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A search for H-chondritic chromite grains in sediments that formed immediately after the breakup of the L-chondrite parent body 470 Ma ago

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Abstract

A large abundance of L-chondritic material, mainly in the form of fossil meteorites and chromite grains from micrometeorites, has been found in mid-Ordovician 470 Ma old sediments globally. The material has been determined to be ejecta from the L chondrite parent body breakup event, a major collision in the asteroid belt 470 Ma ago. In this study we search the same sediments for H-chondritic chromite grains in order to improve our understanding of the extraterrestrial flux to Earth after the asteroid breakup event. We have used SIMS in conjunction with quantitative SEM/EDS to determine the three oxygen isotopic and elemental compositions, respectively, of a total of 120 randomly selected, sediment-dispersed extraterrestrial chromite grains mainly representing micrometeorites from 470 Ma old post-breakup limestone from the Thorsberg quarry in Sweden and the Lynna River site in Russia. We show that 99% or more of the grains are L-chondritic, whereas the H-chondritic fraction is 1% or less. The L-/H-chondrite ratio after the breakup thus was >99 compared to 1.1 in today's meteoritic flux. This represents independent evidence, in agreement with previous estimates based on sediment-dispersed extraterrestrial chromite grain abundances and sedimentation rates, of a two orders of magnitude higher post-breakup flux of L-chondritic material in the micrometeorite fraction. Finally, we confirm the usefulness of three oxygen isotopic SIMS analyses of individual extraterrestrial chromite grains for classification of equilibrated ordinary chondrites. The H- and L-chondritic chromites differ both in their three oxygen isotopic and elemental compositions, but there is some overlap between the groups. In chromite, TiO_2 is the oxide most resistant to diagenesis, and the combined application of TiO_2 and oxygen three-isotope analysis can resolve uncertainties arising from the compositional overlaps.

1. INTRODUCTION

Abundant extraterrestrial material of L-chondritic composition has been discovered in mid-Ordovician sediments worldwide, reflecting a two orders of magnitude enhanced

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flux of such material to Earth following the breakup of the L-chondrite parent body in the asteroid belt 470 Ma ago (e.g., Schmitz et al., 2001, 2003, 2008). The material consists of fossil meteorites (1–21 cm in diameter, Schmitz et al., 1996, 2001; Tassinari et al., 2004) and fossil micrometeorites (~63–250 μm in diameter, Schmitz et al., 2003, 2008; Schmitz and Häggström, 2006), as well as impactor material from the Lockne impact structure in Sweden (Alwmark and Schmitz, 2007). The only relict, common original minerals in these objects are extraterrestrial chromite and chrome-spinel (abbreviated ECs hereafter). Most fossil meteorites, sediment-dispersed EC (SEC) grains and the impactor EC grains from Lockne have been classified as equilibrated L-chondritic based on major and minor elemental compositions of chromite and, in rare cases, its silicate inclusions (Schmitz et al., 1996, 2001, 2003, 2008; Tassinari et al., 2004; Schmitz and Häggström, 2006; Alwmark and Schmitz, 2009; Lindskog et al., 2012). This classification was confirmed initially for a batch of ~100 chromite grains from a single fossil meteorite Gol 001 by oxygen isotopic analysis using laser-assisted fluorination mass spectrometry (Greenwood et al., 2007). Ion microprobe oxygen isotopic analyses of individual chromite grains further confirmed a common L-chondrite parent body for five fossil meteorites, 15 SEC grains from two different sediment beds at the Thorsberg quarry in Sweden, nine SEC grains from two beds from the Puxi River formation in China (Heck et al., 2010), and seven EC grains from the Lockne impactor (Schmitz et al., 2011). This and other independent lines of evidence such as a sediment age-matching gradient of short cosmic-ray exposure ages of fossil L-chondrites (Heck et al., 2004, 2008) ties the origin of the overabundant extraterrestrial material to the L-chondrite parent body breakup (LCPB). See Schmitz (2013) for a comprehensive review on this subject. There is only one known extraterrestrial specimen from these sediments with a different composition, a fossil meteorite tentatively classified as winonaite-like (Schmitz et al., 2014).

Although chromites from the different equilibrated ordinary chondrite groups (L, H, and LL) differ in their major and minor element compositions, there is also some spread and overlap (Bunch et al., 1967). Thus, only the average composition of an assemblage of grains can give information about whether any group dominates an assemblage (Schmitz et al., 2001). The advantage of oxygen isotope ion microprobe analysis is the capability, with some caveats as discussed in the present paper, to determine whether an individual chromite grain belongs either to the H group or the L or LL groups (Heck et al., 2010). Chromites from the L and the LL groups have partially overlapping oxygen isotopic compositions, but rare silicate inclusions can differentiate individual grains from these groups (Alwmark and Schmitz, 2009).

