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Reconstructed using sediment-dispersed extraterrestrial spinels

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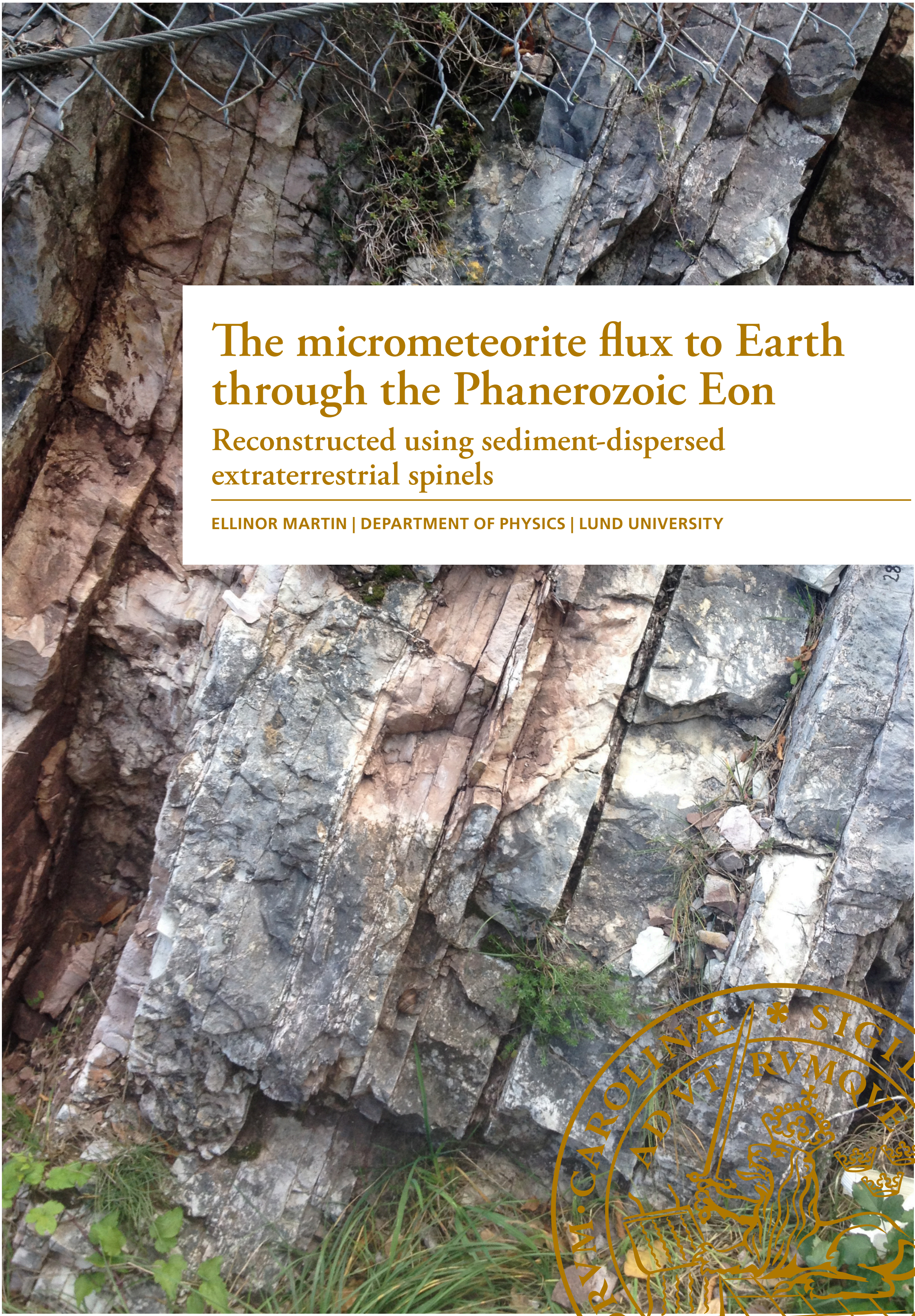

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by

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LUND UNIVERSITY

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Abstract The purpose of this thesis is to add an astronomical component to the history and evolution of Earth by reconstructing the micrometeorite flux to Earth at different time intervals during the Phanerozoic Eon, using sediment-dispersed extraterrestrial spinel group minerals as a proxy. Chromite and chrome spinel are common refractory members of the spinel group, occurring in both extraterrestrial and terrestrial rocks. Their chemistry is indicative both of the petrogenesis of the rock and type of host meteorite. A meteorite on Earth's surface decays relatively quickly, and with the exception of chrome spinel the minerals composing the meteorite are replaced. By the dissolution of large samples of condensed pelagic sediments, and the extraction and analysis of chrome spinel, the flux of different meteorite types in different geological times can be determined.

Covered in nine papers, nine sedimentary sections located in Sweden, Italy, Austria, United States, France, and Russia, deposited during seven different time windows were studied: the mid-Ordovician, late Silurian, late Devonian, early and late Cretaceous, and early Paleogene.

The main objectives in this thesis are to search for spinel grains and describe the flux of micrometeorites in: late Silurian sediments following the L-chondrite parent body (LCPB) breakup in the mid-Ordovician (paper II); Turonian (late Cretaceous) sediments in the Bottaccione section, Italy, within and below the "K3" ^{3}He-anomaly, possibly linked to dust from large lunar impacts (paper III); and Albian-Aptian (early Cretaceous) sediments in search for the lunar Tycho crater ejecta, formed ~109 Ma ago (paper VIII).

Additional aims of this thesis, are to search for spinel grains and describe the flux of micrometeorites in: early Cretaceous, with the potential of finding grains from the LL chondritic Baptistina family-forming event (paper I); late Devonian, during a large biotic crisis (paper V); a multiproxy-approach to resolve the timing of the LCPB breakup and the causality with terrestrial climatic and biotic turnovers (paper VI); early Paleogene after the Cretaceous-Paleogene mass extinction 66 Ma ago (paper VII), including a zircon provenance study that helps to resolve the origin of terrestrial chrome spinels (paper IV); and lastly the terrestrial crater record is compared to the spinel data from the Phanerozoic (paper IX).

Results: in the late Silurian, L chondrites still dominate the flux of ordinary chondrites but is almost back to background levels; in the Turonian ^{3}He anomaly, no lunar grains were found but there is a dominance of H chondritic grains and a ca. 5-fold increase in achondritic grains that could be signs of perturbations and smaller collisions in the asteroid belt. Several levels contain translucent Fe-rich MgAl spinel not previously detected; in the Aptian and Albian, only one tentatively lunar grain was found indicating that the Tycho-forming event could be older than 109 Ma.

In summary, from the extracted equilibrated ordinary chondritic spinels, only one major breakup event is recorded during the Phanerozoic, the LCPB breakup. The flux of micrometeorites from this event continues well into the Devonian Period. The record is intercepted with a few minor, factor of two increase of H-chondritic grains during the time between ca. 60 and 170 Ma ago, and 500 Ma ago. The flux of achondritic micrometeorites were likely more common in earlier times. The sediment-dispersed spinel approach has proven to be a reliable proxy for the micrometeorite flux during geological time. The development to also characterize the flux in smaller size fractions and that of carbonaceous micrometeorites would improve the characterization of the overall flux in ancient times.

Key words chromite, chrome spinel, micrometeorites, Phanerozoic, asteroid breakup, ordinary chondrites, ^{3}He anomalies, lunar impacts, ice age, impact craters, zircons.

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Cover photo front: The Late Cretaceous ^{3}He-rich limestone in the Bottaccione section, Italy.

Cover photo back: Dark shale of the oceanic anoxic event (OAE) 2– “Livello Bonarelli” – in the Bottaccione section, Italy.

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To Edward and Idun

Contents

List of publications

This thesis is based on the following papers:

I. **Meteorite flux to Earth in the Early Cretaceous as reconstructed from sediment-dispersed extraterrestrial spinels**
B. Schmitz, P.R. Heck, W. Alvarez, N.T. Kita, S.S. Rout, A. Cronholm, C. Defouilloy, **E. Martin**, J. Smit, F. Terfelt.
Geology, v. 45, p. 807-810 (2017)
doi: 10.1130/G39297.1

Author contribution: *Took part in the sample retrieval in field, spinel-data processing and compilation. Contributed to the final text.*

II. **From the mid-Ordovician into the Late Silurian: Changes in the micrometeorite flux after the L chondrite parent breakup**
E. Martin, B. Schmitz, H.-P. Schönlaub
Meteoritics & Planetary Science, v. 53, p. 2541-2557 (2018)
doi: 10.1111/maps.13174

Author contribution: Took part in the fieldwork in Sweden, all the sample processing and analyses of the Ordovician sample and spinel grains. Performed analyses of grains in 2 out of 3 Silurian samples. Wrote the first draft of the manuscript and wrote the final text together with the co-authors.

III. **A record of the micrometeorite flux during an enigmatic extraterrestrial ^{3}He anomaly in the Turonian (Late Cretaceous)**
E. Martin, B. Schmitz, A. Montanari
Geological Society of America Special Papers, v. 542, p. 303-318 (2019)
doi: 10.1130/2019.2542(15)

Author contribution: Took part in the planning of the fieldwork and the sample retrieval in Italy. Did most of the sample processing and analyses of the spinel grains. Wrote the first draft of the manuscript and wrote the final text together with the co-authors.

IV. **Zircon provenance analysis from Lower Paleocene pelagic limestones of the Bottaccione section at Gubbio (Umbria-Marche basin, Italy)**
L.E. Aguirre-Palafox, W. Alvarez, S. Boschi, **E. Martin**, B. Schmitz

Geological Society of America Special Papers, v. 542, p. 159-174 (2019)
doi: 10.1130/2019.2542(08)

Author contribution: Took part in the sample retrieval in the field. Extracted zircons from a part of the samples. Responsible for the stratigraphy and creation of figure 1. Edited the final text.

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

Author contribution: Data-processing and interpretations. Constructing most tables, figure 5, and edited the final text.

VI. **An extraterrestrial trigger for the mid-Ordovician ice age: dust from the breakup of the L-chondrite parent body**
B. Schmitz, K.A. Farley, S. Goderis, P.R. Heck, S.M. Bergström, S. Boschi, P. Claeys, V. Debaille, A. Dronov, M. van Ginneken, D.A.T. Harper, F. Iqbal, J. Friberg, S. Liao, **E. Martin**, M.M.M. Meier, B. Peucker-Ehrenbrink, B. Soens, R. Wieler and F. Terfelt
Science Advances, v. 5, p. eaax4184 (2019)
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Author contribution: Took part in the analysis and interpretations of spinel data and discussions. Edited the final text.

VII. **The micrometeorite flux to Earth during the earliest Paleogene reconstructed in the Bottaccione section (Umbrian Apennines), Italy**
S. Boschi, B. Schmitz, **E. Martin**, F. Terfelt
Meteoritics & Planetary Science, v. 55, p. 1615-1628 (2020)
doi: 10.1111/maps.13539

Author contribution: Took part in the sample retrieval in the field. Extraction and analysis of spinel grains from a part of the samples. Spinel-flux calculations and construction of figure 3. Edited the final text.

VIII. **The micrometeorite flux in the Albian/Aptian age (~103-117 Ma): A search for Tycho ejecta in pelagic sediments using chrome spinels**
E. Martin, B. Schmitz, F. Terfelt, L.E. Aguirre-Palafox, W. Alvarez
Geological Society of America Special Papers (*in press*)

Author contribution: Took part in the study design. Analysed spinel grains from a part of the samples. Spinel-data compilation and interpretations.

Wrote the first draft of the manuscript and wrote the final text together with the co-authors.

IX. **Impact-crater ages and micrometeorite paleofluxes compared: Evidence for the importance of ordinary chondrites in the flux of meteorites and asteroids to Earth the past 540 million years**
B. Schmitz, M. Schmieder, S. Liao, **E. Martin**, F. Terfelt
Geological Society of America Special Papers (*in press*)

Author contribution: Spinel-data compilation and interpretations. Responsible for the flux-calculations. Edited the final text.

Extraterrestrial matter and the history of Earth

How much material from space has bombarded Earth in the ancient past, and could this dust have had consequences for our climate, and even evolution of life? This thesis is part of a novel approach to demystify possible dust-forming events in the solar system and to help us understand how extraterrestrial material can affect the environment on Earth. By dissolving large samples of ancient sedimentary limestone in acids and looking for microscopic spinel grains (32-355 µm large), originating from decomposed micrometeorites, the flux of different meteorites, in different times, can be estimated. In this thesis, spinel grains were extracted from limestone sections in several locations in Europe and in the United States. The limestone sections represent the sea floor during different time intervals from ca. 500 million years to ca. 60 million years ago.

In the geological rock record, the fossilized remains of animals that dwelled in the oceans, and on land, tell us stories of speciation, climate and sea-level changes, and mass extinctions. In the sedimentary rocks also lies evidence for a large asteroid impact, as the predominant cause for one of the big five mass extinctions – the end-Cretaceous mass extinction that ended the rule of the dinosaurs and killed 75% of the species. With more than 200 impact craters and a collection of thousands of meteorites, it is evident that Earth is in close connection with the surrounding space. But the magnitude and composition of the ancient meteorite bombardment has until recently been unknown.

Breaking apart

Space dust and meteoroids are formed through collisions between asteroids, and by comets that evaporate as they approach the sun, as well as impacts on planetary surfaces. The asteroid belt between Mars and Jupiter is one of the major source regions where dust is produced. These particles eventually reach Earth and the inner planets. Every year approximately 40 thousand tons of space dust and meteoroids enter the uppermost layer of our atmosphere. As a comparison, this dust would fill more than four Olympic-sized swimming pools!

A large part of this material burns up by the frictional heating when falling through the atmosphere, and some break apart in smaller fragments. Centimetre-sized meteorites rarely reach the ground, and the biggest, kilometre sized fragments (asteroids), impact on Earth even more seldom, at a rate of millions of years apart. There are many kinds of meteorites, divided into different groups and classes. The two main two divisions are chondrites and achondrites. Chondrites are the stony unmelted remnant material that formed early in the formation of our solar system. This includes, for example, ordinary chondrites and carbonaceous chondrites. The achondrites are stony or iron meteorites that come from asteroids (or planets) that have severely melted (differentiated) at some point during their existence. This includes, for example meteorites from the asteroid Vesta, the Moon, and Mars. Cirka 90 percent of the meteorites that fall to Earth today are chondrites, and only 10 percent are achondrites. In addition to these, there are primitive achondrites – meteorites that have preserved either original texture or isotopic composition but have undergone melting to some degree.

Into the deep blue

Meteorites and micrometeorites are mainly collected in hot and cold deserts where they are easy to find. However, as a large part of our planet is covered in water, much of the dust and particles eventually deposit on the ocean floors. Therefore, ancient seafloors, that over time have transformed into limestone and been uplifted, can be mined, and searched for extraterrestrial matter.

On Earth the meteorites weather quickly. The original minerals are exchanged for others or weather away. However, most meteorites contain small amounts of a group of minerals called spinels, which can be found basically intact. Chromite and chrome spinel are the most common variations within the spinel group. Analyses of these minerals can pinpoint the type of meteorite to which it once belonged.

It all began in 1952…

…when quarry workers at the Brunflo quarry, Sweden, found a dark spherical centimetre-sized rock enclosed in a limestone slab they cut in the manufacturing of limestone floors. This turned out to be the very first find of a fossil meteorite.

This meteorite is of a type known as an equilibrated ordinary L chondrite. Cirka 130 fossil meteorites have been found so far, of which a hundred have been analysed. All, but one, belong to this meteorite group. The L chondrite is one out of three subgroups of ordinary chondrites together with H and LL chondrites. The H, L, and LL type chondrites originate from different asteroid parent bodies. The chromite grains within the equilibrated ordinary chondrites have a very defined chemical range, which makes them easy to distinguish from other meteoritic grains.

The ordinary chondrites are one of the most common types of meteorites that fall on Earth today, and many of the recent L chondrites can be dated back to a major disruption of a 100-150 km large asteroid, ca. 466 million years ago, in the

Ordovician Period. This major disruption occurred as a result of a collision between the L chondrite parent body (LCPB) and an unknown celestial body.

These cm-sized fossil meteorites must also have been accompanied by an even greater number of micrometeorites. The surviving spinel grains from these, dispersed throughout the sediment, would thus also be extractable by dissolving small limestone samples in acids from this interval. Several following studies from different sections over the world found the same results: L-chondritic material rained down at dramatically enhanced levels over the entire Earth during at least two million years in the mid-Ordovician Period.

Thesis summary

At one level in the Ordovician sediments from the Hällekis-Thorsberg quarries (paper VI), the number of L-chondritic chromite grains suddenly increase by a hundredfold, together with ^{3}He, a noble-gas implanted from the solar-wind into the finest particles during space-travel. This gigantic explosion of the LCPB must have filled the inner solar system with dust and rock debris that clouded Earth from solar radiation for a few million years. This caused Earth to cool and ice sheets could form on the poles. This can be seen in the rock record as a lowering of the sea-level not long after this event. The diversity of animals on Earth increased during this time – and it is very likely that this dramatic change in solar radiation and the meteorites contribution of nutrients to the sea, stimulated the evolution of animals during the Ordovician Period.

To revisit the breakup of the LCPB, we show in paper II, that a small remnant elevation of L-chondritic chrome-spinel grains in Silurian sediments, was still present – ca. 40 million years after the disruption event. This is in line with dynamical models of how particles continue to collide and decay to finer and finer particles over millions of years. Achondrites made up at least as high of a fraction of the flux as they do today.

In paper V, we searched sediments for spinels deposited during the late Devonian, where one of the five largest mass extinctions on Earth occurred: The Frasnian-Famennian boundary event (ca. 372 Ma ago). An extraterrestrial cause for this event has been inferred by others, based on several large impact craters of this age. Interestingly, the results from the extracted spinels show that L chondrites still dominate the flux of ordinary chondrites, but to a lesser degree than in the Silurian. One of the sampled layers, contain a high abundance in ordinary chondritic chromite, but the layer has the same proportions between the three types of ordinary chondrites as the other layers – inconsistent with the breakup of an asteroid. In several chromite grains there are also noble gases ^{21}Ne and ^{3}He present, which shows that the chromite grains have been very close to the surface inside their host micrometeorite and have been exposed to the solar wind.

