



Fragments of Late Eocene Earth-impacting asteroids linked to disturbance of asteroid belt



Birger Schmitz^{a,b,c,*}, Samuele Boschi^a, Anders Cronholm^a, Philipp R. Heck^{b,d},
Simonetta Monechi^e, Alessandro Montanari^f, Fredrik Terfelt^a

^a Astrogeobiology Laboratory, Department of Physics, Lund University, Sweden

^b Robert A. Pritzker Center for Meteoritics and Polar Studies, The Field Museum of Natural History, Chicago, IL, USA

^c Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Manoa, Honolulu, HI, USA

^d Chicago Center for Cosmochemistry, The University of Chicago, Chicago, IL, USA

^e Department of Earth Sciences, Florence University, Florence, Italy

^f Geological Observatory of Coldigioco, Frontale di Airo, Macerata, Italy

ARTICLE INFO

Article history:

Received 3 February 2015

Received in revised form 4 May 2015

Accepted 5 May 2015

Available online 8 June 2015

Editor: B. Marty

Keywords:

Late Eocene

Popigai crater

helium-3

ordinary chondrite

asteroid belt

ice age

ABSTRACT

The onset of Earth's present icehouse climate in the Late Eocene coincides with astronomical events of enigmatic causation. At ~ 36 Ma ago the 90–100 km large Popigai and Chesapeake Bay impact structures formed within ~ 10 –20 ka. Enrichments of ^3He in coeval sediments also indicate high fluxes of interplanetary dust to Earth for ~ 2 Ma. Additionally, several medium-sized impact structures are known from the Late Eocene. Here we report from sediments in Italy the presence of abundant ordinary chondritic chromite grains (63–250 μm) associated with the ejecta from the Popigai impactor. The grains occur in the ~ 40 cm interval immediately above the ejecta layer. Element analyses show that grains in the lower half of this interval have an apparent H-chondritic composition, whereas grains in the upper half are of L-chondritic origin. The grains most likely originate from the regoliths of the Popigai and the Chesapeake Bay impactors, respectively. These asteroids may have approached Earth at comparatively low speeds, and regolith was shed off from their surfaces after they passed the Roche limit. The regolith grains then settled on Earth some 100 to 1000 yrs after the respective impacts. Further neon and oxygen isotopic analyses of the grains can be used to test this hypothesis.

If the Popigai and Chesapeake Bay impactors represent two different types of asteroids one can rule out previous explanations of the Late Eocene extraterrestrial signatures invoking an asteroid shower from a single parent-body breakup. Instead a multi-type asteroid shower may have been triggered by changes of planetary orbital elements. This could have happened due to chaos-related transitions in motions of the inner planets or through the interplay of chaos between the outer and inner planets. Asteroids in a region of the asteroid belt where many ordinary chondritic bodies reside, were rapidly perturbed into orbital resonances. This led to an increase in small to medium-sized collisional breakup events over a 2–5 Ma period. This would explain the simultaneous delivery of excess dust and asteroids to the inner solar system. Independent evidence for our scenario are the common cosmic-ray exposure ages in the range of ca. 33–40 Ma for recently fallen H and L chondrites.

The temporal coincidence of gravity disturbances in the asteroid belt with the termination of ice-free conditions on Earth after 250 Ma is compelling. We speculate that this coincidence and a general correlation during the past 2 Ga between K–Ar breakup ages of parent bodies of the ordinary chondrites and ice ages on Earth suggest that there may exist an astronomical process that disturbs both regions of the inner asteroid belt and Earth's orbit with a potential impact on Earth's climate.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction and background

The Late Eocene, ~ 37.8 –33.9 Ma ago, was the time when Earth's climate changed into the present “icehouse” state after ~ 250 Ma of “greenhouse” conditions. Although the major change in climate occurred at the Eocene–Oligocene boundary, an accel-

* Corresponding author at: Astrogeobiology Laboratory, Department of Physics, Lund University, Sweden.

E-mail address: birger.schmitz@nuclear.lu.se (B. Schmitz).

erating cooling trend prevailed through the Late Eocene when also the first significant ice sheets on Antarctica formed (Vonhof et al., 2000; Zachos et al., 2001; Bodiselitsch et al., 2004; Lear et al., 2008; Scher et al., 2014; Villa et al., 2014). The Late Eocene was also a period with an enigmatic, enhanced flux of extraterrestrial matter to Earth. The evidence comes primarily from two very large and several medium-sized impact craters, as well as an interval in the sedimentary strata with high concentrations of extraterrestrial ^3He (e.g., Montanari et al., 1993; Farley et al., 1998; Glass and Koeberl, 1999; Whitehead et al., 2000; Koeberl, 2009; Kyte et al., 2011; Paquay et al., 2014). The Popigai crater in northern Siberia is 100 km in diameter and the largest known impact crater post-dating the Cretaceous–Tertiary boundary (Vishnevsky and Montanari, 1999; Whitehead et al., 2000; Koeberl, 2009). The second large astrobleme, Chesapeake Bay in the eastern US, is a structure with a diameter of 85–90 km, but the true crater is ~ 40 km in diameter, with the larger size reflecting collapse of sediment structures (Poag et al., 2004; Kyte et al., 2011). This impact was thus considerably less energetic than the Popigai impact. The Chesapeake Bay and Popigai structures have radiometric ages of 35.5 ± 0.6 and 35.7 ± 0.2 Ma, respectively (Koeberl et al., 1996; Bottomley et al., 1997). The stratigraphic positions of the distal ejecta layers from the craters indicate that the impact events occurred within ~ 10 – 20 ka (Koeberl, 2009). The ejecta layers occur in the middle part of the sedimentary interval enriched in extraterrestrial ^3He , reflecting a ~ 2 Ma period of enhanced flux of small ($< 50 \mu\text{m}$) interplanetary dust particles to Earth (Farley et al., 1998). Three well-dated, medium-sized craters with ages ~ 40 – 35 Ma are Haughton, Mistastin, and Wanapitei (Koeberl, 2009), but there are also a number of craters with larger dating uncertainties of which some could be of Late Eocene age (Earth Impact Database, 2015).

