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A fossil winonaite-like meteorite in Ordovician limestone: A piece of the impactor that broke up the L-chondrite parent body?

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ABSTRACT

About a quarter of all meteorites falling on Earth today originate from the breakup of the L-chondrite parent body ∼470 Ma ago, the largest documented breakup in the asteroid belt in the past ∼3 Ga. A window into the flux of meteorites to Earth shortly after this event comes from the recovery of about 100 fossil L chondrites (1–21 cm in diameter) in a quarry of mid-Ordovician limestone in southern Sweden. Here we report on the first non-L-chondritic meteorite from the quarry, an 8 cm large winonaite-related meteorite of a type not known among present-day meteorite falls and finds. The noble gas data for relict spinels recovered from the meteorite show that it may be a remnant of the body that hit and broke up the L-chondrite parent body, creating one of the major asteroid families in the asteroid belt. After two decades of systematic recovery of fossil meteorites and relict extraterrestrial spinel grains from marine limestone, it appears that the meteorite flux to Earth in the mid-Ordovician was very different from that of today.

1. Introduction and background

Of the meteorites falling on Earth today about 85% are ordinary chondrites, divided based on iron and metal content into the H, L and LL groups. Among these the H and L groups make up 45% each, with the remainder being LL chondrites (Bevan et al., 1998). Since the 1960s it has been known that most of the L chondrites show shock features and K–Ar gas retention ages of ∼470 Ma, reflecting that the parent body of these meteorites broke up in a major collisional event at this time (Anders, 1964; Keil et al., 1995; Bogard, 2011; Swindle et al., 2014). Backtracking the orbits of individual members of asteroid families shows that either the ∼6000 member Flora or ∼1000 member Gefion families may be the residual remains in the asteroid belt (Nesvorný et al., 2002, 2009; Kyte et al., 2011). The breakup has also left prominent traces in Earth's geological record. In 1993, following two chance finds of fossil meteorites in mid-Ordovician marine limestone in Sweden, a systematic search for such meteorites was initiated in the Thorsberg quarry in southern Sweden (Schmitz et al., 2001; Schmitz, 2013). In the quarry, mid-Ordovician limestone is sawed for production of floor plates, among other uses. The lithified sediments were deposited far from land and formed slowly, 2–4 mm Ka^{-1}. It is in the industrial process that the meteorites are recovered, and until today 101 meteorites, 1–21 cm in diameter, have been found, representing ∼98% of all fossil meteorites known to science. The recovered meteorites fell over an area of ∼20 000 m^2 of the sea floor during ∼2 Ma. The limestone beds being sawed and yielding meteorites, however, represent <1 Ma of time. All meteorites except the one discussed in this paper are ordinary chondrites, and they are all (or almost all) L chondrites (Schmitz, 2013). Comparisons with the recent flux of meteorites indicate a flux at least one to two orders of magnitudes higher in the mid-Ordovician (Schmitz et al., 2001). This is also supported by the distribution in strata worldwide of sediment-dispersed, relict

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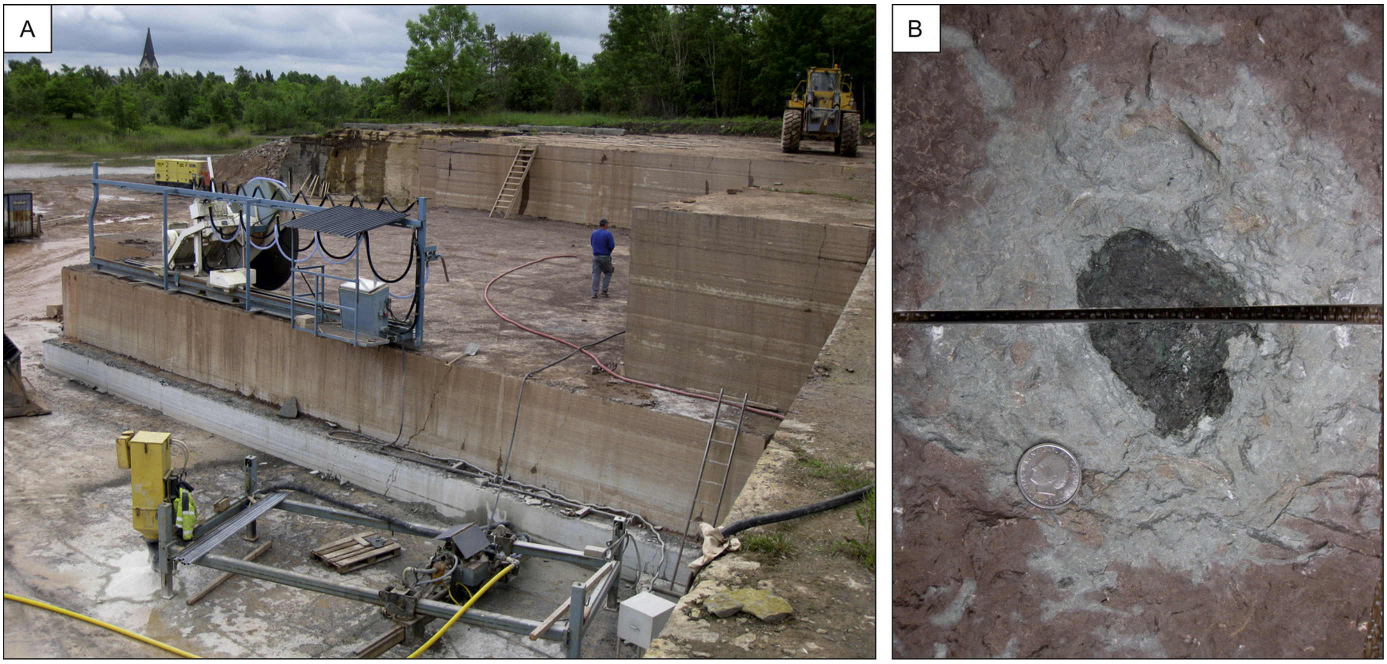