From the studies cited above it is clear that L-chondritic material dominated the meteorite flux ~470 Ma ago; in fact, it obscured any contribution from the background flux. A combined oxygen isotope and elemental composition study with a larger number of samples than previous investigations (e.g., Heck et al., 2010) would provide further constraints on the composition of the flux of extraterrestrial matter to Earth in the mid-Ordovician and would answer the question if the background flux is detectable and distinguishable from LCPB event ejecta with improved sample statistics. Based on noble gas analyses, the SEC grains have been shown to be remnants of micrometeorites (Heck et al., 2008; Meier et al., 2010). Thus, by analyzing oxygen isotopes and elemental compositions of a large number of such grains one can establish a statistically significant estimate of the contribution to the flux from different groups of chrome-spinel bearing micrometeorites and meteorites. The ratio of macroscopic H- to L-chondrites falling on Earth today is ~1 (363 H-chondrites/411 L-chondrites = 0.9; Met. Bull. Database, June 18, 2015, http://www.lpi.usra.edu/meteor/metbull.php). Unmelted and melted micrometeorites were found in Antarctica (e.g., Suavet et al., 2011; Van Ginneken et al., 2012) and melted ones in deep-sea sediments from the Indian Ocean (e.g., Prasad et al., 2015). A fraction of those contain unmelted chromites that were used to classify them. A majority of the chromite-bearing micrometeorites have an L or H chondritic origin but a clear grouping is difficult because of the inherent overlap in elemental compositions of the groups (e.g. Genge, 2008; Van Ginneken et al. 2011) or altered bulk oxygen isotopic composition by a combination of mixing with air and mass-fractionation during atmospheric entry (e.g., Suavet et al., 2011). The number of classified ordinary chondritic recent micrometeorites that contain unmelted chromite is still small and prevents an accurate H/L chondritic ratio to be determined but still allows to conclude that the abundance ratio is not very different from macroscopic meteorites. If one could determine the H/L ratio of extraterrestrial material after the LCPB, and assuming that before this event the ratio was similar to the present, we would obtain a refined perspective of the magnitude of the increase in the L-chondritic flux. The present estimate of the change in flux relies on EC grain abundances in the sediments and estimates of sedimentation rates (e.g., Schmitz and Häggström, 2006). Our study also has the potential to test the idea that ejecta from the LCPB hit other types of ordinary chondritic asteroids and generated secondary ejecta that subsequently hit Earth. To address these ideas, we designed the present study comprising oxygen isotopic analyses of 120 randomly selected SEC grains from different beds formed shortly after the LCPB in southern Sweden and Russia. This adds to the 24 previously analyzed SEC grains from southern Sweden and China (Heck et al., 2010).

2. SAMPLES AND METHODS

2.1. Sample selection

For this study we randomly selected 120 SEC grains (63–250 μm in diameter) from two different localities: 83 SEC grains are from three different sediment beds, Arkeologen (Ark), Golvsten (Gol) and Sextummen (Sex) in the well-studied Thorsberg quarry in southern Sweden. Oxygen isotopes in SEC grains from these beds have been previously studied (Heck et al., 2010); however, here we increase the number of grains by a factor of 5.5. In addition to this, we included 37 SEC grains from the Ly2U bed of the Lynna River section in the St. Petersburg region of northwestern Russia (see Lindskog et al., 2012), with age equivalent to that of the Arkeologen bed at Thorsberg (Fig. 1). The Ly2U bed comprises the interval from 0.13 to 0.23 cm above the base of bed Ly1 in Lindskog et al. (2012). Our sample of 14.5 kg from the Ly2U bed yielded 187 chrome spinel grains >63 μm, of which 173 were identified as typical EC grains and 14 as other chrome spinel. No SEC grains from the Lynna locality have been previously studied for oxygen isotopes.

Because we are here mainly interested in establishing the H/L ratio in the post-LCPB flux we have only used chromite grains that based on their elemental composition are of equilibrated, ordinary chondritic composition (e.g., Bunch et al., 1967; Schmitz et al., 2003, 2008; Wlotzka, 2005; Heck et al., 2010; Lindskog et al., 2012). We justify this choice by the fact that the vast majority of chrome spinels with non-ordinary chondritic element composition in the beds most likely are terrestrial. It would require a major investment in time and resources to analyze a large batch of such grains for oxygen isotopes in order to possibly locate rare extraterrestrial grains that are not from ordinary chondrites. A separate project is planned in order to address this aspect of the post-LCPB micrometeorite flux.

2.2. Sample preparation

The SEC grains were extracted from carbonate sediments using established procedures involving acid dissolution and sieving (Schmitz et al., 2003; Lindskog et al., 2012). Sieved grains from the acid residue were hand picked, placed on carbon tape and qualitatively identified as chromite from equilibrated ordinary chondrites at Lund University with an Oxford Instruments INCA X-Sight energy-dispersive spectrometer (EDS) attached to a Hitachi S-3400N scanning electron microscope (SEM). At Lund University and at the Field Museum SEC grains and grains