The Late Eocene ^3He anomaly and associated impacts were originally proposed to reflect a comet shower from a random perturbation of the Oort comet cloud (Farley et al., 1998; Farley, 2009). This scenario was supposed to best explain the ~ 2 Ma duration of the enhanced flux of fine-grained ^3He -rich dust to Earth. Also the simultaneous delivery of large projectiles and fine-grained interplanetary dust reconciles best with models for cometary events. An asteroid breakup was ruled out because following such an event the ejected dust moves directly to Earth by Poynting–Robinson drag, whereas the km-sized fragments need to drift into an orbital resonance before being redirected to an Earth-crossing orbit. Thus the km-sized asteroids will arrive on Earth typically several million years after the fine-grained dust (Zappalà et al., 1998). Tagle and Claeys (2004, 2005), however, challenged the comet scenario and suggested the breakup of an L-chondritic asteroid in the asteroid belt as an alternative source of Late Eocene ^3He and impactors. They based their claims on platinum-group element (PGE) analyses of melt rock in the Popigai crater (Tagle and Claeys, 2004, 2005), but more elaborated evaluation of the PGE data show that they may be consistent with any type of ordinary chondrite (i.e., H, L or LL) (Farley, 2009; Kyte et al., 2011). There are also other uncertainties around PGE signatures, related to element fractionation in the condensing impact plume or during sediment diagenesis (Schmitz et al., 2011). It has also been speculated that following an L-chondritic asteroid breakup, a shower of smaller asteroids to the Earth–Moon system ejected large amounts of ^3He -rich fine-grained lunar regolith that settled on Earth (Fritz et al., 2007). The most compelling data so far as to the causes of the Late Eocene events comes from Cr-isotopic analyses of distal ejecta from the Popigai crater (Kyte et al., 2011). These data constrain the origin of this impactor to be an ordinary chondritic asteroid. The authors speculated that the Popigai impactor and excess ^3He may be related to the breakup of the Brangäne asteroid, with an assumed H-chondritic composition. Based on astronomical observations this

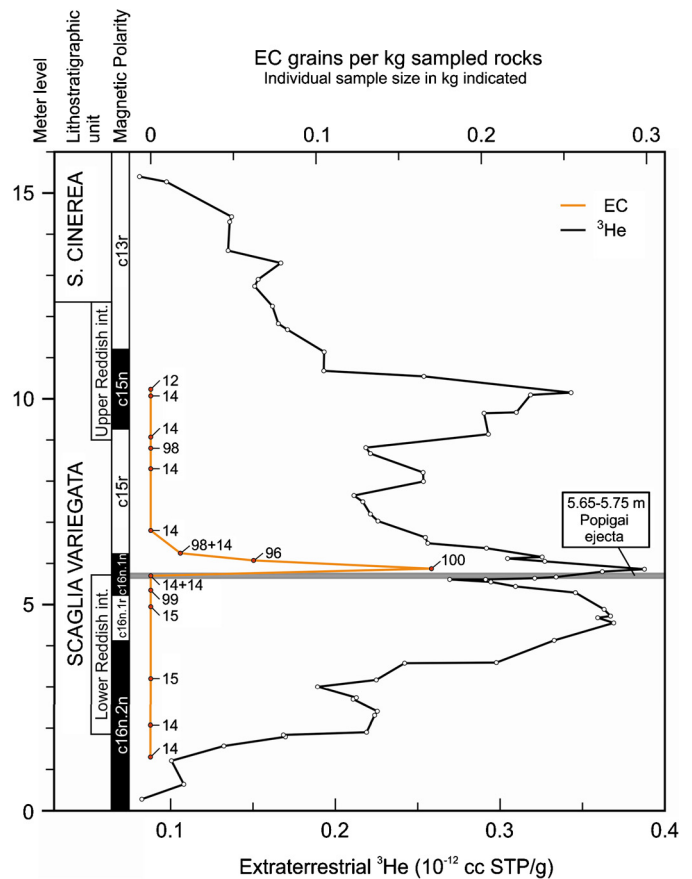


Fig. 1. Profiles for the Massignano section of extraterrestrial ^3He concentrations (black curve) (Farley et al., 1998) and the total number of recovered EC grains per kg sediment (orange curve) in this study and by Schmitz et al. (2009). Indicated in numbers on the latter curve are the masses in kilogram of the samples searched for EC grains. Magnetostratigraphy after Jovane et al. (2007).

body broke up at $\sim 50 \pm 40$ Ma (Nesvorný et al., 2005) and is the only major family-forming event involving an S-type (i.e. ordinary chondritic) asteroid that is a potential match for Late Eocene ^3He and impactors.

In a previous study we aimed at testing the hypothesis of a Late Eocene major L-chondrite breakup event by searching for L-chondritic chromite grains over the ^3He -rich interval in the pelagic sediments of the Massignano section in central Italy (Schmitz et al., 2009). This is the section where some of the most detailed studies of the Late Eocene extraterrestrial events have been performed, including the original reconstruction of the ^3He anomaly (Farley et al., 1998) (Fig. 1). A major breakup event in the Late Eocene would have given a chromite signature in the sediment similar to that following the breakup of the L-chondrite parent body in the mid-Ordovician 470 Ma ago (Schmitz et al., 2003; Schmitz, 2013). Slowly formed marine sediments from immediately after this event contain up to ten L-chondritic chromite grains (63 – $250 \mu\text{m}$) per kg of sediment, attesting to a very high flux of L-chondritic matter to Earth. Chromite makes up $\sim 0.25\%$ of ordinary chondrites and is the only common mineral in this meteorite type that survives weathering on Earth. In our previous study at Massignano we searched for chromite grains in 167 kg of rock from 12 levels within the 14 m stratigraphic range of the ^3He anomaly. We found only one ordinary chondritic chromite grain, arguing against a major breakup event similar to that in the mid-Ordovician. The single grain recovered occurred in a sample ~ 45 cm above the Popigai ejecta layer. This finding prompted us to continue the search for extraterrestrial spinels, but at a higher resolution. Therefore, in the present study a total of 491 kg of

Table 1
EC and OC grains (>63 μm) recovered in Massignano section.

Sample depth (m)	Sample weight (kg)	No. EC grains	No. OC grains	OC/kg rock
10.25–10.35	11.6	0	34	2.9
10.00–10.15	14.0	0	28	2.0
9.00–9.15	14.1	0	71	5.0
8.60–9.00	98.4	0	90	0.9
8.20–8.40	14.2	0	36	2.5
6.70–6.90	14.1	0	24	1.7
6.15–6.25	14.0	1	22	1.6
6.15–6.40	97.6	1	331	3.4
6.00–6.15	96.4	6	122	1.3
5.75–6.00	99.9	17	165	1.7
5.70–5.80	13.8	0	16	1.2
5.60–5.65	13.9	0	35	2.5
5.10–5.40	99.0	0	248	2.5
4.80–5.10	14.6	0	19	1.3
3.05–3.35	15.0	0	22	1.5
1.95–2.20	13.9	0	29	2.1
1.25–1.35	13.9	0	32	2.3
Total:	658.4	25	1324	2.0

limestone, in addition to the previous 167 kg, were collected in the Massignano section with a focus on the interval around the Popigai ejecta bed.

