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Disruption of the L chondrite parent body: New oxygen isotope evidence from Ordovician relict chromite grains

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Abstract

Mid-Ordovician fossil meteorites found in the Thorsberg quarry, southern Sweden, are believed to have been deposited during a period of enhanced meteorite flux following the fragmentation of the L chondrite parent body. During diagenesis, the fossil meteorites were largely replaced by a secondary mineral assemblage. However, primary chromite grains have been preserved. High-precision oxygen isotope analysis by laser-assisted fluorination has been undertaken in order to confirm the chemical group (H, L or LL) to which the fossil meteorites belong. To test our methodology, chromites extracted from recent ordinary chondrite falls (Holbrook L6, Appley Bridge LL6 and Kernouve H6) have been analyzed and these show that ordinary chondrites can be classified into their respective groups (H, L, or LL) using the oxygen isotopic composition of chromite alone. Results from the Golvsten 001 meteorite demonstrate that this sample is an equilibrated L chondrite. The uniform major and minor element composition of chromites throughout the southern Swedish fossil meteorite section means that it is highly probable that all are L chondrites. High-precision oxygen isotope analysis of relict chromites thus further strengthens the link between the fossil meteorites and the disruption of the L chondrite parent body. The evidence presented here demonstrates that relict chromite grains survive diagenesis and can be used to classify ancient meteoritic material. Analysis of such fossil grains may prove to be a powerful tool, not only in the case of the mid-Ordovician event, but also in examining changes in the relative distribution of meteorite groups throughout geological time.

Keywords: fossil meteorites; oxygen isotopes; Ordovician meteorites; L chondrites; ordinary chondrites; L chondrite parent body; relict chromite grains; meteorite classification; Thorsberg quarry; Golvsten 001 meteorite

1. Introduction

The majority of L chondrites show textural evidence of severe shock and display (U–Th)/He and K–Ar ages, indicating a major degassing event approximately 500 Ma ago (Heymann, 1967; Bogard, 1995). These features are believed to result from the catastrophic disruption of the L chondrite parent asteroid (Haack et al.,

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[✠] Robert Hutchison died on 26 January 2007 when this paper was in the final stages of preparation. Robert was an ever enthusiastic and inspirational colleague. All who met him were given a warm smile and the benefit of his impressive scientific knowledge and understanding. We would like to dedicate this paper to his memory.

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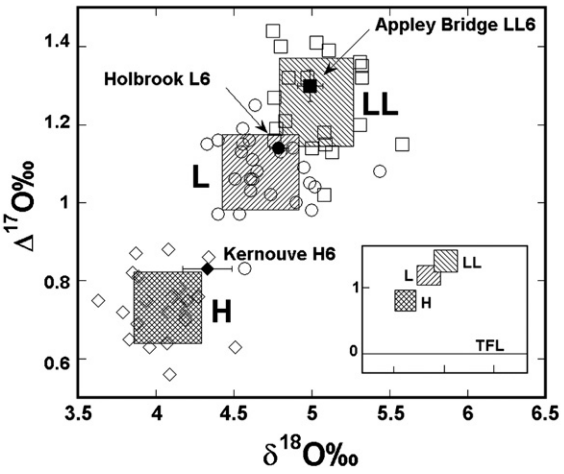

Fig. 1. Plot of whole-rock δ^{18}O versus Δ^{17}O for equilibrated ordinary chondrites. Open symbols are for data obtained by conventional techniques (diamonds: H4-6, circles L4-6, boxes: LL4-6 (Clayton et al., 1991). Filled symbols are for analyses by laser-assisted fluorination (this study). Shaded boxes represent the 1σ error on the whole-rock group mean values for analyses obtained by conventional techniques (Clayton et al., 1991)). Error bars shown for the laser-assisted fluorination analyses are 1σ on the mean of replicate analyses. The inset diagram shows the position of the Terrestrial Fraction Line (TFL) with respect to the H, L and LL 1σ group mean error boxes.

1996). The high abundance of fossil meteorite material in ~470 Ma sediments exposed in the Thorsberg quarry, Kinnekulle, southern Sweden has been linked to this event and indicates a meteorite flux at least two orders of magnitude greater than present day rates (Schmitz et al., 1997, 2001; Heck et al., 2004). A genetic link between the disruption of the L chondrite parent body and the Swedish fossil meteorites has been further strengthened by recent ^{40}Ar–^{39}Ar studies of shocked L chondrites, which yield an age for the break-up event of 470±6 Ma (Korochantseva et al., 2007). This date overlaps the revised stratigraphic age of the mid-Ordovician meteorite-bearing strata of 467±1.6 Ma (Gradstein et al., 2004; Korochantseva et al., 2007). Dynamical modelling indicates that disruption of a ~200 km diameter body may have been the source both of the fossil meteorites and the Flora family of asteroids (Nesvorný et al., 2007).