Fig. 1. The Thorsberg quarry and the Mysterious Object. (A) Thorsberg quarry on June 15, 2013. See Fig. 2 for names of different beds. The Österplana church is seen in the back. (B) The Mysterious Object from the Glaskarten 3 bed. The meteorite is 8 × 6.5 × 2 cm in size. It was found in the youngest quarried bed of the Thorsberg quarry, at the top of the section.

L-chondritic chromite grains (63–250 μm in diameter), representing the ancient flux of micrometeorites (Schmitz et al., 2003; Schmitz and Häggström, 2006; Heck et al., 2008, 2010; Cronholm and Schmitz, 2010; Meier et al., 2010, 2014; Lindskog et al., 2012; Schmitz, 2013).

In the collection of fossil meteorites there has until now been no second type of meteorite that could represent the impactor that hit the L-chondrite parent body. Neither do we know of any other type among recently fallen meteorites with gas retention ages of 470 Ma, similar to the L chondrites (Bogard, 2011). Establishing the character of the impactor could give insights about whether the breakup, and possibly also coeval environmental perturbations on Earth, are related to a large-scale astronomical event affecting the entire solar system (Schmitz, 2013). For example, if the impactor was a comet this could reflect a general perturbation of the orbits of Oort cloud comets and an increase in the comet flux to the inner solar system (Perryman, 2009). One would also expect that in the systematic recovery of fossil meteorites, sooner or later a meteorite representing the non-L-chondritic background flux would be found. On June 26, 2011 the quarry workers were removing limestone beds of low industrial quality from the upper part of their quarry. In the quarry's uppermost bed, Glaskarten 3, the quarry workers identified an 8 × 6.5 × 2 cm prominent gray clay inclusion as a fossil meteorite (Figs. 1–2). All fossil meteorites are almost completely replaced mainly by calcite and clay minerals, and spinel minerals are the only common relict components (Schmitz et al., 2001). Based on spinel analyses, it was soon obvious that this meteorite, with the working name Mysterious Object (MO), is of a completely different kind than the ordinary chondrite meteorites so far found. Here we discuss the possible origin of the MO based on analyses of elements and O and Ne isotopes in its spinels as well as concentrations and isotopes of Os in MO whole-rock. Based on the results, that hint at a winonaite-like origin, we also studied, for comparison, the spinel fraction of recently fallen meteorites that could be analogues to the MO.

2. Materials and methods

For detailed information on materials and methods, see Supplementary Online Material, only a summary is given here. The elemental compositions of chrome spinel grains from the MO and three recent winonaites, Winona, NWA 725 and NWA 4024, were determined with a scanning electron microscope (SEM) equipped with a calibrated energy dispersive spectrometer (EDS). The analyses were performed on polished surfaces, and a cobalt standard was used to control instrumental drift. Eight chrome spinel grains from the MO and a similar number from one of the L chondrites from the same quarry were prepared for oxygen-three isotopic analysis using multicollector secondary ion mass spectrometry (SIMS). Five MO grains and six L chondrites grains proved suitable for analysis. A primary Cs^+ ion beam with a spot size of ~10 μm was used to sputter O-ions from the grains. The three oxygen isotopes were collected in multicollection mode using Faraday cups for ^{16}O and ^{18}O and an electron multiplier for ^{17}O. The data were standardized using Burma spinel. This is not ideal, because there is evidence of a matrix effect related to iron content in spinels (Heck et al., 2010). However, the L-chondrite spinels plot very close to the average O-isotope composition for bulk L chondrites, giving us confidence that our standardization is reasonable. In addition, matrix effects are mass-dependent and will move the compositions along a slope ~0.52 line on an oxygen three-isotope plot. We are primarily interested in $\Delta^{17}O$ (defined as $\delta^{17}O - 0.52 \times \delta^{18}O$), the distance that an object plots away from the terrestrial mass-fractionation line, so conclusions are not sensitive to mass-dependent variations (see Supplementary Online Material for details). Helium and Ne isotopes were measured in each of seven chrome spinel grains from the MO with an ultrahigh sensitivity noble gas mass spectrometer. Two small (12 and 43 mg) aliquots of the bulk MO meteorite were analyzed for Os and Os isotopes by inductively coupled plasma mass spectrometry (ICPMS) using different methods in two different laboratories.