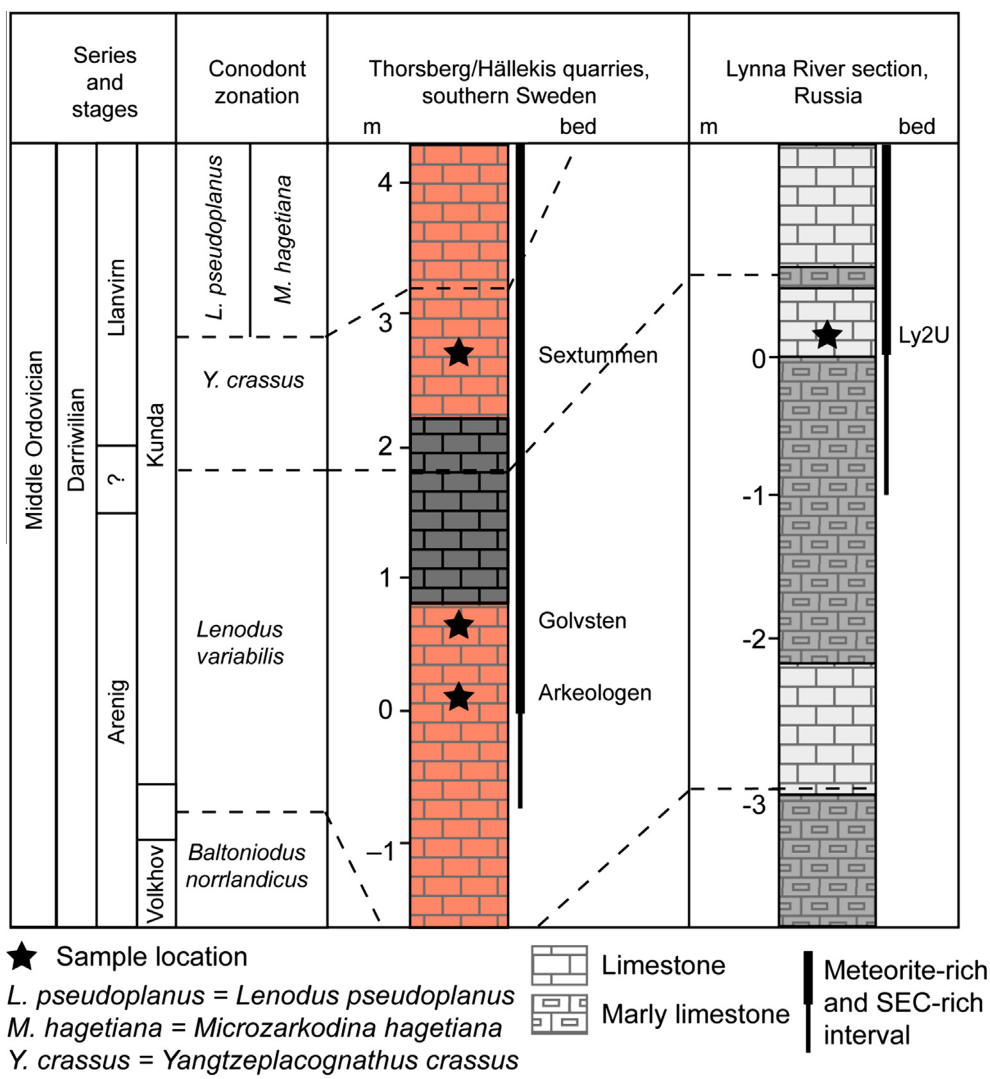

Fig. 1. Schematic stratigraphic columns at Lynna River, Russia and Thorsberg/Hällekis quarries, Sweden, sample locations, and correlations of beds based on biochronology. The SEC-rich interval (black vertical bar) has a range of 1–2 million years. Stratigraphic information from Schmitz et al. (2008) and Lindskog et al. (2012).

of the oxygen-isotope chromite standard UWCr-3 (Heck et al., 2010) were then mounted in epoxy and polished until suitable for secondary ion mass spectrometry (SIMS) following the method described in Heck et al. (2010). Polishing quality was monitored with a Bruker 3D microscope at the Keck-II facility of the NUANCE Center of Northwestern University. We repolished mounts if the relief between mineral grains and epoxy surface was above ~2 μm to minimize topographic mass fractionation effects, as described by Kita et al. (2009).

All polished mounts were gold-coated and subsequently imaged with a Zeiss EVO 60 SEM at the Field Museum in secondary electrons to record topography and in backscattered electrons (BSE) to map compositional contrast prior to SIMS analysis.

2.3. SIMS three oxygen isotope analyses

Oxygen isotopes from individual chromite grains were analyzed with a Cameca IMS-1280 SIMS at the University of Wisconsin-Madison (WiscSIMS Laboratory). Analytical procedures were very similar to the ones used in our previous study (Heck et al., 2010) and are optimized to obtain high-precision measurements of oxygen isotopes. We used a primary Cs^+ ion beam of 4.8 ± 0.4 nA in a total potential of ~20 kV, resulting in a $\sim 10 \times 15$ μm spot size. Charge compensation was achieved with an electron gun and mass resolving power was set to ~5000. Secondary ions of all stable oxygen isotopes $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ were analyzed in multicollection mode. The magnetic field was stabilized with a nuclear magnetic resonance (NMR) magnetometer to better than ±10 ppm within 48 h. As for our previous study we analyzed each spot twice to obtain sufficient precision on $^{17}O/^{16}O$ ratios. Unknowns were bracketed with analyses of the centrally mounted UWCr-3 standard. The magnitude of the $[^{16}O^{1}H]^-$ peak was recorded after each spot analysis and used to correct for a tailing interference on the $^{17}O^-$ peak. The average correction and standard deviation was 0.2 ± 0.3‰. In most cases the difference between the corrections from the two analyses of the same spot is small as illustrated in EA-Fig. 1. In the present study we reject all data with a tailing correction >1.1‰ (EA-Fig. 1). For more details on the analytical procedure we direct the reader to section §3.1.2 in Heck et al. (2010).

