron (BSE) images of polished grains show that most grains in the >63 μm fraction, 25 of 34 (74%), are heterogeneous in composition (Table 2), i.e., the compositional variation within the grain is larger than 2σ standard deviation. Among the 28–63 μm grains 30 of 49, i.e., 61% are heterogeneous (Table 3). Comparisons of spot analyses in heterogeneous >63 μm grains, with BSE-images, show that the lighter areas mostly contain higher amounts of Cr. The Cr-variation shows different patterns, which may be more or less prominent (Fig. 5a-f). Some grains show a patchy pattern (Fig. 5a-b), one grain has a pattern that looks similar to the patchy grains, but is

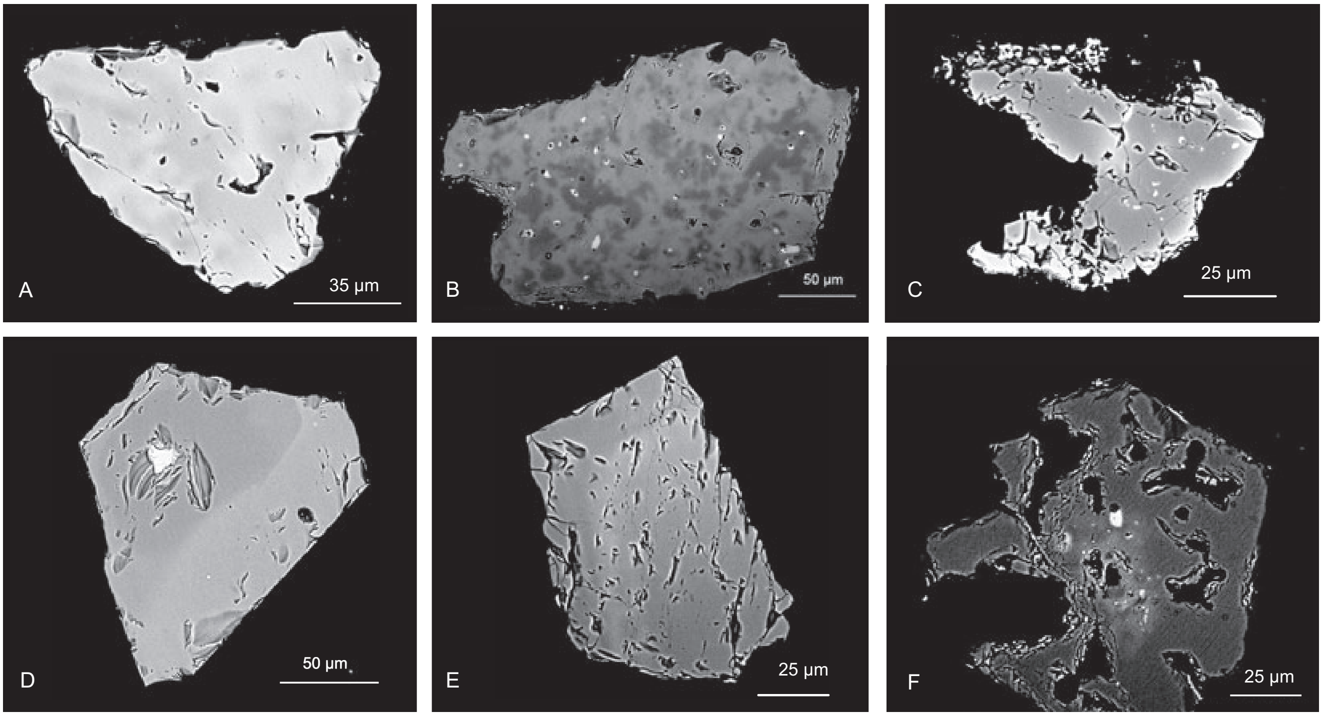

Fig. 5. Spinel grains with Cr-variation >2σ standard deviations of the oxide wt% are considered heterogeneous; SEM-BSE images visualize the variations where areas with lower amounts of heavy elements are darker and vice versa. For grain identification, see Table 2. A) Patchy heterogeneity with smooth transitions (grain 2:1). B) Patchy heterogeneity with more distinct transitions, this grain also has rounded inclusions (the bright spots) containing Si, Ca, Mg and Ti which is likely diopside (grain 3:3). C) This grain is Cr-homogeneous, but the Fe-content increases toward grain boundaries and cracks, with small rounded bright inclusions, containing Ca and Ti in equal amounts, presumably perovskite (Grain 2:5). D) Grain with two distinct zones of different Cr-content, the left area, which may be a core due to its rounded appearance, is less Cr-rich than the right, the grain also has a triangular, bright, Si-, Ca-, and Mg-dominated inclusion, most likely diopside (grain 2:6). E) Chevron-zoned grain with alternating bands of higher/lower Cr-content (grain 2:9) and F) Cr-poor grain with a patchy center of higher Cr-content and small rounded inclusions of varying compositions; Si-, Ca-, and Mg-containing are possibly diopside, Fe-rich with some Ni but no S which may be Fe-Ni metal, and a Ca-Si containing unidentified mineral (grain 3:17).

