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Late Eocene ^{3}He and Ir anomalies associated with ordinary chondritic spinels

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Abstract

During the late Eocene there was an enigmatic enhancement in the flux of extraterrestrial material to Earth. Evidence comes from sedimentary ^{3}He records indicating an increased flux of interplanetary dust during ca. 2 Myr, as well as two very large impact structures, Popigai (100 km diameter) and Chesapeake Bay (40–85 km), that formed within 10–20 kyr at the peak of the ^{3}He delivery. The Massignano section in Italy has one of the best sedimentary records of these events, including a well-defined ^{3}He record, an Ir-rich ejecta bed related to the Popigai impact event, and two smaller Ir anomalies. Recently we showed that the Popigai ejecta is associated with a significant enrichment of chromite grains (>63 μm) with an H-chondritic elemental composition (17 grains in 100 kg of rock). Most likely these grains are unmelted fragments from the impactor. Slightly higher up (ca. 20 cm) in the section, where a small Ir anomaly possibly related to the Chesapeake Bay impact has been measured, we found a weak enrichment in L-chondritic grains (8 grains in 208 kg of rock). Here we report an extended data set increasing the total amount of sediment dissolved in acid and searched for extraterrestrial chromite grains from 658 to 1168 kg. In altogether 760 kg of background sediment from 17 levels over 14 m of strata outside the interval corresponding to the Popigai and Chesapeake Bay impacts, we only found 2 extraterrestrial chromite grains. Both grains have L-chondritic compositions and were found in a 100 kg sample from the ca. 10.25 m level in the section where the second of the smaller Ir anomalies has been reported. A correlation appears to exist between Ir, ^{3}He and chromite from ordinary chondrites. We also report oxygen three-isotope measurements of the extraterrestrial chromite grains associated with the Popigai ejecta and confirm an H-chondritic composition.

The new results strengthen our scenario that the upper Eocene ^{3}He and Ir enrichments originate from the asteroid belt rather than the Oort cloud as originally proposed when the ^{3}He anomaly was discovered. The generally low background concentrations of extraterrestrial chromite through the section speak against any major single asteroid breakup event such as in the mid-Ordovician after the break-up of the L-chondrite parent body. Instead the data reconcile with a small, possibly a factor of 2–3, increase in the flux of extraterrestrial material to Earth, but of both H- and L-chondritic composition. We also

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report the composition of all the 2310 terrestrial chrome spinel grains recovered, and show that their chemical composition indicates a dominantly regional ophiolitic source. Four anomalous chrome spinel grains with high Ti and V concentrations were found in the Popigai ejecta. These grains originate from Siberian Traps basalts in the Popigai crater at the time of impact.

Keywords: Late Eocene; Popigai crater; Helium-3; Ordinary chondrite; Extraterrestrial chromite

1. INTRODUCTION

In the late Eocene epoch, during the Priabonian stage, ~37.8–33.9 Myr ago, the first significant ice sheets began to form on Antarctica, meaning that after 250 Myr of "greenhouse" conditions our planet began to drift into the present "icehouse" state (Zachos et al., 2001). There was also an enhanced flux of extraterrestrial matter to Earth, shown primarily by a sedimentary ^{3}He anomaly reflecting an enhanced flux of small (<3–35 μm) interplanetary dust particles over ~2 Myr (Farley et al., 1997, 1998; Farley, 2009). Additional evidence includes two large impact craters that formed during the peak of the ^{3}He flux to Earth and several medium sized craters (Koeberl, 2009). The Popigai impact structure, with a radiometric age of 35.7 ± 0.2 Myr, in Siberia is with 100 km diameter the largest known impact structure post-dating the Cretaceous–Paleogene boundary (Bottomley et al., 1997; Vishnevsky and Montanari, 1999; Whitehead et al., 2000; Koeberl, 2009). The Chesapeake Bay impact structure in the eastern US formed about 10–20 kyr after the Popigai structure from a less energetic impactor (Koeberl, 2009). The large diameter, ca. 85 km, of the Chesapeake Bay structure reflects collapse of sediment formations around a central crater 35–40 km in diameter (Poag et al., 2004; Catchings et al., 2008; Kyte et al., 2011). For more detailed reviews of the late Eocene extraterrestrial signatures and climate change, see Koeberl (2009) and Schmitz et al. (2015) and references therein.

The ^{3}He anomaly and associated craters were originally considered to represent a comet shower generated from a random perturbation of the Oort cloud (Farley et al., 1998; Farley, 2009). Platinum-group element (PGE) abundances in Popigai impact melt rocks (Tagle and Claeys, 2004) and Cr, Ni, and Co inter-element ratios in clinopyroxene spherules (Glass et al., 2004a), indicated instead an asteroidal source similar to type L and LL ordinary chondrites. More detailed evaluation, however, showed that although the PGE data are consistent with an ordinary chondrite, the resolution of the approach is not sufficient to distinguish between the different groups of ordinary chondrites, i.e., H, L and LL (Farley, 2009). Chromium isotope analyses of the distal ejecta from the Popigai crater confirmed that the impactor must have been an ordinary chondrite (Kyte et al., 2011). Kyte et al. suggested that both the Popigai impact structure and the ^{3}He anomaly are related to the formation of the Brangäne asteroid family. The Brangäne parent body shows the S-type spectra associated with ordinary chondrites, and its breakup has been estimated at 50 ± 40 Myr ago. These authors also speculated that the Brangäne parent body is H-chondritic because of common cosmic ray exposure ages of ca. 35 Myr for recently fallen H chondrites. Schmitz et al. (2015) recovered abundant unmelted extraterrestrial chromite (EC) grains in the 40 cm stratigraphic interval immediately above the Popigai impact ejecta in the Massignano section, central Italy (Fig. 1). In the lower part of this interval 17 chromite grains with H-chondritic elemental composition were found in 100 kg of sediments. In the upper part of the interval 8 L-chondritic chromite grains were found in 208 kg of sediment. In 350 kg of background sediment representing 13 levels through the 14 meter thick ^{3}He-rich interval at Massignano no EC grains were found. The H-chondritic grains are clearly associated with the Popigai ejecta, and most likely represent unmelted fragments of the impactor, probably from the regolith. The L-chondritic grains occur approximately at the level where one would expect to find ejecta from the Chesapeake Bay impact event, suggesting a possible origin from this impactor. Chesapeake Bay ejecta is widespread in the eastern Atlantic, but at Massignano none has been recorded (Glass, 2002; Glass et al., 2004b).

In the present study a total of 510 kg of sedimentary rock was collected in the Massignano section and searched for chrome spinels in addition to the previous 658 kg studied by Schmitz et al. (2009, 2015). A primary objective with the new samples has been to produce a more robust estimate of the "background" concentrations of extraterrestrial spinels in the section. A secondary objective has been to constrain in greater detail the stratigraphic relation between the Popigai ejecta and the abundant chondritic spinel grains recovered. Hence, we have searched a 100 kg sample of the ejecta bed itself for chrome spinels. We have also analyzed 5 EC grains recovered from immediately above the Popigai ejecta for oxygen three-isotopes with secondary ion mass spectrometry. This approach has previously been used with success to identify the detailed origin of EC grains (Heck et al., 2010, 2016). We also present and discuss the full data set on the elemental composition of 2338 opaque chrome spinel grains, of which 28 are clearly extraterrestrial, recovered from the late Eocene part of the Massignano section in the present study and in Schmitz et al. (2009, 2015).