2. Materials and methods

Three of the new samples, each of ~ 100 kg, were collected at succeeding levels beginning at the top of the Popigai ejecta layer, at the 5.75 m level in the section, and covering the entire overlying 65 cm of section (Fig. 1). Two background samples, each ~ 100 kg large, were collected at the 5.10 and 8.60 m levels. Meter levels in the Massignano section are marked by iron plates, but some of these markers have lately disappeared. The Popigai impact ejecta does not represent a distinct bed and can be difficult to demarcate in the field. Montanari et al. (1993) place the base at 5.61 m, whereas Paquay et al. (2014) measure enhanced iridium concentrations over the interval from 5.64 to 5.73 m. Huber et al. (2001) state that the “impactoclastic” layer occurs between levels 5.64 and 5.72 m. Our level 5.75 m in the present study coincides with a change from reddish gray to plain gray sediments, but this color change can best be seen in fresh rock exposures. There may be uncertainties of a few centimeters when comparing sample depths between our previous study (Schmitz et al., 2009) and the present study.

All samples have been carefully cleaned, then dissolved in 6 M HCl in our lab specially designed for dissolution of large rock samples. The residue >63 μm was recovered by sieving and subjected to 11 M HF at room temperature for two days. From the HF residues all opaque chrome spinel grains were picked under a stereo light microscope, then embedded in epoxy, polished and analyzed for element composition with a calibrated SEM-EDS instrument (Schmitz et al., 2009). The analytical approach and the classification of chrome spinel grains into extraterrestrial (EC) or terrestrial (or “other chrome spinel” = OC) based on their chemical composition is further discussed in the Supplementary Online Material. Our approach relies on that chromite in equilibrated ordinary chondrites has a very narrow and unique range in elemental composition, and thus can be readily discriminated from chrome spinels from other sources (Schmitz, 2013).

3. Results

In 658 kg of sediment from the ^3He -rich interval at Massignano we have found a total of 1349 opaque chrome spinel grains (Table 1; Fig. 1). Of these, only 25 have the typical EC composition

and they were all found in the 308 kg of sediment representing the 65 cm interval immediately above the Popigai ejecta (Fig. 2). In the 350 kg of sediment from the remainder of the section no EC grains were found. The 1324 chrome spinel that do not have the typical EC composition are all, or almost all, of terrestrial origin. There are no major changes in the composition of the terrestrial grains through the section. Their chemical composition indicates an ophiolitic source, probably the Sardo–Corso massif to the west.

In the interval that contains EC grains, from 5.75 to 6.40 m, the grains show an apparent tailing-off trend, with 17, 6 and 2 grains in the three vertically succeeding ~ 100 -kg large samples. However, the chemical results show that the situation is more complex and that two events close in time probably are registered (Fig. 3). The 17 EC grains in the sample from 5.75–6.00 m, immediately above the Popigai ejecta bed at ~ 5.64 – 5.73 m, represent a significant enrichment in EC. This is clear when considering the relatively high average sedimentation rate at Massignano, ~ 1 cm per ka (Farley et al., 1998; Brown et al., 2009). Condensed limestone of earliest Paleocene age in the Gubbio section, central Italy, formed on average about four times slower than the Late Eocene sediments at Massignano. The Gubbio limestone contains only ~ 3 EC grains per 100 kg of rock, which is considered to represent the background flux of EC grains (Cronholm and Schmitz, 2007). This means that the background flux at the Massignano section would yield $\sim 1 \pm 1$ EC grain per 100 kg sediment. The 17 EC grains per 100 kg of sediment in the 5.75–6.00 m interval thus reflect an enhanced flux by a factor of ~ 17 . In comparison, the mid-Ordovician EC abundance after the breakup of the L-chondrite parent body, normalized to the circa three times higher sedimentation rates at Massignano, lies typically in the range 30–170 EC grains per 100 kg, a factor 2–10 higher than in the Late Eocene. In the mid-Ordovician the signature of the chromite rain endures through many (>10) meters of section, but at Massignano only over a few decimeters. These differences confirm that there was no Late Eocene asteroid breakup of the same magnitude as the one 470 Ma ago (Schmitz et al., 2009).

The chemical composition of the 17 EC grains from immediately above the Popigai ejecta indicates that all or almost all of these grains have an H-chondritic origin (Fig. 3) (Supplementary Table 1). We have analyzed several 1000 EC grains from Ordovician sediments that formed after the breakup of the L-chondrite parent body (Schmitz, 2013). Although chromite chemistry is susceptible to partial diagenetic alteration, some aspects are very stable no matter the diagenetic conditions. Particularly the Ti, and to some extent also Al, concentrations are indicative of the origin of grains.

