

# LUND UNIVERSITY

### Relict silicate inclusions in extraterrestrial chromite and their use in the classification of fossil chondritic material

Alwmark, Carl; Schmitz, Birger

Published in: Geochimica et Cosmochimica Acta

DOI: 10.1016/j.gca.2008.12.006

2009

Link to publication

Citation for published version (APA):

Alwmark, C., & Schmitz, B. (2009). Relict silicate inclusions in extraterrestrial chromite and their use in the classification of fossil chondritic material. Geochimica et Cosmochimica Acta, 73(5), 1472-1486. https://doi.org/10.1016/j.gca.2008.12.006

Total number of authors: 2

#### **General rights**

Unless other specific re-use rights are stated the following general rights apply:

- Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the
- legal requirements associated with these rights.

· Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

You may not further distribute the material or use it for any profit-making activity or commercial gain
 You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: https://creativecommons.org/licenses/

#### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

**PO Box 117** 221 00 Lund +46 46-222 00 00

Paper IV



Available online at www.sciencedirect.com



Geochimica et Cosmochimica Acta 73 (2009) 1472-1486

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

### Relict silicate inclusions in extraterrestrial chromite and their use in the classification of fossil chondritic material

### Carl Alwmark\*, Birger Schmitz

Department of Geology, University of Lund, Sölvegatan 12, SE-22362 Lund, Sweden

Received 12 September 2008; accepted in revised form 7 December 2008; available online 24 December 2008

#### Abstract

Chromite is the only common meteoritic mineral surviving long-term exposure on Earth, however, the present study of relict chromite from numerous Ordovician (470 Ma) fossil meteorites and micrometeorites from Sweden, reveals that when encapsulated in chromite, other minerals can survive for hundreds of millions of years maintaining their primary composition. The most common minerals identified, in the form of small ( $\leq 1-10 \mu m$ ) anhedral inclusions, are olivine and pyroxene. In addition, sporadic merrillite and plagioclase were found.

Analyses of recent meteorites, holding both inclusions in chromite and corresponding matrix minerals, show that for olivine and pyroxene inclusions, sub-solidus re-equilibration between inclusion and host chromite during entrapment has led to an increase in chromium in the former. In the case of olivine, the re-equilibration has also affected the fayalite (Fa) content, lowering it with an average of 14% in inclusions. For Ca-poor pyroxene the ferrosilite (Fs) content is more or less identical in inclusions and matrix. By these studies an analogue to the commonly applied classification system for ordinary chondritic matrix, based on Fa in olivine and Fs in Ca-poor pyroxene, can be established also for inclusions in chromite. All olivine and Ca-poor pyroxene inclusions (>1.5  $\mu$ m) in chromite from the Ordovician fossil chondritic material plot within the Lchondrite field, which is in accordance with previous classifications. The concordance in classification together with the fact that inclusions are relatively common makes them an accurate and useful tool in the classification of extraterrestrial material that lacks matrix silicates, such as fossil meteorites and sediment-dispersed chromite grains originating primarily from decomposed micrometeorites but also from larger impacts.

© 2008 Elsevier Ltd. All rights reserved.

#### 1. INTRODUCTION

This is the first report on silicate inclusions in chromite from recent chondrites as well as in  $\sim$ 470 Ma old fossil meteorites (Schmitz et al., 2001) and coeval sediment-dispersed chondritic chromite grains (Schmitz et al., 2003; Schmitz and Häggström, 2006). We demonstrate how these inclusions can be used for assessing the meteorite group from which the host chromite grain originates.

The majority of studies on fossil meteoritic material focus on the Middle and Late Ordovician; a period where the meteorite influx to Earth was enhanced by up to two orders of magnitude (Schmitz et al., 2001). At ~470 Ma the disruption of the L-chondrite parent body occurred (Anders, 1964; Korochantseva et al., 2007), and the high abundance of fossil meteoritic material in sediments from this time has been related to this event, based partly on the L-chondritic composition of relict chromite grains (Schmitz et al., 2001, 2003; Schmitz and Häggström, 2006). Because meteoritic material on the Earth surface is rapidly altered or weathered away, with the exception of chromite (FeCr<sub>2</sub>O<sub>4</sub>), constituting 0.05–0.5 wt% of recent chondrites (Keil, 1962), the classification of the fossil chondritic material in these studies has been based mainly on elemental and O-isotopic composition of chromite (e.g., Schmitz et al., 2001; Alwmark and Schmitz, 2007; Greenwood et al., 2007). Both these

<sup>\*</sup> Corresponding author.

E-mail address: carl.alwmark@geol.lu.se (C. Alwmark).

<sup>0016-7037/\$ -</sup> see front matter  $\circledast$  2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.gca.2008.12.006

methods have limitations; the element composition of chromite tends to overlap between respective chondrite groups, making classification of single meteorites uncertain, and Oisotopic measurements generally require large samples of chromite grains, although *in situ* oxygen isotope measurements on individual grains using secondary ion mass spectrometry (SIMS) are under development.

Here we show that, when encapsulated in relict chromite, other minerals, e.g., olivine and pyroxene, can survive for hundreds of millions of years maintaining their primary composition. Previous work on inclusions in spinel-group minerals of extraterrestrial origin is sparse, only comprising a few studies of silicate inclusions in chromite from SNC meteorites (e.g., Goodrich and Harvey, 2002) and one study dealing with Al-rich diopside and partially enclosed olivine in Al-rich spinel from the carbonaceous chondrite Murchison (CM2; Simon et al., 1994). However, numerous studies on inclusions in terrestrial chromite have shown that the composition of olivine and pyroxene inclusions in chromite differ systematically from the composition of the olivine and pyroxene of the matrix, with a general trend of higher Mg, Cr and sometimes Ni in the former (e.g., Talkington et al., 1984; Lorand and Ceuleneer, 1989; McElduff and Stumpfl, 1991; Melcher et al., 1997). Studying recent chondrites where both matrix and chromite-enclosed olivine and pyroxene are present, it is possible to determine whether compositional differences exist for extraterrestrial material as well. An analogue to the well established classification system for ordinary chondrites, founded on the fact that olivine and Ca-poor pyroxene in equilibrated (type 4-6) ordinary chondrites have specific ranges of chemical composition depending on group (H, L, LL; e.g., Mason, 1963; Keil and Fredriksson, 1964; Gomes and Keil, 1980; Rubin 1990), can then be established based on the inclusions. This would create an independent tool in the classification of fossil chondrites and sediment-dispersed extraterrestrial chromite grains originating from decomposed micrometeorites (Heck et al., 2008) and chondritic fragments related to impact events (Alwmark and Schmitz, 2007), when no matrix silicates are preserved or present.

#### 2. MATERIALS AND METHODS

In this study we have examined inclusions in coarse chromite grains from 12 classified recently fallen equilibrated (type 4-6) ordinary chondrites of the different groups (H, L and LL), seven fossil meteorites from the Thorsberg quarry in southern Sweden (the Österplana meteorites), the Brunflo fossil meteorite from the Gärde quarry in central Sweden and in sediment-dispersed extraterrestrial (ordinary chondritic) chromite (EC) grains (63-355 µm) from four different limestone samples from the Thorsberg and Gullhögen quarries in southern Sweden. The samples are listed in Table 1. The Thorsberg quarry meteorites have previously been classified as L chondrites, based on their chromite element composition, chondrule sizes and in one case oxygen isotopic composition (Schmitz et al., 2001; Bridges et al., 2007; Greenwood et al., 2007). The Brunflo meteorite has formerly been assigned to the H-chondrite group (Thorslund et al., 1984), but a recent study by Alwmark and Schmitz (2008) shows that it belongs to the L group, founded, for example, on mean chondrule size. The sediment-dispersed EC grains have been interpreted as originating from mainly L-chondritic material; this is based primarily on the chromite element composition (Schmitz et al., 2003; Schmitz and Häggström, 2006).

Samples in the form of thin sections and polished slabs for the recent meteorites, and as separated chromite grains mounted in epoxy and polished flat, in the case of the fossil meteorites and the sediment samples, were searched for inclusions in the chromite using a scanning electron microscope (Hitachi S-3400N) with a backscatter detector. Quantitative elemental analyses of the inclusions as well as the host chromite and, in the case of recent meteorites, on matrix minerals, were carried out with an energy dispersive spectrometer (Inca X-sight from Oxford instruments) with a Si-detector linked to the scanning electron microscope. Cobalt was used for standard; the acceleration voltage was 15 kV and the beam current ca. 2 nA. The precision of the analyses was between 1% and 4% for major elements. The accuracy was controlled by repeated analyses of various reference minerals (Table 2). X-ray mapping was carried out on grains and inclusions suspected to be heterogeneous. A field emission scanning electron microscope (Jeol-JSM-6700F) was used for high resolution backscatter and secondary electron imaging of the inclusions. An estimate of the frequency of inclusions in the various samples was performed by counting the number of inclusion-bearing chromite grains in comparison to the inclusion-free. Chromite <5 µm in diameter or with an aggregate structure were excluded from the count.