2. GEOLOGICAL BACKGROUND

In the Massignano section the Global Boundary Stratotype Section and Point (GSSP) for the Eocene–Oligocene boundary was defined by Premoli Silva and Jenkins (1993). The section is located near Ancona (northeastern Apennines, Italy), in an abandoned quarry on the Ancona-Sirolo road of the Cònero Regional Natural Park

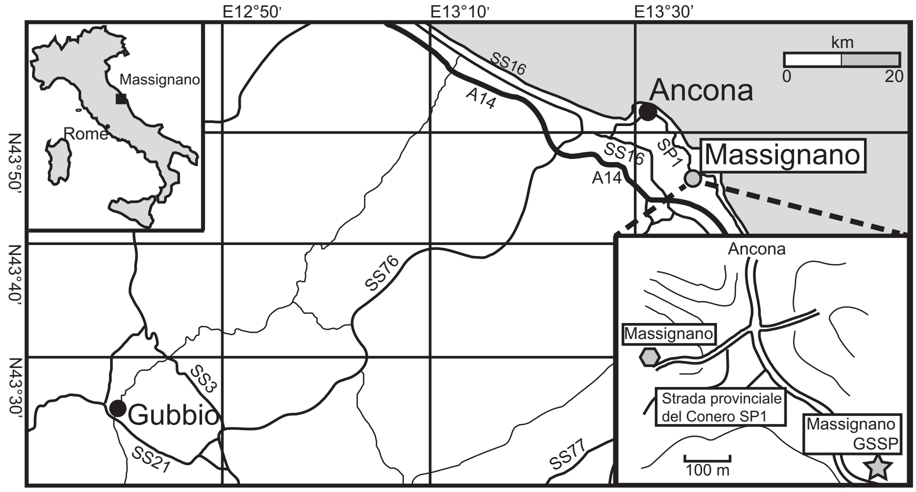


Fig. 1. Map of area around Ancona (eastern central Italy) and location of the Massignano section.

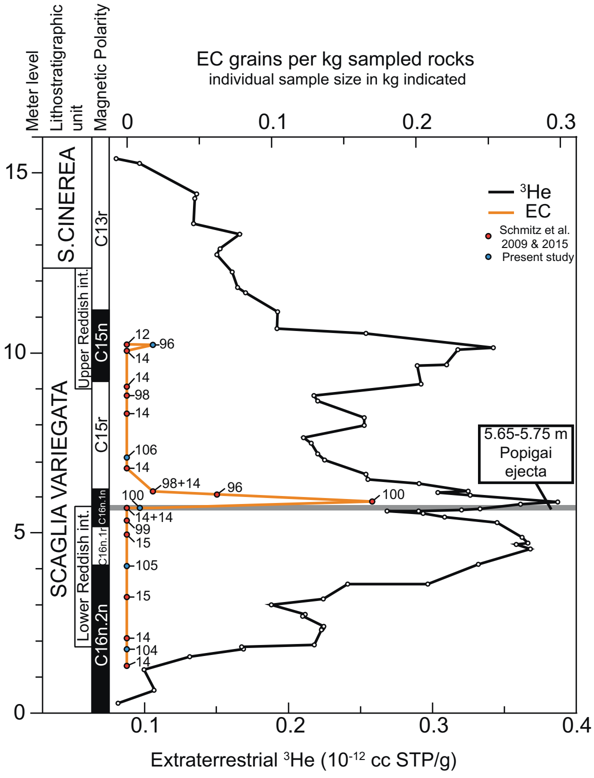


Fig. 2. Profiles for the Massignano section of extraterrestrial ^{3}He concentrations (black curve) (Farley et al., 1998) and the total number of recovered EC grains per kg sediment (orange curve) in the present study and by Schmitz et al. (2009, 2015). Indicated in numbers on the latter curve are the sizes in kilogram of the samples searched for EC grains. Sample points marked in blue are new for the present study. Magnetostratigraphy after Jovane et al. (2007).

near the village of Massignano (Fig. 1). The section comprises two different formations: Scaglia Variegata and Scaglia Cinerea (Fig. 2), which were deposited in the entire Umbria-Marche basin. During the end of the Eocene and the beginning of the Oligocene these pelagic, biomicritic limestones and marly limestones were deposited in the upper part of a lower bathyal setting, at a paleodepth of 1000–1500 m (Coccioni and Galeotti, 2003). The original reconstruction of the late Eocene ^{3}He anomaly was performed in this section (Farley et al., 1998; Fig. 2). In the section meter levels are marked by metal plates, but the markings have deteriorated over the years. The Popigai ejecta bed does not represent a discrete bed and its detailed extent can be difficult to demarcate in the field, thus different authors have given slightly different stratigraphic locations. According to Montanari et al. (1993) and Huber et al. (2001) the ejecta covers the interval from 5.61–5.72 m. In a high-resolution study, Paquay et al. (2014) measured the highest Ir concentrations, 200–465 ppt, in the interval 5.64–5.73 m, but Ir content remains high at 100–200 ppt, up to 5.85 m. The Popigai ejecta bed is also characterized by abundant shocked quartz, micrometer-sized Ni-rich spinels, and so called pancake spherules, about 100–600 μm in size and made up of iron-rich smectite (Clymer et al., 1996; Pierrard et al., 1998; Glass et al., 2004b). The Ni-rich spinels formed from the vapor cloud generated by the impact and are typically very small, <1–20 μm, compared to the >63 μm spinel grains dealt with by us. The pancake spherules represent weathered clinopyroxene-bearing spherules of the type that is found in the Popigai ejecta bed elsewhere. Two other, smaller (100–330 ppt) iridium anomalies were detected at meter levels 6.15 and 10.25 (Montanari et al., 1993; Bodiselitsch et al., 2004). However, Paquay et al. (2014) in their high-resolution Os, Ir and ^{187}Os/^{188}Os isotope profiles across these levels, were not able to reproduce the iridium anomalies. Although there is confusion as to whether there indeed are two iridium anomalies in addition to the one in the Popigai ejecta at 5.65 m, all authors agree that there is no independent evidence for impact such as shocked quartz, Ni-rich spinels, or spherules associated with the 6.15 and 10.25 m levels.

3. MATERIALS AND METHODS

3.1. Chromite separations and element analyses

For this study a total of five ~100 kg limestone samples were collected in the Scaglia Variegata Formation in the Massignano section. Three "background" samples were collected at 1.60, 4.00 and 7.10 m, respectively. One sample spans the Popigai ejecta layer from 5.60 to 5.75 m and one spans the 10.10–10.40 m interval, in which one of the two smaller iridium anomalies were measured by Montanari et al. (1993) and Bodiselitsch et al. (2004). Our 5.75 m level corresponds to a color change from reddish to gray, but the change is evident only in the fresh rock.

The five samples were washed to remove weathered superficial material, and then decalcified in 6 M hydrochloric acid at room temperature. The decalcified residue >63 μm was recovered by sieving and then leached in 11 M hydrofluoric acid at room temperature. The acid-insoluble fraction in the size range 63–355 μm was isolated and searched with a binocular microscope for opaque black grains that are suspected to be chrome spinel. Such grains were picked with a fine brush, mounted on carbon tape and then preliminary analysed in an unpolished state for major and trace elements with a scanning electron microscope (SEM) equipped with a calibrated energy-dispersive spectrometer (EDS). All grains confirmed to be chrome spinels by the preliminary analyses were mounted in epoxy resin and polished using a 1 μm diamond slurry. Quantitative elemental analysis was then performed on the polished grains.

