Microbeam characterization of volatile-rich clasts - a tool to constrain early parent body hydrothermal processes

A Dissertation

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Summary

Meteoritic breccias can contain material that is not yet available in current meteorite collections as individual rocks. These materials can significantly contribute to answering questions related to the formation, environment, and evolution history of planetary bodies. Volatile-rich clasts are a great example of material that occurs in brecciated meteorites and can be used to answer questions related to the above mentioned topics.

Volatile-rich clasts in general are characterized by abundant volatile-bearing secondary formed minerals and can be subdivided into two main types: 1) The CM-like type, which contains chondrules with accretionary rims, tochilinite-cronstedtite intergrowths (TCI), carbonates, and Fe-Ni sulfides dispersed in a very fine phyllosilicate matrix. 2) The CI-like type clasts that contain a fine-grained phyllosilicate matrix with embedded magnetite, Fe-Ni sulfides, carbonates, accessory minerals, and very rarely chondrules or fragments of them. The mineralogy of the two types of clasts shows a strong association to the well-known CM and CI chondrites, respectively. However, it is unclear whether the volatile-rich clasts are actually similar to the analogue chondrites or whether they represent material that is not yet present in our meteorite collections. The goal of this thesis is to not only characterize the volatile-rich clasts and investigate the differences between the clasts and the chondrites, but also to obtain a better understanding of the associated parent body processes, such as; (i) the source and extent of the thermal histories (ii) the timing and source(s) of hydrothermal alteration (iii) the degree of equilibration and origin of sulphides within the parent bodies.

To resolve these processes, we apply a variety of analytical methods. Raman carbon thermometry of organic matter dispersed in the matrix was used to resolve the thermal history in terms of heating source, peak temperatures, extent, and influence of heating on highly volatile element isotope compositions of the volatile-rich clasts and analogue meteorites. Additionally, the formation processes of sulfides were investigated using S isotope compositions of the abundant Fe-Ni sulfides in the CI- and CM-like clasts. Finally, the Mn-Cr ages of dolomite in CI-like clasts and calcite in CM-like clasts were ascertained to constrain the timing of hydrothermal alteration among the clasts and chondrites.

The estimated peak temperature of the organic matter indicates that CI-like clasts experienced an average peak temperature of 65 ± 25 °C; very similar to the CM-like clasts with an average of 70 ± 25 °C. The CM and CI carbonaceous chondrites in this study experienced similar temperatures between 50 °C and 75 °C. The peak temperatures were most likely the result of ^{26}Al decay that triggered hydrothermal alteration. No evidence was found, that indicates additional heating by impacts or interaction with the host rock leading to a higher peak temperature than during their formation. Considering the thermal histories and the mineralogy it seems that the clasts and chondrites represent similar material. The S isotope compositions of sulfides, however, show a completely different result. Although the S isotope compositions of Fe-Ni sulfides in CM chondrites and CM clasts are very similar, the S isotope compositions of sulfides in CI-like clasts and

those in CI chondrites are considerably different. Moreover, CI-like clasts have negative $\delta^{34}S$ values, whereas the CI chondrites have positive $\delta^{34}S$ values. The difference between these two materials, although having a similar mineralogy and thermal history, is the first evidence that the parent bodies of the CI-like clasts sampled different (S) isotopic reservoirs. For this reason, CI-like clasts can better be referred to as C1 clasts.

