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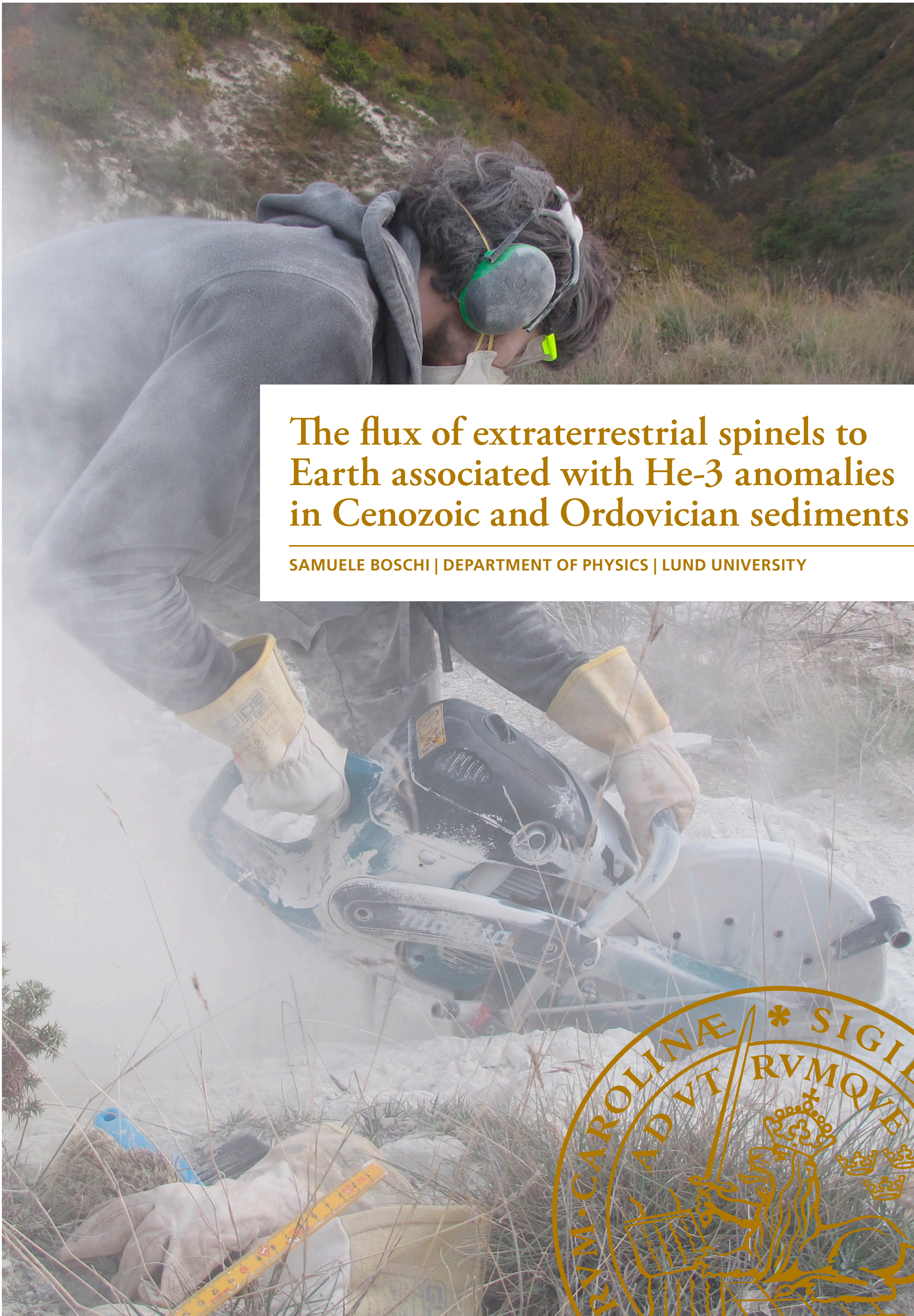

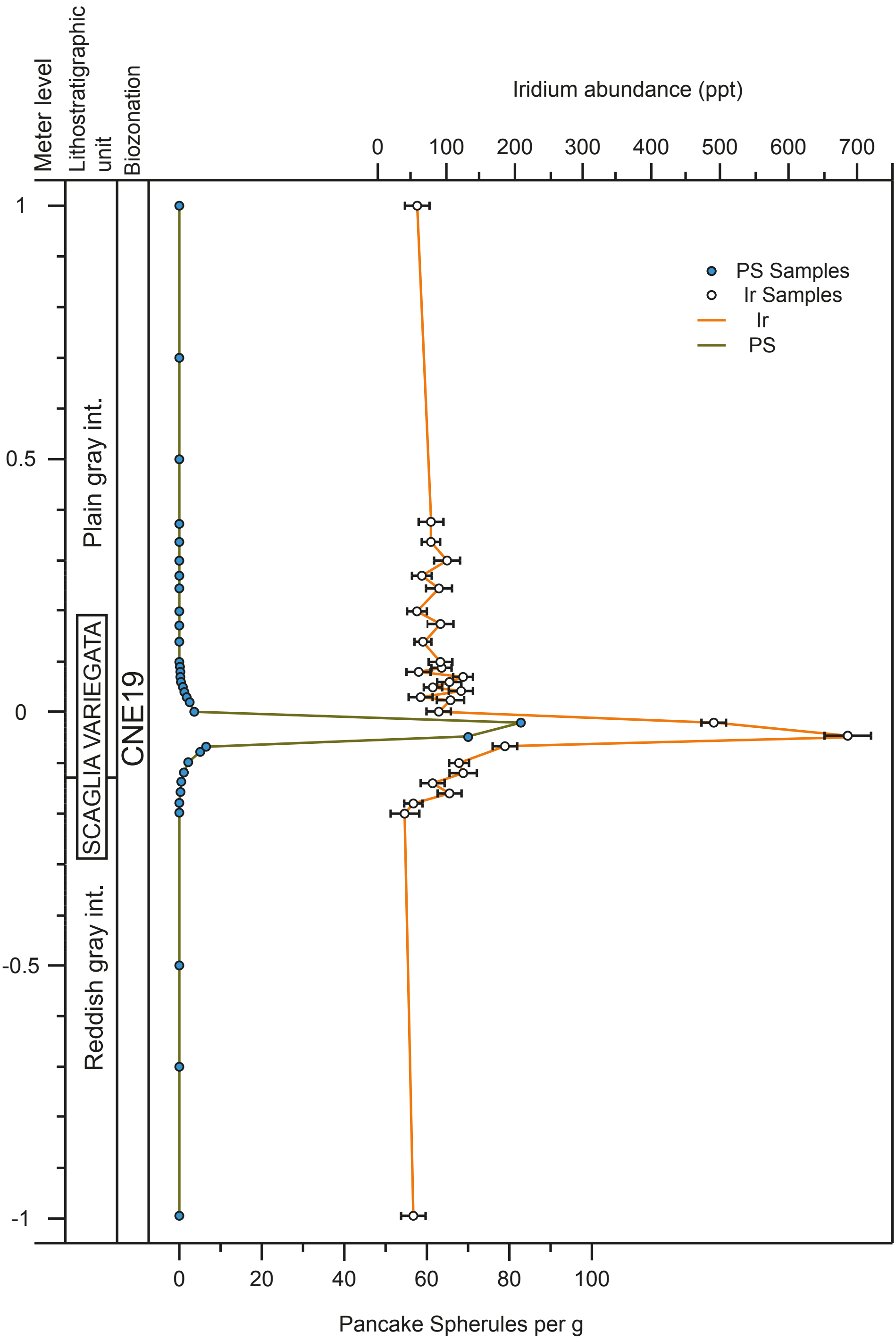

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The flux of extraterrestrial spinels to Earth associated with He-3 anomalies in Cenozoic and Ordovician sediments

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Samuele Boschi

LUND UNIVERSITY

DOCTORAL DISSERTATION

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Abstract The main goal of this thesis is to reconstruct the flux of extraterrestrial matter to Earth in specific time intervals of our past in order to add an astronomical dimension to the understanding of Earth's history. To accomplish this, extraterrestrial chrome-spinel grains have been extracted and analysed. Moreover, analyses of other proxies of extraterrestrial matter e.g. iridium in Cenozoic sediments, have been carried out. Relict spinel grains from extraterrestrial material dispersed in sediments can be used to reconstruct variations in the flux of the different meteorite types to Earth through the ages. Falls of meteorites are rare on Earth's surface and those that fall decay rapidly due to weathering. However, almost all types of meteorites contain a tiny fraction of spinel minerals that survive weathering and they can be recovered after a laboratory acid-dissolution treatment of large limestone samples. The spinel approach can give detailed information on the types of extraterrestrial matter that fell on Earth at specific times in the geological past. Variations in flux and types of meteorites may reflect breakups in the asteroid belt of the parent bodies for different meteorite types known and not yet known as well as possible large-scale orbital pertubations of planets and other celestial bodies in the solar system.

Other goals of this thesis are: (1) describe the Popigai impactoclastic layer in a new Italian section; (2) study the detrital rounded zircon grains from lower Paleocene pelagic limestones of the Bottaccione section in order to constrain the origin of co-occuring terrestrial chrome spinels; (3) resolve whether the mid-Ordovician L-chondritic parent body breakup directly affected Earth's climate and biota. (4) search for extraterrestrial spinels and classify the terrestrial chrome spinels recovered in the late Miocene Monte dei Corvi section.

The late Eocene marine sedimentary rocks at Massignano, Italy, were analysed for equilibrated, ordinary chondritic chromite (EC) content, yielding 28 EC grains (>63 µm) in a total of 1168 kg of rock. Most of these EC grains occur in the ~40 cm interval immediately above the Popigai ejecta layer. Element analyses reveal that grains in the lower half of this interval have an apparent H-chondritic composition, whereas L-chondritic grains dominate in the upper half. We argued that the grains may originate from the regoliths of the Popigai and the Chesapeake Bay impactors, respectively. The Popigai ejecta layer was recovered for the first time in a new Italian location at Monte Vaccaro. Due to the low content of diluting terrestrial chrome spinels in this section, it is ideal to investigate the small size fraction (32-63 µm), and thus resolving the late Eocene event in greater detail. The early Paleocene interval at the Bottaccione section shows a dominance of H-chondritic grains that is possibly is related to na H-chondritic parent body breakup during the late Cretaceous epoch. In the same interval detrital zircons were recovered and U-Pb analyses suggest that the mostly eolian terrigenous material originated from arid regions in northern Africa and southern Europe. In the Monte dei Corvi section (late Miocene), no extraterrestrial grains >63 µm could be recovered from an interval rich in ^{3}He. The L-chondritic parent body breakup (LCPB) occurred in the mid-Ordovician and was probably connected to ice-age conditions at that time. The ice age conditions are indicated by an eustatic sea-level fall related to global cooling triggered by the dust from the LCPB breakup**.**

Key words: chromite, He-3 anomaly, Cenozoic, mid-Ordovician, asteroid breakup, ordinary chondrites, Popigai ejecta, iridium anomaly, zircons, ice age.

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Cover illustration front: Fieldwork in the Monte Vaccaro section, Italy. Photo by Fredrik Terfelt.

Cover illustration back: Figure (Paper III) showing the interval studied at the Monte Vaccaro section (lithostratigraphy, biostratigraphic zonation, sample locations, impact spherules or pancake spherules [PS], and Ir distribution profile).

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Table of Contents

List of Publications **8**
Author's Contribution **10**
Popular Scientific Summary **11**
1 Introduction **14**
2 Aim of the Thesis **16**
2.1 Extraterrestrial Chrome-spinel Approach 16
2.2 Specific Goals 18
3 Materials and Methods **20**
3.1 Separation of Cr spinels and chemical analyses 20
3.2 Iridium, spherules and shocked quartz 21
3.3 Iridium analyses 21
3.4 Separation of zircons and chemical analyses 22
4 Geological Settings **24**
4.1 The Massignano section, Ancona, central Italy 25
4.2 The Monte Vaccaro section, Piobbico, central Italy 26
4.3 The Monte dei Corvi section, Monte Conero, central Italy 27
4.4 The Bottaccione section, Gubbio, central Italy 27
4.5 The Hällekis-Thorsberg section, Kinnekulle, southern Sweden 28
5 Summary of Papers **30**
5.1 Paper I 30
5.2 Paper II 30
5.3 Paper III 32
5.5 Paper IV 34
5.6 Paper V 35
5.7 Paper VI 36
5.8 Paper VII 37
6 Conclusions **38**
7 References **42**
Acknowledgements **50**

List of Publications

PAPER I:

Title: Fragment of late Eocene Earth-impacting asteroids linked to disturbance of asteroid belt.

Authors: Schmitz, B., Boschi, S., Cronholm, A., Heck, P.R., Monechi, S., Montanari, A., and Terfelt, F.

Journal: Earth and Planetary Science Letters, v. 425, p. 77-83 (2015).

PAPER II:

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

Authors: Boschi, S., Schmitz, B., Heck, P.R., Cronholm, A., Defouilloy, C., Kita, N.T.,Monechi, S., Montanari, A., Rout, S.S., and Terfelt, F.

Journal: Geochimica et Cosmochimica Acta, v. 204, p. 205-218 (2017).

PAPER III:

Title: Popigai impact ejecta layer and extraterrestrial spinels recovered in a new Italian location—The Monte Vaccaro section (Marche Apennines, Italy).

Authors: Boschi, S., Schmitz, B., Terfelt, F., Ros, L., Elfman, M., Kristiansson, P., Sulas, C., Monechi, S., and Montanari, A.

Journal: Geological Society of America Special Paper v. 542, p. 355-367 (2019).

PAPER IV:

Title: Distribution of chrome-spinel grains across the ^{3}He anomaly of the Tortonian Stage at the Monte dei Corvi section, Italy.

Authors: Boschi, S., Schmitz, B., and Montanari, A.

Journal: Geological Society of America Special Paper v. 542, p. 383-391 (2019).

PAPER V:

Title: Zircon provenance analysis from lower Paleocene pelagic limestones of the Bottaccione Section at Gubbio (Umbria-Marche basin, Italy).