The quantitative elemental analyses were performed with an Oxford Inca X-sight energy-dispersive spectrometer with a Si detector, mounted on a Hitachi S-3400 scanning electron microscope. Cobalt was used as standard to monitor drift of the instrument. An acceleration voltage of 15 kV, a sample current ~1 nA, and a counting live-time of 80 s was used. Precision of analyses was typically better than 1–4%. Analytical accuracy was controlled by repeated analyses of the USNM 117075 (Smithsonian) chromite reference standard (Jarosewich et al., 1980).

3.2. Grain classification, EC versus OC

In the present study we divided the Cr-rich spinels recovered from the sediment samples in two main groups: extraterrestrial chromite (EC) and "other" Cr-rich chrome spinel grains (OC). The EC grains have narrowly defined ranges for Cr_2O_3 (~55–60 wt%), FeO (~25–30 wt%), Al_2O_3 (~5–8 wt%), TiO_2 (~1.4–3.5 wt%), V_2O_3 (~0.6–0.9 wt%), and MgO (~1.5–4 wt%) (Schmitz and Häggström, 2006; Schmitz, 2013). We stress that for a grain to be classified as an EC grain, it has to have a composition within the defined ranges for all the elements listed. The definition for EC grains used here covers the type of common (>63 μm) chromite in equilibrated (petrographic types 4–6) ordinary chondrites, however, other meteorite types contain spinels with elemental compositions outside the defined ranges (Schmitz, 2013, and references therein).

The OC grains have a wide compositional range, and in studies of chrome spinel grains dispersed in sediments the majority or all of the OC grains tend to have a terrestrial origin. A difference between most types of extraterrestrial and terrestrial chrome spinels is that the former often contain significantly higher vanadium concentrations. We have therefore characterized all recovered OC grains with more than 0.45 wt% V_2O_3 in a subcategory, the "OC-V" grains. By this approach it is easier to obtain an idea of whether the Massignano section registers any increased flux in chrome-spinel rich extraterrestrial matter of other classes than ordinary chondritic.

3.3. Oxygen isotopic analyses

We also recovered 5 EC grains >63 μm with the purpose to be used for oxygen isotopic analyses. These EC grains were recovered specifically for this study from the ca. 15 cm interval immediately above the Popigai ejecta. The grains were mounted in epoxy with the oxygen isotope standard UWCr-3 (Heck et al., 2010), polished and carbon-coated to be suitable for element analyses with SEM-EDS as described above. Grain mounts were polished a second time, and flatness was monitored with a white light profilometer (Bruker 3D Microscope). Mounts were carbon coated for secondary ion mass spectrometer (SIMS) analyses. Oxygen isotopes from the 5 EC grains were analyzed with a Cameca IMS-1280 instrument at the University of Wisconsin-Madison (WiscSIMS Laboratory). We used analytical procedures very similar to the ones used in our previous studies optimized to obtain high-precision measurements of oxygen three-isotope ratios (Heck et al., 2010, 2016). We used a primary Cs^+ ion beam of ~5 nA resulting in a spot size of 15 × 20 μm. An electron gun was used for charge compensation and mass resolving power was set to ~5000. Secondary ions of all stable oxygen isotopes ^{16}O, ^{17}O, and ^{18}O were analyzed in multicollection Faraday cup detectors (Kita et al., 2010). We analyzed one spot per grain, but in order to obtain sufficient precision on $\Delta^{17}O$ ($=\delta^{17}O - 0.52 \times \delta^{18}O$) values we analyzed each spot twice, as in our previous studies. Ten analyses of 5 EC grains were bracketed with 12 analyses of UWCr-3 standard grains. All grains are mounted together at the center of the 25 mm diameter epoxy mount. The magnitude of the $^{16}O^1H^-$ peak was recorded automatically after each spot analysis and was used to correct for the tailing interference on the $\delta^{17}O$ values, which was always less than 0.1‰ (average correction ± 1SD = 0.058 ± 0.005‰). The corrections from the two analyses of the same spot were identical within error. Because the corrections and their variability were very small no data had to be rejected. Molar fractions of the Al_2MgO_4 end member in chromite determined from EDS analysis were used in the correction procedure of SIMS instrumental biases for $\delta^{17}O$ and $\delta^{18}O$ values. For more details on the analytical procedure we direct the reader to Section 3.1.2 in Heck et al. (2010). Post-SIMS SEM imaging confirmed all SIMS analysis spots were within the chromite grains and of regular shape, thus no data had to be rejected on this basis either.

Table 1
EC, OC and OC-V grains (>63 µm) recovered in the Massignano section.[§]

Sample depth (m)	Sample weight (kg)	No. EC grains	No. OC grains[#]	OC/kg rock	No. OC-V grains	OC-V/OC
10.25–10.35[*]	11.6	0	34	2.75	2	0.062
10.10–10.40	95.7	2	262	2.68	6	0.023
10.00–10.15[*]	14.0	0	28	2.00	0	0
9.00–9.15[*]	14.1	0	71	4.75	4	0.059
8.60–9.00[*]	98.4	0	90	0.89	2	0.022
8.20–8.40[*]	14.2	0	36	2.25	4	0.125
7.10–7.40	105.8	0	247	2.24	10	0.042
6.70–6.90[*]	14.1	0	24	1.70	0	0
6.15–6.40[*]	97.6	1	331	3.34	5	0.015
6.15–6.25[*]	14.0	1	22	1.50	1	0.047
6.00–6.15[*]	96.4	6	122	1.18	6	0.070
5.75–6.00[*]	99.9	17	165	1.59	6	0.038
5.60–5.75	99.8	1	316	3.02	15	0.049
5.70–5.80[*]	13.8	0	16	1.07	2	0.142
5.60–5.65[*]	13.9	0	35	2.37	2	0.060
5.10–5.40[*]	99.0	0	248	2.43	10	0.029
4.80–5.10[*]	14.6	0	19	1.23	1	0.056
4.00–4.25	104.7	0	92	0.86	2	0.022
3.05–3.35[*]	15.0	0	22	1.26	3	0.157
1.95–2.20[*]	13.9	0	29	2.08	0	0
1.60–1.90	103.9	0	69	0.60	7	0.101
1.25–1.35[*]	13.9	0	32	2.23	1	0.031
Total:	1168.3	28	2310	2.00	88	0.047

OC-V = other chrome spinel with $\geqslant$ 0.45% V_2O_3. See further main text.

[§] EC = equilibrated ordinary chondritic chromite; OC = other chrome spinel.

[#] Including OC-V grains.

[*] Data from Schmitz et al. (2009, 2015).

4. RESULTS

In a total of 1168 kg of limestone collected in the Massignano section we have found 2338 opaque chrome spinel grains of which 28 are EC grains, including also the data from Schmitz et al. (2009, 2015) (Table 1, Fig. 2, Supplementary Table 1). The elemental composition of all recovered EC grains is given in Table 2. Twenty-five of these grains have been recovered in the previous studies in the ca. 40 cm interval immediately above the Popigai ejecta. In the three "background" samples of ca. 100 kg each from the levels 1.60, 4.00 and 7.10 m that are new for this study we found no EC grains. In the 100-kg-sample that spans the Popigai ejecta over the interval 5.60–5.75 m we recovered one EC grain. In the 10.10–10.40 m interval where one of the smaller Ir anomalies has been measured we recovered two EC grains. The results confirm earlier results that EC grains generally are very rare in the Massignano section (Schmitz et al., 2009, 2015). Of the 28 grains found only 2 are from outside the stratigraphic interval associated with the Popigai and Chesapeake Bay impacts (Table 1). Particularly the 17 grains from 100 kg of sediment in the 5.75–6.00 m interval represent a clear positive anomaly, but also the 6 grains (plus 2 in the immediately overlying beds) in 96 kg of the 6.00–6.15 m interval appear significant.

