The meteorite flux to Earth in the Early Cretaceous as reconstructed from sediment-dispersed extraterrestrial spinels

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ABSTRACT

We show that Earth's sedimentary strata can provide a record of the collisional evolution of the asteroid belt. From 1652 kg of pelagic Maiolica limestone of Berriasian-Hauterivian age from Italy we recovered 108 extraterrestrial spinel grains (32-250 μm) representing relict minerals from

coarse micrometeorites. Elemental and oxygen-three isotope analyses were used to characterize the grains, providing a first-order estimate of the major types of asteroids delivering material at the time. Comparisons are made with meteorite-flux "windows" in the Ordovician before and after the L-chondrite parent-body breakup. In the Early Cretaceous about 80% of the extraterrestrial spinels originate from ordinary chondrites. The ratios between the three groups of ordinary chondrites, H, L, LL, appear similar to the present, ~1:1:0.2, but differ significantly from Ordovician ratios. We see no signs of a hypothesized Baptistina LL-chondrite breakup event. About 10% of the grains in the Maiolica originate from achondritic meteorite types that are very rare (<1%) on Earth today, but that were even more common in the Ordovician. Because most meteorite groups have lower spinel content than the ordinary chondrites, our data indicate that the latter did not dominate the flux during the Early Cretaceous to the same extent as today. Based on studies of three windows in deep time we argue that there may be a gradual long-term (a few 100 Myr) turnover in the meteorite flux from dominance of achondrites in the early Phanerozoic to ordinary chondrites in the late Phanerozoic, interrupted by short-term (a few Myr) meteorite cascades from single asteroid breakup events.

INTRODUCTION

Much knowledge about the history of life, climate, tectonics, magnetic polarity and chemistry of seawater has accumulated during the past two centuries from studies of Earth's sedimentary strata. With the discovery of the asteroid impact at the Cretaceous-Tertiary (K-T) boundary and its effects on life (Alvarez et al.,

1980) an interest has grown in integrating astronomical and geological perspectives. A new approach that can relate ancient events in the skies to coeval events on Earth is the search for relict spinel minerals from micrometeorites and meteorites in condensed sediments (Schmitz, 2013). The method has so far been primarily applied in reconstructions of the Ordovician L-chondrite parent-body breakup (LCPB), the largest documented collisional event in the asteroid belt in the past 3 Gyr (Schmitz et al., 2003). This breakup probably led to the formation of one of the major asteroid families, with the Gefion family being the prime candidate (Nesvorný et al., 2009). The event has been dated by ^{40}Ar-^{39}Ar analyses of recently fallen L-chondrites to ~470 Ma (Korochantseva et al., 2007; Weirich et al., 2012), but the most precise relative date is given by an abrupt two-orders-of magnitude increase worldwide in sand-sized chromite grains with L-chondritic composition in Middle Ordovician sediments (Schmitz et al., 2003; Heck et al., 2016). According to the 2012 Geological Time Scale the spinel increase occurs at a stratigraphic level with an age of 466±1 Ma (Cooper and Sadler, 2012).

By dissolving 100-kg-sized samples of condensed sediments from different time periods in various acids the highly refractory extraterrestrial spinel minerals can be concentrated. The recovered grains typically contain high concentrations of solar-wind noble gases, indicating that they dominantly represent fragments of coarse micrometeorites (Heck et al., 2008; Meier et al., 2010). Pelagic carbonates are the best material for sampling the population of extraterrestrial chromite grains, because of their low content of detrital minerals that obscure the extraterrestrial fraction and the ease with which they can be dissolved in acid. As a part of a larger effort to create "windows" into the meteorite flux to Earth at different times during the Phanerozoic (Schmitz, 2013), we focus here on a part of the Lower Cretaceous

(145-133 Ma) Maiolica limestone in central Italy. This pelagic limestone is exceptionally "clean", i.e. having very low contents of terrestrial mineral grains, making it useful for reconstructions of the micrometeorite flux even in the small spinel size ranges, such as the 32-63 μm range primarily used here. Because some meteorite types contain common spinel grains mainly in the small (<63 μm) rather than in larger (>63 μm) size fractions a more representative picture of the ancient meteorite flux can be gained if grains from the smaller size fraction are studied. From a total of 1652 kg of limestone collected at 13 different levels in the earliest Berriasian to early Hauterivian Maiolica Formation we recovered 108 extraterrestrial spinel grains (Fig. 1). By three-oxygen isotope and elemental analyses of the grains we can obtain the very first insights into what types of meteorites fell on Earth at other times than today and in the mid-Ordovician. These data can be used to test and develop models on the dynamics of meteorite transport from the asteroid belt to Earth and how the asteroid belt has evolved over time. For example, here we add perspectives on Bottke et al's (2007) hypothesis, based on astronomical data, that a ~170-km-diameter asteroid broke up between 190 and 140 Ma leading to the formation of the Baptistina asteroid family, one of the youngest major asteroid families in the inner main asteroid belt.

MAIOLICA STRATIGRAPHY AND SEDIMENTOLOGY

Pelagic calcareous ooze dating back to the Jurassic covers large areas of the present sea floor, but cannot be used for our purposes, because spinel extraction would destroy large amounts of precious core material without yielding a statistically significant number of spinel grains. We are therefore restricted to studying pelagic carbonates exposed in outcrop. Probably the best place in the world to find exposures of rocks of this kind is in the Umbria-Marche Apennines of central Italy, with pelagic carbonates (limestones, dolomites, and marls) representing most of the 165-Myr interval from the Pliensbachian to the Oligocene. These rocks are exposed in bands on the flanks of sub-parallel anticlines over a roughly square area almost 100 km on a side. Earth-history studies of many kinds have been carried out on these rocks beginning with Renz (1936), and a recent compilation is given by Menichetti et al. (2016).