# 2.1. Evaluation of analytical techniques—size becomes a factor

The majority of the samples hold inclusions with a minimum diameter large enough to be analyzed without being affected by secondary fluorescence, i.e., contamination from the host chromite. In Fig. 1 the minimum diameter of various olivine, Ca-poor pyroxene and plagioclase inclusions from the samples are plotted against their content of  $Cr_2O_3$  (wt%). It is shown that the lower size limit of inclusions, in order to attain non-contaminated data, is  $\sim$ 3 µm with the present settings. Therefore, in the tables only analyses on inclusions  $>3 \mu m$  have been included in the average composition of respective sample. Our approach is only valid if the thickness of the inclusion is greater than the penetration depth of the electron beam, in this case approximated to  $<2 \,\mu m$  based on the acceleration voltage used and average atomic number of the minerals in question. The results in Fig. 1 indicate, however, that all of the inclusions with a diameter  $>3 \,\mu m$  had thicknesses  $>2 \ \mu m$ .

In a few samples, where only chromite grains with inclusions  $<3 \mu m$  have been found inclusions in the size range  $1.5-3 \mu m$  were used for analysis, but with a correction for contamination because of secondary fluorescence. The correction was done by subtracting the Cr content together with a quantity of other contaminating elements, proportional to the Cr content of the host chromite. Due to the in-

	No. of chromite grains $(>5 \ \mu m)$	No. of chromite grains with 1 or more incl.	Frequency $(\%)^{a}$	Olivine	Ca-poor pyroxene	Ca-rich pyroxene	Merrillite	Plagioclase	Total # of inclusions	Olivine# <sup>f</sup>
Recent meteorites										
Dimmitt H4	30	5	17	12	6	3			24	
Kesen H4	17	3	18	1	4				5	
Forest City H5	25	9	24	3	9		1		10	
Estacado H6	38	9	16	3	8	4	б	1	19	0.34
Awere L4	19	σ	16	1	1	2			4	
Floyd L4	20	5	25	9	4	2			12	
Mbale L5-6	28	S	18	11	4	9	5	2	28	
Holbrook L6	42	7	17	5	2	2	5	4	18	
New Concord L6	31	5	16	4	1				5	0.69
Naryilco L/LL6	44	8	18	5	1	9			12	
Appley Bridge LL6	30	8	27	7	2			1	10	
Dhurmsala LL6	42	L	17	12	2	1	2		17	0.82
Fossil meteorites										
Österplana 003 (Ark	24	1	4	1					1	
003) <sup>b</sup>										
Österplana 009 (Ark	23	4	17			1	8		6	
ر600°										
Osterplana 030 (Bot 001) <sup>b</sup>	19	1	5				-			
Österplana 032 (Bot	17	1	9	1					1	
003) <sup>b</sup>										
Österplana 034 (Flo 001) <sup>b</sup>	15	1	7		1				1	
Österplana 036 (Sex	19	2	11	$2^{\mathrm{d}}$			3		5	
002) <sup>b</sup>	!					I			I	
Osterplana 038 (Sex	17	3	18	]c		1			7	
w-1) Brunflo	36	9	17	14		8			22	
Sediment samples										
Arkeologen 0.21 m	54	7	4					5	5	
(Gullhögen)					,					
Golvsten 0.62 m	58	Ω.	5	7	7				4	
Sextummen 2.58 m	26	1	4		1c				1	
(Thorsberg)										
Sextummen 2.73 m	21	1	5	1					1	

<sup>a</sup> Number of chromite grains with one or more inclusions of total number of chromite grains. <sup>b</sup> Synonym names. <sup>c</sup> Not plotted in Fig. 8 due to the heterogeneous composition owing to secondary alterations. <sup>d</sup> One of the inclusions not plotted in Fig. 8 due to the small size (<1.5 µm). <sup>e</sup> Not plotted in Fig. 8 due to the small size (<1.5 µm). <sup>f</sup> Mean olivine/(olivine + Ca-poor pyroxene) of the different groups (H, L, LL).

1474

C. Alwmark, B. Schmitz/Geochimica et Cosmochimica Acta 73 (2009) 1472–1486

Table 2	
The average element concentration and stand	ard deviation $(1\sigma)$ of reference standards.

	Olivine		Forsterite		Diopside		Chromite	
	Reference <sup>a</sup>	This study	Reference <sup>a</sup>	This study	Reference <sup>a</sup>	This study	Reference <sup>b</sup>	This study
No. of analyses	_	5	_	5		5	_	5
MgO	49.42	$49.22\pm0.21$	56.54	$56.16\pm0.31$	16.10	$16.01\pm0.22$	15.2	$14.99\pm0.35$
SiO <sub>2</sub>	41.25	$41.30\pm0.24$	42.73	$42.55\pm0.27$	52.70	$52.93 \pm 0.23$		_
CaO			0.01	bd	25.27	$25.11\pm0.19$		_
$Cr_2O_3$			< 0.01	bd	< 0.01	bd	60.5	$60.49 \pm 0.56$
MnO			< 0.01	bd	0.06	$0.06\pm0.09$	0.11	$0.26\pm0.09$
FeO	8.73	$8.96\pm0.14$	0.60	$0.56\pm0.07$	3.27	$3.11\pm0.04$	13.04	$13.03\pm0.31$
NiO	0.39	$0.40\pm0.20$						
$Al_2O_3$			< 0.01	bd	1.00	$1.14\pm0.06$	9.92	$10.02\pm0.17$
TiO <sub>2</sub>			0.01	bd	0.29	$0.38\pm0.04$		
Na <sub>2</sub> O			< 0.01	bd	0.17	$0.21\pm0.05$		
K <sub>2</sub> O	—	—	0.01	bd	0.02	bd	—	—
Total	99.79	$99.95\pm0.44$	99.90	$99.27\pm0.60$	98.88	$99.06\pm0.46$	98.77	$98.79\pm0.55$
0	4	4	4	4	6	6	4	4
Mg	1.800	1.79	1.980	1.98	0.891	0.88	0.74	0.73
Si	1.007	1.01	1.004	1.01	1.956	1.96		
Ca		_	_	_	1.005	0.99		
Cr		_	_	_		bd	1.56	1.56
Mn		—		_	0.002	0.00	0.00	0.01
Fe	0.180	0.18	0.012	0.01	0.101	0.10	0.35	0.35
Ni	0.008	0.01		_		_		
Al				_	0.044	0.05	0.38	0.38
Ti		_	_	_	0.008	0.01		
Na		—		_	0.012	0.01		
K	_			_	0.001	bd		
Cation sum	2.993	2.99	2.996	2.99	4.020	4.00	3.03	3.03
Fa (mol%)	9.1	$9.2\pm0.2$	0.6	$0.5\pm0.0$	_	_		
Fs (mol%)		_		_	5.2	$5.1 \pm 0.0$		_
Wo (mol%)	_	_	_	_	50.3	$50.2\pm0.5$	_	

bd, below detection limit.

<sup>a</sup> Commercial standards #1494 from Micro-analysis Consultants Ltd.

<sup>b</sup> USNM 117075 chromite reference standard, Jarosewich et al. (1980).

crease in contamination and with that the uncertainty of analysis, with decrease of inclusion size, the lower size limit for the corrections to be acceptable is here considered to be 1.5 µm, i.e., compositional data on inclusions <1.5 µm is regarded as semi-quantitative and not included in the tables. In the case of olivine and pyroxene, the consistently high Cr content in all inclusions  $>3 \mu m$ , implies that secondary fluorescence is not accountable for all of the Cr, i.e., both olivine and pyroxene inclusions hold a factual content of Cr, thus when correcting olivine and pyroxene analysis for grains >1.5 to  $<3 \mu m$ , not all Cr is subtracted. The fraction kept corresponds to the Cr<sub>2</sub>O<sub>3</sub> content of the non-contaminated larger inclusions, this being an average of 1.7 wt% for olivine and 1.6 wt% for pyroxene. For olivine inclusions corrections where only required for one fossil meteorite sample (Österplana 036) and for Ca-poor pyroxene inclusions in one sediment sample (Golvsten 0.62 m).

#### 3. RESULTS

Inclusions are present in chromite in both the recent and fossil meteorites as well as in the sediment-dispersed EC grains (Table 1). The all dominating minerals of the inclusions are olivine, pyroxene, merrillite and plagioclase, in that order. Other, more sporadic occurrences include Cl-apatite, rutile and troilite. A gradual increase in olivine and decrease of Ca-poor pyroxene inclusions from H through L to LL can be seen in the recent chondrites, which is in accordance with the modal composition of the different groups' matrix composition (Van Schmus, 1969; Hutchison, 2004). No trend with petrographic type can be discerned.

The number of inclusions within each grain varies from solitary grains to randomly distributed clusters of over 20 (Fig. 2a and b). Inclusions of different minerals within the same host grain are common, individual inclusions, however, are generally monomineralic. No difference in composition of chromite with inclusions compared to chromite free of inclusions is detectable. The frequency of inclusion-bearing chromite to inclusion-free in the recent meteorites varies from 16% to 27%, with an average of ~19%, no trend related to group or type is seen (Table 1). The presence of inclusions in the fossil meteorites and the sediment-dispersed grains is significantly less common, spanning between 4–18% and 4–5%, with an average of ~10% and ~4.5%, respectively (Table 1). These numbers, both



Fig. 1.  $Cr_2O_3$  content in inclusions vs. inclusion size. Note that the chromium content in olivine and Ca-poor pyroxene becomes constant ( $\sim$ 1–2 wt%) in inclusions >3  $\mu$ m, whilst it drops to zero in plagioclase.