Authors: Aguirre-Palafox, L.E., Alvarez, W., Boschi, S., Martin, E., and Schmitz, B.

Journal: Geological Society of America Special Paper v. 542, p. 159-174 (2019).

PAPER VI:

Title: An extraterrestrial trigger for the mid-Ordovician ice age: dust from the breakup of the L-chondrite parent body.

Authors: Schmitz, B., Farley, K.A., Goderis, S., Heck, P.R., Bergström, S.M., Boschi, S., Claeys, P., Debaille, V., Dronov, A., van Ginneken, M., Harper, D.A.T., Iqbal, F., Friberg, J., Liao, S., Martin, E., Meier, M.M.M., Peucker-Ehrenbrink, B., Soens, B., Wieler, R., and Terfelt, T.

Journal: Science Advances v. 5, no. 9, eaax4184 (2019).

PAPER VII:

Title: The micrometeorite flux to Earth during the earliest Paleogene reconstructed in the Bottaccione section (Umbrian Apennines) Italy.

Authors: Boschi, S., Schmitz, B., Martin, E., and Terfelt, F.

Journal: Manuscript.

Author's Contribution

PAPER I: I took part in the samples collection field trip, prepared some of the samples and analysed most of them. I contributed to the interpretation of the data and helped to write the paper.

PAPER II: I was responsible for collecting the samples at the section. I conducted most samples preparation processes, analysed all the data and wrote the manuscript with input from the co-authors.

PAPER III: I discovered the impact ejecta in the Monte Vaccaro section. I was responsible for planning and collecting samples at the section, and conducted all the sample preparation for different analyses (chromite, impact spherules, shocked quartz and iridium). I described and recovered impact spherules and shocked quartz, analysed the chromite grains and wrote the manuscript with input from the co-authors.

PAPER IV: I took part in planning the field trip and collecting the samples, conducted the preparation of the samples, analysed the data and wrote the manuscript with input from the co-authors.

PAPER V: I took part in the samples collection field trip, reviewed the manuscript and was responsible for the lithological and sedimentological description of the section. I am responsible for the main figure in the paper.

PAPER VI: I prepared some of the samples and did most of the analyses of the chromites and interpreted the data. I reviewed the manuscript and contributed in the writing process.

PAPER VII: I took part in the first samples collection field trip and was responsible for planning the second field trip and collecting samples. I prepared most of the samples, analysed some of the grains and wrote the manuscript with input from the co-authors.

Popular Scientific Summary

The tradition is that geologists look down at Earth and astronomers look up at the sky, however, a new approach can relate events in the skies to events on Earth by looking down into the terrestrial sediments. The astronomical events can play an important role in climate changes and evolution of life on Earth. This new approach can combine geology, biology and astronomy together and creating a true "astrogeobiosphere" perspective (astrogeobiology research field). The discovery of a global iridium anomaly at the Cretaceous-Paleogene boundary (K-Pg, 66 Ma ago) (Alvarez et al. 1980; Smit and Hertogen, 1980) was crucial for the development of the astrogeobiology field. The K-Pg Ir anomaly was interpreted as evidence for impact of an asteroid or comet ~10 km diameter causing one of the largest species mass extinction in Earth's history. Since the Alvarez et al. (1980) and Smit and Hertogen (1980) studies a number of new methods have been developed that facilitate the searching for asteroid or comet impact signatures in sedimentary rocks. The most common methods are: iridium and osmium concentrations, chromium isotope anomalies, glassy spherule-beds, shocked quartz, Ni-rich spinels, ^{3}He concentrations and extraterrestrial chromite grains concentration/types.

In this thesis, the extraterrestrial chromite approach was used to reconstruct the flux variation in different intervals of time of our past. Chromite belongs to a group of highly resistant minerals called spinels, which are relatively common in ordinary stony asteroids. The extraterrestrial materials that fell in the sea were incorporated into the calcareous sediments on the sea floor. By accumulation and consolidation the calcareous sediments became sedimentary rock (limestone). The limestone was uplifted by Earth's internal forces (tectonics) and today these sedimentary rocks are cropping out on land (sedimentary rock section). The sediment can record enrichments of ^{3}He and iridium isotopes, which are rare elements on the surface of Earth but more abundant in extraterrestrial material.

The core of this thesis is based on extracted extraterrestrial chromite grains from over 3355 kg of rock collected from five different geological sections. The rocks collected were dissolved in different strong acids and the insoluble residue, containing the chromite grains, was investigated under a binocular microscope. The chromite grains are completely unaffected by the harsh Earth environment during millions of years as well as by the tough acid leaching. Terrestrial chromite grains are also common minerals dispersed in the sediment and they have a wide range in chemical composition. Although terrestrial and extraterrestrial chromite has a similar appearance and similar size range, the extraterrestrial chromite grains have a narrow well-defined chemical composition that enable an unambiguous differentiation between terrestrial and extraterrestrial grains.

This thesis aims at linking the history of Earth in a specific interval to the astronomical realm, by recording extraterrestrial chrome-spinel grains and other extraterrestrial proxies in Cenozoic (early Paleocene, late Eocene and late Miocene) and mid-Ordovician sediments. These periods are characterized by enhanced flux of ^{3}He-enriched interplanetary dust particles to Earth. In the late Miocene Monte dei Corvi section (from 11.63 to 5.33 Ma ago), Italy, no extraterrestrial chromite grains were recovered and during the early Paleocene (from 66 to 61.6 Ma ago) a special type of chromite grain from iron-rich stony asteroids called H-chondrites dominated and was found in correspondence with an inferred ^{3}He anomaly peak at the Bottaccione section, Italy. Mineral analyses from this section suggest that the terrigenous material originated from the large arid region of Northern Africa and from the exposed semi-arid areas of southern Europe.

The largest documented asteroid disruption event in the late solar system history was the breakup of the L-chondrite parent body (LCPB) at ~466 Ma ago. After the LCPB there was a boost in the flux of the most fine-grained material representing three to four orders of magnitude higher concentrations compared to that of much younger sediments (~36 and ~91 Ma old). Extraordinary amounts of dust during >2 Ma following the L-chondrite breakup can be connected with a cooling trend of the Earth which triggered Ordovician icehouse conditions and a global sea-level fall.

The late Eocene (37.8–33.9 Ma ago) was a time which recorded an enhancement of the extraterrestrial flux to the Earth. The evidence come primarily from ^{3}He-rich sediments, an iridium anomaly and several medium- to large-sized impact structures, including the Popigai impact crater (100 km in diameter, located in Siberia) and the Chesapeake Bay impact crater (40–85 km, located on the North-America east coast). The Massignano section in Italy was the first location where all these extraterrestrial features were recovered and described. In the present project, the Popigai ejecta layer (material from the impact event that is thrown up in the atmosphere and later deposited) was recovered from another locality in Italy (Monte Vaccaro section, Piobbico), representing the first new discovery of this layer after the original characterization at the Massignano section (papers III). In papers I and II of this thesis, the Massignano section was investigated and sampled to recover extraterrestrial chrome-spinel grains. In this section most of the extraterrestrial grains were recovered in the ~40 cm interval immediately above the Popigai ejecta layer. In the lower part of the interval the grains showed an H-chondritic composition and the upper part recorded an L-chondritic (with lower iron content than the H-type) dominance. We speculate that the extraterrestrial grains may originate from the loose surface material of the Popigai and the Chesapeake Bay impactors, respectively. The data hint at an asteroid shower involving different types of stony asteroids. This can possibly be explained by gravitational disturbances of the asteroid belt, located between Mars and Jupiter.

The late Miocene epoch or Tortonian age (Paper IV) recorded an exceptional event: a collisional disruption of the >150 km diameter asteroid that created the Veritas family 8.3 ± 0.5 Ma ago in the asteroid belt. This event increased the flux of interplanetary dust particles rich in ^{3}He to the Earth. In Paper IV three ~100 kg samples were collected in the Monte dei Corvi section within the ^{3}He peak interval. In total 1151 chrome spinel grains were recovered in the Monte dei Corvi section but none of the grains has an extraterrestrial origin. This negative result implies that the Miocene ^{3}He flux is associated with the breakup of a carbonaceous chondritic body such as the Veritas family forming event.

The mid-Ordovician (Paper VI) time was characterized by the breakup of the L-chondrite parent body in the asteroid belt, a biodiversification event and an ice age. In Paper VI we investigated marine limestone exposed in the composite Hällekis-Thorsberg section at Kinnekulle in southern Sweden. The results of all the parameters studied show that ice-age conditions in the mid-Ordovician, postulated by other research groups were triggered or intensified by the LCPB breakup. This icehouse condition can be explained by an eustatic sea-level drop related to global cooling sparked by the dust from the LCPB breakup.

In Paper VII we reconstructed the flux of extraterrestrial material in the early Palaeocene interval at the Bottaccione section, Gubbio Italy. The Bottaccione section, Italy, with its famous and well-studied pelagic sequence spanning the Jurassic to the late Eocene is ideal for reconstructing the micrometeorite flux to Earth using sediment-dispersed, refractory chrome-spinel grains. For the present study 633 kg of marine limestone was collected from the early Paleocene part of the section and searched for chrome-spinel grains. The results indicate that during the early Paleocene, the H-chondritic grains strongly dominated the meteoritic flux over L and LL grains. The early Paleocene study results together with the Turonian data indicate the presence of an anomalous period connected with an enhanced flux of H-chondritic matter. During the Turonian an H-chondritic parent body break up possible took place.

In conclusion, the late Eocene and early Paleocene periods show H-chondritic dominance. The Paleocene data together with previous data for the late Cretaceous suggest an H-chondritic parent body break up during the late Turonian. In the mid Ordovician the extraordinary amounts of dust in the entire inner solar system related with the L-chondrite breakup, cooled Earth and triggered Ordovician icehouse conditions and sea-level fall.

1 Introduction

Geology is the science that studies the Earth (geo means earth, and logy means study of) and astronomy is the branch of science, which deals with celestial objects, space, and the physical universe as a whole. Geology involves studying rocks, features and structures present on the Earth as well as the physical processes of our planet in order to understand how it has changed over time, its origin and history. Traditionally, geology and astronomy have been considered two separate subjects. For example, in the past the geologists regarded Earth as a more or less closed system. Only recently it has been accepted that astronomical events can play a crucial role in the evolution of life on Earth (e.g. Alvarez et al., 1980; Alvarez et al., 2003; Alvarez et al., 2019). Evidence of this astronomical influence is represented by numerous craters on the Earth's surface related to impacts of extraterrestrial objects. A new approach can relate events in the solar system to events on Earth, by looking down into Earth's sedimentary record.

The accretion of extraterrestrial matter through Earth history is a new cross-disciplinary research field (see Peucker-Ehrenbrink and Schmitz, 2001). The extraterrestrial features recovered in Earth's sedimentary record can link together the geobiosphere and the astrosphere. This combined with classical astronomy creates a true "astrogeobiosphere" perspective. As summarized by Schmitz (2013) at the early stages of this research field a few visionaries realized that the evolution of animals on Earth could be affected by cosmic events. For example, Nininger (1942) argued that faunal extinctions during Earth history could be connected to impacts of large extraterrestrial bodies. Schindewolf (1954, 1963) suggested that the evolution is not gradual as proposed by Darwin but rather is characterized by a series of mass extinction and diversification events. The breakthrough came with the discovery of an iridium (Ir) anomaly at the K-Pg boundary at the Bottacione section, Italy (Alvarez et al., 1980) and in the Spanish section of Caravaca (Smit and Hertogen, 1980). The K-Pg Ir anomaly was interpreted as reflecting an impact of a major extraterrestrial body causing one of the largest species mass extinction events in Earth history. The idea that the demise of the dinosaurs was due to a comet or asteroid impact, however, was proposed repeatedly during the 20th century (De Laubenfels, 1956; McLaren, 1970; Urey, 1973). Alvarez et al. 1980 for the first time related the impact event hypothesis with evidence recorded in the Earth's sediments. This theory has now withstood thirty years of intense testing (Schulte et al., 2010). A 10 km-sized impactor hit the Yucatan peninsula, Mexico 66 Ma ago forming the ~150–200 km large Chicxulub crater (Kring et al., 1991; Hildebrand et al., 1991). The event eradicated the dinosaurs after their ~165 Ma successful existence on this planet (Lyson et al., 2011), but also seriously affected most groups of common marine invertebrates.

After the discovery of the iridium anomaly at the K-Pg boundary (Alvarez et al., 1980 and Smit and Hertogen, 1980), several other methods have been developed for searching signatures of extraterrestrial events in the sedimentary record. To measure the concentration of iridium and osmium in the sediment is the most used proxy (Paquay et al., 2008; Miller et al., 2010; Ravizza and VonderHaar, 2012). Other proxies used are: chromium isotope anomalies (Kyte et al., 2011), impact related spherule-beds (Smit and Klaver 1981; Glass 2002; Glass and Burns1988; Glass and Simonson, 2012; Krull-Davatzes et al., 2012; Alvarez 2019), shocked quartz (Claymer et al., 1996; Bron and Gostin, 2012), and Ni-rich spinels formed on Earth in impact vapor clouds (Robin and Molina, 2006). The variations in flux to Earth of extraterrestrial debris in the macro-meteorites to fine dust size fraction was reconstructed by a few studies. For example, ^{3}He has been used for tracing variations in the flux of interplanetary dust particles (Farley et al., 2012). Recovery of fossil meteorites in Ordovician limestone (Schmitz et al., 2001) is so far the only method to reconstruct macro meteorite fluxes.

Here, the focus is on recovering and studying the extraterrestrial chrome spinels dispersed in sediments of different geological epochs in order to reconstruct the evolution of the astrogeobiosphere.

