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A single asteroidal source for extraterrestrial Ordovician chromite grains from Sweden and China: High-precision oxygen three-isotope SIMS analysis

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Abstract

We examined oxygen three-isotope ratios of 48 extraterrestrial chromite (EC) grains extracted from mid-Ordovician sediments from two different locations in Sweden, and one location in south-central China. The ages of the sediments (~470 Ma) coincide with the breakup event of the L chondrite parent asteroid. Elemental compositions of the chromite grains are generally consistent with their origin from L or LL chondrite parent bodies. The average $\Delta^{17}O$ (‰-deviation from the terrestrial mass-fractionation line, measured *in situ* from 15 µm spots by secondary ion mass spectrometry; SIMS) of EC grains extracted from fossil meteorites from Thorsberg and Brunflo are 1.17 ± 0.09‰ (2σ) and 1.25 ± 0.16‰, respectively, and those of fossil micrometeorites from Thorsberg and Puxi River are 1.10 ± 0.09‰, and 1.11 ± 0.12‰, respectively. Within uncertainty these values are all the same and consistent with the L chondrite group average $\Delta^{17}O = 1.07 \pm 0.18$‰, but also with the LL chondrite group average $\Delta^{17}O = 1.26 \pm 0.24$‰ (Clayton et al., 1991). We conclude that the studied EC grains from correlated sediments from Sweden and China are related, and most likely originated in the same event, the L chondrite parent body breakup. We also analyzed chromites of modern H, L and LL chondrites and show that their $\Delta^{17}O$ values coincide with averages of $\Delta^{17}O$ of bulk analyses of H, L and LL chondrites. This study demonstrates that *in situ* oxygen isotope data measured by SIMS are accurate and precise if carefully standardized, and can be used to classify individual extraterrestrial chromite grains found in sediments.

1. INTRODUCTION

The breakup of the parent body of the L chondrite meteorite group is the best documented asteroid disruption event of younger solar system history (Anders, 1964; Heymann, 1967; Keil et al., 1994; Bogard, 1995; Haack et al., 1996). This event led to degassing of the parent body which is reflected in a prominent ^{40}Ar–^{39}Ar age peak at ~0.5 Ga in recently fallen L chondrites (e.g., Bogard, 1995). Such a large age peak is not seen in any other group of meteorites in the last billion years. Many L chondrite meteorites also show extensive shock features, attributed to the violent collision leading to the breakup of the parent asteroid (Heymann, 1967). The most promising place to find direct fragments of the primary breakup event is in well-preserved marine sediments. A systematic search in an active quarry of Ordovician limestone of ~470 Ma in southern Sweden (Thorsberg quarry near Kinnekulle, ~160 km northwest of Göteborg; Fig. 1) led to the discovery of more than 87 relict, fossil meteorites, many found on different hardground surfaces (Schmitz et al.,

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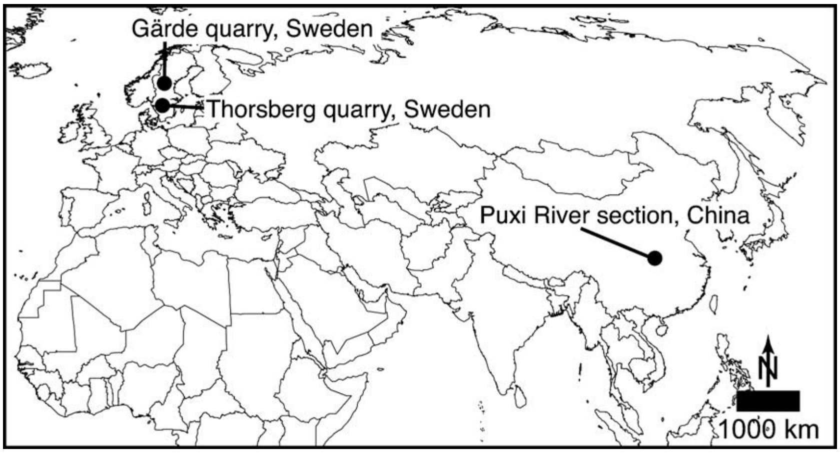

Fig. 1. Sampling locations: Thorsberg quarry, Kinnekulle, southern Sweden, Gärde quarry, central Sweden and Puxi River section, south-central China.

2001, 2009). During diagenesis the original meteorite mineralogy has been almost completely altered, except for the very resistant mineral chromite ($FeCr_2O_4$).

Besides the 87 fossil meteorites from Thorsberg (Schmitz et al., 2001, 2009), two other Ordovician fossil meteorites have been described: Brunflo, the first described mid-Ordovician fossil meteorite (Thorslund and Wickman, 1981; Thorslund et al., 1984) found in the Gärde quarry in central Sweden ~600 km north of Thorsberg, and Gullhögen 001 from Billingen mountain in southern Sweden ~35 km southeast of Thorsberg (Tassinari et al., 2004). Thousands of sediment-dispersed extraterrestrial chromite (SEC) grains were recovered from the same sediments at Thorsberg and from sediments of similar age at other locations in southern Sweden (Schmitz et al., 2003, 2008; Schmitz and Häggström, 2006), in central Sweden (Alwmark and Schmitz 2009a) and in south-central China (Schmitz et al., 2008). These SEC grains are rich in light noble gases from solar wind and are interpreted as remnants of fossil micrometeorites (Heck et al., 2008; Meier et al., 2009). The large number of micrometeorites found within a relatively small volume of sediment (abundance ~1–6 grains per kg of rock compared to 0.01 grains per kg in older Ordovician sediments where no meteorites were found and in much younger Cenozoic sediments; Cronholm and Schmitz, 2007) led Schmitz et al. (2001, 2003) to estimate the post-breakup flux of extraterrestrial matter to Earth to be about two orders of magnitude higher than today.

The base of the meteorite-rich bearing sediment bed at Thorsberg, Arkeologen, is in the *Lenodus variabilis* Conodont Zone and has an age of 467.3 ± 1.6 Ma according to the Geologic Time Scale 2004 (Cooper and Sadler, 2004). The temporal coincidence of the deposition of these sediments with the L chondrite parent body breakup event (improved age 470 ± 6 Ma; Korochantseva et al., 2007), has led to the hypothesis that the meteorites and micrometeorites are fragments produced during the breakup event (Schmitz et al., 2001, 2003). This hypothesis has been substantiated by the discovery of unusually short cosmic-ray exposure ages of the fossil meteorites (~0.1–1 Myr; Heck et al., 2004) and the observation that the exposure ages systematically increase with decreasing sediment ages (dated by conodont biochronology and sedimentation rates). This correlation suggests that the meteorites were generated in a single event and subsequently arrived on Earth at different times (Heck et al., 2004, 2008). The short exposure ages can be explained by recent dynamical model simulations of the breakup event (Nesvorný et al., 2009).

