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 three oxygen 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 were made with meteorite-flux time “windows” in the Ordovician before and after the L-chondrite parent-body breakup. In the Early Cretaceous, ~80% of the extraterrestrial spinels originated 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 found 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 have been a gradual long-term (a few hundred million years) 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 million years) 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-Paleogene (K-Pg) 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 space 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 by. (Schmitz et al., 2003). This breakup probably led to the formation of one of the major asteroid families (Nesvorny et al., 2009). The event has been dated by 40Ar-39Ar analyses of recently fallen L chondrites to 470 ± 6 Ma (Korochantsyeva et al., 2007), but the most precise relative date is given by an abrupt two-orders-of-magnitude increase worldwide in sand-sized L-chondritic chromite grains in mid-Ordovician sediments (Schmitz et al., 2003; Heck et al., 2016).

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). 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, detrital 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. From a total of 1652 kg of limestone from the earliest Berriasian to early Hauterivian Maiolica Formation, we recovered 108 extraterrestrial spinel grains (Fig. 1). Using three oxygen isotope and elemental analyses of the grains, we obtained the very first insights into what types of meteorites fell on Earth at times other 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 an ~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.

MATERIALS AND METHODS

Samples were collected from 12 beds in two stratigraphically separated groups along the 240-m-thick Monte Acuto section of the Maiolica limestone in central Italy (43°27.83′N, 12°40.27′E). We collected a total of 513 kg from four beds in the Berriasian part of the section, and 1015 kg from eight beds in the late Valanginian to early Hauterivian part (Fig. 1). The size of the individual samples varied between 103 and 433 kg (plus one sample of 27 kg). One additional sample from the Bosso section, 12 km northwest of Monte Acuto, weighed 124 kg. The rocks were dissolved in HCl (6 M) and HF (11 M) at room temperature in the Astrogeobiology Laboratory specially built for separation of extraterrestrial minerals from sediments. After sieving at mesh sizes 32 and 63 μm, opaque Cr-spinel grains were identified by handpicking under the binocular microscope and...
**Results**

Among the total of 108 extraterrestrial Cr-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 (Table 1; Tables DR1 and DR2). In the >63 μm fraction, only two extraterrestrial grains were found; both were EC grains. In the 32–63 μm fraction, based on element analyses alone, we found 79 grains with clear EC elemental composition. Oxygen-isotopic analysis was performed on 46 of these grains, confirming that they are all ordinary chondritic grains (Fig. 2).

The division of the 81 recovered EC grains into their three subgroups, based entirely on their TiO₂ content, is given in Table 2. The reason for using TiO₂ is the substantially larger data set for grains having been analyzed for TiO₂ compared to Δ²⁰⁷⁰⁷⁰. These data were compared with estimates based on the same approach for EC grains from the mid-Ordovician before and after the LCPB, as well as the proportions among recent meteorite falls following the Meteoritical Bulletin Database. From our comparisons of divisions based on either TiO₂ or Δ²⁰⁷⁰⁷⁰, as well as both parameters combined, we know that the main trends based on TiO₂ alone, can be seen in all three approaches (Table DR3).

Of the 27 OC-V grains in the 32–63 μm fraction, 17 grains could be analyzed for three oxygen isotopes. Of these, 13 gave Δ²⁰⁷⁰⁷⁰ values separated at 2 standard deviations (SD) from the terrestrial fractionation line (TFL), i.e., indicating a meteoritic origin (Fig. 2). Four of the grains show Δ²⁰⁷⁰⁷⁰ indistinguishable from the TFL, but we argue that these grains nevertheless originate from achondritic meteorite types that have Δ²⁰⁷⁰⁷⁰ values at or very close to the TFL. 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 2 SD) the TFL, with Δ²⁰⁷⁰⁷⁰ values of −0.4‰. Altogether, the six OC-V grains with values at or just below the TFL 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 subsequent qualitative scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) element analysis. From all samples, all (OC-V) and "all other chrome spinel" (OC). The basis for this is that with a Cameca IMS 1280 secondary ion mass spectrometer (SIMS) in narrow elemental composition and can readily be identified based on an analytical standard UWCr-3 (Heck et al., 2017). Element concentrations of the samples were also collected and analyzed in order to determine if any Mg-Al spinels were present.

Polished epoxy mounts were prepared for all Cr-spinels together with an analytical standard UWCr-3 (Heck et al., 2017). Element concentrations were analyzed quantitatively with a calibrated Oxford-Link EDS mounted on a Hitachi SEM. Isotopes of ⁶⁰⁰⁰, ⁶⁰⁰⁰, and ⁶⁰⁰⁰ were analyzed with a Cameca IMS 1280 secondary ion mass spectrometer (SIMS) in three separate sessions with the procedures similar to Heck et al. (2017). We determined parts per thousand deviations from Vienna standard mean ocean water (VSMOW) as δ⁴⁰⁰ and δ⁴⁰⁰, and as Δ²⁰⁷⁰⁷⁰⁷⁰⁷⁰ from the terrestrial mass-fractionation line (= δ²⁰⁷⁰⁷⁰⁷⁰⁷⁰ − 0.52 × δ⁴⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰), the latter being the main indicator for an extraterrestrial origin.

