Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone at Gubbio, Italy: The flux of unmelted ordinary chondrites

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Abstract—The distribution of sediment-dispersed extraterrestrial (ordinary chondritic) chromite (EC) grains (>63 μm) has been studied across the latest Maastrichtian and Paleocene in the Bottaccione Gorge section at Gubbio, Italy. This section is ideal for determining the accumulation rate of EC because of its condensed nature and well-constrained sedimentation rates. In a total of 210 kg of limestone representing eight samples of 14–28 kg distributed across 24 m of the Bottaccione section, only 6 EC grains were found (an average of 0.03 EC grains kg\(^{-1}\)). In addition, one probable pallasitic chromite grain was found. No EC grains could be found in two samples at the Cretaceous-Tertiary (K-T) boundary, which is consistent with the K-T boundary impactor being a carbonaceous chondrite or comet low in chromite. The average influx of EC to Earth is calculated to ~0.26 grain m\(^{-2}\) kyr\(^{-1}\). This corresponds to a total flux of ~200 tons of extraterrestrial matter per year, compared to ~30,000 tons per year, as estimated from Os isotopes in deep-sea sediments. The difference is explained by the EC grains representing only unmelted ordinary chondritic matter, predominantly in the size range from ~0.1 mm to a few centimeters in diameter. Sedimentary EC grains can thus give important information on the extent to which micrometeorites and small meteorites survive the passage through the atmosphere. The average of 0.03 EC grain kg\(^{-1}\) in the Gubbio limestone contrasts with the up to ~3 EC grains kg\(^{-1}\) in mid-Ordovician limestone that formed after the disruption of the L chondrite parent body in the asteroid belt at ~470 Ma. The two types of limestone were deposited at about the same rate, and the difference in EC abundance gives support for an increase by two orders of magnitude in the flux of chondritic matter directly after the asteroid breakup.

INTRODUCTION

Recent empirical evidence indicates the existence of short periods during the Phanerzoic with significantly increased flux of extraterrestrial matter to Earth (Farley et al. 1998, 2006; Schmitz et al. 1996, 2001, 2003). Such flux increases have been predicted to result from, for example, gravity perturbations of the orbits of comets in the Oort cloud (e.g., Hills 1981; Hut et al. 1987; Matese et al. 1995) or parent body breakup events in the asteroid belt (Zappalà et al. 1998; Nesvorny et al. 2006). The finding of more than fifty fossil meteorites in mid-Ordovician marine limestone at Kinnekulle in southern Sweden supports an increase in the flux of meteorites by one to two orders of magnitude following the disruption of the L chondrite parent body in the asteroid belt ~470 Myr ago (Schmitz et al. 1996, 2001). The fossil meteorites have been shown to be pseudomorphosed L chondrites (Schmitz et al. 2001; Bridges et al. 2007; Greenwood et al. 2007) and their relict chromite grains show cosmic-ray exposure ages that support an origin from an asteroid breakup event (Heck et al. 2004). A mid-Ordovician increase in the meteorite flux is further supported by the distribution of sediment-dispersed extraterrestrial (ordinary chondritic) chromite (EC) grains (63–355 μm) in condensed limestone strata from southern Sweden (Schmitz et al. 2003; Schmitz and Häggström 2006). The search for fossil meteorites is time-consuming and requires screening of thousands of cubic meters of limestone, whereas sediment-dispersed EC grains can be searched in samples of 10–50 kg. Chromite is highly resistant to weathering and it is one of the rare relict minerals of fossil meteorites (Thorslund et al. 1984). The sediment-dispersed EC grains represent residues of primarily small, 0.1 mm to ~1 cm ordinary chondrites that decomposed on the sea floor (Schmitz et al. 2003; Heck et al., Forthcoming). Recent ordinary chondrites contain on average ~0.25 wt% chromite (FeCr\(_2\)O\(_4\)) (Keil 1962) and constitute ~80% of the total meteoritic influx (Bevan et al. 1998). The EC can be readily distinguished from terrestrial chromite by a
characteristic and unique major and trace element composition (Thorslund et al. 1984; Nyström et al. 1988; Roeder 1994; Schmitz et al. 2001). Extraterrestrial chromite shows minor variations in composition related to types H, L, and LL of host meteorite (Bunch et al. 1967; Schmitz et al. 2001; Wlotzka 2005). Hence, EC grains dispersed in sediments can be useful for determining both ancient accretion rates of ordinary chondritic material and variations in the types of ordinary chondrites reaching Earth (Schmitz et al. 2003).

In mid-Ordovician condensed strata in southern Sweden, limestone beds that formed after the disruption of the L chondrite parent body contain typically 1–3 EC grains per kg limestone, whereas in 379 kg of limestone that formed during the ~5 Myr immediately prior to this event, only 5 EC grains were found (Schmitz and Häggström 2006). Hence, EC grains dispersed in sediments can be useful for determining both ancient accretion rates of ordinary chondritic material and variations in the types of ordinary chondrites reaching Earth (Schmitz et al. 2003).