The observation of different parent bodies with similar mineral compositions and peak temperatures can be used to constrain a key process in the early solar system; hydrothermal alteration. To constrain whether hydrothermal alteration was a near-contemporaneous event among parent bodies in the outer solar system, or whether it consisted of multiple events, Mn/Cr ages of carbonates were determined. Additionally, Mn/Cr ages will also be used to determine if the isotopic differences between C1 clasts and CI chondrites are caused by a dissimilarity in hydrothermal processes and thus the formation of the secondary formed minerals. The formation age of carbonates in CM, CR, $C2_{ung}$, and CI chondrites as well as those in C1 and CM clasts correspond adequately to heat produced during the ^{26}Al decay. This indicates that the carbonates in the majority of the material precipitated 2-6 Ma after CAI (Calcium-aluminium-rich inclusion) formation from a hydrothermal fluid induced from ice that melted during the heat production of ^{26}Al decay. Not all samples analyzed in this dissertation revealed an age due to the lack of ^{53}Cr enrichments. This lack of ^{53}Cr is most likely a result of small-scale localized differences of Mn/Cr concentrations in the fluid from which the carbonates precipitated. It is therefore plausible, that the small nature and the limited amount of available carbonates in the C1 clasts resulted in a sample bias where only carbonates that precipitated from low $^{53}Cr/^{52}Cr$ and $^{55}Mn/^{52}Cr$ fluid domains were analyzed.

In summary, this dissertation shows that the mineralogy and thermal history of volatile-rich clasts and the CM and CI chondrites are similar and point toward a low-temperature (<100 °C) hydrothermal formation. Isotopic studies however, still show significant differences between C1 clasts and CI chondrites and suggest that C1 clasts originate from spatially separated parent bodies that sampled different isotopic reservoirs compared to CI chondrites. Additionally, Mn/Cr ages of carbonates in various chondrites and clasts suggest that hydrothermal alteration was a near-contemporaneous event among different parent bodies in the outer solar system induced by ^{26}Al decay.

Zusammenfassung

Meteoritische Brekzien können gelegentlich Material enthalten, das in aktuellen Meteoritensammlungen nicht als individuelle Proben verfügbar ist. Diese Materialien können einen wesentlichen Beitrag zur Beantwortung von Fragen im Zusammenhang mit der Entstehung und Entwicklungsgeschichte von planetaren Körpern leisten. Volatilreiche Einschlüsse sind ein hervorragendes Beispiel für Material, das in brekziierten Meteoriten vorkommt und können verwendet werden, um Fragen im Zusammenhang mit den oben genannten Themen zu beantworden.

Volatilreiche Einschlüsse sind im Allgemeinen durch sekundär gebildete volatil-haltige Minerale gekennzeichnet und können in zwei verschiedene Typen unterteilt werden: 1) Der CM-artige Typ, der Chondren mit akkretionären Rändern, Tochilinit-Cronstedtit-Verwachsung (TCI), Karbonate und fein verteilte Fe/Ni-Sulfide in einer sehr feinen Schichtsilikatmatrix enthält. 2) Der zweite Typ ist der CI-artige Typ und besteht aus einer feinkörnige Schichtsilikatmatrix, jedoch mit Magnetit, Fe/Ni-Sulfiden, Karbonaten, akzessorischen Mineralen und sehr selten auch Chondren oder Fragmente von diesen. Die Mineralogie der beiden Typen von Einschlüssen zeigt eine starke Assoziation zu den bekannten CM- bzw. CI-Chondriten. Sind die volatil-reichen Einschlüsse tatsächlich den CI und CM Chondriten ähnlich oder handelt es sich um Material, das in unseren Meteoritensammlungen noch nicht vorhanden ist?

Das Ziel dieser Arbeit is nicht nur, die volatilreichen Klasten zu charakterisieren und die Unterschiede zwischen Klasten und Chondriten zu Untersuchen, sondern auch, um ein besseres Verständnis für die übergeordneten Prozesse dieser Materialien zu erlangen, so wie; (i) die Quelle und das Ausmass der thermischen Vergangenheit (ii) der Zeitpunkt und die Quelle(n) der hydrothermalen Alteration (iii) das Equillibrium und die Herkunft der Sulfide in den Mutterkörpern.