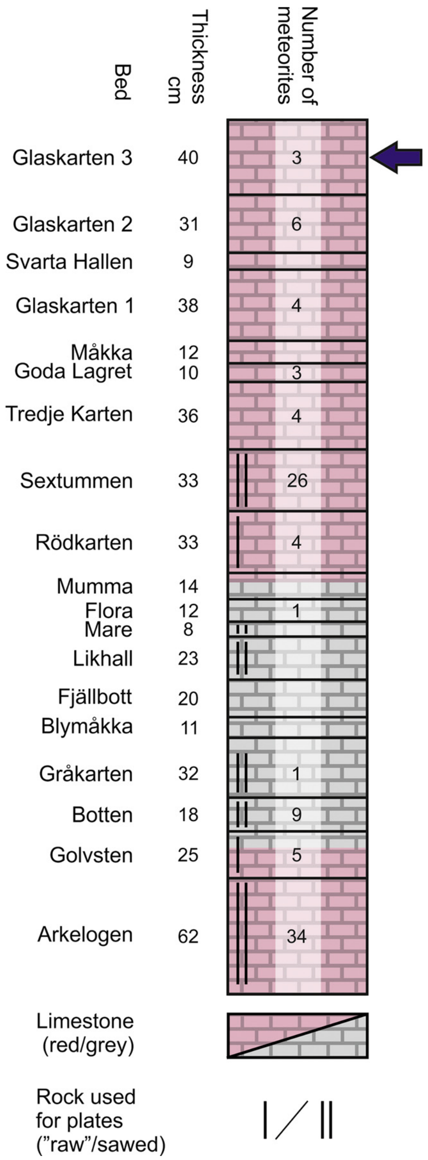

Fig. 2. Distribution of fossil meteorites in the Thorsberg quarry by June 2013. The position of the Mysterious Object is marked by the arrow. The division of the column in different beds is based on tradition used by quarry workers.

3. Results

The MO whole-rock Os concentrations and isotopes data as well as the chrome-spinel O and Ne isotopes clearly confirm that it is a fossil meteorite, and not a volcanic bomb or any other terrestrial material. The MO contains about 50 opaque chrome spinel grains >63 µm per gram meteorite, which is below the range (∼100–3800 grains/g) of chromite content in equilibrated L-chondrites (Bjärnborg and Schmitz, 2013). We found that Winona and NWA 4024 contain about similar concentrations of large chrome spinel grains as the MO, but in NWA 725 they are significantly more abundant. Most MO spinel grains recovered are 60–90 µm large, but rare grains up to 200 µm in the longest axis do exist. This is similar to the grains in Winona and NWA 4024, but in NWA 725 they are often much larger, up to 500 µm. The MO chrome spinel grains have a very different appearance than those in equilibrated ordinary chondrites, but resemble those in recent winonaites. The MO grains are commonly euhedral with large crystal surfaces, and show a tendency for octahedral shapes. We searched also for transparent Mg–Al spinels (>28 µm), a characteristic component of the more common types of carbonaceous chondrites (Simon et al., 2000; Bjärnborg and Schmitz, 2013), but none were found. Neither did we find such Mg–Al spinel grains in the recent winonaites studied.

The individual chrome spinel grains of the MO are in general homogeneous in elemental composition, but there are significant differences between grains, see Figs. 3 and 4 and Supplementary Tables S1–S7. Most grains have Al_2O_3 content in the range 20–30 wt%, Cr_2O_3 35–45 wt%, FeO 23–28 wt% and MgO 4–6 wt%, but there is also a small population with ∼70 wt% Cr_2O_3, and low Al_2O_3, 0.2 wt%. The composition of the MO spinels is very different from the narrow and characteristic compositional range of chromite in equilibrated ordinary chondrites, e.g., $Al_2O_3 \sim 5$–8 wt%, $Cr_2O_3 \sim 55$–60% and FeO ∼ 25–30 wt% (Schmitz et al., 2001; Cronholm and Schmitz, 2010; Schmitz, 2013). Chrome spinel grains from recent winonaites are equilibrated and show only minor compositional variations within individual meteorites, but large variations between different meteorites (Fig. 3). The MO grains show much higher Al_2O_3 and significantly lower Cr_2O_3 concentrations than the grains from recent winonaites. The MO grains show some similarities, such as high Al_2O_3 and Cr_2O_3, to chrome spinel grains from a winonaite-related clast found in the Villalbeto de la Peña L6 chondrite (Bischoff et al., 2013; see further below) (Fig. 4).