Analyses of major and minor elements showed that well-preserved extraterrestrial chromite grains extracted from the fossil meteorites and representing micrometeorites have compositions consistent with chromites of recently fallen L and LL chondrites (Schmitz et al., 2001, 2003; Schmitz and Häggström, 2006). Major element analyses of inclusions of original meteoritic silicate minerals (pyroxenes and olivines) found to occur in some mid-Ordovician extraterrestrial chromite grains confirm an L rather than LL chondritic origin of the material (Alwmark and Schmitz, 2009b). Texturally well-preserved but pseudomorphed chondrules (Schmitz et al., 2001) allow an additional comparison with recent meteorites. Mean diameters of fossil chondrules in sections of six fossil meteorites from Thorsberg (0.5 ± 0.1 μm, 1 SD; Bridges et al., 2007) are more consistent with mean diameters of recent L chondrites (~0.5 mm), than LL (~0.6 mm) or H chondrites (~0.3 mm; Rubin, 2000). However, the mean chrondrule size method can only be applied where the textural information is preserved. Also, fossil micrometeorites are much more abundant than fossil meteorites, and therefore more readily found, cannot be classified this way.

Another approach to classification is to determine the oxygen-isotopic composition of the chromite grains from fossil meteorites and micrometeorites. It has been observed by Clayton et al. (1976) that the oxygen-isotopic compositions and the classification of meteorites are fairly coherent. The permil-deviation of the sample's isotopic composition from the mass-dependent terrestrial mass-fractionation line (TFL) defined in three isotope space can be used to distinguish different meteorite groups and is approximately expressed as $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ (Clayton et al., 1991), with $\delta^{17}O = [(^{17}O/^{16}O)_{sample}/[^{17}O/^{16}O]_{VSMOW} - 1] \times 1000$ and $\delta^{18}O = [(^{18}O/^{16}O)_{sample}/[^{18}O/^{16}O]_{VSMOW} - 1] \times 1000$, where "VSMOW" stands for "Vienna standard mean ocean water".

Greenwood et al. (2007) reported a single analysis of oxygen three isotopes in chromite from a fossil meteorite by laser-assisted fluorination. This pioneering study consumed more than 100 chromite grains mixed together and weighing a total of 0.9 mg. The chromites were extracted from the fossil meteorite Österplana 029 (alias Gol 001). The average value of $\Delta^{17}O$ of the 100 chromite grains from Gol 001 ($1.07 \pm 0.10‰$) is consistent with modern L chondrites (and LL chondrites within 2σ uncertainty) and linked Gol 001 to the L chondrite parent body breakup (Greenwood et al., 2007). However, possible oxygen isotopic variability within and among chromite grains from Gol 001 and the oxygen-isotopic compositions of other fossil meteorites and micrometeorites are not known. The laser fluorination method is limited to bulk analyses of relatively large samples and cannot determine the oxygen-isotopic compositions of single sediment-dispersed grains that are smaller than 300 μm in diameter and might represent individual micrometeorite falls. Single grain analyses are necessary to compare SEC grains deposited at different times and at different locations to each other and to fossil meteorites. Finer-scale analysis is important to determine the origin of the grains through time and space. Furthermore, these samples are extremely rare and precious (0.01–3 extraterrestrial chromite grains per kg of limestone; Schmitz and Häggström, 2006), and therefore, single grain analyses are desirable to preserve material. However, oxygen isotope studies on the micron to sub-mm scale with high, sub-permil precision are required to distinguish between the different groups of ordinary chondrites, the H, L and LL chondrites. Such analyses are challenging because of the low abundance of ^{17}O and ^{18}O (e.g., Kita et al., 2004, 2009).

2. SAMPLES

Twelve fossil meteorites from southern and central Sweden were selected for study, as well as sediment-dispersed extraterrestrial chromite grains from two sediment beds from southern Sweden with two correlated sediment beds in south-central China (Fig. 1). Sample preparation techniques are described in Section 2.5.

2.1. Thorsberg quarry, southern Sweden

Eleven fossil meteorites from 7 different sediment beds and limestone from two different sediment beds were collected in the active Thorsberg quarry near Kinnekulle in southern Sweden (Figs. 1 and 2; Schmitz et al., 1996, 2001, 2003; Schmitz and Häggström, 2006).

We follow the nomenclature of sediment beds at Thorsberg used by quarry workers as is common in the literature on these fossil meteorites. The fieldnames of the meteorites are abbreviated bed names and sequential numbering. These names link the meteorites to the sediment beds and therefore preserve the temporal context, in contrast to the formal names that simply reflect the locality.

The meteorite-rich beds of marine limestone at Thorsberg remain undeformed and have not been inclined since their deposition in the mid-Ordovician. It has been established for the forty meteorites found in this quarry by 2001 that they represent at least twelve different falls, since they commonly lie on different hardground surfaces (Schmitz et al., 2001) and have different cosmic-ray exposure ages (Heck et al., 2004). Cosmic-ray exposure ages have been determined for four (Ark 002 alias Österplana 002; Ark 030 alias Österplana 044; Gol 001; Sex 003 alias Österplana 037) of the eleven Thorsberg meteorites studied here, and for meteorites found in two other beds which contained three meteorites studied here (see Fig. 2; Goda 002; Gla 002, 003; Österplana aliases TBD). Osmium concentrations, and $^{187}Os/^{188}Os$ ratios have been determined in two of the meteorites studied here (Gol 001, Sex 003) and are very similar to values obtained from recent falls of ordinary chondrites (Schmitz et al., 2001). Average elemental compositions of chromites from fossil meteorites were reported in Schmitz et al. (2001) and of SEC grains in Schmitz and Häggström (2006). Here, SEC grains extracted from 10 to 30 kg limestone samples from the Golvsten bed (Gol SEC) and from the middle of the Sextummen bed (Sex-m) have been selected for study (Fig. 2). The samples are about 2 m apart in sediment depth and occur in the respective centers of two adjacent conodont zones, *L. variabilis* and *Yangtzeplacognathus crassus*, respectively.

2.2. Gärde quarry, central Sweden

Brunflo, the first Ordovician fossil meteorite described (Thorslund and Wickman, 1981; Thorslund et al., 1984), was found in the Gärde quarry near Brunflo in Jämtland, central Sweden (Fig. 1). The enclosing sediments are of the *Eoplacognathus suecicus* – *Scalpellodus gracialis* Conodont Subzone, roughly 5 million years younger than the base of the Arkeologen at Thorsberg (Fig. 2). Small pieces of the meteorite were extracted from the main mass at the Swedish Natural History Museum in Stockholm (Alwmark and Schmitz, 2009a). In the current study four chromite grains extracted from Brunflo were investigated.

2.3. Puxi River section, south-central China

Limestone samples (10–30 kg) from two different sediment beds from the Puxi River section near Yichang, Hubei province, south-central China were collected (Figs. 1 and 2; Schmitz et al., 2008). The two samples are ~4 m apart in vertical distance and occur at the bottom and the top, respectively, of the conodont zone *Y. crassus*. This is the same conodont zone encompassing the Sextummen bed at Thorsberg (Fig. 2).