2.4. Post-SIMS imaging and quantitative EDS analyses

After SIMS analyses the gold coating was carefully removed using 0.25 μm diamond paste on a polishing cloth. Subsequently, mounts were carbon-coated and all grains were imaged again in the Field Museum's Zeiss Evo 60 SEM to confirm that no SIMS crater was irregular and no irregularities like cracks or epoxy were sampled. All craters were regular and no spot analysis needed to be rejected on this ground. Major and minor elemental compositions of the chromite grains were analyzed quantitatively with an Oxford Instruments X-Max 50 silicon-drift EDS detector at the Field Museum at 15 kV in several sessions with currents ranging from 0.5 to 1 nA. Beam stability was monitored throughout the session by intermittently measuring copper tape located at the edge of the mount and a UWCr-3 standard located in the center of each mount. Several spots on each grain were analyzed and unknowns were bracketed with UWCr-3 chromite analyses. Standardization, matrix corrections and data analysis were performed with Oxford Instruments AZtec software.

3. RESULTS

3.1. Oxygen isotope ratios

We investigated 120 EC grains and 31 grains of UWCr-3 chromite standards for oxygen isotopes with a total of 519 analyses (Table 1 and Table EA-1, electronic appendix). The $\Delta^{17}O$ values distinguish chromite grains by comparing them to known chondritic sources. Therefore, we discuss oxygen three-isotope data as $\Delta^{17}O$ ($=\delta^{17}O - 0.52 \times \delta^{18}O$), instead of $\delta^{18}O$ and $\delta^{17}O$ values, while all three values are shown in Table 1 and EA-1.

The majority of the EC grains (113) have $\Delta^{17}O$ values from 0.8‰ to 1.5‰ with an average of 1.05 ± 0.16‰ (SD). This places them directly onto the group $\Delta^{17}O$ average of equilibrated L chondrites (Figs. 2 and 3), which is at 1.07 ± 0.09‰ (Clayton et al., 1991). Six further EC grains have $\Delta^{17}O$ values ranging from 0.67 ± 0.27‰ to 0.78 ± 0.21‰. Their compositions are consistent with those of equilibrated H chondrites, which have a group average of 0.73 ± 0.09‰ (Figs. 2 and 3). Within 2SD uncertainties, the $\Delta^{17}O$ values of five of these six grains overlap with the L-chondritic range.

Table 1
The average oxygen isotopic compositions of analyzed sediment-dispersed extraterrestrial chromite (SEC) grains (n = number of grains analyzed). δ-values in ‰ deviation from UWCr-3 standard value, Δ-values in ‰ deviation from the terrestrial fractionation line. Sex = Sextummen bed; Gol = Golvsten bed; Ark = Arkeologen bed; Ly2U = Lynna River 2U bed.

Locality and bed name		$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$
Thorsberg quarry				
Sex	$n = 38$; 1SD	-2.16 ± 0.57	-0.13 ± 0.30	0.99 ± 0.16
Gol	$n = 18$; 1SD	-2.69 ± 0.83	-0.27 ± 0.40	1.11 ± 0.23
Ark/Sex	$n = 27$; 1SD	-1.88 ± 0.46	0.11 ± 0.30	1.09 ± 0.16
Lynna River				
Ly2U	$n = 37$; 1SD	-1.86 ± 0.90	0.07 ± 0.47	1.04 ± 0.11

The lowest $\Delta^{17}O$ value of 0.3 ± 0.1‰ was obtained from grain EC21-gr13. This value is between those of H chondrites and terrestrial fractionation line (TFL). While the OH correction for this grain was on the higher side (1.1 ± 0.1‰; $N = 4$), the correction was within our accepted range (see Fig. EA-1). The cause for such a $\Delta^{17}O$ value remains unclear. The simplest explanation for this would be that the SIMS analysis included a crack filled with epoxy or possibly a terrestrial alteration phase that resulted in a mixed signal. Although the polished grain cross-section shows some epoxy-filled cracks these areas were avoided by SIMS analysis and there is no evidence for having included another phase from our pre/post-SIMS SEM survey nor can it be excluded, as the SIMS-sampled volume itself was not imaged tomographically. We can exclude that mixed analyses occurred for most other grains, otherwise our distribution would have been shifted systematically towards lower $\Delta^{17}O$ values and the total average would be below the L chondrite $\Delta^{17}O$ group average.

$\Delta^{17}O$ values of some of the grains fall into the range that is occupied by both L and LL chondrites. However, the distribution of obtained $\Delta^{17}O$ values more closely resembles the distribution of values from L chondrites rather than from LL chondrites (Fig. 3). For reference, we also observe that most of our $\Delta^{17}O$ data from SECs and the analytical standard UWCr-3 obtained during the same session with the same analytical conditions can be fit with a Gaussian distribution reasonably well (Fig. 3).

The average $\Delta^{17}O$ and $\delta^{18}O$ values between the different beds and localities overlap within 1σ (Fig. 2). The range of $\delta^{18}O$ values is largest for Lynna River SECs (−5.8 to −0.4‰) and smallest for Ark/Sex SECs (−3.3 to −1.3‰). The range of $\Delta^{17}O$ values is smallest in Lynna River SECs and largest in Sex SECs (Table 1).

3.2. Elemental compositions

Elemental compositions of the analyzed grains (Table 2, Table EA-1) are close to the averages of previously measured SEC grains from correlated sediment beds in Sweden, China and Russia and are consistent with L-chondritic composition (Fig. 4). The most diagnostic oxide in chromite for classification purposes is TiO_2. As observed in all previous studies of SECs (e.g., Schmitz and Häggström, 2006), TiO_2 and V_2O_3 are most robust and inert to diagenetic alteration and therefore most diagnostic of all oxides to identify ordinary chondritic SECs. Although the ranges of TiO_2 concentrations in chromites from H, L and LL chondrites overlap to some degree, the distribution is different with distinct averages for H, L and LL chondrites, in contrast to V_2O_3 where the ranges of the three ordinary chondrite group overlap more widely. Compositions of TiO_2 in our SEC sample set average at 3.0 wt%, range from 1.7 wt% to 3.6 wt% and, similar to $\Delta^{17}O$, the distribution is most consistent with an L-chondritic composition (Fig. 4). This is different than the distribution of TiO_2 of chromites from modern micrometeorites (Fig. 5, and Van Ginneken et al., 2012; Prasad et al., 2015), which reflects different sources.

