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Abstract: We have reconstructed the distribution of extraterrestrial chrome spinels in a marine limestone section across the Frasnian-Famennian stratotype section at Coumiac in southern France, providing the first insights on the types of micrometeorites and meteorites that fell on Earth at this time. The data can test whether the small cluster of roughly coeval, large impact structures is related to an asteroid breakup and shower with possible bearings also on the late Devonian biodiversity crisis. A total of ~180 extraterrestrial spinel grains (>32 um) were recovered from 957 kg of rock. Noble-gas measurements of individual grains show high solar-wind content, implying an origin from decomposed micrometeorites. Element analyses indicate a marked dominance of ordinary chondritic over achondritic grains, similar to the recent flux. The relation between H, L and LL meteorites is ~29-58-13%, similar to the late Silurian flux, ~31-63-6%, but different from the distribution, ~45-45-10%, in the recent and the Cretaceous flux. Our data show no indication of a generally enhanced late Devonian micrometeorite flux that would accompany an asteroid shower. However, in a single limestone bed that formed immediately before the Upper Kellwasser horizon, that represents the main end-Frasnian species-turnover event, we found an enrichment of ~10 ordinary chondritic grains (>63 um) per 100 kg of rock, compared to the ~1-3 grains per 100 kg that characterize background. The anomalously abundant grains are of mixed H, L and LL types and may be related to an enhanced flux of extraterrestrial dust during postulated minima in both the 405 ka and 2.4 Ma Earth-orbit eccentricity cycles at the onset of the Upper Kellwasser event. In the present solar system the dust accretion at Earth is the highest at eccentricity minima because of the spatial distribution of dust bands of the zodiacal cloud. Besides this small grain anomaly the data here and in previous studies support a stable meteorite flux through the late Silurian and Devonian, in contrast to the mid-Ordovician, when achondritic meteorites that are rare on Earth today were common, followed by the influx of a flood of debris related to the breakup of the L-chondrite parent body. Our accumulated data for six time windows through the Phanerozoic indicate that the ordinary

chondrites make up a major fraction in the meteorite flux since at least the mid-Ordovician. We note that the sources in the asteroid belt of the H and L meteorites, the two most common types of meteorites today and through much of the Phanerozoic, remain elusive.

Letter to Editor and response to comments by reviewers. Re: EPSL-D-18-01496 "The micrometeorite flux to Earth during the Frasnian-Famennian transition reconstructed in the Coumiac GSSP section, France" by Schmitz et al.

Dear Editor McKinnon:
Please find the revised version of our manuscript "The micrometeorite flux to Earth during the Frasnian-Famennian transition reconstructed in the Coumiac GSSP section, France".

We appreciate your editorial handling. This indeed is a lengthy, technical submission on a new approach that also requires knowledge over a broad range of disciplines (asteroid dynamics, mineralogy, cosmochemistry, stratigraphy, etc.).

In the revised manuscript we have followed your advice and reduced the number of figures and tables from 12 to 10 by moving Figure 5 and Table 3 to the Supplementary File. We have also reduced the total number of references from 61 to 55 (including the addition of one reference) and, as suggested, we moved previous section 4.4 to the Supplementary File.

We have carefully considered all the comments by the two reviewers. Their main area of expertise appears to be the general stratigraphic context of the Frasnian-Famennian event. From some of their comments it appears that misunderstandings have arisen because of a lack of background knowledge that we have taken for granted. The minor changes in the revised text therefore mainly aim at better explaining our approach and reasoning to readers who are not familiar with the details of e.g. asteroid dynamics or meteorite classification. Changes in the revised manuscript are marked in red.

Below the reviewer comments are given in italics, followed by our replies in regular font.

Reviewer #1: RECOMMENDATION:
I do not recommend publication of the paper in Earth and Planetary Science Letters in its present form. The reasoning behind this recommendation is given in full in the next section of this review.

SPECIFIC COMMENTS
What is the purpose of the present study? In reading the paper two different purposes appear to be present:
(1) The addition of new data to the goal of constructing a micrometeorite-flux profile for the entire Phanerozoic.
(2) The testing of the hypothesis that the Frasnian-Famennian (Late Devonian) extinctions were associated with an anomalous asteroid shower.

If the purpose of the study is goal (1), then the paper should be published as a valuable contribution to science. However, it should be published in a focused specialty journal (like Meteoritics and Planetary Science or Geochimica et Cosmochimica Acta) and not in a broad-spectrum journal like Earth and Planetary Science Letters.

Reply: The reviewer is right in so far that there are different conclusions originating from our study, but the purpose of the project has been to perform the first reconstruction of the micrometeorite flux across the Frasnian-Famennian transition. This goal is obvious from the title of the paper. The paleometeorite research field is still very young, and prior to the present study knowledge about the flux only existed for five brief time windows during Earth's long history. We believe that there is an interest among readers of EPSL also in following our research on how the meteorite flux has evolved through the ages. Many readers may even think of this as the more exciting part of the paper.

If the purpose of the study is goal (2), then the paper would have the broad-interest focus of Earth and Planetary Science Letters but the paper fails to accomplish this goal because it does not rigorously test the hypothesis it seeks to test. The reasoning behind this assessment of the paper is as follows:

The paper explicitly provides a null hypothesis, H(0) = no asteroid shower occurred during the late Frasnian, but fails to explicitly provide the predictions necessary to demonstrate the alternative hypothesis H(a) = an asteroid shower did occur during the late Frasnian. For H(a), how many micrometeorite grains per 100 kg of strata are necessary to be present in order to demonstrate that an asteroid shower occurred?

For H(0) this is clear in Table 4: the normal flux is around 0.18 log grains per cubic meter per thousand years (or 1 to 3 grains per 100 kg of strata, as stated in the text of the paper and Table 1). And indeed, the micrometeorite flux in the late Frasnian is higher: around 0.7 log grains per cubic meter per thousand years (or around 8 to 11 grains per 100 kg of strata, as stated in the text and Table 1). Thus H(0) can be rejected -- but can H(a) be accepted?

Apparently not, but the reason for rejecting H(a) is not given. Instead, a new H(a2) is proposed with no justification being given for its proposal: H(a2) = an enhanced flux of extraterrestrial dust did occur during the late Frasnian.

Thus the reader is never told what measurements would have justified accepting H(a), or why the observed anomaly of 8 to 11 grains per 100 kg of strata is only indicative of "an enhanced flux of extraterrestrial dust", H(a2), and not an asteroid shower, H(a). The paper cannot be published until this serious error is corrected.

Reply: It is true that one researcher, McGhee (2001), previously has proposed that there is an asteroid shower across the F-F transition, which is a very interesting hypothesis that inspired our study. But there is no "serious error" in our paper. Based on the reviewer's concern, however, we realize that we need to be more explicit in our explanation why the small (factor of three) EC anomaly in one bed cannot be explained by an asteroid shower. We felt this was implicit in the previous draft, but obviously the reasons need to be more clearly spelled out for readers without knowledge about the dynamics of asteroid showers. In Section 4.2 entitled "A small EC anomaly in beds 31c-e" we have therefore added the sentences marked in bold below (page 17, lines 411 etc):

"This rules out a relation to one larger meteorite fragment trapped in the sea-floor sediment or the local disruption of a small asteroid in the atmosphere or in the ocean. **The mixed**

assemblage of grains with different classifications originating from a variety of sources also rules out a relation to an asteroid shower from a breakup in the asteroid belt, because such an event would have led to a significant increase only in one type of grains. An asteroid breakup is also ruled out by the fact that the enrichment of extraterrestrial grains occurs only in one bed, representing at the most 100 ka. This can be compared with the breakup of the L-chondrite parent body, when the flux of L-chondritic large chromite grains stays enhanced by two orders of magnitudes for more than 2 Ma (Schmitz, 2013). A simple explanation to the EC-grain enrichment would be that the beds 31c-e are somewhat more condensed....etc."

We do not agree with the reviewer that no justification is given for the alternative explanation for the small enhancement of grains in bed 31c-e right at the F-F boundary. The second half of section 4.2 (a full page of text!) outlines in detail the justification of the alternative explanation. It appears that the reviewer somehow has missed this part. Based on the independent reconstruction of Earth's orbital position during the F-F event by De Vleeschouwer *et al.* the prediction could even have been made of a small enhancement of extraterrestrial spinels in bed 31c-e. The explanation given may not be the "final truth", but it is the best explanation for now adhering to the Occam's razor principle. Judging from the comment by the reviewer we believe a problem with the previous draft was that the connection between orbital eccentricity and enhanced meteorite flux was not explained in the abstract. The sentence below in bold has therefore been added to the abstract (page 2, lines 40-42):

"The anomalously abundant grains are of mixed H, L and LL types and may be related to an enhanced flux of extraterrestrial dust during postulated minima in both the 405 ka and 2.4 Ma Earth-orbit eccentricity cycles at the onset of the Upper Kellwasser event. **In the present solar system the dust accretion at Earth is the highest at eccentricity minima because of the spatial distribution of dust bands of the zodiacal cloud.** Besides this small anomaly...."

Other inexplicable errors occur in the study. Figure 4 gives only 6 pre-Today geologic-time data points, yet Table 6 lists data from 3 additional geologic horizons -- why were the two Late Cretaceous data points (data from Martin et al. 2019) and the additional post-LCPB Mid-Ordovician data point (data from Heck et al. 2016, 2017) not plotted in the Figure 4 Phanerozoic flux summary?