Um diese Prozesse zu verstehen, wurden verschiedene Methoden angewandt. Raman-Kohlenstoffthermometrie von in der Matrix verteiltem organischem Material wurde verwendet, um den temperatur Entwicklung bezüglich der Wärmequelle, maximal Temperaturen, Ausmaß, und Einfluss auf leichtflüchtige Elementisotopezusammesetzungen der volatilreichen Einschlüsse und den CI und CM Meteoriten aufzulösen. Zusätzlich wird die Bildung von Sulfiden untersucht mit den S-Isotopenzusammensetzung der häufig vorkommenden Fe/Ni-Sulfide in den CI- und CM-artigen Einschlüssen. Schließlich wird das Mn/Cr-Alter von Dolomit in CI-artigen Einschlüssen und von Calcit in CM-artigen Einschlüssen bestimmt, um das Alter der wässrigen Alteration der Einschlüsse und das der Chondrite zu bestimmen.

Die maximale Temperatur der Einschlüsse basierend auf der Organik zeigt, dass CI-ähnliche Einschlüsse eine durchschnittliche Temperatur von 65 ± 25 °C aufweisen; sehr ähnlich zu den CM-artigen Einschlüssen mit einem Durchschnitt von 70 ± 25 °C. Die kohligen CM und CI Chondrite in dieser Studie zeigen ähnliche Temperaturen zwischen 50 °C und 75° C. Die Höchsttemperaturen in diesen Proben waren

höchstwahrscheinlich das Ergebnis des Zerfalls von ^{26}Al, der die wässrige Alteration auf dem Mutterkörper auslöste. In diesen Proben wurden keine Hinweise gefunden, die auf eine weitere Erwärmung durch Impakte oder Wechselwirkungen mit dem Wirtsgestein hinweisen. In Anbetracht der thermischen Vorgeschichte und der ähnlichen Mineralogie scheinen die Einschlüsse und die Chondrite dasselbe Material zu sein. Die S-Isotopenzusammensetzungen von Sulfiden zeigen jedoch ein völlig anderes Bild. Trotz sehr ähnlicher S-Isotopenzusammensetzungen von Fe/Ni-Sulfiden in CM-Chondriten und CM-Einschlüssen unterscheiden sich die S-Isotopenzusammensetzungen zwischen CI-artigen Einschlüssen und CI-Chondriten erheblich. Zusammenfassend ist festzuhalten, dass die CI-artigen Einschlüsse in einem ähnlichen negativen δ^{34}S-Bereich liegen wie die CM-Einschlüsse und CM-Chondriten, jedoch zeigen die CI-Chondriten generell positive δ^{34}S Werte. Dieser Unterschied zwischen zwei Materialien mit einer ähnlichen Mineralogie und thermischen Vorgeschichte könnte der erste Hinweis darauf sein, dass die CI-artigen Elternkörper der Klasten verschiedene (S) Isotopen-Reservoire beprobten.

Die Existenz verschiedener Mutterkörper mit einer ähnlichen Mineralogie und ähnlicher thermischer Vergangenheit kann dazu genutzt werden, um einen entscheidenden Prozess im frühen Sonnensystem zu verstehen; hydrothermale Alteration. Um festzustellen, ob die hydrothermale Alteration der verschiedenen Mutterkörper zur gleichen Zeit stattfand oder es sich um verschiedene Ereignisse gehandelt hat, wurden die Mn/Cr-Alter der gesamten Karbonate bestimmt. Zusätzlich können die Mn/Cr-Alter dazu genutzt werden, die isotopie Unterschiede zwischen C1 Einschlüssen und CI Chondriten auf einen zeitlichen Unterschied und damit auf die Bildung der sekundären Minerale zurückzuführen. Die Mn/Cr-Alter der Karbonate in CM, CR, ungruppierten C2 und CI Chondriten sowie die Alter der C1 und CM-artigen Einschlüssen überlappen mit den Altern für den Zerfall von kurzlebigem ^{26}Al und der damit verbundenen Aufheizung. Aufgrund von nicht nachweisbaren Anreicherungen von ^{53}Cr zeigen nicht alle in dieser Dissertation analysierten Proben ein Alter. Diese nicht nachweisbare Anreicherung von ^{53}Cr ist aller Wahrscheinlichkeit nach das Ergebnis von lokalen Unterschieden in den Mn/Cr Konzentrationen des Fluids aus dem die Karbonate ausgefällt wurden. Es ist wahrscheinlich, dass die geringe Größe der Einschlüsse sowie Anzahl an Karbonaten in C1-artigen Einschlüssen zu Stichprobenverzerrungen führten und dadurch nur solche Karbonate analysiert wurden, die aus Fluiden mit niedrigem ^{53}Cr/^{52}Cr und ^{55}Mn/^{52}Cr ausgefallen sind.