2 Aim of the Thesis

2.1 Extraterrestrial Chrome-spinel Approach

The chrome spinel approach has its roots in a fossil meteorite discovery in the middle Ordovician, ~462 Ma old marine limestone from the Brunflo quarry, central Sweden (Schmitz, 2013). The spinel grains recovered in the meteorites proved to be extremely resistant to weathering and alteration in the terrestrial environment (Thorslund et al., 1984; Nyström et al., 1988) and they can be recovered from sediments of almost any age over the past 3.5 Ga (Schmitz et al., 2003; Schmitz and Häggström, 2006; Cronholm and Schmitz, 2007, 2010). In the mid-Ordovician period (~466 Ma ago) the L-chondritic parent body breakup in the asteroid belt left a signature in the geological record (Schmitz et al., 2001, 2003, 2008) and the development of the spinel approach relies on the studies of marine sediments that formed in this period. The extraterrestrial chrome-spinel method, however, can be applied to any time in Earth's history for which there are slowly accumulated sediments available. This approach can determinate the class, group and even petrologic type of the meteorite from which the sediment-dispersed extraterrestrial spinel grain originated (e.g., Schmitz et al., 2001, 2003; Alwmark and Schmitz, 2009; Heck et al., 2010).

Chromite belongs to a group of highly resistant accessory minerals called spinels, which are the most abundant oxides in equilibrated ordinary chondrites (Rubin, 1997). The chondrite meteoritic group is part of the stony (or stone) meteorites. The stony meteorites are the most common meteoritic type, and they are further divided into chondrites (> 95%) and achondrites (< 5%) based on presence of chondrules in the matrix. Chondrules are small spherical inclusions that represent the oldest solid matter within our solar system. Chondrites are also divided in three classes: ordinary (95.7%), carbonaceous (3.1%) and enstatite (0.7%) chondrites, respectively. The ordinary chondrites are the most common meteorites that fall on the Earth today. Following the olivine, pyroxene and metal compositions, the ordinary chondritic group can be subdivided into three subgroups (H, L and LL) (Bunch et al., 1967; Afiattalab and Wasson, 1980; Rubin, 1997). The "H" and "L" stand for high and low iron, respectively; whereas "LL" stands for low iron and low free metal content.

The chromite grains recovered in equilibrated ordinary chondrites (EC) (Fig. 1), have narrowly defined ranges for Cr_2O_3 (~53.0-62.0 wt%), FeO (~23.0-32.0 wt%),

Al_2O_3 (~4.5-8.5 wt%), MgO (~1.3-4.5 wt%), V_2O_3 (~0.55-0.95 wt%), and TiO_2 (~1.40-4.50 wt%) (Schmitz and Häggström, 2006; Schmitz, 2013). The EC grains can be dived into the three subgroups depending of their TiO_2 content; H $\leq$ 2.5 wt%, L = 2.51-3.39 wt% and LL $\geq$ 3.40 (Heck et. al., 2016, Schmitz et. al., 2017). The EC classification can also be performed with oxygen-3-isotopic analysis, but it has been shown that the TiO_2 separation approach is as effective as the oxygen isotopic analyses (Heck et al., 2016).

Terrestrial chromium-rich spinels are also common in sediments and in terrestrial rocks. They are often found in relation with peridotite and other layered ultramafic intrusive rock, as well as metamorphic rocks (Barnes and Roeder, 2001). Although extraterrestrial and terrestrial chromite have similar optical appearances (black opaque grains) and similar size range (Fig. 1), they can easily be distinguished from each other by their elemental composition. The EC grains have a narrow chemical composition, as described above, and terrestrial chromium-rich spinels have a wide compositional range very rarely overlapping with that of the EC grains.

The EC grains are also divided into four informal groups (F1-F4) based on the amount of fractures (Alwmark et al., 2011) representing different levels of exposure to chock. The groups are F1: unfractured (Fig. 1A), F2: slightly fractured (Fig. 1B), F3: moderately fractured (Fig. 1C), and F4: heavily fractured (Fig. 1D). This classification does not show a unique distribution trend and there is not a group that is more common than the other.

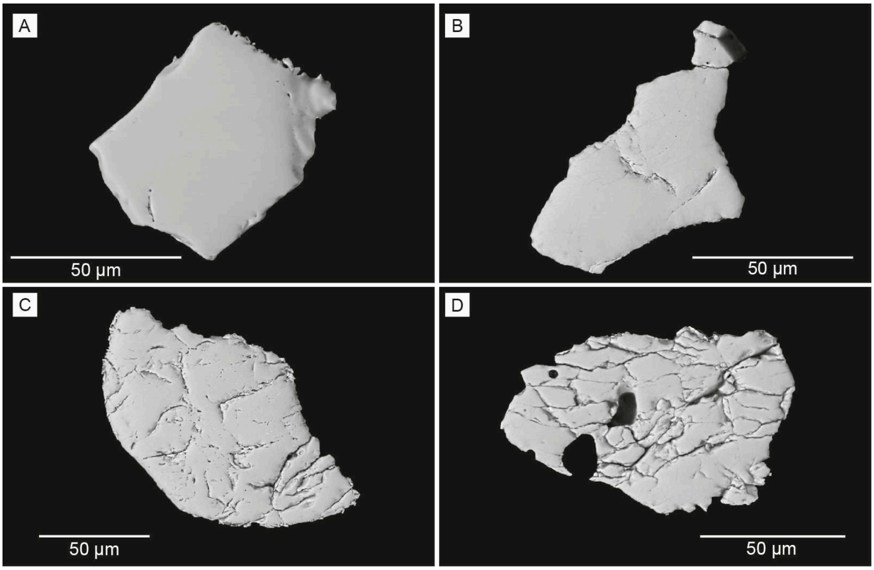

Figure 1. Back-scattered electron images for polished, representative extraterrestrial chromite grains from the Massignano section. (A) Grain of fracture type F1, unfractured. (B) Grain of fracture type F2, slightly fractured. (C) Grains of fracture type F3, moderately fractured. (D) Grains of fracture type F4, heavely fractured.

2.2 Specific Goals

The purpose of the thesis is to investigate extraterrestrial spinels in Cenozoic and mid-Ordovician sediments in order to reconstruct variations in the meteorite flux to Earth. The research links the history of the asteroid belt to the history of Earth. To accomplish this, substantial fieldwork and laboratory work has been carried out. Topics discussed in the thesis have been formulated accordingly:

I) Search for extraterrestrial spinels at the Massignano section at a higher resolution than in a previous study (Schmitz et al., 2009). In the study a total of 491 kg of limestone, in addition to the previous 167 kg (Schmitz et al., 2009), were collected in the Massignano section with a focus on the interval around the Popigai ejecta bed.

II) Search for extraterrestrial chrome spinels in addition to the previous studies by Schmitz et al. (2009, 2015). A primary objective was to produce a more robust estimate of the ‘‘background” concentrations of extraterrestrial spinels in the section. A secondary objective was to constrain in greater detail the stratigraphic relation between the Popigai ejecta and the abundant chondritic spinel grains recovered. 5 extraterrestrial chrome-spinel grains recovered from immediately above the Popigai ejecta were also analysed for oxygen three-isotopes with secondary ion mass spectrometry. We presented and discussed 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).

III) Investigate a new Italian location, the Monte Vaccaro section, ~90 km west of Massignano, in order to search for the Popigai ejecta layer. The impact ejecta layer was discovered in the Monte Vaccaro section and is characterized by abundant pancake spherules, a prominent Ir anomaly, and shocked quartz, just like at Massignano. We also reported the occurrence of extraterrestrial chromite grains in the Monte Vaccaro section, and we show that this section is much better suited for reconstructions of the micrometeorite flux to Earth as compared to the Massignano section.

IV) Recover extraterrestrial chromite grains at the Monte dei Corvi section (Tortonian-early Messinina) connected with a ^{3}He anomaly, corresponding to the approach carried out for the late Eocene ^{3}He anomaly in the nearby Massignano section (Boschi et al., 2017). The late Miocene ^{3}He anomaly is similar in duration and magnitude to that in the late Eocene. There is a prominent 9–7 Ma peak in the cosmic-ray exposure ages of recent H-chondrite falls and finds (Wieler and Graf, 2001); therefore, a major goal was to test if the Tortonian ^{3}He anomaly was related to an H-chondrite breakup event.

V) Study the detrital rounded zircon grains recovered from the lower Paleocene pelagic limestones of the Bottaccione section. By using U-Pb zircon geochronology analyses, identify and geographically constrain the provenance of the emplaced eolian terrigenous dust material, and in turn reconstruct prevalent wind patterns over the Umbria-Marche basin during the early Paleocene. This also helps in constraining the origin of the terrestrial chrome-spinel grains in the samples.

VI) Resolve whether the LCPB breakup directly affected Earth's climate and biota, using new, high-resolution, multiparameter data (chrome spinel, He and Os isotopes) to locate the precise level in the sedimentary strata that corresponds to the LCPB break up event. These data were compared with previous noble-gas data for chromite grains from large fossil meteorites (Heck et al., 2004, 2008), which can be used for an impartial appraisal of the timing of the LCPB breakup.

VII) Reconstruct the extraterrestrial flux during the early Paleocene. The data provide the first insight on the types of micrometeorites and interplanetary dust particles that fell on Earth during the early Paleocene epoch.

3 Materials and Methods

3.1 Separation of Cr spinels and chemical analyses

The sample processing was performed at the Astrogeobiology Laboratory, especially designed for dissolution of large rock samples and to separate microscopic spinels (www.astrogeobiology.org). All samples were carefully washed to remove weathered superficial material and dirt, and then decalcified in large 500-liter barrels with 6 M hydrochloric acid. The residue was sieved at 32 µm in order to wash out the fine clay minerals and leached in 11 M hydrofluoric acid at room temperature to remove silicates for two days. After sieving them again at 32 µm, the samples were treated with sulfuric acid to dissolve natural hydroxide minerals and laboratory-induced calcium fluoride. The insoluble residue was further density separated with LST liquid (lithium heteropolytungstate) and the low-density organic material was burned in a furnace at 550 °C for 10 hours. The final, heavy residue was separated into two size fractions; 32-63 µm and 63-355 µm, respectively. Both size fractions were searched under a binocular microscope and the black opaque grains deduced to be chrome-spinel grains were picked with a fine brush and transferred onto a carbon tape. The grains were analysed semi-quantitatively in an unpolished state both for major and for trace elements with a calibrated energy-dispersive spectrometer (EDS) attached to a scanning electron microscope (SEM). The grains confirmed to be chrome spinels by the preliminary analyses were mounted in epoxy resin together with analytical standard UWCr-3 (Heck et al., 2010) and polished using 1 µm diamond paste.

In order to assess the quality of our analyses we analysed some chrome-spinel grains both at the Vienna Natural History Museum and at the Astrogeobiology Laboratory, Lund University. In Vienna the element concentrations were analysed quantitatively by wavelength dispersive spectroscopy using a JEOL "Hyperprobe" JXA 8530-F field-emission electron microprobe (FE-EPMA) after a careful back-scattered electron imaging examination for zoning, inclusions and weathering processes. An accelerating voltage of 15 kV, a beam current of 20 nA, 1 µm beam diameter and a counting time of 10 s, giving approximately 250.000 counts, for peak and 5 s for background were used for all element Kα lines. The results for each individual chrome-spinel grain represents the average of three to five separate spot analyses, ensuring better statistics and reproducible data. Precisions of concentration analyses for each element were typically better than 1 rel.% of measured values. In Lund, a minor fraction of our recovered grains was analysed with the same SEM/EDS approach at Lund University as in our previous studies of chrome spinels (e.g., Schmitz et al., 2017; Martin et al., 2018). The recovered grains were analysed with an Oxford Inca X181 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 were used. Precision of analyses was typically better than 1–4 %. Analytical accuracy was controlled by analyses of the USNM 117075 (Smithsonian) chromite reference standard (Jarosewich et al., 1980).

3.2 Iridium, spherules and shocked quartz

In order to measure the iridium content in the interval studied, ~3 g of each sample collected were ground to a fine powder in an ultraclean agate mortar. Clean quartz sand was ground between the different samples in order to avoid any cross-contamination between samples. Samples suspected to have high iridium concentrations were ground last. About 10 g aliquots of each sample were dissolved in hydrochloric acid, and the insoluble residues >63 µm were searched under a binocular microscope for pancake spherules, which were recovered and counted. In order to verify the presence and abundance of shocked quartz grains relative to non-shocked grains, 300 g samples were collected. The samples were dissolved in 10% diluted HCl, and the residue material >63 µm was carefully sprinkled on a petrographic slide and covered with index oil. Each slide was examined using a petrographic microscope, and the grains characterized by one or more sets of planar structures possibly representing shock-induced planar deformation features (PDFs) were counted.

3.3 Iridium analyses

The Ir analyses were performed with the triplet coincidence iridium spectrometer built at the Nuclear Physics Division, Lund University, Lund, Sweden. The instrument represents an improvement of the Luis-W.-Alvarez- Iridium Coincidence Spectrometer built at the Lawrence Berkeley National Laboratory in the 1980s (Alvarez et al., 1982). This triplet Ir spectrometer measures low concentration of Ir, typically 10 ppt and upward, in neutronactivated samples. 200 mg aliquots of sample mass were sealed in Heraeus Suprasil quartz ampoules. The ampoules were irradiated at the Hoger Onderwijs Reactor in Delft, Netherlands. The samples were irradiated for 18 h with a thermal neutron flux of 2.5 x 1013 n/cm^2/s. Together with the samples, there were two standards of DINO-1 (Alvarez et al., 1982). A more thorough technical description of the triplet coincidence iridium spectrometer is found in paper III.

To extract the Ir signal to be used to calculate the concentration in the sample, the procedure was:

(1) Select events with three gamma rays within 1 ns.

(2) Require that the three gamma rays, ordered after energy, should be within a given sphere in three-dimensional gamma space.

(3) Plot the three gamma energies in individual spectra, and apply the following selection criteria for the events to pass: All individual gamma energies are within 10 keV of the respective peak value 296 keV, 308 keV, or 316 keV.

(4) Extract the number of counts in the one and only peak ranging around 921 ± 30 keV.

(5) Subtract the non-negligible background signal; since the background is dominated by signals from decays of Sc, Co, and Cs, it can be directly calculated from the measured amounts of these elements.

(6) If desired, extract signals of other elements in a similar way using either double or triple coincidences. In the case of Hf, the non-negligible half-life in the decay chain was also used, with typical sensitivity in the ppb range.