In the early Cretaceous (133–145 Ma ago, paper I), the Baptistina asteroid family with LL chondritic composition is inferred to have formed. In this paper, chemical analysis was combined with oxygen-isotopic analysis. Equilibrated ordinary chondrites are at "normal" low levels like today, as well as the proportion between the three types (H, L, and LL), but higher amounts of achondritic micrometeorites compared with today. Additionally, LL type chromite from the Baptistina LL chondrite parent-body breakup with inferred age between 140 and 190 Ma ago, was not detected within these sediments – implying that the asteroid did not break up during the sampled interval and must be much older.

Lunar impacts and ^{3}He anomalies

Evident from the cratered lunar surface, meteoroids and asteroids have also bombarded the Moon during the eons. Numerical models have shown that a large part of the ejected lunar material from these impacts reaches the Earth's atmosphere in a quite short time of ca. 50 thousand years. In paper VIII, sediments from the Pacifica Quarry, California, early Cretaceous (ca. 103–117 Ma ago) were sampled, in search for lunar chrome spinel originating from the 85 km wide, 109-million-year-old Tycho crater. The age of the crater, however, is uncertain over a large interval, but finding lunar grains in limestone samples of known age would aid in the precise dating of the Tycho crater, which in turn is used when dating planetary surfaces. As the lunar regolith contains spinel with high titanium content, such grains were of particular interest. The search for chrome spinel in samples, taken every meter in 30 meters of the section, only generated one potential lunar grain. Based on the location of the sample in the section, this grain is likely not from a large impact. This could imply that the Tycho crater is older than 117 Ma. Among chromite from ordinary chondrites, H dominated over L and LL.

In paper III, we investigated the spinel content in late Cretaceous (ca. 90–94 Ma ago) sediments from the Bottaccione section in Italy. Here, elevated extraterrestrial ^{3}He is recorded over 15 m of the section, representing approximately 1.5 Ma. A hypothesis is that multiple asteroids bombarding the Moon ejected ^{3}He-rich lunar dust that settled on Earth. Lunar rocks usually contain spinel with a high titanium content, however, we found that H-chondritic grains dominate inside the anomaly. There is also a factor of ca. five increase in grains from various achondrites, as well as an enrichment of transparent iron-rich MgAl-spinels in certain samples, but no lunar-like grains were found. We argue that the size-fraction we search is much too large to detect a flux increase corresponding to a factor four increase in ^{3}He, since larger particles generally are fewer in number compared to the finest dust that carry the ^{3}He.

The Bottaccione section was revisited in paper VII, where the flux of extraterrestrial material during the early Paleocene (ca. 61.6–66 Ma ago) was reconstructed. The results show that the H-chondritic grains strongly dominated the meteoritic flux among the ordinary chondrites. This result together with the result from the Turonian age (paper III), indicate an unusual time connected with an enhanced flux of H-chondritic matter. In this paper, we argue that this might indicate an H-chondritic parent body break up or smaller collision during the ^{3}He anomaly in the Turonian. However, H-chondritic grains also dominate during the early

Cretaceous (paper VIII), and additional spinel data from the ^{3}He-interval, show a slightly lower dominance of H-chondritic grains. These data, along with shock ages of present-day H chondrites, indicate that collisions on H-chondritic asteroids began even earlier. A study of extracted zircon mineral grains from this same interval and samples (paper IV), shows that the terrestrial wind-blown material within these sediments mainly originate from the large arid region of Northern Africa and from semi-arid areas of southern Europe. Except for an ash-layer with pristine zircons from volcanic eruptions, most zircons originate from magmas related to orogenic events. These results also suggest that the terrestrial chrome spinel in paper VII, could have similar origin.

Lastly, in paper IX, the Phanerozoic crater record on Earth was compared to the complete spinel data of which this thesis constitutes a part. This showed that the data for both craters and spinels agree; during the Phanerozoic, it is only the breakup of the L chondrite parent body that produced a detectable increase in the number of both craters and spinels. This is surprising considering the multitude of asteroid family-forming events during this time, that, based on the accepted models of meteorite delivery, should have propelled rock fragments towards Earth.

In summary, the biggest event during this time is the breakup of the LCPB in the mid-Ordovician period, that left a significant mark from all sizes of rock fragments. The amount of incoming dust must have had profound effects on the living environments during this time. This dominance continued through the Silurian into the Devonian. H-chondritic meteorites dominate the flux among equilibrated ordinary chondrites in the Cambrian, Jurassic, Cretaceous, and early Paleocene, which indicate several collisional events on H-chondritic parent asteroids. The study of the ^{3}He anomaly during the late Cretaceous did not support the lunar-impact hypothesis but does not necessarily disprove it either. The 5-fold increase in achondritic grains, and the iron-rich MgAl-spinels could hold clues for what occurred during this interval. The achondritic chrome-spinels and perhaps also the MgAl-spinels analysed in this thesis could provide a more detailed picture of the ancient meteorite flow with further analyses, such as oxygen or chromium isotope analysis.

Utomjordisk materia och jordens historia

Hur mycket materia från rymden har bombarderat jorden i det förflutna och kan detta rymdstoft påverkat vårt klimat och till och med livets utveckling? Denna avhandling är en del av en ny forskningsmetod som syftar till att upptäcka urtida kollisioner mellan himlakroppar i solsystemet, vilket kan hjälpa oss att förstå hur utomjordisk materia kan påverka livet på jorden. Genom att lösa upp stora prover av sedimentär kalksten i syror och leta efter mikroskopiska spineller (32–355 µm stora), ett mineral som härstammar från vittrade mikrometeoriter, kan flödet av olika meteoriter i olika tider bestämmas. I denna avhandling har spinellkorn från kalkstenssektioner på flera platser i Europa och i USA extraherats. Kalkstenssektionerna representerar havsbotten under olika tidsintervaller från ca 500 miljoner år till ca 60 miljoner år sedan.

I de geologiska lagerföljderna finns fossiliserade rester av djur som levde i haven och på land, och som berättar historier om artbildning, klimat- och havsnivåförändringar och massutdöende. Här finns även bevis för att ett stort asteroidnedslag var den dominerande orsaken till ett av de fem stora massutdöendena i slutet av Krita för 66 miljoner år sedan, som satte stopp för dinosauriernas herravälde och utplånade 75% av jordens djurarter. Med mer än 200 dokumenterade nedslagskratrar och en samling av tusentals meteoriter är det uppenbart att jorden i allra högsta grad påverkas av händelser i och utanför vårt solsystem. Men omfattningen och sammansättningen av det förhistoriska meteoritflödet har fram till nyligen varit okänd.

På kollisionskurs

Rymdstoft och meteoroider bildas genom kollisioner mellan asteroider, av kometer som avdunstar när de närmar sig solen, samt genom asteroidnedslag på planeters ytor. Asteroidbältet mellan Mars och Jupiter är en av de huvudsakliga regionerna där meteoroider produceras. Dessa partiklar når så småningom jorden och de inre planeterna. Varje år når tiotusentals ton av rymddamm och meteoroider det översta lagret av vår atmosfär. Som en jämförelse skulle dessa fylla mer än fyra olympiska simbassänger!

En stor del av materialet brinner upp av friktionsvärmen när det faller genom atmosfären och en del bryts isär i mindre fragment. Centimeterstora meteoriter når marken relativt sällan, och nedslag från kilometerstora fragment (asteroider) sker lyckligtvis betydligt mer sällan, med miljontals år emellan. Det finns många typer av meteoriter, indelade i olika grupper och klasser. De två huvudsakliga indelningarna är kondriter och akondriter. Kondriter är stenmeteoriter som härstammar från asteroider som aldrig hettats upp tillräckligt (differentierat) för att producera en kärna, mantel och jordskorpa. De här meteoriterna har bevarat sin ursprungliga textur och solsystemets tidiga sammansättning. Här ingår exempelvis ordinära kondriter och kolkondriter. Akondriter är sten- eller järnmeteoriter som kommer från asteroider (eller planeter) som har smält, eller differentierat, någon gång under sin existens, exempelvis meteoriter från asteroiden Vesta, månen och Mars. Ungefär 90 procent av meteoriterna som faller till jorden idag är kondriter, och endast tio procent är akondriter. Utöver dessa finns även primitiva akondriter – meteoriter som bevarat ursprunglig textur eller isotopsammansättning, men som delvis smält vid något tillfälle.

Ner i havsdjupen

Meteoriter och mikrometeoriter hittas främst i varma och kalla öknar där de är lätta att hitta. Men eftersom en stor del av vår planet är täckt av vatten, hamnar mycket av partiklarna i haven och införlivas med havsbottnen. Därför kan gamla havssediment, som med tiden har förvandlats till kalksten och lyfts upp över havsnivån, brytas och sökas igenom efter utomjordisk materia.

På jorden vittrar meteoriterna snabbt och de ursprungliga mineralerna byts ut mot andra. De flesta meteoriter innehåller dock små mängder av en grupp mineraler som kallas spinell och som bevarats i princip helt oförändrade. Kromit och kromspinell är de vanligaste varianterna inom spinellgruppen. Kemiska analyser av dessa mineral kan fastställa vilken typ av meteorit som de en gång tillhört.

Allt började 1952…

…när arbetare vid Brunflo kalkstensbrott i Sverige hittade en mörk centimeterstor sten inuti en kalkstensplatta, som de sågar ut i tillverkningen av kalkstensgolv. Detta visade sig vara det allra första fyndet av en fossil meteorit.

Meteoriten var en så kallad ordinär L-kondrit. Cirka 130 fossila meteoriter har hittats hittills, varav hundra har analyserats. Alla utom en tillhör denna meteoritgrupp. L-kondriter är en av tre undergrupper av ordinära kondriter tillsammans med H- och LL-kondriter. Dessa tre undergrupper innehåller olika mängd järn och härstammar från olika asteroidkroppar. Proportionerna mellan dessa tre grupper utgör av dagens meteoritflöde cirka 45, 45 och 10% av respektive H, L och LL kondriter. Kromitkornen hos de ordinära kondriterna har en väldefinierad kemisk sammansättning, vilket gör dem lätta att skilja från andra extraterrestriska kromitkorn.

De ordinära kondriterna är en av de vanligaste typerna av meteoriter som faller på jorden idag. Många av L-kondriterna kan dateras tillbaka till splittringen av en 100–150 km stor asteroid för ungefär 466 miljoner år sedan. Denna explosion inträffade genom en gigantisk kollision mellan den L-kondritiska föräldrakroppen (LCPB- ”L Chondrite Parent Body”) och en hittills okänd himlakropp.

De centimeter-stora fossila meteoriterna måste också ha åtföljts av ett ännu större antal mikrometeoriter. De överlevande spinellkornen från dessa, spridda i sedimentet, skulle därmed också kunna hittas vid upplösning av kalksten från samma intervall. Flera studier från olika sektioner från olika delar av världen kom fram till samma resultat: stora mängder L-kondritiska meteoriter regnade ner över jorden under minst 2 miljoner år i mitten av Ordovicium.

Sammanfattning av avhandlingen

I en nivå i de ordoviciska sedimenten från stenbrotten Hällekis-Thorsberg (artikel VI) ökar antalet L-kondritiska kromitkorn plötsligt hundrafaldigt, tillsammans med ^{3}He, en ädelgas som introducerats av solvinden i de minsta partiklarna under deras färd genom rymden. Denna gigantiska explosion av LCPB måste ha fyllt det inre solsystemet med damm och stenar som skuggade jorden från en del solinstrålning i flera miljoner år. Detta ledde till att jorden kyldes ned och is kunde bildas på polerna. Nära i tiden efter denna händelse kan en havsnivåsänkning ses i de sedimentära avlagringarna. Mångfalden bland olika djurgrupper ökade också under denna tid – och det är troligt att den dramatiska förändringen i solinstrålningen och meteoriternas bidrag av näringsämnen till haven stimulerade djurens utveckling under Ordovicium.

För att återknyta till LCPB, visar vi i artikel II att L-kondritiska kromitkorn, extraherade från siluriska sediment, fortfarande dominerar över H- och LL-korn – cirka 40 miljoner år efter uppbrottet av LCPB i Ordovicium. Detta är i linje med dynamiska modeller av hur partiklar fortsätter att kollidera och brytas ner till finare och finare partiklar under miljontals år. Akondriter utgör en tiondel av flödet och liknar därmed dagens flöde av akondriter.

I artikel V undersökte vi sammansättningen av spinellkorn i sediment som avsattes i slutet av Devon (ca 372 milj. år sedan), då ett av de fem största massutdöendena på jorden skedde: Frasnian-Famennian utdöendet. Baserat på flera stora nedslagskratrar under den här tiden, har vissa forskare föreslagit en extraterrestrisk orsak till massutdöendet. Intressant nog visar våra resultat att kromitkorn från L kondriter fortfarande dominerar flödet bland de ordinära kondriterna, men i en mindre utsträckning än i Silur. Ett av de provtagna lagren innehåller ett högre antal kromitkorn från ordinära kondriter, men proportionerna mellan H, L och LL är de samma som i de andra proverna, vilket är oförenligt med en fragmentering av en stor asteroid. I flera kromitkorn förekommer även ädelgaserna ^{21}Ne och ^{3}He vilket innebär att kromitkornen suttit mycket nära ytan i mikrometeoriter och varit exponerade för solvinden.

I tidig Krita (133–145 milj. år sedan, artikel I), förmodas det att asteroidfamiljen Baptistina med LL-kondritisk sammansättning bildats. I denna studie kombinerades kemisk elementanalys med syre-isotopanalys. Resultaten visar att ordinära kondriter är på "normalt" låga nivåer som idag, liksom proportionerna mellan de tre undergrupperna H, L och LL. Akondritiska kromspineller utgör dock en större andel av flödet jämfört med idag. En ökning av LL-kondritisk kromit från uppbrottet av Baptistina-familjens föräldrakropp kunde inte hittas. Detta innebär att asteroiden inte bröts upp under det provtagna intervallet och är sannolikt mycket äldre.

^{3}He och asteroidnedslag på månen

Månens yta är täckt med kratrar från meteoroider och asteroider som har bombarderat månen under dess existens. Beräkningar har visat att en stor del av det utslungade månmaterialet från dessa nedslag når jordens atmosfär på en relativt kort tid. I artikel VIII provtogs sediment från äldre Krita (103–117 milj. år sedan) i Pacifica-stenbrottet i Kalifornien, på jakt efter titan-rika spineller från den 85 km breda, 109 miljoner år gamla Tycho-kratern på månen. Kraterns ålder är dock osäker över ett stort intervall, så att hitta månkorn i kalkstensprover av känd ålder skulle bidra till en mer exakt datering av Tycho-kratern, som i sin tur används vid datering av planetära ytor. Då månens yta innehåller spinell med hög titanhalt, var sådana korn särskilt intressanta. I prover tagna varje meter i 30 m av sektionen hittades endast ett potentiellt månkorn. Baserat på provets placering i sektionen är kornet sannolikt inte från något större nedslag. Detta innebär att Tycho-kratern skulle kunna vara äldre än 117 milj. år. Bland kromit från ordinära kondriter dominerar H över L och LL.

I artikel III undersökte vi sammansättningen av spinellkorn i sediment från yngre Krita (ca 90–94 milj. år sedan) från Bottaccione-sektionen i Italien. I dessa sediment finns förhöjda halter av ^{3}He över ca 15 m av sektionen (vilket motsvarar ungefär 1,5 milj. år). En tidigare hypotes om ^{3}He-anomalin är att flera asteroidnedslag på månen slungat ut ^{3}He-rikt månstoft som sedan sedimenterat på jorden. Vi fann att H-kondritiska korn dominerar inuti ^{3}He-intervallet. Det finns även en femfaldig ökning av kromspinell från olika akondriter, liksom ett stort antal genomskinliga järnrika MgAl-spineller. Dock hittades inga titan-rika korn. Antingen beror inte ^{3}He-ökningen i sedimenten på nedslag på månen, eller så är storleksfraktionen vi arbetar med (>32 µm) för stor för att upptäcka en ökning av månspinellkorn motsvarande den 4-faldiga ökning av ^{3}He, eftersom de större partiklarna från kollisioner, i allmänhet är färre i antal jämfört med det finaste dammet som bär ^{3}He.

Bottaccione-sektionen återbesöktes i artikel VII, där flödet av utomjordiskt material under tidig Paleocen (ca 61–66 milj. år sedan) rekonstruerades. Resultaten visar att H-kondritiska korn dominerade meteoritflödet bland ordinära kondriter. Det här resultatet tillsammans med resultatet från artikel III, indikerar en tid med ökat flöde av H-kondritiska mikrometeoriter. I artikel VII argumenterar vi för att en H-kondritisk föräldrakropp brutits upp eller utsatts för mindre kollisioner med början under ^{3}He-intervallet i yngre Krita. Dock dominerar H-kondritiska korn även under äldre Krita (artikel VIII), och ytterligare spinelldata från ^{3}He-intervallet visar på en något lägre dominans av H-kondritiska korn. Dessa tillsammans med argonåldrar av nutida H-kondriter indikerar att kollisioner på H-kondritiska asteroider började ännu tidigare. En dateringsstudie av zirkoner från samma intervall och prover (artikel IV) visar att det terrestriska materialet i dessa sediment huvudsakligen transporterats med luftströmmar från den stora torra regionen i Nordafrika och från halvtorra områden i södra Europa. Förutom ett asklager med zirkoner från vulkanutbrott, kommer de flesta zirkoner från magmor relaterade till bergskedjebildningar. Dessa resultat tyder också på att de terrestriska spinellkornen i artikel VII, kan ha ett liknande ursprung.

Slutligen i artikel IX, jämfördes terrestriska nedslagskratrar med den fullständiga spinelldatan, där denna avhandling utgör en del. Dessa visar på en samstämmighet; under Fanerozoikum är det bara uppbrottet av LCPB som producerat en detekterbar ökning av både kratrar och spineller. Detta är förvånande med tanke på att det finns många fler asteroidfamiljer som bildades under denna eon, som också borde ha ökat meteoritflödet till jorden.

Sammanfattningsvis, var den största händelsen under denna tid är uppbrottet av LCPB i Ordovicium. Den lämnade ett betydande avtryck på jorden, från de största fragmenten till de allra minsta. Mängden inkommande damm måste ha haft djupgående effekter på livsmiljöerna under denna tid. Dominansen av L-kondritiska mikrometeoriter fortsatte genom Silur ända in i Devon. H-kondriter dominerar flödet bland ordinära kondriter i Kambrium, Jura, Krita och tidig Paleocene. Det indikerar att det kan ha skett flera kollisioner på en H-kondritisk föräldra-asteroid. Studien av ^{3}He intervallet under sen Krita bekräftade inte hypotesen om asteroidnedslag på månen, men motbevisar inte nödvändigtvis den heller. Den 5-faldiga ökningen av akondritiska korn och de järn-rika MgAl-spinellerna skulle kunna vara ledtrådar till ursprunget av ^{3}He. Akondritiska kromspineller och MgAl-spineller som analyserats i avhandlingen skulle genom till exempel syre- eller krom-isotop-analys, kunna ge en mer detaljerad bild av det uråldriga meteoritflödet.