The major and minor elemental composition of EC21-gr13, which has the lowest $\Delta^{17}O$ value, is typical of L chondrites.

4. DISCUSSION

4.1. Are there H-chondritic grains in L chondrite-rich post-breakup sediments?

Finding non-L-chondritic SECs in mid-Ordovician post-LCPB sediments would be intriguing and is necessary to

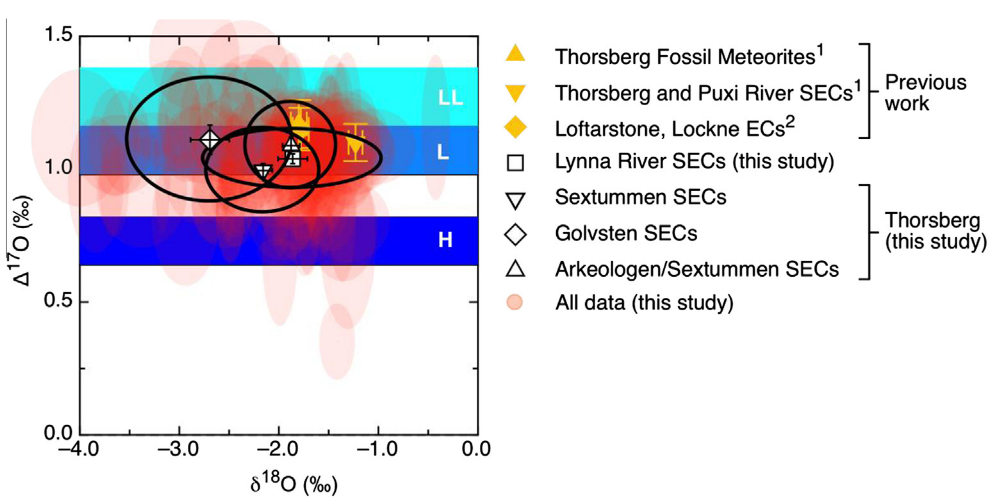

Fig. 2. Values of $\Delta^{17}O$ and $\delta^{18}O$ of all SEC grains analyzed in this study. Individual data points and their 2σ errors are shown as transparent orange ellipses. Areas with more data points increase in orange intensity. Average values of beds are shown as black open symbols with 2SE error bars and 2SD ellipses; averages from previous studies are shown as yellow symbols with 2SE error bars. [1]Thorsberg and Puxi River data are from Heck et al. (2010); [2]Lockne data is from Schmitz et al. (2011). In all figures blue fields represent average $\Delta^{17}O$ compositions for equilibrated H, L, and LL chondrites (petrologic types 4 to 6) determined by Clayton et al. (1991). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