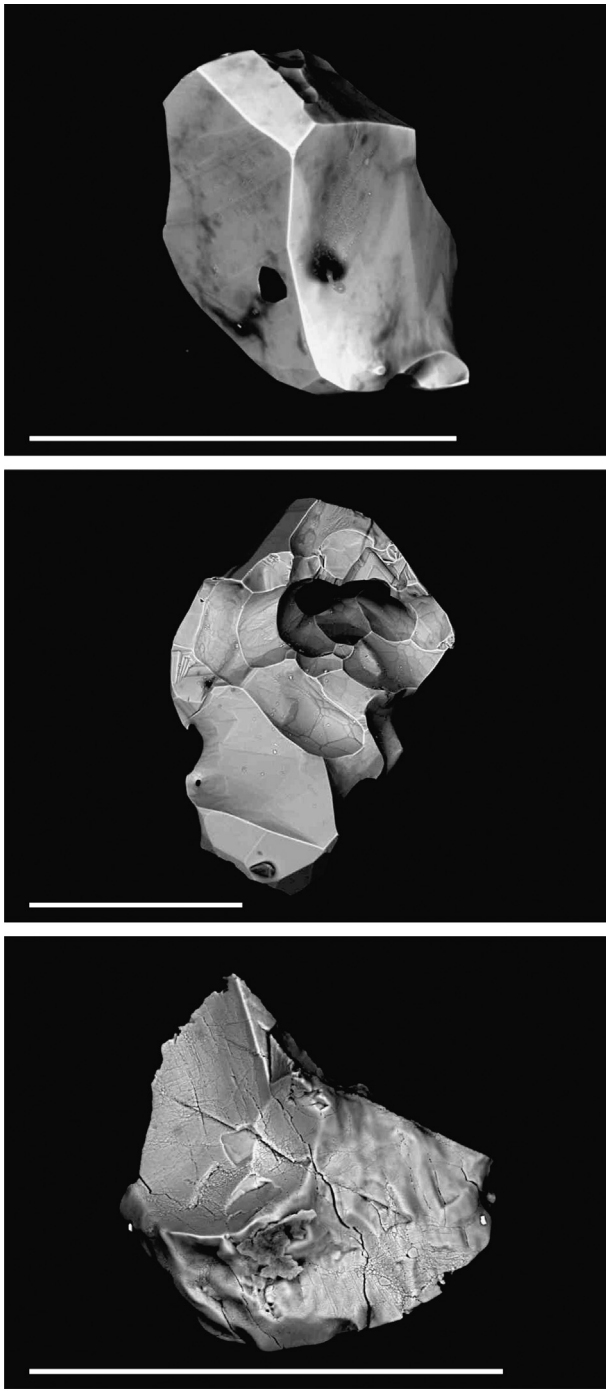


Fig. 2. Three EC grains from the 5.75–6.00 m interval in the Massignano section. Scale bars are 100 μm wide.

These elements in the 17 grains from just above the Popigai ejecta plot with H-chondritic chromite. The grain assemblage clearly has a different composition compared to the L-chondritic grains from the Ordovician. Quite surprisingly the 8 grains from the three samples (with a total weight of 208 kg) in the next succeeding interval (6.00–6.40 m) plot dominantly in the field of L-chondritic chromite. Although there is some overlap in the composition of the grains between the lower and upper interval, there is an obvious general difference. For example, all 17 grains in the lower sample have MgO concentrations >3.5 wt% and FeO <27.3 wt%, whereas only one of the 8 grains in the overlying interval shows such values. Although TiO_2 and Al_2O_3 for the grains in the lower

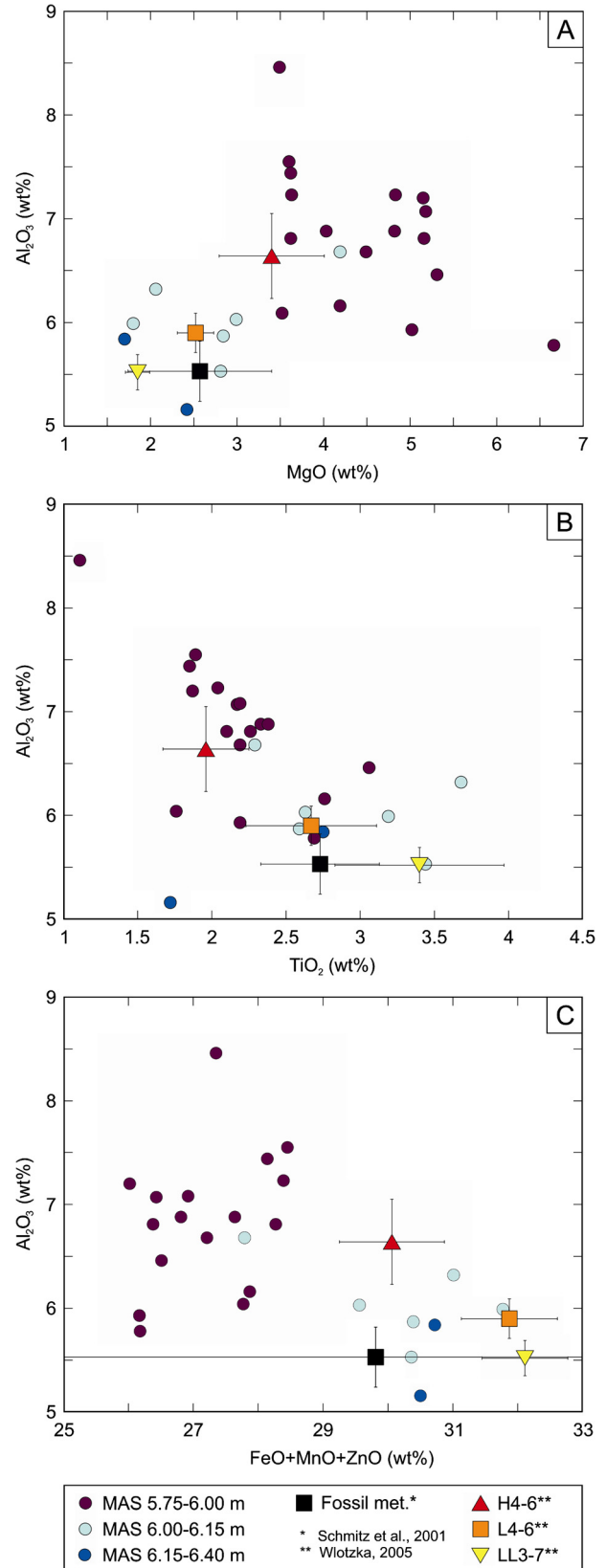


Fig. 3. Elemental composition of EC grains from the Massignano section and chromite grains from recent H, L, and LL chondrites (Wlotzka, 2005) and mid-Ordovician fossil meteorites. Standard deviations are shown for data on fossil and recent meteorites.

sample clearly indicate an H-chondritic origin, the FeO values are a few percent lower than in such chromite (Fig. 3). Previous studies have shown that during diagenesis FeO is the least stable of the oxides in chromite (Schmitz et al., 2001), and this could explain the data. Further oxygen three isotopic analyses or studies of inclusions in the grains are required to ascertain an H-chondritic origin (Schmitz, 2013).