The referee is correct that three of the data points of Table 6 are not plotted in Figure 4, but again, this is not an error. The Heck et al. "Post-LCPB" data point is for the same stratigraphic level as the Post-LCPB data point of Martin et al. 2018 that is used in Figure 4. But the Martin *et al.* point builds on 444 analyses compared to 119 in Heck *et al.* and is therefore more reliable from a statistical perspective. However, the comparison between the Heck *et al.* and Martin *et al.* data in Table 6 (now 5) is important, because the Heck division builds on both Δ17O and TiO2 analyses, whereas the Martin division is based only on TiO2. Table 6 (now 5) shows that the two approaches give about the same result.
The two data points in Table 6 (now 5) for the late Cretaceous (Martin et al., 2019) have not been included in Figure 4 because they deal with a very special case, i.e. the change in flux during a short-term He-3 anomaly of enigmatic origin. In order to clarify we have added the following text to the caption of the figure "**The Turonian data of Table 5 have not been**

included in the plot because these data relate partly to a period of anomalous flux in connection with an enigmatic ^{3}He anomaly (see, Martin et al., 2019)."

Then, Table 4 lists two additional data points from the Late Cretaceous (Late Maastrichtian) and Early Paleogene (Danian; data from the Cronholm and Schmitz 2007 flux study) that are not listed in Table 6 and that do not occur in Figure 4.

Again, this is no error, but our approach involves complex considerations, just like many other advanced empirical approaches, compare e.g. with the complexities of the zircon U/Pb dating. We understand that it can be difficult for readers to follow the detailed reasoning, but everything is clear if one reads the text carefully. Table 4 (now 3) and Figure 4 describe two completely different things: Table 4 (now 3) gives the flux of "equilibrated ordinary chondrites" (i.e. H, L and LL grains) in the >63 micron fraction, whereas Figure 4 describes only the flux of L chondrites through the ages, based on grains in both the 32-63 and the >63 micron fractions. Figure 4A gives the percentage of L chondrites among the three groups of ordinary chondrites (H, L and LL) from Table 6 (now 5). The percentages from Table 6 (i.e. 5) are used to estimate the absolute flux of L chondritic material from the estimated total flux of ordinary chondrites in Table 4 (i.e. 3). The early Danian and Late Maastrichtian have only been studied for grains in the >63 micron fraction yielding six EC grains in 210 kg of rock. This is enough for a reasonable flux estimate (ca. 2-4 grains per 100 kg of rock as stated in Table 4, i.e. 3) but six grains are far too few grains for an estimate of the proportions of L, H and LL grains in the flux. We think all this will be obvious to anyone who invests time in a careful reading of the manuscript, also in its previous form. It would only burden the text to try to further explain what is already said. EPSL is a scientific journal, and we can expect that the readers know the difference between an "L chondrite" and an "equilibrated ordinary chondrite".

However, in order to minimize the potential confusion we have now added text and changed the first four lines of discussion section 4.1 as follows (pages 13-14, lines 325-328: "**We now have data for the total flux of extraterrestrial chrome spinel for nine Phanerozoic time windows (from a total of 4567 kg of sediment) (Table 3), but only for six of these windows do we have sufficient data to constrain in greater detail the types of meteorites represented in the flux.(Tables 4, 5).**"

Further, in the text, the bottom of page 3 and top of page 4 gives a list of the "so far published first-order reconstructions of the flux of meteorites to Earth" (quoted from the authors, page 3, lines 74 and 75). This list includes the Martin et al. (2019) and Heck et al. (2016, 2017) data that are not included in Figure 4, but the list does not contain the Cronholm and Schmitz (2007) flux study that is listed in Table 4 (but not included in Figure 4). Last, this list also states that additional data exist for the Late Eocene -- in a study by Boschi et al. (2017). These data are not given in either Table 4 or 6, or in Figure 4.

Again, the referee has missed that Figure 4 only deals with the flux of L chondrites, and that not all the studies listed have provided robust information on the specific aspects dealt with in the specific tables or figure referred to by the reviewer. However, we have removed the reference to the late Eocene data of Boschi from the list on page 4, line 79 because this is a special case, see below.

Data for the micrometeorite-flux levels during the Late Eocene would be particularly important, as this is a time interval in which a shower of asteroids did occur -- including the Chesapeake Bay, Toms Canyon, and Popigai impactors (Farley et al. 1998, Science 280:1250-1253; a study that is not cited by the authors), which produced craters with 85 km, 20 km, and 100 km diameters, respectively. Perhaps this time interval might provide data for a definitive measure of micrometeorite flux levels associated with an asteroid shower, H(a), as opposed to asteroid "dust", H(a2).

Yes, the referee is absolutely right and the subject is dealt with in detail in one of our papers referred to in the manuscript: Boschi *et al.* (2017), *Late Eocene 3He and Ir anomalies associated with chondritic spinels.* GCA 204, 205-218. This is a much more recent paper than the Farley et al. (1998) and provides an update of the issue. The Farley paper is centrally referred to in the Boschi paper so we see no reason to add this reference here. Unfortunately, the results of Boschi show that it is not easy to reconstruct the micrometeorite flux in the late Eocene because of the admixture of grains from the large impactors. We have several projects ongoing trying to resolve the issue.

Reviewer #2
This reviewer only had a few comments directly in the manuscript. Line numbers refer to previous version.

Line 32: We have followed the advice of the reviewers and split the long sentence into two sentences.

Line 89: We have added the reference De Vleeschouwer et al., 2017 to the text also at this spot. The paper was referred to already in our previous submission, but only in section 4.2.

Line 131: Our approach works best in condensed sediments (condensed = slowly formed) and this is stated elsewhere in the text.

Line 178: We agree that the OC acronym (for "other chrome spinel") is a little bit problematic so we have changed to OtC and OtC-V throughout.

Line 448: There may be problems with these reports of microtektites. Their origin has not been confirmed.

Line 510: As we have learnt from the LCPB story and modelling of asteroid breakups and delivery of material, an enhanced flux of micrometeorites will prevail after a breakup for about two million year, whereas the larger fragments will be delayed by up to 30 million years because they have to drift into an orbital resonance before entering Earth-crossing orbits.

Line 534: We have not repeated the numbers for the Cretaceous flux in the Conclusion section. This would be to return to too detailed information again.

***Highlights (for review)**

Highlights for review:

- First data on the meteorite flux to Earth during the Frasnian-Famennian bioevent.
- No support of asteroid shower, but comet shower cannot be ruled out.
- Meteorite flux supports eccentricity minimum in Earth's orbit at bioevent.
- First picture of the variations in meteorite flux through the Phanerozoic.
- Ordinary chondrites made up a major fraction of the flux since at least 466 Ma ago.

The micrometeorite flux to Earth during the Frasnian-Famennian transition reconstructed in the Coumiac GSSP section, France

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ABSTRACT

We have reconstructed the distribution of extraterrestrial chrome spinels in a marine limestone section across the Frasnian-Famennian stratotype section at Coumiac in southern France, providing the first insights on the types of micrometeorites and meteorites that fell on Earth at this time. The data can test whether the small cluster of roughly coeval, large impact structures is related to an asteroid breakup and shower

with possible bearings also on the late Devonian biodiversity crisis. A total of ~180 extraterrestrial spinel grains (>32 μm) were recovered from 957 kg of rock. Noble-gas measurements of individual grains show high solar-wind content, implying an origin from decomposed micrometeorites. Element analyses indicate a marked dominance of ordinary chondritic over achondritic grains, similar to the recent flux. The relation between H, L and LL meteorites is ~29-58-13%, similar to the late Silurian flux, ~31-63-6%, but different from the distribution, ~45-45-10%, in the recent and the Cretaceous flux. Our data show no indication of a generally enhanced late Devonian micrometeorite flux that would accompany an asteroid shower. However, in a single limestone bed that formed immediately before the Upper Kellwasser horizon, that represents the main end-Frasnian species-turnover event, we found an enrichment of ~10 ordinary chondritic grains (>63 μm) per 100 kg of rock, compared to the ~1-3 grains per 100 kg that characterize background. The anomalously abundant grains are of mixed H, L and LL types and may be related to an enhanced flux of extraterrestrial dust during postulated minima in both the 405 ka and 2.4 Ma Earth-orbit eccentricity cycles at the onset of the Upper Kellwasser event. In the present solar system the dust accretion at Earth is the highest at eccentricity minima because of the spatial distribution of dust bands of the zodiacal cloud. Besides this small grain anomaly the data here and in previous studies support a stable meteorite flux through the late Silurian and Devonian, in contrast to the mid-Ordovician, when achondritic meteorites that are rare on Earth today were common, followed by the influx of a flood of debris related to the breakup of the L-chondrite parent body. Our accumulated data for six time windows through the Phanerozoic indicate that the ordinary chondrites make up a major fraction in the meteorite flux since at least the mid-Ordovician. We note that the sources in the asteroid belt of the H and L meteorites, the two most common types of meteorites today and through much of the Phanerozoic, remain elusive.

1. Introduction

Classical geologists have a record of interpreting the deep-time history of life and Earth as a more or less closed system. It took them a long time to accept that many of Earth's craters are related to impacts of comets or asteroids rather than volcanism (Koeberl, 2001), and there was considerable reluctance to accept the proposal of Alvarez et al. (1980) that an asteroid impact 66 Ma ago caused the demise of the Mesozoic fauna. Astronomers describe a dynamic universe around us, with processes that potentially could affect the solar system, such as nearby passing stars, supernova explosions, giant molecular clouds, dark matter, galactic mergers, and more (e.g., Perryman, 2018). Generally, the solar system has been considered stable through its late history, with large-scale astronomical processes at the most affecting comets in the outer Oort cloud (Rampino and Haggerty, 1996). Some models suggest that there may also have been disturbances in the solar system because of chaotic transitions in the planetary orbits (Haeys et al., 2010). Such disturbances could be related, for example, to the interaction of the outer gaseous and the inner rock planets. The major problem in any attempts to tie Earth's history to astronomical events is the difficulty of obtaining empirical data about the precise timing of events in space relative to events on Earth. For the past years we have developed an empirical approach that, based on studies of Earth's sedimentary record, can provide glimpses into what went on in space when the sediments formed (Schmitz, 2013). We search for relict, acid resistant minerals from meteorites and micrometeorites that fell in the past and became embedded in sea-floor sediments. One could say we search for "needles in the haystack" but use acids that dissolve terrestrial silicates and carbonates to "burn down the haystack" in order to find the rare extraterrestrial grains. Using this approach we have so far published first-order reconstructions of the flux of meteorites to Earth in the mid-Ordovician, before and after the breakup in the asteroid belt of the parent body of the L-chondritic meteorites (Schmitz et al., 2003; Heck et al. 2016, 2017), late Silurian (Martin et al., 2018), lower Cretaceous (Schmitz et al., 2017) and Turonian (Martin et al., 2019).