Oxygen three-isotope analysis is a powerful tool to classify meteorites (Clayton, 1993). The oxygen isotopic compositions of the MO chrome spinels are clearly distinct from those of modern and fossil L chondrites (Heck et al., 2010). The compositions of MO spinels are also distinct from other ordinary chondrites, CR, CV, and CO carbonaceous chondrites, and acapulcoites and lodranites (Fig. 5). Instead, the MO spinels define a trend very similar to meteorites of the winonaite group (Fig. 5) (Greenwood et al., 2012). The MO spinels overlap with the upper end of the range for ureilites, but ureilites typically do not contain spinels, and those that do have only a few very tiny spinels in shock-melt pockets (Berkeley et al., 1980). The field for bulk CM2 chondrites also lies in the same region as the ureilites, but the bulk oxygen compositions are not the appropriate ones for this comparison. CM2 chondrites are mechanical mixtures of two types of material: (1) a high temperature component consisting of calcium–aluminum-rich inclusions, chondrules, and isolated olivine and pyroxene grains and (2) fine-grained hydrous matrix consisting primarily of phyllosilicates. The high-temperature component has oxygen compositions lying on the CCAM line toward more ^{16}O-rich compositions, and its spinels are mostly Mg–Al spinel (not seen in the MO). The low-temperature component plots just below the CCAM line but to the upper right, mostly off of Fig. 5 (Clayton and Mayeda 1984, 1999). The $\delta^{17}O$ and $\delta^{18}O$ values for the MO have a relatively large spread along the winonaite array (Fig. 5). Some of this scatter may be due to variations in instrumental mass fractionation due to cracks and topography of the measured spinel grains (e.g., Kita et al., 2009). Some of the scatter may also reflect minor diagenetic alteration of the grains.

The whole-rock samples of the MO show high Os concentrations, 800–1200 ng/g, and low $^{187}Os/^{188}Os$ ratios of 0.123–0.132, similar to the Thorsberg quarry fossil ordinary chondrites (72–1280 ng/g; 0.126–0.175) as well as recent ordinary chondrites (420–1050 ng/g; 0.127–0.131) (Meisel et al., 1996; Schmitz et al., 2001). Similarly, the recently fallen winonaites, Pontlyfni and Tierra Blanca, have 780 and 1220 ng/g Os, respectively (Davis et al., 1977; Kallemeyn and Wasson, 1985).

We calculated ^{3}He and ^{21}Ne production rates (P_3 and P_{21}, respectively) using an elemental production rate model (Leya and Masarik, 2009) for a meteoroid radius of 25 cm and a shielding depth of 10 cm as in Heck et al. (2004, 2008). Using these production rates, cosmic-ray exposure (CRE) ages of 0.9 ± 0.3 Ma and