2.4. Chromite from modern meteorites

To test our experimental method we have selected two well-characterized H chondrite meteorites (Hessle H5; Guareña H6), two L chondrites (Ergheo L5; New Concord L6) and an LL chondrite (St-Séverin LL6). Chromite standard grains (UWCr-2) were mounted either into the meteorite thin

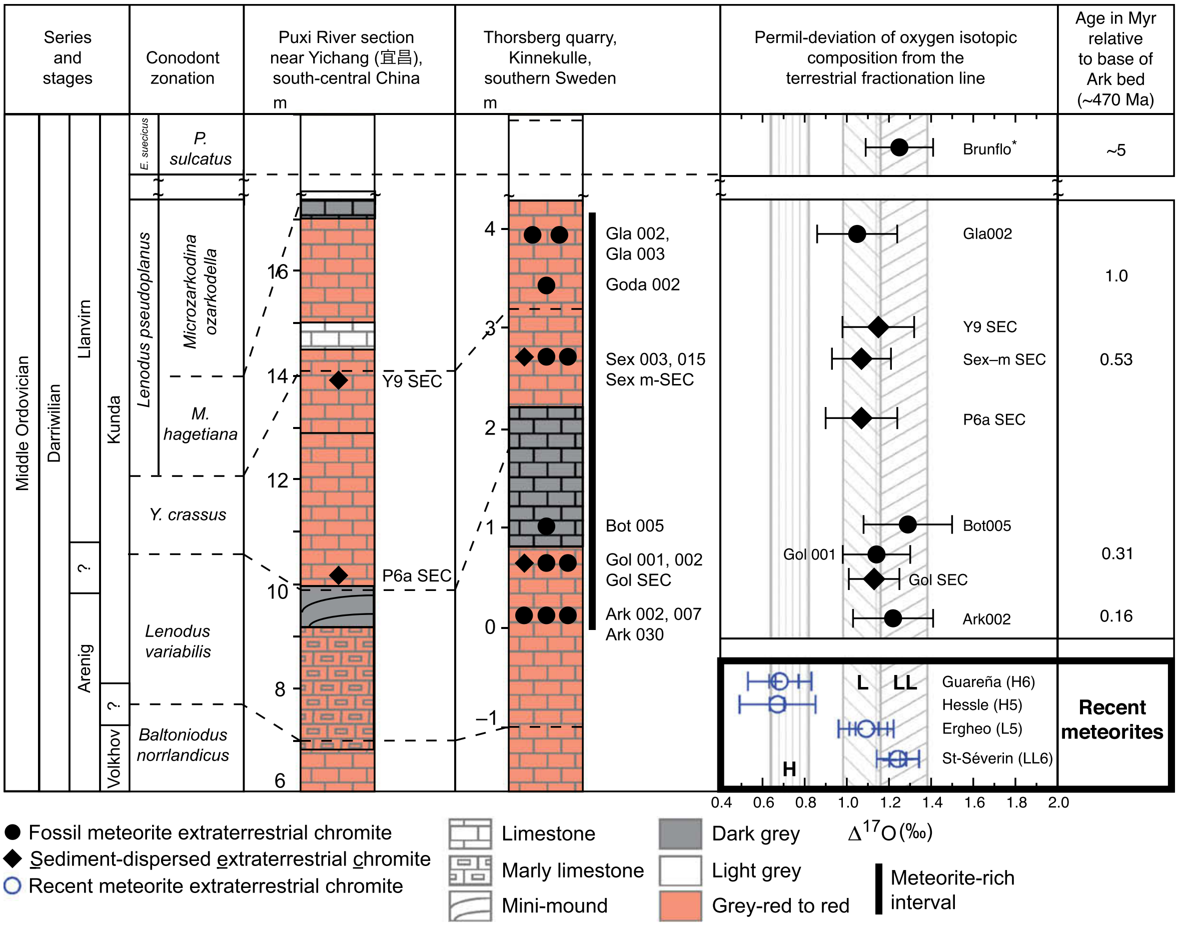

Fig. 2. Stratigraphic columns of the two outcrops sampled at the Puxi River section, near Yichang, south-central China and at the Thorsberg quarry, near Kinnekulle, southern Sweden. Sediments are correlated with conodont zones (dashed lines; after Schmitz et al. (2008)). Approximate locations of extraterrestrial chromite grain samples in the stratigraphic column are shown as solid circles (fossil meteorites) and as diamond symbols (SEC grains). The meteorite-rich interval (black vertical bar) starts at the base of the Arkeologen bed and extends to ~1–2 million year younger sediments of the Glaskarten bed. Cosmic-ray exposure ages of meteorites are shown as relative ages (Heck et al., 2004) except for *Brunflo where the relative age was determined by sediment age (see text). The Arkeologen bed was deposited at ~470 Ma (see text). SIMS analyses of the permil-deviations of the oxygen-isotopic composition ($\Delta^{17}O$; weighted averages) of the extraterrestrial chromite grains relative to the terrestrial mass-fractionation line are shown. Error bars are 2σ and include analytical uncertainties and uncertainties of the $^{16}O^{1}H$ interference correction. For modern ordinary chondrites (falls), individual analyses (vertical bars) are shown in addition to average values (open circles). Patterns are the standard deviations centered on the averages of $\Delta^{17}O$ values for H, L, LL chondrites (falls), respectively, reported by Clayton et al. (1991). Ark, Arkeologen; Gol, Golvsten; Bot, Botten; Sex, Sextummen; Goda, Goda Lagret; Gla, Glaskarten. *E. suecicus*, *Eoplacognathus suecicus; P. sulcatus*, *Panderodus sulcatus; M. hagetiana*, *Microzarkodina hagetiana; Y. crassus*, *Yangtzeplacognathus crassus.*

sections or epoxy mounts. Chromite grains were identified *in situ* using a Hitachi S-3400 scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM/EDS).

2.5. Sample extraction and preparation

Chromites from fossil meteorites and fossil micrometeorites were extracted by crushing and acid dissolution as outlined in Schmitz et al. (2003), Schmitz and Häggström (2006), and Alwmark and Schmitz (2009a). The acid insoluble residue >63 μm was then repeatedly searched under the light microscope and chromite grains were picked with a fine brush. The unpolished grains were mounted on carbon tape and analyzed qualitatively with EDS to verify their extraterrestrial origin based on their elemental composition, in particular diagnostic are high Ti and narrow ranges of V concentrations (Alwmark and Schmitz, 2009a).

Polished sections of extraterrestrial chromite (EC) grains were prepared in 25 mm epoxy resin mounts for secondary ion mass spectrometry (SIMS) analyses. These EC and standard chromite grains (UWCr-2 and UWCr-3, see below) were mounted within the central 10 mm diameter area. Some EC grains are quite brittle and display numerous internal fractures. Therefore, some material was lost during polishing. Data quality of SIMS analyses critically depends on the flatness and low relief of the analyzed surface (Kita et al., 2009). Therefore, polishing relief of chromite against epoxy surface was measured using a Zygo NewView surface profilometer and for most samples was less than 2 μm, but never exceeded 3 μm in any sample. After polishing the mount was rinsed with ethanol and water, dried in a low-vacuum oven, and then carbon-coated.