Here we report our reconstructions of the meteorite flux to Earth in the late Devonian based on extraterrestrial spinel-grain abundances across the Lower and Upper Kellwasser events in the Frasnian-Famennian (F-F) boundary stratotype section at Coumiac in southern France (Klapper et al., 1993). The F-F boundary event is ranked among the five most important biodiversity crises during the Phanerozoic (McGhee et al., 2013). Ammonites, trilobites, corals, brachiopods and placoderm fish experienced heavy extinction, with tropical faunas suffering the most (Stanley and Luczaj, 2015). The mid-to-late Devonian coral-stromatoporoid reef communities, that built the largest reef complexes in Earth history, collapsed entirely. The diversity declines are step-wise and associated with two distinct event beds, the Lower and Upper Kellwasser beds seen in many sections worldwide (Pujol et al., 2006; Le Houedec et al., 2013, De Vleeschouwer et al., 2017). The two beds are associated with major positive C-isotope anomalies, and formed during reducing conditions, possibly because of enhanced biological productivity. There is no simple explanation to the F-F biodiversity collapse, but there is data indicating that significant global cooling accompanied the faunal crisis (Joachimski and Buggish, 2002; Stanley and Luczaj, 2015). Some authors argue that during the end-Frasnian the cooling began that evolved into the large, late Devonian-to-mid-Permian Gondwanaland ice age (e.g., McGhee, 2014). Tests have been made to determine whether the crisis was triggered by the impact of a large extraterrestrial body, but searches for impact-ejecta tracers, such as Ir, Os isotopes, shocked quartz or Ni-rich magnesioferrite spinel, have given negative results, at least for the stratigraphic interval across the main extinction phase (McGhee et al., 1986; Girard et al., 1997). Relating to the temporal coincidence of the late Devonian biodiversity crisis with several prominent asteroid or comet impact features McGhee (2001) explained the crisis with the "multiple impact hypothesis". There is evidence of at least four large impacts in the late Devonian-early Carboniferous, e.g. the Siljan (52 km in diamter), Woodleigh (40 km), and Charlevoix (54 km) structures and the Alamo impact breccia (Morrow et al., 2009; Earth Impact Database, 2018). McGhee pointed out the similarity of the late Devonian case with late Eocene environmental change that is accompanied by multiple major impacts (e.g., Boschi et al., 2017).

If the multiple impact features observed at or around the late Devonian reflect an asteroid shower following a breakup event in the asteroid belt such a shower would likely be accompanied by an enhanced flux of micrometeorites. Such a connection has been observed in Earth's geological record regarding the breakup in the mid-Ordovician of the ~150 km large parent body of the L-chondritic meteorites (e.g., Schmitz, 2013). Following this event the flux of micrometeorites to Earth increased by two orders of magnitude and remained at this high level for at least 2 Ma. Modeling indicates that the peaks in the fluxes of micrometeorites and asteroids from a breakup may partly have a time lag because of different transport mechanisms in space, with some of the larger impactors arriving up to 30 Ma after a breakup (Zappalà et al., 1998). This is seen in the geological record, where there is roughly a tenfold enhancement of small impact craters with ages in the ca. 30 Ma time interval after the L-chondrite parent body breakup (LCPB) (Schmitz et al., 2001; Bergström et al., 2018, 2019).

The Coumiac section is considered to represent one of the most complete successions across the F-F event and has been studied in great detail for many stratigraphic parameters (e.g., Le Houedec et al., 2013). The section contains the type of condensed pelagic limestones that can be used for searches of extraterrestrial spinels, but during our studies of the section, we realized that it is extremely rich in terrestrial chrome-spinel grains that overprint the extraterrestrial signal. This makes the section less ideal for searches of extraterrestrial spinels in the small size fraction (32-63 μm), and we focus here on the >63 μm fraction, which contains fewer terrestrial spinels.

2. Materials and methods

For detailed information on samples, analytical methods and division of grains into different groups, see Supplementary Online Material, only a summary is provided below.

2.1. Samples and grain separation

We have searched for chrome-spinel grains in a total of 898 kg of limestone from the late Devonian section exposed in the Coumiac quarries in the Montagne Noire region of southern France (Fig. 1). The Upper Coumiac Quarry contains the Global Stratotype Section and Point for the base of the Famennian stage. The samples were collected in the Upper Coumiac Quarry, except for a ~100 kg-sized block of the goniatite-rich Upper Kellwasser bed that was found loose on the floor of the Lower Coumiac quarry. Here we also report the results for two mid-Devonian (Givetian age) samples with a total weight of 58.4 kg from the Marble Quarry Nord at Pic de Bissous in the Montagne Noire region.

The limestone samples were dissolved in HCl (6 M) and HF (11 M) at room temperature in the Astrogeobiology Laboratory (Lund, Sweden) specially built for separation of extraterrestrial minerals from sediments. After sieving at mesh sizes 32 and 63 μm, opaque chrome-spinel grains were identified by handpicking under a binocular microscope and subsequent qualitative element analysis with scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) on unpolished grains. Because of the large amounts of diluting terrestrial chrome-spinel grains in most beds we only studied the >63 μm fraction, but in two samples (beds 20 and 31e) extraterrestrial grains could be recovered also from the 32-63 μm fractions. In both samples the recovery of extraterrestrial grains from the smaller size fraction was incomplete because of the extremely tedious approach. This excludes comparisons in this size interval of grain abundances and flux rates with other time periods. The additional small grains, however, can be used to improve the statistical basis when establishing the ratios between H, L and LL micrometeorite types in the flux. From previous studies we know that there may typically be 15-30 extraterrestrial grains in the 32-63 μm fraction for every such grain in the 63-355 μm fraction. However, terrestrial grains tend to become increasingly more abundant relative to meteoritic grains in smaller the size fraction, and problems with dilution can become insurmountable. We also collected all the chrome-spinel grains in both the 32-63 and >63 μm fractions from one of the two Givetian limestone samples, where the terrestrial spinel contribution is smaller.

2.2 Division of grains and definitions

Equilibrated, ordinary chondritic chromite (EC) has a very distinct and narrow elemental composition and can readily be identified based on this criterion alone (Schmitz, 2013). The EC grains can be further divided into the three groups H, L, and LL based on their oxygen isotope and TiO_2 content, but here we only use the latter parameter (see, Heck et al., 2017; Schmitz et al., 2017; Martin et al., 2018, 2019). The grains that are not EC grains are divided into two main categories, "other Cr spinel" (OtC) and "other Cr spinel with ≥0.45 wt% V_2O_3 and Cr_2O_3/FeO ≥1.45" (OtC-V) grains. The OtC grains are generally dominantly or entirely of terrestrial origin, whereas the OtC-V grains in this type of sedimentary environment typically originate from meteorites other than equilibrated ordinary chondrites (Heck et al., 2017; Schmitz et al., 2017). The type of grains here referred to as OtC grains have in our previous studies been referred to as OC grains, but we now change acronym in order to avoid confusion with OC as being used for "ordinary chondrites" in other research.

2.3 Element concentration analyses

The recovered chrome-spinel grains were mounted in epoxy resin, and polished flat using 1 µm diamond paste. Element concentrations were analysed quantitatively by wavelength dispersive spectroscopy at the Vienna Natural History Museum using a JEOL “Hyperprobe” JXA 8530-F field-emission electron microprobe (FE-EPMA) after a careful back-scattered electron imaging examination for zoning, inclusions and weathering processes. An accelerating voltage of 15 kV, a beam current of 20 nA, 1 µm beam diameter and a counting time of 10 s, giving approximately 250,000 counts, for peak and 5 s for background were used for all element Kα lines. The results for each individual chrome-spinel grain represents the average of three to five separate spot analyses, ensuring better statistics and reproducible data. Precisions of concentration analyses for each element were typically better than 1 rel.% of measured values.

The following synthetic compounds Al_2O_3, Cr_2O_3, TiO_2, NiO, and metallic Co were used as standards for Al, Cr, Ti, Ni and Co, respectively. Natural minerals vanadinite, $Pb_5(VO_4)_3Cl$, gahnite, $ZnAl_2O_4$, tephroite, Mn_2SiO_4 and Marjalahti olivine $(Mg,Fe)_2SiO_4$ were used as standards for V, Zn, Mn, Mg and Fe, respectively. The mean (calculated for 450 analyses points) detection limits (in ppm) for measured elements (with standard deviation in parenthesis) of chrome-spinel matrix and above measuring parameters, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni and Zn are 104(7), 118(8), 203(12), 391(37), 444(37), 291(21), 282(47), 349(23), 328(17) and 580(29), respectively.