1. Introduction

Since the dawn of humankind, the sky has played a key role in the concepts and understanding of reality and has had a high cultural significance. In early civilizations, the celestial sphere was divine, and astronomical events could only be understood as sublime messages from the gods (Koestler, 1959; Hoskin et al., 1999). Thus, astronomy is one of the oldest sciences. In contrast, geology is one of the youngest, and in such, space and Earth have, up until recently, been considered isolated entities. During our planet's existence, continents have formed and drifted, sea levels have risen and fallen, life has evolved, thrived and, at some devastating moments in time, nearly been eradicated by sudden global shifts in the living environments – so called mass extinctions (e.g., Raup and Sepkoski, 1982; Ceballos et al., 2017; Vajda et al., 2020). In addition to this brief portrait of Earth's extensive history, the formation of the planets, collisions between celestial bodies, and the continuous bombardment of meteorites on Earth's surface must be added for a full understanding of how our planet has evolved. The knowledge of the flux of meteorites and asteroids to Earth is growing. About 200 terrestrial impact craters with impact ages ranging from ca. 2 Ga ago until recent times, are known as of today (Schmieder and Kring, 2020). The collection of micrometeorites and meteorites, mainly collected from desert regions such as Antarctica, and northern Africa, now amounts to more than 65,700 specimens (Meteoritical Bulletin Database - accessed the 1st of July 2021). The collection encompasses the flux of meteorites the past two million years (Drouard et al., 2019).

The classification of meteorites is complex, and dependent on the physical characteristics and chemical composition. At the upper level of hierarchy, meteorites are divided into chondrites and achondrites. Chondrites are rocks with preserved solar-like compositions and primordial textures, such as chondrules and calcium-aluminium inclusions (CAIs). Chondrites make up ca. 86% of the meteorite falls. Achondrites are igneous rocks or breccias thereof, from differentiated asteroids and planetary bodies. These constitutes the remainder of the recent meteorite falls. There are also a few meteorites, termed primitive achondrites, that have textures suggesting they were partially molten, or melt-residues, but with chemical or oxygen-isotopic compositions close to chondritic (Prinz et al., 1983; Weisberg et al., 2006; Gounelle, 2011).

The overarching goal of this thesis is to investigate different geological times during the Phanerozoic Eon and determine the composition and relative magnitude of the micrometeorite flux to Earth using spinel as a proxy. Spinel is a group of oxide minerals, where chrome spinel and chromite are two varieties that constitute a small part of most meteorite types (Anders, 1964; Rubin, 1997), as well as terrestrial mafic and ultramafic igneous rocks (Roeder, 1994). Chrome spinel and chromite are refractory minerals that form at high temperatures, are opaque to brown in colour, and readily distinguished among other mineral grains during the retrieval process. Chrome spinel is only scarce in carbonaceous meteorites, that instead more often contain translucent MgAl-rich spinel (Bjärnborg and Schmitz, 2013; Lenaz et al., 2019). Equilibrated ordinary chondrites, one of the most common types of meteorites falling on Earth today, have one of the highest abundances of chromite grains >32 µm (Heck et al., 2017). Additionally, chromite from equilibrated ordinary chondrites also has a narrow range in chemical composition, making them ideal for determining the flux of such meteorites.

The bulk of the extraterrestrial matter that reaches Earth's surface are the smallest particles – interplanetary dust particles (IDPs) <10 µm, and micrometeorites, ~10 to 2000 µm across (Rubin and Grossman, 2010). Micrometeorites are of importance for understanding the composition of the Solar System as they represent a wide range of meteorite types. Their compositions can constrain their source region, which are relevant in constructing models of delivery mechanisms of dust to Earth (Folco and Cordier, 2015). Different size fractions of the micrometeorites represent slightly different compositions. The smallest micrometeorites (<100 µm) are dominated by carbonaceous chondrites, which are more brittle and hence fracture into smaller particles during atmospheric entry. With increasing sizes, ordinary chondrites become more common, and resemble the flux of larger meteorites (Rochette et al., 2008; Van Ginneken et al., 2012; Cordier and Folco, 2014; Folco and Cordier, 2015). Based on Ne- and He-isotopic studies of sediment-dispersed chrome spinel, most of the grains found in condensed pelagic limestone originate from micrometeorites (Heck et al., 2008; Schmitz et al., 2019a), in the coarse size fraction >300 µm (Heck et al., 2017).

The pelagic sedimentary records on Earth, contain a plethora of information regarding changes in both the paleo-oceans and terrestrial realm. Variations of carbon and oxygen isotopes give insights into climate and sea-level changes due to cyclic fluctuations in Earth's orbit around the Sun, i.e., Milankovitch cycles. A key discovery, spurring the research field of planetary science and astrogeobiology, was the iridium-rich clay layer distributed globally, that marks the end of the Cretaceous Period ca. 66 Ma, and the demise of the dinosaurs (Alvarez et al., 1980; Smit and Hertogen, 1980; Smit, 1999). Early on, it was argued that mass-extinctions could be consequences of large impacts (Nininger, 1942), and that the sudden mass-extinction at the Cretaceous-Paleogene (K-Pg) boundary was one of them, but the hard evidence had been missing (De Laubenfels, 1956; Urey, 1973). Iridium is an element enriched in meteorites compared to rocks on Earth. The amounts of iridium, and the co-occurrence of shocked quartz, which can only form during the immense pressures of an asteroid impact, were solid evidence for an impact involving a ca. 10 km sized bolide (Alvarez et al., 1980; Smit and Hertogen, 1980). The crater was the last of evidence to be connected, discovered in the Yucatan peninsula, south of the Gulf of Mexico (Hildebrand et al., 1991).

2. Background and aims

2.1 Fossil meteorites and sediment-dispersed chrome spinel

The approach of searching for extraterrestrial spinels in ancient marine sediments started with the fortuitous encounter of a fossil meteorite in mid-Ordovician limestone from the Brunflo quarry in central Sweden, in 1952. This was presented to geology professor Per Thorslund by the quarry owners. Preparing thin sections of the clast and sending it for examination by a petrographer, the clast was incorrectly identified as a terrestrial ultra-mafic rock. The plate was set aside for nearly 30 years until researcher Frans Wickman started conducting an inventory of impact craters (Thorslund and Wickman, 1981). In re-examination of chondrule textures and analysis of chromite, the chromium rich end-member of the spinel group minerals, the clast was determined to be an equilibrated ordinary chondrite tentatively of H-type (Thorslund et al., 1984). Recent studies, however, determined the Brunflo to be an L4-type chondrite based on the size of the chondrules, maximum diameter of chromite (Alwmark and Schmitz, 2009), and O-isotopic composition (Heck et al., 2010), which is in agreement with the chemical composition and the high influx of L-chondritic meteorites at this time (Schmitz, 2013).

Before the discovery of the Brunflo meteorite, even though meteorite falls were considered to likely have occurred during Earth's ancient past, there were even speculations that meteorite falls were a recent phenomenon (i.e., no falls before late Paleogene, e.g., (Paneth, 1956). Until today, about 130 fossil meteorites have been recovered in the Swedish quarries (Fig. 1A). Out of a hundred analysed specimens, 99 belong to the equilibrated ordinary L chondrites. The single non-chondritic specimen belongs to an extinct type of primitive achondrite (Schmitz et al., 2014; Schmitz et al., 2016).

Building on the prevalence of such numerous amounts of cm-sized meteorites found during this time, and the ^{40}Ar-^{39}Ar retention ages of ca. 470 Ma ago for many of the recent L chondrites (Anders, 1964; Swindle et al., 2014), there must also be an even more numerous amounts of micrometeorites within the limestone. Based on this idea, taking just a few kilograms from any part of this interval that produced the fossil meteorites, and dissolving the sample in acids would produce extraterrestrial chrome-spinel grains (Fig. 1B). This proved to be the case, and the research field of sediment-dispersed spinel grains was born (Schmitz et al., 2003).

From the sediments we extract spinel grains from both extraterrestrial and terrestrial sources. These can generally be separated based on their contents of vanadium, as this element tends to be more abundant in meteorites compared to terrestrial rocks. The extraterrestrial grains more often are euhedral compared to terrestrial grains due to differences in transportation (Cronholm and Schmitz, 2010). As mentioned previously, chromite from equilibrated ordinary chondrites (petrological type 4-6) has a defined narrow chemical composition. This can easily distinguish them from other chrome spinel found dispersed in sediments, based on their chemistry alone. Chrome spinel occurring in unequilibrated ordinary chondrites (mainly petrological type 3) have a wider range in compositions (Wlotzka, 2005). These, together with spinel grains from achondrites and primitive achondrites need further analysis, such as oxygen-, and chromium isotopic analysis (Greenwood et al., 2007; Schmitz et al., 2016; Heck et al., 2017).

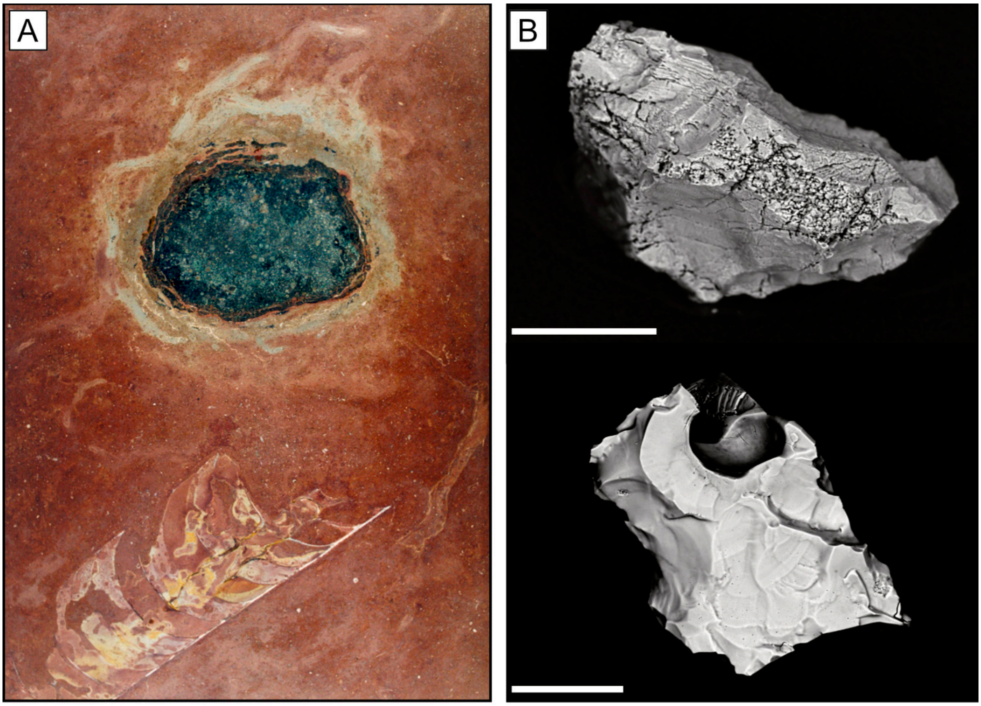

Figure 1. Extraterrestrial material incorporated in limestone. A) One of the ca. 130 fossil meteorites found in the Thorsberg quarry, Sweden (photo: B. Schmitz). B) Scanning electron microscopic backscatter image of two unpolished sediment-dispersed L-chondritic chromite grains, extracted from the mid-Ordovician Komstad Limestone Formation, within the upper *Asaphus expansus* Trilobite Zone, in the Killeröd Quarry (site b). Scale bars = 50 µm.

2.2 Aims of the thesis

The aim of the thesis is to describe the flux of micrometeorites during different time intervals of the Phanerozoic Eon. The results are presented in nine appended papers of which three are derived from main projects as a first author, presented in papers II, III, and VIII. Papers I, IV, V, VI, VII, and IX are those that I have co-authored. In order of publication year, the goal of each paper is formulated below:

I) Reconstruct the micrometeorite flux during the Early Cretaceous (133–145 Ma ago), as documented by the pelagic Maiolica limestone in the Monte Acuto and Bosso River sections in Italy. This time interval could potentially host spinel grains from the Baptistina LL-chondrite breakup event, 190 ± 30 Ma ago.

II) Reconstruct the micrometeorite flux during the Silurian Period following the LCPB in the Ordovician Period. Two sections with similar sedimentation rates and depositional environments were compared. The Silurian samples were retrieved from the Cellon section in Austria, and the mid-Ordovician sample was retrieved from the Killeröd quarry in southern Sweden. These two sections have similar sedimentation rates and depositional environment, which make them ideal for comparison of spinel grain-assemblages and grain alterations.

III) Reconstruct the micrometeorite flux over a ^{3}He-anomaly recorded in the Turonian Stage, Late Cretaceous of the Bottaccione section. Lunar dust ejected from impacts on the Moon is a possible source for the excess ^{3}He in the sediments. Samples were retrieved over an interval of ca. 30 m, both from below and within the ^{3}He anomaly to be able to compare the spinel assemblages from the two intervals.

IV) Analyse the detrital rounded zircon grains recovered from the lower Paleocene pelagic limestones of the Bottaccione section. These were extracted from the same samples as in paper VII. By using U-Pb zircon geochronology analyses, the emplaced aeolian terrigenous dust material can be identified and the provenance geographically constrained. Based on this, the prevalent wind patterns over the Umbria-Marche basin during the early Paleocene can be reconstructed. The results will aid in constraining the origin of the terrestrial chrome-spinel grains within the samples (presented in paper VII).

V) Reconstruct the micrometeorite flux during the Late Devonian, recorded in the Coumiac quarries, Montagne Noire region, France. One of the five largest mass extinctions on Earth occurred in this time: the Frasnian-Famennian boundary event (ca. 372 Ma ago).

VI) Resolve if the LCPB breakup directly affected Earth's climate and biota, using new, high-resolution, multiparameter data (e.g., chrome spinel, He, and Os isotopes) to locate the precise level in the sedimentary strata corresponding to the LCPB breakup event. Samples were taken from the Hällekis-Thorsberg quarry sections, Sweden, with complementary spinel data from the Lynna River section in Russia. The micrometeoritic spinel data was compared with previous noble-gas data for chromite grains from large fossil meteorites (Heck et al., 2004; Heck et al., 2008), which can be used for an impartial appraisal of the timing of the LCPB breakup.

VII) Reconstruct the flux of extraterrestrial matter during the early Paleocene (ca. 61.6–66.0 Ma ago) as documented in the Bottaccione section, Italy. The data provides the first insights on the types of micrometeorites that fell on Earth during this epoch.

VIII) Search for lunar spinel grains from the impact ejecta of the ca. 109 Ma old Tycho crater. Small samples were retrieved every meter over a ca. 30 m interval (ca. 103–117 Ma ago, Albian-Aptian age) of the Calera Limestone in the Pacifica Quarry section, California, with the ambition to find a few lunar grains from the flux of lunar micrometeorites from this ejecta.

IX) Comparative study of the terrestrial crater record and the complete spinel-data obtained for the Phanerozoic Eon. This comparison offers a comprehensive overview on the flux of both coarse micrometeorites and asteroid-sized bolides to Earth during this time, and possibly provide new insights on the delivery mechanisms of meteorites from the asteroid belt.

3. Materials and methods

3.1 Field work and sample retrieval

Micrometeorites that have settled on the seafloor is intermixed with the terrestrial particles. In condensed pelagic sediments deposited far away from the shore, in tranquil conditions, reworking of the sediment by waves and currents are minimal, and the time-average for a sample is larger, i.e., a sediment with low accumulation represents more time which in turn can yield more extraterrestrial spinels. The offshore environment also results in lower intermixing of terrestrial spinels in the size range >32 µm, which facilitates the extraction of extraterrestrial spinel grains. Below 32 µm, the terrestrial contribution has shown to exceed and obscure the extraterrestrial portion. In paper V, the Devonian sediments turned out to host large numbers of terrestrial chrome spinels even in the 32-63 µm fraction, which caused us to use only the fraction >63 µm.

3.2 Separation of spinels

The sample processing was conducted at the Astrogeobiology Laboratory at Lund University. This facility is designed specifically for processing large sample volumes. In the first step, each sample is weighed and carefully washed to remove weathered material, lichen, and dirt, then decalcified in 500-liter barrels with 6 M hydrochloric acid (Fig. 2A). The residual sediment is left to settle at the bottom of the barrel so that excess HCl could be pumped out. The residue is neutralized with NaCl salts. The residue is then sieved at 32 µm in order to wash out the fine clay minerals and leached in 11 M hydrofluoric acid at room temperature for two days to remove silicates. After additional sieving at 32 µm, the samples are treated with sulfuric acid to dissolve natural hydroxide minerals and laboratory-induced calcium fluoride. The insoluble residue is then density separated with LST liquid (lithium heteropolytungstate dissolved in water), and the low-density fraction is burned in a furnace at 550 °C for 10 hours to remove organic material. The final, heavy residue is separated into two size fractions: 32-63 µm and 63-355 µm. Both size fractions are searched under a binocular microscope (Fig. 2B) and the opaque grains deduced to be chrome-spinel grains, and transparent grains tentatively being spinel *sensu stricto*, are picked with a fine brush and transferred onto a carbon tape. The grains are 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 are mounted in epoxy resin (Fig. 2C) together with analytical standard UWCr-3 (Heck et al., 2010) and polished flat using 1 µm diamond paste and coated with carbon.

