Determining the impactor of the Ordovician Lockne crater: Oxygen and neon isotopes in chromite versus sedimentary PGE signatures

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ABSTRACT

Abundant chromite grains with L-chondritic composition in the resurge deposits of the Lockne impact crater (458 Myr old; dia. ~10 km) in Sweden have been inferred to represent relict fragments of an impactor from the break-up of the L-chondrite parent body at 470 Ma. This view has been challenged based on Ir/Cr and platinum group element (PGE) patterns of the same resurge deposits, and a reinterpretation of the origin of the chromite grains. An impactor of the non-magmatic iron meteorite type was proposed instead. Here we show that single-grain oxygen and noble-gas isotope analyses of the chromite grains from the resurge deposits further support an origin from an L-chondritic asteroid. We also present PGE analyses and Ir/Cr ratios for fossil L-chondritic meteorites found in mid-Ordovician marine limestone in Sweden. The L-chondritic origin has been confirmed by several independent methods, including major element and oxygen isotopic analyses of chromite. Although the meteorites show the same order-of-magnitude PGE and Cr concentrations as recent L chondrites, the elements have been redistributed to the extent that it is problematic to establish the original meteorite type from these proxies. Different

PGE data processing approaches can lead to highly variable results, as also shown here for the Lockne resurge deposits. We conclude that the Lockne crater was formed by an L-chondritic impactor, and that considerable care must be taken when inferring projectile type from PGEs in sedimentary ejecta deposits.

1. Introduction

Abundant fossil, L-chondritic meteorites in marine limestone from a mid-Ordovician (470 Ma) quarry in Sweden, and a two orders-of-magnitude increase in L-chondritic micrometeorites in sedimentary strata of the same age worldwide, provide strong evidence for a breakup of the L-chondrite parent body in the asteroid belt at that time (Schmitz et al., 1996, 2001, 2008; Cronholm and Schmitz, 2010; Heck et al., 2010). Already in the 1960s the young K-Ar gas retention ages of many recently fallen L chondrites were inferred to reflect a major parent-body breakup event at around 500 Ma (Anders, 1964). Recently, refined $^{40}Ar/^{39}Ar$ measurements of L chondrites indicate an age of 470 ±6 Ma for the event, which is the same age as for the sediments rich in L-chondritic material (Korochantseva et al., 2007). Although there is robust evidence for a dramatic increase in the flux of micrometeorites and meteorites to Earth for a few million years after the breakup event, model predictions of a coeval increase in the flux of larger L-chondritic asteroids to Earth are more difficult to test (Zappalà et al., 1998). Prominent changes around 470 Ma in Earth's fauna, such as the onset of the Great Ordovician Biodiversification Event (Schmitz et al., 2008), as well as an order-of-magnitude overrepresentation of mid-Ordovician impact craters among Earth's well-dated craters (Schmitz et al., 2001) give some support for an asteroid shower. More robust evidence, however, must come from studies of impact ejecta layers in the geological record, and from identifying the type of impacting projectiles. The problem is that large projectiles tend to become completely vaporized upon impact, leaving behind only a chemical fingerprint that may be fractionated by various processes and thus difficult to interpret. In rare cases pieces of the impactor are preserved, like in the Eltanin or Morokweng impact events (Kyte, 2002; Maier et al., 2006), allowing safe identification of projectile type. For one mid-Ordovician impact crater, the well-preserved, ca. 10 km diameter Lockne crater (458 Ma) in central Sweden, Alwmark and Schmitz (2007) reported an extreme enrichment of extraterrestrial chromite grains in the resurge deposits, the so called Loftarstone. More than 75 extraterrestrial chromite grains per kg of Loftarstone were found, which is three to four orders of magnitude more grains than in normal marine limestone. The chromite grains have an L-chondritic element composition and hence were interpreted as relict fragments of an impactor related to the 470 Ma L-chondrite breakup event. Tagle et al. (2008) challenged this view based on Ir/Cr and platinum group element (PGE) ratios of the Loftarstone, as well as a reinterpretation of the compositional signature of the chromite grains. They suggested that the impactor was a non-magmatic iron meteorite (NMI). This is a viable suggestion considering that PGE signatures of sedimentary ejecta have been shown to be usable under some conditions to identify projectile types (e.g., Evans et al., 1993).

In order to further constrain the origin of the Lockne crater we present here single-grain oxygen and noble gas isotopic data for the purported L-chondritic chromite grains from the Loftarstone. High precision oxygen isotopic analyses of fossil extraterrestrial chromite has proven to be a reliable method to identify precursor meteorite types (Greenwood et al., 2007; Heck et al., 2010). Neon isotopes can discern if an extraterrestrial chromite grain originates from a micrometeorite (solar-wind implanted Ne), meteorite (cosmic-ray Ne) or the interior of an extraterrestrial body with a size greater than the penetration depth (> ca. 2 m) of galactic cosmic rays (Heck et al., 2008; Meier et al., 2010). We also present PGE and Ir/Cr data for mid-Ordovician fossil meteorites for which the L-chondritic origin has been confirmed based on independent proxies, e.g. oxygen isotopes, element composition and silicate inclusions in chromite, and petrography including chondrule appearances. In light of these data we discuss the utility of PGE patterns in sediments for determining impactor types.