4. Discussion

Most likely the 17 grains from immediately above the Popigai ejecta originate from the dust trail of this impactor. The Popigai impactor was on the order of 5 ± 2 km in diameter (Tagle and Claeys, 2005; Kyte et al., 2011; Paquay et al., 2014). Its encounter with the gravity of the Earth–Moon system may have shed off substantial amounts of asteroid debris already at distances of 10,000–20,000 km from Earth. Asteroids entering within the Roche limit get affected by tidal gravity, and anything between loss of surface material to complete disruption of the asteroid may happen (Richardson et al., 1998; Nesvorný et al., 2010; Tóth et al., 2011; Schunova et al., 2014; Yu et al., 2014). Recent space missions to asteroids Itokawa and Eros (mean diameters 0.3 and 17 km, respectively) have shown that small to large asteroids have a significant layer of loose regolith or “rubble-pile” debris on their surface (Murdoch et al., 2013). Model simulations show that regolith avalanches are expected on asteroids affected by Earth’s gravity (Yu et al., 2014). There are a number of tidal effects that can disturb the surface of an asteroid during a planetary encounter, for example, the tidal torque may spin up an asteroid, and centrifugal forces exceeding the asteroids gravity may move the regolith (Nesvorný et al., 2010).

If we assume that one would find worldwide the same number of Popigai-derived EC grains per surface area as at Massignano, then a regolith-layer about 30 cm thick would have had to be shed off a 5 km Popigai impactor in order to explain the occurrence of the EC grains on Earth. For the estimate we used chromite data for ordinary chondrites (1000 grains $>63 \mu\text{m}$ per gram) from Björnberg and Schmitz (2013). Considering that the average thickness of the regolith of Eros is estimated at 20–40 m (Robinson et al., 2002) the ~ 30 cm of regolith shed off from the Popigai impactor may only represent a small fraction of the entire regolith layer on such a body. The Late Eocene impacting asteroids may have approached Earth at comparatively low speeds increasing the tidal effects. The fact that the EC grains at Massignano are found in the interval above the ejecta and not within it can be explained by a delayed settling within a few 100 to 1000 yrs after the first encounter with Earth’s gravity. One would not expect abundant EC grains in the ejecta bed itself because all original minerals were destroyed when the asteroid vaporized upon impact. Instead the ejecta layer contains abundant dendritic Ni-rich magnesioferrite spinel grains that formed when the impact vapor cloud condensed (Pierrard et al., 1998). It should be noted that the Massignano section is bioturbated and vertical redistribution of single grains can take place (Huber et al., 2001).

The origin of the 8 dominantly L-chondritic chromite grains in the overlying 6.00–6.40 m interval is more enigmatic, but likely they originate from the dust trail of the Chesapeake Bay impactor. In the Late Eocene there are two widespread impact ejecta layers that based on biostratigraphy formed within ~ 10 –20 ka (Glass and Koeberl, 1999; Koeberl, 2009). The lower ejecta bed from the Popigai event probably has a global distribution. It is characterized by clinopyroxene-bearing spherules, so called mikrokrystites. This is the same bed that is enriched in iridium, magnesioferrite spinels and shocked quartz at Massignano, but the mikrokrystites are completely weathered, flattened and replaced by clay minerals. The younger of the two ejecta layers represents the less energetic

Chesapeake Bay impact and has a more restricted geographic distribution, from the northwestern Atlantic to the Caribbean Sea. The bed contains glassy microtektites and unmelted impact debris including shocked quartz. No definitive traces of this ejecta have so far been discovered at Massignano. A second, very small Ir anomaly in the section, measured ~ 50 cm above the Popigai ejecta bed, is not always reproducibly detected (Bodiselsitch et al., 2004; Paquay et al., 2014). With an average sedimentation rate of ~ 1 cm per ka at Massignano, the Chesapeake Bay ejecta would occur about 10–20 cm above the Popigai ejecta. Thus the observed vertical distance of ~ 10 –20 cm between the two groups of EC grains can readily be reconciled with the difference in time between the Popigai and Chesapeake impacts.

The scenario with breakups of both H- and L-chondritic bodies in the Late Eocene asteroid belt receives further support from cosmic-ray exposure (CRE) ages of recently fallen meteorites. The L chondrites show a major peak in their CRE ages at ~ 40 Ma ago, which is also their largest peak for the entire Cenozoic (Wieler and Graf, 2001). The peak coincides with a small peak in K–Ar gas retention ages for the same meteorites (Marti and Graf, 1992). There is thus evidence from recent meteorites of a significant L-chondrite breakup event around 40 Ma ago (but it is an event much smaller than the one 470 Ma ago, see e.g., Swindle et al., 2014). The H chondrites show a prominent, maximum peak in CRE ages around 7–8 Ma ago, but also a major peak at ~ 33 –36 Ma ago (Graf and Marti, 1995; Wieler and Graf, 2001; Kyte et al., 2011). The CRE ages for recent meteorites have uncertainties typically in the range 10–20% because of uncertainties in many underlying assumptions in the approach (Marti and Graf, 1992; Farley, 2009). Uncertainties in CRE ages are largely dominated by unknown shielding conditions of a sample, including depth of sample within the meteoroid and size of the meteoroid. It is not likely that this would create systematic differences in CRE ages of two random populations of meteorites. Hence the different CRE ages of ~ 35 and ~ 40 Ma ago for the H and L chondrites, respectively, most likely represent at least two different events separated by one to a couple of million years. The important point here is that also the CRE ages of recent meteorites indicate perturbations of both H and L chondrite parent bodies in or around the Late Eocene and over a protracted period of time.

Our results concur with previous Cr-isotope and PGE data suggesting that the Popigai impactor was an ordinary chondrite (Tagle and Claeys, 2005; Kyte et al., 2011), but the discovery of chromite from apparently two different types of ordinary chondrites is not consistent with an origin from one major family-forming breakup event. Kyte et al. (2011) base their idea of a Late Eocene breakup of an H-chondritic Brangäne parent-body on the peak in CRE ages of ~ 33 –36 Ma for many of the recent H chondrites. But they point out that the relatively small Brangäne family also lies too far from an orbital resonance to deliver large bodies from a breakup event within the same short time scales that the fine-grained dust would need to drift to Earth. We suggest instead based on our findings and the CRE ages that a Late Eocene asteroid and dust shower to the inner solar system was triggered by an episode of gravitational perturbations of asteroid orbits in the asteroid belt. This may have affected primarily a region where many smaller ordinary chondritic asteroids resided. The asteroids were rapidly perturbed into an orbital resonance position. The frequency in collisions increased over a few million years, which could explain both the protracted ^3He signature in Earth’s sedimentary record as well as the simultaneous delivery of dust and km-sized bodies to Earth. Perturbations of asteroid orbits and orbital resonances may be triggered, for example, by unusual planetary alignments or changes in the motions of the inner planets (Varadi et al., 1999, 2003), or by the interplay of chaos between the outer and the inner planets (Hayes et al., 2010). Long-term integrations of planetary orbits have indicated