Petrographic and textural analysis (Schmitz et al., 2001; Bridges et al., in press) confirm that all the Ordovician fossil meteorite samples so far studied are ordinary chondrites, ranging in petrographic grade from 3 to 6. Most of their original silicate mineralogy has been replaced by pseudomorphs (primarily calcite, barite and phyllosilicates). However, relict chromites have largely survived diagenesis (Schmitz et al., 2001). The major and minor element variation in these chromites is broadly consistent with their host meteorite being either L or LL group. However, to be confident that the Swedish samples are related to the L chondrite breakup event requires a more precise classification in terms of their compositional class (H, L or LL) than is possible using such chemical data alone.

For recent ordinary chondrites whole-rock oxygen isotope analysis has proved to be a reliable classification tool capable of assigning individual meteorites to their appropriate H, L or LL groups (Clayton et al., 1991; Folco et al., 2004). The method is based on the fact that ordinary chondrites display an increase in both δ^{18}O and Δ^{17}O (explanation of δ and Δ notation given in Section 2) from H group (lowest values) through L group to LL group (highest values) (Fig. 1). The whole-rock assemblage used to undertake such a classification is predominantly composed of silicates, whereas in the fossil meteorites the only primary phase remaining is chromite. In this paper, we present the results of a study using chromite alone to classify Ordovician fossil meteorites. Obtaining sufficient chromite (222 grains) to make this analysis involved a major effort in terms of mineral separation and subsequent SEM-EDS analysis of each individual grain. As a control, chromites were also extracted from three recent ordinary chondrites falls (H, L and LL) and their oxygen isotope composition determined. The analysis of the recent falls provides a basis for assessing the extent to which the fossil chromites preserve a record of their original isotopic composition and hence are able to furnish reliable information about the compositional class of their host meteorite.

2. Methods

Chromite grains were extracted by acid dissolution from an approximately 7 g sample of the Golvsten 001

Fig. 2. Slab of limestone from the Golvsten bed split along a bedding plane, showing the fossil meteorite from which the chromites used in this study were extracted.

meteorite. This meteorite was chosen because both the SEM characteristics and major element chemistry indicated that its chromites are particularly well preserved. Moreover, this meteorite is relatively rich in chromites, thus providing enough material on which to undertake the acid dissolution work. The Golvsten 001 meteorite measures 6 × 9 × 2 cm (Fig. 2) and is the only specimen located within the Golvsten bed, which immediately overlies the more meteorite-rich Arkeologen bed (Schmitz et al., 2001).

Previously, the oxygen isotope composition of chromite has been used to study iron meteorites (Clayton and Mayeda, 1996). Classification work on ordinary chondrites is almost exclusively based on whole-rock analyses, which are dominated by the contribution from the silicate fraction, mainly olivine, pyroxene and feldspar. To our knowledge, high-precision oxygen isotope classification studies of ordinary chondrites using chromite grains alone have not previously been reported. To test the feasibility of this approach, in addition to the Ordovician fossil meteorite, chromites were extracted from ~10 g samples of three recent ordinary chondrite falls: Holbrook L6, Appley Bridge LL6 and Kernouve H6.

The fossil meteorite sample was dissolved in 6 M HCl at room temperature. Chromite grains > 63 μm were picked from the residue with a fine brush under the light microscope. Samples of the three observed falls were gently crushed with a mortar and pestle, then submitted to leaching first in HCl (6 M, 20 °C) and thereafter in HF (18 M, 20 °C, 72 h). After leaching, all grains were examined under the light microscope in order to ensure that they were free from impurities. All recovered chromite grains, both fossil and recent, were individually analyzed by SEM-EDS methods to confirm their chromite composition and purity. Grains were mounted on carbon tape without any coating, and the shortest possible analysis time was used (<10 s) to avoid