Fig. 2. Backscattered electron images of inclusions. (a) Solitary Ca-poor pyroxene inclusion in chromite grain from fossil meteorite Österplana 034. (b) Numerous inclusions of olivine and Ca-rich pyroxene in chromite from fossil meteorite Brunflo. (c) Close-up of (b). Rounded olivine and Ca-rich pyroxene inclusions and two altered inclusions containing secondary clay minerals. Note the association of the altered inclusions with cracks.

for the recent, fossil and sediment-dispersed grains, must be treated as an absolute minimum due to the fact that the grains have only been examined in a single cross-section. The discrepancy in frequency between the recent and fossil grains is mainly the result of that semi-encapsulated inclusions in the latter have been altered or replaced, typically to serpentine or clay minerals. This is a circumstance seen in the frequent association of the altered/replaced inclusions with cracks and veinlets (Fig. 2c). These inclusions, doubtlessly secondary, have not been included when calculating the frequency of inclusion-bearing chromite. The lesser occurrence of inclusions in the sediment-dispersed grains in comparison to the fossil meteorite grains is most likely the effect of more extensive alteration in the former. The sediment-dispersed grains have been interpreted as originating mainly from micrometeorites (Heck et al., 2008), thus possibilities for external influences and alteration is likely to be greater than in the more sheltered chromite of the proper fossil meteorites. In a couple of instances alteration has only affected the inclusions partially, i.e., along the boundary, resulting in a chemical zoning (see below).

#### 3.1. Olivine

#### 3.1.1. Recent chondrites

Olivine inclusions are present in chromite from all the recent chondrites and is the most abundant type of inclusion. The olivine inclusions are subhedral to anhedral, often spherical. They range in size from <1 to  $15 \mu$ m, though typically between 2 and 5  $\mu$ m and the contact towards the chromite is sharp (Fig. 3a and b). The average compositions of the inclusions as well as matrix olivine from the recent meteorites are shown in Table 3. The composition of the matrix olivine in the recent chondrites is homogenous within each sample and the fayalite (Fa) content is in accordance with the established ranges for the different groups (H, L, LL; Fig. 4; Brearley and Jones, 1998, and references



Fig. 3. Backscattered electron images of inclusions. (a) Chromite grain in Holbrook (L6) with olivine and plagioclase inclusions. (b) Close-up of (a). (c) Solitary olivine inclusion in an EC grain from sediment sample Sextummen 2.73 m. (d) Partially altered olivine inclusion in an EC grain from sediment sample Golvsten 0.62 m. (e) Close-up of (d). The alteration rim consists of iron oxide (light colored) and serpentine (dark gray).

therein). The meteorite Naryilco has previously been classified as an L/LL6 (Wlotzka, 1992); our results with a Fa content of 24.3 mol% and a ferrosilite (Fs) content of 20.2 mol%, point to it being an L rather than an LL. Common for all the olivine inclusions is the presence of  $Cr_2O_3$  (~1.5–2.3 wt%); the matrix olivine holds no or very small amounts of  $Cr_2O_3$  (<0.3 wt%). When comparing the composition of matrix and chromite-enclosed olivine, it becomes clear that the latter is enriched in Cr and Mg, on behalf of foremost Fe, i.e., the Fa content is consistently 10–20% lower, with an average of ~14%, in the inclusions than in the matrix (Fig. 4).

#### 3.1.2. Fossil meteorites and sediment-dispersed EC grains

Inclusions of olivine in chromite are found in five of the eight fossil meteorites (Österplana 003, 032, 036, 038 and Brunflo) and in two of the four sediment samples (Golvsten 0.62 m and Sextummen 2.73 m; Table 4 and Fig. 3c). In one chromite grain from Österplana 003 one olivine inclusion is present; it is elliptical, 2 µm in diameter and has a heterogeneous composition, with an enrichment of Fe along the rim. This is probably due to a partial alteration, where the olivine has been broken down to what appears to be an iron oxide and serpentine (Fig. 3d and e). Although the grain might have a primary composition in the core, it is too small to analyze quantitatively. A solitary olivine inclusion in one chromite grain from Österplana 032 is 3.2 µm in size, spherical in shape and has a homogenous composition with a Fa content of 20.8 mol% and  $\sim$ 1.4 wt% Cr<sub>2</sub>O<sub>3</sub>. In the Österplana 036 sample, two homogenous, anhedral inclusions, one solitary and one accompanied by a few merrillite inclusions (see below), in two different chromite grains, are found. One of the inclusions, after correction due to its small size (2.6 µm) has a Fa content of 18.3 mol%. The other inclusion is too small to be analyzed quantitatively (<1.5  $\mu$ m. One chromite-enclosed olivine is found in the sample from Österplana 038. The inclusion is spherical and only 0.8  $\mu m$  in diameter and thus not analyzed quantitatively. The minute inclusion is accompanied by three even smaller blebs  $\sim 0.2-0.3 \,\mu m$ , suspected to be olivine as well and one Ca-rich pyroxene (see below). A total of 14 olivine inclusions distributed over five chromite grains are found in the Brunflo sample. All the inclusions are homogenous, anhedral, mostly spherical with a minimum diameter ranging between 0.9 and 3.5 µm. In three of the grains the olivine appears as solitary inclusions, sometimes accompanied by altered inclusions. The two other chromite grains hold three and eight olivine inclusions, respectively. The grain with eight inclusions is also the home of several Ca-rich pyroxenes (see below) as well as some altered inclusions (Fig. 2b and c). The average composition for Brunflo, based on analyses on four olivine inclusions, i.e., the ones  $>3 \mu m$ , gives a Fa content of 21.3 mol%, and  $\sim$ 2.3 wt% Cr<sub>2</sub>O<sub>3</sub>. The three inclusions in the EC grains of the sediment samples are all relatively large ( $\sim 6 \,\mu m$ ) and solitary. The two Golvsten 0.62 m inclusions are anhedral and subhedral, respectively, and have heterogeneous compositions, exhibiting alteration rims analogous to that of the inclusion in Österplana 003. However, contrary to the Österplana 003 inclusion, both these are considered to have a large enough central part displaying a primary composition making them valid for analysis, giving an average Fa content of 21.3 mol% and 2.0 wt% Cr<sub>2</sub>O<sub>3</sub>. The Sextummen 2.73 m inclusion is anhedral and has a homogenous composition with a Fa content of 20.4 mol% and 2.3 wt% Cr<sub>2</sub>O<sub>3</sub>.

#### 3.2. Pyroxene

#### 3.2.1. Recent chondrites

Second to olivine, pyroxene is the most common inclusion. Two distinct types are present; Ca-poor pyroxene (Table 5) and Ca-rich pyroxene (diopside; Table 6). The Ca-poor pyroxene is the most abundant; but Ca-rich pyroxene is proportionally considerably more common in inclusions than in the matrix. According to Hutchison (2004) Ca-rich pyroxene constitutes only  $\sim 6\%$  of ordinary chondrites, i.e., Ca-rich pyroxene seems to be overrepresented in the inclusions. Both types of pyroxene form monomineralic subhedral to anhedral inclusions, typically in the size range of 1-5 µm in diameter (Fig. 5a and b), with distinct contacts to the chromite host. As in the case of olivine, all the pyroxene inclusions contain a minor amount of chromium; 1.0-2.0 wt% Cr2O3, no chromium is present in the matrix pyroxenes. The pyroxene inclusions have a composition typical for ordinary chondrites, apart from chromium, and are homogenous within each sample. Ca-poor pyroxene inclusions have a high enstatite (En) content (73-84 mol%), low wollastonite (Wo) content (0.5-2.0 mol%) and occasionally minor amounts of MnO (<0.7 wt%). The Fs/En/Wo ratios of the Ca-poor pyrox-