In the Umbria-Marche sequence, the first four stages of the Lower Cretaceous (Berriasian-Barremian, ~145-125 Ma) are represented by the Maiolica formation, a pure white pelagic limestone having a fine-grained texture reminiscent of majolica pottery, with abundant beds and nodules of chert, mostly black or dark grey, and rare partings of black clay. This unit, ~400 m thick in basinal settings and ~100 m thick on fault-block seamounts, has proven difficult to correlate, date, and study because of the near-absence of distinctive marker beds, the lack of distal volcanic ashes and thus of datable contemporaneous mineral grains, the absence of planktic foraminifera, which had not yet evolved, the rarity of ammonites and other macrofossils, and the presence of slump units in the basins and probably of corresponding hiatuses on structural highs. However, for our purposes the Maiolica is ideal, easily dissolving with small residues from which refractory spinel grains can be collected.

All but one of our samples from the Maiolica Formation come from the 240-m-thick Monte Acuto section, extending from 43° 27.830'N, 12° 40.270'E to 43° 27.842'N, 12° 40.745'E, in cuts along the road from Chiaserna to the pass between Monte Acuto and Monte Catria. Here the Maiolica is well exposed as steeply-dipping beds, with the exception of the covered uppermost part of the formation. In the Monte Acuto section, Channell et al. (1995) determined the M-sequence geomagnetic polarity zonation and tied it to nannofossils events and ammonite zones for the Hauterivian and the uppermost Valanginian. Faraoni et al. (1997) in a painstaking study, recovered many ammonites and presented an ammonite zonation for all of the Valanginian and small portions of the underlying Berriasian and the overlying Hauterivian. Moreover, Sprovieri et al. (2006) studied the cyclostratigraphy of the Monte Acuto section using carbon isotopes, tying this record to the known biozonation and magnetostratigraphy. The average sedimentation rate for the Maiolica limestone in the Monte Acuto section is about 25 m/Myr, based on a measured thickness of 137 m of sediments representing the 5.5 Myr Valanginian Stage. It is likely that the bedding in the section reflects precession cycles. The entire late Berriasian to early Hauterivian section at Monte Acuto corresponds to ca. 9.4 Myr (ca. 141.2 -131.8 Ma) and comprises 453 beds, giving an average of 20.75 kyr/bed.

The oldest (ca. 145 Ma) of our Maiolica Formation samples was collected ca. 3 m above the Maiolica-Diaspri formational contact, i.e. close to the Jurassic-Cretaceous boundary, in the Bosso River section along the Pianello-Cagli road, 12 km northwest of Monte Acuto (Kudielka et al., 2002).

MATERIALS AND METHODS

Grain separation

Samples were collected from twelve beds in two stratigraphically separated groups along the Monte Acuto road section (Fig. 1, and GSA Data Repository Tables DR1 and DR2). A total of 513 kg were collected from four beds in the Berriasian part of the section, and 1015 kg were collected from eight beds in the late

Valanginian to early Hauterivian part. The size of the individual samples varies between 103 and 433 kg (plus one sample of 27 kg). The additional sample from the Bosso section weighed 124 kg. The rocks were dissolved in HCl (6 M) and HF (11 M) at room temperature in the Lund University Astrogeobiology Laboratory specially built for separation of extraterrestrial minerals from ancient sediments. After sieving at mesh sizes 32 and 63 μm opaque chrome-spinel grains were identified by picking under the binocular microscope and subsequent qualitative SEM/EDS element analysis (see below). In some cases after the HF treatment we needed to add other leaching (HNO_3 or H_2SO_4) or density (LST) separation steps in order to remove pyrite and/or organic material. From all samples also all transparent, colorless or pink to red grains were collected and analysed with SEM/EDS in order to determine if any Mg-Al-spinels were present.

Oxygen isotope and element analysis

Polished epoxy mounts were prepared with all Cr-spinels found together with a centrally mounted analytical standard UWCr-3 (Heck et al. 2010). A Bruker white light interferometric 3D microscope at Northwestern University was used to verify that grain-to-epoxy topography was kept below 3 μm (on average 2 μm) after polishing to minimize mass-dependent isotope fractionation effects during SIMS analysis. Element concentrations were analyzed quantitatively with a calibrated Oxford-Link energy-dispersive spectrometer mounted on a Hitachi scanning electron microscope (SEM/EDS), see Schmitz et al. (2009) for details. Isotopes of $^{16}O^-$, $^{17}O^-$ and $^{18}O^-$ were analyzed with a Cameca IMS 1280 SIMS at the WiscSIMS Laboratory at the University of Wisconsin-Madison in three separate sessions with the procedures similar to Heck et al. (2010, 2016, 2017), but with different primary beam sizes (12 μm to 19 μm) to accommodate different grain sizes. This procedure includes analysis and correction for the hydride tailing interference on $^{17}O^{-}$ and bracketing with our analytical standard UWCr-3. We determine parts per thousand deviations from VSMOW as $\delta^{18}O$, $\delta^{17}O$ and from the terrestrial mass-fraction line as $\Delta^{17}O$ (=$\delta^{17}O$ – 0.52 × $\delta^{18}O$), the latter being the main indicator for an extraterrestrial origin. The external reproducibility (spot-to-spot, 2SD) of $\Delta^{17}O$ measurements of standards was 0.2-0.3‰ during the analyses of the unknowns. We obtained valid results from a total of 86 sediment-dispersed chromite and chrome-spinel grains (of which 77 grains are 32-63 μm large, and 9 grains >63 μm).