GEological SEtting

The Bottaccione Gorge with its famous and well-studied pelagic sequence of the middle Cretaceous to the Eocene (e.g., Arthur and Fischer 1977; Alvarez et al. 1980) is located in the Umbria-Marche Apennines, central Italy, directly north of the medieval town of Gubbio (43°22′N, 12°35′E, along the state road SS298 to Scheggia; see Fig. 1). Our sampled interval belongs to the ~325 m thick Scaglia Rossa Formation, which extends from the early Turonian to the middle Eocene (Arthur and Fischer 1977; Monechi and Thierstein 1985). The upper part of this formation consists predominantly of pink to red homogenous limestone and marly limestone that have been thoroughly bioturbated and compacted prior to cementation. The pristine condition of the Scaglia Rossa is explained by the apparent absence of intrusions and thermal alterations in the area (Arthur and Fischer 1977). Agglutinated foraminifera indicate that during the late Cretaceous and Paleocene, the Gubbio/Umbria-Marche basin had a deep bathyal position with a water depth of 1500–2500 m (Kuhnt 1990). Pelagic conditions are also
Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone indicated by abundant calcareous nannofossils and foraminifera, an aeolian clay and silt component, high planktic/benthic ratio in foraminifera, and extremely low concentrations of organic carbon (Arthur and Fischer 1977; Montanari 1991). In about 50 samples spanning from the Turonian to early Paleocene, Kuhnt (1990) noted the absence of terrigenous detrital material in grain fractions larger than 63 μm.

It is generally considered that the sedimentation rates were extremely low in the Gubbio area from the top Cretaceous (6–10 mm kyr⁻¹) to the lowermost Paleocene limestone (2–5 mm kyr⁻¹) (Montanari and Koeberl 2000). For the Paleocene epoch, Arthur and Fischer (1977) suggest an average sedimentation rate of 2.4 mm kyr⁻¹. Mukhopadhyay et al. (2001b) suggest average sedimentation rates on the order of 4–6 mm kyr⁻¹ for the latest Cretaceous and 2–3 mm kyr⁻¹ for the early and middle Paleocene. Their helium isotopic data show that the flux of extraterrestrial ³He to Earth is constant within a factor of ~2 across the K-T boundary and the early and middle Paleocene. Bulk rock ³He concentrations vary by a factor of ~4, reflecting mainly short-term variations in sedimentation rates (Fig. 2).

The Bottaccione Gorge section became famous as the first section shown to contain enhanced iridium levels (3–6 ppb) at the K-T boundary (Alvarez et al. 1980). The iridium originates from a carbonaceous chondritic asteroid or a comet (diameter of ~10 km) that impacted on the Yucatán Peninsula, Mexico (Hildebrand et al. 1991; Shukolyukov and Lugmair 1998). The K-T boundary in the Bottaccione Gorge section is marked by a 1–2 cm thick dark clay layer underlain by a white bleached limestone zone, ~20–50 cm thick. This zone is related to more reducing sediment conditions when increased
amounts of organic material reached the sea floor during the K-T boundary event (Lowrie et al. 1990; Montanari and Koeberl 2000). With the exception of the thin foraminiferal P0 zone, the Bottaccione Gorge section contains an essentially complete succession of biozones across the K-T transition (Smit 1982). The P0 zone is absent or unrecognizable in most of the Umbria-Marche locations, possibly reflecting slow sedimentation rates combined with thorough bioturbation, which would mix tests from the thin P0 zone and the overlying foraminiferal zones (Montanari and Koeberl 2000). Previous studies of the K-T boundary clay worldwide have located excess amounts of impact-related cosmic spinels and shocked quartz, but according to Montanari and Koeberl (2000), “despite its fame . . . the Bottaccione K-T clay is one of the worst known in the Umbria-Marche region in terms of preservation and suitability for a high-resolution microstratigraphic study.” The clay is affected by shearing caused by flexural slip folding and suffers from contamination by the surrounding soil. Common spinel-bearing spherules and shocked quartz have instead been found in the best preserved boundary clay at Petriccio only ~30 km north of Gubbio (Montanari 1991). However, this site is no longer easily accessible.

MATERIALS AND METHODS

Seven large limestone samples ranging from 27.7 to 28.3 kg plus one sample of 13.8 kg, for a total of 210 kg, were collected from 7.15 m below the K-T boundary clay to 17.18 m above it (Fig. 2). One sample of 28.3 kg spanned the 20 cm of section starting 1 cm above the base of the K-T boundary clay; another sample of 13.8 kg spanned the 10 cm of bleached strata immediately underlying the clay. The remaining samples (depths in meters relative to the K-T boundary clay: −7.15 to −6.90, −6.90 to −6.65, +2.10 to +2.40, +5.98 to +6.05, +11.15 to +11.40, +16.85 to +17.18 m) were regarded as representing “background levels” not influenced by the K-T boundary event. The stratigraphically lowest sample is dated to the planktonic foraminiferal Abathomphalus mayaroensis zone of the latest Maastrichtian (Premoli Silva 1977). The youngest sample at 17 m is dated to the lowest part of the planktonic foraminiferal P4 zone (Premoli Silva 1977) or calcareous nannofossil zone NP5 (Monechi and Thierstein 1985) (Fig. 2).