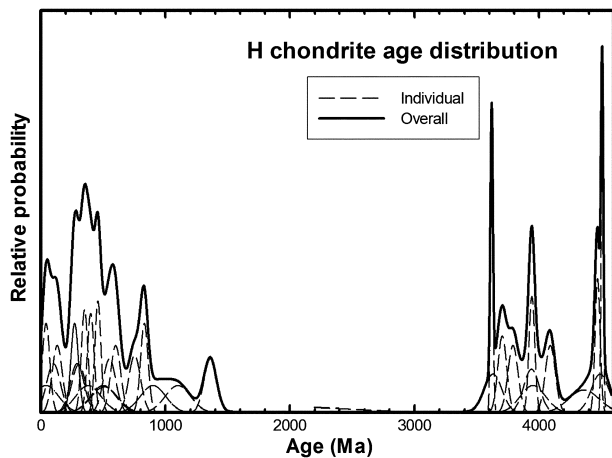


Fig. 4. K–Ar ages of recent H chondrites, from Swindle et al. (2014). The plot shows individual probability distribution for ages of individual meteorites (dashed line) and a combined probability distribution (solid line) for all of the data. The diagram takes into account the uncertainties in the individual data points in a graphical way by giving each data point equal area. There are essentially no impact resetting events recorded for H chondrites between 1.3 and 3.5 Ga ago; see further Swindle et al. (2014) and Schmitz (2013).

that orbits in the inner solar system behave chaotically. Varadi et al. (2003) noted a potential chaos-related transition between different dynamical regimes around 65 Ma ago, and speculated about a relation to the impactor that hit Earth at the Cretaceous–Tertiary (K–T) boundary. Today, empirical evidence has accumulated suggesting that the K–T impactor was a lonely stray object, whereas the evidence is mounting in favor of an asteroid shower in the Late Eocene.

If indeed an asteroid shower in the Late Eocene was triggered by minute changes in the orbits of the inner planets, these changes could have left also a signal in Earth's climate. Brown et al. (2009) observe a disturbance over the ^3He -rich interval in the Massignano section of the orbitally controlled cyclicity in calcite, but this could represent overprinting climatic effects of repeated asteroid impacts. It is generally accepted that Earth's climate variations are primarily astronomically driven, i.e. diurnal, seasonal and Milankovitch cycles, but the fundamental transition after 250 Ma of greenhouse to icehouse climate in the Late Eocene is generally explained in terms of Earth-bound causes, such as the closing or opening of different seaways or changes in atmospheric CO_2 (Zachos et al., 2001). Our data cannot alone challenge such explanations in favor of astronomical causation, but an additional argument comes from the K–Ar ages of recently fallen ordinary chondrites (Swindle et al., 2014). These meteorites show an enigmatic bimodal pattern with gas-retention ages either >3.4 Ga or <1.5 Ga (and mostly <1 Ga) (Fig. 4). The many young ages indicate that major collisions involving ordinary chondrites were much more common in the past 1 Ga than in the 1 Ga before that. The period on Earth from ca. 2 to 1 Ga before the present, sometimes referred to as the Boring Billion (Hazen, 2012), does not have any documented ice age, and there is only one confirmed impact crater from this long period (for a detailed discussion, see Schmitz, 2013). It is compelling that both the ordinary chondrites and Earth's climate show a similar trend, with stability in the period 2 to 1 Ga before the present, followed by a period of instability up to the present. In the past ~ 0.8 Ga there have been seven or eight major ice age episodes, starting with the Snowball Earth glaciations. The onset of Snowball Earth coincides approximately with the formation of the Copernicus crater, the largest young (<2 Ga) crater on the Moon. This crater formed ~ 0.8 Ga ago (Bogard et al., 1994) and some evidence indicate that it formed during an as-

teroid shower (Zellner et al., 2009). Only the ordinary chondrites among recent meteorites show common young (<1 Ga) gas retention ages, indicating that only the inner asteroid belt may have been affected by gravity perturbations. Shoemaker (1998) argued based on lunar and terrestrial crater abundances that “the long-term average cratering rate may have increased late in geological time, perhaps as much as a factor of two” (see also, McEwen et al., 1997). If ordinary chondrites have been the dominating type of projectile impacting Earth, as indicated by the present study and previous work on the mid-Ordovician, then the bimodal distribution of gas retention ages of the recently fallen ordinary chondrites lends support for an increase in the impact rate the past ca. 0.8 Ga or so. Some support for this scenario comes also from studies of craters on the Moon, where Kirchoff et al. (2013) have noticed “lulls” in the impact rate >600 Ma long and approximately coinciding with the Boring Billion years. Dating uncertainties for the lunar craters, however, add complexities to the issue. The ordinary chondrites clearly dominate the meteorite flux today, and a major fraction of them originate from the Late Eocene or mid-Ordovician events. If one takes these two events out, the recent meteorite flux (and most likely also the asteroid flux) would have been significantly lower. The breakup of the Baptistina asteroid family at 160 Ma ago has been suggested to have increased the flux of km-sized bodies by at least a factor of two over the last 100 Ma (Bottke et al., 2007), however, there is no known obvious link between any of the recent common meteorite types and this event (see further Schmitz, 2013).

5. Conclusions

In the Massignano section we find two types of relict chromite grains from ordinary chondrites in the beds just above the ejecta layer from the Popigai impact. The grains most likely represent preserved fragments from the extraterrestrial bodies that created the large Popigai and Chesapeake Bay impact craters in the Late Eocene. Elemental analyses of the chromite grains indicate an H- and L-chondritic composition, respectively, of the two impactors. Thus the enigmatic extraterrestrial signatures in Earth's Late Eocene geological record may neither represent a comet shower nor an asteroid shower related to a single, major breakup event, as previously suggested. Instead the data hint at an asteroid shower involving different types of ordinary chondrites. Further oxygen and neon isotope analyses, however, are required to test this hypothesis. A multi-type asteroid shower can be explained by gravitational perturbations of the asteroid belt, possibly associated with chaos-related transitions between different solar-system dynamical regimes. Such perturbations that are synchronous on a general geological–astronomical time scale with a drastic change in Earth's climate from a greenhouse to icehouse state may indicate a connection. Changes in the orbits of the inner planets may be reflected in the collisional history of asteroids with orbits sensitive to such changes.