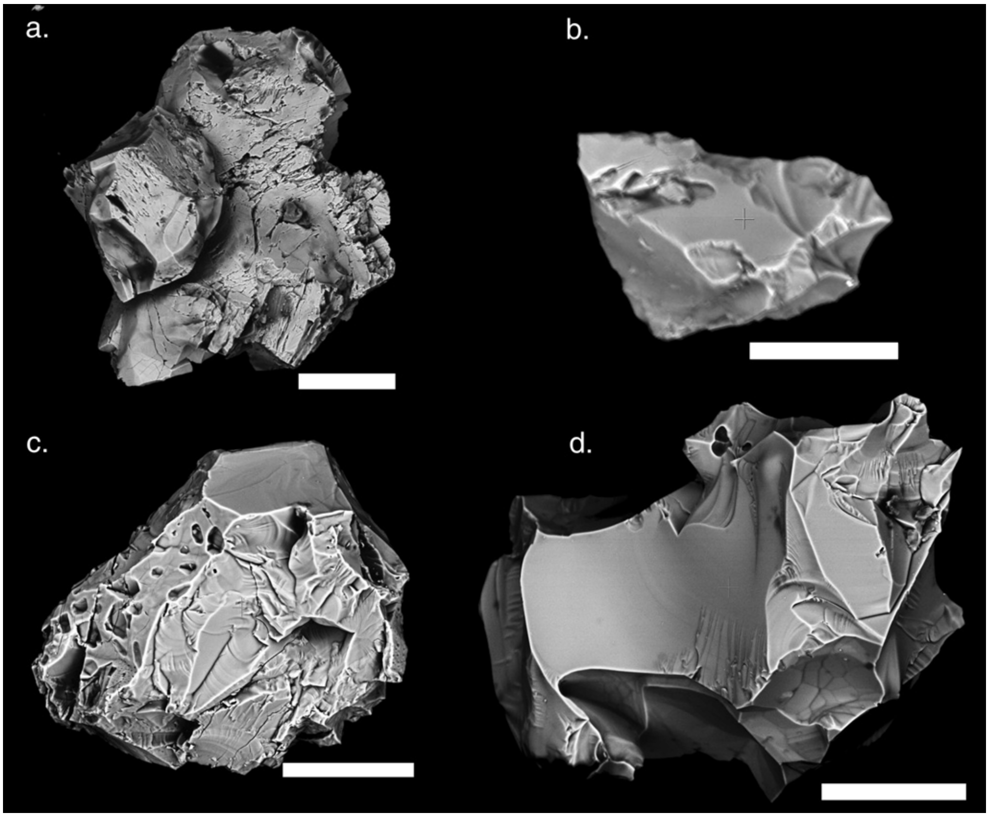

Fig. 3. Back-scattered electron images of chromites extracted from recent ordinary chondrite falls and Swedish fossil meteorite. a. Golvsten 001 meteorite fossil chromite scale 100 μm. b. Chromite from Holbrook (L6) scale 30 μm. c. Chromite from Appley Bridge (LL6) scale 50 μm. d. Chromite from Kernouve (H6) scale 50 μm. Apart from some etched pits on the edge of the Appley Bridge (LL6) chromite all of the grains display relatively pristine morphologies. The size of the chromites from the Golvsten 001 meteorite are particularly large, which lends support to the evidence from oxygen isotopes that this sample is a highly equilibrated type.

affecting the composition of the grains. After analysis, grains were washed in ethanol and distilled water. SEM images of representative chromite grains from the fossil meteorite and all three chondrite falls are shown in Fig. 3. Oxygen isotope analysis of the chromite grains was undertaken by laser-assisted fluorination at the Open University (Miller et al., 1999).

One issue encountered during the course of this study was obtaining a large enough chromite sample to ensure that the oxygen yield would be sufficient to give the precision required to discriminate between L, LL and H groups. The first batch of material processed from the Golvsten 001 meteorite yielded 22 chromite grains (average grain-size ca. 100 μm diameter) weighing 0.12 mg. With a theoretical oxygen yield of 28.6% for $FeCr_2O_4$, this would have given only 34 μg of oxygen, whereas our normal range for silicates is approximately 500 to 1200 μg. As a consequence, further batches of material were processed and a total of 222 relict chromite grains extracted, with a sample mass of 1.59 mg. In the final event, only about 0.9 mg of the relict grains were run for oxygen isotope analysis, as this was deemed sufficient for classification purposes, allowing some material to be retained for other ongoing studies.

Isotope ratio measurements are given using the standard δ notation, so that $\delta^{18}O=((^{18}O/^{16}O_{sample}/^{18}O/^{16}O_{ref})-1)\times 1000$ and similarly for $\delta^{17}O$ using the $^{17}O/^{16}O$ ratio. Values are expressed as per mil (‰) deviation from the international reference standard V-SMOW (Vienna-Standard Mean Ocean Water). On an oxygen three-isotope diagram, in which $\delta^{18}O$ is plotted against $\delta^{17}O$, samples related to each other by mass dependent fractionation processes define linear arrays, with a slope of approximately 0.52 (Clayton, 1993; Clayton and Mayeda, 1996). Thus, silicate rocks on Earth plot as such an array which is generally referred to as the Terrestrial Fractionation Line (TFL) (Clayton and Mayeda, 1996; Rumble et al., 2007). In meteorite studies the TFL is a useful reference for assessing the degree to which extraterrestrial material departs from the isotopic composition of the Earth's oxygen reservoir (Clayton and Mayeda, 1996; Rumble et al., 2007). The term $\Delta^{17}O$ is used to quantify the extent to which a sample deviates from the TFL and is defined as $\Delta^{17}O=\delta^{17}O-0.52\delta^{18}O$ (Clayton and Mayeda, 1996). For ease of comparison with previous oxygen isotope studies of ordinary chondrites (Clayton et al., 1991) this conventional definition of $\Delta^{17}O$ is used throughout this paper, rather than the mathematically more rigorous formulation proposed by Miller (2002).