The eight samples studied were decalcified in 6 M hydrochloric acid at room temperature and then sieved at 32 μm. The residual fractions were leached in 18 M hydrofluoric acid at room temperature and separated into three size fractions (32–63, 63–355, and >355 μm) by sieving and drying. Some samples contained common coal particles and were burned at 550 °C for 24 h to destroy the coal. The coal particles are removed since they resemble the chromite grains. Tests have confirmed that the heating does not affect the major and trace element chemistry of the chromite grains. The middle size fraction (63–355 μm) was scrutinized under a stereomicroscope and suspected chromite grains were collected with a fine brush. The grains were first mounted on carbon tape and preliminarily analyzed in an unpolished state for major and trace elements. The grains were thereafter mounted in epoxy resin and polished before final elemental analysis. For polishing, Struer’s alumina paste (standard quality) mixed with water was used on a spinning polishing cloth (Buehler). For a few grains that were destroyed during the polishing phase, we use the results for unpolished grains. Quantitative elemental analyses were conducted with an energy dispersive spectrometer (INCA x-sight, Oxford Instruments) with a Si detector linked to a Hitachi S-3400N scanning electron microscope (SEM). Samples were analyzed at an acceleration voltage of 15 kV, a beam 1–2 μm in diameter, and a counting live-time of 80 s. Cobalt was used as a standard; the precision (reproducibility) of analyses was typically within 1–4%. Analytical accuracy was controlled by repeated analyses of the USNM 117075 chromite (Smithsonian) reference standard (Jarosewich et al. 1980).

DISTRIBUTION AND ORIGIN OF CHROME SPINELS

The distribution of sediment-dispersed chrome-rich spinel grains (63–355 μm) in the Bottaccione Gorge section is shown in Fig. 2 and the chemical composition is shown in Tables 1–4. We follow the procedures outlined by Schmitz and Hägström (2006) and divide the chrome-rich spinels into two groups: extraterrestrial (equilibrated ordinary chondritic) chromite (EC) and “other” chromium-rich spinels (OC). Under the binocular microscope, the EC and OC grains cannot be distinguished from each other, but they differ in chemical composition. The EC grains are characterized primarily by high Cr₂O₃ contents, ~55–60 wt%, FeO concentrations in the range of ~25–30 wt%, low Al₂O₃ at ~5–8 wt%, and low MgO concentrations of ~1.5–4 wt%. The most discriminative feature, however, is that they plot in narrow ranges of V₂O₅ (~0.6–0.9 wt%) and TiO₂ (~2.0–3.5 wt%) concentration. For a grain to be classified as an EC grain, it has to have a composition within or very close to the defined ranges for all the elements listed above. The OC grains, on the other hand, have a wide compositional range. In most cases they have a terrestrial origin, but some grains may represent rare types of extraterrestrial spinels.

In total, only 6 EC and 14 OC grains were retrieved from 210 kg of limestone (Tables 1–4). No chrome-rich spinels were present in the two samples at the K-T boundary (0 to −0.10 m and +0.01 to +0.20 m). Instead, the 6 EC grains were found in 4 samples evenly distributed through the section. The highest concentrations of EC and OC grains were found in the sample at +2.10 m, which contained 3 EC and 8 OC grains. The average EC and OC concentrations in the section are 0.029 and 0.067 grains kg⁻¹ limestone,
Table 1. The element concentration (wt%) of extraterrestrial chromite (EC) grains from this study.

<table>
<thead>
<tr>
<th>Gubbio EC grains&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>MgO</th>
<th>TiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>FeO</th>
<th>MnO</th>
<th>ZnO</th>
<th>Total</th>
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<tbody>
<tr>
<td>−0.90 to −0.65 m</td>
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<tr>
<td>#1</td>
<td>59.53</td>
<td>7.48</td>
<td>3.03</td>
<td>2.20</td>
<td>0.81</td>
<td>22.52</td>
<td>1.05</td>
<td>2.58</td>
<td>99.2</td>
</tr>
<tr>
<td>+2.10 to 2.40 m</td>
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<tr>
<td>#1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>56.27</td>
<td>5.27</td>
<td>6.08</td>
<td>1.67</td>
<td>0.60</td>
<td>28.45</td>
<td>0.71</td>
<td>0.95</td>
<td>100.0</td>
</tr>
<tr>
<td>#2</td>
<td>59.91</td>
<td>6.30</td>
<td>4.78</td>
<td>1.86</td>
<td>0.51</td>
<td>24.92</td>
<td>n.d.</td>
<td>1.14</td>
<td>99.4</td>
</tr>
<tr>
<td>#3</td>
<td>57.38</td>
<td>6.94</td>
<td>4.30</td>
<td>2.36</td>
<td>0.64</td>
<td>24.14</td>
<td>0.89</td>
<td>2.24</td>
<td>98.9</td>
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<tr>
<td>+5.98 to 6.05 m</td>
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<tr>
<td>#1</td>
<td>59.56</td>
<td>6.14</td>
<td>2.11</td>
<td>3.20</td>
<td>0.65</td>
<td>25.25</td>
<td>0.67</td>
<td>0.51</td>
<td>98.1</td>
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<td>+11.15 to 11.40 m</td>
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<tr>
<td>Mean (with s.d.)</td>
<td>58.94 ± 1.75</td>
<td>5.78 ± 1.11</td>
<td>4.38± 1.88</td>
<td>2.35 ± 0.58</td>
<td>0.67 ± 0.12</td>
<td>24.87 ± 1.99</td>
<td>0.68 ± 0.36</td>
<td>1.37 ± 0.84</td>
<td>99.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Depth relative to the K-T boundary in the Bottaccione Gorge section, Gubbio.