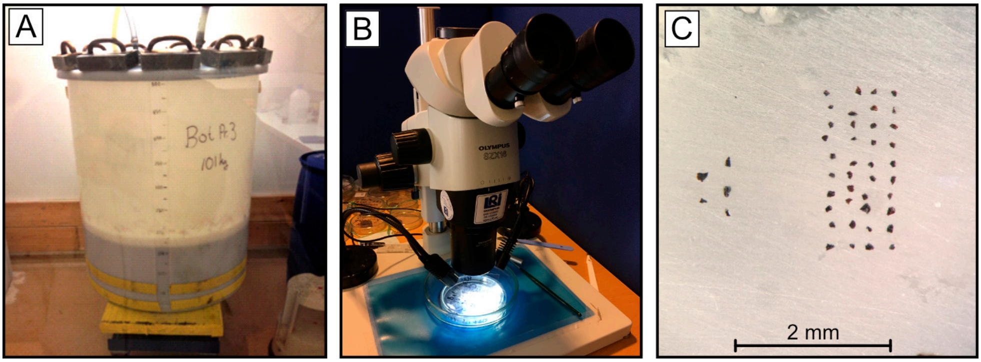

Figure 2. The first steps in the processing of limestone samples. A) Cleaned samples are put in a 500 L barrel and decalcified with HCl acid, residual is seived at 32 µm and further treated with HF acid. B) After seiving, the residual material is separated in two size-fractions in petri-dishes and scanned beneath a stereo microscope and hand-picked with a fine brush. C) Spinel grains are mounted in epoxy resin and polished with diamond paste.

3.3 Chemical analyses

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 backscattered 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, grains are analysed with the same SEM/EDS approach at Lund University as in previous studies of chrome spinels (e.g., (Cronholm and Schmitz, 2010; Schmitz et al., 2015; Boschi et al., 2017). The grains were analysed with an Oxford Inca X-Sight energy-dispersive spectrometer with a Si detector mounted on a Hitachi S-3400 scanning electron microscope. Cobalt was used as standard to monitor drift of the instrument. An acceleration voltage of 15 kV, a sample current of ~1 nA, and a live-time counting of 80 s were used for each analysis spot. 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).

3.4 Division of spinel grains

Based on the results from the chemical analysis, the grains were divided into one out of four categories:

(1) Equilibrated ordinary (petrological type 4-6) chondritic chromite (EC), which have distinct chemical ranges of: Cr_2O_3 ~53.0-62.0 wt%; FeO ~23.0-32.0; Al_2O_3 ~4.5-8.5; MgO ~1.3-4.5; V_2O_3 ~0.55-0.95; and TiO_2 ~1.4-4.5 wt%, as first defined by Schmitz and Häggström (2006), with revised ranges by Schmitz et al. (2017) (paper I). If one or two of the oxides slightly deviate from these ranges, the grain is still considered EC, but are marked red in data tables.

(2) If oxides deviate more substantially (e.g., because of diagenetic alteration) but based on overall chemistry, likely are from equilibrated ordinary chondrites, they are marked as Outlier-EC grains. This grain category was first introduced in paper II where the alteration was notable and were subsequently excluded from flux calculations in papers II and III due to their deviation from the distinct chemical ranges of EC grains. In later publications these grains are incorporated into the main EC category but marked with a footnote in the supplementary data tables.

(3) Grains that have a non-EC composition are assigned to “other chrome spinel” (OtC) grains, except those with high V_2O_3 content that are classified as OtC-V grains. The OtC grains are likely terrestrial as terrestrial grains typically have lower contents of vanadium compared to meteorites. Support for this is found in oxygen-isotopic analysis by (Schmitz et al., 2017), where at least 21 of 23 OtC grains were on the terrestrial fractionation line (TFL).

(4) The OtC grains with V_2O_3 content ≥0.45 wt% and a Cr_2O_3/FeO ratio ≥1.45 are denoted as OtC-V grains (former OC-V). They typically originate from meteorite types other than equilibrated ordinary chondrites. In very rare cases they may also have a terrestrial origin (e.g., ultramafic volcanic rocks, such as komatiites). Grains with V_2O_3 >0.45 wt% and a Cr_2O_3/FeO ratio <1.45 have previously been considered likely terrestrial, and therefore classified as OtC. However, as lunar grains often have Cr_2O_3/FeO ratio <1.45, these types of grains were of particular interest in paper VIII. The classification system used here has evolved over time. The OtC and OtC-V grain categories have replaced the OC and OC-V grain categories used in earlier papers. The acronyms have been changed to avoid confusion with the use of the acronym OC for "ordinary chondrite" in other research fields.

3.4.1 Division of EC grains in H, L, and LL groups

The TiO_2 content can be used to divide the EC grains further into the ordinary chondritic groups; H: ≤2.5 wt%, L: 2.51-3.39 wt%, and LL: ≥3.40 wt% TiO_2, as demonstrated by Heck et al. (2016). The TiO_2 content of each group follows a Gaussian distribution, with ca. 10% overlap between the groups. The average TiO_2 content of the H, L and LL group is ~2.2, 2.7, and 3.4 wt%, respectively. The cut-off limits between the three groups are chosen arbitrarily but must be used consistently for comparison between studies of these kinds. The EC classification into subgroups can also be done with oxygen-3-isotopic analysis, but it has been shown that the TiO_2 approach is as efficient as using oxygen isotopes (Heck et al., 2016). The advantage of using both oxygen isotopes and TiO_2 is that uncertainties from compositional overlaps in respective approach can be resolved in greater detail.

3.5 Flux calculations

The extraterrestrial flux (EF) is calculated as a function of the mean sedimentation rate (SR) of the section, the mean bulk density of limestone (ρ) and the number of grains found per kilogram (N), and expressed as the number of EC-grains deposited within a square meter during a time span of a thousand years (grains m^{-2} ka^{-1}) (eq: 1):

$$\mathrm{EF} = SR \times \rho \times \mathrm{N} \qquad (1)$$

The mean sedimentation rate is expressed as millimetres per thousand years and is either taken from the literature of the specific study location or estimated based on the thickness of the section between age constrained datums. The mean bulk density of limestone is expressed as grams per cubic centimetres and varies between 2.3 and 2.7 g cm^{-3} depending on parameters such as porosity and impurities (Schön, 2011). In paper II the bulk densities were calculated for small rock samples by obtaining their volume indirectly from their displacement of water in a graduated cylinder. In subsequent papers, a mean bulk density of 2.5 g cm^{-3} was used for comparison between studies.

4. Geological settings

In the projects of this thesis, samples from nine sedimentary sections were studied in Sweden, Russia, Austria, Italy, France, and the United States (Fig. 3). The sections are listed in chronological order of the sampled intervals from oldest to youngest. The sections for the other time windows included in paper IX are not accounted for here.

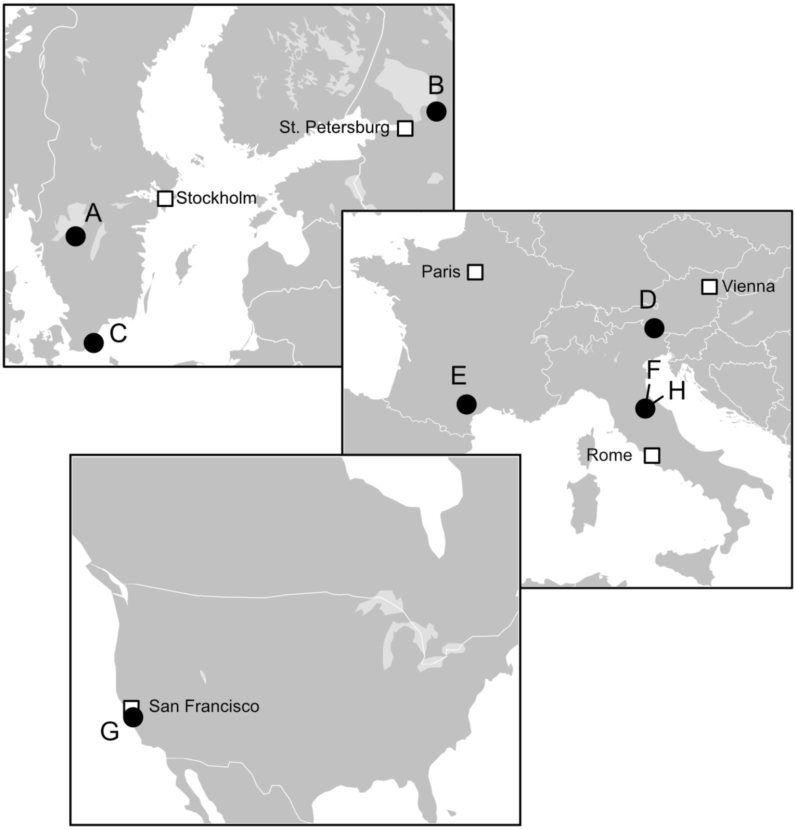

Figure 3. The locations of the studied sections. A) The two mid-Ordovician sections in the Hällekis and Thorsberg quarries, Sweden. B) The mid-Ordovician Lynna River section, Russia. C) The mid-Ordovician Killeröd quarries, Sweden. D) The Silurian Cellon section, Austria. E) The Late Devonian Coumiac GSSP section, France. F) The Early Cretaceous Monte Acuto and Bosso River sections. G) The Early Cretaceous Pacifica Quarry section, United States. H) The Late Cretaceous to Paleogene Bottaccione section, Italy.

4.1 The Hällekis and Thorsberg sections, Kinnekulle, southern Sweden, and Lynna River section, western Russia

Situated southeast of Lake Vänern, Kinnekulle is a 306 m high plateau mountain, consisting mainly of sedimentary rocks of Cambrian to Silurian age. In paper VI, the Thorsberg quarry (58°34'45"N, 13°25'46"E) and the Hällekis quarry (58°36'26"N, 13°23'38"E) near the town of Hällekis were studied (Fig. 3A and Fig. 4A). The Middle Ordovician succession is dominated by limestone deposited in a relatively shallow epicontinental sea that covered most of the Baltoscandian shield during this time (Lindström, 1971). These days the Hällekis quarry is abandoned but was one of the largest active limestone quarries in Sweden. This quarry consists of ~50 m thick succession of the red homogeneous "Orthoceratite limestone", an organic-poor sediment that formed at very low sedimentation rates (2 ± 1 mm ka^{-1}) (Lindström 1971, 1979; (Schmitz et al., 1996). Except for the 1.2-1.4 m thick ubiquitous band of grey Täljsten interval, the colour of the massive limestone beds varies from red to brownish red throughout the section. Abundant hardground surfaces are present, representing periods of nondeposition (Lindström, 1979). The stratigraphically contemporaneous Thorsberg quarry is still active but exposes only ~6 m of the mid-Ordovician rock record. It is from this quarry the ca. 130 fossil meteorites have been found (Schmitz et al., 2001; paper VI).

The Lynna River section (Fig. 3B and Fig. 4B) is located in the St. Petersburg region of north-western Russia (60°0'39"N, 32°33'49"E). It is time equivalent with the Hällekis-Thorsberg sections and represents distal parts of the Ordovician epicontinental sea. The section comprises ca. 10 meters of mid-Ordovician strata, including the uppermost Dapingian through lowermost middle Darriwilian global stages (Volkhov and Kunda regional stages) (eg., Dronov et al. 2005; Dronov & Mikuláš 2010). The section consists of grey limestone alternating with marly horizons. Glauconitic grains and hardgrounds are common, notably in the lower part of the section.

Figure 4. The mid-Ordovician sections. A) The abandond Hällekis Quarry exposing the red orthoceratite limestone. B) The Lynna River section exposed on the river sides, western Russia. C) The Killeröd Quarry section "site b", an organic-rich, darker version of the orthoceratite limestone.

4.2 The Killeröd section, southern Sweden

In paper II, one 100-kg-sample of the Komstad Limetone was taken from the Killeröd section, located in southeast Scania, Sweden, around 13 km west of the town Simrishamn, in an abandoned quarry (55°34'20″N, 14°7'54″E). The sample was extracted from a ca. 12 cm thick bed of the smaller Killeröd quarry "site b" in the upper *A. expansus* Trilobite Zone (Fig 3C and Fig. 4C), within level +35 of

Nielsen (1995) and from levels 9.71–9.84 m in Häggström and Schmitz (2007). The section is proposed as the paratype section of the mid-Ordovician Komstad Limestone, as the type-section in the Komstad quarries, 1 km west of Killeröd, is essentially inaccessible (Nielsen, 1995). The Komstad Limestone is a darker variety of the otherwise reddish “orthoceratite limestone”, as in the Thorsberg and Hällekis sections 350 km north of Killeröd. The Komstad Limestone is an organic-rich wackestone/packstone with intercepting layers of lighter coloured marly limestone and thinner clay-rich bands. The thickness of the Komstad Limestone in the Killeröd area is estimated to a minimum of 15 m (Nielsen 1995) and spans the Volkhov and Kunda Baltoscandian regional stages. The orthoceratite limestone formed at depths of below one hundred to several hundred meters (Lindström, 1963; Jaanusson, 1973; Chen and Lindström, 1991; Nielsen, 1995; Lindskog, 2014).

4.3 The Cellon section, southern Austria

In paper II, three samples weighing a total of 350 kg were extracted from the Cellon section. The section is the stratotype section for Silurian rocks in the Southern Alps (Fig. 3D and Fig. 5). It is situated in the Central Carnic Alps in an avalanche gorge, ca. 400 m from road 110 on the Austrian side of the Austrian-Italian boarder (46°36'32″N, 12°56'31″E). It is accessible by a short walk from Plöcken Pass/Passo di Monte Croce Carnico. The section comprises upper Ordovician to lower Carboniferous rocks representing the so-called Plöcken facies, a shallow to relatively deep marine carbonate sequence. More than 40 m of Silurian “Orthoceras limestone” crop out here, spanning the interval from the late Llandovery to the Pridoli (Brett et al., 2009; Corradini et al., 2014). Since the pioneering work by Geyer (1894), many geological studies have been carried out here, where Walliser (1964) laid the biostratigraphic framework. The “Orthoceras limestone” in the section varies in colour from black to red reflecting deposition under oxic to anoxic conditions. The average sedimentation rate for the Kok and Alticola formations studied here is ~4 mm ka^{-1} based on the thicknesses of the Ludfordian and Gorstian stages.

Figure 5. The Silurian Cellon section. It is located in a steep avalanche gorge in the Central Carnic Alps, near the Italian-Austrian border. Photo credit B. Schmitz.

4.4 The Coumiac GSSP section, southern France

In paper V, a total of 898 kg of limestone was extracted from the Late Devonian section exposed in the Coumiac quarries in the Montagne Noire region of southern France (Fig. 3E). The section is located a few kilometres northeast of Cessenon-sur-Orb (43°28'13"N, 3° 3'49"E). The Upper Coumiac Quarry contains the Global Stratotype Section and Point (GSSP) for the base of the Famennian stage (Klapper et al., 1993). The sequence consists of well-bedded pelagic micrites and calcilutites of red-tinted near-vertical beds. The succession is complete through the middle Frasnian to late Famennian. The Frasnian-Famennian boundary is drawn between Beds 31g and 32a (House et al., 2000).

Hemipelagic limestone of the Middle Devonian Series (middle to upper Givetian) is exposed in the marble quarry on the northern slope of Pic de Bissous ca. three km north of Cabrières (43°36'5"N, 3°21'22"E). The succession has been long known as an important Middle Devonian fossil locality. The succession is overturned 180° but is not disturbed by tectonics. The hematite-rich red limestone contains goniatites, orthocones, and crinoid remains (Feist and Klapper, 1985; Aboussalam and Becker, 2001). The samples for paper V were collected in the Upper Coumiac Quarry, except for a ~100 kg-sized block of the goniatite-rich Upper Kellwasser bed that was found loose on the floor of the Lower Coumiac quarry. Two samples with a total weight of 58.4 kg were extracted from Pic de Bissous.

4.5 The Monte Acuto and Bosso River sections, central Italy

In paper I, samples of Early Cretaceous limestone were extracted from the Monte Acuto (43° 27'83"N, 12° 40'27"E) and Bosso River sections in the Umbria-Marche Apennines of central Italy (Fig. 3F and Fig. 6). This is probably the best place in the world to find exposures of rocks of pelagic carbonates representing most of the 165-Myr interval from the Pliensbachian to the Oligocene. Earth-history studies of many kinds have been carried out on these rocks beginning with Renz (1936), and a recent compilation given by Menichetti et al. (2016). In the Umbria-Marche sequence, the first four stages of the lower Cretaceous (Berriasian-Barremian, ~145-125 Ma) are represented by the Maiolica Formation, a pure white pelagic limestone with a fine-grained texture, abundant black to dark grey beds and nodules of chert, and sporadic partings of black clay. This unit consists of a ~400 m thick sequence deposited in basinal settings and a ~100 m thick sequence deposited on fault-block seamounts. It has been difficult to correlate, date, and study because of the near absence of distinctive marker beds and lack of distal volcanic ashes. However, Channell et al. (1995) determined the M-sequence geomagnetic polarity zonation and tied it to nannofossils events and ammonite zones for the Hauterivian and the uppermost Valanginian. Faraoni et al. (1997) were able to establish an ammonite zonation for all of the Valanginian and small portions of the underlying Berriasian and the overlying Hauterivian. Finally, (Sprovieri et al., 2006) studied the cyclostratigraphy of the Monte Acuto section using carbon isotopes, tying this record to the known biozonation and magnetostratigraphy.

All samples except one were extracted from the 240-m-thick Monte Acuto section exposed in cuts along the road from Chiaserna to the pass between Monte Acuto and Monte Catria. The average sedimentation rate for the Maiolica limestone in the Monte Acuto section is about 25 mm ka^{-1}, based on a measured thickness of 137 m of sediments representing the 5.5 Ma long Valanginian Stage. The entire Late Berriasian to Early Hauterivian section at Monte Acuto corresponds to ca. 9.4 Ma (ca. 141.2 -131.8 Ma ago) and comprises 453 beds, giving an average of 20.75 ka per bed. The oldest of the samples (ca. 145 Ma ago) was extracted from ca. 3 m above the Maiolica-Diaspri formational contact, i.e., close to the Jurassic-Cretaceous boundary, in the Bosso River section along the Pianello-Cagli road, 12 km northwest of Monte Acuto (Kudielka et al., 2002).

Figure 6. The white pelagic Maiolica limestone exposed in the Monte Acuto section along the road from Chiaserna to the pass between Monte Acuto and Monte Catria.

4.6 The Pacifica Quarry section, California, USA

The Calera Limestone is exposed in two quarries on the San Franciscan Peninsula: the Permanente and the Pacifica quarries. The latter is situated at 37°36'49"N and 122°29'45"W, just north of the town Pacifica, ca. 20 km south-southwest of San Francisco, California (Fig. 3G). The quarry is located on the southern side of the Calera Hill, immediately north of Rockaway Beach. Following further quarrying, the appearance of the section face has changed somewhat since the work of Sliter (1999), who established the biostratigraphic age constraints of the limestone. In addition to Sliter's study, there have only been a few studies of the Pacifica section, including palaeomagnetism (Tarduno et al., 1985), and structural geometry and deformational history (Larue et al., 1989). The section spans approximately 26 million years over ca. 75 meters and comprises strata from the early Aptian to the late Cenomanian. There is an unconformity at the Aptian-Albian boundary stretching from ca. 110 Ma to 114 Ma ago. Present is also a horst that repeats a circa three-meter part of the section, which encompasses the upper black shale layer ("Thalmann Event").