In Schmitz et al. (2015) we used TiO_2 content to determine an H-chondritic composition for the 17 grains from the lower part of the interval rich in EC grains. The FeO values, however, are lower than typical in H-chondritic chromite, which motivated us to perform the oxygen three-isotope analyses of the grains. These analyses and elemental results for the five new grains recovered from the lower EC-rich interval clearly confirm an H-chondritic composition (Table 3a,b; Fig. 3 and 4). We use $\Delta^{17}O$ ($=\delta^{17}O - 0.52 \times \delta^{18}O$) values instead of $\delta^{18}O$ and $\delta^{17}O$ values, an approach that has worked well in our previous studies of chromites from both recent and fossil meteorites (Heck et al., 2010, 2016). The five EC grains have $\Delta^{17}O$ values from 0.50‰ to 0.84‰ with an average of 0.67 ± 0.17‰ (Table 3a) that matches the H-chondritic group average of 0.73 ± 0.09‰ (Clayton et al., 1991).

Even though the grains in the lower EC-rich interval are H-chondritic, the 8 grains from the upper part of the EC-rich interval show a clear L-chondritic origin based on TiO_2 content (Schmitz et al., 2015). Because of the rarity of EC grains in the upper interval and also the often cracked condition of these grains (see below) we only aimed for oxygen isotopic analyses of grains from the lower interval. However, the oxygen isotopic analyses in this and our other studies of EC grains (e.g., Schmitz et al., 2011; Heck et al., 2010, 2016; Heck et al., 2017) show that the approach of using TiO_2 for distinguishing H- from L-chondritic chromite is reliable, albeit with some caveats as discussed below and in Heck et al. (2016). In TiO_2 versus Al_2O_3 plots, as well as in the other elemental plots, the two grains recovered in this study from the 10.10–10.40 m interval clearly plot in the L-chondritic field (Table 2; Fig. 3). The single EC grain recovered in this study from the Popigai ejecta (5.60–5.75 m) interval plots with the H-chondritic grains

Table 2
Element concentrations (wt%) in extraterrestrial Cr-spinels from Massignano section. All analyses by SEM-EDS, see Section 3.

Grain	MgO	Al_2O_3	TiO_2	V_2O_3	Cr_2O_3	MnO	FeO	ZnO	Total
Mas 5.60–5.75 m									
Cr 1	5.62	7.91	3.69	0.70	55.8	n.d.	26.0	n.d.	99.66
Mas 5.75–6.00 m[*]									
Cr 1	6.66	5.78	2.69	0.63	58.1	0.68	25.5	n.d.	99.99
Cr 2	3.62	6.81	2.10	0.69	59.2	1.04	26.9	0.33	100.6
Cr 3	3.52	6.04	1.76	0.71	60.5	1.25	26.1	0.43	100.3
Cr 4	3.63	7.23	2.04	0.78	58.4	1.05	27.3	n.d.	100.4
Cr 5	3.62	7.44	1.85	0.72	58.2	0.98	27.2	n.d.	100.0
Cr 6	3.49	8.46	1.11	0.71	59.1	1.09	26.0	0.26	100.2
Cr 7	4.19	6.16	2.76	0.73	58.7	0.72	26.8	0.34	100.4
Cr 8	3.60	7.55	1.89	0.74	58.1	1.01	27.2	0.26	100.3
Cr 9	5.15	7.20	1.87	0.76	59.0	0.93	25.1	n.d.	99.97
Cr 10	5.16	6.81	2.26	0.73	59.2	0.77	25.4	0.16	100.6
Cr 11	5.02	5.93	2.19	0.77	60.1	1.08	25.1	n.d.	100.1
Cr 12	5.31	6.46	3.06	0.66	58.1	0.58	25.7	0.22	100.2
Cr 13	4.83	7.08	2.19	0.69	58.4	0.99	25.9	n.d.	100.1
Cr 14	5.18	7.07	2.17	0.75	58.4	0.95	25.3	0.18	99.99
Cr 15	4.82	6.88	2.38	0.67	59.1	0.77	26.0	n.d.	100.7
Cr 16	4.03	6.88	2.33	0.62	59.2	0.84	26.8	n.d.	100.7
Cr 17	4.49	6.68	2.19	0.63	59.2	0.99	26.2	n.d.	100.4
Mas 6.00–6.15 m[*]									
Cr 1	2.99	6.03	2.63	0.75	57.9	0.86	28.7	n.d.	99.87
Cr 2	2.84	5.87	2.59	0.81	58.9	0.83	29.2	0.41	101.4
Cr 3	4.19	6.68	2.29	0.65	59.4	0.89	26.9	n.d.	101.0
Cr 4	2.06	6.32	3.68	0.81	57.7	0.82	30.2	n.d.	101.6
Cr 5	2.81	5.53	3.44	0.67	57.9	0.75	29.6	n.d.	100.7
Cr 6	1.80	5.99	3.19	0.87	57.1	0.84	30.6	0.31	100.8
Mas 6.15–6.40 m[*]									
Cr 1	1.70	5.84	2.75	0.78	58.8	0.66	30.1	n.d.	100.6
Cr 2	2.42	5.16	1.72	0.71	58.9	1.29	28.9	0.36	99.40
Mas 10.10–10.40 m									
Cr 1	2.07	5.24	3.59	0.63	56.8	0.81	30.5	n.d.	99.81
Cr 2	1.89	6.34	2.96	0.78	57.5	0.62	30.1	n.d.	100.1

[*] From Schmitz et al. (2009, 2015).

Table 3a
Oxygen isotope composition of extraterrestrial chromite from the Massignano section.

Sample name	$\delta^{18}O$‰	±2σ[§]	$\delta^{17}O$‰	±2σ[§]	$\Delta^{17}O$‰	±2σ[§]
Popigai-Mass01	−2.18	0.60	−0.63	0.37	0.50	0.13
Popigai-Mass02	−2.19	0.60	−0.81	0.37	0.70	0.13
Popigai-Mass03	−2.44	0.60	−0.51	0.37	0.76	0.13
Popigai-Mass04	−2.57	0.60	−0.42	0.37	0.77	0.13
Popigai-Mass05	−2.57	0.60	−0.49	0.37	0.84	0.13
Mean ± 2SD	−2.47	0.39	−0.57	0.31	0.71	0.26
Uncertainty of the mean[#]		0.17		0.14		0.12

[§] External reproducibility of bracket standard analysis ($n = 6$).

[#] Largest of 2σ errors of each analysis or 2SD of 5 analyses divided by square root of 5.

for MgO, Al_2O_3 and FeO, but it has a high TiO_2 (3.69 wt%) content which would indicate an L, or even LL, chondritic origin. Although TiO_2 is the most diagnostic oxide to classify ECs from ordinary chondrites (average TiO_2 content for different groups is: H 2.2 wt%, L 2.7 wt% and LL 3.4 wt%), there is a compositional overlap between the groups hence the method does not allow the identification of single grains. Based on the general chemical resemblance of the grain from the ejecta interval with the common H-chondritic grains in the immediately overlying interval, except for TiO_2, all the grains most likely have the same origin (Fig. 3). The grain in the ejecta could have moved downward through bioturbation (see e.g., Huber et al., 2001), or it could originate from the uppermost or transi-

Table 3b
Element concentrations (wt%) in extraterrestrial chromite grains used for oxygen isotope analyses.