2.6. Oxygen-isotope chromite standards

Instrumental bias on SIMS oxygen isotope analyses is sensitive to major-element composition of the unknown samples (compositional matrix effect; e.g., Eiler et al., 1997; Riciputi et al., 1998; Valley and Kita, 2009). Therefore, the composition of the standard used should match the composition of the sample as closely as possible. To our knowledge, no chromite standard for high-precision *in situ* O-isotope analyses has been previously reported. We therefore evaluated chromite minerals from five different chromitite rocks from southern Africa. Polished sections of the chromitites were prepared and analyzed with a CAMECA SX-51 electron probe microanalyzer (EPMA) and an IMS-1280 SIMS at the University of Wisconsin-Madison (see Section 4), and tested for elemental and O isotope homogeneity. Two chromites (UWCr-2 and UWCr-3), both from chromitites of the Eastern Bushveld Complex, South Africa, turned out to be homogeneous in elemental composition and were subsequently investigated with SIMS. Oxygen isotope SIMS analyses revealed that both grain-to-grain and spot-to-spot 2 SD-reproducibilities were 0.3‰ in δ^{18}O and 0.2‰ in Δ^{17}O for both chromites (Electronic annex EA-1-1, Fig. EA-2-1), consistent with a typical reproducibility achieved in the WiscSIMS laboratory (Kita et al., 2009). Therefore, they have been chosen as standards and were analyzed with conventional gas-source mass spectrometry (see next Section) to obtain reference δ^{18}O values in VSMOW-scale. Small chips (<5 g) were broken off decimeter-sized samples, crushed to sub-mm-size in a mortar, sieved, and then leached in cold concentrated (49%) HF for two days to remove silicates. Chromite grains (diameters a few hundred μm) were then handpicked. An epoxy grain mount for SIMS analysis was prepared as described above and analyzed for major and minor elemental concentrations with the EPMA (see Section 3.3. below and Electronic annex EA-1-2). UWCr-2 is from a ~1 m thick chromitite layer from the Steelport seam at Farm Winterveld (Cameron, 1977) with a chromite-spinel volume fraction of >97%; and UWCr-3 is from a chromitite at Annex Grootboom with ~70% chromite-spinel volume fraction, both from the ore collection of E. N. Cameron at the University of Wisconsin-Madison. In a simple two-spinel endmember system UWCr-2 and UWCr-3 are 71% and 64% chromite, respectively, and 29% and 36% $MgAl_2O_4$, respectively. Analytical data in weight percent are given in Electronic annex EA-1-2.

3. ANALYTICAL PROCEDURE

3.1. High-precision oxygen isotope analyses by IMS-1280 SIMS

3.1.1. Analytical conditions

The IMS-1280 SIMS at the University of Wisconsin (WiscSIMS Laboratory) was used for the high-precision oxygen three-isotope analyses. The instrumental setup and analytical procedures are based on previous developments for sub-permil precision oxygen isotope analyses by IMS-1280 for both oxygen two and three isotope analysis (Kita et al., 2009; Valley and Kita, 2009), which are applied to various cosmochemical studies (e.g., Downes et al., 2008). The instrumental parameters were optimized for the highest possible precision with a moderate sized spot size (~15 μm) as described in Kita et al. (2009). A ~5 nA primary Cs^+-beam in a 20 kV total potential was focused to a 10 × 15 μm ellipse at the sample surface (Fig. 3). Charge compensation was achieved with a normal incidence electron gun, which generated an electron cloud close to the sample. Mass resolving power was set to ~5000. Secondary ions of $^{16}O^-$, $^{17}O^-$ and $^{18}O^-$ were measured simultaneously with three faraday cup (FC) detectors, L′2, FC2 (fixed axial detector), and H1, respectively. FC2 and H1 detectors were connected to amplifiers equipped with $10^{11}\,\Omega$ resistors, while L′2 was connected to an $10^9\,\Omega$ resistor due to the high $^{16}O^-$ signal. The movable FC detectors L′2 and H1 were aligned relative to the fixed FC2 detector every 12 h and the magnetic field was stabilized with a nuclear magnetic resonance (NMR) magnetometer, to better than ±10 ppm during the analysis session of 48 h.

3.1.2. Analytical procedure

Prior to each analysis, the sample surface was presputtered for 100 s during which time the secondary ion beam

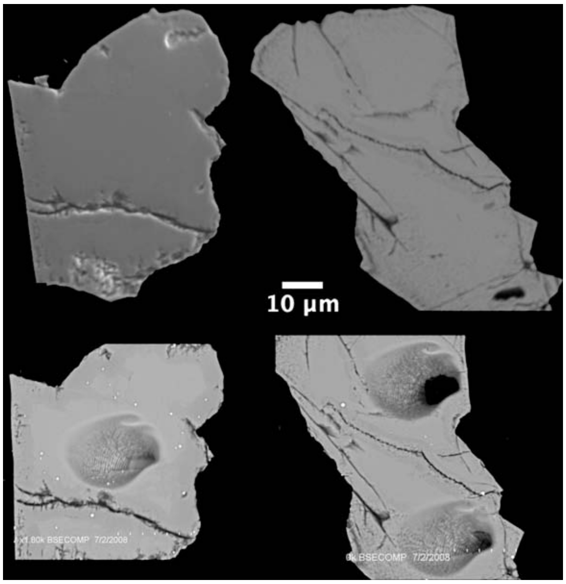

Fig. 3. SEM-BSE images of polished extraterrestrial chromite grains from the Sextummen bed at the Thorsberg quarry, southern Sweden (left column) and from the Y9 bed, Puxi-River formation, south-central China (right column). SEM images of all grains were recorded prior (upper row) and after (lower row) SIMS analysis. Sputtering craters in chromites always exhibit ripples, independent of the crystallographic orientation of the chromite. The upper crater in the lower right image penetrated the grain and hit epoxy, resulting in a strong $[^{16}O^1H]^-$ mass peak whose tail interfered with the ^{17}O mass peak and resulted in a δ^{17}O-correction of 0.9‰ leading to rejection of the data.

was centered relative to the field aperture and detectors. In order to preserve sample material, presputtering was done with a lower primary ion beam current of ~0.1 nA. Our aim was to resolve differences of $\Delta^{17}O$ as small as 0.1‰. The 2 SD error of $\Delta^{17}O$ from a single analysis was on average 0.3‰. To improve the precision for $\Delta^{17}O$, two analyses per spot were performed. However, measured $\delta^{17}O$ and $\delta^{18}O$ values change with the depth of the sputtering crater and are mass fractionated, while $\Delta^{17}O$ values were constant. We therefore report mean values of $\delta^{17}O$ and $\delta^{18}O$ from the first analysis at each spot, which comprises 20 analytical cycles, whereas $\Delta^{17}O$ is calculated from both, the first and second analysis. Eight to 12 sample analyses were bracketed with 12 analyses of the UWCr-2 chromite running standard in the same mount. The instrumental bias is corrected according to UWCr-2 data according to the method described in Kita et al. (2009).

After each SIMS analysis, the magnitude of the $[^{16}O^{1}H]^{-}$ peak was recorded to correct for any tailing interference with the $^{17}O^{-}$ peak. The intensity ratio of the $[^{16}O^{1}H]^{-}$ signal at the position of the ^{17}O peak center ("OH tailing interference") and the center of the $[^{16}O^{1}H]^{-}$ mass peak has been determined to be $2.9(+0.5/-0.3) \times 10^{-5}$ during the same analysis session (Fig. EA-2-2). The uncertainty resulting from the 10 ppm maximum drift of the NMR-controlled magnetic field has been included into the error of the OH tailing interference correction, and is reported as part of the uncertainties of the interference-corrected $\delta^{17}O$ and $\Delta^{17}O$ values. We define this calculated uncertainty as 2σ. The corrections of the OH tailing interference with $\delta^{17}O$ and the reproducibility (2SD) of $\Delta^{17}O$ of chromite standard analyses are better than 0.07‰ and 0.27‰, respectively (Table EA-1-4). All values are reported as ‰ relative to VSMOW unless stated otherwise.