For further details on materials and methods, including a summary on the sedimentology of the Maiolica Formation, see the GSA Data Repository.¹

**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 then be further divided into the three groups H, L, and LL based on their oxygen isotope and TiO₂ content (see following). The remaining Cr-spinel grains were divided into two groups, “other chrome spinel with 0.45 wt% V₂O₃ (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 were further subdivided based mainly on their oxygen isotopic composition.

The three groups of ordinary chondrites, H, L, and LL, have different average values of Δ²⁰⁷⁰⁷⁰ (0.73‰, 1.07‰, and 1.26‰, respectively; Clayton et al., 1991) and TiO₂ (2.2, 2.7, and 3.4 wt%, respectively; Schmitz, 2013). Around these averages, the Δ²⁰⁷⁰⁷⁰ and TiO₂ values are spread following a Gaussian distribution, but the distributional tails overlap (Heck et al., 2016). The exact ranges for dividing grains based on TiO₂ and/or Δ²⁰⁷⁰⁷⁰ can in principle be arbitrarily set, but they must be used consistently when comparing different time periods.

**Table 1**

| Type of chrome spinel | Before LCPB Ordovician no. (%) of grains | Early Cretaceous no. (%) of grains | Today % of flux | Ratios | EC/OC-V |
|----------------------|--------------------------------------|--------------------------------|----------------|--------|---------|
| EC                   | 23 (56)                              | 81 (75)                        | 90             |        | 1.5     |
| OC-V                 | 15 (37)                              | 27 (25)                        | 9              | 9      | 3       |
| AC-low-V             | 3 (7)                                | ?                              | <1             | 1      |         |

¹GSA Data Repository item 2017273, Item DR1 and Tables DR1–DR6 (additional data and descriptions of methods), is available online at http://www.geosociety.org/datarepository/2017/, or on request from editing@geosociety.org.
have $\Delta^{17}O$ values similar to ordinary chondrites, despite having an elemental composition significantly outside the defined EC range. The grains have $\Delta^{17}O$ values spanning the range from H- to LL-chondritic meteorites (0.48‰ to 1.49‰) and may originate from unequilibrated ordinary chondrites, i.e., petrographic types 3–4. The last six of the OC-V grains analyzed for $\Delta^{17}O$ have anomalously low $\Delta^{17}O$ values, in the range $-1.80^{\circ}e$ to $-3.78^{\circ}e$, indicating that they originate from primitive (e.g., winonaites, lodranites, acapulcoites) or ungrouped or anomalous achondrites that are very rare on Earth today (see following). In summary, 12 of the 17 OC-V grains analyzed for oxygen isotopes, and 21 have $\Delta^{17}O$ values right on the TFL within $\pm 2$ SD (Table DR2). Two of the grains lie slightly off the TFL ($-0.31^{\circ}e \pm 0.18^{\circ}e$, and $0.34^{\circ}e \pm 0.21^{\circ}e$), which could indicate an extraterrestrial origin, but the element compositions of the grains are similar to that of typical terrestrial OC grains in the section.

The Berriasian part of the Monte Acuto section has higher concentrations of EC grains, 7.0 per 100 kg rock, 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 supports the view that all of the OC-V grains are extraterrestrial. In the Monte Acuto section, all except three of the 88 OC grains were found in the younger part of the section.

Because acid residues of the Maiolica limestone are so clean, it has been possible to also quantify the amount of transparent Mg-Al-spinels. In some of the more common carbonaceous chondrite meteorite types that fall on Earth today (e.g., CM and CV types), Mg-Al-spinels are common in the 32–63 μm fraction and dominate over opaque Cr-spinels (Schmitz, 2013). Only one Mg-Al-spinel grain was found in our samples, which is significant for the interpretation of the origin of the other Cr-spinel grains (see following). The single grain was found in Bed 406 together with many terrestrial zircons. This fact and the low $V_{O_2}$ content (<0.3 wt%) of the grain indicate that it is most likely of terrestrial origin.