2. Materials and methods

The chromite grains (ca. 63-100 μm in diameter) studied here originate from the two Loftarstone samples FF2 and FF4 collected at the edge of the inner Lockne crater (see figure 1 in Sturkell, 1998, for sample locations). The samples contain 2.5 and 2.0 ppb Ir, respectively (Sturkell, 1998). Alwmark and Schmitz (2007) recovered abundant extraterrestrial chromite grains from sample FF2, however, because of shortage of this material 50 g of sample FF2 and 300 g of sample FF4 were used for the present study. The procedure of recovering grains was the same as in Alwmark and Schmitz (2007) except that the HCl- and HF-leached residue fractions were not heated to remove coal, because this could have an effect on the noble gases.

Seven chromite grains with L-chondritic element composition according to Alwmark and Schmitz (2007) were selected from the Loftarstone for O isotope analysis, using a CAMECA IMS-1280 ion microprobe at the WiscSIMS Laboratory, University of

Wisconsin-Madison (Kita et al., 2009). The grains were mounted in the center of 25 mm epoxy plugs with chromite standards UWCr-2 and UWCr-3 and polished to a flat low-relief surface (Heck et al., 2010). We performed oxygen-three-isotope analyses on the grains using the same instrument setup and analytical conditions as in the approach optimized for chromite analyses by Heck et al. (2010). The primary ion beam at 5 nA intensity was focused to a 15 μm spot. In total 10 analyses, bracketed by standard analyses, were obtained on the chromite grains. We are able to achieve precisions of $\leq$0.3‰ (2SD) for $\delta^{18}O$ and $\delta^{17}O$ and ~0.2‰ for $\Delta^{17}O = (\delta^{17}O – 0.52 \times \delta^{18}O)$ from single spot analysis. The contribution of OH^- interference to $^{17}O^-$ was typically less than 0.1‰ and the uncertainties of the correction on $^{17}O/^{16}O$ ratios were insignificant (<0.05‰). This precision is sufficient to distinguish H versus L or LL chondrites. Values of $\Delta^{17}O$ from chromite grains from recently fallen H, L and LL chondrites, analyzed during the same session and reported by Heck et al. (2010), fell onto $\Delta^{17}O$ group averages obtained from bulk meteorite fluorination analysis (Clayton et al., 1991), and demonstrate the reliability of our analytical method (Fig. 1). The seven polished grains were also analysed for major and minor elements with a CAMECA SX-51 electron probe microanalyzer (EPMA) at UW-Madison. For further details on the SIMS and EPMA procedures, see Heck et al. (2010).

In addition six L-chondritic chromite grains from the Loftarstone, each grain weighing between 1 and 4 µg, were analyzed for cosmogenic ^3He and ^{21}Ne at ETH-Zürich. As the amount of cosmogenic noble gases was expected to be very small, due to the small size of the grains, an ultra-high-sensitivity mass spectrometer and a low-blank extraction line were used for the measurements. The mass spectrometer concentrates gases into the ion source by a molecular drag pump (compressor), which gives a ca. two orders of magnitude higher sensitivity than the same instrument without a compressor ion source (Baur, 1999). Detection limits were ~$4*10^{-16}$ cm^3 STP for ^{21}Ne and ~$2*10^{-16}$ cm^3 for ^3He, and are defined as the 2σ scatters of the blank. For further details on the instrument, analytical procedures and calculations, see Heck et al. (2004, 2008) and Meier et al. (2010).

The selection of the 13 chromite grains discussed above was based on semi-quantitative element analyses of unpolished, whole grains, using an energy-dispersive spectrometer (Inca X-sight from Oxford instruments) with a Si detector, mounted on a Hitachi S-3400 scanning electron microscope at Lund University. Cobalt was used for standard, see Alwmark and Schmitz (2009a) for further details. The analyses are mostly of sufficient quality to determine if a grain has an ordinary chondritic composition. Grains were discarded if there was any doubt of a chondritic origin.