(7) Finally, normalize all data to the DINO-1 standard that followed the samples throughout the process. In this way, the effects of neutron flux and exact irradiation time are eliminated.

3.4 Separation of zircons and chemical analyses

At the Astrogeobiology laboratory at Lund University, recovery of the zircon grains was a fortunate by-product of the study of chromite grains for the determination of the kinds of meteorites that have fallen on Earth through time (see separation of Cr spinels and chemical analyses section). Suspected zircon grains were handpicked with a fine brush and then analysed for the presence of zirconium and silicon using an energy-dispersive spectrometer (EDS) attached to a scanning electron microscope (SEM).

At the Arizona LaserChron Center, located at the University of Arizona, the Bottaccione zircon grains were transferred onto a sticky tape surface along with zircon-standard grains of known ages: FC-1 (1099 Ma), SLM (563.5 Ma), and R33 (420 Ma). A 1-inch-diameter epoxy mount with these grains was prepared, ground to a depth of ~20 µm and then polished with the help of a MiniMet 1000 Grinder-Polisher and a VibroMet 2 Vibratory Polisher. Cathodoluminescence (CL) images using a Gatan ChromaCL2 detector, and Backscattered electrons (BSE) images obtained from the Hitachi 3400N SEM, were taken to improve the selection of spot locations preceding isotopic analysis and subsequently aid in the interpretation of results. U-Pb zircon geochronology analyses were conducted by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a Photon Machines Analyte G2 excimer laser equipped with HelEx ablation cell that uses a spot diameter of 20 μm. The ablated material was then carried into the plasma source of an Element 2 HR ICPMS, and signal intensities were measured with an SEM.

4 Geological Settings

In the present project, five geological sections were investigated (Fig. 2); one located in Sweden and four in Italy (Fig. 2A, B). The sections' geological settings are listed and described below according to this thesis papers order: Massignano section (Fig. 2A, 3A), Monte Vaccaro section, Piobbico (Fig. 2A, 3B), Monte dei Corvi section (Fig. 2A, 3C), Bottaccione section, Gubbio (Fig. 2A, 3D) and Hällekis-Thorsberg section (Fig. 2B, 3E).

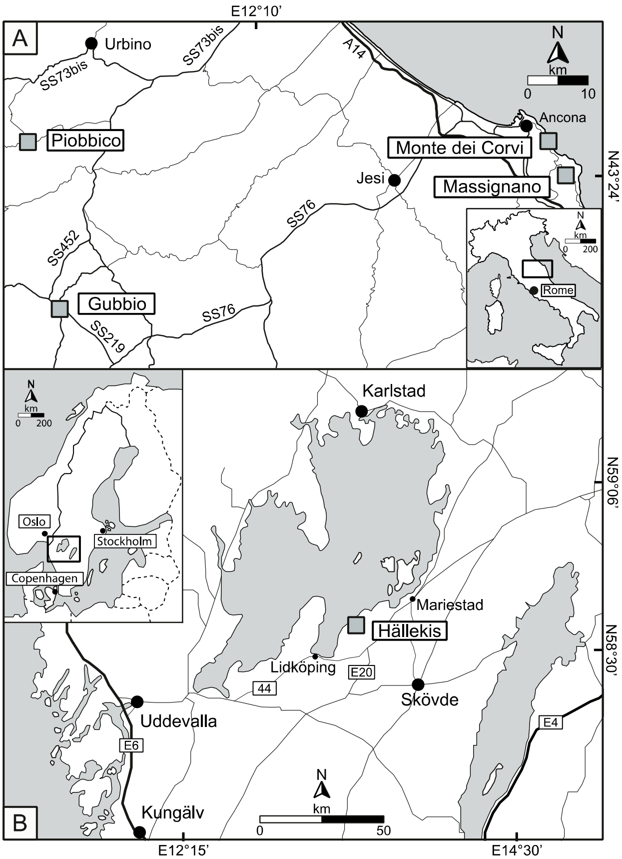

Figure 2. (A) Map of estern central Italy and geographical location of Massignano, Monte dei Corvi, Gubbio and Piobbico areas. (B) Maps of Sweden (Västergötaland) and geographical location of the Hällekis quarry.

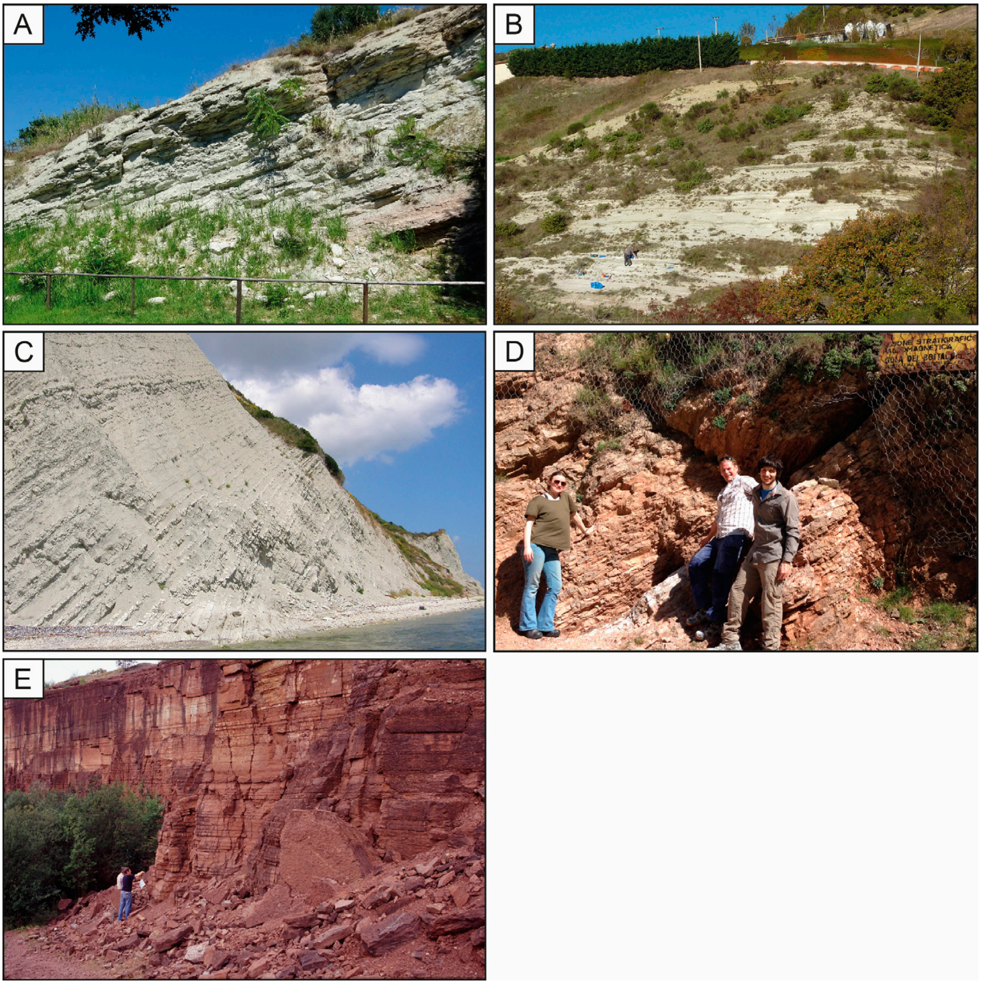

Figure 3. (A) The Massignano section, Ancona, eastern central Italy. (B) The Monte Vaccaro section, Piobbico, central Italy. (C) The Monte dei Corvi section, Ancona, eastern central. (D) Cretaceous-Paleocene (K-Pg) boundary at the Bottaccione section, Gubbio, central Italy. (E) The Hällekis section, Kinnekulle, southern Sweden.

4.1 The Massignano section, Ancona, central Italy

The Massignano section is the Global Boundary Stratotype Section and Point (GSSP) for the Eocene–Oligocene boundary (Premoli Silva and Jenkins, 1993). The section is located in an abandoned quarry on the Ancona-Sirolo road of the Conero Regional Natural Park near the village of Massignano, Ancona (northeastern Apennines, Italy) (Fig. 2A, 3A). The section comprises two different formations: Scaglia Variegata and Scaglia Cinerea, which were deposited in the entire Umbria-Marche basin. At the Eocene/Oligocene transitional time interval, these pelagic, biomicritic limestones and marly limestones were accumulated in the upper part of a lower bathyal setting representing 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. 4). 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 positions for this bed. According to Montanari et al. (1993) and Huber et al. (2001) the ejecta occurs in the 5.61-5.75 m interval. 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 stays high (100–200 ppt), up to 5.85 m (Fig. 4). The Popigai ejecta bed is also characterized by 1– 20 µm sized Ni-rich spinels formed from the vapor cloud generated by the impact, shocked quartz, and 100–600 µm sized iron-rich smectite informally referred to as pancake spherules (Clymer et al., 1996; Pierrard et al., 1998; Glass et al., 2004). The pancake spherules represent weathered clinopyroxene-bearing spherules of the type that is found in the Popigai ejecta bed elsewhere. Two smaller (100–330 ppt) iridium anomalies were detected at meter levels 6.15 and 10.25 (Montanari et al., 1993; Bodiselitsch et al., 2004). Although there are uncertainties with regard to the causation of the two additional iridium anomalies, there seem to be no independent evidence for impact such as shocked quartz, Ni-rich spinels, or spherules associated with the 6.15 and 10.25 m levels.

4.2 The Monte Vaccaro section, Piobbico, central Italy

The Monte Vaccaro section is located near the town of Piobbico (43°35′20″N, 12°28′28″E) (Fig. 2A). The section appears very similar to the Massignano section, as well as the no-longer- accessible Contessa quarry section near Gubbio described by Montanari and Koeberl (2000). The Monte Vaccaro section consists of two formations (Fig. 3B): the Scaglia Variegata and Scaglia Cinerea, which were deposited during the late Eocene and early Oligocene in a lower bathyal setting of the Umbria-Marche pelagic basin at a paleodepth of ~1000–1500 m (Coccioni and Galeotti, 2003). At Massignano and at Gubbio, the uppermost Scaglia Variegata Formation is composed of alternations of reddish and greyish, more or less marly limestones. One of the more prominent shifts in colour from red to grey occurs right at the level of the impact ejecta bed (Fig. 5). The lithology is similar at Monte Vaccaro, and, in fact, we found the impactoclastic layer placed a few centimeters below the level of the last prominent colour change, from reddish-grey to plain grey (Fig. 5). All throughout the Umbria-Marche region, the lower part of the Scaglia Cinerea Formation is composed of plain greenish-grey, more or less marly limestones (Coccioni et al., 2008). As shown here and by Sulas (2017), the Monte Vaccaro section spans the same interval as the Massignano section, i.e., calcareous nannofossil zones NP19–20 to NP21 of Martini (1971), CP15a to CP16.

4.3 The Monte dei Corvi section, Monte Conero, central Italy

The Monte dei Corvi section is located ~8 km south of Ancona, Italy, and it represents the global stratotype section and point (GSSP) for the Tortonian Stage (Hilgen et al., 2005) (Fig. 2A, 3C). During the mid-Miocene, pelagic sedimentation in the Umbria-Marche basin was interrupted by the arrival of siliciclastic turbidites from the Alps, namely, the Marnosa Arenacea Flysch. This interruption did not occur in the easternmost part of the Umbria-Marche basin, along the anticlinal Adriatic promontory between the city of Ancona and Monte Conero (Montanari et al., 1997, 2017, and references therein). In this area, turbidite-free, hemipelagic carbonates spanning the entire Miocene Epoch up to the early Pliocene are well exposed on the cliffs of the Conero Riviera (Fig. 3C). The siliciclastic component is made up of hemipelagic, terrigenous silt and clay of alluvial origin. The interval studied here comprises only the Tortonian upper part of the Schlier Formation (Fig. 6). This unit consists of a rhythmic alternation of prominent marls and marly limestones with recessive sapropelic horizons (Montanari et al., 1997; Hilgen et al., 2003; Hüsing et al., 2010) (Fig. 6). In this stratigraphic interval, there is a distinctive brownish member (up to meter level 127.8), which consists of an alternation of grey-blue and brown marly layers (Fig. 6).

4.4 The Bottaccione section, Gubbio, central Italy

The pelagic sequence at the Bottaccione Gorge, Gubbio (central Italy), is probably the most prominent and well-studied section across the Cretaceous-Paleogene (K-Pg) boundary in the world (Premoli Silva, 1977; et al., 1980; Lowrie et al., 1990). Here Alvarez et al. (1980) discovered an iridium anomaly at the K-Pg boundary, later connected to an impact crater on the Yucatán Peninsula, Mexico, 66 Ma ago (Hildebrand et al., 1991; Shukolyukov and Lugamir 1998; Schulte et al., 2010; Lyson et al., 2011). The Bottaccione section is located in the central part of Italy in the Umbro-Marche Apennines, directly northeast of the town of Gubbio (43°22′ N, 12°35′ E, along the state road SS298 to Scheggia; see Fig. 2A). It extends for more than 400 m and it includes pelagic limestones from the uppermost Jurassic to the uppermost Paleogene. In the Bottaccione section, the K-Pg boundary is represented by a 1-2 cm thick dark clay layer underlain by a white bleached limestone zone, ~20-50 cm thick (Fig. 3D). This zone is probably related to more reducing sediment conditions when increased amount of organic material reached the sea floor during the K-Pg event (Lowrie et al., 1990; Montanari and Koeberl, 2000). The K-Pg boundary has a worldwide distribution and the clay layers contains excess amount of impact-related spherules and shocked quartz (Montanari and Koeberl, 2000).