Despite the complexities of faulting and unconformities in the section, Sliter (1999) calculated the sedimentation rates of the biozones that were adequately complete. In the Aptian part of the section, the sedimentation rate varies between 4.4 mm ka^{-1} (Leupoldina cabri Zone), 2.8 mm ka^{-1} (Globigerinelloides ferreolensis Zone), and 3.5 mm ka^{-1} (G. algerianus Zone). In the Albian, mostly represented by the nearly complete Ticinella primula Zone, the rate is 2.8 mm ka^{-1} (Sliter, 1999). The average sedimentation rate for these four zones combined is 3.4 mm ka^{-1}.

4.7 The Bottaccione Gorge section, Gubbio, Italy

The pelagic Bottaccione Gorge section is likely the most well-studied locality in the world that covers the Cretaceous-Paleogene boundary (Renz, 1936; Alvarez et al., 1977; Premoli Silva, 1977). The section is located in the Umbria-Marche Apennines, central Italy (Fig. 3H), along the state road SS298 northeast of the medieval town of Gubbio (Fig. 7A; 43°22′N, 12°35′ E). It is a classical section consisting of nearly 400 m of pelagic limestone strata from the uppermost Jurassic to the uppermost Oligocene and has been of key importance for the development of the Cretaceous and Paleogene chronostratigraphy (Galeotti et al., 2015). The Bottaccione section has frequently been visited by earth scientists during many decades, pioneered by the biostratigraphic foundation laid out by Renz (1936); see also Luterbacher (2016). The section is world famous for the discovery of the iridium anomaly clay layer that marks the end of the Cretaceous Period (Fig. 7B), attributed to the impact of a 10-km-diameter asteroid leading to the demise of the dinosaurs (Alvarez et al., 1980). It is also in this section that several ^{3}He anomalies have been detected (Farley et al., 2012).

In papers III and VII, samples were taken from the 325 m thick Scaglia Rossa Formation, which includes strata from the Early Turonian to the Latest Ypresian. The Scaglia Rossa Formation consists of mainly pink, homogeneous biomicritic, pelagic limestones and marly limestones containing radiolarian cherts (Arthur and Fischer, 1977; Montanari et al., 1989). The sedimentation in the Umbria-Marche basin occurred at middle to lower bathyal depths of 1500–2500 m (Arthur and Fischer, 1977; Galeotti et al., 2004). The Turonian R1 Member has an estimated sedimentation rate of ~10 mm ka^{-1}, based on a thickness of 40 m of the Turonian Stage (Arthur and Fischer, 1977; Cohen et al., 2013), consistent with the 10.5 mm ka^{-1} estimated by spectral analysis (Batenburg et al., 2016). After the K-Pg boundary the sedimentation rate decreases, and the average sedimentation rate for the R3 member in the lower Paleocene is 4.3 mm ka^{-1} (Sinnesael et al., 2016).

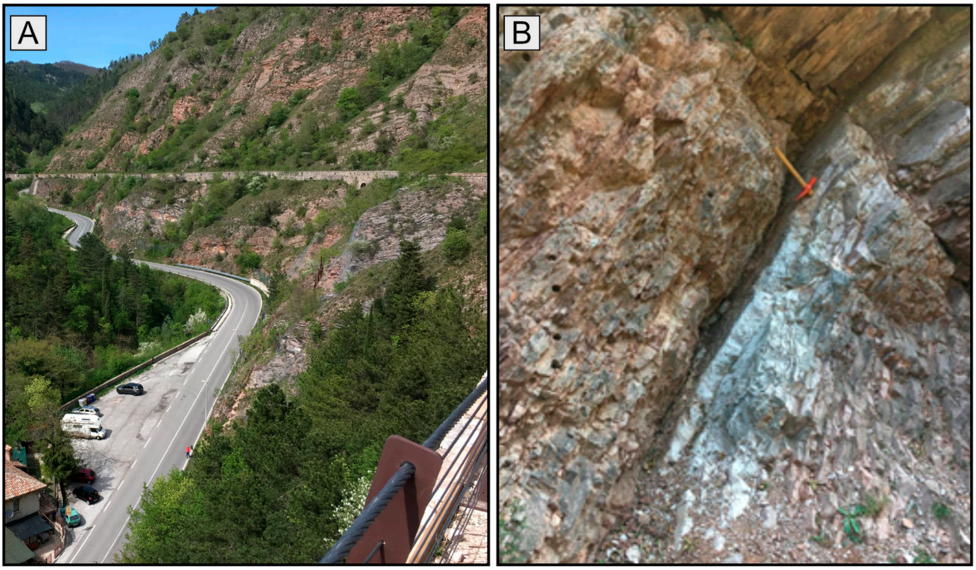

Figure 7. The classical Tethyan Bottaccione Gorge section. A) Seen from the medieval aquaducts just north of the town of Gubbio. Pelagic rocks deposited in the Cretaceous Tethyan sea can be seen cropping out on both sides of the gorge along the road. B) The iridium-rich clay layer that marks the Cretaceous-Paleogene boundary in the Bottaccione Gorge section lies just around the bend at the end of the road in A. The ~2 cm thick clay is underlain by a zone of bleached white limestone, possibly related to more reducing sediment conditions when increased amount of organic material reached the sea floor after the K-Pg event (Lowrie et al., 1990).

5. Summary of papers

5.1 Paper I

Title: Meteorite flux to Earth in the Early Cretaceous as reconstructed from sediment-dispersed extraterrestrial spinels
Authors: B. Schmitz, P.R. Heck, W. Alvarez, N.T. Kita, S.S. Rout, A. Cronholm, C. Defouilloy, E. Martin, J. Smit, F. Terfelt
Journal: Geology, v. 45, p. 807-810 (2017)

In this paper the aim was to determine the meteorite flux to Earth in the Early Cretaceous and to investigate if the LL chondritic Baptistina family forming event (ca. 140–190 Ma ago), could be detected. We recovered 108 extraterrestrial spinel grains (>32 µm) in 1652 kg of the Italian pelagic Maiolica limestone. Elemental and three oxygen isotope analyses were used, providing a first-order estimate of the major types of asteroids delivering material during this time. The results show that ~80% of the extraterrestrial spinels originated from ordinary chondrites. The ratios between the three groups of ordinary chondrites, H, L, LL, are similar to the present ratio of ~1:1:0.2. We found no signs of a hypothesized Baptistina LL-chondrite breakup event in these sediments. About 10% of the grains in the Maiolica originate from achondritic meteorite types that are very rare (<1%) on Earth today but were even more common in the Ordovician. Because most meteorite groups have lower spinel content than the ordinary chondrites, the data indicate that the latter did not dominate the flux during the Early Cretaceous to the same extent as today. Based on the spinel studies published prior to this study, we argued that there may have been a gradual long-term (a few hundred million years) turnover in the meteorite flux, from dominance of achondrites in the early Phanerozoic to ordinary chondrites in the late Phanerozoic, interrupted by short-term (a few million years) meteorite cascades from single asteroid breakup events.

5.2 Paper II

Title: From the mid-Ordovician into the Late Silurian: Changes in the micrometeorite flux after the L chondrite parent breakup
Authors: E. Martin, B. Schmitz, H.-P. Schönlaub
Journal: Meteoritics & Planetary Science, v. 53, p. 2541-2557 (2018)

In this paper we present the first reconstruction of the micrometeorite flux to Earth in the Silurian Period (ca. 425 Ma ago). We searched 321 kg of condensed, marine limestone from the late Silurian Cellon section, southern Austria, for chrome-spinel grains from micrometeorites that fell on the ancient sea floor. A total of 155 extraterrestrial spinel grains (10 grains >63 µm, and 145 in the 32–63 µm fraction) were recovered. For comparison, we also searched 102 kg of similar limestone from the mid-Ordovician Komstad Formation in southern Sweden. This limestone formed within ~1 Ma after the breakup of the L chondrite parent body (LCPB) in the asteroid belt. In this sample we found 444 extraterrestrial spinel grains in the >63 µm fraction and estimate a content of at least 7000 such grains in the 32–63 µm fraction. Our results show that in the late Silurian, ~40 Ma after the LCPB, the flux of ordinary equilibrated chondrites had decreased by two orders of magnitude, almost down to background levels, of which the L-chondritic micrometeorites has waned off significantly, from >99% in the post-LCPB mid-Ordovician to ~60% in the late Silurian, with ~30% H-, and ~10% LL-chondritic grains. In the late Silurian, primitive achondrite abundances appear similar to today.

5.3 Paper III

Title: A record of the micrometeorite flux during an enigmatic extraterrestrial ^{3}He anomaly in the Turonian (Late Cretaceous)
Author: E. Martin, B. Schmitz, A. Montanari
Journal: Geological Society of America Special Papers, v. 542, p. 303-318 (2019)

In this paper we wanted to study the contents of extraterrestrial spinel over a ca. 2 Ma interval of elevated ^{3}He (“K3”) in the Turonian (ca. 90–92 Ma), recorded in the Bottaccione section, Italy. The ^{3}He anomaly has an unusually spiky and temporal progression not readily explained by present models for delivery of extraterrestrial dust to Earth. From ca. 30 m of the limestone succession a total of 979 kg of rock from levels below and within the ^{3}He excursion yielded 603 spinel grains (32–355 µm). Of those, 115 represent equilibrated ordinary chondritic chromite (EC). Within the ^{3}He excursion, there is no change in the number of EC grains per kilogram of sediment, but H-chondritic grains dominate over L and LL grains (70%, 27%, and 3%), contrary to the interval below the excursion, where the relation between the three groups (50%, 44%, and 6%) is more similar to today and to the Early

Cretaceous. Intriguingly, there is also a factor-of-five increase of vanadium-rich chrome spinels within the ^{3}He anomaly, likely originating from achondritic and unequilibrated ordinary chondritic meteorites. Additionally, some layers within the anomaly are enriched with transparent Fe-rich MgAl spinels not previously detected. Their composition does not match with spinel from carbonaceous chondrites but has better match with both terrestrial marble high-T spinel and unequilibrated chondritic chrome spinel. Previous suggestions that the ^{3}He anomaly is related to a comet or asteroid shower possibly associated with dust-producing lunar impacts are not supported by our data. Instead, the spinel data preliminary indicates a more general disturbance of the asteroid belt, where different parent bodies or source regions of micrometeorites were affected at the same time. An additional number of spinel grains need to be recovered and oxygen isotopic analyses of grains are required to better resolve the origin of the ^{3}He anomaly.

5.4 Paper IV

Title: Zircon provenance analysis from Lower Paleocene pelagic limestones of the Bottaccione section at Gubbio (Umbria-Marche basin, Italy)
Authors: L.E. Aguirre-Palafox, W. Alvarez, S. Boschi, E. Martin, B. Schmitz
Journal: Geological Society of America Special Papers, v. 542, p. 159-174 (2019)

When extracting chrome-spinel grains from the early Paleocene samples for paper VII, zircon grains were also separated. Dating detrital zircon grains from sands and sandstones has become an important technique for determining sediment provenance and dispersal patterns. We believe this to be the first provenance study of zircon grains extracted from large samples of pelagic limestone. In paper IV, these zircon grains were dated with U-Pb analyses by conducting laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The recovered zircons included both euhedral crystals interpreted as airborne ash from volcanic eruptions of the same age as the sediment in which they were found, and rounded zircons interpreted as windblown detrital material with a history of sediment transport, probably derived from desert regions. Samples from five levels in the 12 m immediately above the Cretaceous-Paleogene boundary in the section, yielded detrital zircon grains with ages clustered in eight bands extending back to the Neoarchean. A previous study of this outcrop using proxies for the noncarbonate detrital content had suggested a source region for this dust either in North Africa or in Central Asia. A comparison of our dates from the actual dust grains with geochronological studies from the literature suggests source regions in North Africa and/or the Iberian Peninsula, rather than in Central Asia. With this conclusion, we considered the orogenic events that may have produced each of the eight age bands, the specific source regions that may have supplied zircons from each age group, and the implications for paleoclimate (especially aridity) and paleo-wind conditions during this time.

5.5 Paper V

Title: The micrometeorite flux to Earth during the Frasnian–Famennian transition reconstructed in the Coumiac GSSP section, France
Authors: B. Schmitz, R. Feist, M.M.M. Meier, E. Martin, P.R. Heck, D. Lenaz, D. Topa, H. Busemann, C. Maden, A.A. Plant, F. Terfelt
Journal: Earth and Planetary Science Letters, v. 522, p. 234-243 (2019)

In this study, 180 extraterrestrial chrome-spinel grains were extracted in 957 kg of marine limestone (formed ca. 374–372 Ma ago) from the Frasnian–Famennian stratotype section at Coumiac, southern France. The data could test whether the small cluster of roughly coeval, large impact structures is related to an asteroid breakup and shower with possible bearings on the late Devonian biodiversity crisis. Noble-gas measurements of individual grains show high solar-wind content, implying an origin from decomposed micrometeorites. Element analyses indicate a dominance of ordinary chondritic over achondritic grains, similar to the recent flux. The relation between H, L and LL meteorites is ~29–58–13%, similar to the late Silurian flux, ~31–63–6%. The data show no indication of an enhanced late Devonian micrometeorite flux that would accompany an asteroid shower. However, in a single limestone bed formed immediately before the Upper Kellwasser horizon, that represents the main end-Frasnian species-turnover event, we found an enrichment of ~10 ordinary chondritic grains (>63μm) per 100 kg of rock, compared to the ~1–3 grains per 100 kg that characterise the background flux. The anomalously abundant grains have H, L, and LL proportion as the other samples in the section and may be related to an enhanced flux of extraterrestrial dust during postulated minima in both the 405 ka and 2.4 Ma Earth-orbit eccentricity cycles at the onset of the Upper Kellwasser event. In the present solar system, the dust accretion at Earth is the highest at eccentricity minima because of the spatial distribution of dust bands of the zodiacal cloud. Besides this, the data here and in previous studies support a stable meteorite flux through the late Silurian and Devonian, with a steady decline in L chondrites following the L chondrite parent body breakup.

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

Journal: Science Advances, v. 5, p. eaax4184 (2019)

The breakup of the L-chondrite parent body in the asteroid belt 466 Ma ago still delivers almost a third of all meteorites falling on Earth. In this paper, a multiproxy approach, consisting of extraterrestrial chromite, ^{3}He, bulk Al_2O_3, and Os isotopic data for Ordovician sediments, show that the breakup took place just at the onset of a major, eustatic sea level fall previously attributed to an Ordovician ice age. Shortly after the breakup, the flux to Earth of the most fine-grained, extraterrestrial material increased by three to four orders of magnitude. In the present stratosphere, extraterrestrial dust represents 1% of all the dust and has no climatic significance. The extraordinary amounts of dust in the entire inner solar system during >2 Ma following the LCPB breakup cooled Earth and triggered Ordovician icehouse conditions, sea level fall, and major faunal turnovers related to the Great Ordovician Biodiversification Event.

5.7 Paper VII

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

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

Journal: Meteoritics & Planetary Science, v. 55, p. 1615-1628 (2020)

The aim of this study was to describe the micrometeorite flux using chrome spinel during the earliest Paleogene. This study was extended from a previous study of Cronholm and Schmitz (2007). From a total of 843 kg of limestone, 86 extraterrestrial spinel grains (12 grains >63 µm, and 74 in the 32–63 µm fraction) was recovered. Ordinary chondrites dominated over achondritic meteorites similar to the recent flux, but H chondrites dominated over L and LL chondrites (69%, 22%, and 9%, respectively). This H-chondrite dominance is similar to that recorded within the ^{3}He anomaly (70%, 27%, and 3%) in the Turonian, but different from just before the anomaly, as well as in the early Cretaceous, where ratios are similar to the recent flux (~45%, 45%, and 10%). The K-Ar isotopic ages of recently fallen H chondrites indicate a small impact event on the H-chondrite parent body ~50 to 100 Ma ago. We tentatively suggested that this event is recorded by the Turonian ^{3}He

anomaly, resulting in an H-chondrite dominance among ordinary chondrites that extended into the Paleocene. Additionally, the sample spanning the 20 cm above the K–Pg boundary did not yield any spinel grains related to the K–Pg boundary impactor.

5.8 Paper VIII

Title: The micrometeorite flux in the Albian/Aptian age (~103-117 Ma): A search for Tycho ejecta in pelagic sediments using chrome spinels
Authors: E. Martin, B. Schmitz, F. Terfelt, L.E. Aguirre-Palafox, W. Alvarez
Journal: Geological Society of America Special Papers (*in press*)

Numerical models of meteorite delivery from impacts on the Moon have demonstrated that the impact event forming the lunar crater Tycho (~85 km diameter; ~109 Ma old) would have delivered considerable amounts of ejected material to Earth. The ejecta, containing lunar Ti- and V-rich chrome spinels, would have been distributed globally and admixed with sea-floor sediments over a few meters of a typical marine stratigraphic interval. In order to locate such ejecta, samples weighing ~12-25 kg each, with one-meter spacing were extracted over a ~30-meter interval of the deep-sea formed Calera Limestone, Albian and Aptian age (ca. 103-117 Ma ago), from the Pacifica Quarry, south of San Francisco.

In a total of 689 kg of limestone, 1154 chrome-spinel grains were found. Of these, 319 contain >0.45 wt% V_2O_3, of which 227 originate from equilibrated ordinary chondrites. The majority of the other 92 grains with >0.45 wt% V_2O_3 are most likely from different types of achondritic meteorites. Among these, there were 11 particularly Ti-rich chrome-spinel grains. The elemental abundances of these grains were compared with chrome spinel from lunar, HED and R-chondritic meteorites. This showed that only one of these grains could potentially be of lunar origin. The bulk of the other grains likely originate from HED meteorites based on oxygen isotopic analysis of similar grains in previous studies. Grains with TiO_2 >10 wt%, common among lunar spinels, were not found, further supporting an HED source for the Ti-rich grains. In summary, Albian and Aptian strata in the Pacifica quarry do likely not record any major lunar impact event. Either the timing of the impact is located within a ~110-114 Ma ago unconformity in the middle part of the section or the impact is likely older than the studied interval.