Whole-rock samples (ca. 40-70 mg) of fossil L chondrites from mid-Ordovician marine limestone in Sweden (Schmitz et al., 2001) were analysed for PGEs at Woods Hole Oceanographic Institution by isotope dilution with ICP-MS after NiS fire assay preconcentration according to methods described in Hassler et al. (2000) and Peucker-Ehrenbrink et al. (2003). The following meteorites were analysed: Österplana 003, 008, 009, 019, 027, 032, 035 and Gullhögen 001 (Connolly et al., 2007). Concentrations were calculated using one (Ir), two (Ru, Pd, Pt), or three (Os) isotope ratios, and concentrations based on multiple ratios typically agree to better than 10% (Ru) and 5% (Pd, Pt). External reproducibility of PGE data was investigated by multiple analyses of standard reference materials (SRM) with certified PGE concentrations (Pd, Pt). The most homogenous of the SRM we tested with moderate low PGE concentrations is the Trembley Lake Diabase (TDB-1). The average values and reproducibility (95% confidence interval) of this standard is 122±5 pg Os/g, 78±5 pg Ir/g, 4.4±0.2 ng Pt/g, and 24.8±1.0 ng Pd/g (see Peucker-Ehrenbrink et al., 2003 for details). Certified or provisional values for this SRM are 5.8 ng Pt/g, 22.4 ng Pd/g (both certified), 150 pg Ir/g (provisional). Total procedural blanks contribute less than 1% of the total analyte.

3. Chemical and isotopic signatures

3.1 Loftarstone chromite grains

The oxygen isotope results for chromite grains from the Loftarstone are summarized in Table 1, and compared with oxygen isotope results for recently fallen H, L and LL meteorites in Fig. 1. It is clear that the Loftarstone grains show typical L or possibly LL composition. The grains also show the same oxygen isotopic composition as chromite grains from fossil Österplana meteorites (Heck et al., 2010). The $\Delta^{17}O$ SIMS data for the Loftarstone chromite show little variability (0.11‰, 2SD; n=10) and average at 1.15 ±0.08‰ (weighted average based on individual 2SD errors). This is consistent with $\Delta^{17}O$ of chromite from modern Ergheo L5 fall (1.09 ±0.07‰, weighted average as above, Heck et al., 2010), and with the $\Delta^{17}O$ group average of modern L or LL chondrites (1.07 ±0.18‰, 2SD; n=26; 1.26 ±0.24‰, 2SD, respectively) (Clayton et al., 1991). Oxygen isotope ratios of the Loftarstone chromite grains lie on a mass-dependent fractionation line within the analytical uncertainty, while the weighted average is similar to that of Ergheo L5 (Fig. 1).

The $\Delta^{17}O$ value of the Loftarstone grains (1.15 ±0.08‰) is clearly distinct from $\Delta^{17}O$ of NMI meteorites (–0.48 ±0.20‰; 2SD; n=23), including IAB and IIICD irons, analyzed by Clayton and Mayeda (1996). Oxygen and nitrogen isotopes of silicate inclusions of some magmatic iron meteorites of type IIE are consistent with H chondrite data (Clayton et al., 1983; Mathew et al., 2000). However, we can clearly distinguish H chondrites from L and LL chondrites, and can exclude from that observation alone a IIE origin of the Loftarstone chromites. There is not even a remote possibility that the abundant chromite in the Loftarstone could have an NMI origin.

The elemental concentrations determined with EPMA for the grains analysed for O isotopes are presented in Table 2. The results are very similar to results for the 73 extraterrestrial chromite grains recovered from the Loftarstone by Alwmark and Schmitz (2007), and chromite grains from 26 mid-Ordovician fossil meteorites analysed by Schmitz et al. (2001). The data in tables 1 and 2 allow a detailed grain-by-grain comparison of oxygen isotopic composition and elemental composition. No correlation of $\delta^{18}O$, $\delta^{17}O$, or $\Delta^{17}O$ with any measured element concentration is observed.

The noble gas results for six chromite grains from the Loftarstone are shown in Table 3, and compared with similar data for extraterrestrial and terrestrial chrome spinels from meteorite-rich mid-Ordovician limestone. The Loftarstone grains show no or very low concentrations of ^{3}He and $^{20,21,22}Ne$, i.e. the grains have acquired no or insignificant amounts of cosmogenic, solar or nucleogenic noble gases. This is in clear contrast to other extraterrestrial chromite grains recovered from mid-Ordovician sediments. Sediment dispersed chromite grains representing parts of micrometeorites typically contain 3-4 orders of magnitude higher concentrations of solar noble gases (Heck et al., 2004; 2008; Meier et al., 2010). Chromite from fossil meteorites instead contain significant concentrations of cosmic-ray induced neon. Terrestrial chrome spinel grains from mid-Ordovician sediments, on the other hand, show a similar absence of ^{3}He or $^{20,21,22}Ne$ as the Loftarstone grains (Meier et al., 2010). The semi-quantitative analyses by SEM-EDS of the six chromite grains used for the destructive noble gas analyses are presented in Table 4. Despite the lower quality of the analyses it is obvious, based on previous experience, that the grains originate from ordinary chondrites. Over the years our group has screened in excess of a thousand unpolished chromite grains in order to identify chondritic grains by means of semi-quantitative SEM-EDS analyses. Subsequent high-quality analyses of the grains after polishing have always confirmed the preliminary assessment (e.g., Schmitz et al., 2001; Cronholm and Schmitz, 2010).