The samples studied belonging to the Scaglia Rossa formation represents the middle part of the Bottaccione pelagic succession, from the early Turonian to the Ypresian (Arthur and Fischer, 1977; Monechi and Thierstein, 1985; Montanari et al., 1989) (Fig. 7). The formation consists of pink biomicritic limestone made up of planktonic foraminiferal tests suspended in a coccolith matrix with a terrigenous component of silt and clay considered to be of eolian origin (Arthur and Fischer, 1977; Johnsson and Reynolds, 1986) (Fig. 7). Agglutinated foraminifera indicate that during the late Cretaceous and Paleocene, the sedimentation in the Umbria/Marche basin occurred at a paleo depth of 1500-2500 m (Arthur and Fisher, 1977; Kunhnt, 1990). This formation is characterized by a number of marly horizons interbedded with the typical limestone of this formation (Arthur and Fischer, 1977; Montanari et al., 1989).

4.5 The Hällekis-Thorsberg section, Kinnekulle, southern Sweden

Kinnekulle is a 306 m high table mountain situated southeast of Lake Vänern, Västergötaland, formed primarily by sedimentary rocks of lower Cambrian to lower Silurian age (Fig. 2B). The middle Ordovician succession is dominated by limestone deposited in a shallow epicontinental sea that covered most of the Baltoscandian shield during this period (Lindström et al., 1971, 1979). The best exposure of the Orthoceratite Limestone at Kinnekulle occurs in the abandoned quarry at Hällekis-Thorsberg (lat. 58”37’N, long. 13”24’E) (Fig. 2B). This abandoned quarry consist of ~50 m thick succession of the red homogeneous Orthoceratite Limestone, an organic-poor sediment that formed at a very low sedimentation rate (2 ± 1 mm ka^{-1}) (Lindström et al. 1971, 1979; Schmitz et al. 1996) (Fig. 3E). The colour of the massive limestone beds varies from red to brownish red throughout the section, with the exception of the 1.2-1.4 m thick, grey Täljsten interval (Fig. 3E, 8).

The limestone succession in the Hällekis Quarry is contemporaneous with strata in the nearby Thorsberg Quarry (Fig. 2B) that has yielded >130 fossil meteorites.

All, except one of these meteorites are L chondrites and have been recovered over the entire 5 m stratigraphic interval quarried at Thorsberg, starting at the base of the bed colloquially referred to as ‘Arkeologen’. Measurements of ^{21}Ne in chromite grains from meteorites at different levels in the quarry have given sequentially longer cosmic ray exposure (CRE) ages, from ca. 0.1 to 1.2 Ma, with increasing stratigraphic height (Heck et al., 2004; Heck et al., 2008). This pattern is due to the circumstance that all meteorites originated from a single breakup event and reached Earth at different times and, hence, were exposed differentially to cosmic rays. The age succession is consistent with the average sedimentation rates for the strata, generally accepted to be in the order of 2 to 4 mm ka^{-1} [e.g., (Schmitz et al., 2014)]. The ^{21}Ne data place the LCPB breakup at a stratigraphic level between ~0.4 and 1.2 m below the base of the Arkeologen bed.

5 Summary of Papers

5.1 Paper I

Title: Fragments of late Eocene Earth-impacting asteroids linked to disturbance of asteroid belt.

Authors: Schmitz, B., Boschi, S., Cronholm, A., Heck, P.R., Monechi, S., Montanari, A., and Terfelt, F.

Journal: Earth and Planetary Science Letters, v. 425, p. 77-83 (2015).

Summary: The late Eocene, or Priabonian (~37.8–33.9 Ma ago) was a time characterized by an enhanced flux of extraterrestrial matter to the Earth. The evidence comes from two major and several minor impact craters, at least two microtectite-microkrystite layers, shocked quartz, iridium anomalies and a stratigraphic interval of elevated ^{3}He (extraterrestrial) sediment. The Massignano section, Italy, records all of these extraterrestrial signatures.

In this study a total of 658 kg of sediment from the ^{3}He-rich interval were collected at the Massignano section. In 1324 grains recovered in the section, only 25 grains have a typical extraterrestrial composition and they were all found in the 308 kg samples collected from the 65 cm interval immediately above the Popigai ejecta layer (Fig. 4). The chemical composition of 17 of these grains indicates that all or almost all are of H-chondritic origin and probably associated with the Popigai impact (Fig. 4). The remaining 8 extraterrestrial grains have an L-chondritic composition and are probably associated with the Chesapeake Bay impact.

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 support an asteroid shower involving different types of ordinary chondrites.

5.2 Paper II

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

Authors: Boschi, S., Schmitz, B., Heck, P.R., Cronholm, A., Defouilloy, C., Kita, N.T., Monechi, S., Montanari, A., Rout, S.S., and Terfelt, F.

Journal: Geochimica et Cosmochimica Acta, v. 204, p. 205-218 (2017).

Summary: In this article we report an extended chromite grain data set from samples collected in the Massignano section. In Schmitz et al. (2015), a total of 25 extraterrestrial chromite grains from ~210 kg of sample was recovered in the interval corresponding to the Popigai and Chesapeake Bay impacts (Fig. 4). In the present study 760 kg were analysed outside the impact layers and only 2 extraterrestrial chromite grains were found (Fig. 4). Both grains have L-chondritic compositions and they were found in a 100 kg sample from a level in the section where a second, smaller Ir anomaly has been reported. An oxygen three-isotope measurement of the extraterrestrial chromite grains associated with the Popigai ejecta confirmed an H-chondritic composition.

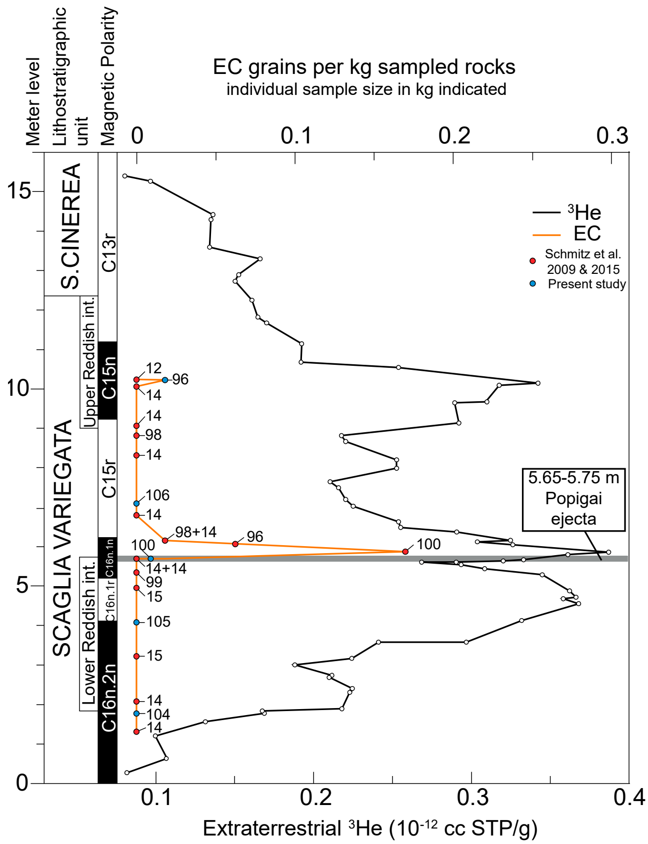

Figure 4. Profiles for the Massignano section of extraterrestrial ^{3}He concentrations (black curve) (Farley et al., 1998) and the total number of recovered EC grains per kg sediment (orange curve) in the present study and by Schmitz et al. (2009, 2015). Indicated in numbers on the latter curve are the sizes in kilogram of the samples searched for EC grains. Sample points marked in blue are new for the present study.

5.3 Paper III

Title: Popigai impact ejecta layer and extraterrestrial spinels recovered in a new Italian location—The Monte Vaccaro section (Marche Apennines, Italy).

Authors: Boschi, S., Schmitz, B., Terfelt, F., Ros, L., Elfman, M., Kristiansson, P., Sulas, C., Monechi, S., and Montanari, A.

Journal: Geological Society of America Special Paper 542, p.355-367 (2019).

Summary: The Popigai (100 km in diameter) and the Chesapeake Bay (40-85 km) impact structures formed within a time span of 10-20 ka and characterizes together with a ^{3}He interplanetary dust anomaly, the Late Eocene (Priabonian) enhanced flux of extraterrestrial matter to Earth. The Popigai impact structure is located in Siberia and it has a radiometric age of 35.7 ± 0.5 Ma. The ejecta from the impact crater has been recovered in late Eocene sediments in the Massignano section, near Ancona, Italy (Montanari et al., 1993) (Fig. 4). The ejecta layer in the Massignano section is not represented by a distinct bed and can thus be difficult to distinguish in the field. The impact layer is associated with an iridium anomaly, shocked quartz, and abundant altered clinopyroxene-bearing spherules called pancake spherules. Recently we showed that the ejecta is also associated with a significant enrichment of H-chondritic chromite grains (>63 µm) possibly representing unmelted fragments of the impactor (Boschi et al., 2017).

In this article, the Popigai ejecta layer was discovered in a new Italian location at the same biostratigraphic level as in the Massignano section, representing the first record of this event outside the Massignano section. The Popigai ejecta layer in the Monte Vaccaro section contains shocked quartz, abundant pancake spherules and an iridium anomaly of 700 ppt, which is three times higher than the peak measured in the ejecta layer at Massignano (Fig. 5). The Monte Vaccaro biostratigraphy was established on calcareous nannoplankton and it shows a good correlation with the Massignano section. Preliminary analyses of chromite from a 100 kg sample collected just above the Popigai ejecta layer showed an enrichment of H-chondritic grains.

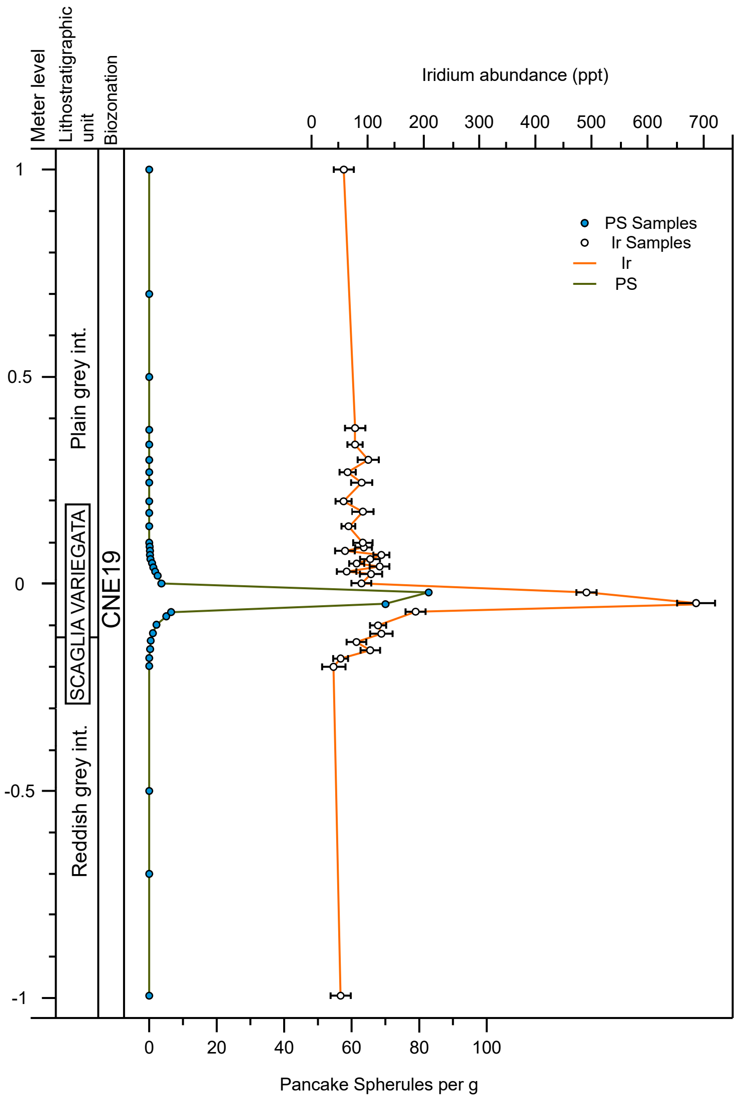

Figure 5. Monte Vaccaro section interval studied at high resolution (lithostratigraphy, biostratigraphic zonation, sample locations, pancake spherules [PS], and Ir distribution profile).

5.4 Paper IV

Title: Distribution of chrome-spinel grains across the ^{3}He anomaly of the Tortonian Stage at the Monte dei Corvi section, Italy.

Authors: Boschi, S., Schmitz, B., and Montanari, A.

Journal: Geological Society of America Special Paper 542, p. 383-391 (2019).

Summary: The Miocene Epoch was a time when the northern Apennines accretionary wedge was built up and the present day ocean-climate system configuration took shape (Montanari et al., 2017). The Messinian (late Miocene) recorded a salinity crisis, and during the late Tortonian there was another exceptional event that might have affected the global climate and ecology system: a collisional disruption of the >150 km diameter asteroid that created the Veritas family 8.3 ± 0.5 Ma ago in the asteroid belt. This event increased the flux of interplanetary dust particles rich in ^{3}He to the Earth (Farley et al., 2006). The late Miocene ^{3}He anomaly has been registered in two drill cores from the Ocean Drilling Program (ODP); ODP site 926 (Atlantic Ocean) and ODP site 757 (Indian Ocean). An additional record comes from the late Tortonian-early Messinian Monte dei Corvi section near Ancona, Italy (Montanari et al., 2017).

Three 100 kg samples across the ^{3}He anomaly in the Tortonian stage at Monte dei Corvi section, Italy, were collected and analysed for extraterrestrial spinels (Fig. 6). In this study none of the chromite grains recovered have an extraterrestrial origin (Fig. 6). The terrestrial grains were analysed and classified in order to understand the possible geneses area.