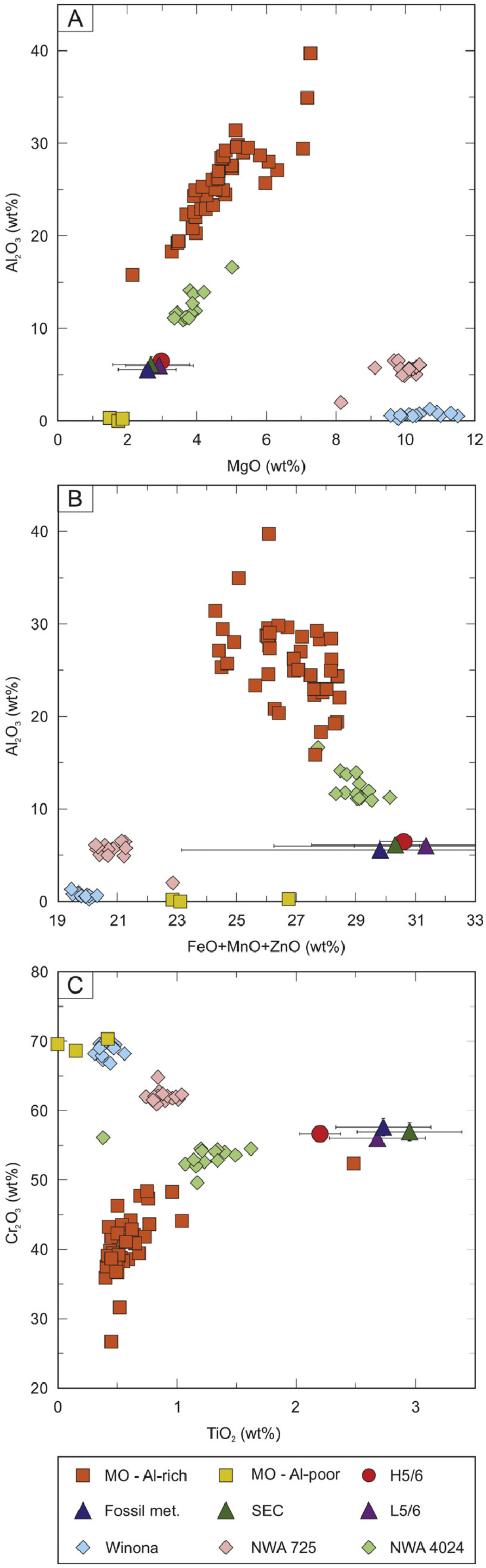

Fig. 3. Element compositions of chrome spinels in Mysterious Object, recent winonaites (Winona, NWA 725, NWA 4024), recent H5/6 and L5/6 chondrites, and Ordovician fossil meteorites, and of sediment-dispersed Ordovician chromite (SEC). For data and references, see Supplementary Tables S1–S5 and S7.

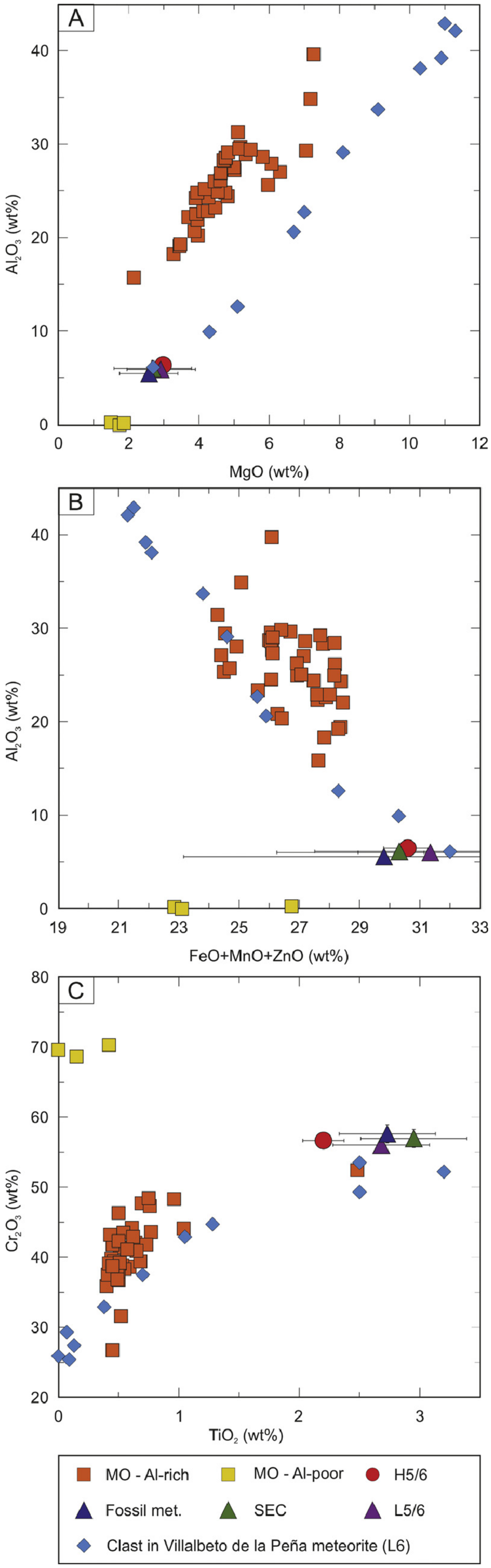

Fig. 4. Element compositions of chrome spinels in Mysterious Object, a winonaite-related clast in Villalbeto de la Peña, recent H5/6 and L5/6 chondrites, and Ordovician fossil meteorites, and of sediment-dispersed Ordovician chromite (SEC). For data and references, see Supplementary Tables S4–S7.