The average	element conc	entration and	1 standard de	viation (1c	5) of olivine i	n matrix and	inclusions in e	chromite fror	n 12 recent c	hondrites.				
	Dimmit H4		Kesen H4		Forest City F	HS	Estacado H6		Awere L4		Floyd L4		Mbale L5-6	
	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion
Size (µm)	-	> 3 5	-	- >3	-	ر ع	-	د ع	6	- >3	- 9	>3 6	- 9	- ^ <u>-</u> 3
# MgO	$^{4}_{41.76 \pm 0.30}$	$43.41 \pm 0.69$	$^{4}_{43.63} \pm 0.20$	1 44.04	$^{4}_{42.61} \pm 0.28$	$\frac{2}{43.15 \pm 1.13}$	$42.33\pm0.20$	$^{2}$ 43.78 ± 0.28	$38.21 \pm 0.22$	1 40.08	$39.26 \pm 0.71$	$41.32\pm0.64$	$38.71 \pm 0.59$	$40.62 \pm 1.10$
$SiO_2$	$38.88\pm0.18$	$38.64\pm0.37$	$40.21\pm0.22$	39.53	$39.58\pm0.22$	$38.62\pm0.05$	$39.16\pm0.23$	$38.95\pm0.06$	$37.51\pm0.48$	38.12	$38.11\pm0.52$	$38.70\pm0.53$	$38.14\pm0.72$	$38.48\pm0.45$
$Cr_2O_3$	pq	$1.65\pm0.39$	þq	1.87	pq	$1.67\pm0.09$	pq	$1.57\pm0.12$	þq	1.52	$0.31\pm0.30$	$1.60\pm0.17$	þq	$1.64\pm0.20$
MnO	$0.50\pm0.06$	$0.41\pm0.25$	$0.20\pm0.41$	pq	$0.25\pm0.29$	$0.23\pm0.32$	þd	$0.51\pm0.06$	pq	pq	$0.45\pm0.23$	$0.34\pm0.27$	$0.50\pm0.27$	$0.30\pm0.35$
FeO	$18.02\pm0.40$	$15.07\pm0.86$	$15.31\pm0.61$	13.01	$17.12\pm0.16$	$15.21\pm0.30$	$17.26 \pm .0.30$	$15.12\pm0.02$	$22.92\pm0.38$	19.97	$20.84\pm0.37$	$18.15\pm0.47$	$21.80\pm0.26$	$19.08\pm0.92$
Total	$99.16\pm0.79$	$99.18\pm0.47$	$99.35\pm0.62$	98.46	$99.57 \pm 0.46$	$99.18 \pm 1.25$	$98.75\pm0.46$	$99.91 \pm 0.17$	$98.63\pm0.31$	69.69	$98.97 \pm 1.11$	$100.11 \pm 0.78$	$99.14\pm0.95$	$100.12 \pm 0.51$
0;	4 •	4 •	4 •	4 •	4 ·	4 •	4 ·	4 •	4	4 • 1	4	4	4 ·	4
Mg	1.60	1.65	1.64	1.66	1.62	1.65	1.62	1.66	10.1	1.55 2	1.53	1.58 25	10.1	1.50
SI	1.00	0.98	1.01	1.00	1.01	0.99	1.01	0.99	0.99	0.99	1.00	0.99	1.00	0.99
Ċ	pq	0.03	pq	0.04	pq	0.02	pq	0.03	pq	0.03	0.01	0.03	pq	0.03
Mn	0.01	0.01	0.01	pq	0.01	0.01	pq	0.01	pq	þq	0.01	0.01	0.01	0.01
Fe	0.39	0.32	0.32	0.28	0.37	0.33	0.37	0.32	0.51	0.43	0.46	0.39	0.48	0.41
Cation sum	3.00	2.99	2.98	2.98	2.99	2.98	3.00	3.01	3.01	3.00	3.01	2.99	3.00	3.00
Fa (mol%)	$19.6\pm0.38$	$16.2\pm0.9$	$16.4\pm0.7$	14.4	$18.4\pm0.3$	$16.5\pm0.5$	$18.7\pm0.1$	$16.2\pm0.1$	$25.2\pm0.5$	21.8	$23.0\pm0.4$	$19.8\pm0.5$	$24.0\pm0.5$	$20.9\pm1.2$
Fa diff. (%) <sup>b</sup>	17.3		12.2		10.3		13.4		13.5		13.9		12.9	
	Holbroo	k L6		New Con	cord L6		Naryilco L/LI	.6	Ar	ppley Bridge	LL6	Dhu	ırmsala LL6	
	Matrix	Inc	dusion	Matrix	Incl	usion	Matrix	Inclusion	U W	atrix	Inclusion	Mat	rix	Inclusions
Size (µm)		~			$\stackrel{\scriptstyle <}{\sim}$			~3			~3			~3
#a	9	4		4	4		9	б	9		4	4		9
MgO	$37.76 \pm 0$	0.42 39.	$76\pm0.68$	$38.26\pm0$	.23 40.8	$39\pm0.84$	$38.62\pm0.39$	$39.31 \pm$	0.73 34	$.30 \pm 0.24$	$36.40\pm0$	.56 36.7	$1\pm0.36$	$38.32\pm0.52$
SiO,	$38.07 \pm 0$	0.45 37.	$95\pm0.49$	$38.33 \pm 0$	.33 38.5	$54\pm0.18$	$38.44\pm0.34$	$37.91 \pm$	0.54 38	$21 \pm 0.16$	$39.10\pm0$	.16 38.0	$7 \pm 0.33$	$37.67 \pm 1.22$
$Cr_2O_3$	pq	1.5	$5\pm0.23$	pq	1.78	$3 \pm 0.14$	þd	$1.32 \pm 0$	.31 bd		$1.98\pm0.2$	pd 03		$1.59\pm0.07$
MnO	$0.39\pm0.$	33 0.3	$9\pm0.08$	$0.27 \pm 0.2$	32 0.26	$5\pm0.30$	$0.47\pm0.24$	$0.50\pm 0$	.11 0.0	$07\pm0.20$	$0.25\pm0.2$	29 0.12	$\pm 0.25$	$0.58\pm0.11$
FeO	$23.33 \pm 0$	0.27 19.	$92\pm0.74$	$22.20 \pm 0$	.03 17.7	$74 \pm 1.12$	$21.89\pm0.32$	$19.78 \pm$	0.70 26	$.35\pm0.46$	$21.70\pm0$	.83 24.3	$1\pm0.37$	$21.91\pm0.80$
Total	$99.55 \pm$	1.11 99.	$58 \pm 1.15$	$99.06\pm0$	.28 99.2	$21\pm0.61$	$99.36\pm0.50$	$98.83 \pm$	1.07 98	$.93 \pm 0.75$	$99.42\pm0$	.39 99.2	$1 \pm 1.07$	$99.88\pm1.87$
0	4	4		4	4		4	4	4		4	4		4
Mg	1.48	1.5	4	1.50	1.57	1	1.50	1.53	1.3	25	1.42	1.45		1.49
Si	1.00	0.9	6	1.01	0.99	•	1.01	0.99	1.0	12	1.02	1.01		0.98
Cr	pq	0.0	3	pq	0.04	-	pq	0.03	pq		0.04	pq		0.03
Mn	0.01	0.0	1	0.01	0.01		0.01	0.01	0.0	0	0.01	0.00		0.01
Fe	0.51	0.4	3	0.49	0.38	~	0.48	0.43	0.5	69	0.48	0.54		0.48
Cation sum	3.00	3.0	0	3.00	2.99	•	2.99	3.00	2.9	8	2.97	2.99		2.99
Fa (mol%) Fa diff. (%) <sup>b</sup>	$\begin{array}{c} 25.7\pm0\\ 14.4\end{array}$	.1 22.	$.0 \pm 0.8$	$24.6 \pm 0.2$ 20.3	2 19.6	$5 \pm 1.4$	$24.3\pm0.2$ 9.5	$22.0 \pm 0$	.7 30.	$.1 \pm 0.4$ .9	$25.3 \pm 1.0$	) 27.1 10.3	$\pm 0.2$	$24.3 \pm 0.5$
bd, below de	tection limit.													

Table 3

1478

C. Alwmark, B. Schmitz/Geochimica et Cosmochimica Acta 73 (2009) 1472-1486

 $^a$  Number of grains analyzed.  $^b$  The difference (%) in Fa content between matrix and inclusions.



Fig. 4. Fa content in olivine and Fs content in Ca-poor pyroxene in matrix and inclusions in chromite of various recent chondrites. The gray boxes represent the established ranges of Fs and Fa in Ca-poor pyroxene and olivine, respectively, determined for the three groups (H, L, LL) of ordinary equilibrated chondrites (Brearley and Jones, 1998, and references therein).

Table 4

The average element concentration and standard deviation  $(1\sigma)$  of olivine and Ca-poor pyroxene inclusions in chromite from fossil meteorites and sediment samples.