Another uncertainty of the correction for the OH tailing interference comes from an instability of the $[^{16}O^{1}H]^{-}$ signal during the analysis. Since we recorded the magnitude of the $[^{16}O^{1}H]^{-}$ signal after each analysis, we cannot detect fluctuation of the magnitude of the $[^{16}O^{1}H]^{-}$ signal. The source of OH causing the $[^{16}O^{1}H]^{-}$ interference is most likely water and hydrocarbons released at high vacuum from the sample mount and sample itself. It is often suspected that water is released if the primary ion beam hits an internal crack in the target mineral. However, we did not observe a correlation between the OH signal and the number of cracks, the accumulated length of cracks, or the surface area covered by cracks in the sputtering crater as observed after analysis by SEM. Some analyses with no cracks visible in SEM images of the sputtering craters had large OH signals, which lead to tailing interferences of >1‰, while some craters with up to six cracks had very low OH signals, leading to corrections of <0.5‰. To eliminate ambiguity of the correction of OH tailing interference with the $^{17}O^{-}$ peak, we rejected all data with OH tailing corrections >0.5‰ (Fig. EA-2-3) or if values of $\Delta^{17}O$ of two analyses in the same spot differ by more than 1‰. All samples were imaged with SEM before and after SIMS analyses (e.g., Fig. 3).

Two chromite standards, UWCr-2 ($Sp_{0.29}Chr_{0.71}$) and UWCr-3 ($Sp_{0.36}Chr_{0.64}$), and pure $MgAl_2O_4$ spinel standard "Spinel#1" (Kita et al., 2007) were used to evaluate matrix correction for the instrumental bias. The results are shown for oxygen isotope analyses both by SIMS (Electronic annex EA-1-1 and EA 1-4) and laser-assisted fluorination (LF; Electronic annex EA-1-3) as well as EPMA analyses (Electronic annex EA-1-2 and EA-1-5). From these results, we estimate that instrumental bias for EC grains is only 0.3‰ higher in $\delta^{18}O$ relative to UWCr-2 (see EA-3-1). The uncertainty of this 0.3‰ correction is of the same magnitude as the spot-to-spot analytical uncertainty. Furthermore, the correction applies to the values of $\delta^{18}O$ and $\delta^{17}O$, but will not affect values of $\Delta^{17}O$, which are most important for meteorite classification of L chondrites. Therefore, no additional correction for the instrumental bias has been applied to the EC data.

3.2. Laser-assisted fluorination oxygen isotope analyses of chromite standards

Chips of the new UWCr-2 and UWCr-3 standards were analyzed in the Stable Isotope Laboratory at the University of Wisconsin. Gas extraction was achieved by laser-heating of ~2 mg samples in a BrF_5 atmosphere. After cryogenic purification, CO_2 was measured with a Finnigan MAT 251 mass spectrometer (Valley et al., 1995; Spicuzza et al., 1998). For chromite, normal protocols for laser fluorination produced low yields. In order to increase yields, BrF_5 pressures during lasing were increased from ~0.1 to ~0.45 atm. Our experiments indicate that the yield increases with increasing amounts of reagent, converging at 92–97% with a pressure of ~46 kPa BrF_5 (0.45 atm) in the fluorination chamber before laser irradiation. Values of $\delta^{18}O$ are not reproducible with yields less than 90% and are not considered reliable. The $\delta^{18}O$ values of UWCr-2 and UWCr-3 are 4.59 ± 0.17‰ (2SD) and 3.85 ± 0.14‰ (2SD) VSMOW, respectively (EA-1-3). The $\delta^{18}O$ value determined for UWCr-2 is consistent with $\delta^{18}O$ values of chromites (4.3–4.8‰; Li et al., 2005) from the Merensky Reef also from the Bushveld Complex obtained by conventional $\delta^{18}O$ analysis of mg-size samples.

3.3. Electron microprobe elemental analyses

Elemental compositions of Ordovician extraterrestrial chromite grains and chromite and spinel standards were measured with a Cameca SX-51 electron probe microanalyzer (EPMA) at the University of Wisconsin-Madison. Analysis was performed with a 20 nA electron beam at 20 keV. Kα-peaks of the following elements were detected with five tunable wavelength dispersive spectrometers: Mg, Al (TAP); Ti, Cr (PET); Fe, Zn, V, Mn (LIF). Integration times for each element were 10 s on peak and 10 s off peak. Data reduction and corrections were performed with the Probe for Windows software. The V peak was corrected for interference by Ti by measuring the Ti peak on synthetic TiO_2 (Donovan et al., 1993). Background correction for Ti, V, Cr, Zn was linear, i.e. the background was measured on both sides of the peak, and average for Mg, Al, Mn, Fe, i.e. the background was measured on the high λ side of the peak twice and averaged. Measurements were calibrated with the following standards: USNM 117075 chromite for Mg, Al, Cr; USNM 114887 magnetite for Fe; Minas Gerais rutile for Ti; synthetic manganese olivine for Mn, USNM 145883 gahnite for Zn; and LGM-P7 V metal for V. ZAF or φ(ρZ) matrix correction was applied (Armstrong, 1988) with mass absorption coefficients from the LINEMU/CITZMU dataset. Data with oxide totals <96 wt% were rejected. Two to three spots per grain were analyzed. If more than one analysis per grain resulted in an oxide total >96%, the arithmetic mean is reported.

4. RESULTS

4.1. Three oxygen isotope compositions

Averages of oxygen isotopic analyses with OH corrections of <0.5‰ are given in Table 1 and are shown in Figs. 2 and 4. Data with interference corrections larger than 0.5‰ scatter by ±1‰ compared to data with low OH corrections. In some cases the OH signal was presumably variable during a single analysis, probably due to cracks or contributions of OH-bearing phases that might change as sample was sputtered. The two analyses per spot give us a way to monitor the OH signal at two instances. We reject all data with OH tailing corrections >0.5‰ (Fig. EA-2-3), or if the difference before OH correction between $\Delta^{17}O_{raw}$ of two analyses of the same spot was larger than 1‰. The complete oxygen isotope dataset, including analyses that have been rejected (53% of all analyses) due to large OH corrections >0.5‰, is listed in Electronic annex EA-1-4.

We report the oxygen-isotopic composition of 4 fossil meteorites from 4 different sediment beds in the Thorsberg quarry in southern Sweden (we rejected data from 5 meteorites because of large OH interference corrections), of the fossil meteorite Brunflo from slightly younger sediments of the Gärde quarry in central Sweden, and of 15 analyses of SEC grains from Thorsberg (26 analyses were rejected) and 9 analyses of SEC grains from Puxi River, south-central China (12 analyses were rejected) from sediments of the similar age (Fig. 2). Values of $\Delta^{17}O$ of chromites from the modern ordinary chondrite falls Guareña (H6), Ergheo (L5) and St-Séverin (LL6) are consistent within 0.08–0.11‰ with Clayton et al.'s (1991) $\Delta^{17}O$ values of bulk analyses of these meteorites (see Table 1).