Zusammengefasst zeigt diese Dissertation, dass sich die volatil-reichen Einschlüsse, sowie die CM und CI Chondrite in ihrer Mineralogie als auch in den Temperaturen der Alteration ähneln und auf eine Niedrigtemperatur-Hydrothermalbildung (<100 °C) hindeuten. Isotopenstudien zeigen jedoch, dass signifikante Unterschiede zwischen den CI Chondriten und den C1-artigen Einschlüssen existieren und dass letztere von einem räumlich getrennten Mutterkörper stammen, der unterschiedliche Isotopen Reservoire beprobt als der Mutterkörper der CI Chondrite. Weiterhin zeigen die Mn/Cr-Alter der Karbonate aus verschiedenen Chondriten und Einschlüssen, dass die hydrothermale Alteration durch den Zerfall von ^{26}Al selbst auf verschiedenen Mutterkörper zu sehr ähnlichen Zeiten im äußeren Sonnensystem stattfand.

“Once I blazed across the sky,
Leaving trails of flame;
I fell to earth, and here I lie -
Who'll help me up again?

-A Shooting Star”

— Johann Wolfgang von Goethe

Chapter 1

Introduction

1.1 This thesis in the TRR170 framework

The thesis presented here is a part of the collaborative research program "TRR 170 - Late Accretion onto Terrestrial Planets" funded by the Deutsche Forschungsgemeinschaft (DFG). The aim of this large collaboration between different universities is to increase our understanding of the late-accretion history of the terrestrial planets from 4.5-3.8 Ga. This is achieved by 1) constraining the timing and distribution of basin forming impacts on the Moon to improve basic parameters of the cratering chronology in the early solar system, 2) quantify the mass of the material accreted between 4.5-3.8 Ga, 3) characterize the composition of late accreted material, 4) refine our current estimate of the present-day budget of a spectrum of critical volatile- and metal-loving elements in Earth, Moon, and in other terrestrial planets, 5) test the hypothesis that late-accreted material was volatile-rich and had a similar composition as material delivered towards the end of the main planetary building stages prior to 4.5 Ga, and 6) develop quantitative models for the evolution of the terrestrial planets in the relevant time interval.

To achieve these goals, the program has been divided into three main research topics that consist of various subprojects:

- The timing of late accretion, which includes the subprojects related to chronometric investigations of the moon, lunar cratering chronology, lunar impact populations, and the inventory and evolution of lunar basins.
- The chemical budget, which includes the research topics; highly siderophile elements (HSE) and siderophile volatile elements (SVE) in ancient lunar impactites, stable isotope fractionation of sulfur, tellurium, and palladium, nucleosynthetic isotopic anomalies in siderophile elements, atmo- and hydrophile elements in Earth and Moon, and the early-formed volatile-rich clasts in meteorite breccias.
- Geodynamic implications, which include, partitioning of siderophile volatile elements during core formation, modeling giant impacts and liquid metal behavior, ^{182}W heterogeneities in the Earth's mantle, thermo-chemical evolution of the early Earth-Moon system, and early interior-surface-atmosphere interaction on terrestrial planets.

This thesis is part of the B5 subproject: "Early-formed volatile-rich clasts in meteorite breccias" and is subdivided in two parts: In the first part we examine the internal structure and compositional variability of these clasts, which provides chemical details about the fragments' constituents and reveals how they might define their hosts' bulk signals. The second part of the project determines the bulk chemical characteristics of the clasts that may have contributed to the current volatile inventories of the terrestrial planets. Since volatile-rich clasts are a relatively newly discovered material the goals of the B5 subproject are to (i) characterize the mineralogy of volatile-rich clasts (ii) constrain formation environments and processes (iii) compare volatile-rich clasts to known meteorites in terms of mineral and isotope composition (iv) determine whether volatile-rich clasts could have contributed to the volatile budget of the terrestrial planets.