3. Results

3.1. Precision of small sample analyses

To evaluate overall precision when analysing small oxygen samples a number of test runs were carried out using the PSRI obsidian oxygen isotope secondary standard (Miller et al., 1999). The results obtained are summarised in Table 1. Also shown in Table 1 is an average of 62 normal-sized (~2 mg) obsidian standards run over a twelve-month interval that overlapped the period during which the chromites were analyzed. In

Table 1

Whole-rock samples and standards	N [a]	μg [b]	$\delta^{17}O$‰	1σ	$\delta^{18}O$‰	1σ	$\Delta^{17}O$‰	1σ
Kernouve (H6)	2	696–779	3.09	0.08	4.33	0.16	0.83	0.00
Holbrook (L6)	2	699–777	3.63	0.04	4.79	0.06	1.14	0.01
Appley Bridge (LL6)	2	648–885	3.89	0.00	4.99	0.08	1.30	0.04
PSRI Obsidian (range 800–1200 μg oxygen)	62	1043	3.80	0.04	7.26	0.07	0.02	0.02
PSRI Obsidian (range 100–300 μg oxygen)	7	199	3.97	0.10	7.61	0.20	0.01	0.02
Chromite samples	N [a]	μg [b]	$\delta^{17}O$‰	1σ [c]	$\delta^{18}O$‰	1σ [c]	$\Delta^{17}O$‰	1σ [c]
Kernouve (H6)	1	124	0.58	0.10	−0.25	0.20	0.71	0.05
Holbrook (L6)	1	45	0.28	0.20	−1.65	0.40	1.14	0.10
Appley Bridge (LL6)	1	72	0.58	0.20	−1.13	0.40	1.16	0.10
Fossil Meteorite (Golvsten bed)	1	214	0.95	0.10	−0.23	0.20	1.07	0.05

[a] N = Number of individual laser-assisted fluorination analyses.

[b] μg = micrograms of oxygen liberated from sample. The single values quoted for the obsidians represent the mean value of all the analyses undertaken.

[c] Quoted errors for the chromite samples are estimates based on the results from a range of standards, including the small-sized aliquot PSRI obsidian runs given above.

terms of precision and reproducibility these large samples are indistinguishable from the previously reported results for the PSRI obsidian standard (Miller et al., 1999) and indicate that the system was operating satisfactorily throughout this period. The small oxygen samples (100–300 μg O_2) show decreased precision compared to the larger ones, with a small shift to higher δ^{17}O and δ^{18}O values (Table 1). However, Δ^{17}O values of the small and large oxygen samples are identical and the magnitude of the δ^{17}O and δ^{18}O shifts insufficient to have any significant influence on the chromite characterisation work.

3.2. Laser-assisted fluorination compared to conventional analysis techniques

At present, a representative dataset of oxygen isotope analyses for each of the three ordinary chondrite iron groups (H, L and LL) has only been collected by conventional techniques, i.e. using externally-heated nickel bombs (Clayton et al., 1991). A systematic study using laser-assisted fluorination is only available for H group samples (Folco et al., 2004). However, it is clear from the results of this study that laser fluorination and conventional techniques give comparable results for the H group chondrites, with laser fluorination yielding somewhat higher precision (Clayton et al., 1991; Folco et al., 2004). The effectiveness of laser fluorination techniques in separating ordinary chondrites into their respective iron groups is further shown by analysis of three recent falls: Kernouve (H6), Holbrook (L6) and Appley Bridge (LL6). Results are given in Table 1 and plotted on Fig. 1. Both Holbrook (L6) and Appley bridge (LL6) plot within the 1σ error box for their respective iron groups. Kernouve (H6) plots slightly outside the H group 1σ box. However, the good separation between the H and L groups on Fig. 1 means that the oxygen isotope analysis for Kernouve can be used to unambiguously assign it to the H group. These results again demonstrate that oxygen isotope analysis by laser-assisted fluorination is a reliable classification tool for ordinary chondrites.