Acknowledgements

This study was supported by a European Research Council – Advanced Grant to B.S. We thank K. Deppert, P. Eriksson, and P. Kristiansson for general support that made the study possible. Discussions on the Late Eocene events with G. Ravizza have been inspiring. Excellent support in the laboratory was provided by F. Iqbal. The association “Le Montagne di San Francesco” provided logistical support in Italy. The helium data were kindly provided by K. Farley. Reviews by B. Bottke, C. Koeberl and R. Wieler helped to substantially improve the manuscript.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2015.05.041>.

References

- Björnberg, K., Schmitz, B., 2013. Large spinel grains in a CM chondrite (Acfer 331): implications for reconstructions of ancient meteorite fluxes. *Meteorit. Planet. Sci.* 48, 180–194.
- Bodiselsch, B., Montanari, A., Koeberl, C., Coccioni, R., 2004. Delayed climate cooling in the Late Eocene caused by multiple impacts: high-resolution geochemical studies at Massignano, Italy. *Earth Planet. Sci. Lett.* 223, 283–302.
- Bogard, D.D., Garrison, D.H., Shih, C.Y., Nyquist, L.E., 1994. ^{39}Ar – ^{40}Ar dating of two lunar granites: the age of Copernicus. *Geochim. Cosmochim. Acta* 58, 3093–3100.
- Bottke, W.F., Vokrouhlický, D., Nesvorný, D., 2007. An asteroid breakup 160 Myr ago as the probable source of the K/T impactor. *Nature* 449, 48–53.
- Bottomley, R., Grieve, R.A.F., York, D., Masaitis, V., 1997. The age of Popigai impact event and its relation to events at Eocene–Oligocene boundary. *Nature* 338, 365–368.
- Brown, R.E., Koeberl, C., Montanari, A., Bice, D.M., 2009. Evidence for a change in Milankovitch forcing caused by extraterrestrial events at Massignano, Italy, Eocene–Oligocene boundary GSSP. *Spec. Pap., Geol. Soc. Am.* 452, 119–138.
- Cronholm, A., Schmitz, B., 2007. Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone at Gubbio, Italy: the flux of unmelted ordinary chondrites. *Meteorit. Planet. Sci.* 42, 2099–2109.
- Earth Impact Database, 2015. <http://www.passc.net/EarthImpactDatabase/>.
- Farley, K.A., 2009. Late Eocene and late Miocene cosmic dust events; comet showers, asteroid collisions, or lunar impacts? *Spec. Pap., Geol. Soc. Am.* 452, 27–35.
- Farley, K.A., Montanari, A., Shoemaker, E.M., Shoemaker, C.S., 1998. Geochemical evidence for a comet shower in the Late Eocene. *Science* 280, 1250–1253.
- Fritz, J., Tagle, R., Artemieva, N., 2007. Lunar helium-3 in marine sediments: implications for a late Eocene asteroid shower. *Icarus* 189, 591–594.
- Glass, B.P., Koeberl, C., 1999. Ocean Drilling Project Hole 689B spherules and upper Eocene microtektite and clinopyroxene-bearing spherule strewn fields. *Meteorit. Planet. Sci.* 34, 197–208.
- Graf, T., Marti, K., 1995. Collisional history of H chondrites. *J. Geophys. Res., Planets* 100, 21247–21263.
- Hayes, W.B., Malykh, A.V., Danforth, C.M., 2010. The interplay of chaos between the terrestrial and giant planets. *Mon. Not. R. Astron. Soc.* 407, 1859–1865.
- Hazen, R.M., 2012. *The Story of Earth – The First 4.5 Billion Years from Stardust to Living Planet*. Penguin Books, New York. 306 pp.
- Huber, H., Koeberl, C., King Jr., D.T., Petruny, L.W., Montanari, A., 2001. Effects of bioturbation through the Late Eocene impactoclastic layer near Massignano, Italy. In: Buffetaut, E., Koeberl, C. (Eds.), *Geological and Biological Effects of Impact Events (Impact Studies)*. Springer-Verlag, Berlin, pp. 197–216.
- Jovane, L., Sprovieri, M., Florindo, F., Acton, G., Coccioni, R., Dall’Antonia, B., Dinarès-Turell, J., 2007. Eocene–Oligocene paleoceanographic changes in the stratotype section, Massignano, Italy: clues from rock magnetism and stable isotopes. *J. Geophys. Res., Planets* 112, B11101.
- Kirchoff, M.R., Chapman, C.R., Marchi, S., Curtis, K.M., Enke, B., Bottke, W.F., 2013. Ages of large lunar impact craters and implications for bombardment during the Moon’s middle age. *Icarus* 225, 325–341.
- Koeberl, C., 2009. Late Eocene impact craters and impactoclastic layers—an overview. *Spec. Pap., Geol. Soc. Am.* 452, 17–26.
- Koeberl, C., Poag, C.W., Reimold, W.U., Brandt, D., 1996. Impact origin of the Chesapeake Bay structure and the source of the North American tektites. *Science* 271, 1263–1266.
- Kyte, F.T., Shukolyukov, A., Hildebrand, A.R., Lugmair, G.W., Hanova, J., 2011. Chromium-isotopes in Late Eocene impact spherules indicate a likely asteroid belt provenance. *Earth Planet. Sci. Lett.* 302, 279–286.
- Lear, C.H., Bailey, T.R., Pearson, P.N., Coxall, H.K., Rosenthal, Y., 2008. Cooling and ice growth across the Eocene–Oligocene transition. *Geology* 36, 251–254.
- Marti, K., Graf, T., 1992. Cosmic-ray exposure history of ordinary chondrites. *Annu. Rev. Earth Planet. Sci.* 20, 221–243.
- McEwen, A.S., Moore, J.M., Shoemaker, E.M., 1997. The Phanerozoic impact cratering rate: evidence from the farside of the Moon. *J. Geophys. Res., Planets* 102, 9231–9242.
- Montanari, A., Asaro, F., Michel, H.V., Kennett, J.P., 1993. Iridium anomalies of late Eocene age at Massignano (Italy), and ODP Site 689B (Maud Rise, Antarctic). *Palaios* 8, 420–437.
- Murdoch, N., Rozitis, B., Green, S.F., Michel, P., de Lophem, T.-L., Losert, W., 2013. Simulating regoliths in microgravity. *Mon. Not. R. Astron. Soc.* 433, 506–514.