actually homogeneous in Cr-content and is instead heterogeneous in FeO (Fig. 5c). Other grains show a Cr-pattern with distinct areas of varying Cr-content (Fig. 5d), which may be similar to chevron zonation (Fig. 5e). One grain has a diffuse Cr-rich core and otherwise homogeneous Cr-content (Fig. 5f). A few grains have gradational Cr-enrichments. The within-grain variations are often large; 5 wt% difference between minimum and maximum Cr_2O_3 content is not uncommon (Fig. 4 and Tables 2 and 3). Homogeneous grains (with a Cr-variation lower than the 2σ standard deviation of the wt%) are colorless or blue and have a low Cr_2O_3 content.

Inclusions are relatively common (Fig. 5a–f), and some in the >63 μm grain fraction were analyzed semiquantitatively. Most inclusions have high amounts of Ca, several are rich in Si, Ca, and Mg, some with enrichments of Ti. These may be pyroxene, some are perhaps diopside. Some are rich in Ca and Si with enrichment also in Al. Others are rich in Ca and Ti and are likely perovskite. A few are very rich in Ca and show minor excesses in Mg and Zn. Some inclusions contain Fe and Ni and may be Fe-Ni metal (the Fe-Ni ratio is 7–10:1).

Opaque Cr-Spinel Grains in Acfer 331

In the two >63 μm residues not one single opaque Cr-spinel grain was found, whereas the one 28–63 μm residue searched for grains contained a total of 260 Cr-spinel grains, i.e., 65 grains per gram meteorite. The grains are dark colored to black and opaque, or weakly translucent. Most are angular (Fig. 6a) and octahedron grains are common (Fig. 6b). Chemical analyses of 25 randomly selected grains showed that they are Cr- and Fe-rich; Cr_2O_3 44.4–61.7 wt%, FeO 21.2–31.3 wt%, and have lower amounts of Mg and Al; MgO 2.4–9.1 wt% and Al_2O_3 0.5–22.6 wt% (Fig. 7, Table 4). Other elements measured are TiO_2, 0.4–1.6 wt%, V_2O_3 up to 1.0 wt%, SiO_2 up to 0.5 wt%, and in some grains there is MnO up to 1 wt%. Most grains, 22 of 25, are heterogeneous, a few grains show clear zoning patterns (Fig. 6c). The within-grain variation is generally 1–5 wt%