3.3. Chromite analyses

The oxygen isotope results obtained for the chromites extracted from the Ordovician fossil meteorite and the three recent falls are given in Table 1 and plotted on Fig. 4. Also shown on Fig. 4, as shaded zones, are the ±1σ errors on the Δ^{17}O group mean values for H, L and LL ordinary chondrites (Clayton et al., 1991). In terms of their δ^{18}O values chromites from both the fossil meteorite and recent falls are up to 6.4‰ mass fractionated relative to their respective whole-rock values (Table 1). However, it remains valid to plot on Fig. 4 the ±1σ Δ^{17}O variation seen in average H, L and LL chondrites (Fig. 1). This is because mass-dependant relationships on plots of Δ^{17}O against δ^{18}O are represented by horizontal lines. Thus, the upper and lower Δ^{17}O values used to define the H, L, LL boxes on Fig. 1 can be extrapolated to lower values of δ^{18}O as horizontal lines on Fig. 4 and still remain valid despite the significant levels of isotopic fractionation present.

As seen previously on Fig. 1, there is a clear separation between the H and L groups with respect to their Δ^{17}O values, whereas the L and LL chondrites display a small degree of overlap at the 1σ level. In terms of the chromites extracted from previously classified falls, the analysis for Kernouve (H6) plots well within the H chondrite field. Holbrook (L6) plots in the L field, but close to the boundary with the LL field and Appley Bridge (LL6) plots on the overlap between the L and LL field. Also shown on Fig. 4 are the results for the Ordovician chromites, which plot well within the L chondrite field. The relict grains were the largest of the extraterrestrial samples run in this study (214 μg O_2, Table 1). The principal conclusion to be drawn from the oxygen isotope analysis of the fossil chromite grains (Table 1, Fig. 2) is that the Swedish Ordovician

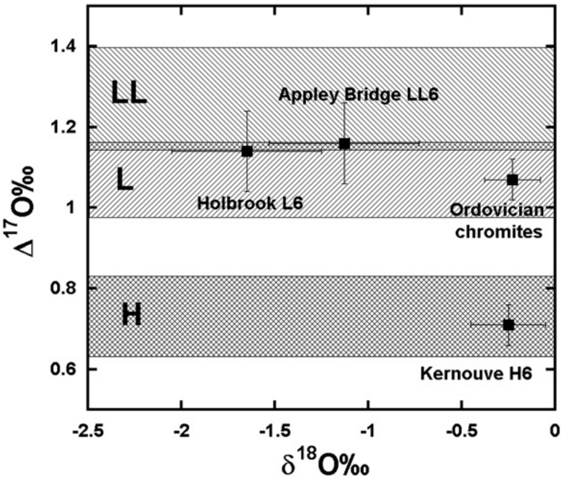

Fig. 4. Plot of δ^{18}O versus Δ^{17}O for chromite grains obtained from recent meteorite falls and from the Golvsten 001 Ordovician fossil meteorite. The shaded boxes are the 1σ error on the H, L and LL whole-rock group mean values obtained by conventional techniques (Clayton et al., 1991). Error bars on the chromite analyses are 1σ .The analysis for the Ordovician chromites falls centrally within the L group box and hence further strengthens the case that these samples were derived from the break-up of the L group parent asteroid.

Table 2a
Calculated temperatures for recent falls and fossil meteorite

		$\delta^{18}O_{\text{whole-rock}}$	$\delta^{18}O_{\text{olivine calculated}}$ [a]	$\delta^{18}O_{\text{chromite}}$	$\Delta_{\text{chromite–olivine}}$	T (°C) [b]
Kernouve	H6	4.33	3.80	−0.25	−4.05	558
Holbrook	L6	4.79	4.26	−1.65	−5.91	383
Appley Bridge	LL6	4.99	4.46	−1.13	−5.59	407
Fossil meteorite		4.70 [c]	4.17	−0.23	−4.40	517

[a] $\delta^{18}O_{\text{olivine calculated}}=\delta^{18}{}_{\text{Whole Rock}} - 0.53$.

[b] Temperatures calculated using calibrations of Zheng (1991, 1993).

[c] Average L chondrite $\delta^{18}O$ value from Clayton et al. (1991) is used as $\delta^{18}O_{\text{whole-rock}}$ value for the fossil meteorite.

meteorites can be unequivocally classified as L group ordinary chondrites.

4. Discussion

4.1. How pristine are the fossil chromites?

The Ordovician fossil meteorites from Sweden have been extensively altered, such that their original mineralogy has been almost completely replaced by a secondary assemblage of calcite, barite and phyllosilicates (Schmitz et al., 2001). The only primary phase present in these samples is chromite. In view of the pervasively altered nature of these meteorites, it is important to try and assess just how pristine are the remaining chromite grains. A detailed study of major and minor element variation in the fossil chromites (Schmitz et al., 2001) did reveal some compositional variation that would appear to reflect diagenetic alteration. In particular, the negative correlation between FeO and ZnO (as well MnO) in some relict grains (Schmitz et al., 2001) suggests that FeO can be replaced by ZnO and MnO during diagenesis. However, in other respects the elemental variation displayed by fossil chromites shows a remarkably good match to chromites from recent ordinary chondrites (Schmitz et al., 2001).