- Nesvorný, D., Jedicke, R., Whiteley, R.J., Ivezi, Z.K., 2005. Evidence for asteroid space weathering from the Sloan Digital Sky Survey. *Icarus* 173, 132–152.
- Nesvorný, D., Bottke, W.F., Vokrouhlický, D., Chapman, C.R., Rafkin, S., 2010. Do planetary encounters reset surfaces of near Earth asteroids? *Icarus* 209, 510–519.
- Paquay, F.S., Ravizza, G., Coccioni, R., 2014. The influence of extraterrestrial material on the late Eocene marine Os isotope record. *Geochim. Cosmochim. Acta* 144, 238–257.
- Pierrard, O., Robin, E., Rocchia, R., Montanari, A., 1998. Extraterrestrial Ni-rich spinel in upper Eocene sediments from Massignano, Italy. *Geology* 26, 307–310.
- Poag, C.W., Koeberl, C., Reimold, W.U., 2004. The Chesapeake Bay Crater, Geology and Geophysics of a Late Eocene Submarine Impact Structure. Springer, Heidelberg. 522 pp.
- Richardson, D.C., Bottke Jr., W.F., Love, S.G., 1998. Tidal distortion and disruption of Earth-crossing asteroids. *Icarus* 134, 47–76.
- Robinson, M.S., Thomas, P.C., Veverka, J., Murchie, S.L., Wilcox, B.B., 2002. The geology of 433 Eros. *Meteorit. Planet. Sci.* 37, 1651–1684.
- Scher, H.D., Bohaty, S.M., Smith, B.W., Munn, G.H., 2014. Isotopic interrogation of a suspected late Eocene glaciation. *Paleoceanography* 29, 628–644.
- Schmitz, B., 2013. Extraterrestrial spinels and the astronomical perspective on Earth’s geological record and evolution of life. *Chem. Erde – Geochem.* 73, 117–145.
- Schmitz, B., Tassinari, M., Peucker-Ehrenbrink, B., 2001. A rain of ordinary chondritic meteorites in the early Ordovician. *Earth Planet. Sci. Lett.* 194, 1–15.
- Schmitz, B., Håggström, T., Tassinari, M., 2003. Sediment-dispersed extraterrestrial chromite traces a major asteroid disruption event. *Science* 300, 961–964.
- Schmitz, B., Cronholm, A., Montanari, A., 2009. A search for extraterrestrial chromite in the late Eocene Massignano section, central Italy. *Spec. Pap., Geol. Soc. Am.* 452, 71–82.
- Schmitz, B., Heck, P.R., Alwmark, C., Kita, N.T., Meier, M.M.M., Peucker-Ehrenbrink, B., Ushikubo, T., Valley, J.W., 2011. Determining the impactor of the Ordovician Lockne crater: oxygen and neon isotopes in chromite versus sedimentary PGE signatures. *Earth Planet. Sci. Lett.* 306, 149–155.
- Schunova, E., Jedicke, R., Walsh, K.J., Granvik, M., Wainscoat, R.J., Haghhighipour, N., 2014. Properties and evolution of NEO families created by tidal disruption at Earth. *Icarus* 238, 156–169.
- Shoemaker, E.M., 1998. Long-term variations in the impact cratering rate on Earth. *Geol. Soc. (Lond.) Spec. Publ.* 140, 7–10.
- Swindle, T.D., Kring, D.A., Weirich, J.R., 2014. $^{40}\text{Ar}/^{39}\text{Ar}$ ages of impacts involving ordinary chondrite meteorites. *Geol. Soc. (Lond.) Spec. Publ.* 378, 333–347.
- Tagle, R., Claeys, P., 2004. Comet or asteroid shower in the Late Eocene? *Science* 305, 492.
- Tagle, R., Claeys, P., 2005. An ordinary chondrite impactor for the Popigai crater, Siberia. *Geochim. Cosmochim. Acta* 69, 2877–2889.
- Tóth, J., Veres, P., Kornos, L., 2011. Tidal disruption of NEAs – a case of Příbram meteorite. *Mon. Not. R. Astron. Soc.* 415, 1527–1533.
- Varadi, F., Ghil, M., Kaula, W.M., 1999. Jupiter, Saturn, and the edge of chaos. *Icarus* 139, 286–294.
- Varadi, F., Runnegar, B., Ghil, M., 2003. Successive refinements in long-term integrations of planetary orbits. *Astrophys. J.* 592, 620–630.
- Villa, G., Fioroni, C., Persico, D., Roberts, A.P., Florindo, F., 2014. Middle Eocene to Late Oligocene Antarctic glaciation/deglaciation and Southern Ocean productivity. *Paleoceanography* 29, 223–237.
- Vishnevsky, S., Montanari, A., 1999. The Popigai impact crater (Arctic Siberia, Russia): geology, petrology, geochemistry, and geochronology of glass-bearing impactites. *Spec. Pap., Geol. Soc. Am.* 339, 19–60.
- Vonhof, H.B., Smit, J., Brinkhuis, H., Montanari, A., 2000. Late Eocene impacts accelerated global cooling? *Geology* 28, 687–690.
- Whitehead, J., Papanastassiou, D.A., Spray, J.G., Grieve, R.A.F., Wasserburg, G.J., 2000. Late Eocene impact ejecta: geochemical and isotopic connections with the Popigai impact structure. *Earth Planet. Sci. Lett.* 181, 473–487.
- Wieler, R., Graf, T., 2001. Cosmic ray exposure history of meteorites. In: Peucker-Ehrenbrink, B., Schmitz, B. (Eds.), *Accretion of Extraterrestrial Matter Throughout Earth’s History*. Kluwer Academic, New York, pp. 221–240.
- Wlotzka, F., 2005. Cr spinel and chromite as petrogenetic indicators in ordinary chondrites: equilibration temperatures of petrologic types 3.7 to 6. *Meteorit. Planet. Sci.* 40, 1673–1702.
- Yu, Y., Richardson, D.C., Michel, P., Schwartz, S.R., Ballouz, R.-L., 2014. Numerical predictions of surface effects during the 2029 close approach of Asteroid 99942 Apophis. *Icarus* 242, 82–96.
- Zachos, J., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science* 292, 686–693.
- Zappalà, V., Cellino, A., Gladman, B.J., Manley, S., Migliorini, F., 1998. Asteroid showers on Earth after family breakup events. *Icarus* 134, 176–179.
- Zellner, N.E.B., Delano, J.W., Swindle, T.D., Barra, F., Olsen, E., Whittet, D.C.B., 2009. Evidence from $^{40}\text{Ar}/^{39}\text{Ar}$ ages of lunar impact glasses for an increase in the impact rate ca. 800 Ma ago. *Geochim. Cosmochim. Acta* 73, 4590–4597.