Division of grains and definitions

We divide our grains into different meteorite groups based on a combination of elemental and isotopic data. Grains from equilibrated ordinary chondrites (EC) have a very distinct and narrow elemental composition and can readily be identified on this criterion alone (Schmitz, 2013). The EC grains can then be further divided into the three groups H, L and LL based on their oxygen isotope and TiO_2 content (see below). The remaining chrome-spinel grains are divided into two groups, "other chrome spinel with ≥0.45 wt% V_2O_3" (OC-V) and "all other chrome spinel" (OC). The basis for this is that most Cr-spinels from meteorites are rich in V, whereas V-rich (>0.5 wt%) terrestrial Cr-spinels are generally rare. The OC-V and OC grains are further subdivided based mainly on their oxygen isotopic composition, but element composition can also give clues about their origin. Sometimes the shape of a grain can also be indicative. In many sedimentary environments far from the shore, terrestrial grains are rounded, having been transported on the sea floor over long distances, whereas extraterrestrial grains that fell on the site are angular (cf., Cronholm and Schmitz, 2010).

The three groups of ordinary chondrites, H, L, and LL, have different average values of $\Delta^{17}O$ (0.73, 1.07, 1.26‰) and TiO_2 (2.2, 2.7, 3.4 wt%, respectively) (Clayton et al., 1991; Bunch et al., 1967; Schmitz et al., 2001). Around these averages the $\Delta^{17}O$ and TiO_2 values are spread following a Gaussian distribution, but the distributional tails overlap (Heck et al., 2016). There is no indication that a grain lying in the tail of the TiO_2 distribution lies in the corresponding tail of the $\Delta^{17}O$ distribution. Rare grains may have H-chondritic $\Delta^{17}O$, but LL-chondritic TiO_2 and vice versa (Tables DR3 and DR4). The exact definitions of the ranges for dividing grains based on TiO_2 and/or $\Delta^{17}O$ can in principle be arbitrarily set, but must be used consistently when comparing different time periods.

RESULTS

Among the total of 108 extraterrestrial chrome spinel grains (32-250 μm large) recovered, 81 are clearly equilibrated ordinary chondritic (EC) and 27 are vanadium-rich grains (OC-V) probably originating from other types of meteorites (Tables 1, DR1 and DR2). In the >63 μm fraction only two extraterrestrial grains were found; both are EC grains (Tables DR1 and DR2). In the 32-63 μm fraction, based on element analyses alone, we found 79 grains with clear EC elemental composition. Oxygen-isotopic analyses of 46 of these grains confirmed that they all are ordinary chondritic (Fig. 2).

The division of the 81 recovered EC grains into their three groups using definitions as outlined above and in the Data Repository, is given in Table 2. The data are compared with estimates based on the same approach for EC grains from the mid-Ordovician before and after the L-chondrite parent-body breakup, as well as the proportions among recent meteorite falls following the Meteoritical Society data base. In Table 2 we base the division of the EC grains entirely on their TiO_2 content. The reason for this is the substantially larger data set for grains having been analyzed for TiO_2 compared to $\Delta^{17}O$. In Tables DR3 and DR4 we compare the outcome of divisions based on either TiO_2 or $\Delta^{17}O$, as well as both parameters combined. We conclude that the main trends based on TiO_2 alone, can be seen in all three approaches. This is expected, because overlap effects between $\Delta^{17}O$ and TiO_2 cancel out.

There is no significant difference between the ratios of the three ordinary chondrite groups between the Berriasian and the late Valanginian-Hauterivian part of the section (Table DR2). In the earliest Berriasian sample from the Bosso section, however, H-chondritic grains dominate among the 8 EC grains found, but this may be a local effect from e.g. the fall of a single larger H-chondritic micrometeorite containing several chromite grains.

Of the 27 OC-V grains in the 32-63 μm fraction, 17 grains could be analyzed for oxygen-three isotopes (Tables 3 and DR2). Of these, 13 gave $\Delta^{17}O$ values separated (at 2SD) from the terrestrial fractionation line, i.e. indicating a meteoritic origin. Four of the grains show $\Delta^{17}O$ indistinguishable from the terrestrial fractionation line, but we argue that the grains nevertheless originate from achondritic meteorite types that have $\Delta^{17}O$ values at or very close to the terrestrial fractionation line. There is nothing in our data or the general paleogeographic setting that indicates that the types of rare terrestrial rocks that potentially could yield V-rich Cr-spinels existed in the study region in the Early Cretaceous. Two of the 17 OC-V grains analyzed lie clearly below (at 2SD) the TFL with $\Delta^{17}O$ values of -0.4‰. The altogether six OC-V grains with values at or just below the terrestrial fractionation line may originate from the howardite, eucrite, diogenite (HED) types of meteorites, or from primitive or ungrouped achondrites. Five of the 17 OC-V grains analyzed have $\Delta^{17}O$ values similar to ordinary chondrites despite having an elemental composition significantly outside the range that we use to define equilibrated ordinary chondritic grains. The grains have $\Delta^{17}O$ values spanning the range from H- to LL-chondritic (0.48‰ to 1.49‰). The grains may originate from unequilibrated ordinary chondrites, i.e. petrographic types 3-4, however, they are puzzling because we have not seen such grains among hundreds of mid-Ordovician sediment-dispersed extraterrestrial grains previously studied by us. This may reflect that in this study we deal mainly with the smaller size fraction, 32-63 µm, instead of >63 µm as in previous work. The last six of the OC-V grains analyzed for $\Delta^{17}O$ have anomalously low $\Delta^{17}O$ values, in the range -1.80‰ to -3.78‰, indicating that they originate from primitive (e.g., winonaites, lodranites, acapulcoites,) or ungrouped or anomalous achondrites that are very rare on Earth today (see below). In summary, twelve of the 17 OC-V grains analyzed for oxygen isotopes are from achondrites, and five from (unequilibrated?) ordinary chondrites.