3.2 PGEs in fossil meteorites and Loftarstone

The results of PGE analyses of the nine small whole-rock pieces from eight fossil L chondrites are shown in Table 5 and compared with PGE data from the literature for recently fallen, fresh L chondrites. The L-chondrite classification of the fossil meteorites is based on studies of the element and oxygen isotopic composition of chromite (Schmitz et al., 2001; Heck et al., 2010), the composition of olivine and pyroxene inclusions in the chromite (Alwmark and Schmitz, 2009b), and the average size distribution of relict chondrule textures (Bridges et al., 2007). Most of the fossil meteorite samples show similar high, or even higher, PGE concentrations as recent meteorites, e.g. 450-940 ng/g Ir in the fossil meteorites compared to 385-490 ng/g Ir in recent L chondrites. The fossil meteorites are almost completely pseudomorphed by secondary minerals, and chromite is the only relict component known (Nyström and Wickman, 1991; Schmitz et al., 2001). Some of the meteorite pieces have Ir concentrations as low as 60-200 ng/g, i.e. they have lost 50 to 90 percent of their original inventory. Other pieces show up to a factor two higher PGE concentrations than recent meteorites. These data suggest considerable redistribution of PGEs.

In Fig. 2 we show that the fossil L-chondrite samples give highly variable PGE patterns, with no or only little resemblance to the patterns of recent unweathered L chondrites. As a central argument for an NMI impactor of the Lockne crater, Tagle et al. (2008) use the Ru/Ir ratio measured in the Loftarstone. They show that recent L chondrites have ratios in the range between 1.42 and 1.62, and that the corresponding ratio, based on regression slopes, in the Loftarstone lies at 2.00 ±0.11, outside the L-chondritic range but in accord with an NMI impactor. The Ru/Ir ratios of the fossil L chondrites in Fig. 2 and Table 5 vary between 1.00 and 3.83, however, none of the nine ratios fall in the range for recent L chondrites. It would not have been possible to establish the L-chondritic origin of the fossil meteorites from the individual PGE patterns, despite the fact that much of the original PGEs are preserved. We attempted also regression analyses of the data (e.g., Ru/Ir, Pt/Ir, Pd/Ir, Pt/Pd, Pt/Ru, Pd/Ru), but the scatter in the data is too large to give any significant information about precursor meteorite type from the regression slopes. Apparently diagenesis has dramatically altered the original ratios for each individual sample. However, despite the large spread in platinum group inter-elemental ratios, the *average* PGE content of the nine samples is close to identical to that from recent, fresh L chondrites (Table 5; Fig. 2). The average Ru/Ir value is 1.57, i.e. perfectly L-chondritic.

4. Discussion

4.1 Chromite for projectile identification

Only for very few craters larger than 1.5 km has the impactor type been established, mainly because physical pieces of the impactors generally are missing (see, Alwmark and Schmitz, 2007; Tagle et al., 2008; Tagle and Claeys, 2005). The extremely abundant chromite grains with L-chondritic composition in the Loftarstone were interpreted by Alwmark and Schmitz (2007) as representing relict physical fragments of an impactor in relatively deep water (ca. 500 m). Using a grossly exaggerated scale when presenting the chromite major element data of Alwmark and Schmitz (2007), Tagle et al. (2008) highlighted some minor deviations for some grains relative to the "ideal" L-chondritic composition. Based on this they questioned the L-chondritic origin of the grains, but suggested no other likely origin. Alwmark and Schmitz (2007) argue that the chromite in the Loftarstone sometimes shows minor deviations from a typical L-chondritic composition, related to hydrothermal alteration of the grains after the impact, but on the whole the majority of the grains still show a clear L-chondritic elemental signature, as now also confirmed by O-isotopic analyses. The NMI meteorites do not contain common chromites of the type found in the Loftarstone (Bunch et al., 1970). It is noteworthy that the Loftarstone is the sediment with the highest content of extraterrestrial chromite ever observed. It contains on the order of one extraterrestrial chromite grain per 0.01 kg rock, in contrast to one grain per 100 kg for slowly formed (ca. 2 mm kyr^{-1}) limestone from periods in Earth's history not influenced by the excess flux of meteoritic matter immediately following the break-up of the L-chondrite parent body (Schmitz and Häggström, 2006; Cronholm and Schmitz, 2007, 2010). In condensed sediments formed within the first few million years after the break-up event, the concentrations are 1-3 grains per kg (Schmitz and Häggström, 2006). The absence of cosmogenic ^{3}He and $^{20,21,22}Ne$ in the chromite grains from the Loftarstone indicates that they have not been exposed to galactic cosmic rays. This is to be expected for extraterrestrial material that has been transported to Earth in a large body (asteroid), as the penetration depth of galactic cosmic rays is on the order of 1-2 m. For the Lockne impactor, which had an approximate size of ~600 m in diameter (Ormö and Lindström, 2000), this means that only ca. 2% of the chromite grains could have been exposed to galactic cosmic rays as they would have been situated in the outermost two meters of the body. The results also indicate that the chromite grains are not reworked grains derived from the enhanced rain of micrometeorites in the mid-Ordovician. Such grains almost always contain solar wind Ne (Heck et al., 2008; Meier et al., 2010). In this alternative explanation, micrometeoritic chromite grains dispersed in the target rock would have lost their solar wind Ne either during impact, because of elevated temperature and pressure, or due to hydrothermal activity in the crater after the impact. However, while the solar wind Ne, which is only implanted a few nm into the surface of a grain, might be easily lost that way, complete loss of noble gases, including cosmogenic Ne, requires more or less total melting of the grains. Most grains show a perfect, unaltered L-chondritic major element and oxygen isotopic composition, disproving melting and pointing towards an initial deficiency in such gases. Degassing of the Loftarstone chromite grains on million year time scales after the impact event is neither a likely scenario, since the long-term burial heating history in the Lockne region was not very different from that at other sites in Sweden, e.g. Kinnekulle, where extraterrestrial chromite grains in sediments have retained all or most of their solar-wind and cosmogenic gases until today (Heck et al., 2008; Meier et al., 2010).