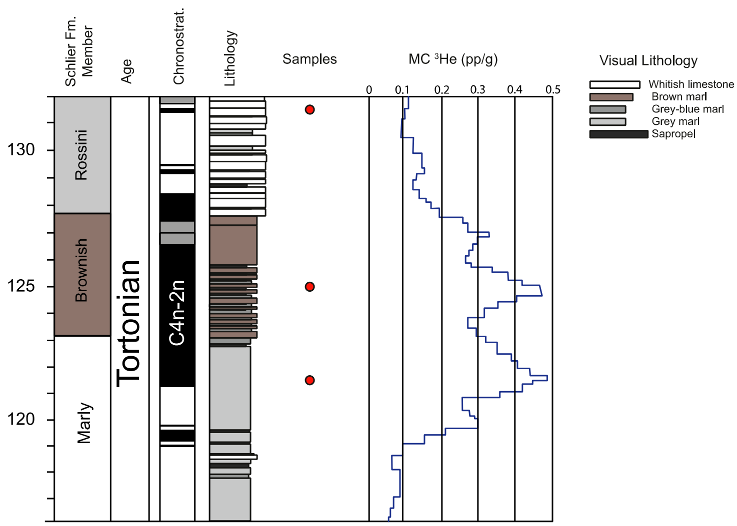

Figure 6. Stratigraphic scheme of Monte dei Corvi (MC) beach section (ages in Ma on left). Chronostratigraphy and lithostratigraphy are after Hüsing et al. (2007, 2009); extraterrestrial ^{3}He concentration profi le is by Montanari et al. (2017); and samples locations are from this work (Paper IV).

5.5 Paper V

Title: Zircon provenance analysis from lower Paleocene pelagic limestones of the Bottaccione Section at Gubbio (Umbria-Marche basin, Italy).

Authors: Aguirre-Palafox, L.E., Alvarez, W., Boschi, S., Schmitz, B., and Martin, E.

Journal: Geological Society of America Special Paper 542, p. 1–16 (2019).

Summary: The advances in U-Pb geochronology methods have not only improved the accuracy for dating the zircon grains but it has become an important geological technique for determining sediment provenance and dispersal patterns.

In this paper detrital zircon grains with ages back to the Neoarchean (2.8-2.5 Ga ago) were recovered from the samples immediately above the Cretaceous-Paleogene boundary at Gubbio, Italy (Fig. 7). In a previous study, using proxies for the non-carbonate detrital content, a source region for this dust from either North Africa or Central Asia was proposed. Our data, however, suggests source regions in North Africa and/or the Iberian Peninsula, rather than in Central Asia.

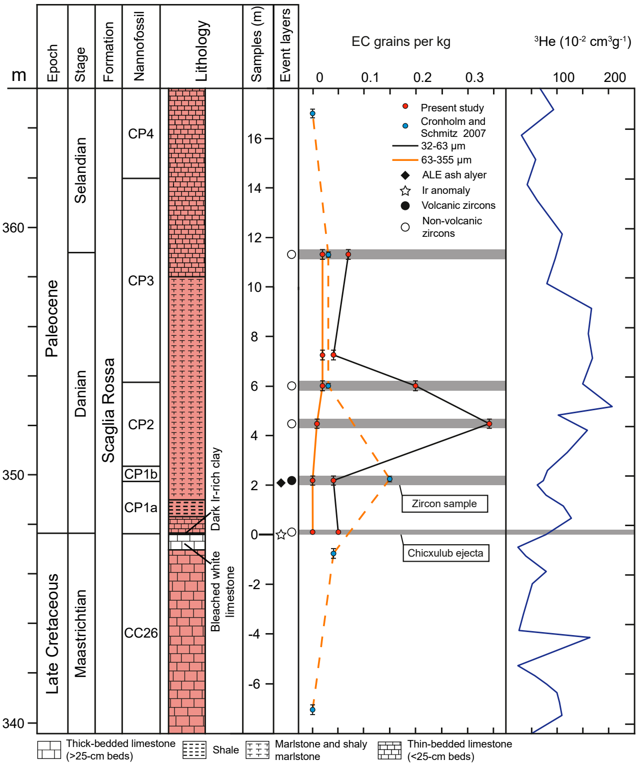

Figure 7. Samples distribution, number of zircons and extraterrestrial (EC) chromite grains per kg of rock across the Bottaccione section. Lithology after Arthur and Fischer (1977), nannofossil stratigraphy from Monechi and Thiersten (1985), and helium isotopic distribution from Mukhopadhyay et al. (2001).

5.6 Paper VI

Title: An extraterrestrial trigger for the mid-Ordovician ice age: dust from the breakup of the L-chondrite parent body.

Authors: Schmitz, B., Farley, K.A., Goderis, P., Heck, P.R., Bergström, S.M., Boschi, S., Claeys, P., Debaille, V., Dronov, A., van Ginneken, M., Harper, D.A.T., Iqbal, F., Friberg, J., Liao, S., Martin, E., Meier, M.M.M., Peucker-Ehrenbrink, B., Soens, B., Wieler, R., and Terfelt, F.

Journal: Science Advances v. 5, no. 9, eaax4184 (2019).

Summary: The largest documented asteroid disruption event in the late solar system history was the L-chondrite parent break up ~466 Ma ago (Fig. 8). This event still delivers almost a third of all meteorites falling on Earth today. An eustatic sea-level fall was recorded just after the major asteroid break up. This sea-level fall has been attributed to an Ordovician ice age in a previous study. The new extraterrestrial chromite and ^{3}He data for Ordovician sediments show a plausible correlation with the L-chondritic breakup and the sea level change (Fig. 8). After the breakup, the fine-grained extraterrestrial material flux to Earth increased by three to four orders of magnitude. The shielding effect of extraordinary amounts of dust in the entire inner solar system during >2 Ma following the L-chondrite breakup cooled Earth and triggered Ordovician icehouse conditions and sea-level fall (Fig. 8).

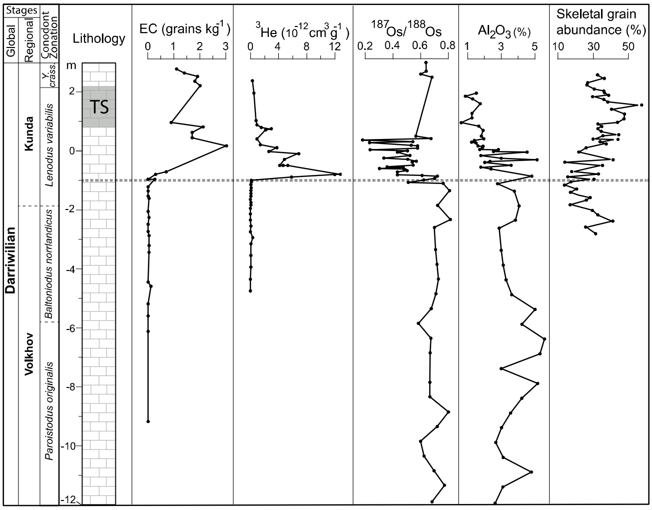

Figure 8. The lower part of the Hällekis Quarry section with plots of bulk-rock concentrations of equilibrated, ordinary chromite (EC) grains, ^{3}He and Al_2O_3, and $^{187}Os/^{188}Os$ ratios. In the far-right column skeletal grain abundance according to (Lindskog et al., 2014, 2017) is shown. The chromite, and He and Os isotopes data confirm a sudden increase in extraterrestrial material in the sediment at -1 m, whereas the Al_2O_3 and skeletal grain abundances illustrate the change to a more clean and coarse-grained limestone that can be used for production of industrial limestone slabs. The coarsening of the sediment reflects stronger hydrodynamic forcing due to a more shallow enviroment leading to winnowing of the fine fraction. TS = Täljsten lowstand deposit.

5.7 Paper VII

Title: The micrometeorite flux to Earth during the earliest Paleogene reconstructed in the Bottaccione section (Umbrian Apennines) Italy.

Authors: Boschi, S., Schmitz, B., Martin, E., and Terfelt, F.

Journal: Manuscript.

Summary: The boundary between the Cretaceous and Paleogene periods (K-Pg) (66 Ma ago) marked an important shift in Earth's history. The K-Pg event resulted in one of the major Phanerozoic mass extinctions, caused by the impact of a large asteroid/comet body (diameter of ~10 km) on the Yucatán Peninsula, Mexico (Alvarez et al., 1980; Smit and Hertogen, 1980; Montanari, 1991; Schulte et al., 2010). The basis for the theory of a global mass extinction at the end of the Cretaceous Period is connected to a dramatically elevated concentration of iridium, which can be found in a clay boundary interval that is present all over the world (Alvarez et al., 1980; Smit and Hertogen, 1980; Montanari, 1991). Enhanced Ir concentration in the K-Pg boundary layer was first described by Alvarez et al. (1980) at the Bottaccione section, Gubbio, Italy (Fig. 2A, 3D).

Another interesting feature of the section is that several peaks of elevated extraterrestrial helium-3 (^{3}He) have been recorded here (Mukhopadhyay et al., 2001; Farley et al., 2012). Four intervals of elevated ^{3}He have been recorded in the Bottaccione section limestone; three in the late Cretaceous and one small in the early Paleocene, of which only the early Paleocene interval is considered in the present study (Fig. 7).

In this study, a total of 633 kg of sedimentary rocks were collected in the Bottaccione section and searched for chrome spinel grains with the aim of reconstructing the extraterrestrial flux during the early Paleocene time (Fig. 7). The samples analysed contain 63 spinel grains in the 63-355 µm size fraction and 1378 grains in the 32-63 µm size fraction. Of those, 12 and 78 grains represent equilibrated ordinary chondritic chromite, respectively. The results indicate that during the early Paleocene, the H-chondritic grains dominated the meteoritic flux over L and LL grains (74%, 17% and 9%). These results are similar to the data from the Cretaceous flux measured within the ^{3}He anomaly (70, 27 and 3%) but different from the meteorites distribution in the Cretaceous before and after the ^{3}He anomaly and in the recent flux (~45, 45 and 10%). The data from the Turonian together with the early Paleocene may represent an anomalous period connected with an enhanced flux of H-chondritic matter.

6 Conclusions

This thesis deals with the significance of the sediment-dispersed extraterrestrial chrome spinels recovered in limestone collected in different sections through the Cenozoic Era. We aim to reconstruct and evaluate the flux in the Cenozoic, by recovering extraterrestrial chromite grains at the Bottaccione (early Paleocene), Massigano and Monte Vaccaro (late Eocene) and Monte dei Corvi (late Miocene) sections.

Though a fundamental part of this study is focused on recovering EC grains in the Cenozoic era, other significant results includes: the Popigai impact ejecta recovered in a new Italian location (Monte Vaccaro), description of the Monte Vaccaro section from a stratigraphical viewpoint (biostratigraphy and lithology), terrestrial chrome spinel grain classification, U-Pb geochronology of zircons in the early Paleocene period and the mid-Ordovician LCPB break up event ice age association. The general conclusions of this thesis are:

I) The extraterrestrial chrome spinel grains recovered in the Massignano section in the interval with enhanced ^{3}He concentrations 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 that time (paper I and II). Two significant peaks in EC grain abundance in the the Massignano section were recorded and interpreted as associated with the Popigai impact ejecta and the Chesapeake Bay impact, respectively (Fig. 4). Elemental analyses of the chromite grains indicate an H- and L-chondritic composition, respectively, of the two impactors. 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.

II) The Popigai ejecta layer (late Eocene) was recovered and described in a new Italian location - the Monte Vaccaro section (Fig. 5). This new record represent the first time that the Popigai layer was found elsewhere after its original characterization at the Massignano section.

The ejecta layer in the Monte Vaccaro section contains shocked quartz, abundant pancake spherules with Ni-rich spinel crystals, and an iridium anomaly of 701 ± 39 ppt (over a background of ~55 ppt), which is three times higher than the peak Ir measured in the ejecta layer at in the Massignano section (Paper IV) (Fig. 5).

III) In order to better constrain the EC flux during the late Eocene, a pilot sample (105 kg) was collected from just above the ejecta layer in the Monte Vaccaro section. This sample was characterized by an enrichment of H-chondritic chromite grains. Because of its condensed nature and low content of terrestrial spinel grains, the Monte Vaccaro section holds great potential for reconstructions of the micrometeorite flux to Earth during the late Eocene using spinels (Paper IV).

IV) The ^{3}He flux in the early Paleocene has been considered nearly constant except for a small spike measured at ~61 Ma (Mukhopadhyay et al., 2001). The single ^{3}He spike has traditionally been interpreted as associated with sedimentation rates rather than an astronomical event (Fig. 7). The K-Pg boundary also marked a drop in sedimentation rate from 10 mm ka^{-1} (Maastrichtian) to 4.3 mm ka^{-1} (Danian) (Coccioni et al., 2012; Sinnesael et al., 2016). The early Paleocene study results together with the Turonian data indicate the presence of an anomalous period connected with an enhanced flux of H-chondritic matter. During the Turonian an H-chondritic parent body break up possible took place in the late solar system history. This even after the initial break up, it formed fragments that continue to collide (Cascade model event) and they produced different extraterrestrial fluxes to Earth. These fluxes were connected with the three ^{3}He peaks in the Turonian sedimentary record. The H-chondritic parent body breakup event is also confirmed by K-Ar isotopes ages, which place such event around ca. 50-100 Ma ago.

V) Detrital zircons were recovered in the early Paleocene at the Bottaccione section (Fig. 7). The mineral analyses suggest that the mostly eolian terrigenous material originated from the large arid region of Northern Africa and exposed semi-arid areas of southern Europe. This result is supported by zircon populations of Variscan (270-350 Ma ago) and peri-Gondwana magmatism (440-500 Ma ago) ages, which in the North African region are not strongly represented in detrital zircon studies. The process that might control the zircon transportation is the latitudinal movement of the prevalent westerlies over larger timescales. This, along with the aridification of areas of the southern European terranes could have promoted the erosion and accumulation of dust material for later eolian transport eastward into the Umbria-Marche carbonate succession.

The study shows that detrital zircon geochronology and provenance analyses of zircon grains, extracted by the dissolution of large quantities of pelagic limestones, can be useful in the reconstruction of prevalent paleowind patterns over a large geographical region. Such knowledge can further aid in other fields, for instance cyclostratigraphy, paleoclimatology and paleobiology.

VI) The mid-Ordovician time was characterized by the L-chondritic parent body break up that still delivers meteorites today. After this event there was a three to four order of magnitude incensement in the flux of the most fine-grained material (Fig. 8).