We also recovered a total of 33 and 65 grains in the >63 and 32-63 µm fractions, respectively, classified as "other Cr-spinel" (OC) grains meaning that they have a different composition than the EC grains, but with V_2O_3 concentrations <0.45 wt%. These grains are almost certainly terrestrial, except for possibly two of them. We analyzed 23 of them for oxygen isotopes and 21 have $\Delta^{17}O$ values right on the terrestrial fractionation line within ~2SD. Two of the grains lie slightly off the terrestrial fractionation line (-0.31±0.18, and 0.34 ±0.21), which could indicate an extraterrestrial origin, but the element compositions of the grains are similar to that of the typical terrestrial OC grains in the section.

The Berriasian part of the Monte Acuto section has higher concentrations of ordinary chondritic grains, 8.8 per 100 kg, compared to 3.5 per 100 kg in the younger Valanginian-Hauterivian part of the section. The ratio OC-V versus EC grains is about the same, 0.3, throughout the entire section, which represents a strong argument that all or most of the OC-V grains are extraterrestrial. In the Monte Acuto section all except three of the 88 OC grains found, were found in the younger part of the section. There is also a trend with various terrestrial acid-resistant grains, including zircons, being generally more abundant and larger in the younger part. The single sample from the very earliest Berriasian in the Bosso River section is relatively rich in both EC and OC grains (Table DR2).

Because acid residues of the Maiolica limestone are so clean it has been possible to quantify also the amount of transparent Mg-Al-spinels. In some of the more common carbonaceous chondritic meteorite types that fall on Earth today (e.g., CM and CV types) Mg-Al-spinels are abundant in the 32-63 μm fraction and strongly dominate over opaque Cr-spinels (Bjärnborg and Schmitz, 2013, and references therein; Table DR5). In the Maiolica limestone there are several types of rare transparent terrestrial minerals, like zircon and corundum, that appear similar to Mg-Al-spinels under the light microscope. We have picked every such transparent grain and analyzed them by SEM/EDS for elemental composition. Only one Mg-Al-spinel grain was found, a fact significant for the interpretation of the origin of the other Cr-spinel grains (see below). The single grain was found in Bed 406 together with many zircons. This fact and the low V_2O_3 content (<0.3 wt%) of the grain indicates that it is most likely of terrestrial origin.

DISCUSSION

Flux of meteorites through the Phanerozoic

Before the present study the only periods in deep time for which we knew something about the types of meteorites that commonly fell on Earth are for the mid-Ordovician after and before the LCPB (Schmitz et al., 2001, 2003; Schmitz, 2013; Heck et al., 2016, 2017). The addition here of a third "window" in the geological record adds an important new perspective, but interpretations and any generalizations must be preliminary awaiting the results for additional time windows and further developments of the approach. Perhaps the most important result so far is that it indeed is possible to obtain quantitative insights into the history of the asteroid belt from Earth's sedimentary record.

The ratio of ordinary chondritic/achondritic meteorites in the Early Cretaceous (~3) lay somewhere between the ratios for the mid-Ordovician before the LCPB (~1.5) and the recent (~10) (Table 1). It appears that the background meteorite flux may have evolved gradually over the Phanerozoic, from being dominated by achondrites to the present situation where the ordinary chondrites dominate (>80% of all meteorite falls) and Cr-spinel-rich achondrites (other than the ~8% HED meteorites) are very rare, representing less than one per cent. Even if the ordinary chondrites may have had a more subordinate role at times, our data show that they likely have always represented an important fraction of the flux.

There may be a trend also for the flux of ordinary chondrites through the Phanerozoic (Table 2). Within the resolution of our approach the ratios between the different groups of ordinary chondrites in the Early Cretaceous (~1:1:0.2) are identical to the ratios today (~1:1:0.2). In the mid-Ordovician after the LCPB the

EC grains are 100% (or close to) L-chondritic. The 8% and 6% H- and LL-chondritic grains given in Table 2 most likely reflect L grains in the tails that overlap in TiO_2 content with the "neighbor groups". Heck et al. (2016) analysed 120 post-LCPB EC grains for oxygen isotopes and found that ≥99% of the grains were L-chondritic. Before the LCPB the LL chondrites (based on 215 EC grains analyzed for TiO_2) represent about 30% of the ordinary chondritic flux, compared to ca. 10% in the Early Cretaceous and today (Tables 2 and DR6; Heck et al., 2017). The L and H chondrites share the remaining 70% of the pre-LCPB flux in about equal proportions. The high relative abundance of LL chondrites in the pre-LCPB meteorite assemblage probably reflects the tail of the meteorite flux related to the breakup of the LL-chondritic Flora family ca. 1 Ga (see Heck et al., 2017). With its ~14,000 members this is one of the largest asteroid families (Nesvorný et al., 2015).