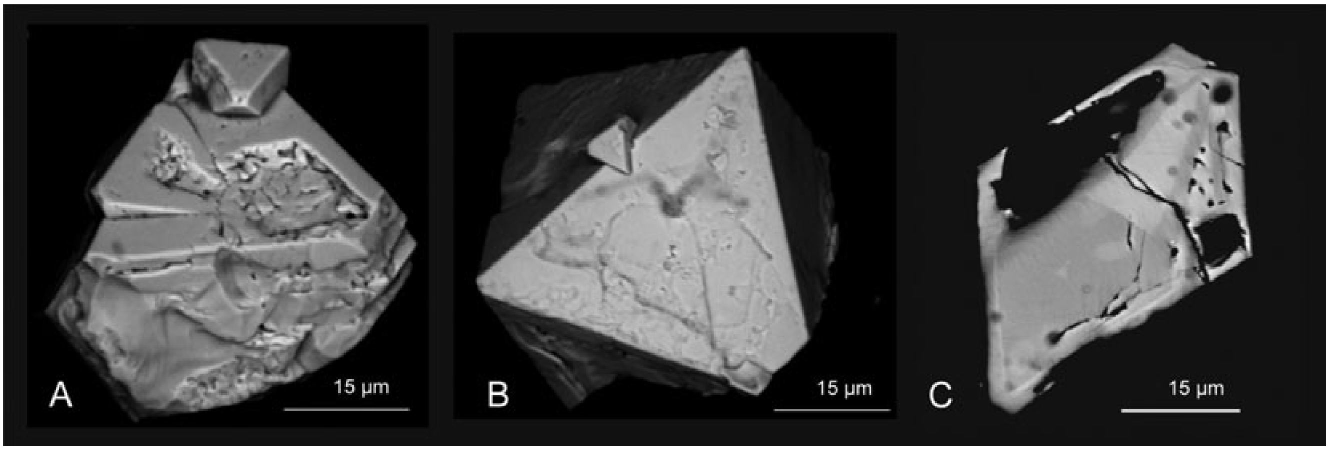

Fig. 6. The Cr-rich spinel grains are mostly (A) angular, but (B) euhedral, octahedron grains are also common. Grains are imaged with SEM. C) Most Cr-rich spinel grains are heterogeneous in composition, and some show distinct zoning with SEM-BSE-imaging (grain 7, Table 4).

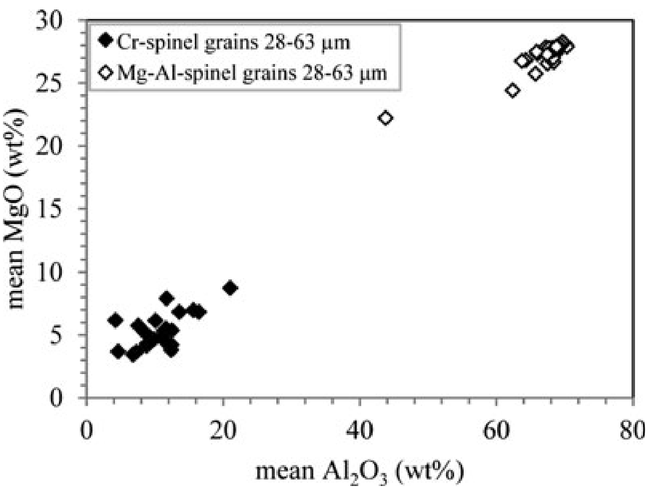

Fig. 7. The Cr-rich spinel grains are distinctly separated from the Mg-Al-spinel grains considering the major element content. The mean of the wt% of MgO and Al_2O_3 content of all grains analyzed in the 28–63 μm fraction are presented in this plot.

but may be higher reaching around 10 wt% for Cr_2O_3 (Table 4). The FeO contents vary generally with a few wt%. The TiO_2 contents show variations of 0.1–1.1 wt % within the grains and the V_2O_3 contents vary with 0.1–0.4 wt%. Almost all grains have narrow ranges for maximum TiO_2 and V_2O_3 concentrations, 0.6–1.6 wt% and 0.5–1.0 wt%, respectively. Inclusions found in the Cr-spinel grains consist of Fe-Ni sulfide, olivine, and other unidentified phases.

Chromite in Fossil and Recent L-Chondrites

The nine fossil meteorites contain variable concentrations of chromite grains >63 μm, spanning from 77 to 3764 grains per gram meteorite (Table 5). Three meteorites contain between 1542 and 3764 grains per gram meteorite. Two meteorites are low in chromite, between 77 and 158 grains per gram, and four meteorites contain intermediate concentrations, 366–691 grains per gram. Ghubara L4-6 meteorite is a breccia and two different samples were examined individually; in one 5.16 g matrix sample 42 chromite grains were found, and in one 1.69 g inclusion (L4 type) 14 chromite grains were found. Thus, both Ghubara samples gave 8 grains per gram. The Lundsgard L6 meteorite is rich in chromite >63 μm, with approximately 1100 grains per gram.

DISCUSSION

Tracing the Ancient Flux of CM Micrometeorites

The most encouraging result in our study is the unexpectedly high abundance of spinel grains, 130 Mg-Al- and 65 Cr-spinel grains per gram meteorite, in the 28–63 μm fraction of Acfer 331. From this it appears that it would be realistic to recover relict micrometeoritic CM spinel grains from ancient sediments; however, there are many potential caveats to be considered. To be a good tracer, a mineral must be durable in the wet and oxidizing terrestrial environment, occur in enough quantities in the larger size fractions of a meteorite, and have some specific features that can be used for identification. Undoubtedly, spinel is a highly durable mineral, which is shown by its acid resistance and high hardness, and also its occurrence in, for example, terrestrial placer deposits together with other durable minerals such as ilmenite, rutile, and zircon (Lumpkin 2001; Pownceby 2005; Pownceby and Bourne 2006).