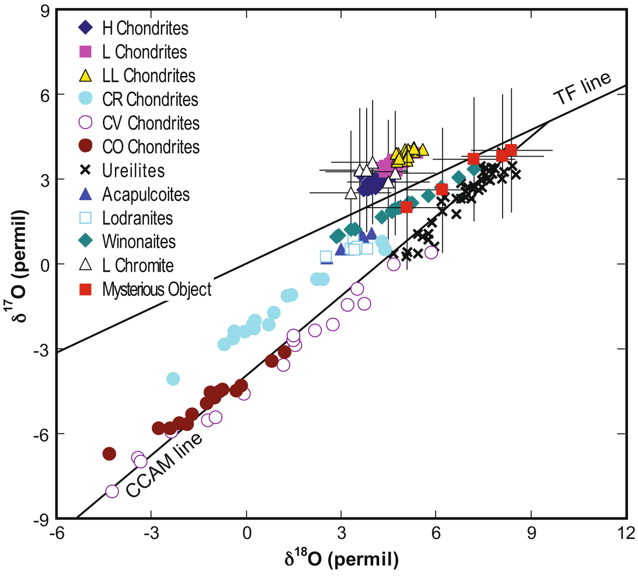

Fig. 5. Oxygen isotopic compositions. Results obtained in this study for chrome spinels from a fossil L chondrite and from the Mysterious Object are compared to the oxygen isotopic compositions of a variety of meteorite types. The L-chondrite data agree well with the values for recently fallen, bulk L chondrites. The Mysterious Object is clearly distinct from almost all meteorite types. Winonaites and the chrome spinels from the Mysterious Object lie along a single trend just below TF (terrestrial fractionation) line. (CCAM line = carbonaceous chondrite anhydrous mineral line.) Data from Clayton et al. (1991), Clayton and Mayeda (1996, 1999), and Greenwood et al. (2012).

1.1 ± 0.4 Ma were calculated from cosmogenic ^{3}He and ^{21}Ne concentrations, respectively (Supplementary Tables S8–S9). While all elements present in chrome spinel grains produce ^{3}He in about equal amounts (within one order of magnitude), ^{21}Ne is predominantly produced by spallation reactions on Mg and, to a lesser extent, on Al. Four grains with high Mg and Al concentrations, as determined by SEM-EDS, also released higher ^{21}Ne amounts, while the three grains low in Mg and Al released less ^{21}Ne (Supplementary Figure S1). This confirms that the ^{21}Ne in the grains is of predominantly cosmogenic origin. For ^{3}He, there is a more simple dependency on mass, as expected.

Opaque chrome spinels with high (20–30%) Al_2O_3 also exist in lunar rocks (Papike et al., 1998), but the high Os concentrations of the MO as well as the Os and O isotope data clearly rule out such an origin. Rare and/or small (<63 μm) Al_2O_3-rich chrome spinels also exist, e.g. in Rumuruti chondrites (Bischoff et al., 2011) and in unequilibrated ordinary chondrites (Holstein et al., 2013), but such meteorites contain also other more common types of spinels that have not been found in the MO. The O isotopic results also exclude that the MO originates from any of these meteorite groups. The eucrite Pasamonte contains chrome spinel with high Al_2O_3 (Bunch and Keil, 1971), but eucrites are low in platinum group elements (Warren et al., 1996).

4. Discussion

The combined data, concentrations and isotopes of Os in whole rock as well as element and O isotope compositions of the separated spinels, show that the MO is of a meteorite type that has no documented equivalent among the ~49 000 recent meteorites known today. Although the oxygen isotopic compositions of the MO are most similar to the bulk compositions of the rare winonaites, the precision of the data is not very good, leaving a significant uncertainty in assigning the MO to the winonaites. In addition, the spinel composition (Al-rich) is clearly different from that (Mg-rich) of the three winonaites studied by us (Figs. 3 and 4; Supplementary Tables S1–S7). There are other meteorite types with somewhat similar oxygen isotopic compositions, but other characteristics of these objects do not match the MO. Enstatite chondrites and achondrites plot along the terrestrial fractionation (TF) line, but these meteorites do not contain chromite or other oxide minerals. Eucrites also have oxygen isotopes that plot near the TF line, but these meteorites are depleted in siderophile elements. Acapulcoites and lodranites, which, like winonaites are primitive achondrites, have Δ^{17}O values near those of winonaites (Fig. 5) (Greenwood et al., 2012), but are slightly more ^{16}O-rich and their spinels have different compositions. The MO shows some similarities to a black, unusual cm-sized winonaite-related xenolith in the Villalbeto de la Peña meteorite that fell in 2004 in Spain (Bischoff et al., 2013). This meteorite was first classified as a shocked L6 chondrite, but after the discovery of the xenolith it was reclassified as a metamorphosed, polymict L-chondritic breccia. The xenolith is the only material known to us that is similar both in oxygen isotopes and chrome spinel composition (Al-rich) to the MO. It may have been incorporated in the breccia long before the breakup of the L-chondrite parent body, judging from hydrothermal metamorphism and shock veins cutting through it as well as the adjacent rock (Dyl et al., 2012; Bischoff et al., 2013).