1.2 Distribution of highly volatile elements during solar system formation

During the very early stages of the solar system, volatile elements were enriched in the outer solar system while the inner solar system was depleted. This discrepancy is observed most broadly in giant gas planets that are composed of abundant volatile-elements in the outer solar system, whereas the inner planets are comparatively depleted in volatiles and have a rocky nature.

A similar distribution can be observed among different meteorite groups that we currently have in meteorite collections. We can distinguish rocky, differentiated meteorites (ureilites, angrites, enstatite, and ordinary chondrites), the so-called non-carbonaceous chondrites (NC) and the carbonaceous chondrites (CC; such as CI and CM chondrites). These two different types of meteorites show significant differences in their mineralogy and evolutionary processes. Both CC and NC types can be differentiated. CC meteorites, apart from CC iron meteorites, are in general often composed of a mixture of primary minerals and volatile-bearing secondary minerals that indicate the presence of fluids during formation. The NC chondrites are mostly 'dry' meteorites and are often composed of primary minerals (such as chondrules in ordinary chondrites), and can regularly have a magmatic origin (e.g., angrites).

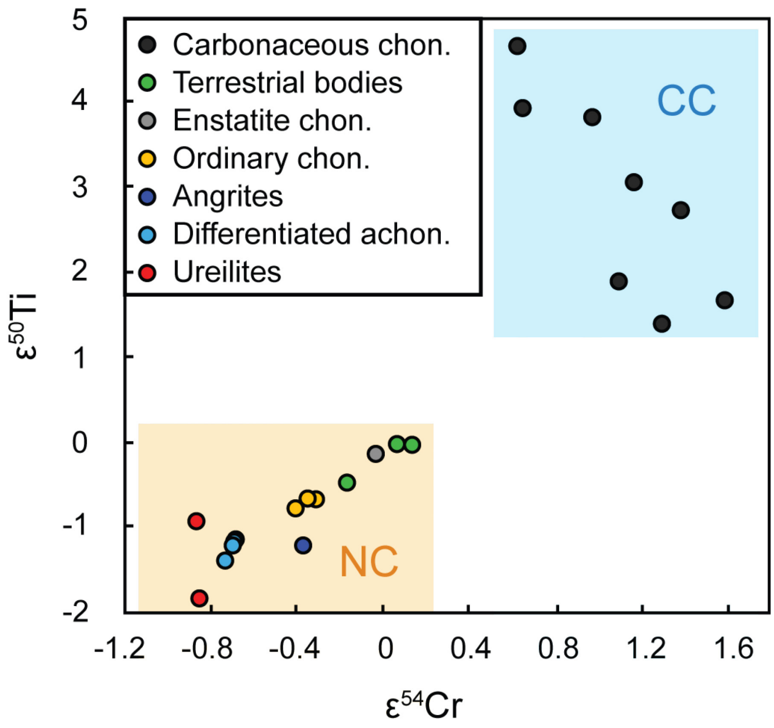

Fig. 1.1: ε^{50}Ti vs ε^{54}Cr plot for carbonaceous chondrites and non-carbonaceous chondrites modified after Warren et al. (2011b).

Wasson (1988) was the first author that suggested that the large differences in refractory-lithophile-element composition were caused because NC and CC are formed at a large spatial difference from each other. Warren et al. (2011a) and (2011b) speculated that the CC chondrites originate from the outer solar system, beyond the snow line based on the mineralogy (Wood 2005).

A comparison of ε^{54}Cr vs ε^{50}Ti very clearly portrays an isotopic dichotomy between NC and CC meteorites. This can also be seen in other isotope combinations, for example, O, Mo, Ni, and Ti (Fig. 1.1; Warren 2011a; 2011b).