5.9 Paper IX

Title: Impact-crater ages and micrometeorite paleofluxes compared: Evidence for the importance of ordinary chondrites in the flux of meteorites and asteroids to Earth the past 540 million years

Authors: B. Schmitz, M. Schmieder, S. Liao, E. Martin, F. Terfelt

Journal: Geological Society of America Special Papers (*in press*)

In this paper, the complete spinel data acquired over the years were compared to the terrestrial crater record. Although the ~200 impact craters known on Earth represent only a small fraction of the craters originally formed, the available data suggest an excess by one order-of-magnitude of craters, by number, in the interval ~470-440 Ma ago in the Ordovician. Most of these "excess" craters may be related to the breakup of the L-chondrite parent body (LCPB) in the asteroid belt 465.8 ± 0.3 Ma ago. This is the only obvious peak in the crater-age record that can currently be attributed to an asteroid shower and breakup event. Spatial crater densities in regions with high potential for crater preservation (e.g., Canada, Scandinavia) support a one order-of-magnitude increase in the flux of large (>0.1 km) impactors following the LCPB breakup. A similar pattern as seen in the cratering record has emerged in the studies of the micrometeoritic chrome-spinel flux through the Phanerozoic, with so far only one major spike in the flux, associated with the LCPB breakup. Similarly, the record of K-Ar and (U-Th)/He gas-retention ages of recently fallen meteorites only indicates one major breakup, the LCPB event, during the Phanerozoic. This is surprizing since astronomical backtracking studies of the orbits of asteroid family members indicate about 70 major family-forming breakups within the past ~540 Ma. These, apparently, have not left any clear imprint in Earth's geological record. The chrome-spinel grains recovered in our studies dominantly represent large micrometeorites (>300 µm) and as such also are representative of the flux of larger meteorites to Earth. An observed nearly constant flux to Earth of ordinary chondritic chrome-spinel grains throughout the Phanerozoic, except after the LCPB event, indicates that the present situation with a clear dominance of ordinary chondritic matter in the large micrometeorite and meteorite fractions has prevailed at least for the last 540 Ma. This is also supported in our samples by generally high ratios of ordinary chondritic chrome-spinel grains compared to other types of meteoritic spinel. The chrome-spinel data together with the abundance of fossil meteorites (1-20 cm in diameter) on the Ordovician seafloor, sets an upper limit at one order of magnitude in the increase following the LCPB in flux of large >0.1 km-diameter L-chondritic projectiles to Earth. We argue that the origin of impactors to Earth during the past 540 Ma has mirrored the flux of large micrometeorites and meteorites, with ordinary chondrites being an important, or most likely, the dominant (in numbers) component throughout.

6. Discussion

6.1 The flux of equilibrated ordinary, H, L, and LL chondrites

From the seven time-windows presented in this thesis, together with the complete spinel data from the 15 time windows covered in paper IX and Terfelt and Schmitz (2021), the equilibrated ordinary chondrites appear to have dominated the flux of coarse micrometeorites and meteorites during most of the past 500 Ma (Fig. 8). From the spinel data, the LCPB breakup is the only recorded massive family-forming event during this time. This correlates with both the terrestrial crater record (Schmieder and Kring, 2020) and a distinct peak in Ar-Ar ages in many of the recent L chondrites (Fig. 9; Swindle et al., 2014).

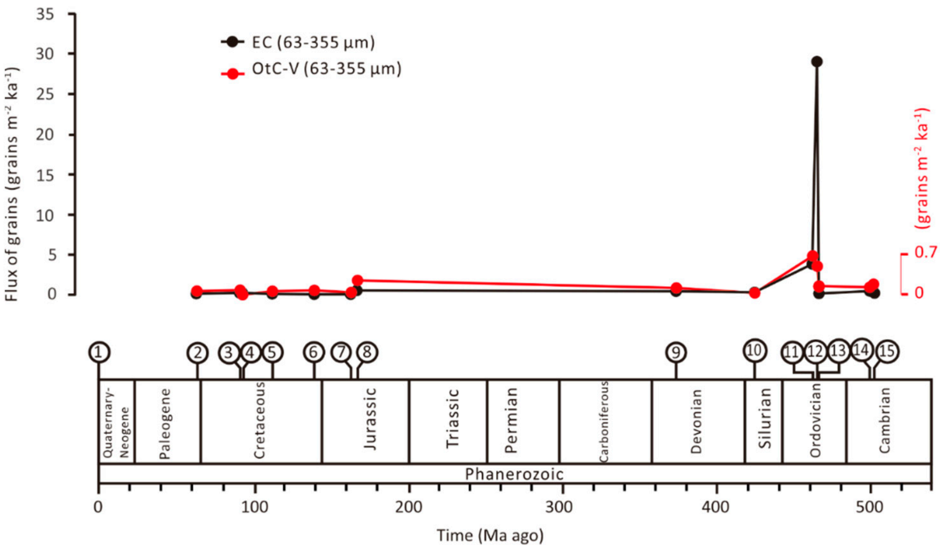

Figure 8. Extraterrestrial flux data from the 15 Phanerozoic time windows based on the >63 µm fraction. Note the two different scales. In many instances, like in the Early Cretaceous (6), Jurassic (7)(8), mid-Ordovician pre-LCPB (13), and the Cambrian (14 and 15), the flux of OtC-V grains appear to have been more pronounced compared to the recent flux of meteorites. The two synchronous Pre-LCPB time windows almost overlap with each other, and are therefore labeled as a single one (no. 13). Number references of the time-windows: 1, Recent flux of meteorites (Meteoritical Database, 2021); 2, Paper VII; 3, Paper III and Terfelt and Schmitz (2021); 4, Paper III; 5, Paper VIII; 6, Paper I; 7 and 8, Terfelt and Schmitz 2021; 9, Paper V; 10, Paper II; 11, Alwmark and Schmitz (2009); 12, Paper II; 13, Paper VI, Paper I, and Heck et al. (2017); 14 and 15, Terfelt and Schmitz (2021). Modified from fig. 4 in Paper IX.

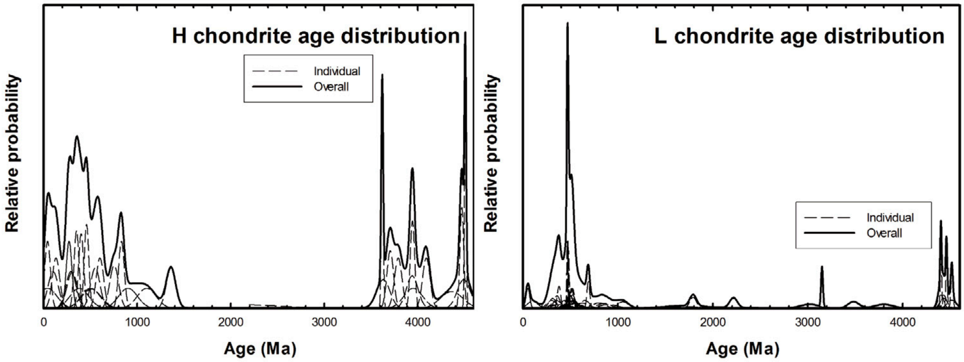

Figure 9. Age distributions among recent H and L chondrites. H chondrites have several smaller peaks in gas retention ages during the past 500 Ma, whereas L chondrites have one distinct peak around 500 Ma. Figures from Swindle et al. (2014).

The H chondritic spinel grains dominate over L (and LL) in several of the time-windows between 60 and 170 Ma ago, and ca 500 Ma ago. As seen in Fig. 10A, the curve for L chondritic grains decline after the LCPB breakup in the Ordovician, and at some point, before or around 170 Ma ago in the Jurassic, there is a shift, and a new time regime starts, where H chondritic grains dominate over L. A similar tendency can be seen in the Ar-Ar ages of recent ordinary chondrites, illustrated in Fig. 10B. In paper VII, we tentatively suggested that the dominance of H chondritic grains in the early Paleocene and Turonian ^{3}He anomaly, was a consequence of a collision on the H chondrite parent body that occurred in the Turonian. The plot of Ar-Ar ages of H chondrites (Fig. 9 and Fig. 10B) shows three peaks at ca. 280, 355, and 450 Ma ago, which could be records of multiple collisions (Swindle et al., 2014). There is also a smaller broader peak in ages the last 100 Ma (Graf and Marti, 1995). Additionally, there are two craters with ages around the time for the Turonian ^{3}He anomaly: The 91 ± 7 Ma old Steen River impact structure, Canada (Walton et al., 2016; Walton et al., 2017), and the 89.0 ± 2.7 Ma old Dellen impact structure, Sweden (Deutsch et al., 1992). There is also the younger, 73.3 ± 5.3 Ma old Lappajärvi impact structure, likely produced by an H-chondritic projectile (Tagle et al., 2007). However, with only a few craters, the timing could very well be coincidental. New additional data from the ^{3}He anomaly presented in Terfelt and Schmitz (2021), shows that H-chondritic grains dominated in the anomaly but to a lesser degree than previous data suggested, which, together with the Ar-Ar ages for H chondrites, could indicate that the Late Cretaceous ^{3}He anomalies are not directly linked to H chondrites, contrary to the proposition in paper VII.

Partial resetting of the Ar-Ar clock is also a common issue, where trapped Ar from incomplete degassing gives older ages. This is the case for recent L chondrites with ages around 500 Ma ago – where the breakup event itself, as recorded in the sediments, took place 465.76 ± 0.30 Ma ago (Liao et al., 2020). This could also be the case for the three peaks in ages of H chondrites, where the younger age is the true age, and that there was only one thermal event on the H-chondrite parent body around 300 Ma ago. This would have occurred in the time where there is no spinel data available (between ca. 170 and 370 Ma ago). The peak in ages around 450 Ma ago is not recorded by the EC grains within the Silurian sediments, but it is possible that a small event during this time would be overprinted by the dominance in L chondrites that still prevailed during the Silurian.

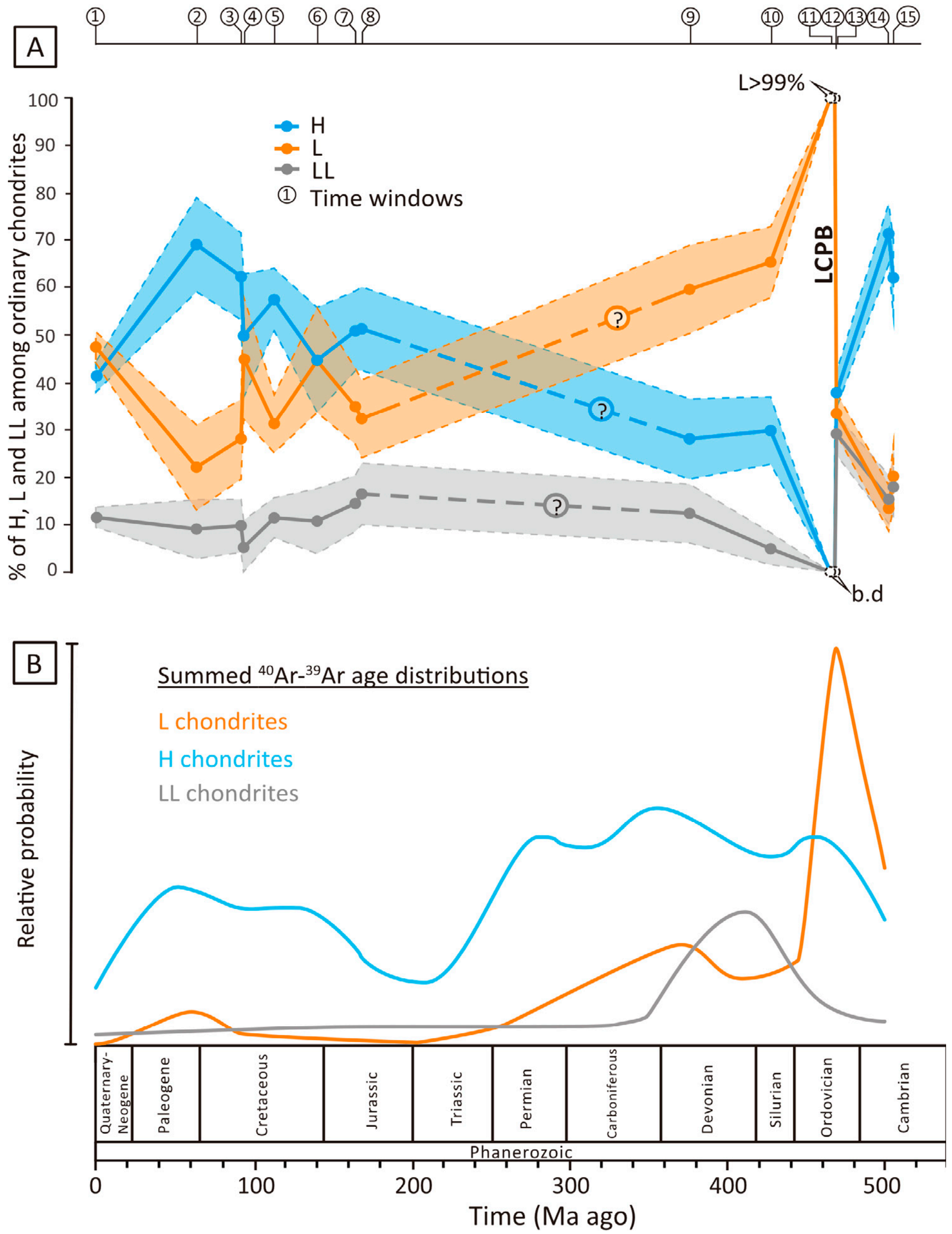

Figure 10. Comparison between the equilibrated ordinary chondritic chromite (EC) grains and the Ar-Ar ages of recent ordinary chondrites. A) Percentage of H, L and LL chondrites among ordinary chondrites during 15 Phanerozoic time windows studied and today. Based on table 2 in paper IX and Terfelt and Schmitz (2021). Based on both the small (32–63 µm) and the large (>63 µm) fraction of EC grains, after a 10-percent-overlap correction of TiO_2. Colored shadow regions indicate 1σ uncertainties evaluated through binomial probability. Dashed bold lines and question marks represent extrapolated percentages. Numbers of time windows as in Fig. 8. Modified from fig. 4 in paper IX B) shows the summed probability in Ar-Ar ages of recent ordinary chondrites during the past 500 Ma, derived from Fig. 9 (Swindle et al., 2014).

The LL chondrites are the rarest among recent ordinary chondrites and in such there are fewer shock ages obtained from this group. Different from H and L, LL chondrites display two very distinct peaks around 4200-4350 Ma ago indicating an early collisional event around this time. However, for the past 500 Ma, the data for the LL chondrites is too scares to argue for any event to have occurred (Swindle et al., 2014). Except for the rare occurrences in pre-LCPB strata and one of the Devonian beds, the LL chondrites appear to be at a steady state of ca. 10% among the ordinary chondrites throughout the Phanerozoic, with no indication of any collisional event during this time.

6.2 ^{3}He anomalies and lunar impacts

The record of extraterrestrial ^{3}He have been established for marine sediments representing the past 100 Ma (Farley et al., 1998; Mukhopadhyay et al., 2001; Farley et al., 2006; Farley et al., 2009; Farley et al., 2012). Within this record, several peaks of elevated ^{3}He have been detected. These elevations of ^{3}He are represented by particles <35 μm (Farley et al., 1997), mostly IDPs <10 μm, and to a lesser extent of micrometeorites (Mukhopadhyay and Farley, 2006; Brook et al., 2009). Apart from spinel minerals, these particles are liberated from fragmentations of all types of celestial bodies, both asteroids and comets. Sediments in which three of these ^{3}He anomalies occur have been searched for extraterrestrial spinel, of which one (K3) in the Late Cretaceous is covered in paper III. The other anomalies searched for spinel occur in the late Miocene (Boschi et al., 2019) and late Eocene (Schmitz et al., 2015; Boschi et al., 2017).

The spinel grains extracted within the K3 event differ from those extracted in the sediments below the anomaly. The amount of EC grains was of equal amounts both within and below the anomaly but the average percentage for H chondritic grains were higher within the anomaly. The other extraterrestrial (OtC-V) grains are a factor of five more common within the anomaly and could have affinity with achondrites or unequilibrated ordinary chondrites. Fe-rich MgAl-spinel grains occur in high numbers in several samples within the anomaly, but none below. The MgAl spinels have a composition that differs from lunar equivalents analysed in e.g., Apollo 14 and Luna 20 samples, but where the latter lunar spinels contain >2 wt% Cr_2O_3 (Roedder and Weiblen, 1972; Haggerty, 1973). The average size of spinel grains in carbonaceous chondrites is generally <32 μm, but there are reports of spinel grains exceptionally large, as those found in Murchison (CM) and Allende (CV3) (Simon et al., 1994; Simon et al., 2000). These also contained a large amount of Cr_2O_3, however, which is only minor, at most, in the MgAl-spinels found in K3. Spinels inside calcium-aluminium-rich inclusions from unequilibrated chondrites can have similar composition (Bischoff and Keil, 1983; Wlotzka, 2005). However, they are usually smaller than 32 μm and spinel with minor contents of Cr_2O_3 appear to be less common compared to the accompanying Cr spinels. The other possibility is that they are terrestrial. Although terrestrial spinels with similar composition appear to be somewhat rare, they are reported in island arc basalts (Arculus and Wills, 1980; Della-Pasqua et al., 1995) and marble units associated with contact metamorphism (Janardhan et al., 2001). The high Ti- and V-rich chrome spinels that would be expected from ejected lunar regolith were not found, hence a lunar impact scenario could not be confirmed A possible explanation for the absence of such grains could be that the size distribution of material liberated by impacts follow a power law, where only the finest particles that retain most of the ^{3}He increase by a factor-of-four, which might not correspond to a detectable increase in the larger fractions.