Table 4. Chemical composition (wt%) of the opaque Cr-spinel grains sizes 28–63 μm.

			MgO		Al_2O_3		Cr_2O_3		FeO		TiO_2		V_2O_3		SiO_2
Grain	Cr-zoning	n*	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Max
1	het	4	5.7	6.5	7.8	11.2	52.7	56.9	24.5	25.0	0.7	0.8	0.5	0.8	0.4
2	het	4	3.4	3.5	6.5	7.2	55.7	57.5	28.6	30.3	0.9	1.2	0.5	0.9	0.3
3	het	4	4.5	5.1	9.9	14.4	48.5	52.8	24.4	27.3	0.7	0.9	0.6	0.7	0.4
4	het	5	5.6	7.6	6.3	16.3	50.0	59.1	25.2	27.0	0.8	1.3	0.6	0.9	0.3
5	het	5	4.6	5.4	10.9	11.5	52.5	53.7	26.8	27.2	0.6	1.0	0.5	0.9	0.3
6	het	3	3.5	4.1	12.0	12.8	47.3	49.3	29.5	31.3	0.9	1.0	0.5	0.9	0.2
7	het	4	3.2	7.1	0.6	12.0	51.6	59.4	24.8	29.5	1.0	1.5	0.6	1.0	0.4
8	het	3	5.2	5.7	12.1	13.0	49.0	50.2	26.4	27.3	1.2	1.3	0.7	0.9	0.4
9	het	4	7.5	8.3	11.2	12.6	52.3	53.7	21.2	22.9	0.6	0.7	0.4	0.8	0.3
10	het	4	5.3	5.8	10.3	13.3	48.9	51.9	25.8	28.2	0.5	1.4	0.5	0.8	0.5
11	het	4	6.5	7.4	15.8	17.6	45.6	47.3	25.8	27.8	1.1	1.4	0.3	0.6	0.3
12	het	4[a]	2.4	5.6	0.5	12.8	50.5	60.1	25.1	28.9	0.4	1.3	0.6	0.8	0.3
13	het	6[a]	3.7	4.4	11.8	12.9	46.9	47.9	28.4	29.5	0.9	1.1	0.5	0.7	0.3
14	het	4	3.7	4.7	8.3	9.5	53.3	56.2	26.4	28.8	0.4	1.0	0.6	0.7	0.3
15	hom	5	4.7	5.3	10.6	11.5	51.2	51.6	26.8	27.4	1.2	1.5	0.6	0.9	0.3
16	het	4	6.0	7.8	14.2	17.2	44.6	47.9	24.0	26.1	1.0	1.4	0.5	0.9	0.4
17	het	5	4.0	4.9	10.9	11.7	50.5	52.0	26.6	28.1	0.7	1.0	0.5	0.9	0.4
18	het	4	8.3	9.1	19.3	22.6	44.4	46.5	22.8	24.2	0.5	0.6	b.d	0.5	0.3
19	het	3	5.7	6.6	3.1	5.1	60.5	61.7	23.2	24.4	0.4	0.8	b.d	0.6	b.d
20	het	4	4.4	5.1	9.1	9.3	53.1	55.9	27.0	27.5	0.7	0.8	0.4	0.6	0.4
21	het	6	4.6	5.7	4.2	11.3	53.9	58.5	25.9	28.2	0.5	1.6	0.5	0.9	0.3
22	hom	3	4.1	4.2	8.5	9.0	52.9	53.6	27.7	28.6	1.1	1.3	0.5	0.7	0.4
23	hom	4	3.4	4.0	7.0	7.5	53.7	54.5	28.9	29.9	0.8	1.2	0.6	0.8	0.3
24	het	3	4.2	5.4	9.7	10.0	52.0	53.3	27.0	27.5	0.6	0.9	0.4	0.5	0.5
25	het	3	3.9	6.3	6.3	14.3	49.6	57.2	26.0	27.2	0.8	1.0	0.7	1.0	0.4

het = heterogeneous Cr-content; hom = homogeneous Cr-content; n* = number of analyses.
Analyses shown have sums 95–102 wt%. See Table 2 for further information.
[a]Analyses with sums 94–102 wt%.