It was recently proposed that the separation of the two isotopically distinct reservoirs was caused by the formation of proto-Jupiter (Kruijer et al. 2017), where the growing core of proto-Jupiter served as a barrier hindering mixing of the two different reservoirs (Lambrechts et al. 2014; Morbidelli et al. 2015; Andrews et al. 2016). The Grand Tack model (Walsh et al. 2011) where Jupiter and Saturn migrate inward is currently the best explanation for mixing NC and CC reservoirs resulting in breccias containing both outer and inner solar system material.

1.3 Meteoritic breccias

The first ever use of the term "meteoritic breccia" can be traced back to 1843 and has since been the subject of intensive research (Partsch 1843). Due to the increased interest in the origin and processes that formed meteoritic breccias, meteoritic breccias were subdivided into two main types; 1) Monomict breccias, that contain fragments or lithologies in the matrix that have a similar composition and origin, and 2) polymict breccias that contain fragments that have a different composition and origin compared to the matrix (Wahl 1952).

Keil (1982) effectively listed multiple reasons as of why it is important to study brecciated meteorites and what we can learn from them. To summarize, I will list the main reasons that are directly applicable to this dissertation: 1) The abundance of different rock types in one meteorite might suggest whether different meteorite classes come from a multitude of separate, compositionally homogenous parent planetesimals or coexisted in one or only a few parent bodies. 2) Clasts in breccias allow us to recognize new rock types not represented in meteorites as individual stones. 3) Meteorite breccias can shed light on how they have been formed and give information on their thermal history, as well as impact and cratering mechanisms that can be related to other planetary objects.

Over the years many different kinds of meteorite breccias have been observed and described. One example are monomict meteorite breccias, for instance many CI chondrites (e.g., Ivuna, Orgueil, Tonk, Alais). Even though they consist of roughly the same minerals they can still be subdivided into slightly different CI lithologies, in terms of mineral abundance and composition. Morlok et al. (2006) subdivided 113 CI chondrite fragments of four different CI chondrites into eight different fragment groups that were all chemically different and had different mineral abundances. The same brecciation features can also be observed in some CM chondrites such as Cold Bokkeveld, Nagoya, or LON 94101 (Bischoff et al. 2017).

Another example of meteoritic breccias are complicated breccias such as Kaidun and Almahatta Sitta, which are the foremost specimens. Almahatta Sitta is classified as a polymict ureilite breccia and contains EL, EH, H, L, LL, R, and C lithologies (e.g., Horstmann and Bischoff 2014; Bischoff et al. 2010; 2012; 2014; 2015; 2016; Horstmann et al. 2010; Zolensky et al. 2010; Fioretti et al. 2017; Goodrich et al. 2014; 2017). Studies of this exceptional meteorite suggest that the meteorites found in the strewn field were all individual fragments that broke up along their original boundaries in the atmosphere. These individual fragments were suggested to originate from centimeter-sized, loosely agglomerated material that made up asteroid 2008 TC3 (Bischoff et al. 2010). Kaidun is a similar complicated breccia and consists of EH3-5, EL3, CV3, CM1-2, CI, and R chondrite fragments (Ivanov 1989; Zolensky and Ivanov 2003) that may have a similar origin (Bischoff et al. 2010). These two meteoritic breccias might be important samples to explain the mixing of the NC and CC reservoirs mentioned in the previous paragraph.

The last examples are less complicated polymict breccias that usually contain one or two foreign types of lithologies distributed throughout the samples. Polymict ureilites are meteorites that can often be associated with this appearance. They can contain ordinary chondrite fragments (e.g., Jaques and Fitzgeral 1982; Prinz et al. 1986; 1987; 1988; Ikeda et al. 2000; 2003; Goodrich et al. 2004; Ross et al. 2010), angrite-like clasts (Jaques and Fitzgeral 1982; Prinz et al. 1986; 1987; Ikeda et al. 2000; Goodrich and Keil 2002; Cohen et al. 2004; Kita et al. 2004), and even carbonaceous chondrite clasts (e.g., Patzek et al. 2018).