<sup>b</sup>The grain was lost during polishing, and is only represented by preliminary pre-polish measurements. The elemental values have been normalized from the original total of 92.8 wt%.

n.d. = not detected.

Table 2. The average element concentration (wt%, with standard deviation) of EC grains from this and previous studies.

<table>
<thead>
<tr>
<th></th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>MgO</th>
<th>TiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>FeO</th>
<th>MnO</th>
<th>ZnO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment-dispersed EC grains</td>
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</tr>
<tr>
<td>Gubbio section, Italy; 6 grains (this study)</td>
<td>58.9 ± 1.75</td>
<td>5.78 ± 1.11</td>
<td>4.38 ± 1.88</td>
<td>2.35 ± 0.58</td>
<td>0.67 ± 0.12</td>
<td>24.9 ± 1.99</td>
<td>0.68 ± 0.36</td>
<td>1.37 ± 0.84</td>
<td>99.0</td>
</tr>
<tr>
<td>Thorsberg quarry, Sweden; 276 grains&lt;sup&gt;a&lt;/sup&gt;</td>
<td>57.6 ± 1.58</td>
<td>6.07 ± 0.76</td>
<td>2.58 ± 0.79</td>
<td>3.09 ± 0.33</td>
<td>0.75 ± 0.07</td>
<td>27.4 ± 2.63</td>
<td>0.78 ± 0.20</td>
<td>0.53 ± 0.50</td>
<td>98.8</td>
</tr>
<tr>
<td>Chrome grains from meteorites&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Mid-Ordovician fossil meteorites, Thorsberg quarry; 26 meteorites</td>
<td>57.6 ± 1.30</td>
<td>5.53 ± 0.29</td>
<td>2.57 ± 0.83</td>
<td>2.73 ± 0.40</td>
<td>0.73 ± 0.03</td>
<td>26.9 ± 3.89</td>
<td>1.01 ± 0.33</td>
<td>1.86 ± 2.43</td>
<td>99.0</td>
</tr>
<tr>
<td>Recent H5/6 group chondrites; 11 meteorites</td>
<td>56.6 ± 0.37</td>
<td>6.44 ± 0.14</td>
<td>2.98 ± 0.23</td>
<td>2.20 ± 0.17</td>
<td>0.73 ± 0.02</td>
<td>29.3 ± 0.67</td>
<td>1.00 ± 0.08</td>
<td>0.33 ± 0.05</td>
<td>99.6</td>
</tr>
<tr>
<td>Recent L5/6 group chondrites; 10 meteorites</td>
<td>56.0 ± 0.65</td>
<td>5.97 ± 0.43</td>
<td>2.93 ± 0.97</td>
<td>2.68 ± 0.40</td>
<td>0.75 ± 0.02</td>
<td>30.2 ± 2.23</td>
<td>0.83 ± 0.10</td>
<td>0.30 ± 0.07</td>
<td>99.7</td>
</tr>
</tbody>
</table>

<sup>a</sup>Data from Schmitz and Häggeström (2006).

<sup>b</sup>Data given is the mean of the average composition of typically 10–20 EC grains from each meteorite. Data from Schmitz et al. (2001), modified by Alwmark and Schmitz (2007).
respectively. The EC grains from the Gubbio section are on the whole very similar in composition to both chondrite in recent ordinary chondrites and EC grains found in Ordovician limestone and fossil meteorites at Kinnekulle, Sweden (Schmitz et al. 2001, 2003; Schmitz and Häggström 2006) (see Table 2). Some minor but significant differences exist. The Gubbio grains are often high in ZnO (0.5–2.6 wt%) and on average 2–2.5 wt% lower in FeO than Ordovician chondritic chromite. For the Ordovician fossil meteorites, it has been shown that Zn can replace Fe in the chromite structure during diagenesis (Schmitz et al. 2001); hence, the Gubbio grains appear to be more diagenetically altered than most Ordovician EC grains. The Gubbio EC grains on average have a higher MgO (4.4 wt%) concentration than the Ordovician (2.6 wt% MgO) EC grains. However, only the three grains from the sample at +2.10 m have significantly higher MgO than the Ordovician average EC. Single fossil meteorites at Kinnekulle contain chromite grains with MgO concentrations of ~5–6 wt% rather than the normal ~2–4 wt% (Schmitz et al. 2001). Hence, the three EC grains from the +2.10 m level probably derive from the same meteorite or micrometeorite. The TiO2 concentration of the Gubbio EC grains is on average 0.4–0.7 wt% lower than in Ordovician EC grains. Previous studies have shown that the TiO2 concentration of sediment-dispersed chromite grains in general is very resistant to weathering and diagenesis (Schmitz et al. 2001; Schmitz and Häggström 2006; Alwmark and Schmitz 2007). Chromite in H chondrites is on average ~0.6–0.7 wt% lower in TiO2 than in L chondrites (Bunch et al. 1967; Schmitz et al. 2001; Wlotzka 2005). The Ordovician EC grains predominantly originate from the disruption of the L chondrite parent body at this time, which could explain the higher TiO2. There is no reason to expect that L chondrites dominated the flux in the latest Maastrichtian–Paleocene. Although the majority of the EC grains from Gubbio may derive from H chondrites, the ranges of TiO2 concentrations in recent H and L chondritic chromite overlap; hence, only the average TiO2 content of a large number of sediment-dispersed grains is indicative of precursor chondrite type. Moreover, the three grains in the sample at +2.10 m are low in TiO2 and this affects the average TiO2 concentration disproportionately. The three EC grains at other levels have typical H or L chondritic TiO2 contents. In essence, no conclusions about the relative fluxes of H and L chondrites can be drawn from this small data set.