Values of $\Delta^{17}O$ averaged for each fossil meteorite and for each group of contemporaneous SEC grains are consistent with the range of $\Delta^{17}O$ values of modern L and LL chondrite falls (Fig. 2; Table 1 and Electronic annex EA-1-4). The weighted $\Delta^{17}O$ average of all Ordovician chromite samples of this study is 1.14 ± 0.05‰ and lies in the $\Delta^{17}O$ L and LL range overlap and is closest (within 0.07‰) to the mean $\Delta^{17}O$ of bulk L chondrites analyzed by Clayton et al. (1991). Our $\Delta^{17}O$ of Gol 001 (1.14 ± 0.16‰) is the same within analytical uncertainty as the value obtained by Greenwood et al. (1.07 ± 0.10‰). Values of $\Delta^{17}O$ for chromites from four modern ordinary chondrite falls reported here show that with the $\Delta^{17}O$ precision achieved in this study (<0.2–0.3‰; 2 SD; and 0.1–0.2‰; 2σ; as an average of multiple analyses) H chondrites can be readily distinguished from L and LL chondrites (Fig. 2).

All oxygen isotope data of Gol 002 chromites were rejected because the difference between $\Delta^{17}O_{raw}$ of two analyses of the same spot is larger than 1‰ whereas for other analyses the difference is mostly <0.3‰ (see EA-1-4).

In an oxygen three-isotope diagram (Fig. 4), weighted averages of SIMS data from chromites from modern ordinary chondrites fall onto mass fractionation lines in good agreement with the average compositions of the ordinary chondrites of the corresponding types H, L and LL reported by Clayton et al. (1991). Data from chromites from Thorsberg fossil meteorites, and SEC grains from Thorsberg and Puxi River fall onto the L chondrite mass fractionation line. The $\delta^{18}O$ and $\delta^{17}O$ values of the Thorsberg meteorite chromite are very close to the values determined for Ergheo L5 chromites.

Although the average $\Delta^{17}O$ of chromite from the fossil meteorite Brunflo (1.25 ± 0.16‰) from the Gärde quarry, central Sweden, is higher and falls onto the LL chondrite mass fractionation line (Figs. 2 and 4), within its 2σ uncertainty, however, it is consistent with the range of L chondrite $\Delta^{17}O$ values determined by Clayton et al. (1991). The fayalite and forsterite content, respectively, of olivine and pyroxene inclusions in Brunflo chromite grains give independent evidence for an L rather than an H or LL chondritic origin of this meteorite (Alwmark and Schmitz, 2009b). All other chromite $\Delta^{17}O$ values are also consistent with $\Delta^{17}O$ ranges of LL chondrites. This also applies to the data point defined by the laser-assisted fluorination analysis of a composite of >100 chromites from the fossil meteorite Gol 001 from Thorsberg (Greenwood et al., 2007). The difficulty to distinguish between L and LL chondrites is illustrated by the proximity of the data points defined by $\Delta^{17}O$ of chromites from Ergheo (L5) and St-Séverin (LL6) in Figs. 2 and 4. The difference in $\Delta^{17}O$ between H chondrites and the L and LL chondrites is much larger and a clear distinction between H chondrites and the L and LL chondrites can be made for all samples.

4.2. Minor and major elemental composition

4.2.1. *Fossil meteorites from Thorsberg and SEC grains from Thorsberg and Puxi River*

Elemental compositions of most chromite grains analyzed here fall within the ranges of previously published average compositions of extraterrestrial chromites from Ordovician fossil meteorites and sediments from southern Sweden and are distinct from compositions of terrestrial Cr-rich spinel grains (Schmitz et al., 2001; Schmitz and Häggström, 2006). The analyzed chromite grains have 1.8–4.0 wt% MgO, 4.4–6.8 wt% Al_2O_3, 1.5–3.8 wt% TiO_2 and a narrow range of V_2O_3 (0.5–0.9 wt%) (Electronic annex EA-1-2; Fig. 5). The concentration maxima of the distributions in histograms of MgO, Al_2O_3, TiO_2, V_2O_3 and MnO are consistent with averages and ranges of these oxides in chromite of modern L chondrites (Fig. 5).

Table 1

Oxygen three isotope compositions of extraterrestrial chromite grains. Weighted averages are shown for data with $^{16}O^{1}H$-corrections of less than 0.5‰. Bed names: Ark, Arkeologen; Bot, Botten; Gla, Glaskarten; Goda, Goda Lagret; Gol, Golvsten. Uncertainties are 2σ. A full data table is given in the Electronic annex.

Sample	$\delta^{18}O_{VSMOW}$	±2σ	$\delta^{17}O_{VSMOW}$[a]	±2σ	$\Delta^{17}O_{Avg}$	±2σ total[b]	$^{16}O^{1}H$ corr.[c]	+err	−err	Accepted/rejected[d] $\Delta^{17}O$ analyses
Fossil meteorites, Thorsberg quarry, southern Sweden										
Ark002	−1.93	0.15	0.21	0.20	1.22	0.19	0.04	0.01	0.01	4/0
Bot005	−1.83	0.19	0.34	0.23	1.29	0.21	0.04	0.01	0.01	4/0
Gla002	−1.63	0.18	0.20	0.21	1.05	0.19	0.20	0.04	0.03	4/0
Goda002	−1.59	0.19								0/4
Gol001	−1.77	0.16	0.22	0.18	1.14	0.16	0.38	0.06	0.04	6/2
Thorsberg meteorites	**−1.80**	**0.08**	**0.23**	**0.10**	**1.17**	**0.09**	**0.044**	**0.006**	**0.004**	**18/10**
Brunflo fossil meteorite, Gärde quarry, central Sweden										
Brunflo meteorite	−1.02	0.22	0.72	0.20	1.25	0.16	0.033	0.006	0.004	6/2
Sediment-dispersed grains, Thorsberg quarry, southern Sweden										
Golvsten bed	−1.29	0.13	0.45	0.14	1.13	0.12	0.08	0.02	0.01	6/19
Sextummen bed	−1.23	0.12	0.43	0.15	1.07	0.14	0.11	0.02	0.01	9/7
Average	−1.26	0.09	0.45	0.10	1.10	0.09	0.10	0.01	0.01	15/26
Sediment-dispersed grains, Puxi-River formation, south-central China										
P6a	−0.95	0.18	0.57	0.20	1.07	0.17	0.09	0.02	0.02	4/7
Y9	−1.36	0.18	0.44	0.19	1.15	0.17	0.36	0.08	0.05	5/5
Average	−1.16	0.13	0.50	0.14	1.11	0.12	0.12	0.02	0.02	9/12
All sediment-dispersed grains	**−1.23**	**0.07**	**0.47**	**0.08**	**1.10**	**0.07**	**0.10**	**0.01**	**0.01**	**24/38**
All Ordovician grains	**−1.44**	**0.05**	**0.39**	**0.06**	**1.14**	**0.05**	**0.045**	**0.004**	**0.003**	**48/55**
Recent meteorite falls										
Guareña (H6)	−1.84	0.11	−0.28	0.16	0.68	0.15	0.0045	0.0008	0.0005	6/3
Hessle (H5)	−2.17	0.22	−0.46	0.21	0.67	0.18	0.045	0.008	0.005	4/0
Ergheo (L5)	−1.89	0.15	0.11	0.15	1.09	0.13	0.048	0.007	0.004	8/0
St-Séverin (LL6)	−2.03	0.09	0.18	0.11	1.24	0.10	0.062	0.008	0.005	8/1
Bulk meteorite data (Clayton et al., 1991)										
Guareña (H6)					0.76	0.16				
Ergheo (L5)					0.98	0.16				
St-Séverin (LL6)					1.16	0.16				

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[a] $\delta^{17}O_{VSMOW}$ was calculated as described in the text.