Carbonaceous chondrite clasts have not only been described in polymict ureilites, but also occur in polymict eucrites, howardites, CR chondrites, CH chondrites, H chondrites, and R chondrites. This occurrence is intriguing, since carbonaceous volatile-rich material from the outer solar system reservoir is often incorporated into meteorite material from the inner solar system meteorite reservoir. This in turn means that some processes must have occurred to agglomerate these convincingly different materials together.

1.4 Volatile-rich clasts

Wilkening (1973) was the first to mention the occurrence of carbonaceous chondrite-like material in achondrites. In this specific case, the howardite Kapoeta contained CM chondrite like material. Later, Anders (1978) described the presence of carbonaceous chondrite material in ordinary chondrites. Eventually, even more carbonaceous chondrite material was identified and characterized in numerous different achondritic and chondritic groups. All the carbonaceous clasts described in the brecciated meteorites have affinities with either CR, CI, or CM chondrites (e.g., Mittlefehldt 1994, 2015; Zolensky et al. 1996; Gounelle et al. 2003).

The host meteorites of the CI- or CR-like type clasts that are known to contain the carbonaceous chondrite clasts are brecciated ureilites (e.g., Prinz et al. 1987; Brearley and Prinz 1992; Brearley and Jones 1998; Goodrich and Keil 2002; Goodrich et al. 2004), CR chondrites (e.g., Bischoff et al. 1993b; Endress et al. 1994) CH chondrites (e.g., Bischoff et al. 1993c), H chondrites (e.g., Funk et al. 2011; Briani et al. 2012; Zolensky et al. 2016), and HEDs (e.g., Zolensky et al. 1996; Gounelle et al. 2003). Conversely, CM-like type clasts are often restricted to HED meteorites (Zolensky 1996).

Even though many studies have perceived the so inaccurately called dark clasts, the main conclusions were based on optical observations these clasts in different types of meteorites. Detailed compositional and isotopic studies on a large group of clasts were still missing.

The term "dark clasts" has a variety of meanings in literature (Fig. 1.2). They can resemble dark clasts that are found in the Allende meteorite (Bischoff et al. 1988; 2006), melt inclusions, or even opaque phases. The dark clasts that I discuss in this work and were discussed in Patzek et al. (2018), however, consist unlike the others of abundant volatile-bearing phases and minerals that were precipitated from aqueous fluids and that closely resemble strongly altered carbonaceous chondrites. They We will therefore further be referred to as volatile-rich clasts.

To extend and improve the already existing literature on volatile-rich clasts, Patzek et al. (2018) conducted a large study on the mineral content, texture, and compositions of a significant quantity of volatile-rich clasts in various types of achondritic and chondritic meteorites and concluded that we can distinguish two main types: 1) CI-like clasts that occur in HEDs, polymict ureilites, CR, CH, and H chondrites, and 2) CM-like clasts that were only present in HEDs and ordinary chondrites.