The oxygen isotope data presented here provides a further means of assessing the extent to which the fossil chromite grains were altered during diagenesis. For the recent ordinary chondrite falls $\delta^{18}O_{\text{chromite}}$ values show significant isotopic fractionation, on the order of 4.6‰ to 6.1‰, when compared to measured $\delta^{18}O_{\text{whole-rock}}$ values (Table 2a). This feature is broadly consistent with the fact that all three are equilibrated type 6 chondrites, and hence cooled slowly within their parent body from peak temperatures in the range 750 to 950 °C (Hutchison, 2004). For the fossil meteorite it is not possible to measure a $\delta^{18}O_{\text{whole-rock}}$ value. However, assuming that prior to diagenesis this would have been close to the average L chondrite $\delta^{18}O$ value of 4.7‰ (Clayton et al., 1991), then the measured $\delta^{18}O_{\text{chromite}}$ indicates a similar degree of fractionation for the fossil chromites to that seen in the recent falls, i.e. about 5‰. The degree of isotopic fractionation shown by the fossil chromites is consistent with their host meteorite being a relatively equilibrated type and hence is in agreement with the evidence from relict textures which indicate that the Golvsten 001 meteorite is petrographic type 6 (Bridges et al., in press).

Table 2b
Calculation of average olivine offset from whole-rock composition

Sample	Group	$\delta^{18}O$ [a]	$\delta^{18}O$ [b]	$\delta^{18}O$
		Whole rock	Olivine	Whole rock–olivine
Allegan	H5	3.97	3.37	0.60
Olivenza	LL5	4.88	4.33	0.55
Mocs	L6	4.55	4.10	0.45
Modoc	L6	4.65	4.17	0.48
St. Severin	LL6	4.76	4.19	0.57
MEAN				0.53

[a] Whole-rock data Clayton et al. (1991).

[b] Olivine data Clayton (1993).

The close match between measured $\delta^{18}O$ values for the chromites from both recent and fossil meteorites is strong evidence that the fossil grains did not undergo significant oxygen isotope exchange during diagenesis. This feature is further illustrated by comparing metamorphic temperatures calculated using the measured oxygen isotope whole-rock and chromite values (Tables 2a and 2b). Although we have not directly measured $\delta^{18}O_{\text{olivine}}$ in the recent falls these values can be calculated assuming a constant isotopic offset of 0.53‰ from the associated whole-rock value (Table 2b). Calculated $\Delta_{\text{chromite–olivine}}$ values for both recent falls and the fossil meteorite have been used to derive isotopic closure temperatures using the calibration of Zheng (1991, 1993). For the recent falls these values range from 383 °C to 558 °C, with the fossil meteorite giving a value of 517 °C (Table 2a). Consideration of the analytical errors suggests that the uncertainty on these temperature estimates is in excess of ±50 °C.

While the temperature estimates obtained here are very low compared to those derived by pyroxene thermometry on type 6 ordinary chondrites, which generally give temperatures in excess of 850 °C (McSween and Patchen, 1989; Chamont and McSween, 2000), they are more in keeping with results obtained using olivine–Cr–spinel and olivine–chromite pairs (O'Neill and Wall, 1987; Johnson and Prinz, 1991; Sack and Ghiorso, 1991; Wlotzka, 2005). Although it is unrealistic to draw too many conclusions from the calculations presented in Tables 2a and 2b, they serve to demonstrate that the fossil chromites give comparable results to those from recent falls, and hence do not appear to have been significantly altered by later diagenetic processes. The conodont colour alteration index measured in the Kinnekulle area indicate only weak heating during diagenesis, of at the most 80 to 110 °C. This evidence again supports the conclusion that the fossil chromites from this locality are relatively pristine.