Sample name	MgO	Al_2O_3	TiO_2	V_2O_3	Cr_2O_3	MnO	FeO	ZnO	Total
Popigai-Mass01	3.42	7.37	1.97	0.63	58.3	0.99	27.0	0.33	100.1
Popigai-Mass02	3.57	7.48	1.84	0.79	58.1	1.12	27.1	n.d.	100.0
Popigai-Mass03	3.08	6.54	1.83	0.82	59.0	1.20	27.7	0.43	100.6
Popigai-Mass04	3.08	6.46	2.02	0.82	59.1	0.96	27.7	0.40	100.5
Popigai-Mass05	2.82	6.14	2.16	0.73	59.6	1.17	27.4	0.47	100.5

tional zone of the ejecta interval. Because of the absence of clear bedding at Massignano, and with the large samples that we work with, it is unavoidable that our depth assignments have uncertainties of up to a few centimeters.

The 2310 chrome spinel grains recovered that do not have the typical EC composition and that are classified as OC grains are probably all of terrestrial origin. The average concentration of OC grains in the section is 2 grains per kg of rock, with a range between 0.6 and 4.8 grains per kg (Table 1). There is significant variability in the abundance of grains between different beds and no obvious abundance trend through the section. In order to determine the origin of the OC grains we have plotted their composition following the practice of Barnes and Roeder (2001). All the data from this and previous studies (Schmitz et al., 2009, 2015) have been used. The OC grains plot perfectly in the ophiolitic field and there is no significant variation or change in composition through the section (Fig. 5; Supplementary Fig. 1).

We have searched for outlier grains among the OC grains that potentially could represent other types of extraterrestrial material than ordinary chondrites. Among the OC grains we found 88 grains with >0.45 wt% V_2O_3, i.e., representing our subcategory named "OC-V" grains. The OC-V grains are distributed through the entire section. The majority have comparatively low Cr/Fe ratios (<1.5) and are rich in ferric iron (Fig. 5; Supplementary Fig. 1). Such grains are very likely of terrestrial origin despite their high vanadium content. There are some of the V-rich grains with higher Cr/Fe ratio that could be extraterrestrial but oxygen isotopic analyses would be required to determine this. The samples collected over the Popigai impact ejecta and in the overlying interval rich in ordinary chondritic grains do not show higher percentages of V-rich grains among the OC grains than other levels.

Fritz et al. (2007) suggested that the ^3He anomaly at Massignano is related to regolith ejected from the Moon following repeated asteroid bombardment in the wake of a major parent body breakup in the asteroid belt. Lunar spinels have a very wide compositional range, but grains can typically be much higher in TiO_2 than terrestrial spinels (Papike et al., 1998). Most or many lunar spinels have TiO_2 concentrations >4 wt% and values up to 20 wt% are common. Almost all of our OC grains are very low in TiO_2 (mostly <1.5 wt%). In Table 4 we have compiled the four chrome spinel grains in our total data set (2310 grains) with the highest TiO_2 concentrations. Notably three of the four grains were found in the Popigai ejecta bed (5.60–5.75 m) and the fourth grain comes from the sample immediately on top of the ejecta (5.75–6.00 m). One of the grains from the ejecta has 8.7 wt% TiO_2, and the V_2O_3 content of the grain is remarkably high, 1.6 wt%. As discussed in the next section the grains originate from Siberian Traps basalts in the Popigai crater at the time of impact.

We did not recover any of the abundant Ni-rich spinels that Pierrard et al. (1998) showed are common in the Popigai ejecta bed, not even from the 100 kg of sample spanning the Popigai ejecta. These grains are too small or too fragile to be recovered in our approach.

5. DISCUSSION

Based on our much larger data set than previously published we show that the background concentrations of EC grains at Massignano are even lower, 0 grains per 665 kg sediment, than suggested earlier, 0 grains per 350 kg sediment. This estimate is based on the assumption that the two grains at 10.10 m are impact-related, but if they instead are related to the micrometeorite background flux, then the revised estimate lies at 2 EC grains per 760 kg. In any case the data clearly do not support any orders-of-magnitude enhanced flux of ordinary chondritic micrometeorites, such as after the breakup of the L-chondrite parent body in the mid-Ordovician (see discussion in Schmitz et al., 2009, 2015). The three intervals yielding EC grains are the same three levels that have yielded Ir anomalies, indicating that the recovered grains may be related to Earth-impacting asteroids rather than the background rain of meteoritic dust. The short-lived character of the EC anomalies also support a relation to asteroid impacts rather than to the micrometeorite flux. At least for the abundant H-chondritic grains directly on top (or in the uppermost part) of the Popigai ejecta the relation to an impact event appears obvious. Disregarding the EC-yielding intervals at 5.60–6.40 m and 10.10–10.40, we found no EC grains in 665 kg of rock from 16 levels through the section. It is possible, however, that the two grains from the 10.10–10.40 m interval may rather be related to the background flux of micrometeorites than to an impact event. Considering that only 2 EC grains were found at this level, the association with an (not always reproducible) Ir anomaly may just reflect random coincidence. If we assume that none of the recovered EC grains in our study relate to the micrometeorite background flux, then the number is 0 background EC grains in 1168 kg of rock from 21 samples. Sedimentation rates at Massignano are relatively high, ca. 1 cm kyr^{-1} (Farley et al., 1998; Brown et al., 2009). This means that none or only a few background micrometeorite grains would be expected in this study unless the late Eocene flux of micrometeorites was dramatically enhanced such as after

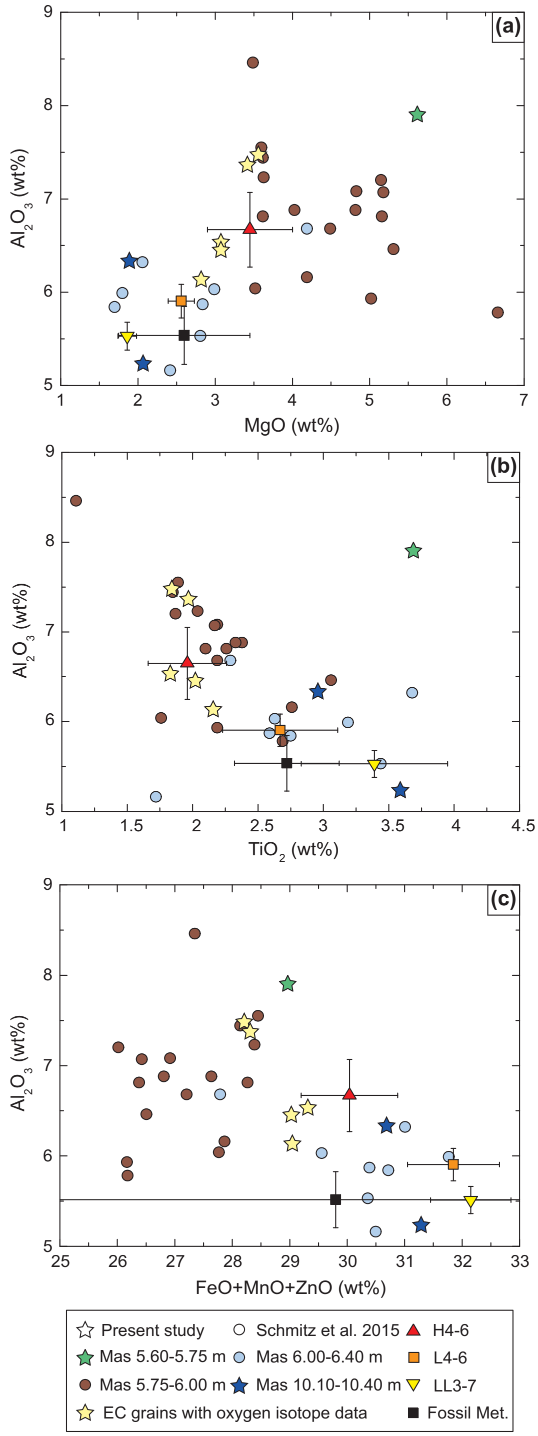


Fig. 3. Elemental composition of EC grains from the Massignano section and chromite grains from recent H, L and LL chondrites (Wlotzka, 2005) and mid-Ordovician fossil meteorites (Schmitz et al., 2001). Standard deviations are shown for data on fossil and recent meteorites. As discussed in the main text, among the analyzed elements only the TiO_2 content is used to discriminate between different types of ordinary chondrites. The general validity of this approach has been confirmed by combined oxygen isotope and TiO_2 analyses on numerous EC grains in Schmitz et al. (2011), Heck et al. (2010, 2016, 2017) and on five EC grains in the present study.