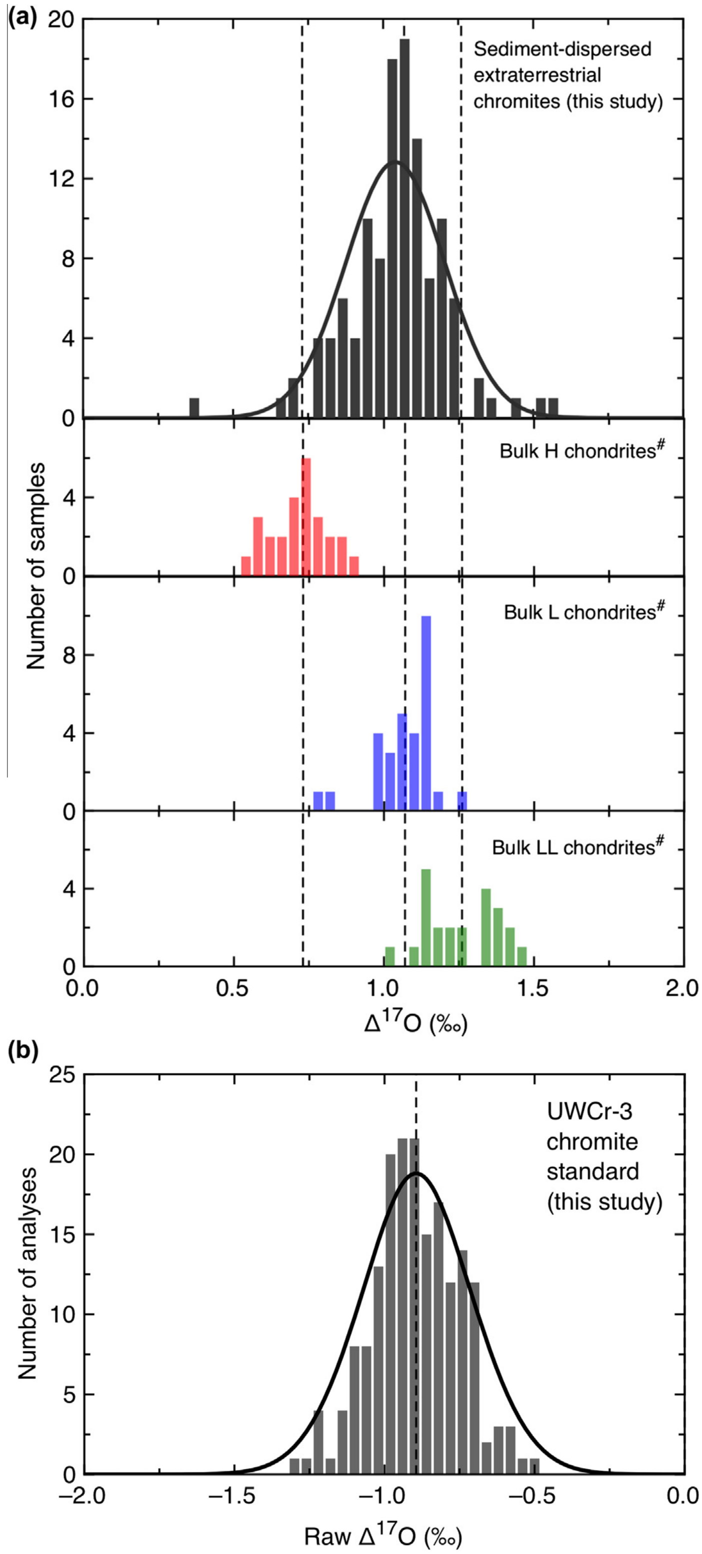

Fig. 3. Histograms of $\Delta^{17}O$ values of (a) SEC grains from this SIMS study compared with published data by Clayton et al. (1991)# obtained from whole rock analyses of equilibrated ordinary chondrites of petrologic type 4 to 6 by laser-assisted fluorination mass spectrometry; (b) and raw values from SIMS analyses of UWCr-3 chromite standards analyzed during the same session as the unknowns in this study. Solid lines are Gaussian fits; vertical dashed lines are averages.

Table 2
The average elemental concentrations in wt% of analyzed SEC grains (n = number of grains analyzed). Intragrain reproducibilities are on average 0.5–0.7 wt% for major elements and 0.1–0.4 wt% for minor elements.

Locality and bed name		MgO	Al_2O_3	TiO_2	V_2O_3	Cr_2O_3	MnO	FeO	ZnO	Total
Thorsberg quarry										
Sex	$n = 38$; 1SD	3.02 ± 0.61	6.29 ± 0.33	2.96 ± 0.31	0.86 ± 0.08	57.76 ± 1.05	0.73 ± 0.15	27.09 ± 1.33	0.47 ± 0.35	99.18
Gol	$n = 18$; 1SD	2.97 ± 0.75	6.44 ± 0.80	2.75 ± 0.46	0.88 ± 0.05	59.12 ± 1.22	0.81 ± 0.16	26.55 ± 2.02	0.76 ± 0.46	100.28
Ark/Sex	$n = 27$; 1SD	2.73 ± 0.54	5.87 ± 0.35	3.10 ± 0.20	0.73 ± 0.05	58.55 ± 0.72	0.73 ± 0.10	27.91 ± 0.85	0.43 ± 0.17	100.05
Lynna River										
Ly2U	$n = 37$; 1SD	2.74 ± 0.82	5.95 ± 0.24	3.13 ± 0.24	0.89 ± 0.07	58.93 ± 0.93	0.68 ± 0.09	25.52 ± 2.54	1.34 ± 2.35	99.18

determine the composition of the non-L-chondritic fraction of the chrome-spinel bearing extraterrestrial flux to Earth immediately following the asteroid breakup event. We found 9 grains, which are nominally consistent with H chondrites, in terms of their $\Delta^{17}O$ values (0.7–0.8‰). Only one of them, EC17-gr25 from Ark/Sex, has a $\Delta^{17}O$ value (0.7 ± 0.1‰) that is typical of H chondrites and does not overlap directly with the $\Delta^{17}O$ range of L chondrites, whereas its TiO_2 concentration of 2.5 ± 0.1 wt% is typical for L chondrites but also overlaps with the H-chondritic range. There are several other grains with similarly low $\Delta^{17}O$ values (EC17-gr09, EC26-gr17, EC17-gr26, EC21-gr27, EC26-gr05, EC22-gr43, EC18-gr23, and EC22-gr13) but their (2 SE) errors are large enough to reach into the range occupied by L chondrites. We argue in the following that possibly all of these grains with low $\Delta^{17}O$ values, are part of the L-chondritic population. The distribution of the TiO_2 data of those 9 grains is in good agreement with the distribution of TiO_2 data from the other, clearly L-chondritic grains from this study (Fig. 4). Based on the overall distribution of $\Delta^{17}O$ and TiO_2 data together (Fig. 3 and EA-Fig. 2) it is likely that most of the grains are L-chondritic with only one grain being H-chondritic, as illustrated in the probability density distributions (EA-Fig. 2).