The extraterrestrial chromite grains in the Loftarstone most likely represent the relict residues of weathered, small pieces of the impactor. When an asteroid impacts in deep water such pieces may escape vaporization as shown by the abundant unmelted meteorite fragments found in sediments from the late Pliocene Eltanin impact site in the Southern Ocean (Kyte, 2002). Based on robust biostratigraphy we know that the Lockne crater formed ca. 10 million years after the first micrometeorites from the break-up of the L-chondrite parent body showered the Earth (Alwmark and Schmitz, 2009a). This time lag is in agreement with modeling simulations of large break-up events showing that the larger, km-sized bodies typically tend to reach Earth on the order of 1-30 million years later than the dust particles (e.g. Zappalà et al., 1998; Dermott et al., 2002). Poynting-Robertson light drag is important in transferring particles <500 μm directly from the asteroid belt to the inner solar system, whereas kilometer-sized objects are ejected to the inner solar system first after having drifted into orbital resonance positions.

4.2 PGEs and Cr for projectile identification

Several studies have previously pointed out the general difficulties of using PGE patterns to determine the type of impactor. Farley (2009) evaluated in detail the claims by Tagle and Claeys (2005) of an L-chondritic impactor for the Popigai crater based on PGE patterns in impact glasses, and showed that the impactor signature is highly sensitive to the assumptions and methods used in the regression. By recomputing the Ru/Ir and Ru/Rh, for example, simply by switching *x* and *y* axes, or by including single data points omitted for unspecified reasons by Tagle and Claeys (2005), Farley (2009) showed that no robust conclusion about projectile type for the Popigai crater can be obtained from the PGEs. Regression slopes may be highly dependent on single outlier data points whereas an average value, like for the PGEs of our fossil meteorite, weights each data point to the same extent. As shown here, the average PGE ratios of the fossil meteorite samples give a clear chondritic pattern, whereas regression slopes following the approach of Tagle et al. (2008) are not usable for determining the origin. This insight led us to calculate the average Ru/Ir value for the 17 samples from the Loftarstone analysed by Tagle et al. (2008; their figure 3). This gives a Ru/Ir ratio of 1.76, rather than the 2.00± 0.11 calculated by Tagle et al. (2008) from regression slopes. The average Ru/Ir value of the Loftarstone thus lies just slightly outside the L-chondritic range, 1.42-1.62, whereas the regression slope for the same data set instead indicates an NMI impactor. We argue that the different results from the two approaches shows, analogous to the Popigai case, that the conclusion of Tagle et al. (2008) about an NMI impactor based on the Loftarstone Ru/Ir regression slopes can not be considered robust. It should be noted that the method of averaging PGEs rather than using slopes will not work in samples that have a large fraction of target PGEs.