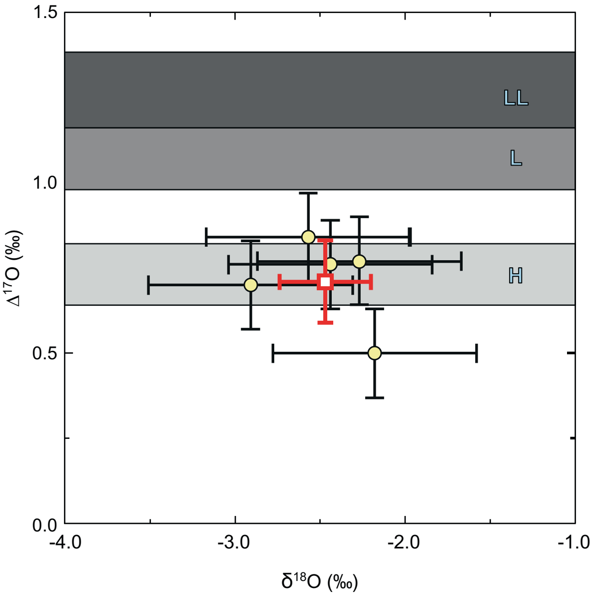
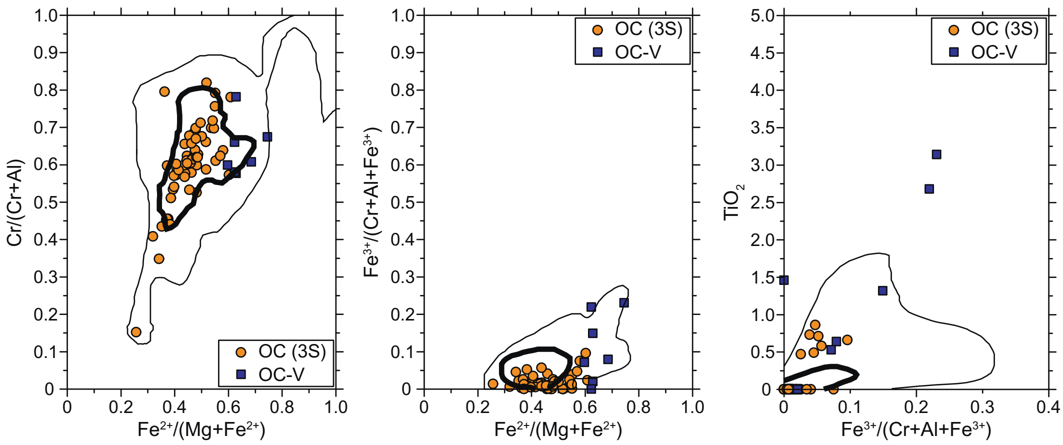


Fig. 4. Values of $\Delta^{17}O$ and $\delta^{18}O$ of all five sediment-dispersed grains analyzed in this study. Individual grain data are shown as open symbols with 2σ errors; average is shown as solid symbol with standard errors. Gray shaded areas are average $\Delta^{17}O$ compositions for equilibrated H, L, and LL chondrites (petrologic types 4–6) determined by Clayton et al. (1991). The terrestrial mass fractionation line is by definition at $\Delta^{17}O$ values of 0‰.

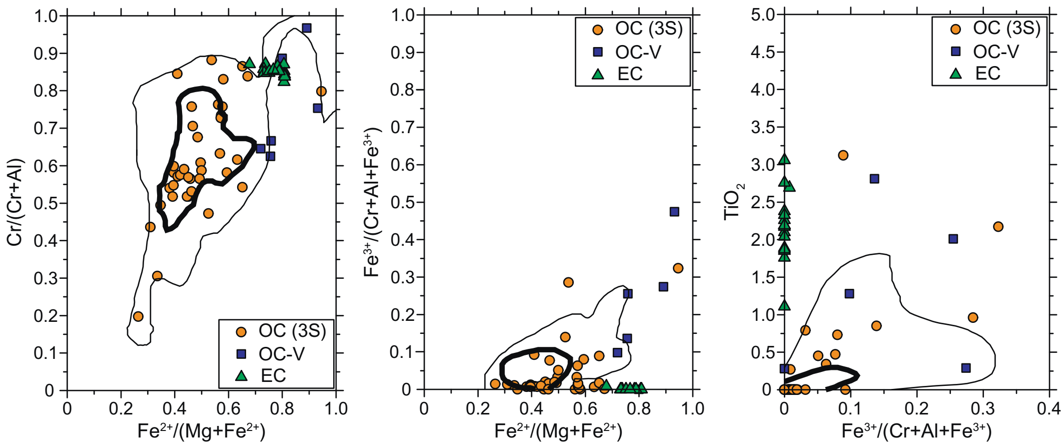
a major breakup event (Schmitz et al., 2009, 2015). Judging from the extraterrestrial ^3He trend in the late Eocene the flux of very fine-grained (<35 µm) interplanetary dust was enhanced by a factor typically in the range 2–4 and up to a maximum of 5 (Farley, 2009). A similar flux enhancement for spinel grains (>63 µm) included in coarse micrometeorites would not necessarily be resolved in our approach here. It cannot be entirely ruled out, however, that our two levels with L-chondritic grains reflect peaks in micrometeorite flux associated with peaks in ^3He from the even finer dust fraction (see below). For comparison, in the mid-Ordovician period after the breakup of the L-chondrite parent body there is a two orders of magnitude increase in L-chondritic fossil meteorites and sediment-dispersed micrometeoritic chromites during at least 1–2 Myr after the breakup (Schmitz, 2013, and references therein; Heck et al., 2016).