	Olivine					Ca-poor pyrox	kene
	Fossil mete	orites		Sediment sampl	es	Fossil met.	Sed. sample
	Öpl 032	Öpl 036 <sup>b</sup>	Brunflo	Golv 0.62	Sex 2.73	Öpl 034	Golv 0.62 <sup>b</sup>
Size (µm)	>3	2.6	>3	>3	>3	>3	>1.5 to <3
# <sup>a</sup>	1	1	4	2	1	1	2
MgO	39.91	42.18	$39.30\pm0.31$	$39.57\pm0.17$	39.71	28.53	$28.84 \pm 0.19$
SiO <sub>2</sub>	38.02	38.50	$38.14\pm0.43$	$38.05\pm0.32$	37.56	54.68	$55.39 \pm 0.56$
CaO	bd	bd	bd	bd	bd	0.69	$0.69\pm0.20$
$Cr_2O_3$	1.44	1.50	$2.34\pm0.15$	$2.02\pm0.09$	2.30	1.79	$1.88\pm0.13$
MnO	0.45	bd	$0.28\pm0.33$	$0.58\pm0.04$	0.44	0.45	bd
FeO	18.72	16.85	$18.95\pm0.86$	$19.22\pm0.13$	18.17	12.85	$13.03\pm0.52$
Total	98.55	99.03	$99.00\pm0.48$	$99.44\pm0.41$	98.18	98.99	$99.83\pm0.20$
0	4	4	4	4	4	6	6
Mg	1.56	1.61	1.52	1.53	1.55	1.54	1.54
Si	0.99	0.99	0.99	0.99	0.98	1.98	1.99
Ca	bd	bd	bd	bd	bd	0.03	0.03
Cr	0.03	0.03	0.05	0.04	0.05	0.05	0.05
Mn	0.01	bd	0.01	0.01	0.01	0.01	bd
Fe	0.41	0.36	0.41	0.42	0.40	0.39	0.39
Cation sum	3.00	3.00	2.98	2.99	2.99	4.00	4.00
Fa (mol%)	20.8	18.3	$21.3\pm1.0$	$21.3\pm0.3$	20.4	_	_
Fs (mol%)	_	_	_	_	_	19.9	$19.9\pm0.7$
Wo (mol%)	—	_	_	_	_	1.5	$1.4\pm0.3$

bd, below detection limit

<sup>a</sup> Number of grains analyzed.

<sup>b</sup> Corrected for secondary fluorescence from the host chromite.

The aver	age element (	concentration	and standard	n ucviation (	10) UL Ca-pur	IT Pytukene II	I IIIaUIV auv							
	Dimmit H4		Kesen H4		Forest City H	H5	Estacado H6		Awere L4		Floyd L4		Mbale L5-6	
	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion	Matrix	Inclusion
Size		>3		>3		>3		>3		>3		>3		>3
#a	9	3	5	2	4	4	4	9	3	1	4	4	4	3
MgO SiO:	$31.06 \pm 0.23$ 56 33 $\pm 0.27$	$30.39 \pm 0.54$ 55 30 $\pm$ 0.33	$31.19 \pm 0.28$ 56 50 $\pm 0.27$	$31.06 \pm 0.13$ 56 17 ± 0.71	$31.02 \pm 0.08$	$30.13 \pm 0.20$	$30.72 \pm 0.27$	$30.34 \pm 0.35$	$28.67 \pm 0.44$ 54.08 ± 0.50	28.83 54.61	$29.61 \pm 0.37$	$29.02 \pm 0.55$ 55 13 $\pm$ 0.00	$29.20 \pm 0.09$	$28.79 \pm 0.11$
CaO <sup>2</sup>	$0.61 \pm 0.03$	$0.51 \pm 0.06$	$0.55 \pm 0.07$	$0.51 \pm 0.05$	$0.46 \pm 0.10$	$0.56 \pm 0.10$	$0.49 \pm 0.06$	$0.47 \pm 0.07$	$0.59 \pm 0.04$	0.54	$0.67\pm0.10$	$0.56 \pm 0.04$	$0.77 \pm 0.12$	$0.54 \pm 0.09$
$Cr_2O_3$	bd 5 2 - 5 11	$1.47 \pm 0.07$	$0.23 \pm 0.34$	$1.64 \pm 0.14$	bd o eo - o oo	$1.58 \pm 0.23$	bd 0.37 - 0.33	$1.57 \pm 0.15$	bd bd	1.29	bd 0.70 - 0.05	$1.24 \pm 0.44$	bd 0.12 - 0.20	$1.76\pm0.14$
FeO	$11.41 \pm 0.21$	$0.42 \pm 0.37$ 11.26 $\pm 0.04$	$10.03 \pm 0.34$	$0.99 \pm 0.61$	$10.48 \pm 0.21$	$0.49 \pm 0.55$ 10.88 $\pm 0.55$	$0.27 \pm 0.32$ 11.51 $\pm 0.10$	$11.10 \pm 0.09$	$0.10 \pm 0.20$ $14.61 \pm 0.20$	13.79	$0.00 \pm 0.00$ 13.19 $\pm 0.39$	$13.64 \pm 0.43$	$13.67 \pm 0.19$	$13.57\pm0.35$
Total	$99.94\pm0.47$	$99.43\pm0.57$	$99.18\pm0.66$	$99.64\pm0.61$	$99.20\pm0.28$	$99.55\pm0.60$	$99.43 \pm 0.66$	$99.10\pm0.43$	$99.01\pm0.55$	99.64	$99.70\pm1.05$	$100.13 \pm 0.77$	$100.02\pm0.53$	$99.92\pm0.50$
0;	9	9	9	9	9	9	9	9	9	9	9	9	9	9
Si Si	1.04	1.01	2.01	1.04	1.64 2.01	1.60	2.00	1.02	1.54 2.00	cc.1 1.97	1.99	cc.1 1.98	2.00	1.98
Ca	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.02
ų;	bd	0.04	0.01	0.05	bd	0.04	bd	0.04	bd î	0.04	bd	0.04	bd	0.05
Mn Fe	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.00	0.02	0.02	0.02	0.02	pq
Cation	4.00	4.00	3.99	4.00	3.99	3.99	4.00	4.00	4.01	4.01 4.01	0.40 4.01	0.40 4.01	4.00	4.00
sum E.	014.0.21	171 + 0.4	157 + 07	151 + 0.2	150-03	707271	171+01	160403	5 U + 6 CC	- 10	105401			207 + 202
rs (mol%)	$10.9 \pm 0.2$	$1.1 \pm 0.4$	$15.2 \pm 0.4$	$0.1 \pm 0.5$	$10.9 \pm 0.7$	$0.0 \pm 0.01$	$1/.1 \pm 0.1$	$10.9 \pm 0.3$	$22.5 \pm 0.5$	21.1	$19.0 \pm 0.4$	$20.1 \pm 0.9$	$7.0 \pm 0.07$	$20.1 \pm 0.3$
Wo	$1.0\pm0.0$	$1.0\pm0.0$	$1.0\pm0.0$	$1.0\pm0.0$	$0.8\pm0.3$	$1.1\pm0.1$	$1.0\pm0.0$	$1.0\pm0.0$	$1.0\pm0.0$	1.0	$1.4\pm0.2$	$1.0\pm0.0$	$1.4\pm0.2$	$1.0\pm0.0$
(mol%)														
	Holl	rook L6		New C	oncord L6		Naryilco L/L	L6	App	ley Bridge I	TL6	Dhu	rmsala LL6	
	Mat	rix	Inclusion	Matrix	I	nclusion	Matrix	Inclusic	nn Mat	rix	Inclusion	Mati	ix	Inclusion
Size (µm)			>3			×3		>3			~3			~3
; # <sup>a</sup>	6 6		2	4			4	1	S.		2	4		2
MgO S:O:S	28.2	$8 \pm 0.16$ $2 \pm 0.44$	$28.17 \pm 0.19$	28.84 ±	± 0.07	8.51	$28.87 \pm 0.23$	28.22	26.7	$4 \pm 0.35$ $2 \pm 0.62$	$25.86 \pm 0.55.04 \pm 0.55.04 \pm 0.55.04$	04 28.33 20 56.20	$0.26 \pm 0.26$	$27.48 \pm 0.56$
CaO CaO	0.00	$\pm 0.12$	$1.26 \pm 0.16$	$0.71 \pm$	0.14 0	-53	$0.88 \pm 0.03$	0.81	1.00	$\pm 0.17$	$0.87 \pm 0.0$	9 0.79	$\pm 0.07$	$0.65 \pm 0.08$
$Cr_2O_3$	pq		$1.62\pm0.09$	pq	1	.60	bd	1.37	pq		$1.40\pm0.0$	6 bd		$1.84\pm0.39$
MnO FeO	0.52	$\pm 0.28$ 3 + 0.23	$0.66 \pm 0.11$ 13 41 + 0 23	$0.63 \pm$ 13.59 +	0.10 0.10	1,46 3 08	$0.49 \pm 0.05$ 13 22 $\pm$ 0.15	0.64 13 78	0.11	$\pm 0.24$ $2 \pm 0.38$	$0.57 \pm 0.0$ 1574 + 0	8 0.49 21 14 80	$\pm 0.05$ 0 + 0.14	$0.64 \pm 0.09$ 14.66 $\pm$ 0.10
)														
Total	99.5 6	$3 \pm 0.75$	$99.90\pm0.32$	99.52 ≟ 6	± 0.70 9	8.44	$99.04\pm0.58$	99.75 6	99.4 6	$0 \pm 0.77$	$99.46 \pm 0.66$	06 100.3	$^{\prime 2}\pm .0.54$	$99.24\pm0.88$
Mg	1.52		1.51	1.54		.54	1.55	1.52	.1 4-1		1.40	1.51		1.50
Si	2.00		1.97	2.00	1	.97	2.00	1.98	2.03		2.01	2.00		1.97
ca Ca	0.04 5.4		0.05	0.03 b.d	00	1.02	0.03	0.03	0.04		0.04	0.03		0.03
Ъ Ч	0.02		0.02	0.02		01	0.02	0.02	0.00		0.02	0.01		0.00
Fe	0.43		0.40	0.41	0	.40	0.40	0.42	0.47		0.48	0.44		0.45
Cation su	un 4.00		4.00	4.00	с, с ,	66.	4.00	4.00	3.97		3.98	4.00		4.01
Fs (mol% Wo (mol%	() 21.5 ∞0 1.9 ±	$\pm 0.2$	$20.5 \pm 0.1$ $2.5 \pm 0.3$	$20.6 \pm 1.4 \pm 0$	0.1 2.	.0 .0	$20.2\pm0.3$ $1.5\pm0.0$	21.3 1.5	24.0	$\pm 0.5$ $\pm 0.3$	$24.9\pm0.4$ $1.8\pm0.4$	22.4 1.5 ≟	$\pm 0.2$	$22.8\pm0.2$ $1.3\pm0.4$
bd, belov <sup>a</sup> Num	w detection li	mit. analvzed												

1480

C. Alwmark, B. Schmitz/Geochimica et Cosmochimica Acta 73 (2009) 1472-1486

Table 6

Representative analyses of Ca-rich pyroxene in matrix and inclusions in chromite from two recent chondrites and of inclusions in chromite from three fossil meteorites.