Table 5. Number of chromite grains >63 μm, in samples of fossil and recent L-chondrites.

Meteorite	Sample weight (g)	No. of grains (#)	#/g
Österplana 063 (Gla3/001)	0.089	335	3764
Österplana 064 (Gla3/002)	0.62	48	77
Österplana 060 (Gla2/004)	0.46	318	691
Österplana 062 (Gla2/006)	0.28	183	654
Österplana 054 (Gla1/002)	0.28	445	1589
Österplana 055 (Gla1/003)	0.093	34	366
Österplana 056 (Gla1/004)	0.72	1110	1542
Österplana 051 (God 002)	0.21	109	519
Österplana 049 (Tre 004)	0.64	101	158
Ghubara L5 matrix	5.16	42	8
Ghubara L4 inclusion	1.69	14	8
Lundsgård L6	0.55	607	1104

Most other minerals occurring in a CM meteorite, such as olivine, pyroxene, and sulfides are much more susceptible to weathering. A few other minerals occurring in meteorites, such as corundum, are also durable but very rare. Our study of the Acfer 331 sample represents the first complete quantification of acid-insoluble Mg-Al- and Cr-spinel grains >28 μm in a CM meteorite. In previous studies, such as by Simon et al. (1994), the spinel grains are chosen by, e.g., color for a certain purpose and thus show only a fraction of the spinel varieties. The ratios between the many different types of spinels observed in Acfer 331 will be helpful in determining whether a spinel assemblage from a fossil meteorite indicates a CM origin.

The size aspect is important because in our reconstructions of the flux of Ordovician, L-chondritic micrometeorites, using as tracer chromite grains in condensed sediments, the ratio of extraterrestrial/terrestrial mineral grains increases with increasing grain size studied (Schmitz et al. 2003; Schmitz and Häggström 2006; Cronholm and Schmitz 2010). Most condensed sediments, like recent deep-sea sediments forming at 1–2 mm per thousand years, are deposited at very large distances from land, and only the most fine-grained, clay-sized particles, i.e., <2 μm, reach these sites by wind or current transport. This means that the "haystack" of terrestrial grains that dilutes the extraterrestrial fraction becomes smaller, the larger the size fraction that is studied. On the other hand, because the larger extraterrestrial grains fall more rarely on Earth, the sample size required to yield such grains has to be larger.

When assessing the feasibility of recovering micrometeoritic CM spinel from sediments we here try to compare the CM spinel abundance with that of chromite in L-chondrites; however, quantifying chromite >63 μm in L-chondrites is not an entirely straightforward task. Based on the quantification attempts here, however, it appears that on an order-of-magnitude scale spinel grains in CM meteorites are about as abundant in the 28–63 μm fraction as "sea-floor durable" chromite in the >63 μm fraction in ordinary chondrites. The nine fossil, and the two recent, L-chondrites analyzed for chromite here contained about 100–1600 chromite grains >63 μm per gram meteorite, but two outlier values of 8 and 3760 grains per gram were also observed. Chromite in ordinary chondrites is chemically very durable, but can be physically quite fragile, particularly after HCl–HF treatment. In the chondrites the mineral typically occurs in aggregates with complex, "straggly" shapes, and anhedral crystal outlines (see e.g., fig. 4 in Bridges et al. 2007). Only some of these aggregates and crystals would break down mechanically in a way that a >63 μm core is left on the sea floor. Both the Mg-Al- and Cr-spinel grains of CM meteorites appear much more physically robust; they often have euhedral crystal outlines and would have a great probability to survive on the sea floor. The amount of chromite in ordinary chondrites is typically given as 0.25% weight percent based on counts in polished sections (Keil 1962), but this gives no information on the number of potentially durable grains >63 μm. The amount of large chromite grains in ordinary chondrites varies significantly, with the higher petrographic types containing higher amounts (Bridges et al. 2007). The typical range over one order of magnitude in chromite content (100–1600 grains per gram) for the L-chondrites studied by us probably reflects both the span from equilibrated L4 to L6 chondrites and variation within petrographic types (Table 5). Bridges et al. (2007) note that the content of chromite grains in thin sections of recent L-chondrites even of the same petrographic type shows large variations. For example, three L4 chondrites studied show up to a factor of 22 difference in the amount of chromite grains >5 μm. The micrometeorite flux to Earth will be a mixture of all petrographic types of chondrites, and considering that the more equilibrated types may represent a larger fraction of the total flux, we estimate that the average chromite content of L-chondritic micrometeorites lies somewhere in the middle part of the range identified by us. Admittedly, there are many uncertainties, but our best estimate is that the amount of sea-floor durable >63 μm chromite grains in L-chondritic micrometeorites on average lies at about 500–1000 grains per gram.