The high concentration of EC grains (17 grains per 100 kg) in the interval 5.75–6.00 m immediately on top of the Popigai ejecta almost certainly relates to the Popigai impactor. Although the span of the ejecta layer is generally given in the literature as 5.61–5.72 m, Paquay et al. (2014) report iridium values in the range 100–200 ppt, i.e., clearly higher than background (typically in the range 40–70 ppt), up to ~5.85 m. Schmitz et al. (2015) suggested that the "delayed" appearance in the strata of the EC grains compared to where the bulk of the micrometer-sized Ni-rich spinels, shocked quartz and pancake spherules occur reflects that the EC grains originate from regolith shed off from the Popigai impactor after it came under the influence of Earth-Moon gravity. Further studies at cm-by-cm strati-

Mas 1.60-1.90 m 103.9 kg



Mas 5.75-6.00 m 99.9 kg



Mas 10.10-10.40 m 95.7 kg

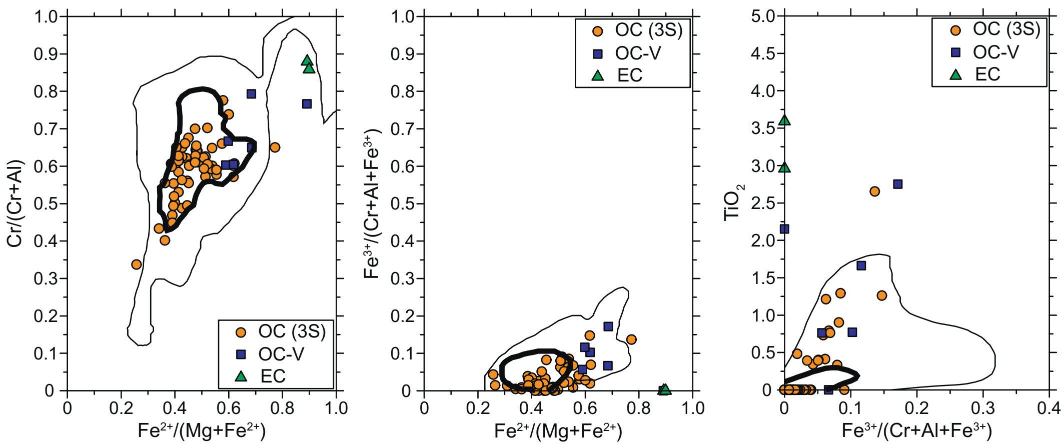


Fig. 5. Chemical composition of the OC, EC and OC-V grains from three representative Massignano samples plotted against the compositional density contour fields within which 50% and 90% of spinels from ophiolitic rocks plot according to Barnes and Roeder (2001). Only results for high-precision analyses (three spots, i.e., "3S" in legend) are used, see Supplementary Table 1. Diagrams for all the samples from the present study and Schmitz et al. (2015) are presented in Supplementary Fig. 1.

graphic resolution, and involving also other sites at some distance from Massignano would help to shed light on this. The H-chondritic EC grains appear very well preserved with few or no cracks (Fig. 6a,b), indicating little or no shock (see, Alwmark et al., 2011). This reconciles with an origin from regolith that was not involved in the impact

Table 4
Element concentrations (wt%) in the four Cr-rich spinel grains with the highest TiO_2 concentrations from the Massignano section.

Grain	MgO	Al_2O_3	TiO_2	V_2O_3	Cr_2O_3	MnO	FeO	ZnO	Total
Mas 5.60–5.75 m									
Cr 1	8.97	11.2	4.39	0.83	39.0	0.59	36.4	n.d.	101.4
Cr 2	7.17	8.11	8.71	1.62	28.0	n.d.	47.1	n.d.	100.7
Cr 3	8.76	12.5	4.90	0.79	33.1	0.52	39.1	n.d.	99.8
Mas 5.75–6.00 m[*]									
Cr 1	1.44	5.36	4.58	0.69	24.4	0.73	62.5	n.d.	99.7

[*] From Schmitz et al. (2015).

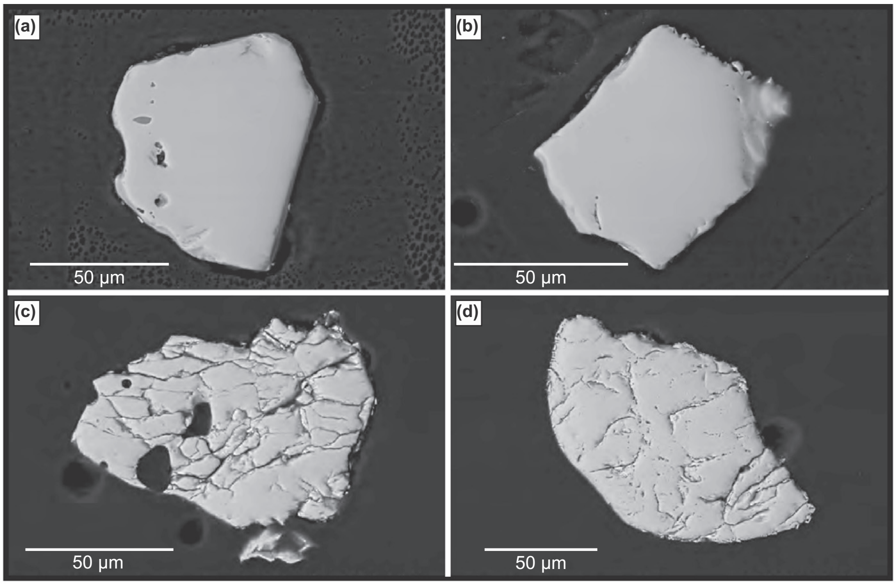


Fig. 6. Back-scattered electron images for polished, representative extraterrestrial chromite grains from the Massignano section. (A, B) H-chondritic grains from sample 5.75–6.00 m, (99.9 kg). (C, D) L-chondritic grains from sample 6.00–6.15 m, (96.4 kg). Note the difference in the abundance of cracks between the H- and L-chondritic grains. The number of cracks in extraterrestrial chromite grains has been shown to be related to shock levels (Alwmark et al., 2011). Polished H-chondritic grains from the Massignano section show smooth surfaces often without any cracks indicating that they have not experienced any significant shock pressure. On the other hand, the L-chondritic grains in the section appear to have undergone similar shock as the L-chondritic grains that fell on Earth after the breakup of the L-chondrite parent body in the mid-Ordovician (Alwmark et al., 2011).

event itself. Determining He and Ne isotopic ratios and concentrations of the EC grains would help to identify a potential regolith origin, and also to establish if extraterrestrial chromite carries helium that may contribute to the ^{3}He anomaly. In Middle Ordovician sediments coarse (>63 μm) EC grains carry high amounts of ^{3}He implanted from the solar wind. These EC grains are predominantly parts of micrometeorites released in the asteroid disruption event, and only a small fraction is from regolith (Heck et al., 2008; Meier et al., 2010). However, it is generally believed that the bulk of the ^{3}He in sediments is carried by much smaller particles (<35 μm) because of their lower heating during atmospheric entry and their higher abundance and larger surface to volume ratios (Farley et al., 1997).

The small enrichments in L-chondritic grains associated with the two more uncertain iridium anomalies in the section also coincide with short-term ^{3}He peaks superposed on the main long-term peak (Fig. 2). The general correlation of the EC occurrences with ^{3}He peaks and iridium anomalies gives a strong indication that the late Eocene extraterrestrial signals ultimately originate from the parts of the asteroid belt where the ordinary chondrites reside and not, as originally proposed by Farley et al. (1998), from the Oort comet cloud. The second smaller peak (8 grains in 208 kg of rock) in EC grains coincides with the precise level corresponding in time to the Chesapeake Bay impact, indicating that the grains may have originated from this event. Ejecta from the Chesapeake Bay impact has so far only been found at sites within a few 1000 km distance from the crater. If on the other hand there exists a global EC signal from this event, this would be consistent with the recovered L-chondrite grains having been shed off the impactor in space at tens of thousand kilometer distance from Earth and falling down all over the Earth. Contrary to the H-chondritic grains the L-chondritic grains often show many cracks (Fig. 6c, d), supporting that the two types of grains have different origins. The L-chondritic grains may still originate from regolith, because their shocked appearance may go back to the time when the L-chondrite parent body broke up 470 Myr ago.