A minor fraction of our recovered grains was analysed with the same SEM/EDS approach at Lund University as in our previous studies of chrome spinels (e.g., Schmitz et al., 2017; Martin et al., 2018). These analyses were performed with a calibrated Oxford-Link energy-dispersive spectrometer (with a Si-detector) mounted on a Hitachi scanning electron microscope. Cobalt was used to monitor drift of the instrument. An accelerating voltage of 15 kV in high-vacuum mode, a sample current ~1-2 nA, and a counting live-time of 80 s were used. The result for each individual chrome-spinel grain represents the average of three separate spot analyses, ensuring better statistics and reproducible data. Precisions of analyses were typically better than 1-4 rel%.

Analytical accuracy both in Vienna and Lund has also been controlled by analyses of the USNM 117075 (Smithsonian) chromite standard (Jarosewich et al., 1980), the UWCr-3 standard (Heck et al., 2016) and internally produced chrome-spinel standards. In the Supplementary Online Material (Table S1) we present comparisons of the results by the different analysis approaches in Vienna and Lund.

2.4 Noble-gas analyses

From bed 31e that contains high concentrations of extraterrestrial grains we separated 26 of the largest grains in the 32-63 μm fraction for noble gas (Ne and He) isotopic analyses at ETH Zürich (Heck et al., 2007; Meier et al., 2010). Nine batches (named a to j) consisting of two Devonian sediment-dispersed EC grains each, and one single grain (named k) were transferred manually into individual holes drilled into an Al sample holder. The holder was then loaded into the sample chamber of the high-sensitivity, compressor-source noble gas mass spectrometer (Baur, 1999) connected to an ultra-low blank extraction line consisting of three cold traps at the temperature of liquid N_2 (two of them containing activated charcoal), and three zirconium alloy getters. Gas extraction was done by heating the grains with a Nd:YAG laser with a wavelength of 1064 nm for 60 s, vaporizing them in the process. The gases were then analysed by a protocol originally developed by Heck et al. (2007), and adapted for the analysis of individual EC grains by Meier et al. (2010). The grain masses (needed for concentrations) were calculated by multiplying a density of 4.4 g/cm^3 with the characteristic volume estimated from the cross-sectional area of the grains measured on SEM images, using the empirical formula given by Meier et al. (2014). The sphere-equivalent diameters of the individual grains range from 40 to 75 µm, the typical batch mass is about 1 µg. A production rate of cosmogenic ^{21}Ne in micrometeoritic chromite (from both solar and galactic cosmic rays) of $6.3 \pm 1.3 \times 10^{-10}$ cm^3 STP g^{-1} Ma^{-1} was used to calculate cosmic-ray exposure (CRE) ages (as in Meier et al., 2014).

3. Results

3.1. Spinel-grain abundances based on element analyses

We recovered in total 49 EC and 13 OtC-V grains >63 μm in 957 kg of rock (Fig. 2; Table 1; Table S1). These grains were found together with ~800 grains classified as OtC grains, of which all or almost all have a terrestrial origin. Some beds are particularly rich in terrestrial chrome-spinel grains, making the search for extraterrestrial grains very tedious even in the >63 μm fraction. For example, in bed 31c eight EC and two OtC-V grains were found together with ~300 OtC grains.

The circa three decimeter thick interval of beds 31c-e just below the goniatite-rich Upper Kellwasser bed 31g (bed 31f is only 2 cm thick) shows a factor of ~3 higher EC grain concentration than the samples from other parts of the Givetian-Famennian sections studied here. In 474 kg of rock from beds 31a-e (most mass from c-e) we found 38 EC grains compared with 11 EC grains in 482 kg of limestone from the other studied Devonian beds. The Upper Kellwasser bed itself at Coumiac also holds low concentrations of EC grains, 5 grains in 195 kg rock.

The in total 109 EC grains recovered from both the 32-63 and 63-355 μm fractions of the late Frasnian beds have been divided into the three groups H, L and LL, based on their TiO_2 content (Table 2). The relation between H-L-LL meteorites for all the grains is ~31-57-17 %, when uncorrected for overlap between the three groups (see also the Discussion section). There is no major or significant difference in this relation between beds 20 and 31e, from which most of the grains were recovered.

Nearly all of the EC grains from the two Givetian samples show strong diagenetic replacement of Fe by Mn and Zn. Although we have previously seen how primarily Zn can replace for Fe in the chromite structure (Schmitz et al., 2001), the

MnO concentrations (up to 11 wt%) in the Givetian chromite grains are exceptionally high, but also ZnO concentrations are high (up to 6 wt%), and always at the expense of FeO (Table S1). Because of the diagenetic overprint we do not use these grains in some of our flux reconstructions.

In the late Devonian the EC/OtC-V ratio lies at about 4, but there is some uncertainty around the meaning of this ratio in the absence of oxygen isotope data (Table 1). The one OtC-V grain from the Upper Kellwasser bed with 12 wt% ZnO may be a diagenetically altered EC grain. Most of the late Devonian OtC-V grains (9 out of 12) were found in beds 31a-e with an average EC/OtC-V ratio of 4.2. Although the OtC-V grains are too few for any robust assessments, the available EC/OtC-V ratios appear relatively stable between different samples and do not decrease in samples that are extremely rich in OtC grains. The covariation between OtC-V and EC grains, and absence of covariation between OtC-V and OtC grains indicate that all or almost all of the OtC-V grains are extraterrestrial. Most likely the EC/OtC-V ratio in beds 31a-e primarily reflects the relation between equilibrated ordinary chondritic and achondritic grains. However, one or a few of the OtC-V grains could also originate from unequilibrated ordinary chondrites (see e.g, Heck et al. 2017; Schmitz et al., 2017). The origin in bed 20 of the two OtC-V grains that were found in the >63 µm fraction together with two EC and 13 OtC grains is very uncertain in the absence of oxygen-isotope data.

The provenance of the OtC grains, which likely all are of terrestrial origin, is discussed in the Supplementary Online Material. The most probable sources could be alkali basalts/lamproites or tholeiitic basalts/boninites (Fig. S1).

3.2. Noble gas results

All grain batches released He and Ne far above the instrumental detection limits (Table S2). The $^{3}He/^{4}He$ ratios on the order of ~10^{-4}, and $^{20}Ne/^{22}Ne$ ratios of about ~11 indicate that He and Ne are derived mainly from solar wind, mass-dependently fractionated by implantation into grain surfaces ("fSW"; see Grimberg et al., 2006). The fact that all nine batches of two grains each did release extraterrestrial noble gases suggests that a large majority of the grains must contain them. The He and Ne concentrations are within the lower part of the range observed previously in individual EC grains from the Ordovician period (Alwmark et al., 2012; Meier et al., 2010, 2014), and in batches of Ordovician EC grains (Heck et al., 2008). The $^{3}He/^{4}He$ ratio can be explained by a mixture of solar wind He and fractionated solar wind He (Fig. 3), except for batches c, d, and e, where there might be a small contribution from radiogenic or terrestrial atmospheric He. In a Ne three isotope plot (Fig. 3), the Devonian EC batches show, on average, more fractionated (i.e., lower) $^{20}Ne/^{22}Ne$ ratios than the Ordovician EC grains. As for the Ordovician EC grains, a large fraction of the Devonian EC-grain batches plot (within uncertainty) at higher $^{21}Ne/^{22}Ne$ ratios than mass-dependently fractionated solar wind would suggest, revealing a contribution of ^{21}Ne-rich cosmogenic Ne (from the exposure of the grains to solar and galactic cosmic rays). The cosmogenic inventories of the different grain batches were resolved by first projecting the grains away from the cosmogenic end-member and onto the solar wind fractionation line, and then subtracting the corresponding non-cosmogenic (solar) ^{21}Ne from the measured amounts. The corresponding nominal CRE ages range from ~0 to ~7 Ma (Table S2).

4. Discussion

We are still in an early phase in building up our understanding of the variations in the abundances and types of extraterrestrial spinels in Earth's geological strata. Interpretations will be preliminary because of a small and slowly growing database. The spinel approach requires substantial investments in time and resources. Interpretations may be complex, for example, chrome-spinel abundances vary in different size fractions in different meteorite types (Heck et al., 2017), therefore it is crucial that all comparisons of spinel abundances between samples account for the size interval considered. We rely also on small differences in the chemistry of the grains, and very detailed and careful calibration of the elemental analyses is imperative.

4.1 Mid-Ordovician to Late Cretaceous meteorite flux

We now have data for the total flux of extraterrestrial chrome spinel for nine Phanerozoic time windows (from a total of 4567 kg of sediment) (Table 3), but only for six of these windows do we have sufficient data to constrain in greater detail the types of meteorites represented in the flux (Tables 4, 5). In this perspective, the Frasnian-Famennian meteorite flux, except the small enrichment of EC grains in beds 31c-e, does not appear anomalous. The meteorite flux, ~0.2 grains >63 µm m^{-2} ka^{-1}, based on the 392 kg of rock in the Frasnian-Famennian interval away from beds 31c-e is similar to that of other periods studied, besides the extremely anomalous situation after the LCPB in the mid-Ordovician.

The EC/OtC-V ratio of ~4 (mainly based on grains in beds 31c-e) indicates that the ratio of ordinary chondrites/achondrites may have been lower than today's ratio of ~10 (Table 4). The ratios were not as low as in the mid-Ordovician before the LCPB, when achondrites probably were as, or even more, abundant than ordinary chondrites (Heck et al., 2017). In mid-Ordovician beds formed about 0.5-1 Ma before the LCPB the EC/OtC-V grain (>63 μm) ratio is as low as 1.5. Because chrome-spinel grains generally are more common in equilibrated ordinary chondrites than in most achondrites, this low ratio may even support a dominance of achondrites. Oxygen-three isotope analyses of the mid-Ordovician OtC-V grains confirm that they dominantly represent different types of achondritic meteorites that are rare on Earth today (Heck et al., 2017). Extraterrestrial spinels from Silurian sediments show an EC/OtC-V ratio of 11 (Martin et al., 2018), and in the Early Cretaceous the ratio is 3 (Schmitz et al., 2017), but these studies rely primarily on grains in the 32-63 μm fraction, so the results are not directly comparable to those of the mid-Ordovician and the late Devonian relying on grains >63 μm.