The many OC-V grains that cannot be assigned to unequilibrated ordinary chondrites likely originate from achondritic meteorites (Table 3). The carbonaceous chondrites (with rare exceptions) contain only low concentrations of opaque spinels in the grain-size ranges we work with compared to ordinary chondrites and most of the achondrites (Table DR5). Because of the clear dominance of transparent Mg-Al-spinels over opaque spinels in carbonaceous chondrites, the scarcity of Mg-Al-spinels in our samples gives support for the interpretation that none of the recovered opaque grains are from carbonaceous chondrites. Iron meteorites, mesosiderites and pallasites contain too low spinel concentrations to be of any significance in this type of study. Rumuruti chondrites are rich in Cr-spinels but have $\Delta^{17}O$ of ca. 2‰, values not observed here. Enstatite chondrites are too reduced to contain significant amounts of any chromium-rich oxides.

In our assemblage of Cr-spinel grains there is a significant amount (>10%) of achondritic grains with $\Delta^{17}O$ values below -2‰ (Tables 3 and DR2). Such achondrites are very rare on Earth today, representing less than a tenth of a percent of the known recent meteorites. In Bed 36 there are three such grains, two grains with $\Delta^{17}O$ close to -2‰ and one grain with a value of -3.8‰. In Bed 40 there are two grains with values of -3.5‰ and almost identical elemental composition, indicating that they may come from the same micrometeorite. In Bed 406 one grain has a $\Delta^{17}O$ value of -3.0‰. These six grains may originate from "extinct" anomalous achondrites similar to the mid-Ordovician fossil meteorite Österplana 065 (Schmitz et al., 2016). Based on Cr and O isotopic analyses this meteorite is believed to originate from a type of meteorite that no longer falls on Earth because its parent body in the asteroid belt has been consumed by collisions (see, Schmitz et al., 2016; Heck et al., 2017). The altogether five OC-V grains with $\Delta^{17}O$ values just below or at the terrestrial fractionation line may originate from primitive achondrites or HED achondrites, the latter having $\Delta^{17}O$ of ca. -0.2‰ and that make up about 8% of the recent flux. The HED achondrites originate from the 4 Vesta asteroid, the second largest asteroid in the asteroid belt

The Baptistina family breakup

We see no apparent signature of the Baptistina (LL-chondritic) asteroid-family forming event. By back-tracking the orbits of asteroids among the members of the Baptistina asteroid family in the inner main belt, Bottke et al. (2007), estimated that at 160 Ma (with an uncertainty range 190-140 Ma) the ~170 km parent-body of the Baptistina asteroid family broke up. Masiero et al. (2012) suggested a revised event age of 190±30 Ma based on astronomical data. This is one of the youngest major asteroid family-forming events documented, resulting in a family of about 2500 members (Nesvorný et al., 2015). Bottke et al. (2007) postulated that the impactors creating the K-T boundary Chicxulub crater on the Yucatan peninsula and the Tycho crater on the Moon around 109 Ma originated from this collisional event. However, refined spectral studies have shown that the Baptistina family members are LL chondrites (Reddy et al., 2014), whereas chromium isotopic measurements of K-T boundary ejecta clearly rule out such an impactor, favoring instead a cometary or carbonaceous (CM type) impactor (Trinquier et al., 2006). Our samples span the range from 145 to 133 Ma, and nowhere in the section do we see any enrichment in LL-chondritic grains, neither do we see any tailing-off trend in LL-grain abundances between the oldest and youngest samples. Our results together with the data of Masiero et al. (2012) constrain the breakup event to have occurred probably between 145 and 210 Ma.

CONCLUSIONS AND SUMMARY

A detailed history of the asteroid belt can be reconstructed from Earth's sedimentary record by recovering extraterrestrial spinels from condensed sediments. The three first "windows" into the meteorite flux in deep time have been reconstructed, providing some insights into the flux in the early Cretaceous as well as immediately before and after the breakup of the L-chondrite parent body in the mid-Ordovician. The background meteorite flux in the early Paleozoic appears to have been significantly different from the flux in the early Cretaceous, which is more similar to today's flux. This general trend was at times overprinted (for 1-10 Myr) by floods of single types of meteorites from occasional major breakup events in the asteroid belt, such as after the LCPB.

ACKNOWLEDGMENTS

The study was supported by an ERC-Advanced Grant (ASTROGEOBIOSPHERE) to B.S. We thank M. Alvarez and L., N. and E. Schmitz for field support, F. Iqbal for laboratory support and A. Montanari for showing us the Bosso River section. P.R.H. acknowledges funding from the Tawani Foundation. We thank B. Strack for maintenance of the Field Museum's SEM laboratory. WiscSIMS is partly supported by the National Science Foundation (EAR03-19230, EAR13-55590). We thank J. Kern for SIMS support. The 3D microscopy was performed in the Keck-II facility of the Northwestern University NUANCE Center, supported by NSEC (NSF EEC-0647560), MRSEC (NSF DMR-1121262), the Keck Foundation, the State of Illinois and Northwestern University.