In addition, estimates based on present day fall statistics suggest the expected H-chondrite abundance should have been very low. For instance, if we assume a 100× higher-than-current flux of L chondrites at the time of deposition of the SEC grains, then we would expect to find only one H-chondritic sample (0.9%) out of 120 samples, if we assume the fraction of H chondrites from background falls was consistent with present observations (42% of current ordinary chondrite falls; Meteoritical Bulletin Database, June 18, 2015). It is also worth noting that in sediments formed immediately before the LCPB at the localities dealt with here we only find on the order of 1–5 EC grains per 100 kg sediment (Schmitz and Häggström, 2006; Lindskog et al., 2012). We can estimate how many H chondritic grains we would find in post-LCPB sediments if we (1) assume the background flux of H-chondritic grains remained constant after the LCPB, (2) assume 42% of all ordinary chondritic material in the background is H chondritic as today (3) using the pre-LCPB ordinary chondritic SEC abundance of 1 to 5 grains per 100 kg of sediment and the post-LCPB abundance of 173 SEC grains in 14.5 kg of sediment. We would then only expect 0.06–0.3 H-chondritic grains in 14.5 kg of post-LCPB sediments. This reasoning builds on the assumption that sedimentation rates were relatively constant through the sections, which is generally supported by lithological and biostratigraphical considerations (e.g., Schmitz, 2013). When we add the 24 L-chondritic SEC grains from sediments of the same interval in Sweden and China from a previous study (Heck et al., 2010) we obtain a total of 142 L-chondritic grains that gives a fraction of 0.7% H-chondritic grains. The present study sets the upper limit for H chondrites to 1%, at least for microscopic material, which is strong evidence – independent of previous estimates – for an at least two orders of magnitude increase in the flux of L-chondritic matter in the micrometeorite fraction following the LCPB.

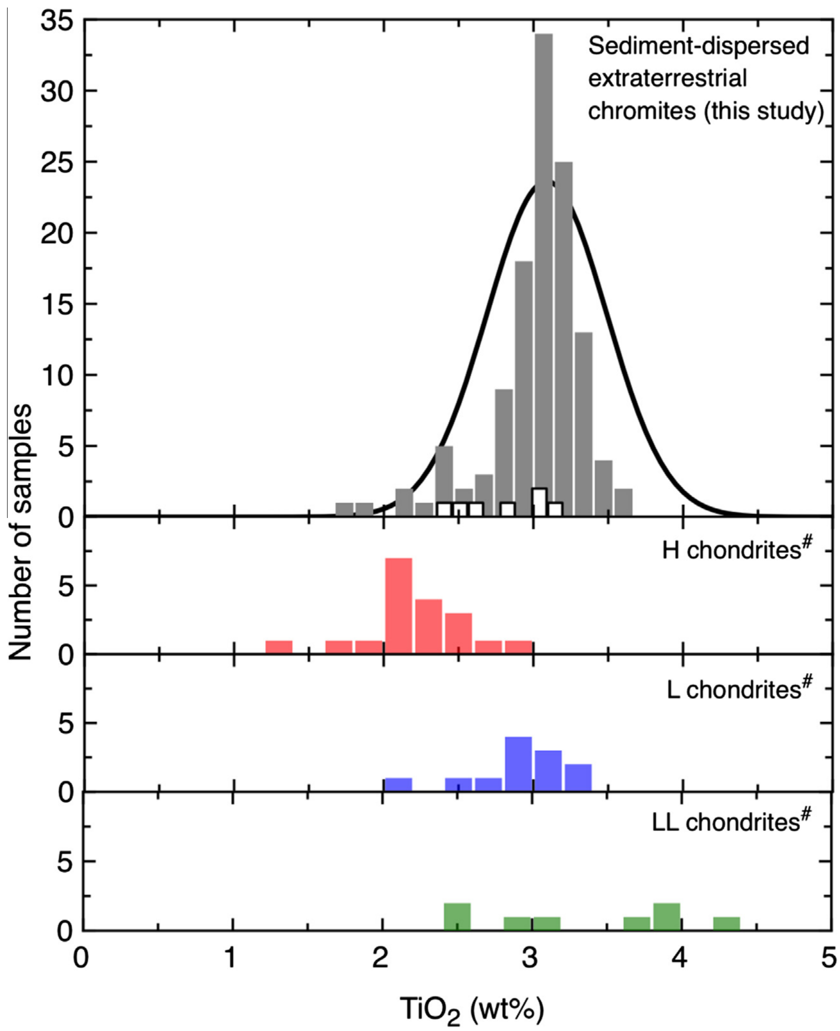

Fig. 4. Histograms and Gaussian fit (solid line) of TiO_2 concentrations of SEC grains from this study compared with published microprobe data# of chromites from equilibrated ordinary chondrites (Snetsinger et al. (1967), Bunch et al. (1967), Wlotzka (2005)). The SEC grains from this study with low $\Delta^{17}O$ values are shown as a white histogram in the top panel.