[b] Total 2 SE on $\Delta^{17}O_{Avg}$ includes analytical uncertainties and uncertainty of $^{16}O^{1}H$-correction.

[c] Weighted averages of $^{16}O^{1}H$-corrections are calculated from corrections <0.5‰.

[d] Data were rejected if the $^{16}O^{1}H$-correction is larger than 0.5‰; for complete data set see Electronic annex.

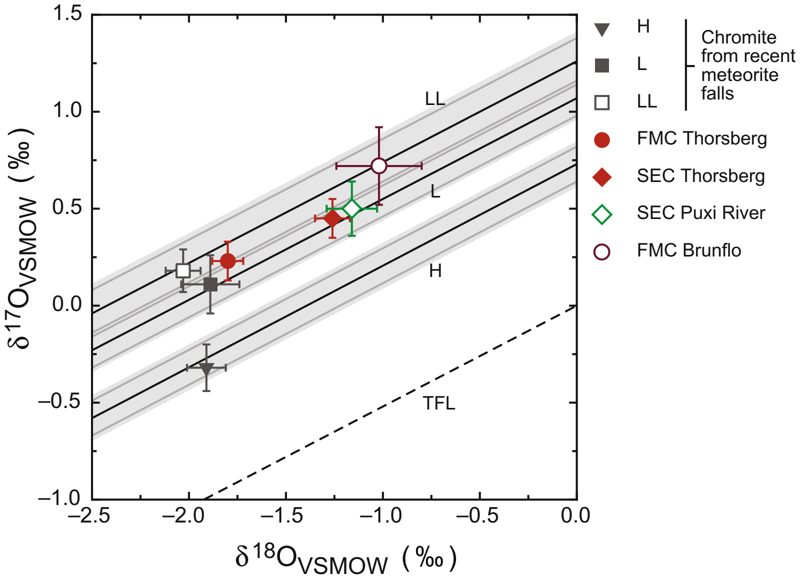

Fig. 4. Oxygen three isotope diagram. Error bars are 2σ. Solid lines labeled H*, L* and LL* are defined by average $\Delta^{17}O$ values of ordinary chondrite data (Clayton et al., 1991); the short lines perpendicular to them show the standard deviation of the individual $\Delta^{17}O$ values within each ordinary chondrite group. FMC, fossil meteorite chromite grains; SEC, sediment-dispersed extraterrestrial chromite grains; TFL. terrestrial mass-fractionation line.

5. DISCUSSION

5.1. Alteration of Ordovician extraterrestrial chromites

Were the extraterrestrial chromites affected by diagenesis during their ~470 Myr residence time in the marine limestone? Based on the conodont color alteration index of Epstein et al. (1977), Nyström et al. (1988) report that the sediments experienced peak temperatures of less than 100 °C. Low sediment temperatures are also required to explain the presence of surface-implanted solar wind He and Ne in the micrometeoritic SEC grains (Heck et al., 2008). If the sediments had experienced higher temperature, the light noble gas He would have been considerably more fractionated relative to the heavier Ne, contrary to the data. We would expect preferential release of He relative to Ne in any mineral if the temperatures were between the closure temperature of He and Ne. Experiments on retention of implanted He and Ne as a function of temperature in olivine and ilmenite (Futagami et al., 1993) show preferential release of He over Ne at low temperatures, but it is problematic to extrapolate diffusion parameters, which depend on different parameters, from studied minerals to unstudied ones (e.g., Farley, 2007). Nevertheless, such low temperatures prove that the O isotopic composition of the chromites was not affected measurably by diffusion (see, Valley (2001)). Furthermore, if oxygen isotopes were exchanged by some other process on Earth, values of $\Delta^{17}O$ would be shifted towards the terrestrial value of 0‰. The tight clustering of $\Delta^{17}O$ values in this study argue that analyses on spots that passed the previously described OH rejection criteria were not measurably affected by terrestrial alteration.

We do not observe a correlation of oxygen isotope data with elemental concentrations. In particular, values of $\Delta^{17}O$ and $\delta^{18}O$ are independent of ZnO concentrations (Fig. 6). Enhancements in ZnO concentration have been attributed to reflect terrestrial alteration of Ordovician EC grains (Schmitz et al., 2001). We show that such alteration does not affect the oxygen-isotopic composition within our analytical uncertainty. We therefore consider our oxygen isotope data for analyses that passed the rejection criteria as accurate and unaffected by alteration.

5.2. Chromite grains from L chondrites

Values of $\Delta^{17}O$ of extraterrestrial chromite grains from the Ordovician fossil meteorites and micrometeorites from Sweden and China are consistent with $\Delta^{17}O$ of L and LL chondrites (Figs. 2 and 4). This conclusion is supported by TiO_2 concentrations in the chromites (Fig. 5). The inability to separate L and LL chondrites is not an analytical limitation but due to the fact that the oxygen isotope compositions and compositional ranges of major and minor elements of some meteorites of the two groups partially overlap. Since many of our data are in the overlapping range of L and LL chondrites we will briefly discuss the hypothetical L/LL meteorite group. There are several modern ordinary chondrite chemical compositions that do not allow distinguishing between the L or LL chondrites. These meteorites have been tentatively designated as L/LL chondrites based on siderophile element concentrations (Kallemeyn et al., 1989), and depending on their fayalite content of olivine and Co concentrations in kamacite (Rubin, 1990). Do these samples form a distinct group of ordinary chondrites and did they originate from a different parent body? Friedrich and Lipschutz (2001) found that L/LL chondrites are enriched in light rare earth elements relative to L and LL chondrites and indeed might represent