REFERENCES CITED

Alvarez, L.W., Alvarez, W., Asaro, F., and Michel, H.V., 1980, Extraterrestrial cause for the Cretaceous-Tertiary extinction: Science, v. 208, p. 1095-1108.

Bjärnborg, K., and Schmitz, B., 2013, Large spinel grains in a CM chondrite (Acfer 331): implications for reconstructions of ancient meteorite fluxes: Meteoritics & Planetary Science, v. 48, p. 180-194.

Bottke, W.F., Vokrouhlický, D., and Nesvorný, D., 2007, An asteroid breakup 160 Myr ago as the probable source of the K/T impactor: Nature, v. 449, p. 48-53.

Bunch, T.E., Keil, K., Snetsinger, K.G., 1967, Chromite composition in relation to chemistry and texture of ordinary chondrites: Geochimica et Cosmochimica Acta, v. 31, p. 1569-1582.

Clayton, R.N., Mayeda, T.K., Goswami, J.N., and Olsen, E.J., 1991, Oxygen isotope studies of ordinary chondrites: Geochimica et Cosmochimica Acta, v. 55, p. 2317-2337.

Cooper, R.A., and Sadler, P.M., 2012, The Ordovician Period, *in* Gradstein, F.M., Ogg, J.G., Schmitz, M.D., and Ogg, G.M., eds., The Geologic Time Scale 2012, Volume 2: Elsevier BV, p. 489-523.

Cronholm, A., and Schmitz, B., 2007, Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone at Gubbio, Italy: the flux of unmelted ordinary chondrites. Meteoritics & Planetary Science, v. 42, p. 2099-2109.

Faraoni, P., Flore, D., Marini, A., Pallini, G., and Pezzoni, N., 1997, Valanginian and early Hauterivian ammonite successions in the Mt Catria group (Central Apennines) and the Lessini Mts (Southern Alps), Italy: Palaeopelagos, v. 7, p. 59-100.

Heck, P.R., Schmitz, B., Baur, H., and Wieler, R., 2008, Noble gases in fossil micrometeorites and meteorites from 470 Myr old sediments from southern Sweden and new evidence for the L chondrite parent body break-up event. Meteoritics & Planetary Science, v. 43, p. 517-528.

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

Heck, P.R., Schmitz, B., Rout, S.S., Tenner, T., Villalon, K., Cronholm, A., Terfelt, F., and Kita, N.T., 2016, A search for H-chondritic chromite grains in sediments that formed immediately after the breakup of the L-chondrite parent body 470 Ma ago: Geochimica et Cosmochimica Acta, v. 177, p. 120-129.

Heck, P.R., Schmitz, B., Bottke, W.F., Rout, S.S., Kita, N.T., Cronholm, A., Defouilloy, C., Dronov, A., and Terfelt, F., 2017, Rare meteorites common in the Ordovician period: Nature Astronomy, v. 1, doi:10.1038/s41550-016-0035.

Korochantseva, E.V., Trieloff, M., Lorenz, C.A., Buykin, A.I., Ivanova, M.A., Schwarz, W.H., Hopp, J., and Jessberger, E.K., 2007, L-chondrite asteroid breakup tied to Ordovician meteorite shower by multiple isochron ^{40}Ar-^{39}Ar dating: Meteoritics & Planetary Science, v. 42, p.113-130.

Kudielka, G., Koeberl, C., Montanari, A., Newton, J., and Reimold, W.U., 2002, Stable-isotope and trace element stratigraphy of the Jurassic/Cretaceous boundary, Bosso River Gorge, Italy, *in* Buffetaut, E., and Koeberl, C., eds., Geological and Biological Effects of Impact Events: Springer Verlag Berlin Heidelberg, p. 25-68.

Masiero, J.R., Mainzer, A.K., Grav, T., Bauer, J.M., and Jedicke, R., 2012, Revising the age for the Baptistina asteroid family using *WISE*/NEOWISE data: The Astrophysical Journal, v. 759, article 14 (14 pp).

Meier, M.M.M., Schmitz, B., Baur, H., and Wieler, R., 2010, Noble gases in individual L-chondritic micrometeorites preserved in an Ordovician limestone: Earth and Planetary Science Letters, v. 290, p. 54-63.

Menichetti, M., 2016, Early Cretaceous tectonic event in the Adria: Insight from Umbria-Marche pelagic basin (Italy), *in* Menichetti, M., Coccioni, R., and Montanari, A., eds., Integrated Stratigraphy of the Late Cretaceous-Paleogene Umbria-Marche Pelagic Basin: Geological Society of America Special Paper, v. 524, p. 35-55.

Nesvorný, D., Vokrouhlický, D., Morbidelli, A., and Bottke, W.F., 2009, Asteroidal source of L chondrite meteorites: Icarus, v. 200, p. 698-701.

Nesvorný, D., Brož, M, Carruba, V., 2015, Identification of dynamical properties of asteroid families, *in* Michel, P., DeMeo, F.E., and Bottke, W.F., eds., Asteroids IV, University of Arizona, Tucson, pp. 297-321.

Reddy, V., Sanchez, J.A., Bottke, W.F., Cloutis, E.A., Izawa, M.R.M., O'Brien, D.P., Mann, P., Cuddy, M., Le Corre, L., Gaffey, M.J., and Fujihara, G., 2014, Chelyabinsk meteorite explains unusual spectral properties of Baptistina Asteroid Family: Icarus, v. 237, 116-130.