In this paper we argue that ice-age conditions in the mid-Ordovician, postulated by other research groups were triggered or intensified by the LCPB breakup. This ice age condition can be explained by an eustatic sea-level fall related to global cooling triggered by the dust from the LCPB breakup (Fig. 8). In Earth's atmosphere today extraterrestrial dust represents about one percent of the total stratospheric dust and has no direct climatic significance. However, if the amount of extraterrestrial dust in the atmosphere for several 100 ka or longer increases by more than a thousand times, this likely will lead to a global temperature drop. Following the LCPB breakup, not only Earth's atmosphere but also interplanetary space in the inner solar system became dusty, further shading Earth from sunlight. Vast amounts of dust in the entire inner solar system during more than 2 Ma following the L-chondrite breakup cooled Earth and prompted Ordovician icehouse conditions and sea-level fall.

VII) No extraterrestrial grains >63 μm were recovered in the ^{3}He enriched interval in the upper Tortonian (late Miocene) Monte dei Corvi section, Italy (Fig. 6). The negative result implies that this ^{3}He anomaly was probably not related to an ordinary chondritic breakup event, but rather associated with the breakup of a carbonaceous chondritic body such as the Veritas family forming event.

All the chrome-spinel grains recovered from the section have a terrestrial origin, and their elemental compositions plot only in the ophiolitic field following the Barnes and Roeder (2001) approach. According to the Picazo et al. (2016) classification, our grains are compositionally compatible with the field of Dinaridic ophiolites. The Dinarides include large masses of ophiolites that are associated with genetically related sedimentary formations. These are among the largest ophiolite complexes built into the western parts of the Alpine–Himalaya orogenic belt (Gealey, 1988; Pamić et al., 2002). The Alps were the source for the siliciclastic turbidites filling up the northwest-southeast–oriented foredeep basin of the Apennines (e.g., the upper Miocene Laga Flysch; see Montanari et al., 2017, and references therein). The Monte dei Corvi area, which was located far to the east and out of the tectonic trough, hemipelagic terrigenous sediment would have been provided by runoff from the Dinarides.

In conclusion, in all Cenozoic sections, extraterrestrial grains are rare and a common problem was to recover a sufficient number of grains to enable statistically robust data.

Based on the EC grain classification in previous studies, four main “regimes” have been identified in the flux of ordinary chondrites through the Phanerozoic (Schmitz et al., 2019): The first is just before the LCPB, where the three types (H, L and LL) make up a third of the flux each. The second is after LCPB where the L chondrites make up more than 99% of the flux. The third is from the late Silurian to the late Devonian and in this time, the L chondrites still dominate (roughly L 60%, H 30% and LL 10%). The last regime spans from the early Cretaceous until today (roughly H 45%, L 45% and LL 10%), and similarly to the first regime, this relation has been assumed to be very stable (Schmitz et al., 2019). It should be noted, however, that during some short-term “events”, the flux might temporarily change. For example, the Turonian interval has recorded a very enigmatic extraterrestrial ^{3}He anomaly dominated for a short time by H chondrites (Martin et al., 2018; Schmitz et al., 2019). During the last regime three extraterrestrial ^{3}He enriched periods have been recovered (early Paleocene, late Eocene and late Miocene). All three ^{3}He periods were studied and described in this thesis. Although no EC grains were recovered in the late Miocene, the early Paleocene and the late Eocene times show H-chondritic grains dominance. Important conclusions are: The early Paleocene together with the Turonian data indicate a presence of an enhanced flux of H-chondritic matter possible related with a H-chondritic parent body breakup during the Turonian. The late Eocene extraterrestrial flux with multi-type asteroid shower was triggered by gravitational perturbations of the asteroid belt, possibly associated with chaos-related transitions between different solar-system dynamical regimes.

Further goals might include the study of the Popigai ejecta layer and the EC grains enrichment in Monte Vaccaro section and in new late Eocene section, preferably not in Italy or at least in a different geological formation than Scaglia Variegata. The problem is that the Scaglia Variegata formation is not ideal for recover chrome spinel due its high sedimentation rate and non-homogeneous lithology. The study of the Monte Vaccaro and a new late Eocene section can confirm the Massignano results and it can add data in order to have better statistics. For example, a possible suitable section is located on the Barbados Island where some glassy impact spherules have been already found connected with the Chesapeake Bay impact event. Another project might involve the measurement of the Ir anomaly associated with the Chesapeake Bay impact event in a new section, for example the Monte Vaccaro section. This anomaly was measured for the first time at Massignano but it is not considered always reproducible.

An important goal to achieve will be to increase the knowledge about extraterrestrial processes and expand the chromite database in order to produce robust results, which can connect geological processes with astronomical events in new geological time intervals. As explained in the introduction section, astrogeobiology is a cross-disciplinary field aiming at creating an integrated history of Earth, the solar system and the galaxy. To accomplish this, extraterrestrial chromite spinel data are combined with geology, astronomy and physics. The already successful outcome of this newly developed research field hold promise for great discoveries in the future.

7 References

Afiattalab, F., Wasson, J.T., 1980. Composition of the metal phases in ordinary chondrites: Implication regarding classification and metamorphism. Geochimica et Cosmichimica Acta 44, 431-446.

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

Alvarez, W., 2003. Comparing the evidence relevant to impact and flood basalt at times of major mass extinctions. Astrobiology 3, 153–161.

Alvarez, W., 2019. A review of the Earth history record in the Cretaceous, Paleogene, and Neogene pelagic carbonates of the Umbria-Marche Apennines (Italy): Twenty-five years of the Geological Observatory of Coldigioco. Geological society of America, Special Paper 542, 1-58.

Alvarez, W., Asaro, F., Michel, H.V., Alvarez, L.W., 1982. Iridium anomaly approximately synchronous with terminal Eocene extinctions. Science 216, 886–888, https://doi.org/10.1126/science.216.4548.886.

Alwmark, C., Schmitz, B., 2009. Relict silicate inclusions in extraterrestrial chromite and their use in the classification of fossil chondritic material. Geochimica et Cosmichimica Acta 73, 1472–1486.

Alwmark, C., Schmitz, B., Holm, S., Marone, F., Stapononi, M.A., 2011. 3-D study of mineral inclusions in chromite from ordinary chondrites using synchrotron radiation X-ray tomographic microscopy—Method and applications. Meteoritics & Planetary Science 46(8), 1071-1081, doi: 10.1111/j.1945-5100.2011.01214.x.

Arthur, M.A., Fischer, A.G., 1977. I. Lithostratigraphy and sedimentology, in Alvarez, W., Arthur, M.A., Fischer, A.G., Lowrie, W., Napoleone, G., Premoli Silva, I., and Roggenthen, W.M., eds., Upper Cretaceous-Paleocene magnetic stratigraphy at Gubbio, Italy. Geological Society of America Bulletin 88 (3), 367-371.

Barnes, S.J., Roeder, P.L., 2001. The range of spinel compositions in terrestrial mafic and ultramafic rocks. Journal of Petrology 42, 2279–2302.

Bodiselitsch, 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 and Planetary Science Letters 223, 283–302.

Boschi, S., Schmitz, B., Heck, P.R., Cronholm, A., Defouilloy, C., Kita, N.T., Monechi, S., Montanari, A., Rout, S.S., Terfelt, F., 2017. Late Eocene ^{3}He and Ir anomalies associated with ordinary chondritic spinels. Geochimica et Cosmochimica Acta 204, 205–218, https://doi.org/10.1016/jgca.2017.01.028.

Bron, K.A., Gostin, V., 2012. The Tookoonooka marine impact horizon. Australia: Sedimentary and petrologic evidence. Meteoritics & Planetary Science 47, 296–318.

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

Clymer, A.K., Bice, D.M., Montanari, A., 1996. Shocked quartz from the late Eocene: Impact evidence from Massignano, Italy. Geology 24, 483–486, https://doi.org/10.1130/0091-7613(1996)024<0483:SQFTLE >2.3.CO;2.

Coccioni, R., Galeotti, S., 2003. Deep-water benthic foraminiferal events from the Massignano Eocene/Oligocene boundary stratotype section and point (central Italy): Biostratigraphic, paleoecologic, and paleoceanographic implications, in Prothero, D.R., Ivany, L.C., Nesbitt, E.A., eds., From Greenhouse to Icehouse: The Marine Eocene-Oligocene Transition. New York, Columbia University Press, 438–452.

Coccioni, R., Montanari, A., Bellanca, A., Bice, D.M., Brinkhuis, H., Church, N., Deino, A., Lirer, F., Macalady, A., Maiorano, P., Mancin, N., McDaniel, A., Monechi, S., Neri, R., Nini, C., Nocchi, M., Pross, J., Rochette, P., Sagnotti, L., Sprovieri, M., Tateo, F., Touchard, Y., Williams, G.L., 2008. Integrated stratigraphy of the Oligocene pelagic sequence in the Umbria Marche basin (northeastern Apennines, Italy): A potential global stratotype section and point (GSSP) for the Rupelian/Chattian boundary. Geological Society of America Bulletin 120, 487–511, https://doi.org/10.1130/B25988.1.

Coccioni, R., Sideri, M., Bancala, G., Catanzariti, R., Frontalini, F., Jovane, L., Montanari, A., Savain, J. 2012. Integrated stratigraphy (magneto-,bio- and chronostratigraphy) and geochronology of the Palaeogene pelagic succession of the Umbria-Marche Basin (central Italy), in Jovane, L., Herrero-Bervera, E., Hinnov, L.A., and Housen, B.A. eds., Magnetic Methods and the Timing of Geological Processes. Geological Society, London, Special Publication 373, 111–131.

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

Cronholm, A., Schmitz, B., 2010. Extraterrestrial chromite distribution across the mid-Ordovician Puxi River section, central China: evidence for a global major spike in flux of L-chondritic matter. Icarus 208, 36–48.

De Laubenfels, M.W., 1956. Dinosaur extinction: one more hypothesis. Journal of Paleontology 30, 207–218.

Farley, K.A., Montanari, A., Shoemaker, E.M., Shoemaker, C.S., 1998. Geochemical evidence for a comet shower in the late Eocene. Science 208, 1250–1253.

Farley, K.A., Vokrouhlicky, D., Bottke, W.F., Nesvorny, D., 2006. A late Miocene dust shower from the breakup of an asteroid in the main belt. Nature 439, 295–297, https://doi.org/10.1038/nature04391.

Farley, K.A., Montanari, A., Coccioni, R., 2012. A record of the extraterrestrial ^{3}He flux through the Late Cretaceous. Geochimica et Cosmochimica Acta 84, 314–328.

Glass, B.P., 2002. Upper Eocene impact ejecta/spherule layers in marine sediments. Chemie der Erde 62, 173–196, https://doi.org/10.1078/0009-2819-00017.

Glass, B.P., Burns, C.A., 1988. Microkrystites: A new term for impact produced glassy spherules containing primary crystallites. In Proceedings of the 18th Lunar and

Planetary Science Conference: Houston, Texas, Lunar and Planetary Institute, 455–458.

Glass, B.P., Simonson, B.M., 2012. Distal impact ejecta layers: spherules and more. Elements 8, 43–48.

Glass, B.P., Liu, S., Montanari, A., 2004. Impact ejecta in upper Eocene deposits at Massignano. Italy. Meteoritics & Planetary Science 39, 589–597.

Gealey, W.K., 1988, Plate tectonic evolution of the Mediterranean–Middle East region. Tectonophysics 155, 285–306, https://doi.org/10.1016/0040-1951(88)90270-3.

Heck, P.R., Schmitz, B., Baur, H., Halliday, A.N., Wieler, R., 2004. Fast delivery of meteorites to Earth after a major asteroid collision. Nature 430, 323-325.

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

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

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

Hildebrand, A.R., Penfiled, G.T., Kring, D.A., Pilkington, M., Camargo, A., Jacobsen, S.B., Boynton, W.V., 1991. Chicxulub crater: A possible Cretaceous-Tertiary boundary impact crater on Yucatan Peninsula, Mexico. Geology 18, 867-871.

Hilgen, F., Abdul Aziz, H., Krijgsman, W., Raffi, I., Turco, E., 2003. Integrated stratigraphy and astrochronology of the Serravallian and Lower Tortonian at Monte dei Corvi (Middle–Upper Miocene, northern Italy). Palaeogeography, Palaeoclimatology, Palaeoecology 199, 229–264, https://doi.org/10.1016/S0031-0182(03)00505-4.

Hilgen, F., Iaccarino, S., Krijgsman, W., Montanari, A., Raffi, I., Turco, E., Zachariasse, W.J., 2005. The global boundary stratotype section and point (GSSP) of the Tortonian Stage (Upper Miocene) at Monte dei Corvi. Episodes 28, 1–12.

Huber, H., Koeberl, C., King, Jr., D.T., Petruny, L.W., Montanari, A., 2001. Effects of bioturbation through the Late Eocene impactoclastic layer near Masignano, Italy. In Geological and Biological Effects of Impact Events (eds. Buffetaut, E., Koeberl, C.). Springer Verlag, Berlin, Impact Studies, 197–216.

Hüsing, S.K., Hilgen, F.J., Aziz, H.A., Krijgsman, W., 2007. Completing the Neogene geological time scale between 8.5 and 12.5 Ma. Earth and Planetary Science Letters 253, 340–358, doi:10.1016/jepsl.2006.10.036.

Hüsing, S.K., Kuiper, K.F., Link, W., Hilgen, F.J., Krijgsman, W., 2009. The Upper Tortonian–Lower Messinian at Monte dei Corvi (Northern Apennines, Italy): Completing a Mediterranean reference section for the Tortonian Stage. Earth and Planetary Science Letters 282, 140–157, https://doi.org/10.1016/j.epsl.2009.03.010.

Hüsing, S.K., Cascella, A., Hilgen, F.J., Krijgsman, W., Kuiper, K.F., Turco, E., Wilson, D., 2010. Astrochronology of the Mediterranean Langhian between 15.29 and 14.17 Ma. Earth and Planetary Science Letters, 290, 254–269, https://doi.org/10.1016/j.epsl.2009.12.002.