When estimating the feasibility of recovering from sediments large spinel grains representing different types of meteorites, one needs to consider also the total flux to the upper atmosphere of the respective micrometeorite type, as well as the fraction of the flux that reaches the sea floor in an unmelted state. The latter relates to many factors, such as velocity, entrance angle, size, and hardness of the micrometeorite. The soft carbonaceous micrometeorites will break up more easily, but the large spinel grains may not be affected. In the large collections of micrometeorites from Antarctic ice unmelted carbonaceous micrometeorites are as abundant, or even more abundant than unmelted ordinary chondritic micrometeorites (e.g., Engrand and Maurette 1998). This fact, together with the quantification of spinel abundances here, indicates that in a weathered assemblage of present-day micrometeorites there may be, on the order of magnitude, about as many 28–63 μm sized spinel grains from carbonaceous meteorites as there will be >63 μm sized chromite grains from ordinary chondrites. Some support for this comes from studies of spinel occurrences in polished mounts of 250 micrometeorites from Antarctic and Greenland ice (Michel-Levy and Bourot-Denise 1992). Probably only a small fraction of unmelted micrometeorites, both carbonaceous and ordinary chondritic, that fall on a sea floor contain a large spinel grain (>28 or >63 μm) that will remain in the sediment after the main mass of the micrometeorite has weathered away. The following calculation gives a rough estimate of how rare such CM micrometeorites may be. There are approximately 135 Mg-Al- and 65 Cr-spinel grains >28 μm per gram CM meteorite. This equals to 1 Mg-Al-Cr-spinel grain >28 μm per 5×10^{-3} g CM meteorite. A micrometeorite of cubic shape with a diameter of 200 μm, a size that is common among micrometeorites (Love and Brownlee 1993), and with the bulk density of 2.2 g cm^{-3} (mean of CM meteorites; Macke et al. 2011; for comparison see e.g., Flynn et al. 1999, McCausland et al. 2011), weighs 1.76×10^{-5} g. This means that 1 in 284 CM micrometeorites would yield a spinel grain >28 μm.

Identifying a CM Spinel Grain

In an acid-extracted assemblage of heavy minerals from a large sediment sample the Mg-Al-spinel grains would be readily identified under a binocular microscope based on their transparency, high refractive index, and color. The blue, pink, and red spinel grains, which make up a significant fraction of Mg-Al-spinel grains in Acfer 331, would be easy to spot. Also the opaque Cr-spinel grains of the CM meteorites have a characteristic appearance, commonly being angular, and with a significant fraction being subhedral-euhedral showing its octahedron shape. SEM-BSE imaging of the grains further shows that they commonly are heterogeneous. These are prominent features that can aid when searching for tracer minerals. Generally, the element composition of most CM spinel grains will not be a good tool of identification, at least not for a single grain; instead the full chemical, mineralogical, and sedimentological context must be considered in the identification process.

In a sediment that was deposited at sufficient distance from land to prevent admixture of common terrestrial, nonauthigenic minerals >28 μm, and that is found to contain a mixture of Mg-Al- and Cr-spinel grains with features and in proportions similar to those described for Acfer 331, it is very likely that the spinel grains originate from decomposed carbonaceous chondritic matter. The absence in the assemblage of other durable, heavy minerals common in most terrestrial rocks would alone indicate a meteoritic origin of the spinel grains. A distinctive feature of a major fraction of the spinel grains of Acfer 331, similarly to the spinel grains of Murchison studied by Simon et al. (1994), is that they have inclusions. Inclusions such as olivine and pyroxene can be instrumental in assessing an extraterrestrial origin for a spinel. Simon et al. (1994) made a detailed study of the inclusions in their large, pink to red and Cr-rich Mg-Al-spinel grains. The majority of the spinel grains contained small anhedral grains of aluminum diopside with 12–24 wt% Al_2O_3 and up to 3.7 wt% TiO_2. The MgO, Al_2O_3, and TiO_2 contents were within the ranges for low-Ti pyroxene from refractory inclusions. Aluminous diopside inclusions were found by Simon et al. (1994) in almost every of their grains with a patchy, core-rim or chevron type zoning, but were absent in the gradationally zoned and homogeneous grains. Olivine, mostly pure forsterite ($Fo_{>99}$) or with $Fo_{95–96}$, was also observed as a common type of inclusion in the spinel grains from Murchison CM meteorite. In addition, glass or Fe-Ni inclusions were found, both with a high discriminative value when assessing whether a spinel is extraterrestrial.