In paper VIII where the Tycho ejecta was searched for in Aptian and Albian sediments, we calculated the amount of grains that we would expect to find in a small 20 kg sample based on the number of spinels found per gram in the lunar meteorite Shisr 162, the size of the crater, the numerical model of lunar meteorite delivery (Gladman et al., 1995), and of the survivability of unmelted lunar material passing through the atmosphere (ca. 70%, Artemieva and Shuvalov [2008]). The first bulk of lunar material would arrive to Earth in the first 50 ka after the impact, representing only ca. 20 cm of strata in the Pacifica section. A 20 kg sample from this layer could contain ca. 250-750 lunar grains. The following million years after the impact about 3-10 grains, and the remainder, ca. 9 Ma less than one grain per sample. Not finding more than one potential lunar grain in the section, we draw the conclusion in paper VIII that the Tycho crater must be either within the hiatus around 110-114 Ma ago, or, more likely, much older than 117 Ma ago. There are, however, possibilities of overestimations of e.g., the amount of accreted mass of ejected unmelted lunar material by Earth, the fraction of unmelted particles during impact, or the rate of survivability of lunar particles during atmospheric entry. In a study by Fritz (2012), several ^{3}He anomalies were tentatively linked with large young lunar craters. The craters suggested to have created the late Eocene (Moore F and Byrgius A) and Miocene (Giordano Bruno) ^{3}He excursions, all with a diameter of ca. 20 km, would have ejected 1-2 orders of magnitude less material compared to the Tycho crater. With the previous calculations of 3-10 grains per 20 kg sample within the first one million year after impact, one or two magnitudes less ejecta material would produce, at most, one grain per sample, which also might explain the absence of lunar grains within the K3 interval in paper III.

7. Conclusions and outlook

For the meteorite types that contain large spinel minerals, the micrometeorite flux has been documented in the papers included in this thesis. In most time windows, the flux is dominated by ordinary chondrites much like today, but in a few times the flux of achondrites and primitive achondrites have been more pronounced, as documented in e.g., the Cambrian, the mid-Ordovician pre-LCPB, and the Jurassic. Since achondritic meteorites have lower abundances of chrome spinel compared to ordinary chondrites, the often-low EC/OtC-V ratios indicate that achondrites sometimes constituted a greater part of the meteorite flux in ancient times compared to today.

The equilibrated ordinary chondritic chromite grains indicate a relatively steady flux during the Phanerozoic. The relation between the three groups H, L, and LL chondrites, were comparable with the recent meteorite flux, with H and L chondrites delivering the bulk of the EC grains. The record is truncated by the enormous increase and dominance of L-chondritic grains after the LCPB in the mid-Ordovician, that extends, and declines all the way into the Late Devonian. At some point in the Jurassic, the flux is instead dominated by H chondritic chromite but to a lesser extent, with a maximum of a factor of two increase among the coarse micrometeorites indicating smaller impact events. The results clearly indicate that there is only one major asteroid breakup event that is distinguishable from the chrome-spinel data and the terrestrial crater record. Present models on meteorite and asteroid delivery to Earth are not consistent with these results, and alternative delivery mechanisms might be needed.

The ^{3}He interval (K3) in the Turonian is likely associated with the factor-of-five increase in OtC-V grains originating from e.g., achondrites or unequilibrated ordinary chondrites. These grains together with the many MgAl-spinel grains, could be analysed further for O-, and Cr-isotopic composition to determine their origin.

The ejecta from the Tycho crater was not found within the sediment samples extracted from the Pacifica Quarry, 103-117 Ma. There is still potential of finding the impact ejecta layer from the Tycho crater, however, considering that the spinel-approach is both time consuming and dependent on appropriate laboratory scaling for the leaching of large samples, establishing ^{3}He profiles might be a more suitable first step.

Although time- and effort-consuming, preferably all the spinel grains, including the OtC, terrestrial category of grains, could be analysed for e.g., O-, and Cr-isotopic composition, as there are likely some extraterrestrial spinel with low vanadium contents. Future developments to characterize the flux in smaller size fractions and that of carbonaceous micrometeorites would improve the characterization of the overall flux in ancient times. Even though there are many more questions left to answer, the results herein document a first reconstruction of the ancient micrometeorite flux to Earth during the Phanerozoic Eon, using spinel as a proxy.

8. Acknowledgements

It is with both joy and a bit of sadness that I now have reached the end of these years as a doctoral student. But I should feel tons lighter, at least. Undertaking research has been a winding road with many ups and downs, both eureka-like moments and painful self-doubt when an idea turned out to be a dead-end street rather than a golden gate. One door opens two other doors, and so on, but luckily, I have had great guidance by my supervisors. I have been very lucky to have gotten a chance to explore this new field of astrogeobiology and the micrometeorite flux in deep time, and for that I am very grateful to my main supervisor Birger Schmitz for entrusting me with these high-risk/high gain projects. Always there for support, feedback, and interesting discussions. Much gratitude to my supervisor Fredrik, that with positiveness and good spirit have answered any question, and pedagogically supervised in the lab. It has been inspirational in how no problem is unsolvable, no matter how big or small. Also demonstrating that clogs can be fashionable anywhere. My gratitude to Anders Cronholm for demonstrations of the SEM, and the cheerful atmosphere in the office. Also, for leaving a mixed cd in the lab that I listened to when sieving got just a tiny bit dull. To my fellow PhD student (now Dr.) Samuele Boschi, thank you for your positive spirits during these years, helpfulness, and inspirational dedication to your projects. I appreciate the many times we spent in the field, the courses we took together and discussions. I also wish to extend my gratitude to your amazing family in Italy, that were so kind in the logistic support with our samples and welcoming in their home. Just wish I would have remembered more Italian words from school – mi dispiace! Thanks to co-worker Faisal Iqbal, for your sincerity and the many philosophical conversations concerning the meaning of life, spirituality, and human nature in general. Best of luck in the future! Working in and being a part of this research team has been very inspirational and there has never been a dull moment in the office or in the field. I would also like to extend my gratitude to the co-authors of the papers in this thesis for all your fine contributions. I had a wonderful time working on these projects and collaborating with all of you. A big thank you to co-supervisor Per Kristiansson for being so welcoming to me and inviting us to the Friday outings that you arranged with the microbeam-people, with Charlotta, Nathaly, Linus, Mikael E, Jan, and others, with shuffleboard and subsequent dinner to one of the many quaint restaurants in Lund.

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9.References

Aboussalam, Z., and Becker, R., 2001, Prospects for an upper Givetian substage: Fossil Record, v. 4, p. 83-99, doi: 10.5194/fr-4-83-2001

Aguirre-Palafox, L.E., Alvarez, W., Boschi, S., Martin, E., and Schmitz, B., 2019, Zircon provenance analysis from Lower Paleocene pelagic limestones of the Bottaccione section at Gubbio (Umbria-Marche basin, Italy), *in* Koeberl, C., and Bice, D.M., eds., 250 Million Years of Earth History in Central Italy: Celebrating 25 Years of the Geological Observatory of Coldigioco: Geological Society of America Special Papers, v. 542**,** doi: 10.1130/2019.2542(08)

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

Alvarez, W., Arthur, M.A., Fischer, A.G., Lowrie, W., Napoleone, G., Premoli Silva, I., and Roggenthen, W.M., 1977, Upper Cretaceous-Paleocene magnetic stratigraphy at Gubbio, Italy; V, Type section for the late Cretaceous-Paleocene geomagnetic reversal time scale: Geological Society of America Bulletin, v. 88, p. 383-389.

Alwmark, C., and Schmitz, B., 2009, The origin of the Brunflo fossil meteorite and extraterrestrial chromite in Mid-Ordovician limestone from the Gärde Quarry (Jämtland, central Sweden): Meteoritics & Planetary Science, v. 44, p. 95-106, doi: DOI: 10.1111/j.1945-5100.2009.tb00720.x

Anders, E., 1964, Origin, age, and composition of meteorites: Space Science Reviews, v. 3, p. 583, doi: 10.1007/bf00177954

Arculus, R.J., and Wills, K.J.A., 1980, The petrology of plutonic blocks and inclusions from the Lesser Antilles Island Arc: Journal of petrology, v. 21, p. 743-799, doi: 10.1093/petrology/21.4.743

Artemieva, N.A., and Shuvalov, V.V., 2008, Numerical simulation of high-velocity impact ejecta following falls of comets and asteroids onto the Moon: Solar System Research, v. 42, p. 329–334, doi: 10.1134/S0038094608040059

Arthur, M.A., and Fischer, A.G., 1977, Upper Cretaceous-Paleocene magnetic stratigraphy at Gubbio, Italy; I, Lithostratigraphy and sedimentology: Geological Society of America Bulletin, v. 88, p. 367-371.

Batenburg, S.J., De Vleeschouwer, D., Sprovieri, M., Hilgen, F.J., Gale, A.S., Singer, B.S., Koeberl, C., Coccioni, R., Claeys, P. and Montanari, A., 2016, Orbital control on the timing of oceanic anoxia in the Late Cretaceous: Climate of the Past, v. 12, p. 1995-2009, doi: 10.5194/cp-12-1995-2016

Bischoff, A., and Keil, K., 1983, Ca-Al-rich chondrules and inclusions in ordinary chondrites: Nature, v. 303, p. 588-592, doi: 10.1038/303588a0

Bjärnborg, K., and Schmitz, B., 2013, Large spinel grains in a CM chondrite (Acfer 331): Implications for reconstructions of ancient meteorite fluxes: Meteoritics & Planetary Science, v. 48, p. 180-194, doi: 10.1111/maps.12050

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

Boschi, S., Schmitz, B., Martin, E., and Terfelt, F., 2020, The micrometeorite flux to Earth during the earliest Paleogene reconstructed in the Bottaccione section (Umbrian Apennines), Italy: Meteoritics & Planetary Science, v. 55, p. 1615-1628, doi: 10.1111/maps.13539

Boschi, S., Schmitz, B., and Montanari, A., 2019, Distribution of chrome-spinel grains across the ^{3}He anomaly of the Tortonian Stage at the Monte dei Corvi section, Italy, *in* Koeberl, C., and Bice, D. M., eds., 250 Million Years of Earth History in Central Italy: Celebrating 25 Years of the Geological Observatory of Coldigioco: Geological Society of America, 542, doi: 10.1130/2019.2542(21)

Brett, C.E., Ferretti, A., Histon, K., and Schönlaub, H.P., 2009, Silurian sequence stratigraphy of the Carnic Alps, Austria: Palaeogeography Palaeoclimatology Palaeoecology, v. 279, p. 1-28, doi: 10.1016/j.palaeo.2009.04.004

Brook, E.J., Kurz, M.D., and Curtice, J., 2009, Flux and size fractionation of ^{3}He in interplanetary dust from Antarctic ice core samples: Earth and Planetary Science Letters, v. 286, p. 565-569, doi: 10.1016/j.epsl.2009.07.024

Channell, J.E.T., Cecca, F., and Erba, E., 1995, Correlations of Hauterivian and Barremian (Early Cretaceous) stage boundaries to polarity chrons: Earth and Planetary Science Letters, v. 134, p. 125-140, doi: 10.1016/0012-821X(95)00111-O

Chen, J., and Lindström, M., 1991, Cephalopod Septal Strength Indices (SSI) and depositional depth of the Swedish Orthoceratite limestone: Geologica et Palaeontologica, v. 25, p. 5-18.

Ceballos, G., Ehrlich, P.R., and Dirzo, R., 2017, Biological annihilation via the ongoing sixth mass extinction signaled by vertebrate population losses and declines: Proceedings of the National Academy of Sciences, v. 114, p. E6089-E6096, doi: 10.1073/pnas.1704949114

Cohen, K.M., Finney, S.C., Gibbard, P.L., and Fan, J.X., 2013, The ICS international chronostratigraphic chart: Episodes, v. 36, p. 199-204,

Cordier, C., and Folco, L., 2014, Oxygen isotopes in cosmic spherules and the composition of the near Earth interplanetary dust complex: Geochimica et Cosmochimica Acta, v. 146, p. 18-26, doi: 10.1016/j.gca.2014.09.038

Corradini, C., Corriga, M.G., Mannik, P., and Schönlaub, H.P., 2014, Revised conodont stratigraphy of the Cellon section (Silurian, Carnic Alps): Lethaia, v. 48, p. 56-71, doi: 10.1111/let.12087

Cronholm, A., and Schmitz, B., 2007, Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone at Gubbio, Italy; the flux of unmelted ordinary chondrites: Meteoritics & Planetary Science, v. 42, p. 2099-2109, doi: 10.1111/j.1945-5100.2007.tb01010.x

Cronholm, A., and 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, v. 208, p. 36-48, doi: 10.1016/j.icarus.2010.02.004

De Laubenfels, M.W., 1956, Dinosaur extinction: One more hypothesis: Journal of Paleontology, v. 30, p. 207-212.

Della-Pasqua, F.N., Kamenetsky, V.S., Gasparon, M., Crawford, A.J., and Varne, R., 1995, Al-spinels in primitive arc volcanics: Mineralogy and Petrology, v. 53, p. 1-26, doi: 10.1007/BF01171944

Deutsch, A., Buhl, D., and Langenhorst, F., 1992, On the significance of crater ages: new ages for Dellen (Sweden) and Araguainha (Brazil). Tectonophysics, v. 216, p. 205-218, doi: 10.1016/0040-1951(92)90167-5

Dronov, A. & Mikuláš, R., 2010, Paleozoic ichnology of St. Petersburg Region: Excursion Guidebook: Geological Institute, Russian Academy of Sciences, Moscow, 70 pp.

Dronov, A., 2005, Introduction to the geology of the St. Petersburg region, *in* Dronov, A., Tolmacheva, T., Raevskaya, E., and Nestell, M., eds., Cambrian and Ordovician of St. Petersburg area, Guidebook of the pre-conference field trip: St. Petersburg State University, Saint-Petersburg, p. 2-15.

Drouard, A., Gattacceca, J., Hutzler, A., Rochette, P., Braucher, R., Bourlès, D., Team, A., Gounelle, M., Morbidelli, A., Debaille, V., Van Ginneken, M., Valenzuela, M., Quesnel, Y., and Martinez, R., 2019, The meteorite flux of the past 2 m.y. recorded in the Atacama Desert: Geology, v. 47, p. 673-676, doi: 10.1130/g45831.1

Faraoni, P., Flore, D., Marini, A., Pallini, G., and Pezzoni, N., 1997, Valanginian and early Hauterivian ammonite successions in the Mt Catria group (Central Apennines) and in the Lessini Mts (Southern Alps), Italy: Palaeopelagos, v. 7, p. 59-100.

Farley, K.A., Love, S.G., and Patterson, D.B., 1997, Atmospheric entry heating and helium retentivity of interplanetary dust particles: Geochimica et Cosmochimica Acta, v. 61, p. 2309-2316, doi: 10.1016/S0016-7037(97)00068-9

Farley, K.A., Montanari, A., Shoemaker, E.M., and Shoemaker, C.S., 1998, Geochemical evidence for a comet shower in the late Eocene: Science, v. 280, p. 1250-1253.

Farley, K.A., Vokrouhlicky, D., Bottke, W.F., and Nesvorny, D., 2006, A late Miocene dust shower from the break-up of an asteroid in the main belt: Nature, v. 439, p. 295-297, doi: 10.1038/nature04391

Farley, K.A., 2009, Late Eocene and late Miocene cosmic dust events: Comet showers, asteroid collisions, or lunar impacts, *in* Koeberl; C., and Montanari, A., eds., The Late Eocene Earth—Hothouse, Icehouse, and Impacts: Geological Society of America Special Papers, v. 452, p. 27-35, doi: 10.1130/2009.2452(03)

Farley, K.A., Montanari, A., and Coccioni, R., 2012, A record of the extraterrestrial He-3 flux through the Late Cretaceous: Geochimica et Cosmochimica Acta, v. 84, p. 314-328, doi: 10.1016/j.gca.2012.01.015

Feist, R. and Klapper, G., 1985, Stratigraphy and conodonts in pelagic sequences across the Middle-Upper Devonian Boundary, Montagne Noire, France: Palaeontographica Abteilung a -Stuttgart-, v. 188, p. 1-18.

Folco, L., and Cordier, C., 2015, Micrometeorites, *in* Lee, M. R. and Leroux, H., eds., Planetary Mineralogy: European Mineralogical Union Notes in Mineralogy, Mineralogical Society of Great Britain and Ireland, v. 15, p. 253-297, doi: 10.1180/EMU-notes.15.9

Fritz, J., 2012, Impact ejection of lunar meteorites and the age of Giordano Bruno: Icarus, v. 221, p. 1183-1186, doi: 10.1016/j.icarus.2012.08.019

Galeotti, S., Kaminski, M., Coccioni, R., and Speijer, R., 2004, High-resolution deep-water agglutinated foraminiferal record across the Paleocene/Eocene transition in the Contessa Road Section (Central Italy), *in* Bubik, M. and Kaminski, M.A., eds., Proceedings of the Sixth International Workshop on Agglutinated Foraminifera (Prague, Czech Republic, September 1-7, 2001): Grzybowski Foundation Special Publication. Grzybowski Foundation, London, UK, v. 8, p. 83-103.

Galeotti, S., Moretti, M., Cappelli, C., Phillips, J., Lanci, L., Littler, K., Monechi, S., Petrizzo, M.R., Silva, I.P., and Zachos, J.C., 2015, The Bottaccione section at Gubbio, central Italy: a classical Paleocene Tethyan setting revisited: Newsletters on Stratigraphy, v. 48, p. 325-339, doi: 10.1127/nos/2015/0067

Geyer, G., 1894, Zur Stratigraphie der paläozoischen Schichtserie in den Karnischen Alpen: Verhand. Geol. Reichsanstalt, v. 3, p. 102–119.

Gladman, B.J., Burns, J.A., Duncan, M.J., and Levison, H.F., 1995, The dynamical evolution of lunar impact ejecta: Icarus, v. 118, p. 302-321.

Gounelle, M., 2011, The asteroid-comet continuum: In search of lost primitivity: Elements, v. 7, p. 29-34, doi: 10.2113/gselements.7.1.29

Graf, T. and Marti, K., 1995, Collisional history of H chondrites: Journal of Geophysical Research: Planets, v. 100, p. 21247-21263, doi: 10.1029/95JE01903

Greenwood, R.C., Schmitz, B., Bridges, J.C., Hutchison, R., and Franchi, I.A., 2007, Disruption of the L chondrite parent body; new oxygen isotope evidence from Ordovician relict chromite grains: Earth and Planetary Science Letters, v. 262, p. 204-213, doi: 10.1016/j.epsl.2007.07.048

Haggerty, S.E., 1973, Luna 20: mineral chemistry of spinel, pleonaste, chromite, ulvöspinel, ilmenite and rutile: Geochimica et Cosmochimica Acta, v. 37, p. 857-867, doi: 10.1016/0016-7037(73)90183-X

Häggström, T., and Schmitz, B., 2007, Distribution of extraterrestrial chromite in Middle Ordovician Komstad Limestone in the Killeröd quarry, Scania, Sweden: Bulletin of the Geological Society of Denmark, v. 55, p. 37-58.