Johnsson, M.J., Reynolds, R.C., 1986. Clay mineralogy of shale limestone rhythmites in the Scaglia Rossa (Turonian-Eocene), Italian Apennines. Journal of Sedimentary Petrology 56, 501-509.

Jarosewich, E., Nelen, J.A. Norberg, J.A., 1980. Reference samples for electron microprobe analysis. The Journal of Geostandards and Geoanalysis 4, 43–47.

Kring, D.A., Hildebrand, A.R., Boynton, W.V., Anonymous, 1991, The petrology of an andesitic melt rock and a polymict breccia from the interior of the Chicxulub structure, Yucatan, Mexico. Proceedings of the Lunar and Planetary Science Conference 22, 755–756.

Krull-Davatzes, A.E., Lowe, D.R., Byerly, G.R., 2012. Mineralogy and diagenesis of 3.24 Ga meteorite impact spherules. Precambrian Research 196–197, 128–148.

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 and Planetary Science Letters 302, 279–286.

Kuhnt, W., 1990. Agglutinated foraminifera of western Mediterranean Upper Cretaceous pelagic limestone (Umbrian Apennines, Italy, and Betic Cordillera, southern Spain). Micropaleontology 36, 297–330.

Lindskog, A., Eriksson, M. E., Pettersson, A. M. L., 2014. The Volkhov-Kunda transition and the base of the Holen Limestone at Kinnekulle, V.sterg.tland, Sweden. GFF 136, 167–171.

Lindskog, A., Eriksson, M. E., 2017. Megascopic processes reflected in the microscopic realm: Sedimentary and biotic dynamics of the Middle Ordovician "orthoceratite limestone" at Kinnekulle, Sweden. GFF 139, 163–183.

Lindström, M., 1971. Vom Anfang. Hochstand und Ende eines Epikontinentalmeeres. Geologische Rundschau 60, 419–438.

Lindström, M., 1979. Diagenesis of Lower Ordovician hardgrounds in Sweden. Geology and Palaeontology 13, 9–30.

Lowrie, W., Alvarez, W., Asaro, F., 1990. The origin of the White Beds below the Cretaceous-Tertiary boundary in the Gubbio section, Italy. Earth and Planetary Science Letters 98, 303–312.

Lyson, T.R., Bercovici, A., Chester, S.G.B., Sargis, E.J., Pearson, D., Joyce, W.G., 2011. Dinosaur extinction: closing the '3 m gap'. Biology Letters 7, 925–928.

Martin, E., Schmitz, B., Schönlaub, H.P., 2018. From the mid-Ordovician into the Late Silurian: Changes in the meteorite flux after the L-chondrite parent breakup. Meteoritics and Planetary Science12, 2541–2557. doi.org/10.1111/maps.13174.

Martini, E., 1971. Standard Tertiary and Quaternary calcareous nannoplankton zonation, in Farinacci, A., ed., Proceedings of the 2nd International Conference Planktonic Microfossils Roma: Rome, Ed. Tecnoscienza 2, 739–785.

McLaren, D.J., 1970. Time, life and boundaries. Journal of Paleontology 44, 801–815.

Miller, K.G., Sherrell, R.M., Browning, J.V., Field, M.P., Gallagher, W., Olsson, R.K., Sugarman, P.J., Tuorto, S., Wahyudi, H., 2010. Relationship between mass extinction and iridium across the Cretaceous-Paleogene boundary in New Jersey. Geology 38, 867–870.

Monechi, S., Thierstein, H.R., 1985. Late Cretaceous-Eocene nannofossil and magnetostratigraphic correlations near Gubbio, Italy. Marine Micropaleontology 9, 419–440.

Montanari, A., 1991. Authigenesis of impact spheroids in the K/T boundary clay from Italy: New constraints for high-resolution stratigraphy of terminal Cretaceous events. Journal of Sedimentary Petrology 61, 315–339.

Montanari, A., Koeberl, C., 2000. Impact Stratigraphy: The Italian Record. Lecture Notes in Earth Sciences: Berlin, Springer, 364 p.

Montanari, A., Chan, L.S., Alvarez, W., 1989. Synsedimentary tectonics in the Late Cretaceous-Early Tertiary pelagic basin of the northeastern Apennines, in Crevello, P., Wilson, J.L., Sarg, R., Reed, F., eds., Controls on Carbonate Platform and Basin Development. SEPM Special Publication 44, 380-399.

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.

Montanari, A., Beaudoin, B., Chan, L., Coccioni, R., Deino, A., DePaolo, D.J., Emmanuel, L., Fornaciari, E.S., Kruge, M., Lundblad, S., Mozzato, C., Portier, E., Renard, M., Rio, D., Sandroni, P., Stankiewicz, A., 1997. Integrated stratigraphy of the Middle to Upper Miocene pelagic sequence of the Conero Riviera (Ancona, Italy), in Montanari, A., Odin, G.S., Coccioni, R., eds., Miocene Stratigraphy: An Integrated Approach: Amsterdam, Elsevier Science B.V., Developments in Paleontology and Stratigraphy 15, 409–450.

Montanari, A., Farley, K.A., Claeys, P., De Vleeschouwer, D., de Winter, N., Vansteenberge, S., Sinnesael, M., Koeberl, C., 2017. Stratigraphic record of the asteroidal Veritas breakup in the Tortonian Monte dei Corvi section (Ancona, Italy). Geological Society of America Bulletin 129, 1357–1376, https://doi.org/10.1130/B31476.1.

Mukhopadhyay, S., Farley, K.A., Montanari, A., 2001. A 35 Myr record of helium in pelagic limestone from Italy: Implications for interplanetary dust accretion from the early Maastrichtian to the middle Eocene. Geochimica et Cosmochimica Acta 65, 653–669.

Nininger, H.H., 1942. Cataclysm and evolution. Popular Astronomy 50, 270–272.

Nyström, J.O., Lindström, M., Wickman, F.E., 1988. Discovery of a second Ordovician meteorite using chromite as a tracer. Nature 336, 572–574.

Pamić, J., Tomljenović, B., Balen, D., 2002. Geodynamic and petrogenetic evolution of Alpine ophiolites from the central and NW Dinarides. An overview: Lithos 65, 113–142, https://doi.org/10.1016/S0024-4937(02)00162-7.

Paquay, F.S., Ravizza, G.E., Dalai, T.K., Peucker-Ehrenbrink, B., 2008. Determining chondritic impactor size from the marine osmium isotope record. Science 320, 214–218.

Paquay, F.S., Ravizza, G., Coccioni, R., 2014. The influence of extraterrestrial material on the late Eocene marine Os isotope record. Geochimica et Cosmochimica Acta 144, 238–257.

Peucker-Ehrenbrink, B., Schmitz, B. (Eds.), 2001. Accretion of Extraterrestrial Matter Throughout Earth's History. Kluwer Academic/Plenum Publishers, New York, 466.

Picazo, S., Müntener, O., Manatschal, G., Bauville, A., Karner, G., Johnson, C., 2016. Mapping the nature of mantle domains in Western and Central Europe based on clinopyroxene and spinel chemistry. Evidence for mantle modifi cation during an extensional cycle. Lithos 266-267, 233-263, https://doi.org/10.1016/j.lithos.2016.08.029.

Pierrard, O., Robin, E., Rocchia, R., Montanari A., 1998. Extraterrestrial Ni-rich spinel in upper Eocene sediments from Massignano, Italy. Geology 26, 307–310.

Premoli Silva, I., 1977. Upper Cretaceous-Paleocene magnetic stratigraphy at Gubbio, Italy; II. Biostratigraphy. Geological Society of America Bulletin 88, 371–374.

Premoli Silva, I., Jenkins, D.G., 1993. Decision on the Eocene-Oligocene boundary stratotype. Episodes 16, 379–382.

Ravizza, G., VonderHaar, D., 2012. A geochemical clock in earliest Paleogene pelagic carbonates based on the impact-induced Os isotope excursion at the Cretaceous-Paleogene boundary. Paleoceanography 27, 3219.

Robin, E., Molina, E., 2006. Chronostratigraphy, composition, and origin of Ni-rich spinel from the Late Eocene Fuente Caldera section in Spain: one impact or more? Meteoritics & Planetary Science 41, 1231–1248.

Rubin, A.E., 1997. Mineralogy of meteorite groups. Meteoritics & Planetary Science 32, 231-247.

Schindewolf, O.H., 1954. Über die möglichen Ursachen der grossen erdgeschichtlichen Faunenschnitte. Neues Jahrbuch für Geologie und Paläontologie, 457–465.

Schindewolf, O.H., 1963. Neokatastrophismus? Zeitschrift der Deutschen Geologischen Gesellschaft 114, 430–445.

Schmitz, B., 2013. Extraterrestrial spinels and the astronomical perspective on Earth's geological record and evolution of life. Chemie der Erde 73, 117–145, https://doi.org/10.1016/j.chemer.2013.04.002.

Schmitz, B., Häggström, T., 2006. Extraterrestrial chromite in Middle Ordovician marine limestone at Kinnekulle, southern Sweden—traces of a major asteroid breakup event. Meteoritics & Planetary Science 41, 455–466.

Schmitz, B., Lindström, M., Asaro, F., Tassinari, M., 1996. Geochemistry of meteoriterich marine limestone strata and fossil meteorites from the lower Ordovician at Kinnekulle, Sweden. Earth Planetary Science Letters 145, 31–48.

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

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

Schmitz, B., Harper, D.A.T., Peucker-Ehrenbrink, B., Stouge, S., Alwmark, C., Cronholm, A., Bergström, S.M., Tassinari, M., Wang, X., 2008. Asteroid breakup linked to mid-Ordovician biodiversification event. Nature Geoscience 1, 49–53.

Schmitz, B., Cronholm, A., Montanari, A., 2009. A search for extraterrestrial chromite in the late Eocene Massignano section, central Italy. Geological Society of America Special Papers 452, 71–82.

Schmitz, B., Huss, G. R., Meier M. M. M., Peucker-Ehrenbrink, B., Church R. P., Cronholm, A., Davies, M. B., Heck, P. R., Johansen, A., Keil K., Kristiansson, P., Ravizza ,G., Tassinari, M., and Terfelt, F., 2014. A fossil winonaite-like meteorite in Ordovician limestone: A piece of the impactor that broke up the L-chondrite parent body? Earth Planetary Science Letters 400, 145–152.

Schmitz, B., Boschi, S., Cronholm, A., Heck, P.R., Monechi, S., Montanari, A., Terfelt, F., 2015. Fragments of late Eocene Earth-impacting asteroids linked to disturbance of asteroid belt: Earth and Planetary Science Letters 425, 77–83, https://doi.org/10.1016/j.epsl.2015.05.041.

Schmitz, B., Heck, P.R., Alvarez, W., Kita, N.T., Rout, S.S., Cronholm, A., Defouilloy, C., Martin, E., Smit, J., Terfelt, F., 2017. The meteorite flux to Earth in the Early Cretaceous as reconstructed from sediment-dispersed extraterrestrial spinels. Geology 45-9, 807-810.

Schmitz, B., Feist, R., Meier, M.M.M., Martin, E., Heck, P.R., Lenaz, D.,Topa, D., Busemann, H., Maden, C., Plant, A.A., Terfelt, F., 2019. The micrometeorite flux to Earth during the Frasnian-Famennian transition reconstructed in the Coumiac GSSP section, France. Earth and Planetary Science Letters 522, 234-243, https://doi.org/10.1016/j.epsl.2019.06.025.

Schulte, P., Alegret, L., Arenillas, I., Arz, J.A., Barton, P.J., Bown, P.R., Bralower, T.J., Christeson, G.L., Claeys, P., Cockell, C.S., Collins, G.S., Deutsch, A., Goldin, T.J., Goto, K., Grajales-Nishimura J.M., Grieve, R.A., Gulick, S.P., Johnson, K.R., Kiessling, W., Koeberl, C., Kring, D.A., MacLeod, K.G., Matsui, T., Melosh, J., Montanari, A., Morgan, J.V., Neal, C.R., Nichols, D.J., Norris, R.D., Pierazzo, E., Ravizza, G., Rebolledo-Vieyra, M., Reimold, W.U., Robin, E., Salge, T., Speijer, R.P., Sweet, A.R., Urrutia-Fucugauchi, J., Vajda, V., Whalen, M.T., Willumsen, P.S., 2010. The Chicxulub asteroid impact and mass extinction at the Cretaceous-Paleogene boundary. science 327-5970, 1214-8, doi: 10.1126/science.1177265.

Shukolyukov, A., Lugmair, G.W., 1998. Isotopic evidence for Cretaceous-Tertiary impactor and its type. Science 282, 927-929.

Sinnesael, M., de Vleeschouwer, D., Coccioni, R., Claeys, P., Frontalini, F., Jovane, L., Savian, J.F., and Montanari, A., 2016. High-resolution multiproxy cyclostratigraphic analysis of environmental and climatic events across the Cretaceous-Paleogene boundary in the classic pelagic succession of Gubbio (Italy), in Menichetti M., Coccioni R., Montanari A. eds., The Stratigraphic Record of Gubbio: Integrated Stratigraphy of the Late Cretaceous–Paleogene Umbria-Marche Pelagic Basin. Geological Society of America Special Paper 524, 115–137.

Smit, J., Hertogen, J., 1980.An extraterrestrial event at the Cretaceous-Tertiary boundary: Nature 285, 198–200, doi:10.1038/285198a0.

Smit, J., and Klaver, G., 1981. Sanidine spherules at the Cretaceous-Tertiary boundary indicate a large impact event. Nature 292, 47–49.

Sulas, C., 2017. From Greenhouse to Icehouse World after the Late Eocene Popigai Impact Event: New Data from Calcareous Nannofossil Analysis on Monte Vaccaro Section [M.S. thesis]. Florence, Italy, University of Florence, 95 p.

Thorslund, P., Wickman, F.E., Nyström, J.O., 1984. The Ordovician chondrite from Brunflo, central Sweden. I. General description and primary minerals. Lithos 17, 87–100.

Urey, H.D., 1973. Cometary collisions and geological periods. Nature 242, 32–33.

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/Plenum Publishers, New York, 221–240.

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