If the Devonian-Carboniferous large impact structures like Siljan and Woodleigh are related to an asteroid shower following a major breakup event in the asteroid belt, there would likely also be a dramatically enhanced flux to Earth of micrometeorites from the body that broke up. However, there are meteorite types, like the carbonaceous chondrites, that generally have low spinel concentrations in the size fractions studied here (e.g., Bjärnborg and Schmitz, 2013). An increase in the flux of spinel-poor micrometeorites would not give a resolvable signal in sediments rich in terrestrial spinels like in this study. Our results thus can only rule out the existence of a shower of the types of micrometetorites and corresponding asteroid types that are rich in chrome spinels. This includes the ordinary chondrites, most types of achondrites, R chondrites, and lunar and martian meteorites. Accordingly, our results cannot rule out, for example, a shower of comets or carbonaceous chondritic asteroids.

Although there appears to have been some significant, and possibly short-term, variations in the ordinary chondrite/achondrite ratio through the Phanerozoic, the three types of ordinary chondrites have generally made up a major fraction of the meteorite flux to Earth at least since the LCPB around ~466 Ma ago. The high abundance of HED achondrites in the pre-LCPB samples was interpreted as the fading trail of the Rheasilvia impact-basin forming event on the HED parent body Vesta (Heck et al., 2017). The unusually abundant primitive achondrites in the pre-LCPB time window represent several types of parent bodies, implying a more complex origin than from a single breakup event. With the present data, we cannot tell whether the high abundance of achondrites relative to ordinary chondrites before the LCPB represents an anomaly in the history of meteorite flux, perhaps related to some kind of astronomical event that led also to the LCPB, or whether these data are representative for the early Phanerozoic. It appears also that at least since the Silurian the relation between the three groups of ordinary chondrites, H, L and LL, has been relatively constant (Table 5). From our data for the six time windows that provide sufficient data we infer that there may have been four different main "regimes" in the flux of ordinary chondrites through the Phanerozoic. At the time just before the LCPB, the three types, H, L and LL, make up about a third each of the flux, followed by a few million years with the L chondrites making up more than 99% of the flux as a result of the LCPB. During the ca. 50 million years spanning from the Late Silurian to the Late Devonian the L chondrites still dominate, making up about 60 %, with the H and LL meteorites representing ~30 and ~10 %, respectively. The flux rate of L chondrites, however, had diminished by two orders of magnitude within a couple of million years after the LCPB (Fig. 4). Both in the early and the late Cretaceous the relation between the three types of ordinary chondrites appears to be similar as today, indicating that also this relation has been a stable feature. Nevertheless, we also have data showing that during shorter "events" there were exceptions to this general pattern, for example, in sediments that formed during an extraterrestrial ^{3}He anomaly with a very enigmatic structure in the Turonian, the H chondrites dominated for a short time (Table 5; Martin et al., 2019). Our data indicate that there may be a general background pattern, on which there are sometimes superimposed signals reflecting short-term events, such as smaller asteroid breakups or major crater-forming events.

There is presently no consensus or robust understanding why the ordinary chondritic meteorites so strongly dominate the flux to the Earth today (e.g., Meibom and Clark, 1999; DeMeo and Carry, 2014; Heck et al., 2017). The spinel data provide growing insight that the situation likely was the same for at least the past ~466 Ma, which does not make the issue less enigmatic. Studies of the present asteroid belt show that today 85% of all meteoritic debris in the inner asteroid belt are related to five major asteroid families, Flora, Vesta, Nysa, Polana and Eulalia (Dermott et al., 2018), but none of these families show a clear relation to the abundant H or L chondrites falling on Earth today.

4.2 A small EC anomaly in beds 31c-e

The ca. 10 EC grains per 100 kg limestone in the ~30 cm limestone interval of beds 31c-e represent a small, but significant anomaly compared both to the other Devonian samples in this study and to similarly condensed strata from other time intervals that we have studied. The grains are of a mixed origin, with similar proportions between H, L, and LL as in the Devonian background flux, and different types of achondritic grains occur in the sample. This rules out a relation to one larger meteorite fragment trapped in the sea-floor sediment or the local disruption of a small asteroid in the atmosphere or in the ocean. The mixed assemblage of grains with different classifications originating from a variety of sources also rules out a relation to an asteroid shower from a breakup in the asteroid belt, because such an event would have led to a significant increase only in one type of grains. An asteroid breakup is also ruled out by the fact that the enrichment of extraterrestrial grains occurs only in one bed, representing at the most 100 ka. This can be compared with the breakup of the L-chondrite parent body, when the flux of L-chondritic large chromite grains stays enhanced by two orders of magnitudes for more than 2 Ma (Schmitz, 2013). A simple explanation to the EC-grain enrichments would be that the beds 31c-e are somewhat more condensed than other parts of the section, but there is no independent sedimentological evidence in support of this view. We have observed similarly high concentrations of EC grains in some single beds throughout the Phanerozoic sedimentary record, such as the *Trypanites* bed in the mid-Ordovician of the Lynna River section in Russia (Heck et al., 2017). Such beds typically show independent and obvious sedimentological, biostratigraphic, and mineralogical evidence of extreme condensation. The F-F interval at Coumiac has been studied in great detail over the decades and there is no indication that the sedimentation rate is lower in beds 31c-e than in surrounding beds. The number of conodont elements, for example, is not significantly different from that in neighboring beds, and the high percentage of juveniles and ramiform elements may exclude sorting processes by strong current activity or gravity flows (Girard and Feist, 1996). If sea-floor hydrodynamic processes had concentrated spinel grains we would have expected the bed to also contain high numbers of the OtC grains that are so abundant throughout the rest of the section, but instead the parts (e.g., bed 31e) of the EC-rich interval has some of the lowest OtC grain concentrations of the F-F beds studied.

It is possible that the abundant grains may reflect a higher rate at which Earth captured extraterrestrial dust particles from different dust bands associated with the zodiacal cloud. The rate at which Earth captures dust in space is dependent on the spatial density of particles near Earth and the geocentric encounter velocity of the particles (Kortenkamp et al., 2001). Studies of the distribution of dust bands in the present solar system show that the capture rate can vary by a factor up to three because of variations in the eccentricity and inclination of Earth's orbit around the Sun. The capture rate is anti-correlated to eccentricity, i.e. at eccentricity minima the dust accretion is the highest (Kortenkamp et al., 2001). De Vleeschouwer et al. (2017) have made detailed reconstructions of the orbital evolution across the F-F transition worldwide and based on their data the Upper Kellwasser event, which is represented by bed 31g, two cm above the top of beds 31c-e, is paced by orbital cycles similar to Mesozoic intervals of environmental upheaval, like the Cretaceous Ocean-Anoxic-Event-2. According to the authors, the Upper Kellwasser event coincides with an unusual minimum in both the 405 ka and 2.4 Ma eccentricity cycles. In such a situation, obliquity prevails over precession, which would also affect climate. With the information at hands, the Occam's razor explanation to the abundant EC grains in beds 31c-e, would be that they reflect that Earth entered into a more dusty area of the solar system in connection with the postulated minima nodes in eccentricity. With combined orbital-cycle studies as those of De Vleeschouwer et al. (2017) and the spinel approach, it may be possible to test whether there is a variation in flux of extraterrestrial dust to Earth related to minima in the eccentricity cycle.

4.3 Noble gases and the origin of the extraterrestrial chromite

The ubiquity of fractionated solar wind He and Ne in Devonian EC grains confirms that they have all been exposed to the solar wind at some point in their history, further corroborating their extraterrestrial origin. There are only two environments in which solar wind exposure of meteoritic materials is common: either as individual dust grains (“micrometeoroids”) in transfer to Earth, or in a regolith layer near the surface of their parent asteroid (where impact gardening leads to their episodic exposure to both the solar wind and galactic cosmic rays). Only a small fraction of the ordinary chondrites falling to Earth today are derived from regoliths (3% of the L chondrites, 8% of the LL chondrites, and 20% of the H chondrites; Bischoff et al., 2018). However, most Antarctic micrometeorites contain fractionated solar He and Ne, and a significant fraction of them derive from ordinary chondritic parent bodies (Osawa et al., 2010; Baecker et al., 2018). While in interplanetary space, micrometeoroids are exposed to bombardment by solar photons, leading to orbital decay on a time-scale of 10^4-10^6 Ma, depending on size, density, and original heliocentric distance (Burns et al., 1979). When they eventually encounter the Earth and enter its atmosphere, silicate particles <300 µm mostly survive entry heating (Love and Brownlee, 1991), limiting the maximal size of the micrometeoroids from which the Devonian EC grains can likely be derived. In Table 6, we list the orbital decay times for spherical chromite (40-80 µm, 4.4 g/cm^3) and silicate (100-1000 µm, 3 g/cm^3) particles from different regions of the asteroid belt and the outer solar system. Particles <300 µm from the inner and middle asteroid belt (i.e., inside 2.8 a.u.), where S-type asteroids, the most likely parent bodies of ordinary chondrites (Nakamura et al., 2011) dominate, should thus reach the Earth in no more than ~2.2 Ma. This age is compatible (within uncertainty) with most of the CRE ages observed in the Devonian EC grain batches. Only two of the EC batches have CRE ages in excess of 2.2 Ma, which indicates that at least some EC grains have seen longer exposure to cosmic-rays, which could point to a regolith origin. However, they might also have traveled in space as part of originally larger (>300 µm), more slowly migrating silicate particles, which were then disrupted by a collision, allowing the smaller fragments to survive entry into the Earth’s atmosphere. For example, it would take a 1 mm-sized particle about ~7 Ma to migrate from the outer edge of the middle asteroid belt (at 2.8 AU) to Earth (Table 6). This age is compatible with the longest CRE age observed in an EC batch. In summary, the observed noble gas record in the Devonian EC grains is fully compatible with the hypothesis that these grains sample the (basic or temporarily enhanced) background flux of ordinary chondritic micrometeorites in the Devonian.