	Recent met	eorites			Fossil meteor	ites	
	Estacado H	16	Mbale L5-6	5	Öpl 009 <sup>a</sup>	Öpl 038	Brunfloa
	Matrix	Inclusion	Matrix	Inclusion	Inclusion	Inclusion	Inclusion
Size (µm)		10		6	1.9	4.6	2.8
Na <sub>2</sub> O	0.50	0.69	0.51	0.45	0.56	0.66	1.14
MgO	17.24	17.04	16.83	16.54	16.83	16.52	14.71
$Al_2O_3$	0.42	0.42	bd	bd	bd	bd	bd
SiO <sub>2</sub>	55.10	53.62	55.48	53.73	53.30	53.76	54.00
CaO	22.38	21.67	23.10	21.7	21.94	21.87	22.63
TiO2	bd	bd	bd	0.59	bd	bd	bd
$Cr_2O_3$	bd	1.91	bd	1.78	1.73	2.04	1.39
FeO	3.87	3.75	3.89	4.24	4.44	4.01	4.49
Total	99.51	99.10	99.81	99.03	98.80	98.86	98.35
0	6	6	6	6	6	6	6
Na	0.04	0.05	0.04	0.03	0.04	0.05	0.08
Mg	0.94	0.93	0.91	0.91	0.93	0.91	0.82
Al	0.02	0.02	bd	bd	bd	bd	bd
Si	2.01	1.98	2.02	1.99	1.98	1.99	2.01
Ca	0.88	0.86	0.90	0.86	0.87	0.87	0.90
Ti	bd	bd	bd	0.02	bd	bd	bd
Cr	bd	0.06	bd	0.05	0.05	0.06	0.04
Fe	0.12	0.12	0.12	0.13	0.14	0.12	0.14
Cation sum	4.01	4.02	3.99	3.99	4.01	4.00	4.00
Fs (mol%)	6.2	6.3	6.2	6.8	7.3	6.5	7.5
Wo (mol%)	45.4	44.8	46.6	45.3	44.8	45.6	48.6

bd, below detection limit.

<sup>a</sup> Corrected for secondary fluorescence from the host chromite.



Fig. 5. Backscattered electron images of inclusions. (a) Inclusions of Ca-poor pyroxene in chromite from meteorite Estacado (H6). (b) Inclusions of Ca-rich pyroxene in chromite from meteorite Estacado (H6). (c) Ca-rich pyroxene inclusions in chromite from fossil meteorite Österplana 038.

enes in the matrix are largely consistent with the defined ranges for the different ordinary chondrite groups (H, L, LL; Fig. 4; Brearley and Jones, 1998, and references therein). However, the Fa content of the chondrites of petrographic type 4 should be regarded with some caution due to the possibility of not being completely equilibrated. The Ca-rich pyroxene inclusions have a composition of  $En_{44-49}Fs_{6-8}Wo_{45-49}$  (mol%), with Na<sub>2</sub>O of 0.5–1.2 wt%, low or no Al<sub>2</sub>O<sub>3</sub> (<0.5 wt%) and no detectable MnO. Apart from the Cr content and contrary to enclosed olivine, the pyroxene displays only minor difference in composition between matrix and inclusions, with no apparent trend (Fig. 4).

#### 3.2.2. Fossil meteorites and sediment-dispersed EC grains

Ca-poor pyroxene is present in one chromite grain from the fossil meteorite Österplana 034 sample and in two chromite grains from sediment samples Golvsten 0.62 m and Sextummen 2.58 m (Table 4 and Fig. 2a). The inclusion from the Österplana 034 sample is spherical with a diameter of 3.5 µm and has a homogenous composition of  $En_{78.6}$ -Fs<sub>19.9</sub>Wo<sub>1.5</sub> (mol%) and a Cr<sub>2</sub>O<sub>3</sub> content of 1.8 wt%. The two Ca-poor pyroxene inclusions, present in one EC grain from the Golvsten 0.62 m sample, are closely spaced, anhedral and homogenous. The inclusions are both <3 µm (1.9 and 1.6 µm) and have a corrected mean composition of  $En_{78.7}Fs_{19.9}Wo_{1.4}$  (mol%) with a Cr<sub>2</sub>O<sub>3</sub> of 1.9 wt%. The inclusion in the EC grain from the Sextummen 2.58 m sample is large (10  $\mu$ m), anhedral and exhibits an alteration rim. The rim is analogous to those found in two of the olivine inclusions, consisting of iron oxide and serpentine (Fig. 6a–c). Despite its large size, no consistent analysis could be carried out on the inclusion due to heterogeneity caused by the partial alteration.

Chromite-enclosed Ca-rich pyroxene has been found in three of the fossil meteorite samples (Österplana 009, 038 and Brunflo; Figs. 2b and c and 5c), but in none of the EC grains of the sediment samples. The inclusions in chromite from the fossil meteorite samples are generally rounded and have a composition similar to the inclusions of the recent chondrites, with  $En_{44-48}Fs_{6.5-7.5}Wo_{45-49}$  (mol%) and 1.4–2.0 wt%  $Cr_2O_3$ . Representative analyses are given in Table 6. The Österplana 009 sample holds one small (1.9 µm) solitary inclusion whilst in Österplana 038 numerous inclusions (<1–5 µm in size) are present in three separate chromite grains. The Brunflo meteorite is the home of eight inclusions, ranging in size from 0.6 to 2.8 µm. Seven of these inclusions are located in the same chromite grain, this being the grain hosting eight olivine inclusions (see above).

#### 3.3. Merrillite

#### 3.3.1. Recent chondrites

Inclusions in chromite of sodium-rich merrillite ( $Na_2Mg_2$ -C $a_{18}P_{14}O_{56}$ ), an anhydrous phosphate and an extraterrestrial variant of the terrestrial mineral whitlockite, are found in five of the recent chondrite samples. The inclusions are generally anhedral with a diameter ranging from 0.5 to 12  $\mu$ m (Fig. 7a). The merrillite has a homogenous composition throughout the samples, both in matrix and in inclusions, and does not display any difference in composition, neither between matrix and inclusions nor between different samples. Representative analyses are given in Table 7.

#### 3.3.2. Fossil meteorites and sediment-dispersed EC grains

Merrillite inclusions have been identified in chromite from three of the fossil meteorite samples (Österplana 009, 030 and 036) but in none of the sediment samples. The inclusions are generally small ( $0.5-2.0 \mu m$ ), anhedral and appear either solitarily (Österplana 009 and 030) or in clusters of 2–4 grains (Österplana 009 and 036; Fig. 7b and c). The inclusions have a composition analogous to the merrillite of both matrix and inclusions in the recent chondrites (Table 7), and are homogenous; implying that the inclusions are unaffected, i.e., have a primary composition.

#### 3.4. Plagioclase

#### 3.4.1. Recent chondrites

Plagioclase inclusions in chromite are relatively rare and have only been identified in one third of the recent chondrite samples. The inclusions are  $1-10 \mu m$  in diameter, subhedral to anhedral and the contact to the host chromite is sharp (Fig. 3a). The chromite-enclosed plagioclase is albitic and shows little variation in chemistry with a composition of An<sub>10-12</sub>Ab<sub>81-85</sub>Or<sub>4-7</sub> (mol%) and low or no FeO



Fig. 6. Backscattered electron images of inclusions. (a) Partially altered Ca-poor pyroxene inclusion (arrow) in EC grain from sediment sample Sextummen 2.58 m. (b) Close-up of (a). (c) Close-up of (b). The alteration rim consist of iron oxide (light colored) and probably serpentine (dark gray).



Fig. 7. Backscattered electron images of inclusions. (a) Merrillite inclusions in chromite from meteorite Dhurmsala (LL6). (b) Merrillite inclusions in chromite from fossil meteorite Österplana 009. (c) Close-up of (b). (d) Plagioclase and secondary mineral inclusions in EC grain from sediment sample Arkeologen 0.21 m.