Table 3. The element concentration (wt%) of other chromium-rich spinel (OC) grains from this study.

<table>
<thead>
<tr>
<th>Gubbio OC grains(^{a})</th>
<th>Cr(_2)O(_3)</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>TiO(_2)</th>
<th>V(_2)O(_3)</th>
<th>FeO</th>
<th>MnO</th>
<th>ZnO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2.10 to 2.40 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>27.61</td>
<td>29.54</td>
<td>15.47</td>
<td>2.08</td>
<td>n.d.</td>
<td>23.80</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.5</td>
</tr>
<tr>
<td>#2</td>
<td>23.80</td>
<td>32.65</td>
<td>15.21</td>
<td>1.80</td>
<td>n.d.</td>
<td>24.19</td>
<td>n.d.</td>
<td>n.d.</td>
<td>97.7</td>
</tr>
<tr>
<td>#3</td>
<td>26.73</td>
<td>31.07</td>
<td>16.00</td>
<td>1.93</td>
<td>n.d.</td>
<td>22.95</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.7</td>
</tr>
<tr>
<td>#4</td>
<td>18.06</td>
<td>30.21</td>
<td>9.70</td>
<td>2.50</td>
<td>n.d.</td>
<td>36.91</td>
<td>0.92</td>
<td>n.d.</td>
<td>98.3</td>
</tr>
<tr>
<td>#5</td>
<td>11.73</td>
<td>38.51</td>
<td>14.80</td>
<td>3.05</td>
<td>n.d.</td>
<td>30.91</td>
<td>n.d.</td>
<td>n.d.</td>
<td>99.0</td>
</tr>
<tr>
<td>#6(^{b}) (grain lost during polishing)</td>
<td>28.67</td>
<td>38.67</td>
<td>15.96</td>
<td>0.26</td>
<td>n.d.</td>
<td>16.44</td>
<td>n.d.</td>
<td>n.d.</td>
<td>100.0</td>
</tr>
<tr>
<td>#7(^{c}) (grain lost during polishing)</td>
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<tr>
<td>#8(^{c}) (grain lost during polishing)</td>
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| +5.98 to 6.05 m           |                |                |     |          |                |     |     |     |       |
| #1                       | 64.27          | 5.83           | 5.42 | n.d.     | 0.56           | 14.20| 0.71| 8.11| 99.1  |
| #2                       | 43.46          | 27.58          | 12.53| n.d.     | n.d.           | 16.34| n.d.| n.d.| 99.9  |
| #3                       | 26.61          | 27.16          | 12.19| 1.73     | n.d.           | 30.35| n.d.| n.d.| 98.0  |
| #4\(^{d}\) (grain lost during polishing) | 42.13 | 30.74 | 12.74 | n.d. | n.d. | 14.56 | n.d. | n.d. | 100.2 |

| +16.85 to 17.18 m         |                |                |     |          |                |     |     |     |       |
| #1                       | 56.79          | 15.27          | 8.08 | n.d.     | n.d.           | 15.00| n.d.| 2.20| 97.3  |

\(^{a}\)Depth relative to the K-T boundary in the Bottaccione Gorge section, Gubbio.

\(^{b}\)The grain was lost during polishing, and is only represented by preliminary pre-polish measurements. The elemental values have been normalized from the original total of 96.4 wt%.

\(^{c}\)Pre-polish measurements of grains #7 and 8 gave similar results as for grains #1, 2, and 3 in the same sample.

\(^{d}\)Pre-polish measurements of grain #4 gave similar results as for grains #1 and 3 in the same sample.

n.d. = not detected.

Table 4. The element composition (wt%) of average pallasitic chromite compared to the OC grain from +5.98 to 6.05 m above the K-T boundary at Gubbio, Italy.