5. Conclusions

Our searches for extraterrestrial spinel grains in strata across the Frasnian-Famennian boundary at the GSSP stratotype section at Coumiac in southern France have not yielded any evidence of a generally enhanced flux of micrometeorites from a breakup event in the asteroid belt that could also explain the small cluster of large impact structures in the late Devonian-early Carboniferous. However, because cometary material and carbonaceous chondrites do not generally contain the types of spinels that we have searched for, the data cannot rule out the existence of a shower of impactors made up of such material.

In one bed immediately below the Upper Kellwasser bed, representing the main animal species-turnover event, we found a small, circa a factor three, enrichment of extraterrestrial spinels originating from H, L, and LL chondrites as well as achondrites. The formation of this bed coincides with an extreme minimum in the eccentricity of Earth's orbit around the Sun, a situation which places the Earth in the center of the zodiacal dust band, which could explain a factor of three increase in the flux of extraterrestrial dust to Earth.

Based on spinel data for six time windows through the Phanerozoic we suggest that the ordinary chondrites have represented a major fraction of the meteorite flux since at least the mid-Ordovician. We tentatively discern four "regimes" in the flux of the ordinary chondrites. Before the LCPB in the mid-Ordovician the three types of ordinary chondrites, H, L and LL, each made up about a third of the flux. Then during a few million years after the LCPB there was an increase by two orders of magnitude in the flux of L chondrites to Earth, with L chondrites making up >99% of the total flux. In the Silurian and the Devonian the absolute flux rates for the L chondrites was down almost at background levels, but they still made up about 60% of the flux. From the early Cretaceous it appears that similar flux conditions as today were established for the ordinary chondrites.

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Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/etc.

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Figure captions

Fig. 1. Map of sampling area for Frasnian-Famennian limestone, with location of the Coumiac quarries.

Fig. 2. Lithostratigraphy of studied interval in the Upper Coumiac Quarry with positions and sizes of samples and number of EC grains >63 μm found. A major faunal turnover occurred when the Upper Kellwasser bed formed.

Fig. 3. Three-isotope diagram (^{20}Ne/^{22}Ne versus ^{21}Ne/^{22}Ne, main panel), and ^{3}He/^{4}He versus ^{4}He concentration diagrams (inset). Noble gas components (open circles) are connected by dashed lines to guide the eye (sources: Busemann et al., 2000; Wieler, 2002; Heber et al., 2009). Ordovician EC grains (from Meier et al., 2010, 2014; Alwmark et al., 2012) are shown as gray solid circles. The EC-grain batches from this work are shown as black solid diamonds. SEC = sediment-dispersed equilibrated ordinary chondritic chromite.

Fig. 4. A) Percentage of L chondrites among ordinary chondrites during five time windows and today. The plot is based on both the small (32–63 μm) and the large

(>63 µm) fraction of EC grains. The Turonian data of Table 5 have not been included in the plot because these data relate partly to a period of anomalous flux in connection with an enigmatic ^{3}He anomaly (see, Martin et al., 2019). B) Total flux of L chondrites through the five time windows until today, based on the >63 µm fraction of EC grains. The flux based on the Late Devonian beds 31a-e is considered to represent an anomaly and plotted off the background trend. The recent flux is assumed to be at/within background values and is set to that of the Early Cretaceous (see, Schmitz et al., 2017). Modified from Martin et al. (2018).

Figure 1

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Figure 2

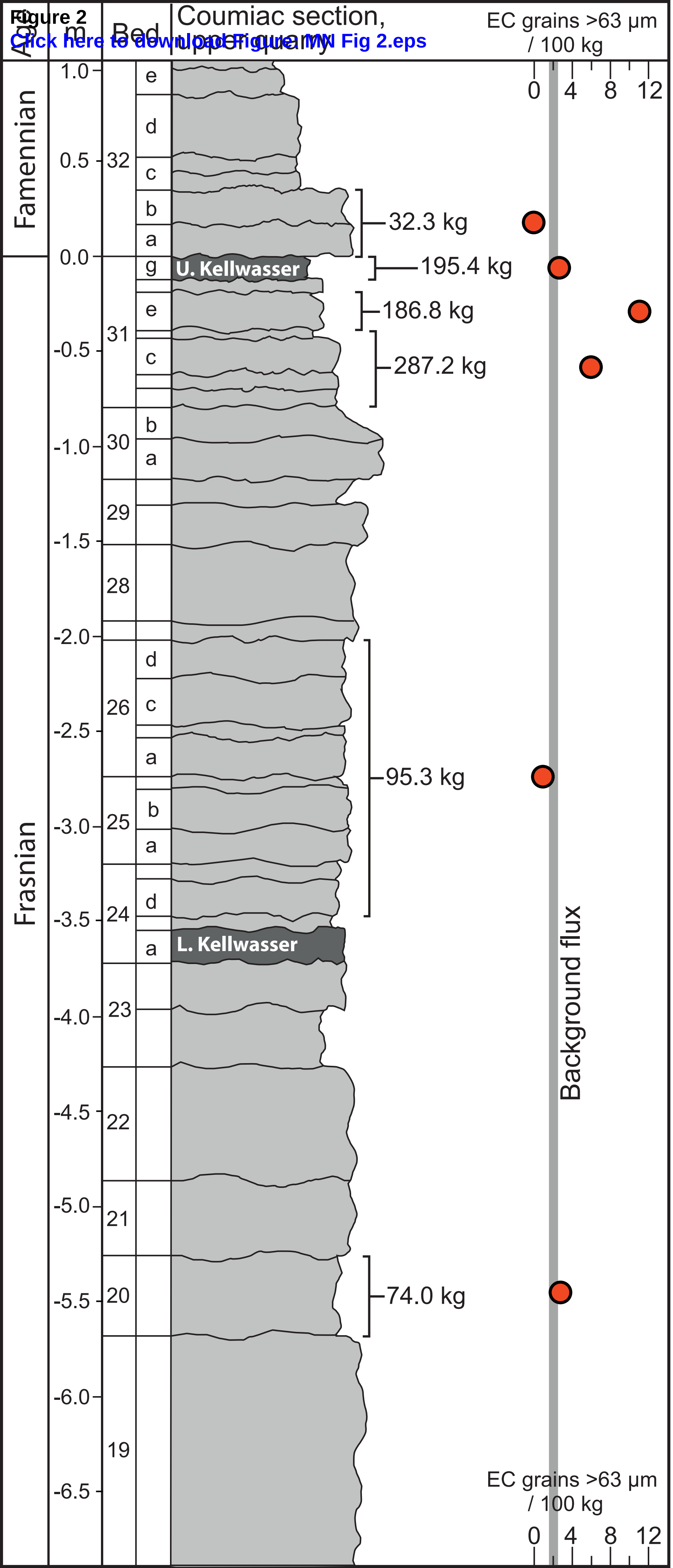

Age
m
Bed
Coumiac section, upper quarry
EC grains >63 µm / 100 kg
0
4
8
12
Famennian
Frasnian
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
32
e
d
c
b
a
31
g
e
c
30
b
a
29
28
26
d
c
a
25
b
a
24
d
a
23
22
21
20
19
U. Kellwasser
L. Kellwasser
32.3 kg
195.4 kg
186.8 kg
287.2 kg
95.3 kg
74.0 kg
Background flux
EC grains >63 µm / 100 kg
0
4
8
12