Renz, O., 1936, Stratigraphische und mikropaläontologische Untersuchungen der Scaglia (Obere Kreide-Tertiär) im zentralen Apennin: Eclogae Geologicae Helvetiae, v. 29, p. 1-149.

Schmitz, B., 2013, Extraterrestrial spinels and the astronomical perspective on Earth's geological record and evolution of life: Chemie der Erde, v. 73, p. 117-145.

Schmitz, B., Tassinari, M., Peucker-Ehrenbrink, B., 2001, A rain of ordinary chondritic meteorites in the early Ordovician: Earth and Planetary Science Letters, v. 194, 1-15.

Schmitz, B, Tassinari, M., and Häggström, T., 2003, Sediment-dispersed extraterrestrial chromite traces a major asteroid disruption event: Science, v. 300, p. 961-964.

Schmitz, B., Cronholm, A., and Montanari, A., 2009, A search for extraterrestrial chromite in the late Eocene Massignano section, central Italy, *in* Koeberl, C., and Montanari, A., eds., The Late Eocene Earth - Hothouse, Icehouse, and Impacts: Geological Society of America Special Paper, v. 452, p. 71-82.

Schmitz, B., Yin, Q.-Z., Sanborn, M.E., Tassinari, M., Caplan, C.E., and Huss, G.R., 2016, A new type of solar-system material recovered from Ordovician marine limestone: Nature Communications, doi:10.1038/ncomms11851.

Sprovieri, M., Coccioni, R., Lirer, F., Pelosi, N., and Lozar, F., 2006, Orbital tuning of a lower Cretaceous composite record (Maiolica Formation, central Italy): Paleoceanography, v. 21, PA4212, doi:10.1029/2005PA001224.

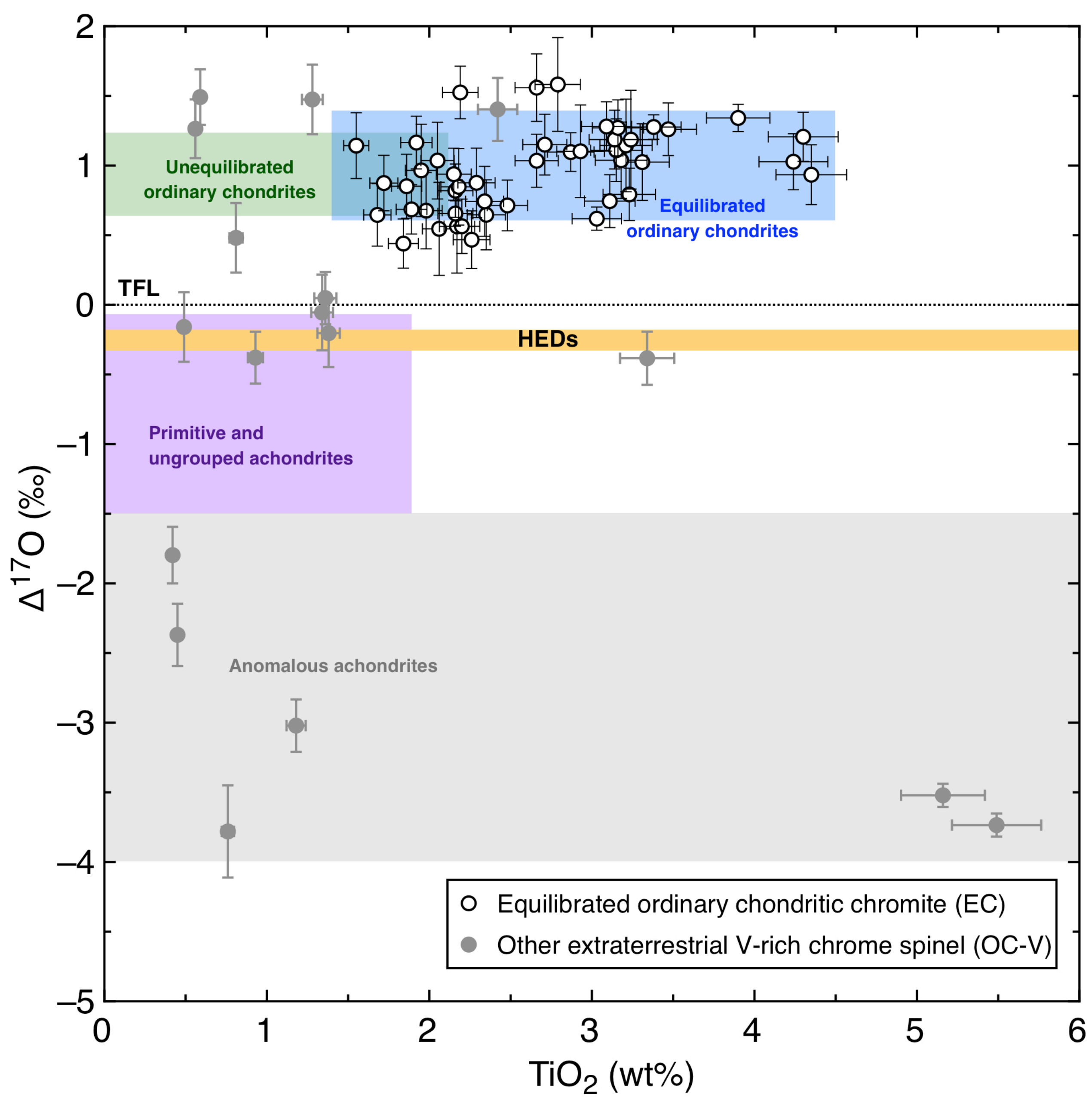
Trinquier, A., Birck, J.-L., and Allègre, C.J., 2006, The nature of the KT impactor. A ^{54}Cr reappraisal: Earth and Planetary Science Letters, v. 241, p. 780-788.