Table 7

Fossil meteorites Recent meteorites Öpl 036<sup>a</sup> Öpl 030<sup>a</sup> Estacado H6 Holbrook L6 Inclusion Matrix Inclusion Matrix Inclusion Inclusion Size (µm) 4.5 4.0 1.8 2.0 2.86 Na<sub>2</sub>O 2.72 2.88 3.00 2.64 2.88 MgO 3.53 3.54 3.57 3.66 3.61 3.61  $P_2O_5$ 46.54 46.45 46.54 45.32 45.70 44.96 CaO 45.67 46.12 46.42 45.98 45.02 45.63 FeO 0.68 1.10 1.16 1.74 0.63 bd Total 99.32 98.95 100.47 99.06 99.07 97.71 0 56 56 56 56 56 56 1.99 Na 1.96 1.82 2.11 1.86 2.04 1.97 Mg 1.96 1.96 1.87 1.95 1.92 Р 13 91 14.00 14 14 14.04 14.05 13 94 Ca 17.36 17.64 17.72 17.86 17.51 17.91 0.19 Fe 0.14 bd 0.33 0.35 0.53 35.42 35.56 35.95 36.18 35.86 36.06 Cation sum

Representative analyses of merrillite in matrix and inclusions in chromite from two recent chondrites and of inclusions in chromite from two fossil meteorites.

bd, below detection limit.

<sup>a</sup> Corrected for secondary fluorescence from the host chromite.

(<0.8 wt%); typical for chondrites of type 4–6 (Table 8; Brearley and Jones, 1998, and references therein). No difference in composition between plagioclase inclusions and matrix plagioclase can be observed.

#### 3.4.2. Fossil meteorites and sediment-dispersed EC grains

Chromite-enclosed plagioclase has not been identified in any of the fossil meteorite samples and only in one sediment sample (Arkeologen 0.21 m). Two EC grains with plagioclase inclusions are present in Arkeologen 0.21 m, in one grain as a relatively large ( $\sim 5 \,\mu$ m) solitary inclusion (Fig. 7d) and in the other as four small inclusions (1– 2  $\mu$ m). All the inclusions are homogenous, anhedral, bordering to spherical, and have compositions similar to the recent chondrites' matrix and inclusions, with An<sub>11</sub> Ab<sub>84</sub>Or<sub>5</sub> (mol%; Table 8).

Table 8

Representative analyses of plagioclase in matrix and inclusions in chromite from two recent chondrites and of one inclusion in chromite from a sediment sample.

	Recent meteori	tes			Sed. sample
	Estacado H6		Holbrook L6		Ark 0.21 m
	Matrix	Inclusion	Matrix	Inclusion	Inclusion
Size (µm)	_	5	_	5	5
Na <sub>2</sub> O	9.56	9.54	9.73	9.66	9.82
Al <sub>2</sub> O <sub>3</sub>	21.24	21.25	20.92	20.76	20.78
SiO <sub>2</sub>	64.59	64.82	66.57	66.24	66.37
K <sub>2</sub> O	1.27	1.16	0.96	0.76	0.82
CaO	2.55	2.44	2.20	2.34	2.36
FeO	0.79	bd	0.63	0.74	bd
Total	100.00	99.21	101.01	100.50	100.15
0	8	8	8	8	8
Na	0.82	0.82	0.82	0.82	0.84
Al	1.11	1.11	1.08	1.07	1.08
Si	2.87	2.88	2.91	2.91	2.92
K	0.07	0.07	0.05	0.04	0.05
Ca	0.12	0.12	0.10	0.11	0.11
Fe	0.03	bd	0.02	0.03	bd
Cation sum	5.02	5.00	4.98	4.98	5.00
An (mol%)	11.9	11.9	10.3	11.3	11.0
Or (mol%)	6.9	6.9	5.2	4.1	5.0

bd, below detection limit.

#### 4. DISCUSSION

Inclusions of olivine, pyroxene, merrillite and plagioclase have been identified in chromite of extraterrestrial origin; both in recent ordinary chondrites as well as in fossil chondrites and sediment-dispersed EC grains. Petrological and mineralogical studies on Brunflo and some of the Österplana meteorites have shown that, with the exception of chromite and chrome spinels, all the original minerals have been replaced by secondary phases during a two-stage alteration process, at first under oxidizing conditions and later, due to deeper burial, reducing conditions (Nyström et al., 1988; Nyström and Wickman, 1991; Schmitz et al., 1996; Hofmann et al., 2000). The secondary phases are dominated by calcite, barite and sheet silicates; with none of the minerals found in the inclusions in chromite present (Nyström et al., 1988; Nyström and Wickman, 1991). This together with the fact that the inclusions in chromite from the fossil meteorites and in the sediment-dispersed EC grains, with a few exceptions due to partial alteration, are identical in both composition and appearance with those of the recent chondrites is a clear indication that the inclusions in the chromite are of primary extraterrestrial origin; furthermore, merrillite is a mineral only present in extraterrestrial material (Rubin, 1997). Thus, the relict nature of the mineral inclusions in chromite makes them valid in the classification of extraterrestrial material where matrix material is absent or altered.

# 4.1. Compositional ranges for olivine and Ca-poor pyroxene inclusions in chromite

The Cr content in the olivine and pyroxene inclusions and the elevated forsterite content, i.e., enrichment of Mg on behalf of Fe, in the former is a common feature in terrestrial equivalents (e.g., Lorand and Ceuleneer, 1989; McElduff and Stumpfl, 1991; Melcher et al., 1997), where it is interpreted as the result of sub-solidus re-equilibration with the enclosing chromite (Lorand and Ceuleneer, 1989; Melcher et al., 1997). Regarding inclusions in chromite in chondrites of the higher petrographic types, the enrichment is most likely contemporary with the entrapment of the inclusions during the formation of chromite through solid state recrystallisation in the matrix due to parent body thermal metamorphism. The small volume of the inclusions compared to the host chromite makes them rather sensitive to this process. Another effect of the entrapment is the rounded, often spherical shape of the inclusions which minimizes the contact towards the host chromite and thus the surface energy.

Apart from the slight modification due to the sub-solidus re-equilibration, the olivine and pyroxene inclusions in the chromite grains of the recent chondrites have a composition analogous to the olivine and pyroxene of the matrix, respectively. For olivine the sub-solidus reequilibration has affected the Mg/Fe ratio, lowering the Fa content in inclusions with an average of  $13.7 \pm 3.1\%$ (1 $\sigma$ ). Accounting for this, the compositional ranges of Fa for olivine inclusions are: H chondrites, Fa<sub>13.8-17.3</sub>; L chondrites, Fa<sub>19.0-22.4</sub>; LL chondrites, Fa<sub>22.4-27.6</sub>. When applying the maximum standard deviation (1 $\sigma$ ) the ranges are: H chondrites, Fa<sub>13,3-17.9</sub>; L chondrites, Fa<sub>18,3-23.2</sub>; LL chondrites, Fa<sub>21,6-28.6</sub>, i.e., a slight overlap between L and LL chondrites (Fig. 8). In the case of Capoor pyroxene, the compositional difference between matrix and inclusions is minor with an average of  $\sim 1\%$ higher Fs content in inclusions. This is considered to be well within the error limits, i.e., the Fs ranges for inclusions are analogous to that of matrix pyroxenes. Hence, the systematic compositional variation of the chromite hosted olivine and the more or less analogous Ca-poor pyroxene, makes it possible to discriminate between the different groups of equilibrated ordinary chondrites based on the composition of olivine and Ca-poor pyroxene inclusions in chromite (Fig. 8).

## 4.2. Classification of the fossil meteorites and the origin of the sediment-dispersed EC grains—evaluation of the new tool

The fayalite and ferrosilite content of chromite inclusions (>1.5  $\mu$ m) of the fossil meteorites and sediment EC samples are plotted in Fig. 8 compared to the newly defined ranges for Fa and Fs in inclusions of the different meteorite groups. The plot includes all data considered reliable, including four of the eight fossil meteorites (Österplana 032, Österplana 034 and Österplana 036 from Thorsberg quarry and the Brunflo meteorite) plus two of the four sediment-dispersed samples (Golvsten 0.62–0.87 m and Sex 2.73–2.83 m).

Meteorites Österplana 032 and Österplana 034 as well as the Brunflo meteorite plot well within the ranges for L chondrites; using the Fs content of Ca-poor pyroxene for Österplana 034 and the Fa content of olivine for Österplana 032 and Brunflo. In the case of the Brunflo meteorite, the Fa number is an average of the four olivine inclusions >3  $\mu$ m. The third meteorite from Thorsberg, Österplana 036, based on Fa content of one olivine inclusion plots within the standard deviation (1 $\sigma$ ) for L chondrites. The composition of olivine in chromite from sediment sample Sex 2.73–2.83 m, and the average of two olivine as well as two Ca-poor pyroxene inclusions from Golvsten 0.62–0.87 m, also fall well within the Lchondritic field.

In summary, all inclusions plot within the L-chondritic field, which is in accordance with the previous classifications for the Österplana fossil meteorites and the sediment-dispersed EC grains (Schmitz et al., 2001, 2003; Schmitz and Häggström, 2006; Bridges et al., 2007; Greenwood et al., 2007) as well as the revised classification of the Brunflo meteorite (Alwmark and Schmitz, 2008). The overall concordance in classification of the fossil meteorites and the sediment-dispersed grains with previous studies implies that the composition of inclusions of olivine and Ca-poor pyroxene in chromite from ordinary equilibrated chondrites can be used in determining meteorite group with no or very little overlap.