There is no known candidate for an impact event corresponding to the two L-chondritic grains at 10.10–10.40 m and associated Ir anomaly. But there are some possible impact events with ages that might fit: Mistastin, Canada (35.8 ± 1 Myr, 28 km diameter), Wanapitei, Canada (37.2 ± 1.2 Myr, 7.5 km) or poorly dated impact events, like Beenchime-Salaaty, Russia (40 ± 20 Myr, 8 km) and Longancha, Russia (40 ± 20 Myr, 20 km) (Earth Impact Database, 2015). The two grains recovered could alternatively, as discussed above, be a reflection of the background meteorite flux. The appearance of these two grains when polished is similar to the L-chondritic grains in the 6.00–6.40 m interval, indicating that the grains have been affected by high shock pressures.

Despite the difference in Ir results by three laboratories across the 6.15 and 10.25 m levels there is no reason to question the quality of the data (Montanari et al., 1993; Bodiselitsch et al., 2004; Paquay et al., 2014). Extraterrestrial debris is very prone to weathering in terrestrial environments, and only spinel grains and PGE carrying nuggets tend to survive in an unaltered condition (Schmitz et al., 2011). Micrometer to submicrometer PGE-carrying grains can be heterogeneously distributed in the sediment. Whether such single grains become incorporated or not in a whole-rock sample used for Ir analyses will have a crucial effect on the outcome. This nugget effect is seen in the data of Paquay et al. (2014) where replicate Ir analyses of samples from the same stratigraphic level at Massignano sometimes give up to a factor 3 different results. The probability to measure a positive Ir anomaly, however, increases the higher the content of Ir-carrying nuggets at a particular level.

The oxygen isotopes and the extended data set in this study support an H-chondritic origin for the Popigai impactor. In our data there is also potential evidence for one or two L-chondritic impactors during the course of the late Eocene ^{3}He anomaly. This would speak against previous explanations of the late Eocene extraterrestrial signature relating it to an asteroid shower from a single parent-body breakup (Tagle and Claeys, 2004, 2005; Kyte et al., 2011). Kyte et al. (2011) based their idea of a late Eocene breakup of an H-chondritic Brangäne parent-body among others on the peak in CRE ages of ~35 Myr for many recent H-chondritic meteorites. The Brangäne family is relatively small and far from an orbital resonance. The breakup would thus not deliver large amounts of extraterrestrial debris to Earth like the much larger breakup of the L-chondrite parent body 470 Myr ago (Heck et al., 2004; Nesvorný et al., 2009; Schmitz, 2013). Schmitz et al. (2015) suggest that the late Eocene asteroid and dust shower to the inner part of the solar system was triggered by an episode of gravitation perturbation of asteroid orbits in the asteroid belt. The process could explain the simultaneous arrival of ^{3}He-carrying interplanetary dust, micrometeorites and km-sized bodies to Earth from different types of asteroid bodies.

The four anomalous OC grains with high Ti and V concentrations associated with the Popigai ejecta could possibly reconcile with a lunar origin, but terrestrial spinels can have similar compositions in some cases (see e.g., data base of Barnes and Roeder, 2001). Stochiometric calculations also indicate that the Fe^{3+}/Fe^{2+} ratio of the four grains are too high for being lunar. The Popigai ejecta bed is rich in material such as shocked quartz from the impact crater that formed on dominantly continental crust and sedimentary cover (Kettrup et al., 2003). The chemical plots of the OC grains at Massignano following Barnes and Roeder (2001) indicate that the bulk fraction in the Popigai ejecta of terrestrial spinels is not different from those at other levels in the Massignano section (Fig. 5; Supplementary Fig. 1). This is in accord with absence of chrome spinels in non-mafic bedrock like the gneisses and sediments dominating at the Popigai impact site. Within the crater, however, there are also a variety of small mafic or ultramafic bodies, including 20–30 m thick piles of volcanogenic mafic rocks scattered on Permian sandstones and related to the Siberian Traps flood basalts (Kettrup et al., 2003). Ultrabasic sheets 10–100 m thick and up to 1–2 km long is also a minor constituent in the gneisses of the crater (Vishnevsky and Montanari, 1999). Compositional data for spinels from Siberian Traps basalts in Barnes and Kunilov (2000) show a high proportion of spinels with unusually high Ti and V oxide values for being terrestrial spinels. Some grains have TiO_2 values in the range 7–10% and V_2O_5 values up to 1.5%. Based on a comparison with the data in Table 2 of Barnes and Kunilov (2000) the four anomalously Ti- and V-rich OC grains in the Popigai ejecta at Massignano almost certainly originate from Siberian Traps basalt in the Popigai crater.

Most of the OC grains in this study have similar compositions as the rare OC grains recovered by Cronholm and Schmitz (2007) in early to middle Paleocene sediments in the Bottaccione Gorge section at Gubbio. The OC grains are much more common in the Massignano section, with on average 2.0 grains kg^{-1} (Table 1) compared to Gubbio limestone, with 0.07 OC grain kg^{-1}. The difference may reflect a more pelagic situation in the Paleocene and development to more hemipelagic conditions in the late Eocene, as indicated also by increasing sedimentation rates. Following the Barnes and Roeder (2001) approach the late Eocene OC grains dominantly plot in the ophiolitic compositional field (Fig. 5; Supplementary Fig. 1). There is no change in the composition of OC grains through the studied interval of the Massignano section, which indicates stability in source area and sediment transport routes in the late Eocene. The OC grains analysed have rounded edges and a general abraded appearance, indicating that they were transported to the sedimentation area in the Umbria-Marche basin. The detailed origin of the regionally derived OC grains is beyond the scope of our study, however, a likely source may be ophiolitic rocks in the Alps massif (see e.g., Principi et al., 2004; Argnani et al., 2006; Franceschi et al., 2015).

6. CONCLUSIONS

Extraterrestrial chrome spinel grains in the interval with enhanced ^{3}He concentrations at Massignano are very rare (in the range 0–2 grains 1000 kg^{-1} of sediments) ruling out more than a factor of 2–3 enhancement in the flux of ordinary chondritic micrometeorites at the time. This argues against a late Eocene major asteroid breakup event. Two significant peaks in EC grains in the Massignano section are recorded associated with the Popigai impact ejecta and the stratigraphic level corresponding to the Chesapeake Bay impact, respectively. The grains may represent regolith gravitationally shed off the impactors on close encounters with the Earth-Moon system. Oxygen isotopic measurements of the grains associated with the Popigai ejecta in this study, and a general evaluation of TiO_2 as indicator for ordinary chondrite group in this and our other studies of EC grains, support a scenario with the Popigai impactor being an H chondrite and Chesapeake Bay probably an L chondrite. Two L-chondritic EC grains were found in this study at the 10.25 m level where previously a third Ir anomaly (in addition to those at the Popigai and Chesapeake Bay impact levels) has been measured. These grains may reflect a third unknown impact event or grains related to the background flux of micrometeorites. The general correlation of ordinary chondritic spinel grains with positive Ir and ^{3}He anomalies through the section represents a strong argument for that the late Eocene extraterrestrial signatures reflect disturbances of the inner asteroid belt rather than the Oort cloud, as originally suggested for the ^{3}He anomaly. The terrestrial chrome spinel grains at Massignano are regionally derived, have an ophiolitic composition and do not change significantly through the section. Four anomalous Ti- and V-rich grains recovered in the Popigai ejecta bed originate from Siberian Traps basalts in the Popigai impact crater.

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The paper was written by SB and BS with input from all coauthors. The recovery and elemental analyses of Cr spinels were performed by SB, BS, AC, and FT. SM and AM contributed on stratigraphy and regional geology. PRH and SSR prepared samples for SIMS and performed the SIMS and post-SIMS analyses, while NK and CD set up SIMS analysis conditions and assisted the analyses.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2017.01.028.

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