All types of primitive achondrites are very rare, and there are significant uncertainties regarding their origin (Benedix et al., 1998, 2000; Greenwood et al., 2012). Different primitive achondrites with similar oxygen isotopic composition could represent separate melting residues from a few differentiated parent bodies, but they could also represent different parent bodies that formed in the same region of the condensing nebula.

A previous study of chromite grains from nine fossil meteorites from six beds across ~3.8 m of vertical distance in the Thorsberg quarry yielded comparatively low ^{21}Ne CRE ages, from ~0.1–0.2 to ~0.8–1.2 Ma (Fig. 6) (Heck et al., 2004, 2008). The CRE ages generally increase upward in the sediment column, with the difference in exposure age between the stratigraphically highest and lowest meteorite (~1 Ma) being similar to the time difference in deposition on the sea floor based on biochronological estimates of sedimentation. The meteorites in the oldest bed quarried, Arkeologen, occur only ~80 cm above the first level with abundant sediment-dispersed EC grains, i.e., the level most likely representing the time for the breakup of the L-chondrite parent body. The young average CRE age, ~0.1 Ma, of the Arkeologen meteorites and the gradual increase upward of the exposure ages, and the identical elemental and oxygen isotopic composition of chromite throughout the section (Schmitz et al., 2001; Heck et al., 2010), conforms with the idea that all meteorites originated from one breakup event, and reached Earth at successively later times (Heck et al., 2004, 2008). The CRE age of ~1 Ma for the MO is similar to the CRE ages measured in fossil meteorites from the youngest strata in the Thorsberg quarry (Fig. 6). The low exposure age of only ~1 Ma, which is much shorter than typically observed in achondrites, e.g., ~20–80 Ma for winonaites (Benedix et al., 1998), but identical to the L-chondritic fossil meteorites in the same sediment beds, strongly suggests that the MO is related to the other meteorites, i.e., it is likely to have been released as a decimeter-sized object during the L-chondrite parent body breakup event. The MO is therefore unlikely to be an unrelated fossil meteorite from the background flux.

We see three different possibilities for the origin of the MO. The first, and our favored scenario, is that the MO represents a fragment of the body that hit and broke up the L-chondrite parent body. Although most of this body probably was vaporized, fragments from the body could have been ejected and reached Earth together with L-chondritic material. About 25 recent winonaites are known and ^{39}Ar–^{40}Ar ages exist for three of them, all showing

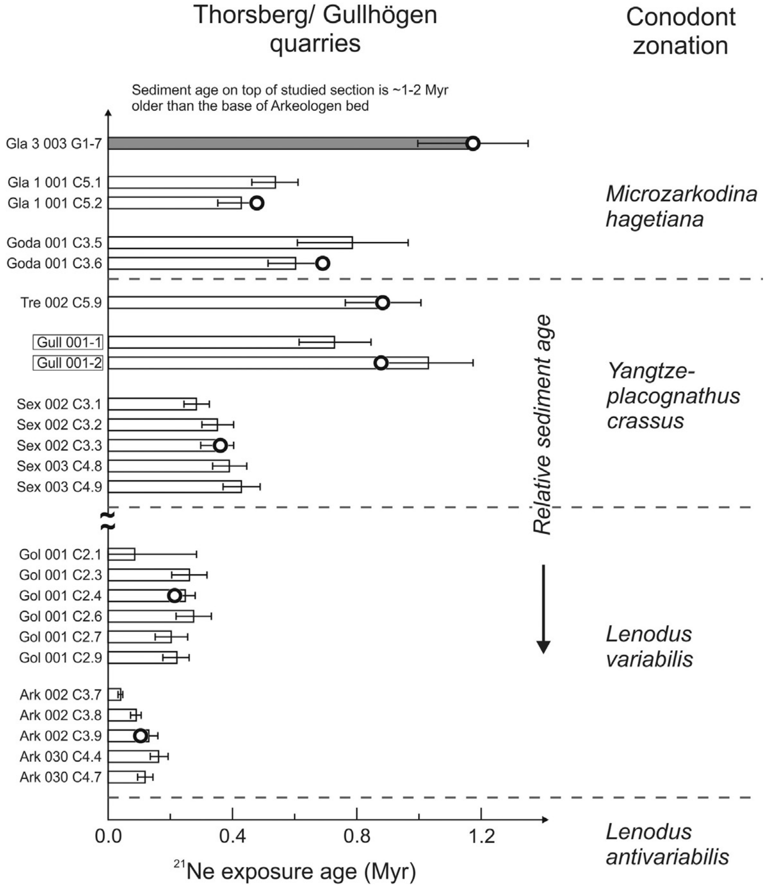

Fig. 6. Cosmic-ray exposure ages for mid-Ordovician fossil meteorites. The Mysterious Object is the Gla 3 003 meteorite at the top of the section. The cosmic-ray exposure ages of the meteorites increase with stratigraphic height in concordance with sedimentation rates as established from conventional biochronology (Heck et al., 2004, 2008). The data indicate that all the fossil meteorites, including the Mysterious Object, originate from a breakup event that took place about 200 Ka before the lowermost beds in the quarry formed. The ^{21}Ne data of Supplementary Table S8 have been recalculated for a correct comparison with the previous data in Heck et al. (2004, 2008).