4.2. How many ordinary chondrite parent bodies are there?

Primarily on the basis of olivine and kamacite compositions, ordinary chondrites are conventionally sub-divided into three groups: H, L and LL (Kallemeyn et al., 1989; Rubin, 1990). These classification techniques are able to uniquely define the H group, but do not show a distinct break between the L and the LL groups. Hence, there is a sub-set of ordinary chondrites which appear to straddle the boundary between the L and LL groups and these have sometimes been given the designation L/LL (Rubin, 1990; Wasson and Wang, 1991). Holbrook has in the past been included in this sub-group (Rubin, 1990; Wasson and Wang, 1991), although it is presently classified as an L6 (Meteoritical Bulletin Database). The transitional character of Holbrook is also reflected in the whole-rock and chromite oxygen isotope values which plot on the overlap between the L and LL fields (Figs. 1, 4). Since the H, L and LL groups are generally considered to originate from distinct parent bodies, the recognition of a sub-group that straddles the boundary between the L and LL fields is problematic. It has been suggested that the L/LL meteorites are a distinct ordinary chondrite grouping derived from a fourth independent parent body (Wasson and Wang, 1991; Fredrich and Lipschutz, 2001). As noted earlier, a representative oxygen isotope dataset for the ordinary chondrites has only been collected by conventional analysis. The relationship between L and LL groups will probably remain unresolved until systematic high-precision oxygen isotope studies by laser-assisted fluorination are available.

In the case of the fossil meteorites the nature of the relationship between the L and LL groups is not a significant issue. The oxygen isotope analysis of the fossil chromites (Fig. 4) plots centrally in the L group field, well away from the overlap with the LL field. Thus, the Ordovician fossil meteorites were not part of a transitional L/LL sub-group as Holbrook may be, but were unambiguously members of the L group.

4.3. Are all the Ordovician fossil meteorites L group?

In this study, we have undertaken high-precision oxygen isotope analysis of chromites extracted from only one Ordovician fossil meteorite. We have been able to show with a high degree of certainty that this meteorite is L group in composition. The question that arises from this is whether it is reasonable to infer that all, or at least the majority, of the other Ordovician fossil meteorites are also L group. The fossil chromite grains show very little variation in Cr_2O_3, TiO_2, Al_2O_3,V_2O_5 and MgO, either within or between different meteorites (Schmitz et al., 2001). As noted previously, MnO, FeO and ZnO do display variation indicative of minor degrees of secondary alteration (Schmitz et al., 2001). In Table 3 the composition of chromite grains from the Golvsten 001 meteorite is compared to the average fossil meteorite value (Schmitz et al., 2001). It is evident from this comparison (Table 3) that the grains analyzed from the Golvsten 001 meteorite have a very similar composition to all the other fossil chromites so far studied. The uniform composition of relict chromites seen in the Swedish Ordovician fossil meteorites, in conjunction with the oxygen isotope data presented here, indicates that all are from a single group, namely the L chondrites.

Table 3
Average composition (wt.%) of chromite from the Golvsten bed compared to average chromite from all of the Ordovician fossil meteorites

	Golvsten bed meteorite [a]	All fossil meteorites [b]
Cr_2O_3	57.00 ± 0.60	57.6 ± 1.30
Al_2O_3	5.59 ± 0.23	5.53 ± 0.29
MgO	2.57 ± 0.18	2.57 ± 0.83
TiO_2	2.93 ± 0.17	2.73 ± 0.40
V_2O_5	0.90 ± 0.08	0.89 ± 0.04
FeO	29.30 ± 0.80	26.94 ± 3.89
MnO	0.78 ± 0.13	1.01 ± 0.33
ZnO	0.36 ± 0.12	1.86 ± 2.43
Total	99.43	99.13

[a] Based on 12 analyses of 10 grains.

[b] Data from Schmitz et al. (2001).

4.4. Implications for the break-up of the L group asteroid

Since 1992, systematic study of mid-Ordovician marine limestone in the Thorsberg quarry has located over fifty fossil meteorites (Schmitz et al., 2001; Bridges et al., in press). In addition to these larger meteorite fragments, sediment-dispersed extraterrestrial chromite grains have been located both in the Thorsberg quarry and in the nearby disused Hällekis quarry (Schmitz and Häggström, 2006). The fossil meteorites recovered from the Thorsberg quarry occur in at least 12 different beds, separated by prominent hardgrounds (Schmitz et al., 2001). Unfortunately, it is not possible to tell whether meteorites within the same bed relate to single, or multiple showers, or to large individual meteorites that broke up in the water column. However, stratigraphic and sedimentologic evidence demonstrates that meteorites in different beds (representing a stratigraphic interval of 1.8 million years) represent distinct fall events. A minimum of 12 meteorite falls over 1.8 Ma at one locality indicates extremely high flux rates compared to present day values. Calculations based on the Thorsberg quarry occurrences indicate that flux rates during the mid-Ordovician were at least two orders of magnitude greater than those prevailing today (Schmitz et al., 2001). It has been suggested that this enhanced flux rate was caused by the disruption of the L chondrite parent body (Schmitz et al., 1997, 2001).