Figure 3

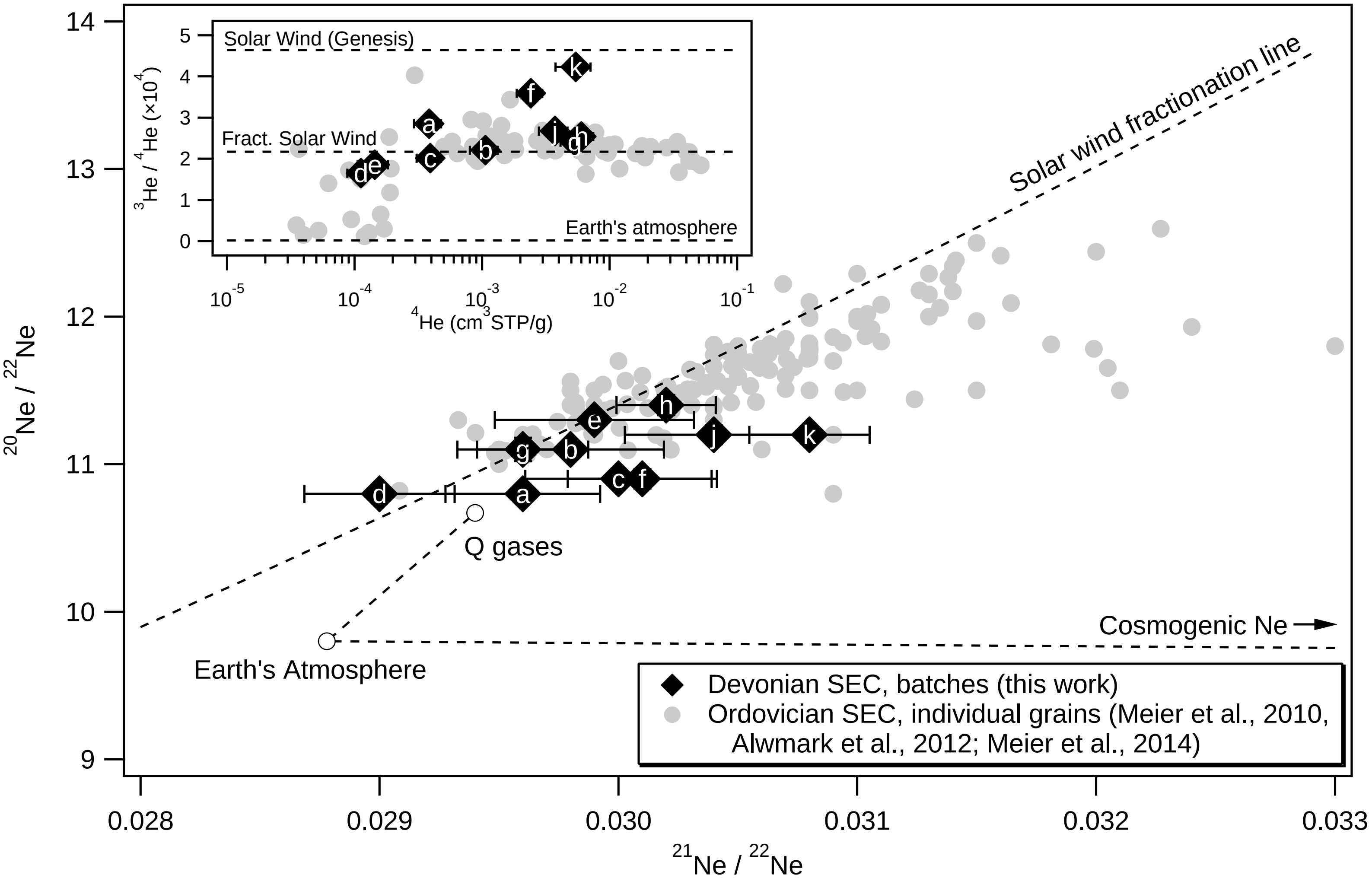
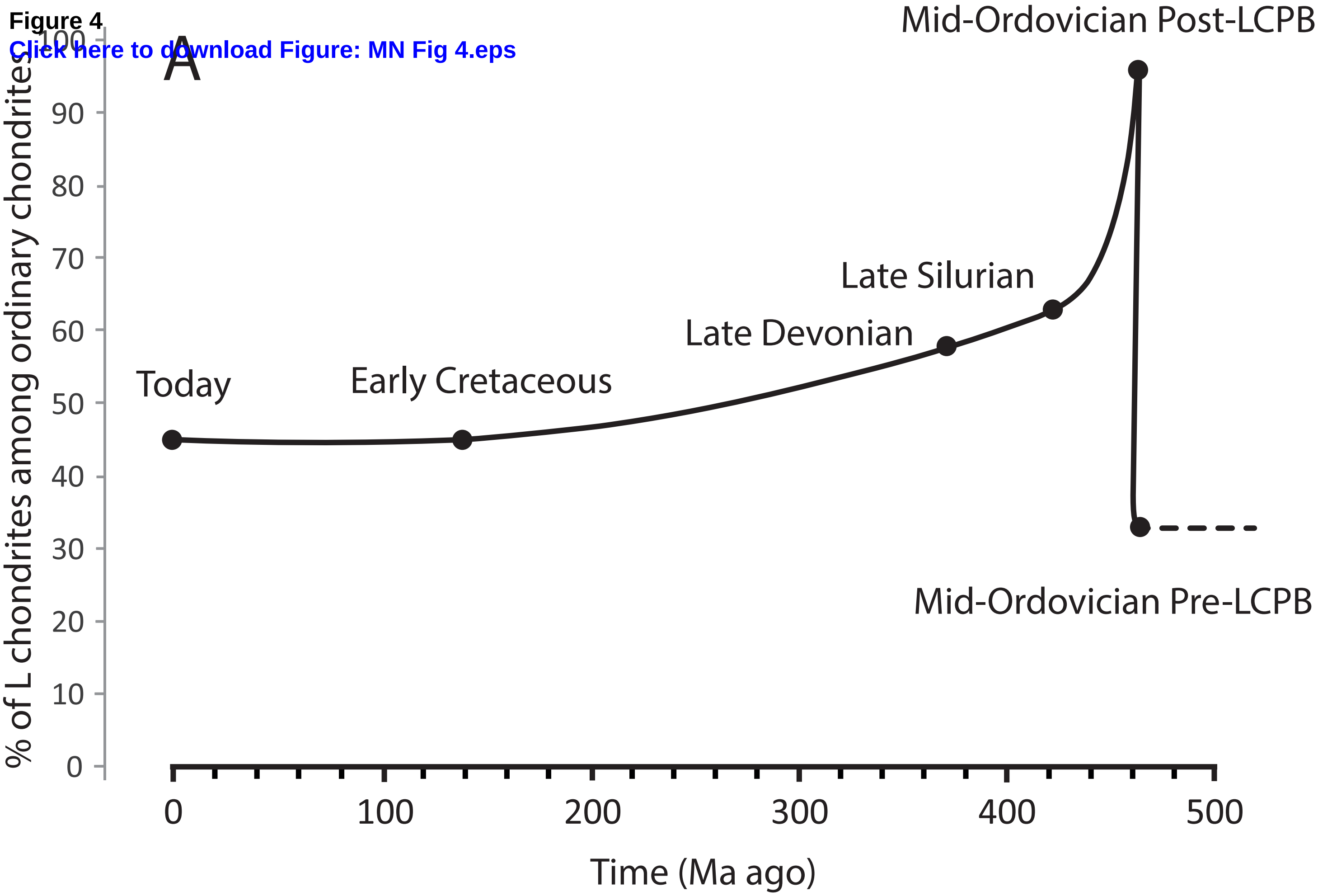

14
13
12
11
10
9
^{20}Ne / ^{22}Ne
0.028
0.029
0.030
0.031
0.032
0.033
^{21}Ne / ^{22}Ne
Solar wind fractionation line
Q gases
Earth's Atmosphere
Cosmogenic Ne →
a
b
c
d
e
f
g
h
j
k
◆ Devonian SEC, batches (this work)
● Ordovician SEC, individual grains (Meier et al., 2010, Alwmark et al., 2012; Meier et al., 2014)
Solar Wind (Genesis)
Fract. Solar Wind
Earth's atmosphere
5
4
3
2
1
0
^{3}He / ^{4}He (×10^{4})
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
^{4}He (cm^{3} STP/g)

Figure 4

Click here to download Figure: MN Fig 4.eps



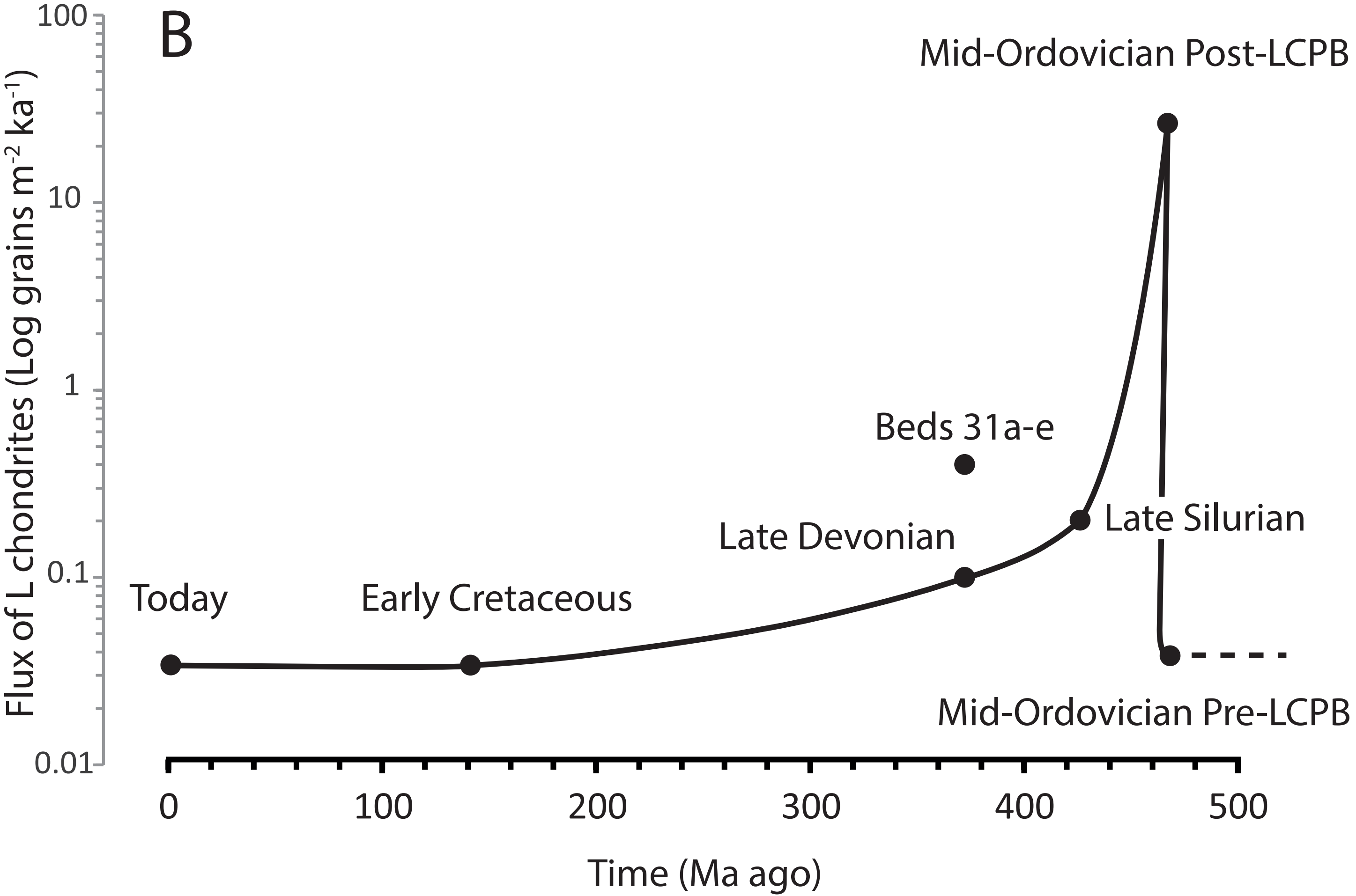


Table 1

Chrome-spinel grains >63 µm in Devonian samples from Montaigne Noir region.