<table>
<thead>
<tr>
<th></th>
<th>Cr(_2)O(_3)</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>TiO(_2)</th>
<th>V(_2)O(_3)</th>
<th>FeO</th>
<th>MnO</th>
<th>ZnO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pallasite(^{a})</td>
<td>64.0</td>
<td>5.6</td>
<td>5.8</td>
<td>0.18</td>
<td>0.54</td>
<td>23.2</td>
<td>0.65</td>
<td>&lt;0.02</td>
<td>99.97</td>
</tr>
<tr>
<td>OC grain from +5.98 m</td>
<td>64.3</td>
<td>5.8</td>
<td>5.4</td>
<td>n.d.</td>
<td>0.56</td>
<td>14.2</td>
<td>0.71</td>
<td>8.1</td>
<td>99.1</td>
</tr>
</tbody>
</table>

\(^{a}\)Data from Bunch and Keil (1971).

n.d. = not detected.
All except 2 of the 14 OC grains originate from the two samples at +2.10 and +11.15 m (Table 3). Most of the OC grains from these samples are similar in composition. They have low Cr/Cr + Al ratios (<0.5), which is in good agreement with a terrestrial origin (Roeder 1994), they are typically high in MgO (12–16 wt%), and they contain no detectable V or Zn. Comparisons of the compositions of the OC grains from Gubbio with chrome spinels from various magmatic provinces as plotted in Barnes and Roeder (2001) indicate an ophiolite provenance, but alternative sources are also plausible. Various magmatic processes, including subduction and possibly plume activity, have occurred in Italy dating back to at least 60–70 Ma (Bell et al. 2004). A more detailed evaluation of the origin of the terrestrial chromite grains from the Gubbio section is beyond the scope of this article.

The two OC grains from the samples at +5.98 and +16.85 m show different compositions compared to those discussed above (Table 3). The origin of the grain from +16.85 m is uncertain and it may be a terrestrial grain. The single OC grain at +5.98 m represents a very special case. It is unusually large (150 × 300 μm) and has a distinct composition almost identical to the average composition of chromites from pallasites (Table 4) (Bunch and Keil 1971). The high Cr₂O₃ (64%), low Al₂O₃ (5.6 wt%), and characteristic V₂O₅ (0.5 wt%) and TiO₂ (0.18 wt%) contents distinguish pallasitic chromite from most terrestrial chromite. The higher ZnO (8.1 wt%) and lower FeO (14.2 wt%) of our OC grain compared to the pallasitic average chromite is readily explained by replacement of Fe by Zn during diagenesis (Schmitz et al. 2001). Pallasitic chromite is also characterized by a larger grain size than in other types of meteorites (Bunch and Keil 1971). The fact that the grain occurs unassociated with any other OC grains in the same sample and the profound difference in composition compared to the terrestrial chrome spinels in the samples above and below also speak in favor of an extraterrestrial origin.

BACKGROUND FLUX OF EXTRATERRESTRIAL CHROMITE

Previous attempts to determine the time-averaged total influx of meteorites and/or smaller extraterrestrial particles to Earth have relied on the density of micrometeoroid hypervelocity impact craters on the Long Duration Exposure Facility (LDEF) satellite (Love and Brownlee 1993), radar micrometeor observations in the upper atmosphere (Mathews et al. 2001), concentrations of platinum group elements, osmium isotopes and ³He in condensed sediments (Farley et al. 1997; Peucker-Ehrenbrink and Ravizza 2000; Peucker-Ehrenbrink 2001; Dalai and Ravizza 2006), iridium concentrations in ice cores (Karner et al. 2003; Gabrielli et al. 2004), micrometeorite abundances in Antarctic ice (Taylor and Lever 2001) and, for meteorites, meteor sky-watch programs (Halliday 2001) and systematic meteorite searches in wind-eroded desert areas (Bland et al. 1996; Bland 2001). The various approaches give flux estimates that sometimes differ significantly. To some extent this can be explained by the different size fractions of the total flux being measured, but methodological problems such as undersampling of larger extraterrestrial particles because of low sample time-area products may in some cases be a problem (see discussion in Peucker-Ehrenbrink and Ravizza 2000). The perhaps best value for the total accreted amount of extraterrestrial matter on the Earth’s surface is 30,000 (±15,000) metric tons per year (Peucker-Ehrenbrink and Ravizza 2000). This is based on Os isotopes in deep-sea sediments and agrees with the estimate of 30,000 (±10,000) tons for the flux measured by the LDEF satellite at altitudes of 330 to 480 km (Love and Brownlee 1993; revised estimate in Engrand and Maurette 1998). Desert meteorite search programs show that the total mass flux to the Earth’s surface for meteorites over the 10 g to 1 kg interval is between 2.9 and 7.3 tons per year, an estimate that agrees well with estimates from sky-watch networks (Bland et al. 1996; Halliday 2001). The large difference between the total and the meteorite-sized flux illustrates that the bulk of the extraterrestrial matter reaches the Earth surface as very small dust particles or micrometeorites (<300 μm), or occasionally as very large impactors (>1–2 km).