ages of >4.4 Ga (Benedix et al., 1998). There is thus no support from these data for a collisional event involving the winonaite parent body. Considering how different the spinels of the MO are in their elemental composition compared to those of recent winonaites, it is possible that the MO represents a related but different asteroid body than the one providing winonaites to Earth today. For example, the IAB iron meteorites show the same oxygen isotopic composition as recent winonaites, and are considered to represent the iron core of the differentiated winonaite/IAB parent body (Benedix et al., 2000). There are many types of related iron meteorites for which no corresponding mantle material is known, reflecting that stony material is ground down in the asteroid belt at a faster rate than an iron core (Wasson and Kallemeyn, 2002). Future research may find rare winonaite-related meteorites with gas retention ages similar to those of L chondrites.

A second possible scenario is that there was a winonaite-like asteroid in the region where the L-chondrite parent body broke up, and that the MO resulted from a ricochet collision during the breakup event. The rarity of winonaite meteorites falling on Earth today, however, argues against the idea of a large winonaite-like body in the region of the asteroid belt from where the ordinary chondrites originate today.

The third scenario would be that the MO was a part of the regolith of the L-chondrite parent body, an idea that concurs with the find of the similar xenolith in Villalbeto de la Peña. Although >16 000 recently fallen L chondrites are known, the only winonaite-related object similar to the MO is the clast in the Villalbeto de la Peña meteorite. This indicates that such material was rare in the regolith of the L-chondrite parent body, and cannot account for the one-in-a-hundred find in the mid-Ordovician meteorite assemblage. The discovery of the MO, however, may raise awareness of a so far overlooked relation between winonaites and L chondrites. The MO chromite grains do not contain solar-wind Ne that can be typical of regolith breccias. Also the very short CRE age of the MO argues against a pre-breakup residence in asteroidal regolith. Neither does the MO contain any L-chondrite chromite grains representing the matrix of such a regolith.

For a parent body of approximately 100 km in radius, in order to obtain one meteorite fall from the (smaller) impactor for every hundred falls from the larger body, an impactor of roughly 20 km radius is required. An N-body calculation of encounter rates within the asteroid belt shows that encounters between 100 km asteroids and 20 km impactors are likely to happen at a rate of about four every Ga (Supplementary Figs. S2–S4). As such encounters have impact speeds many tens of times larger than the surface escape speed of the 100 km asteroid, breakup of both asteroids is likely. Those breakups located close to the orbital resonances are most likely to lead to a series of impacts on the Earth, as orbital elements of objects in the resonances will be perturbed chaotically leaving some fragments on Earth-crossing orbits (Zappalà et al., 1998). Further studies of relict meteoritic spinels in Earth's sedimentary record has the potential to yield an improved understanding of these ancient events in space (Schmitz, 2013).

5. Conclusions

After two decades of a systematic search for meteorites on the ancient Ordovician seafloor ∼100 ordinary chondrites have been recovered, with all (or almost all) of them being L chondrites (Schmitz, 2013). Here we report on the first recovered meteorite, the "Mysterious Object", that is not an L-chondrite, but a winonaite-related meteorite of a kind that has no equivalent among the meteorites found on Earth today. Cosmic-ray exposure ages inferred from the relict chrome spinels indicate that the MO is related to the breakup of the L-chondrite parent body. It may be a fragment of (1) the impactor that broke up the L-chondrite parent body, (2) a nearby winonaite-like asteroid hit by a ricochet from the L-chondrite breakup, or (3) a pre-breakup breccia on the L-chondrite parent body. We favor the first alternative because of the rarity of documented winonaite-bearing breccias among recent L chondrites, lack of solar gases and low cosmogenic gas content of MO spinels, and absence of matrix-related L-chondritic spinels in the MO.

If the MO is a piece of the impactor, then the possible role of a winonaite-related object in one of the major, late collisions in the asteroid belt, an event still providing about a quarter of all meteorites to Earth, together with the extreme rarity of winonaite meteorites today, will be challenging to explain in terms of solar system dynamics and meteorite delivery processes. Based on our empirical data it is clear, however, that the meteorite flux to Earth in the mid-Ordovician was very different from that of today.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.05.034.

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