#### 5. CONCLUSIONS

Primary inclusions of olivine, pyroxene, merrillite and plagioclase have been identified in chromite of extrater-



Fig. 8. Fa content in olivine and Fs content in Ca-poor pyroxene of inclusions in chromite of recent and fossil meteorites and sediment samples. The red boxes represent the newly defined ranges of Fa and Fs in Ca-poor pyroxene and olivine, respectively, of inclusions in chromite, with the red dotted lines being the standard deviation  $(1\sigma)$ . The gray boxes represent the established ranges of Fs and Fa in Ca-poor pyroxene and olivine, respectively, determined for the three groups (H, L, LL) of ordinary equilibrated chondrites (Brearley and Jones, 1998, and references therein).

restrial origin, both in recent and fossil meteorites as well as in sediment-dispersed EC grains. The inclusions are anhedral, commonly rounded, range in size from <1 to 15 µm and vary from solitary to randomly distributed clusters of over 20 inclusions within the same chromite grain. Inclusions of varying composition within the same host grain are common, individual inclusions, however, are monomineralic.

In the case of olivine and pyroxene, sub-solidus reequilibration between inclusion and host chromite during entrapment has altered the composition with an increase in chromium and in olivine also magnesium. The systematic compositional difference in Fa content (with an average 14% lower) in the chromite hosted olivine and the more or less analogous Fs content in Ca-poor pyroxene compared to matrix phases, makes it possible to establish ranges for inclusions analogous to the well established classification system based on Fa in olivine and Fs in Ca-poor pyroxene, for ordinary equilibrated chondrites.

All olivine and Ca-poor pyroxene inclusions (>1.5  $\mu$ m) in chromite from the fossil meteorites and the sediment samples plot within the L-chondritic field using the newly defined ranges, which is in agreement with previous classifications. Thus, the accuracy together with the relatively high frequency of inclusions makes this a good tool in classification of fossil meteorites as well as the origin of sediment-dispersed chromite grains from decomposed meteorites and larger impacts, where no other matrix minerals have survived or are present.

#### ACKNOWLEDGMENTS

We thank A. Lindh for enlightened discussions and criticism. We thank A. Krot and A. Rubin for comments and reviews of the manuscript.

#### REFERENCES

- Alwmark C. and Schmitz B. (2007) Extraterrestrial chromite in the resurge deposits of the early Late Ordovician Lockne crater, central Sweden. *Earth Planet. Sci. Lett.* 253, 291–303.
- Alwmark C. and Schmitz B. (2008) The origin of the Brunflo fossil meteorite and extraterrestrial chromite in mid-Ordovician limestone from the Gärde quarry (Jämtland, central Sweden). *Meteorit. Planet. Sci.* 44.
- Anders E. (1964) Origin, age and composition of meteorites. Space Sci. Rev. 3, 583–714.
- Brearley A. J. and Jones R. H. (1998) Chondritic meteorites. In *Planetary Materials* (ed. J. J. Papike). Mineralogical Society of America, Washington, pp. 3-1–3-398.
- Bridges J. C., Schmitz B., Hutchison R., Greenwood R. C., Tassinari M. and Franchi I. A. (2007) Petrographic classification of mid-Ordovician fossil meteorites from Sweden. *Meteorit. Planet. Sci.* 42, 1781–1789.
- Gomes C. B. and Keil K. (1980) *Brazilian Stone Meteorites*. University of New Mexico Press, Albuquerque.
- Goodrich C. A. and Harvey R. P. (2002) The parent magmas of lherzolitic shergottites ALHA77005 and LEW88516: a reevaluation from magmatic inclusions in olivine and chromite. *Meteorit. Planet. Sci.* 37, A54.

- Greenwood R. C., Schmitz B., Bridges J. C., Hutchison R. and Franchi I. A. (2007) Disruption of the L-chondrite parent body: new oxygen isotope evidence from Ordovician relict chromite grains. *Earth Planet. Sci. Lett.* 262, 204– 213.
- Heck P. R., Schmitz B., Baur H. and Wieler R. (2008) Noble gases in fossil meteorites and meteorites from 470 Myr old sediments from southern Sweden and new evidence for the L chondrite parent body breakup event. *Meteorit. Planet. Sci.* 43, 517–528.
- Hofmann B. A., Nyström J. O. and Krähenbühl U. (2000) The Ordovician chondrite from Brunflo, central Sweden. III. Geochemistry of terrestrial alteration. *Lithos* 50, 305–324.
- Hutchison R. (2004) Meteorites: a Petrologic, Chemical and Isotopic Synthesis. Cambridge University Press, Cambridge.
- Jarosewich E., Nelen J. A. and Norberg J. A. (1980) Reference samples for electron microprobe analysis. *Geostand. Newsl.* 4, 43–47.
- Keil K. (1962) On the phase composition of meteorites. J. Geophys. Res. 67, 4055–4061.
- Keil K. and Fredriksson K. (1964) The iron, magnesium, and calcium distribution in coexisting olivines and rhombic pyroxenes of chondrites. J. Geophys. Res. 69, 3487–3515.
- Korochantseva E. V., Trieloff M., Buikin A. I., Lorenz C. A., Ivanova M. A., Schwarz W. H., Hopp J. and Jessberger E. K. (2007) L chondrite asteroid breakup tied to Ordovician meteorite shower by multiple isochron <sup>40</sup>Ar-<sup>39</sup>Ar dating. *Meteorit. Planet. Sci.* 42, 113–130.
- Lorand J. P. and Ceuleneer G. (1989) Silicate and base-metal sulfide inclusions in chromites from the Maqsad area (Oman ophiolite, Gulf of Oman): a model for entrapment. *Lithos* 22, 173–190.
- Mason B. (1963) Olivine composition in chondrites. *Geochim.* Cosmochim. Acta 27, 1011–1023.
- McElduff B. and Stumpfl E. F. (1991) The chromite deposits of the Troodos Complex, Cyprus: evidence for the role of a fluid phase accompanying chromite formation. *Mineral. Deposita* 26, 307–318.
- Melcher F., Grum W., Simon G., Thalhammer T. V. and Stumpfl E. F. (1997) Petrogenesis of the ophiolitic giant chromite deposits of Kempirsai, Kazakhstan: a study of solid and fluid inclusions in chromite. J. Petrol. 38, 1419–1458.

- Nyström J. O., Lindström M. and Wickman F. E. (1988) Discovery of a second Ordovician meteorite using chromite as a tracer. *Nature* 336, 572–574.
- Nyström J. O. and Wickman F. E. (1991) The Ordovician chondrite from Brunflo, central Sweden. II. Secondary minerals. *Lithos* 27, 167–185.
- Rubin A. E. (1990) Kamacite and olivine in ordinary chondrites: intergroup and intragroup relationships. *Geochim. Cosmochim. Acta* 54, 1217–1232.
- Rubin A. E. (1997) Mineralogy of meteorite groups: an update. Meteorit. Planet. Sci. 32, 733–734.
- Schmitz B. and Häggström T. (2006) Extraterrestrial chromite in Middle Ordovician limestone at Kinnekulle, southern Sweden—traces of a major asteroid breakup event. *Meteorit. Planet. Sci.* **41**, 455–466.
- Schmitz B., Häggström T. and Tassinari M. (2003) Sedimentdispersed extraterrestrial chromite traces a major asteroid disruption event. *Science* 300, 961–964.
- Schmitz B., Tassinari M. and Peucker-Ehrenbrink B. (2001) A rain of ordinary chondrites in the early Ordovician. *Earth Planet. Sci. Lett.* **194**, 1–15.
- Schmitz B., Lindström M., Asaro F. and Tassinari M. (1996) Geochemistry of meteorite-rich marine limestone strata and fossil meteorites from the lower Ordovician at Kinnekulle, Sweden. *Earth Planet. Sci. Lett.* **145**, 31–48.
- Simon S. B., Grossman L., Podosek F. A., Zinner E. and Prombo C. A. (1994) Petrography, composition, and origin of large, chromian spinels from the Murchison meteorite. *Geochim. Cosmochim. Acta* 58, 1313–1334.
- Talkington R. W., Watkinson D. H., Whittaker P. J. and Jones P. C. (1984) Platinum-group minerals and other solid inclusions in chromite of ophiolitic complexes: occurrence and petrological significance. *Tschermaks Min. Petr. Mitt.* 32, 285–301.
- Thorslund P., Wickman F. E. and Nyström J. O. (1984) The Ordovician chondrite from Brunflo, central Sweden. I. General description and primary minerals. *Lithos* 17, 87–100.
- Van Schmus W. R. (1969) The mineralogy and petrology of chondritic meteorites. *Earth Sci. Rev.* 5, 145–184.
- Wlotzka F. (1992) Meteoritical Bulletin, No. 72. Meteoritics 27, 109–117.

Associate editor: Alexander N. Krot

1486