Whereas chromite from ordinary chondrites can readily be distinguished from terrestrial spinel grains based on a very specific, narrow range of elemental composition (Schmitz et al. 2001; Schmitz and Häggström 2006), the CM spinel show a wide compositional range that to a major extent overlaps with the composition of terrestrial spinel. Terrestrial spinel can have a variety of compositions, and occur on Earth in the entire compositional spectrum from chromite to pure Mg-Al-spinel (see Barnes and Roeder 2001). Still, the full spectrum of elemental compositional information about large CM spinel grains acquired here can be diagnostic at least for a tentative assessment of the origin of sediment-dispersed spinel grains. Considering the Cr-content of all the spinel grains in Acfer 331 we find two chemically distinct groups of spinel, i.e., transparent Mg-Al-spinel grains and opaque Cr-spinel grains (Fig. 7).

In the samples most Mg-Al-spinel grains are heterogeneous foremost in Cr. The more Cr-rich of those grains are more commonly heterogeneous (Fig. 4). Heterogeneity of Cr content within spinel grains is, however, common also for terrestrial spinel and can be of both magmatic and metamorphic origin. For instance oscillatory zoning of Cr-spinel considered of magmatic origin studied by, e.g., Allan et al. (1988), grains with a core of either higher or lower Cr-content than the mantling (e.g., Morten et al. 1989), metamorphic rims on chromite, such as rims of green spinel (e.g., Evans and Frost 1975) or enrichment of Cr and Fe^{2+} in rims of chromian spinel due to hydrothermal alteration (Kimball 1990). The opaque Cr-spinel grains have low amounts of Mg and Al, and thus have a composition close to chromite. In fact, in the opaque Cr-rich grains the relatively stable and narrow ranges for maximum TiO_2 and V_2O_3 concentrations, 0.6–1.6 wt% and 0.5–1.0 wt%, respectively, could be highly diagnostic. Euhedral, heterogeneous, opaque Cr-spinel grains with maximum TiO_2 and V_2O_3 in the ranges found here would with a high probability have a carbonaceous chondritic origin, at least if the grains are not associated with other common Cr-spinel showing the wide range of compositions characteristic of terrestrial spinel (see Barnes and Roeder 2001).

Probably the best way of assessing whether an individual spinel grain from the ancient sea floor is extraterrestrial would be to study the O or Cr isotopic composition of the grain (e.g., Clayton and Mayeda 1984; Virag et al. 1991; Simon et al. 1994). The pink to red, and 60–325 μm large, Cr-rich Mg-Al-spinel grains in the study of Simon et al. (1994) have $\delta^{18}O$ close to terrestrial values. From twelve such grains analyzed, Simon et al. (1994) obtained a $\delta^{18}O$ mean of 1.9 ± 2.4‰. On the other hand, oxygen isotopic analyses by Virag et al. (1991) of nine pure Mg-Al-spinel grains in the size 10–30 μm gave a mean $\delta^{18}O$ value of −50‰. The small and pure ^{16}O-rich spinel grains are interpreted as originating from refractory inclusions, whereas the large Cr-rich grains have another origin, perhaps from chondrules (Simon et al. 1994, 2000). In our two size subsets of Acfer 331 Mg-Al-spinel grains, the Cr-rich pink to red spinel grains are significantly less abundant in the smaller size fraction, 28–63 μm. To what extent the oxygen isotopic composition of the CM spinel grains correlates with size or chemistry cannot be deduced with confidence from the literature, however, among the nine small (10–30 µm) spinel grains analyzed by Virag et al. (1991) one grain has a positive $\delta^{18}O$ value; this grain also has higher Cr and Fe than eight ^{16}O-rich grains (see Simon et al. 1994). It is likely that a major fraction of the more pure Mg-Al-spinel grains in the smaller size subset in our study originate from refractory inclusions, and hence have highly distinctive $\delta^{18}O$ signatures, making identification of a sediment-dispersed CM spinel relatively straightforward. In the literature, we have found only one oxygen isotopic analysis of a chromite from Murchison, and a $\delta^{18}O$ value of −22‰ is given (McKeegan 1987; Simon et al. 1994). Further studies of the oxygen isotopic variations, including also $\delta^{17}O$, in CM spinel grains and in particular Cr-spinel grains, are warranted, and the results would further help in the process of identifying the origin of spinel group minerals recovered from sediments.