The Cr/Ir ratios of Loftarstone bulk sediment samples were plotted by Tagle et al. (2008), and mixing lines assuming two-components mixing between target rock and impactor were compared to chondrite-target rock mixing lines (Fig. 3). It was argued that the Loftarstone Cr/Ir regression slope indicates a ratio of 13.1 compared with 7.8 for L-chondrites, a fact used to argue for an NMI impactor. In Table 6 and Fig. 3 we present a compilation from the literature of the Cr/Ir ratios of nine samples from six fossil L chondrites (Schmitz et al., 1996, 1997). It is clear from Fig. 3 that because of element redistribution it is not possible to establish the L-chondritic origin of the fossil meteorites from the Cr/Ir ratios, despite the fact that a major fraction of the Ir and Cr of the meteorites is preserved. The Cr/Ir ratios (x 10^3) of the fossil meteorite samples are highly variable, in the range 5.50 to 37.7 compared to 7.92 for recent L chondrites (Table 6). In a transect of three samples from the central to the outer part of fossil meteorite Österplana 009 there is a gradual shift in Cr/Ir from 5.50 to 11.3 to 32.3, clearly indicating a higher mobility of Ir than Cr during diagenesis. This is further indicated by the decrease in Cr/Ir ratio to 15.4 in the limestone just outside the meteorite, where Ir mobilized from the fossil meteorite was redeposited. We argue that in an open sediment such as the initially porous Loftarstone the observation by Tagle et al. (2008) of slightly higher Cr/Ir ratios than in L chondrites most likely reflects the higher mobility of Ir during early diagenesis, rather than a non-chondritic impactor.

Element mobility during early diagenesis is probably the greatest problem when attempting to use PGE patterns from sedimentary ejecta deposits, however, fractionation in the hot impact plume and during subsequent condensation may also obscure original patterns (e.g., Evans et al., 1993). Post-depositional mobility of PGEs in sediments has been described in several papers, e.g. Colodner et al. (1992) showed that Pt, Re and Ir in abyssal sediments are redistributed by changes in sedimentary redox conditions. Wallace et al. (1990) showed that the PGEs of the Late Proterozoic Acraman impact ejecta similarly were highly mobile and affected by redox chemistry. Evans et al. (1993) compiled PGE data for a large number of continental and marine Cretaceous-Tertiary boundary clays, and concluded that the boundary has a chondritic PGE signature, but only when the integrated values on a global scale are considered. For each individual site non-chondritic values were the rule rather than an exception. This conclusion is similar to that obtained here for the PGEs of the fossil meteorites, i.e. only the integrated value for all samples gives a clear chondritic signature. This also lends support to the significance of the near-chondritic average Ru/Ir ratio of the Loftarstone.

5. Conclusions

High-precision oxygen isotope SIMS analyses confirm that the abundant extraterrestrial chromite grains in the Loftarstone are L (or LL) chondritic (see, Alwmark and Schmitz, 2007). The isotopic results are clearly incompatible with meteorites of the NMI type. Analyses of Cr and PGEs of fossil L-chondritic meteorites show that meteoritic elemental ratios in ancient sedimentary environments are significantly affected by element mobility, and only integration of a large data set can give clues about original ratios. The approach is very sensitive to how the integration is made. We find no robust support for the claim by Tagle et al. (2008) that the Lockne crater was caused by an NMI impactor. The Lockne crater is likely related to the L-chondrite parent body break-up at 470 Ma.

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References

Alwmark, C., Schmitz, B., 2007. Extraterrestrial chromite in the resurge deposits of the early Late Ordovician Lockne crater, central Sweden. Earth Planet. Sci. Lett. 253, 291-303.

Alwmark, C., Schmitz, B., 2009a. The origin of the Brunflo fossil meteorite and extraterrestrial chromite in mid-Ordovician limestone from the Gärde quarry (Jämtland, central Sweden). Meteorit. Planet. Sci. 44, 95-106.

Alwmark, C., Schmitz, B., 2009b. Relict silicate inclusions in extraterrestrial chromite and their use in the classification of fossil chondritic material. Geochim. Cosmochim. Acta 73, 1472-1486.

Anders, E., 1964. Origin, age and composition of meteorites. Space Sci. Rev. 3, 583-714.

Baur, H., 1999. A noble-gas mass spectrometer compressor source with two orders of magnitude improvement in sensitivity. EOS Trans., AGU 46 Abstract F1118.

Bridges, J.C., Schmitz, B., Hutchison, R., Greenwood, R.C., Tassinari, M., Franchi, I.A., 2007. Petrographic classification of Middle Ordovician fossil meteorites from Sweden. Meteorit. Planet. Sci. 42, 1781-1789.

Bunch, T.E., Keil, K., Olsen, E., 1970. Mineralogy and petrology of silicate inclusions in iron meteorites. Contr. Mineral. Petrol. 25, 297-340.

Clayton, R.N., Mayeda, T.K., 1996. Oxygen isotope studies of achondrites. Geochim. Cosmochim. Acta 60, 1999-2017.

Clayton, R.N., Mayeda, T.K., Olsen, E.J., Prinz, M., 1983. Oxygen isotope relationships in iron-meteorites. Earth Planet. Sci. Lett. 65, 229-232.