Sample (bed No.)	Sample weight (kg)	#EC >63 µm	#OtC-V >63 µm	#OtC >63 µm	EC grains/ 100 kg	EC/ OtC-V
Coumiac						
32a-b	32.3	0	0	0	-	-
31g (Kellwasser)	195.4	5	1	29	2.6	5.0
31f	12.1	0	0	9	-	-
31e	186.8	21	5	55	11.2	4.2
31c	98.2	8	2	>200	8.1	4.0
31a-d	189.0	9	2	173	4.8	4.5
30	15.0	0	0	14	-	-
26	16.2	0	0	3	-	-
25b-c	20.4	1	0	43	-	-
24d	58.7	0	0	112	-	-
20	74.0	2	2	13	2.7	-
Total:	898.1	46	12	>651	5.1	3.8
Pic de Bissous						
26C	26.0	1	1	0	-	-
26	32.4	2	0	0	-	-
Total:	*58.4*	*3*	*1*	*0*	-	-

- Number of grains

Table 2

Division of equilibrated ordinary chondritic (EC) grains 32-355 μm large from Coumiac quarries using TiO_2 (wt%)

		H	**L**	**LL**
Bed	TiO_2 (wt%):	≤2.50%	2.51%-3.39%	≥3.40%
31g (n=5)		1	3	1
31e (n=49)		13 *(27%)*	29 *(59%)*	7 *(14%)*
31c (n=8)		2	3	3
31a-d (n=9)		4	3	2
25b-c (n=1)		1	0	0
20 (n=37)		13 *(35%)*	19 *(51%)*	5 *(14%)*
Total (n=109)		**34 *(31%)***	**57 *(52%)***	**18 *(17%)***

Table 3

Flux of equilibrated ordinary chondritic (EC) grains >63 μm during different time windows.

Time window	# EC grains >63 μm	Sample weight (kg)	Grains per 100 kg	Sedimentation rate (mm/ka)	Flux* (grains/m^2 × ka)
Early Danian[1]	5	140	3.6	2.5	0.23
Late Maastrichtian[1]	1	70	1.4	5.0	(0.18)
Late Cretaceous[2]	11	979	1.1	10	0.24
Early Cretaceous[3]	2	1652	0.1	25	0.075
Late Frasnian, Bed 31[4]	38	474	8.0	3.5	0.70
Late Frasnian, except Bed 31[4]	8	392	2.0	3.5	0.18
Middle Devonian, Givetian[4]	3	58	5.1	3.6	(0.47)
Late Silurian[5]	10	321	3.1	4.0	0.32
Post-LCPB Mid-Ordovician[5]	444	102	434.0	2.5	28
Pre-LCPB Mid-Ordovician[6]	5	379	1.3	3.5	0.11

[1] Cronholm & Schmitz (2007), [2] Martin et al. (2019), [3] Schmitz et al. (2017), [4] This study, [5] Martin et al. (2018), [6]Schmitz & Häggström (2006). *Flux estimates in parentheses rely on small sample weights.

Table 4

Comparison of flux of equilibrated ordinary chondrites to other chrome-spinel bearing meteorite types. Modified from Schmitz et al. (2017).

Time window	**EC**[1] # (%) of grains	**OtC-V**[1] # (%) of grains	**AC-low-V**[1] # (%) of grains	**EC/OtC-V ratios**[2]
Today[3]	90	9	<1	10
Late Cretaceous Syn-^{3}He[4]	60 (71)	25 (29)	N.A.	2.4
Late Cretaceous Pre-^{3}He[4]	55 (93)	4 (7)	N.A.	13.8
Early Cretaceous[5]	81 (75)	27 (25)	N.A.	3
Late Devonian[6]	46 (79)	12 (21)	N.A.	3.8
Late Silurian[7]	155 (92)	14 (8)	N.A.	11
Post-LCPB Ordovician[7]	444 (98)	8 (2)	N.A.	56
Pre-LCPB Ordovician[8]	23 (56)	15 (37)	3 (7)	1.5

[1] EC = chromite from equilibrated ordinary chondrite; OtC-V = other chrome spinel with V_2O_3 ≥0.45 wt% and Cr_2O_3/FeO ratios ≥1.45; AC-low-V = chrome spinel from achondrites judging from $\Delta^{17}O$ values, but with V_2O_3 ≤0.44 wt%. N.A. = not applicable.

[2] The ratios for the flux in the deep-time windows are not directly comparable to the ratio for today's flux. Most achondrites and unequilibrated ordinary chondrites have lower contents of chrome spinels (>32 µm) than the equilibrated ordinary chondrites. Comparisons between different time periods should ideally be based only on variations in the types of Cr-spinel grains from sediments. The EC/OtC-V ratios for the two Ordovician and the Devonian windows are based on the >63 µm grain fractions, and the Cretaceous windows on the 32-63 µm fractions.

[3] Fraction of the meteorite flux excluding the recent major meteorite groups poor in large Cr-spinel. The OtC-V category as defined for this row includes all achondrites rich in Cr-spinel with high (>0.5 wt %) V_2O_3, as well as the R chondrites and unequilibrated ordinary chondrites. The AC-low-V category includes achondrites rich in Cr-spinel but with low (<0.45 wt%) V_2O_3. Source: Meteoritical Bulletin database (www.lpi.usra.edu/meteor/).

[4] Martin et al. (2019).

[5] Schmitz et al. (2017).

[6] This study. Based on the >63 µm grain-fraction only.

[7] Martin et al. (2018).

[8] Heck et al. (2017). Based on the >63 µm grain-fraction only.

Table 5

Flux of ordinary chondrites through time. Division of equilibrated ordinary chondritic (EC) grains using TiO$_2$ (wt%) and correction for 10% overlap between the three groups.

		H	**L**	**LL**
Time window	TiO$_2$ (wt%):	≤2.50%	2.51-3.39%	≥3.40%
Late Cretaceous[1]				
	Pre-^{3}He (n=55)	27.4	24.4	3.2
		(50%)	*(44%)*	*(6%)*
	Syn-^{3}He (n=60)	42.3	16.1	1.6
		(70%)	*(27%)*	*(3%)*
Early Cretaceous [n=81][2]		36.2	36.1	8.7
		(45%)	*(44%)*	*(11%)*
Late Devonian, Frasnian [n=109)[3]		31.7	63.2	14.1
		(29%)	*(58%)*	*(13%)*
Late Silurian [n=155][4]		47.4	97.6	10
		(31%)	*(63%)*	*(6%)*
Mid-Ordovician Post-LCPB [n=444][4]		33.2	424.9	-14.1
		(7%)	*(96%)*	*(-3%)*
Mid-Ordovician Post-LCPB [n=119][5]		0.8	120.7	-2.5
		(1%)	*(101%)*	*(-2%)*
Mid-Ordovician Pre-LCPB [n=215][5,6]		81.1	71.0	63.3
		(38%)	*(33%)*	*(29%)*

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[1] Martin et al. (2019), [2] Schmitz et al. (2017), [3] this study, [4] Martin et al. (2018), [5] Heck et al. (2016), [6] Heck et al. (2017).

Footnote: Table 6 shows the percentages of H, L, and LL chondritic EC grains with the 10% overlap between the three groups. The overlaps are calculated and subtracted or added to respective group. When a group has a large percentage, as in e.g. Post-LCPB L group grains, then this can cause a false negative grain count and group percentage in the groups with low percentage.

Table 6
Poynting-Robertson Transfer times (Ma) from the outer solar system to Earth

Diameter, type	1.9 AU	2.5 AU	2.8 AU	3.5 AU	5.2 AU	30 AU
40 µm, chromite	0.16	0.33	0.42	0.70	1.6	56
60 µm, chromite	0.24	0.49	0.64	1.0	2.4	83
80 µm, chromite	0.32	0.65	0.85	1.4	3.2	110
100 µm, silicate	0.28	0.55	0.72	1.2	2.8	95
200 µm, silicate	0.55	1.1	1.4	2.4	5.5	190
300 µm, silicate	0.83	1.7	2.2	3.6	8.2	280
1000 µm, silicate	2.8	5.5	7.2	12	27	950

Caption: typical transfer times from the inner rim of the asteroid belt (1.9 AU), the division between the inner and middle asteroid belt (2.5 AU), the division between the middle and outer asteroid belt (2.8 AU), the outer rim of the asteroid belt (3.5 AU), the Jupiter trojans (5.2 AU) and the inner rim of the Kuiper belt (30 AU), based on Burns et al. (1979). Densities of 4.4 g/cm^3 and 3.0 g/cm^3 were used for chromite and silicate, respectively. All ages given in millions of years (Ma).