Also Cr isotopic analyses of sediment-dispersed spinel grains may be instrumental in determining their origin. Simon et al. (1994) show that spinel grains from Murchison have carbonaceous chondritic Cr isotopic composition, and there is no anomalous Cr present as had been reported by others previously.

CONCLUSIONS

Quantifications of the amounts of large (>28 µm) spinel grains and the detailed proportions between different types of spinel group minerals in different meteorite groups will provide an important tool for classifying fossil meteorites and micrometeorites, in which all other common minerals have weathered away. Based on studies of 470 million year old fossil L-chondrites we have shown that dissolution of recent L-chondrites in strong hydrofluoric acid gives relict spinel assemblages very similar to the spinel assemblages in the sea-floor weathered fossil meteorites.

In CM meteorite Acfer 331 leached in strong hydrofluoric acid we find two chemically distinct groups of large (>28 µm) spinel grains; transparent Mg-Al-spinel and opaque Cr-spinel. One gram of Acfer 331 contains 4–5 Mg-Al-spinel grains >63 µm, 130 Mg-Al-spinel grains 28–63 µm, and 65 opaque Cr-spinel grains 28–63 µm. The Mg-Al-spinel grains can be further divided into two groups, the Cr-rich, commonly pink or red, and the Cr-poor, colorless or blue, grains. Both the transparent Mg-Al- and the opaque Cr-spinel grains are generally heterogeneous in composition within the grains, and there is also a large variability in Cr- and Fe-content between different grains.

The abundance of spinel grains in the 28–63 µm fraction in Acfer 331 lies at the same order-of-magnitude as the abundance of chromite grains >63 µm in ordinary chondrites. Relict such chromite grains have previously been recovered from condensed sediments from the Paleogene and Ordovician. Assuming there was a substantial fraction of CM matter in the ancient micrometeorite flux, like the situation today, it appears feasible to recover also CM spinel grains from acid-residues of ancient sediment, but the 28–63 µm fraction must be used. Ordinary chondritic chromite can readily be identified by a rather unique and narrow range in elemental composition. CM spinel grains, on the other hand, have a complex range of elemental compositions, overlapping to a great extent with the compositions of terrestrial spinel. Most CM Mg-Al-spinel grains, 28–63 µm large, however, will probably have distinctive oxygen isotopic compositions, which will clearly distinguish them from terrestrial spinel grains. The CM Cr-spinel grains can be identified by their commonly euhedral, heterogeneous appearance, narrow ranges of maximum Ti and V contents, and also by their oxygen isotopic composition. To identify a CM spinel from a sediment acid-residue ideally the full chemical, mineralogical, and sedimentological context should be considered.

The data gathered here can be helpful also in searching for spinel grains from relict matter from the asteroid of carbonaceous chondritic (possibly CM) composition that impacted Earth at the Cretaceous-Paleogene boundary.

Acknowledgments—During the progress of this study, we have depended on the skillful and inspiring persons in and around the research group and the Department of Geology, Lund University. We want to thank A. Cronholm, M. M. Meier, S. Frey, P. R. Heck, A. Lindh, C. Alwmark, and A. Lindskog for their irreplaceable contributions and also U. Hålenius for valuable discussions. We thank I. M. Steele for help with EPMA analyses in Chicago. Comments on the submitted manuscript by C. Floss, F. T. Kyte, S. B. Simon, and an anonymous referee were very helpful. The study was supported by grants to B. Schmitz from the Swedish Research Council and the European Research Council, and was performed within the framework of the LUCCI project funded by the Swedish Research Council.

Editorial Handling—Dr. Christine Floss

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