Clayton, R.N., Mayeda, T.K., Goswami, J.N., Olsen, E.J., 1991. Oxygen isotope studies of ordinary chondrites. Geochim. Cosmochim. Acta 55, 2317-2337.

Colodner, D.C., Boyle, E.A., Edmond, J.M., Thomson, J., 1992. Post-depositional mobility of platinum, iridium and rhenium in marine sediments. Nature 358, 402-404.

Connolly, Jr., H.C., Smith, C., Benedix, G., Folco, L., Righter, K., Zipfel, J., Yamaguchi, A., Chennaoui Aoudjehane, H., 2007. The Meteoritical Bulletin, No.92, 2007 September. Meteorit. Planet. Sci. 42, 1647-1694.

Cronholm, A., Schmitz, B., 2007. Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone at Gubbio, Italy: The flux of unmelted ordinary chondrites. Meteoritic. Planet. Sci. 42, 2099-2109.

Cronholm, A., Schmitz, B., 2010. Extraterrestrial chromite distribution across the mid-Ordovician Puxi River section, central China: Evidence for a global major spike in flux of L-chondritic matter. Icarus 208, 36-48.

Dermott, S.F., Durda, D.D., Grogan, K., Kehoe, T.J.J., 2002. Asteroidal dust, in: Bottke, W.F.Jr., Paolicchi, P., Binzel, R.P., Cellino, A. (Eds.), Asteroids III. The University of Arizona Press, Tucson, Arizona, pp. 423-442.

Evans, N.J., Gregoire, D.C., Grieve, R.A.F., Goodfellow, W.D., Veizer, J., 1993. Use of platinum-group elements for impactor identification: Terrestrial impact craters and Cretaceous-Tertiary boundary. Geochim. Cosmochim. Acta 57, 3737-3748.

Farley, K.A., 2009. Late Eocene and late Miocene cosmic dust events: Comet showers, asteroid collisions, or lunar impacts? Geol. Soc. Amer. Spec. Paper 452, 27-35.

Greenwood, R.C., Schmitz, B., Bridges, J.C., Hutchison, R., Franchi, I.A., 2007. Disruption of the L chondrite parent body: New oxygen isotope evidence from Ordovician relict chromite grains. Earth Planet. Sci. Lett. 262, 204-213.

Hassler, D.R., Peucker-Ehrenbrink, B., Ravizza, G.E., 2000. Rapid determination of Os isotopic composition by sparging OsO_4 into a magnetic-sector ICP-MS. Chem. Geol. 166, 1-14.

Heck, P.R., Schmitz, B., Baur, H., Halliday, A.N., Wieler, R., 2004. Fast delivery of meteorites to Earth after a major asteroid collision. Nature 430, 323-325.

Heck, P.R., Schmitz, B., Baur, H., Wieler, R., 2008. Noble gases in fossil micrometeorites and meteorites from 470 Myr old sediments from southern Sweden, and new evidence for the L-chondrite parent body breakup event. Meteorit. Planet. Sci. 43, 517-528.

Heck, P.R., Ushikubo, T., Schmitz, B., Kita, N.T., Spicuzza, M.J., Valley, J.W., 2010. A single asteroidal source for extraterrestrial Ordovician chromite grains from Sweden and China: High-precision oxygen three-isotope SIMS analysis. Geochim. Cosmochim. Acta 74, 497-509.

Kita, N.T., Ushikubo, T., Fu, B., Valley, J.W., 2009. High precision SIMS oxygen isotope analysis and the effect of sample topography. Chem. Geol. 264, 43-57.

Korochantseva, E.V., Trieloff, M., Lorenz, C.A., Buykin, A.I., Ivanova, M.A., Schwarz, W.H., Hopp, J., Jessberger, E.K., 2007. L-chondrite asteroid breakup tied to Ordovician meteorite shower by multiple isochron 40Ar-39Ar dating. Meteorit. Planet. Sci. 42, 113-130.

Kyte, F.T., 2002. Unmelted meteoritic debris collected from Eltanin ejecta in *Polarstern* cores from expedition ANT XII/4. Deep-Sea Res. II, 49, 1063-1071.

Maier, W.D., Andreoli, M.A.G., McDonald, I., Higgins, M.D., Boyce, A.J., Shukolyukov, A., Lugmair, G.W., Ashwal, L.D., Gräser, P., Ripley, E.M., Hart, R.J., 2006. Discovery of a 25-cm asteroid clast in the giant Morokweng impact crater, South Africa. Nature 441, 203-206.

Mathew, K.J., Palma, R.L., Marti, K., Lavielle, B., 2000. Isotopic signatures and origin of nitrogen in IIE and IVA iron meteorites. Geochim. Cosmochim. Acta 64. 545-557.