Extraterrestrial chromite grains dispersed in condensed sediments is a new proxy for the influx of extraterrestrial detritus to Earth and has previously only been applied for mid-Ordovician condensed limestone (Schmitz et al. 2003; Schmitz and Häggström 2006). The average EC content of the Gubbio limestone, 0.029 grain kg⁻¹, is similar to that of mid-Ordovician limestone, (0.013 grain kg⁻¹ for 379 kg) which formed before the disruption of the L chondrite parent body. Based on the Gubbio data, the average influx of EC to Earth is calculated to be ~0.26 EC grain m⁻² kyr⁻¹, using average sedimentation rates of 2.5 mm kyr⁻¹ for the Paleocene and 5 mm kyr⁻¹ for the three Cretaceous samples studied (Arthur and Fischer 1977; Mukhopadhyay et al. 2001b) and a limestone density of 2.7 g cm⁻³. For the mid-Ordovician, before the asteroid breakup event, the estimated flux is ~0.09 EC grains m⁻² kyr⁻¹ but increases dramatically to an average of ~13 EC grains m⁻² kyr⁻¹ after the event (Schmitz and Häggström 2006). We use a sedimentation rate of 2.5 mm kyr⁻¹ for the Ordovician limestone, but this number contains an uncertainty of up to a factor of two. Furthermore, single EC grains can be readily overlooked during the chromite search and coincidental recovery of relic chromite from larger meteorite fragments, such as probably in sample +2.10 m at Gubbio, also adds statistical uncertainty to the flux estimates. We conclude that the normal flux of EC to Earth lies at ~0.1–0.3 grain m⁻² kyr⁻¹.

The flux of EC grains (0.26 grain m⁻² kyr⁻¹) reconstructed at Gubbio corresponds to 4.7 × 10⁻⁴ g of ordinary chondritic, unmelted debris m⁻² kyr⁻¹. For this estimate, we assume that the average EC grain is a cube with...
a diameter of 100 μm; we use a chromite density of 4.6 g cm\(^{-3}\) and an average chromite content for ordinary chondrites of 0.25 wt% (Keil 1962). Many of the EC grains have irregular shapes, but the use of a 100 μm cube in our calculation is reasonable, considering that all grains are >63 μm in at least one dimension and most of the grains have maximum length axes <150 μm. The fact that we only search for chromite grains larger than 63 μm introduces some uncertainty, but for a gross, order-of-magnitude estimate the effect is negligible. Extrapolation to the entire surface of the Earth yields a global flux of ~200 tons of meteoritic matter per year. This is substantially less than the flux of ~30,000 tons based on Os isotopes in deep-sea sediments (Peucker-Ehrenbrink and Ravizza 2000), but significantly more than the 2.9–7.3 tons of meteorites in the 10 g to 1 kg mass spectrum according to desert meteorite abundances (Bland et al. 1996). Based on cosmic spherules from the South Pole Water Well, Taylor and Lever (2001) estimated an annual flux of 2700 ±1400 tons of micrometeorites in the size range 50–700 μm; however, 85% of the spherules were totally melted. Our mass estimate clearly appears realistic in view of these numbers and considering that our EC grains originate predominantly from decomposed unmelted meteorite fragments in the size range of 0.1 mm to a few centimeters (Schmitz et al. 2003; Heck et al., Forthcoming). The full range of the size spectrum and the significance of different size fractions within this spectrum are difficult to assess. Some micrometeorites may have been only marginally larger than the chromite grain itself. At the other end of the mass spectrum, chromite grains were spread over the sea floor by currents and bioturbation from decomposed kilogram-sized meteorites. Some of the chromite grains may derive from bodies 1–100 m in diameter, or even larger, which disrupted in the atmosphere or water column, resulting in micrometeorite and meteorite strewn fields on the sea floor (Lal and Jull 2002; Klekociuk et al. 2005).

Because of atmospheric disintegration of larger meteoroids, the size distribution of objects above the atmosphere is substantially different from that of the material reaching the Earth’s surface (Lal and Jull 2002). In order to understand the processes that regulate the extraterrestrial flux through the atmosphere, it is necessary to understand the distribution of extraterrestrial matter over the different size fractions reaching Earth’s surface. In flux estimates, the EC distribution in sediments appears to be an important complement to, for example, chemical studies of deep-sea sediments that primarily sample the most fine-grained and/or vaporized and recondensed fractions of the extraterrestrial flux (Lal and Jull 2003).

We stress that the flux of unmelted ordinary chondritic matter of 200 tons per year is a first-order estimate that may be refined as larger samples of limestone will be studied in the future. There are some potential methodological problems that have been considered. With the type of well-preserved limestone like at Gubbio or in the mid-Ordovician at Kinnekulle in Sweden, there is good reason to believe that no EC grains have been destroyed over time by diagenesis or weathering (Schmitz and Häggström 2006). The EC grains found only show evidence of minor alteration, such as replacement of a few percent Fe by Zn. We do not find EC grains with, e.g., zoning that characterizes grains from more aggressive diagenetic environments, like in the Locke impact crater where EC grains have been affected by hydrothermal activity (Alwmark and Schmitz 2007). Without grains representing intermediate states of alteration, it is not likely that grains were lost entirely because of diagenesis. Redistribution of EC grains by sea-floor currents may bias the EC grain distribution, but with large samples from several stratigraphic levels, the effect of this process will be smoothed out. Tests with individual chromite grains leached in HF and HCl show that the acids do not destroy the grains, but occasionally grains with fragile structure can break into smaller than 63 μm fragments during the wet sieving. Tests with samples “spiked” with EC grains show that this affects at the most a few percent of all grains.