### DISCUSSION

**Flux of Meteorites through the Phanerzoic**

Before the present study, the only periods in deep time for which information existed about the types of meteorites that commonly fell on Earth were for the mid-Ordovician before and after the LCPB (Schmitz et al., 2003; Schmitz, 2013; Heck et al., 2016, 2017). The addition here of a third “window” adds an important new perspective, but interpretation and generalizations must be preliminary awaiting the results for additional time windows. 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 from Early Cretaceous strata (~3) is somewhere between the ratios for the mid-Ordovician before the LCPB (~1.5) and recent time (~10; Table 1). It appears that the background meteorite flux may have evolved gradually over the Phanerzoic, from being dominated by achondrites to the present situation, where 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 1%. 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 also be a trend in the flux of ordinary chondrites through the Phanerzoic (Table 2). Within the resolution of our approach, the ratios between the different groups of ordinary chondrites in the Early Cretaceous (H:L:LL $\sim 1:1:0.2$) are identical to the ratios today ($\sim 1:1:0.2$). 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 content with the “neighbor groups.” Heck et al. (2016) analyzed 120 post-LCPB EC grains for oxygen isotopes and found that ~29% of the grains were L-chondritic. Before the LCPB, the LL chondrites (based on 215 EC grains analyzed for TIO$_2$) represent ~30% of the ordinary chondritic flux, compared to ~10% in the Early Cretaceous and today (Table 2; Table DR4; 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. The carbonaceous chondrites (with rare exceptions) contain only low concentrations of opaque spinels in the grain-size ranges we analyzed as compared to ordinary chondrites and most of the achondrites (Heck et al., 2017). 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 that none of the recovered opaque grains is from carbonaceous chondrites. Iron meteorites, mesosiderites, and pallasites contain spinel concentrations too low to be of any significance in this type of study. Rumuruti chondrites are rich in Cr-spinels but have δ¹⁷O values not observed here. Enstatite chondrites are too reduced to contain significant amounts of any Cr-rich oxides.

In our assemblage of Cr-spinel grains, there is a significant amount (~10%) of achondritic grains with δ¹⁷O values at or below ~2‰ (Fig. 2; Table DR5). Such achondrites are very rare on Earth today, representing less than a tenth of a percent of the known recent meteorites. In Bed 36, −3.8‰. In Bed 40, there are two grains with values on the early Paleozoic appears to have been significantly different from the flux in the Cretaceous, which is more similar to today’s flux. Achondrites dominated in the early Paleozoic, and ordinary chondrites dominate today. This general trend was at times overprinted (for 1–10 m.y.) by floods of single types of meteorites from occasional major breakup events in the asteroid belt, such as after the LCPB.

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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, doi:10.1126/science.208.4448.1095.

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, doi:10.1038/nature06070.

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, doi:10.1016/0016-7037(91)90107-G.

Faroni, P., Flore, D., Marino, G., pistilli, G., and Pezzoni, N., 1997, Valanginian and early Hauterivian ammonite successions in the Mt. Catria group (Central Apenines) and the Lessini Ms (southern Alps), Italy: Paleopelagos, v. 7, p. 59–100.

Heck, P.R., Schmitz, B., Baur, H., and Wieler, R., 2008, Noble gases in fossil micro-meteorites 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, doi:10.1111/j.1945-5100.2008.tb00669.x.

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 chrome 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, doi:10.1016/j.gca.2015.11.042.

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 Ordo-
vorian period: Nature Astronomy, v. 1, 0035, 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 ⁴⁰Ar–³⁹Ar dating: Meteoritics & Planetary Science, v. 42, p. 113–130, doi:10.1111/j.1945-5100.2007.tb00221.x.

Maserio, J.R., Mainzer, A.K., Grav, T., Bauer, J.M., and Jedidke, R., 2012, Revis-
ing the age for the Baptistina asteroid family using WISE/NEOWISE data: The Astrophysical Journal, v. 759, article 14.

Nesvorný, D., Vokrouhlický, D., Morbidelli, A., and Bottke, W.F., 2009, Asteroidal source of L chondrite meteorites: Icarus, v. 200, p. 698–701, doi:10.1016/j.icarus.2008.12.016.

Nesvorný, D., Brož, M., and Carruba, V., 2015, Identification of dynamical properties of asteroid families, in Michel, P., et al., eds., Asteroids IV: Tucson, University of Arizona, p. 297–321, doi:10.2485/azu_uapress_9780816552131-ch016.

Reddy, V., et al., 2014, Chelyabinsk meteorite explains unusual spectral properties of Baptista asteroid family: Icarus, v. 237, p. 116–130, doi:10.1016/j.icarus.2014.04.027.

Schmittz, 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, doi:10.1126/chemer.2013.04.002.

Schmittz, B., Tassinari, M., and Häggström, T., 2003, Sediment-dispersed extra-
terrestrial chromite traces a major asteroid disruption event: Science, v. 300, p. 961–964, doi:10.1126/science.1082182.

Schmittz, 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 lime-
stone: Nature Communications, v. 7, no.11851, doi:10.1038/ncomms11851.

Trinquier, A., Bürck, J.-L., and Allègre, C.J., 2006, The nature of the KT impactor: A ⁴⁰Ca reappraisal: Earth and Planetary Science Letters, v. 241, p. 780–788, doi:10.1016/j.epsl.2005.11.006.

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