Heck, P.R., Schmitz, B., Baur, H., Halliday, A.N., and Wleler, R., 2004, Fast delivery of meteorites to Earth after a major asteroid collision: Nature, v. 430, p. 323-325, doi: 10.1038/nature02736

Heck, P.R., Schmitz, B., Bauer, H., and 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, v. 43, p. 517–528.

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

Heck, P.R., Schmitz, B., Rout, S.S., Tenner, T., Villalon, K., Cronholm, A., Terfelt, F., and Kita, N.T., 2016, A search for H-chondritic chromite grains in sediments that formed immediately after the breakup of the L-chondrite parent body 470 Ma ago: Geochimica et Cosmochimica Acta, v. 177, p. 120-129, doi: 10.1016/j.gca.2015.11.042

Heck, P.R., Schmitz, B., Bottke, W.F., Rout, S.S., Kita, N.T., Cronholm, A., Defouilloy, C., Dronov, A., and Terfelt, F., 2017, Rare meteorites common in the Ordovician period: Nature Astronomy, v. 1, p. 0035, doi: 10.1038/s41550-016-0035

Hildebrand, A.R., Penfield, G.T., Kring, D.A., Pilkington, M., Camargo Z., A., Jacobsen, S.B., and Boynton, W.V., 1991, Chicxulub Crater: A possible Cretaceous/Tertiary boundary impact crater on the Yucatán Peninsula, Mexico: Geology, v. 19, p. 867-871, doi: 10.1130/0091-7613(1991)019<0867:Ccapct>2.3.Co;2

Hoskin, M. (Ed.), Ruggles, C., Cullen, C., Gingerich, O., Bennet, J.A., and Dewhirst, D., 1999, The Cambridge Concise History of Astronomy: Cambridge University Press, p. 388.

House, M., Becker, R., Feist, R., Flajs, G., Girard, C. and Klapper, G., 2000, The Frasnian/Famennian boundary GSSP at Coumiac, Southern France: CFS Courier Forschungsinstitut Senckenberg, v. 225, p. 59-75.

Jaanusson, V., 1973, Aspects of carbonate sedimentation in the Ordovician of Baltoscandia: Lethaia, v. 6, p. 11-34.

Janardhan, A.S., Sriramguru, K., Basava, S. and Shankara, M.A., 2001, Geikielite-Mg.Al.Spinel -titanoclinohumite association from a marble quarry near Rajapalaiyam area, part of the 550 Ma old Southern Granulite Terrain, Southern India: Gondwana Research, v. 4, p. 359-366, doi: 10.1016/s1342-937x(05)70335-x

Jarosewich, E., Nelen, J.A., and Norberg, J.A., 1980, Reference Samples for Electron Microprobe Analysis*: Geostandards Newsletter, v. 4, p. 43-47, doi: 10.1111/j.1751-908X.1980.tb00273.x

Klapper, G., Feist, R., Becker, R.T., and House, M.R., 1993, Definition of the Frasnian/Famennian Stage boundary: International Union of Geological Sciences, v. 16, p. 433-441, doi: 10.18814/epiiugs/1993/v16i4/003

Koestler, A., 1959, The sleepwalkers: A history of man's changing vision of the universe: London, Hutchinson, p. 592.

Kudielka, G., Koeberl, C., Montanari, A., Newton, J., and Reimold, W.U., 2002, Stable-isotope and trace element stratigraphy of the Jurassic/Cretaceous boundary, Bosso River Gorge, Italy, *in* Buffetaut, E., and Koeberl, C., eds., Geological and Biological Effects of Impact Events: Springer Berlin Heidelberg, p. 25-68, doi: 10.1007/978-3-642-59388-8_3

Larue, D.K., Barnes, I., and Sedlock, R.L., 1989, Subduction and accretion of the Permanente terrane near San Francisco, California: Tectonics, v. 8, p. 221-235, doi: 10.1029/TC008i002p00221

Lenaz, D., Lughi, V., Perugini, D., Petrelli, M., Turco, G., and Schmitz, B., 2019, $MgAl_2O_4$ spinels from Allende and NWA 763 carbonaceous chondrites: Structural refinement, cooling history, and trace element contents: Meteoritics & Planetary Science, v. 54, p. 3089-3100, doi: 10.1111/maps.13400

Liao, S., Huyskens, M.H., Yin, Q.-Z., and Schmitz, B., 2020, Absolute dating of the L-chondrite parent body breakup with high-precision U–Pb zircon geochronology from Ordovician limestone: Earth and Planetary Science Letters, v. 547, p. 116442, doi: 10.1016/j.epsl.2020.116442

Lindskog, A., 2014, Palaeoenvironmental significance of cool-water microbialites in the Darriwilian (Middle Ordovician) of Sweden: Lethaia, v. 47, p. 187-204.

Lindström, M., 1963, Sedimentary folds and the developement of limestone in an early Ordovician sea: Sedimentology, v. 2, p. 243-292.

Lindström, M., 1971, Vom Anfang, Hochstand und Ende eines Epikontinentalmeeres: Geologische Rundschau, v. 60, p. 419-438.

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

Lowrie, W., Alvarez, W., and Asaro, F., 1990, The origin of the White Beds below the Cretaceous-Tertiary boundary in the Gubbio section, Italy: Earth and Planetary Science Letters, v. 98, p. 303-312, doi: 10.1016/0012-821X(90)90032-S

Luterbacher, H., 2016, Otto Renz (1906–1992): Pioneer of the Cretaceous and Paleogene stratigraphy of the Central Apennines: *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 Papers, v. 524, p., doi: 10.1130/2016.2524(02)

Martin, E., Schmitz, B., and Schönlaub, H.-P., 2018, From the mid-Ordovician into the Late Silurian: Changes in the micrometeorite flux after the L chondrite parent breakup: Meteoritics & Planetary Science, v. 53, p. 2541-2557, doi: 10.1111/maps.13174

Martin, E., Schmitz, B., and Montanari, A., 2019, A record of the micrometeorite flux during an enigmatic extraterrestrial ^{3}He anomaly in the Turonian (Late Cretaceous), , *in* Koeberl, C. and Bice, D.M.(eds), 250 Million Years of Earth History in Central Italy: Celebrating 25 Years of the Geological Observatory of Coldigioco: Geological Society of America Special Papers, 542, p. 303-318, doi: 10.1130/2019.2542(15)

Martin, E., Schmitz, B., Alvarez, W., Aguirre-Palafox, L., and Terfelt, F., 2020, Chemistry of sediment-dispersed chrome spinel grains from the Early Cretaceous (Albian/Aptian) Calera Limestone, Pacifica Quarry, California, PANGAEA, doi: 10.1594/PANGAEA.920972

Martin, E., Schmitz, B., Terfelt, F., Aguirre-Palafox, L. E., and Alvarez, W., 2021, The micrometeorite flux in the Albian/Aptian age (~103-117 Ma): A search for Tycho ejecta in pelagic sediments using chrome spinels: Geological Society of America Special Papers (*in press*)

Menichetti, M., 2016, Early Cretaceous tectonic event in the Adria: Insight from Umbria-Marche pelagic basin (Italy), *in* Menichetti, M., Coccioni, R. and Montanari, A., eds., The Stratigraphic Record of Gubbio: Integrated Stratigraphy of the Late Cretaceous–Paleogene Umbria-Marche Pelagic Basin: Geological Society of America, v. 524, doi: 10.1130/2016.2524(04)

Montanari, A., Chan, L.S., Alvarez, W., Crevello, P.D., Wilson, J.L., Sarg, J.F., and Read, J.F.,1989, Synsedimentary Tectonics in the Late Cretaceous-Early Tertiary Pelagic Basin of the Northern Apennines, Italy, Controls on Carbonate Platforms and Basin Development: SEPM Society for Sedimentary Geology, 44**,** doi: 10.2110/pec.89.44.0379

Mukhopadhyay, S., Farley, K.A., and Montanari, A., 2001, A 35 Myr record of helium in pelagic limestones from Italy: Implications for interplanetary dust accretion from the early Maastrichtian to the middle Eocene: Geochimica et Cosmochimica Acta, v. 65, p. 653-669, doi: 10.1016/s0016-7037(00)00555-x

Mukhopadhyay, S., and Farley, K.A., 2006, New insights into the carrier phase(s) of extraterrestrial ^{3}He in geologically old sediments: Geochimica et Cosmochimica Acta, v. 70, p. 5061-5073, doi: 10.1016/j.gca.2006.06.1566

Nielsen, A.T., 1995, Trilobite systematies, biostratigraphy and palaeoecology of the Lower Ordovician Komstad Limestone and Huk Formations, southern Scandinavia: Fossils and Strata, v. 38, p. 1-374.

Nininger, H.H., 1942, Cataclysm and Evolution: Contributions of the Society for Research on Meteorites, v. 3, p. 27-29, doi: 10.1111/j.1945-5100.1942.tb00135.x

Paneth, F.A., 1956, The frequency of meteorite falls throughout the ages: Vistas in Astronomy, v. 2, p. 1681-1686, doi: 10.1016/0083-6656(56)90092-7

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

Prinz, M., Cherukupalli, N., Delaney, J., and Weisberg, M., 1983, Silicates in IAB and IIICD Irons, Winonaites, Lodranites an Brachina: a Primitive and Modified-Primitive Group: Lunar Planet. Sci., v. 14, p. 616-617.

Raup, D.M., and Sepkoski, J.J., 1982, Mass Extinctions in the Marine Fossil Record: Science, v. 215, p. 1501-1503, doi: 10.1126/science.215.4539.1501

Renz, O., 1936, Stratigraphische und mikropalaeontologische Untersuchung der Scaglia (obere Kreide-Tertiaer) im zentralen Apennin: Eclogae Geologicae Helvetiae, v. 29, p. 1-149.

Rochette, P., Folco, L., Suavet, C., Van Ginneken, M., Gattacceca, J., Perchiazzi, N., Braucher, R., and Harvey, R.P., 2008, Micrometeorites from the Transantarctic Mountains: Proceedings of the National Academy of Sciences, v. 105, p. 18206-18211, doi: 10.1073/pnas.0806049105

Roedder, E., and Weiblen, P.W., 1972, Occurrence of chromian, hercynitic spinel (“pleonaste”) in Apollo-14 samples and its petrologic implications: Earth and Planetary Science Letters, v. 15, p. 376-402, doi: 10.1016/0012-821X(72)90038-6

Roeder, P.L., 1994, Chromite: from the fiery rain of chondrules to the Kilauea Iki Lava lake: The Canadian Mineralogist, v. 32, p. 729-746, Rubin, A.E., 1997, Mineralogy of meteorite groups: Meteoritics & Planetary Science, v. 32, p. 231-247, doi: 10.1111/j.1945-5100.1997.tb01262.x

Rubin, A.E., and Grossman, J.N., 2010, Meteorite and meteoroid: New comprehensive definitions: Meteoritics & Planetary Science, v. 45, p. 114-122, doi: 10.1111/j.1945-5100.2009.01009.x

Schmieder, M., and Kring, D.A., 2020, Earth's Impact Events Through Geologic Time: A List of Recommended Ages for Terrestrial Impact Structures and Deposits: Astrobiology, v. 20, p. 91-141, doi: 10.1089/ast.2019.2085

Schmitz, B., Lindström, M., Asaro, F., and Tassinari, M., 1996, Geochemistry of meteorite-rich marine limestone strata and fossil meteorites from the Lower Ordovician at Kinnekulle, Sweden: Earth and Planetary Science Letters, v. 145, p. 31-48.

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

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

Schmitz, B., and Häggström, T., 2006, Extraterrestrial chromite in Middle Ordovician marine limestone at Kinnekulle, southern Sweden—Traces of a major asteroid breakup event: Meteoritics & Planetary Science, v. 41, p. 455-466, doi: 10.1111/j.1945-5100.2006.tb00473.x

Schmitz, B., 2013, Extraterrestrial spinels and the astronomical perspective on Earth's geological record and evolution of life: Chemie der Erde/Geochemistry, v. 73, p. 117-145.

Schmitz, B., Huss, G.R., Meier, M.M.M., Peucker-Ehrenbrink, B., Churche, 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 and Planetary Science Letters, v. 400, p. 145–152.

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

Schmitz, B., Yin, Q.Z., Sanborn, M.E., Tassinari, M., Caplan, C.E., and Huss, G.R., 2016, A new type of solar-system material recovered from Ordovician marine limestone: Nature Communications, v. 7, p. 1-7, doi: 10.1038/ncomms11851

Schmitz, B., Heck, P.R., Alvarez, W., Kita, N.T., Rout, S.S., Cronholm, A., Defouilloy, C., Martin, E., Smit, J., and Terfelt, F., 2017, Meteorite flux to Earth in the Early Cretaceous as reconstructed from sediment-dispersed extraterrestrial spinels: Geology, v. 45, p. 807-810, doi: 10.1130/g39297.1

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

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, F., 2019b, An extraterrestrial trigger for the mid-Ordovician ice age: Dust from the breakup of the L-chondrite parent body: Science Advances, v. 5, p. eaax4184, doi: 10.1126/sciadv.aax4184

Schmitz, B., Schmieder, M., Liao, S., Martin, E., Terfelt, F., 2021, Impact-crater ages and micrometeorite paleofluxes compared: Evidence for the importance of ordinary chondrites in the flux of meteorites and asteroids to Earth the past 540 million years: Geological Society of America Special Papers (*in press*)

Schön, J. H., 2011, Density, Physcial properties of rocks: Elsevier, Great Britain, , v. 8: p. 481.

Simon, S.B., Grossman, L., Podosek, F.A., Zinner, E., and Prombo, C.A., 1994, Petrography, composition, and origin of large, chromian spinels from the Murchison meteorite: Geochimica et Cosmochimica Acta, v. 58, p. 1313-1334, doi: 10.1016/0016-7037(94)90384-0

Simon, S.B., Mckeegan, K.D., Ebel, D.S., and Grossman, L., 2000, Complexly zoned chromium-aluminum spinel found in situ in the Allende meteorite: Meteoritics & Planetary Science, v. 35, p. 215-227, doi: 10.1111/j.1945-5100.2000.tb01770.x

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 Papers, v. 524, p. 115-137, doi: 10.1130/2016.2524(09)

Sliter, W.V., 1999, Cretaceous planktic foraminiferal biostratigraphy of the Calera Limestone, Northern California, USA: Journal of Foraminiferal Research, v. 29, p. 318-339.

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

Smit, J., 1999, The global stratigraphy of the Cretaceous-Tertiary boundary impact ejecta: Annual Review of Earth and Planetary Sciences, v. 27, p. 75-113, doi: 10.1146/annurev.earth.27.1.75

Sprovieri, M., Coccioni, R., Lirer, F., Pelosi, N. and Lozar, F., 2006, Orbital tuning of a lower Cretaceous composite record (Maiolica Formation, central Italy): Paleoceanography, v. 21, doi: 10.1029/2005PA001224

Swindle, T.D., Kring, D.A., and Weirich, J.R., 2014, $^{40}Ar/^{39}Ar$ ages of impacts involving ordinary chondrite meteorites, *in* Jourdan, F., Mark, D. F., and Verati, C., eds., Advances in $^{40}Ar/^{39}Ar$ dating: from archeology to planetarty sciences: The Geological Society of London, Special Publications, 378, doi: 10.1144/SP378.6

Tagle, R., Öhman, T., Schmitt, R.T., Erzinger, J. and Claeys, P., 2007, Traces of an H chondrite in the impact-melt rocks from the Lappajärvi impact structure, Finland: Meteoritics & Planetary Science, v. 42, p. 1841-1854, doi: 10.1111/j.1945-5100.2007.tb00542.x

Tarduno, J.A., Mcwilliams, M., Debiche, M.G., Sliter, W.V., and Blake, M.C., 1985, Franciscan Complex Calera limestones: accreted remnants of Farallon Plate oceanic plateaus: Nature, v. 317, p. 345-347, doi: 10.1038/317345a0

Terfelt, F. and Schmitz, B., 2021, Asteroid break-ups and meteorite delivery to Earth the past 500 million years: Proceedings of the National Academy of Sciences, v. 118, p. e2020977118, doi: 10.1073/pnas.2020977118

Thorslund, P., and Wickman, F.E., 1981, Middle Ordovician chondrite in fossiliferous limestone from Brunflo, central Sweden: Nature, v. 289, p. 285-286, doi: 10.1038/289285a0

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

Urey, H.C., 1973, Cometary collisions and geological periods: Nature, v. 242, p. 32-33, doi: 10.1038/242032a0

Van Ginneken, M., Folco, L., Cordier, C., and Rochette, P., 2012, Chondritic micrometeorites from the Transantarctic Mountains: Meteoritics & Planetary Science, v. 47, p. 228-247, doi: 10.1111/j.1945-5100.2011.01322.x

Vajda, V., Mcloughlin, S., Mays, C., Frank, T.D., Fielding, C.R., Tevyaw, A., Lehsten, V., Bocking, M., and Nicoll, R.S., 2020, End-Permian (252 Mya) deforestation, wildfires and flooding—An ancient biotic crisis with lessons for the present: Earth and Planetary Science Letters, v. 529, p. 115875, doi: 10.1016/j.epsl.2019.115875

Walton, E.L., Sharp, T.G., and Hu, J., 2016, Frictional melting processes and the generation of shock veins in terrestrial impact structures: Evidence from the Steen River impact structure, Alberta, Canada: Geochimica et Cosmochimica Acta, v. 180, p. 256–270, doi: 10.1016/j.gca.2016.02.024

Walton, E.L., Hughes, A., Maclagan, E., Herd, C.D.K., and Dence, M., 2017, A previously unrecognized high-temperature impactite from the Steen River impact structure, Alberta, Canada: Geology, v. 45, p. 291-294 doi: 10.1130/G38556.1

Weisberg, M.K., Mccoy, T.J. and Krot, A.N., 2006, Systematics and evaluation of meteorite classification, *in* Lauretta, D. S., and McSween, H. Y., eds., Meteorites and the Early Solar System II: The University of Arizona Press, p. 19-52.

Wlotzka, F., 2005, Cr spinel and chromite as petrogenetic indicators in ordinary chondrites: Equilibration temperatures of petrologic types 3.7 to 6: Meteoritics & Planetary Science, v. 40, p. 1673–1702.