Weirich, J.R., Swindle, T.D., and Isachsen, C.E., 2012, ^{40}Ar-^{39}Ar age of Northwest Africa 091: more evidence for a link between L chondrites and fossil meteorites. Meteoritics & Planetary Science, v. 47, p. 1324-1335.

FIGURE CAPTIONS

Figure 1. Stratigraphic context of Maiolica Formation, position and size of samples analyzed and number of extraterrestrial chrome spinel grains recovered per kilogram of sediment.

Figure 2. Oxygen isotope and TiO_2 composition for 63 out of in total 108 extraterrestrial chrome spinel grains recovered from the Maiolica Formation. TFL = terrestrial fraction line; HED = howardite, eucrite and diogenite meteorites, with origin from asteroid 4 Vesta. For details on oxygen isotopic analyses, see also Table DR7 and Fig. DR1)



Unequilibrated ordinary chondrites
Equilibrated ordinary chondrites
TFL
HEDs
Primitive and ungrouped achondrites
Anomalous achondrites
Equilibrated ordinary chondritic chromite (EC)
Other extraterrestrial V-rich chrome spinel (OC-V)
Δ17O (‰)
TiO2 (wt%)

TABLE 1. COMPARISON OF FLUX OF EQUILIBRATED ORDINARY CHONDRITES TO OTHER CHROME-SPINEL BEARING METEORITE TYPES

Type of chrome spinel	**Before LCPB Ordovician**[1] *# (%) of grains*	**Early Cretaceous**[1] *# (%) of grains*	**Today**[2] *% of flux*
EC	23 (56)	81 (75)	90
OC-V	15 (37)	27 (25)	9
AC-low-V	3 (7)	?	<1
		Ratios[3]	
EC/OC-V	1.5	3	10

[1]EC = chromite from equilibrated ordinary chondrite; OC-V = other chrome spinel with V_2O_3 ≥0.45 wt%; AC-low-V = chrome spinel from achondrites judging from $\Delta^{17}O$ value below terrestrial fractionation line, but with V_2O_3 ≤0.44 wt%.

[2]Fraction of the flux excluding the recent major meteorite groups poor in large Cr-spinel (Table DR5). The OC-V category as defined for this column 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 (<0.5 wt%) V_2O_3. Source: Meteoritical Bulletin data base (www.lpi.usra.edu/meteor/).

[3]The ratios for the Ordovician and the Cretaceous are not directly comparable to the ratio for todays flux. Most achondrites and unequilibrated ordinary chondrites have significantly lower contents of chrome spinels (>32 μm) than the equilibrated ordinary chondrites (Table DR5). If this could be accounted for, the Ordovician and Cretaceous ratios would be even lower than given here. Ideally, comparisons between different time periods should be based entirely on variations in the types of chrome-spinel grains recovered from sediments.

TABLE 2. DIVISION OF EQUILIBRATED ORDINARY CHONDRITIC (EC) GRAINS USING TiO_2 (wt%).

	H **≤2.50%**	**L** **2.51-3.39%**	**LL** **≥3.40%**
Early Cretaceous (n=81)[1]	36	34	11
%	*44*	*42*	*14*
Mid-Ordovician, post-LCPB (n=119)[2]	10	102	7
%	*8*	*86*	*6*
Mid-Ordovician, pre-LCPB (n=215)[3]	80	71	64
%	*37*	*33*	*30*
Recent falls[4] %	***42***	***47***	***11***

[1]This study, [2]Heck et al. (2016), [3]This study, and Heck et al. (2017), [4]Meteoritical Bulletin data base.

TABLE 3. GRAIN ABUNDANCES FROM DIFFERENT METEORITE TYPES OTHER THAN EQUILIBRATED ORDINARY CHONDRITES BASED ON $\Delta^{17}O$

$\Delta^{17}O$ of grain	**Before LCPB Ordovician**[1] *% of 18 gr.*	**Early Cretaceous**[1] *% of 17 gr.*	**Today**[2] *% of non-EC flux*
$\Delta^{17}O$ = 0.35 to 1.6‰ Unequilibrated ordinary chondrites	0	29	~35
$\Delta^{17}O$ at TFL within 2SD Primitive or ungrouped achondrites, (HEDs, or unusual terrestrial V-rich grains?)	17	24	<1
$\Delta^{17}O$ <0 to -0.49‰ at ~2SD HEDs, primitive or ungrouped achondrites	50	12	~60
$\Delta^{17}O$ < -0.50‰ primitive, ungrouped or anomalous achondrites	33	35	<1
Lunar, martian, R chondrites	0	0	~5
Total	100	100	100

[1]The columns show the division of all extraterrestrial grains analyzed for $\Delta^{17}O$ but with a major element composition different from the chromites of equilibrated ordinary chondrites.
[2]The column shows the approximate fraction of the flux of all achondrites and unequilibrated ordinary chondrites rich in large chrome spinels (Table DR5). Data for recent falls from Meteoritical Bulletin data base (www.lpi.usra.edu/meteor/).