Most L chondrites show evidence of intense shock and appear to have undergone heating during an event with an age of approximately 500 Ma (Heymann, 1967; Bogard, 1995). However, measured ages show considerable spread. Thus, for example, a detailed Ar–Ar study of the Peace River L6 chondrite showed evidence of major Ar degassing and gave a plateau age of 450± 30 Ma (McConville et al., 1988). The upper limit to the age of the Peace River L6 event includes the age of the fossil meteorites. More recent ^{40}Ar–^{39}Ar studies of 5 shocked L chondrites further strengthens the case for a link between enhanced Ordovician flux rates and the disruption of the L chondrite parent body, yielding an age for the break-up event of 470±6 Ma (Korochantseva et al., 2007). The revised stratigraphic age of the mid-Ordovician meteorite-bearing beds is 467±1.6 Ma (Gradstein et al., 2004; Korochantseva et al., 2007). There is therefore good agreement between the shock ages recorded by L chondrites and the stratigraphic age of the fossil meteorite-bearing sediments.

The link between the disruption of the L chondrite parent body and enhanced Ordovician flux rates has been further strengthened by the low cosmic ray exposure ages of the fossil chromites and their systematic increase with decreasing stratigraphic age (Heck et al., 2004). Thus, chromites from the Arkeologen bed, the oldest fossil meteorite-bearing horizon, have exposure ages of about 100,000 years, whereas those in the youngest Goda Lagret and Glaskarten beds approach and sometimes exceed 10^6 years (Heck et al., 2004). These ages are somewhat lower than the exposure ages of L chondrites falling today, which are generally in the range 3 to 60 Ma (Wieler, 2002). The most likely explanation for the relatively short exposure ages of the fossil chromites is that following a major collisional event in the asteroid belt material was directly injected into an orbital resonance and then rapidly ejected on an Earth-crossing orbit. In contrast, the much longer exposure ages of recent meteorites can be explained as the result of relatively slow drift into an orbital resonance subsequent to ejection from their parent asteroid (Heck et al., 2004).

All of the foregoing evidence points to a strong link between the L chondrite disruption event and enhanced mid-Ordovician meteorite flux rates. However, one essential piece of information required to confirm this relationship has until now been lacking, namely the exact classification of the fossil meteorites. The evidence presented here confirms that most, if not all, the fossil meteorites from the Thorsberg quarry are L group ordinary chondrites. In conjunction with the age relationships discussed above, this new data confirms the link between the break-up of the L chondrite parent body at ~470 Ma and the enhanced flux rates that prevailed in the mid-Ordovician. Although the evidence for this event presently comes from a relatively restricted area, this clearly must have been a global phenomenon. Recent work on sediment-dispersed extraterrestrial chromites has demonstrated that the high flux rates seen in the Thorsberg quarry sequence are also present in the nearby Hällekis quarry (Schmitz and Häggström, 2006) and in the Dagerhamn area, approximately 300 km to the southeast (Schmitz et al., 2003). In addition, there is some evidence of an enhanced terrestrial cratering rate at this time (Schmitz et al., 2001). Recent studies of one crater in central Sweden dated at 458 Ma, and therefore potentially related to the disruption of the L chondrite parent body, has led to the identification of dispersed chromites which are chemically similar to those found in L chondrites (Alwmark and Schmitz, 2007).

In mid-Ordovician times the flux distribution of ordinary chondrites would have been totally unlike that seen at the present day, with the H and LL groups being completely swamped by the L chondrites. At other times in Earth history the complement of meteorites reaching the Earth may also have varied markedly from the present day distribution. The delivery of meteorites to Earth is likely to be related to impact events in the asteroid belt and hence should vary with time (Nesvorný et al., 2002, 2007). Until now there has not been a realistic means of assessing how the meteorite distribution might have varied through geological time. With only a modest increase in sensitivity it should soon be possible to measure the oxygen isotopic composition of sediment dispersed chromites with sufficient precision to reliably classify this material. Such a development will, for the first time, allow us to examine how the composition of extraterrestrial material arriving on Earth has changed through geological time.

5. Conclusions

In this paper, we demonstrate that relict chromite grains found in fossil meteorites have survived diagenesis relatively intact, and hence can furnish useful information concerning the original composition of their extraterrestrial source. Oxygen isotope analysis of chromites from the Golvsten 001 meteorite demonstrate this to be L group and by extrapolation indicates that all the Swedish fossil meteorites were also L group chondrites. This result further strengthens the case in favour of the ~470 Ma break-up of the L chondrite parent body being the cause of the enhanced mid-Ordovician meteorite flux. This would clearly have been a global phenomenon. The flux distribution of ordinary chondrites at this time would have been totally unlike that seen today, with the H and LL groups being completely swamped by the L chondrites In future studies, only a modest improvement in analytical sensitivity should allow us to use chromite as a probe for the time-integrated meteorite flux over a much larger slice of Earth's history than is presently possible.

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