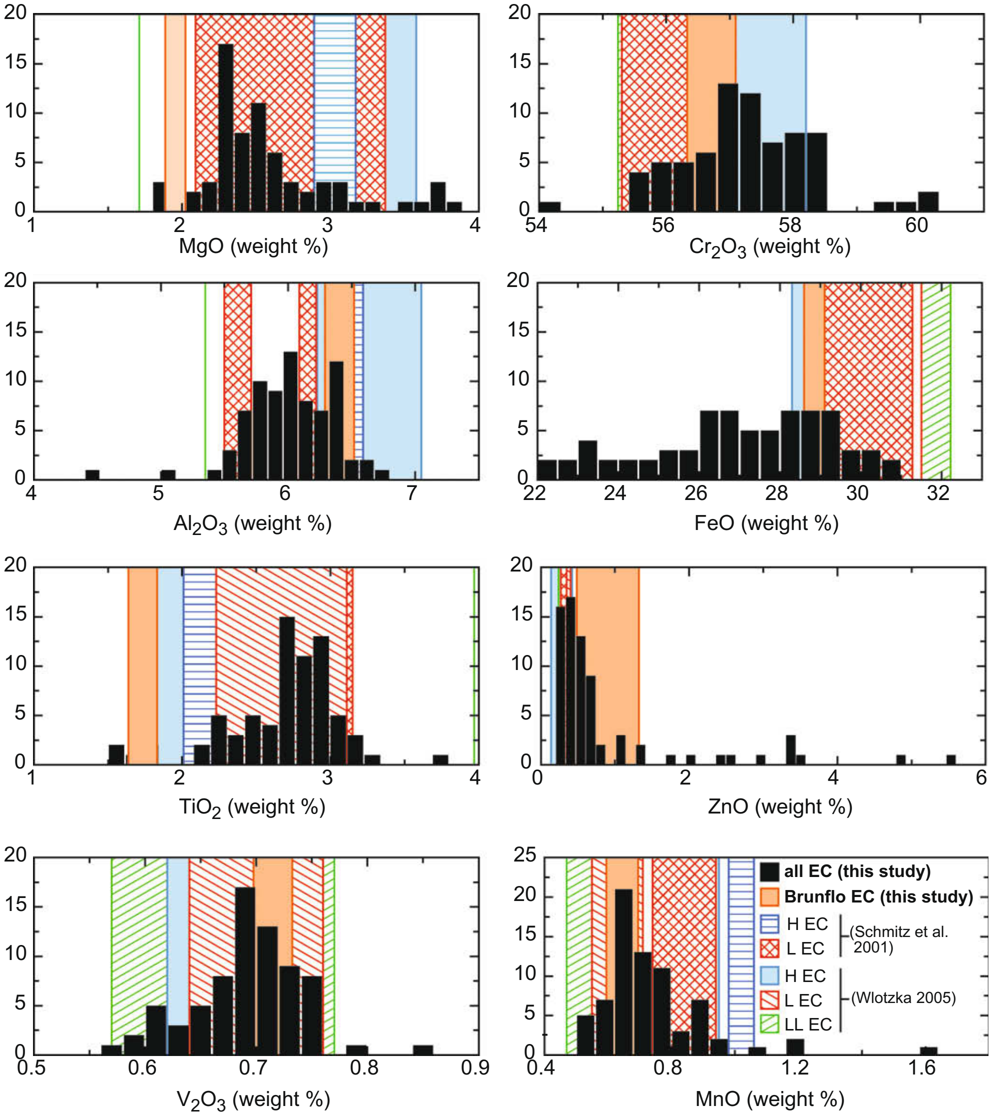

Fig. 5. Histograms of major and minor element concentrations in Ordovician extraterrestrial chromite grains measured by EPMA. We compare the data from Ordovician chromites with average concentrations ±1 standard deviations of concentrations in chromites of modern H, L and LL chondrites (Schmitz et al., 2001; Wlotzka, 2005). Average MgO, Al_2O_3, TiO_2, V_2O_3, MnO and ZnO concentrations of the modern L chondrite chromites coincide with concentration maxima of these oxides in Ordovician extraterrestrial chromites. Brunflo chromite element concentration range is shown for 4 grains analyzed.

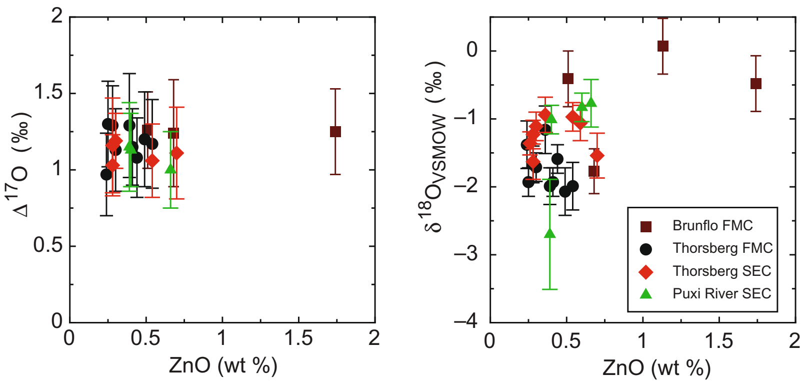

Fig. 6. ZnO concentrations vs. $\delta^{18}O$ and $\Delta^{17}O$. There is no correlation between ZnO and oxygen-isotopic compositions.

a different group. The Catalogue of Meteorites (Grady, 2000) lists 58 L/LL chondrites, representing about 6‰ of all listed L, LL and L/LL chondrites. (U–Th)/He ages of 12 L/LL chondrites were determined by Wasson and Wang (1991) based on data compiled by Schultz and Kruse (1989). Eleven out of the 12 L/LL chondrites have ages $\geqslant$1.7 Ga, and one has an age of 50 Myrs. Such an age distribution is not observed for L chondrites, which mostly have Ar-Ar gas-retention ages of ~500 Ma and seem to originate from a single parent body, which broke-up at that time. Gas-retention ages of the 12 L/LL chondrites are also different to ages of LL chondrites which show a peak at ~1.2 Ga, an age cluster neither observed for L chondrites (Bogard, 1995) nor for L/LL chondrites (Wasson and Wang, 1991). This observation suggests separate parent bodies for the L, LL, and L/LL chondrites that suffered different collisional histories. Distinct L and LL parent body histories are evidenced in the distributions of cosmic-ray exposure ages of modern meteorites that reflect relatively recent impact events on the respective secondary parent asteroids (see compilation by Wieler (2002)). It is unlikely, based on the above-mentioned observations together with the oxygen isotope data presented here and the previous studies of Ordovician ECs, that parent bodies of LL or L/LL chondrites were the sources of the samples studied here.

6. CONCLUSIONS

1. High-precision and accuracy SIMS oxygen three-isotope data of extraterrestrial chromite grains from fossil meteorites and micrometeorites found in a ~2 Myr interval of Ordovician marine limestone of 467.3 ± 1.6 Ma dated with conodont biochronology at Thorsberg in southern Sweden and Puxi River in south-central China provide strong evidence that these chromites formed in a single asteroidal source and were part of fragments generated in the L chondrite parent asteroid breakup 470 ± 6 Ma. The oxygen isotope data are a successful test for the link between the chromites and the asteroid breakup, and are consistent with previous lines of evidence.
2. We confirm that the fossil meteorite Brunflo is an L chondrite instead of an H chondrite with high-precision oxygen three-isotope analyses with SIMS. Brunflo fell ~5 Myr after the L chondrite asteroid breakup event and very likely was formed in this event. This suggests that the elevated impact rate of fragments from the breakup event lasted for at least ~5 Myr, and is consistent with recent numerical model simulation of the L chondrite parent asteroid breakup event.
3. The non-correlation of oxygen isotope data with elemental concentrations and the tightly clustered non-terrestrial values of Δ^{17}O show that terrestrial alteration did not affect the oxygen isotope composition of the studied extraterrestrial chromite grains.
4. We conclude that highly precise and accurate SIMS oxygen three-isotope analysis in conjunction with major and minor element analyses is an effective method to investigate extraterrestrial chromite grains as witnesses of solar system events preserved in sediments. Similar studies are planned on extraterrestrial materials deposited at other times in Earth's history.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.10.027.

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