**CRETACEOUS-TERTIARY BOUNDARY EVENT**

Chemical and isotopic extraterrestrial signatures at the K-T boundary worldwide and coeval species mass extinctions are best explained by the impact of a major extraterrestrial body (~10 km in diameter) at the Yucatán Peninsula, Mexico (e.g., Alvarez et al. 1980; Hildebrand et al. 1991; Arenillas et al. 2006). The globally distributed K-T boundary clay containing iridium, shocked quartz, and spinel-rich microspherules represents compelling evidence for the impact event (Montanari and Koeberl 2000). Chromium isotopic analyses of the boundary clay (Shukolyukov and Lugmair 1998; Trinquier et al. 2006) and studies of a mm-sized weathered meteorite fragment from the K-T boundary in DSDP Hole 576 (Kyte 1998) suggest that the impactor was a carbonaceous chondrite, although a comet can not be ruled out. An important question is whether the K-T boundary impactor was a lone stray object or part of an asteroid or comet shower related to perturbations of solar system gravity (e.g., Hut et al. 1987). An enhanced flux of comets during a few million years can be produced by gravitational perturbations of the Oort Cloud, but the studies by Mukhopadhyay et al. (2001a, 2001b) at Gubbio indicate a near-constant flux of extraterrestrial 3He during the K-T boundary event (Fig. 2), speaking against a comet shower. Varadi et al. (2003) suggest that the K-T impactor may instead have been related to perturbations in the asteroid belt ~65 Myr ago during chaotic transitions in the motions of the inner planets. Any such activity could have increased material transport in the inner solar system, resulting in enhanced accretion rates of cosmic material on Earth. High-resolution Ir analyses across the latest Maastrichtian and earliest
Paleocene strata at Gubbio, show that Ir is only enriched across a narrow interval close to the very K-T boundary, speaking against an extended period with substantially enhanced flux of extraterrestrial matter to Earth (Alvarez et al. 1990). Short vertical tails of enhanced Ir concentrations around the boundary clay most likely reflect redistribution of Ir during bioturbation and diagenesis. To add to this, our chromite searches in samples immediately adjacent to the K-T boundary clay could not find support for any significant increase in the flux of equilibrated ordinary chondritic micrometeorites or meteorites to Earth associated with the K-T event. The absence of >63 μm chromite grains in beds immediately adjacent to the K-T boundary clay at Gubbio also speaks against an equilibrated ordinary chondritic impactor. Although we have not studied the centimeter-thick K-T boundary clay itself, chromite grains in adjacent beds can be expected if they occur in the boundary clay because of the effects of bioturbation and redistribution of material by currents. Alternatively, complete vaporization of an ordinary chondrite during impact could have led to the absence of chromatite. Our results are consistent with a carbonaceous chondritic impactor as suggested based on chromium isotopes. Carbonaceous chondrites only contain trace amounts of chromite, and grains larger than 63 μm are entirely absent or extremely rare (Fuchs et al. 1973; El Goresy 1976; Johnson and Prinz 1991; Rubin 1997), hence our data cannot rule out an increased flux of such material over an extended period.

**CONCLUSIONS**

The influx of extraterrestrial (ordinary chondritic) chromite (>63 μm) to Earth during the latest Maastrichtian and Paleocene has been established at a perfect testing ground, the condensed, pelagic limestones of the Bottaccione Gorge section at Gubbio, Italy. In 210 kg of limestone deposited at ~2.5 to 5 mm kyr⁻¹, we found a total of 6 EC grains, corresponding to an average of 0.03 EC grain kg⁻¹. From well-constrained sedimentation rates, relying on detailed stratigraphic records, we determine the average flux of EC grains to Earth to ~0.26 grain m⁻² kyr⁻¹. This corresponds to a total influx of ~200 tons of extraterrestrial matter to Earth per year, which is realistic considering that the EC grains only record the flux of unmelted ordinary chondritic matter in the size range from ~0.1 mm up to a few centimeters in diameter. The distribution of EC grains in sediments can give information on the extent to which extraterrestrial matter survives the passage through the atmosphere.

The results in this study confirm the extraordinary circumstances recorded in mid-Ordovician (~470 Ma) limestone at Kinnekulle, Sweden, where an increase in EC grains of two orders of magnitude (from ~0.013 to 1–3 EC grains kg⁻¹ limestone) coincides with the coeval disruption of the L chondrite parent body in the asteroid belt. Large limestone samples collected at Gubbio in the immediate stratigraphic vicinity of the 1 cm thick K-T boundary clay contained no EC grains. This shows that there was no increase in the flux of ordinary chondritic matter to Earth during the K-T boundary transition.

The finding of 6 ordinary chondritic and 1 probable pallasitic chromite grain in 210 kg of condensed limestone from Gubbio shows that our approach has promise for retrieving general knowledge about past variations in the meteorite flux to Earth, particularly if methods could be developed for automatic preparation of limestone samples in the size of 100–200 kg.

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**Editorial Handling**—Dr. Timothy Swindle

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