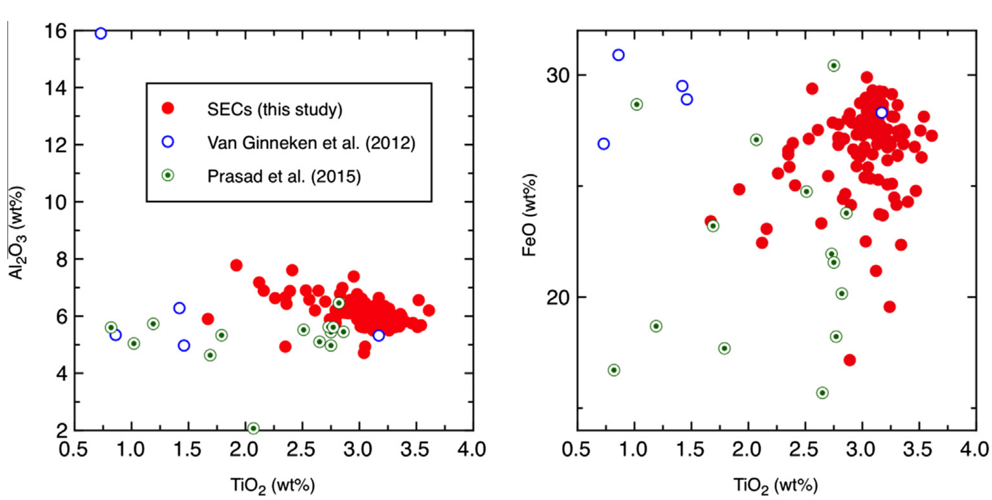

Fig. 5. Comparison of SEC data from this study with TiO_2, Al_2O_3 and FeO concentrations in chromite within modern micrometeorites from two recent studies. The diagrams indicates that the total number of L chondritic and H chondritic grains within modern ordinary chondritic micrometeorites is similar based on TiO_2 contents (also see Fig. 4).

We note that in rare cases H-chondritic inclusions were found within L chondrites, like in the Barwell L6 chondrite (Hutchison et al., 1988). However, based on our current records, the probability of finding such an inclusion in all known L chondrites is ~0.1%. Therefore, the probability of an H-chondritic SEC grain being an inclusion is very low; lower than the probability of being an H-chondritic micrometeorite.

4.2. Are there LL-chondritic grains in L-chondrite-rich post-breakup sediments?

The possibility exists that some of the grains investigated are LL-chondritic because they fall in the natural overlap of the ranges of $\Delta^{17}O$ values and TiO_2 concentrations of L and LL chondrites. However, we think this is highly unlikely for the following reasons: (1) the distribution of $\Delta^{17}O$ values and TiO_2 concentrations best match those of L chondrites; and (2) if we assume the same background fraction of LL chondrites as recent (11% of all current ordinary chondrite falls), and assume a 100× overabundance of L-chondritic material (98%) in the post-LCPB sediments from where our SEC grains were extracted, we would expect virtually no LL-chondritic grains (0.2%) among the 120 samples.

4.3. A chondrule origin for low $\Delta^{17}O$ values?

Kita et al. (2010) reported that chondrules in LL3 chondrites show $\Delta^{17}O$ values of $0.5 \pm 0.9‰$, which is systematically lower than those of bulk LL3 chondrites but similar to bulk H-chondrites. Thus, an alternative explanation of low $\Delta^{17}O$ values in some chromite grains could be that they originated from chromite in chondrules. However, chromite does not occur in most chondrules, except as small grains (⩽10 μm) in FeO-rich chondrules in carbonaceous chondrites (e.g., Jones, 1990). Chromite rarely occurs in chondrules in unequilibrated ordinary chondrites (e.g., Jones, 1990). In contrast, our samples include large chromite grains (>63 μm) or small fragments of large grains and are therefore unlikely to be from chondrules. Although there have been observations of larger (~200 μm) chromite grains in a subset of Cr-rich chondrules in ordinary chondrites, such chondrules are very rare (<0.1% of all ordinary chondrites; Krot and Rubin, 1993). Thus, coarse chromite from Cr-rich chondrules are unlikely to make up a significant fraction of sediment-dispersed chromite grains.

4.4. Implications and new constraints on the composition of the background flux

The data presented here further corroborate the findings in previous studies that the accretion of extraterrestrial material to Earth after the LCPB is dominated by L-chondritic material. We have established upper limits for H-chondritic material of ~0.8 to ~1%. If there were more than one H-chondritic grain this would imply a higher H-chondritic meteorite flux than today. Such a high flux could be qualitatively explained by LCPB ejecta hitting an H-chondritic asteroid that generated secondary fragments that were injected into an orbital resonance resulting in short travel times to Earth, within ~10^5–10^6 years, like the L chondrites (Heck et al., 2004). In such a hypothetical scenario a high total mass of L-chondritic material would be obtained from the large number of fragments produced during the catastrophic collision versus a low total mass from the smaller number of fragments generated as secondary ejecta from an hypothetical H-chondritic asteroid nearby that got hit by L-chondritic projectiles. Numerical simulations could model such a scenario and determine the probability ratio of such secondary ejecta reaching Earth versus the abundant ejecta from the catastrophically disrupted L-chondrite parent body.

Based on all the arguments presented above, we conclude that the flux composition was dominated by L-chondritic material with 1% or less of H-chondritic material. This flux is consistent not only with the work presented here but also with all other observations from extraterrestrial matter in mid-Ordovician sediments. It furthermore predicts that a fossil H-chondritic meteorite could be discovered within the next decade, assuming current fossil meteorite discovery rates.

5. CONCLUSIONS

1. Based on new oxygen isotope data of sediment-dispersed extraterrestrial chromite grains from the Thorsberg Quarry in Sweden and for the first time from the Lynna River locality in Russia we confirm that the extraterrestrial flux to Earth in the mid-Ordovician was dominated by L-chondritic material.
2. For the ordinary chondritic micrometeorites falling on Earth after the LCPB we determine a lower limit for the L-chondritic fraction of 99% and an upper limit for the H-chondritic fraction of 1%.
3. We confirm the usefulness of $\Delta^{17}O$ values from individual chromite grains from equilibrated ordinary chondrites for classification purposes. We note, however, that because of the natural overlap between the different ordinary chondrite groups there can remain an ambiguity regarding classification in some cases. The combined approach of oxygen isotope and TiO_2 analyses can in most cases be used to resolve the origin of single grains.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.11.042.

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