Meier, M.M.M., Schmitz, B., Baur, H., Wieler, R., 2010. Noble gases in individual L chondritic micrometeorites preserved in an Ordovician limestone. Earth Planet. Sci. Lett. 290, 54–63.

Nyström, J.O., Wickman, F.E., 1991. The Ordovician chondrite from Brunflo, central Sweden. II. Secondary minerals. Lithos 27, 167-185.

Ormö, J., Lindström, M., 2000. When a cosmic impact strikes the seabed. Geol. Mag. 137, 67–80.

Peucker-Ehrenbrink, B., Bach, W., Hart, S.R., Blusztajn, J.S., Abbruzzese, T., 2003. Rhenium-osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP Sites 504 and 417/418. Geochem. Geophys. Geosyst. 4, Art. No. 8911; doi 10.1029/2002GC000414.

Schmitz, B, Häggström, T., 2006. Extraterrestrial chromite in Middle Ordovician marine limestone at Kinnekulle, southern Sweden – Traces of a major asteroid breakup event. Meteorit. Planet. Sci. 41, 455-466.

Schmitz, B., Harper, D.A.T., Peucker-Ehrenbrink, B., Stouge, S., Alwmark, C., Cronholm, A., Bergström, S.M., Tassinari, M., Wang, X., 2008. Nature Geoscience 1, 49-53.

Schmitz, B., Lindström, M., Asaro, F., Tassinari, M., 1996. Geochemistry of meteorite-rich marine limestone strata and fossil meteorites from the lower Ordovician at Kinnekulle, Sweden . Earth Planet. Sci. Lett. 145, 31-48.

Schmitz, B., Peucker-Ehrenbrink, B., Lindström, M., Tassinari, M., 1997. Accretion rates of meteorites and cosmic dust in the early Ordovician. Science 278, 88-90.

Schmitz, B., Tassinari, M., Peucker-Ehrenbrink, B. 2001. A rain of ordinary chondritic meteorites in the early Ordovician. Earth Planet. Sci. Lett. 194, 1-15.

Sturkell, E.F.F., 1998. Impact-related Ir anomaly in the Middle Ordovician Lockne impact structure, Jämtland, Sweden. GFF 120, 333-336.

Tagle, R., Claeys, P., 2005. An ordinary chondrite impactor for the Popigai crater, Siberia. Geochim. Cosmochim. Acta 69, 2877-2889.

Tagle, R., Schmitt, R.T., Erzinger, J., 2008. The Lockne impact is not related to the Ordovician L-chondrite shower. Lunar Plan. Sci. Conf. XXXIX, Abs. #1418.

Wallace, M.W., Gostin, V.A., Keays, R.R., 1990. Acraman impact ejecta and host shales: Evidence for low-temperature mobilization of iridium and other platinoids. Geology 18, 132-135.

Wasson, J.T., Kallemeyn, G.W., 1988. Composition of chondrites. Phil. Trans. R. Soc. London, Ser. A, 325, 535-544.

Zappalà, V., Cellino, A., Gladman, B.J., Manley, S., Migliorini, F., 1998. Asteroid showers on Earth after family breakup events. Icarus 134, 176-179.

Figure captions

Fig. 1: Oxygen-three-isotope diagram. Loftarstone chromite individual analyses (open circles) are shown with 2 SD error bars. The weighted Loftarstone average (solid circle) is shown with its weighted average error based on individual 2 SD errors. Gol 001 is a bulk analysis of ca. 100 chromite grains shown with 2 SD error bars from the fossil meteorite Österplana 029 (Gol 001) reported by (Greenwood et al., 2007). Chromite data from recent ordinary chondrites (triangle and box symbols) are weighted averages of SIMS data from Heck et al. (2010). Mass-dependent fractionation lines are shown for terrestrial samples (TFL; dashed line), for average compositions of group H, L and LL bulk ordinary chondrites (Clayton et al., 1991) and NMI meteorites (Clayton and Mayeda, 1996) (solid lines) and their standard deviations (shaded boxes).

Fig. 2: L-chondrite normalized PGE patterns for nine samples from fossil L-chondritic meteorites Öst 003, 008, 009, 019, 027, 032, 035 and Gul 001. Recent L-chondrite data from Wasson and Kallemeyn (1988) and Tagle and Claeys (2005).

Fig. 3: Ir and Cr content of nine samples from fossil L-chondritic meteorites Öpl 001, 007, 009, 011, 030, and 036, compared with mixing lines by Tagle et al. (2008) for assumed two component mix between target rock and impactor for the Loftarstone based on two data

sets. Included in the figure are also expected mixing lines with different chondritic impactors, following Tagle et al. (2008) and Wasson and Kallemeyn (1988). Slopes for the Loftarstone mixing lines were based on Ir contents <4.5 ppb, whereas fossil meteorites contain 100-880 ppb Ir.