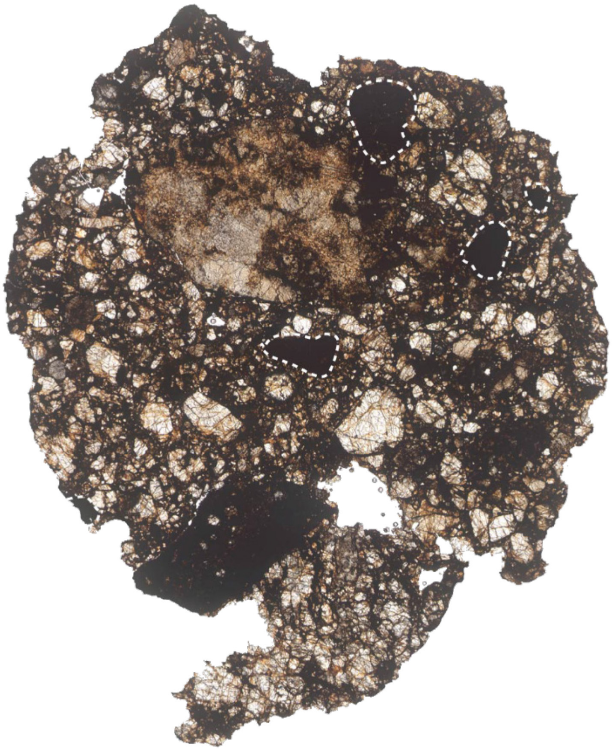

Fig. 1.2: Polymict Ureilitic host rock (DaG 976) that apart from the large olivine crystals of different sizes also contains volatile-rich clasts (circled in white). This figure clearly shows why the volatile-rich clasts need to be differentiated from the term "dark clast" since dark lithologies that look similar are not always volatile-rich clasts.

Mineralogy of volatile-rich clasts

60 CM-like clasts distributed over 15 different HED meteorites were studied by Patzek et al. (2018). Optical microscopy was used to search for the clasts in many thin sections of their potential host meteorites. The fine-grained opaque nature of the grains enables transmitted light to enhance the strong textural contrast of the clasts with the often large olivine- or pyroxene-rich host meteorites (e.g., ureilite, HED). The clasts have a size from <150 µm to ca. 2000 µm and are regularly surrounded by cracks separating them from the host rock. The CM-like clasts have a main mineral composition that is consistent with CM chondrites (e.g., Zolensky 1996). CM-like clasts are dominated by a fine-grained, porous matrix that is composed of serpentine minerals, a wide range of very fine-grained minerals such as silicates, sulfides, and carbonates, and organic matter. This matrix contains varying amounts of tochilinite-cronstedtite intergrowths (TCI) that in some cases occur as fine wavy structures or lump structures. TCI is a prominent feature in CM chondrites, where it consists of the hydrated Fe sulfide tochilinite ($Fe^{2+}_{5\text{-}6}(Mg, Fe^{2+})_5S_6(OH)_{10}$) intergrown with the Fe-rich serpentine cronstedtite ($Fe^{2+}_2Fe^{3+}((Si, Fe^{3+})_2O_5)$ $(OH)_4$).

CM-like clasts frequently contain complete or remnants of silicate chondrules that are often comprised of Mg-rich olivine or pyroxene (Fig. 1.3). A critical observation are the accretionary dust rims that surround these chondrules. Similar accretionary rims have been described in CM chondrites by Metzler et al. (1992). Furthermore, CM-like clasts contain sulfides such as pyrrhotite ($Fe_{1-x}S_x$) or pentlandite ($FeNi_7S_8$) and more rarely P-rich sulfides (e.g., Devouard and Buseck 1997; Gounelle et al. 2003; Nazarov et al. 2009). Other, less abundant, minerals in these type of clasts are carbonates, mainly calcite/aragonite that can contain up to ~4 wt.% Fe, rarely dolomite (Johnson et al. 1993), and spinel.

Over 200 CI-like clasts in 11 polymict ureilites, 9 HEDs, 1 ordinary chondrite, 1 CH chondrite, and 10 CR chondrites have been studied for their mineralogy in Patzek et al. (2018). The overall mineralogy of CI-like clasts in this larger study agrees with earlier literature descriptions (e.g., Prinz et al. 1987; Brearley and Prinz 1992; Brearley and Jones 1998; Goodrich and Keil 2002; Goodrich et al. 2004).

Similar to the CM-like clasts, CI-like clasts are dominated by a fine-grained phyllosilicate matrix. However, unlike CM-like clasts (Fig. 1.3), silicate fragments and especially chondrules are rare. Silicate fragments that were observed have a forsteritic composition similar to the chondrules in CM-like clasts. Additionally, the most prominent minerals in CI-like clasts are magnetite and sulfides. Magnetite occurs as framboids usually around 20 to 50 µm in size with individual magnetite spheres having a diameter between 1 and 10 µm. Occasionally, magnetite forms either irregular grains or spheres that are roughly between 2 and 40 µm in size, as well as smaller plaquettes (1-10 µm).

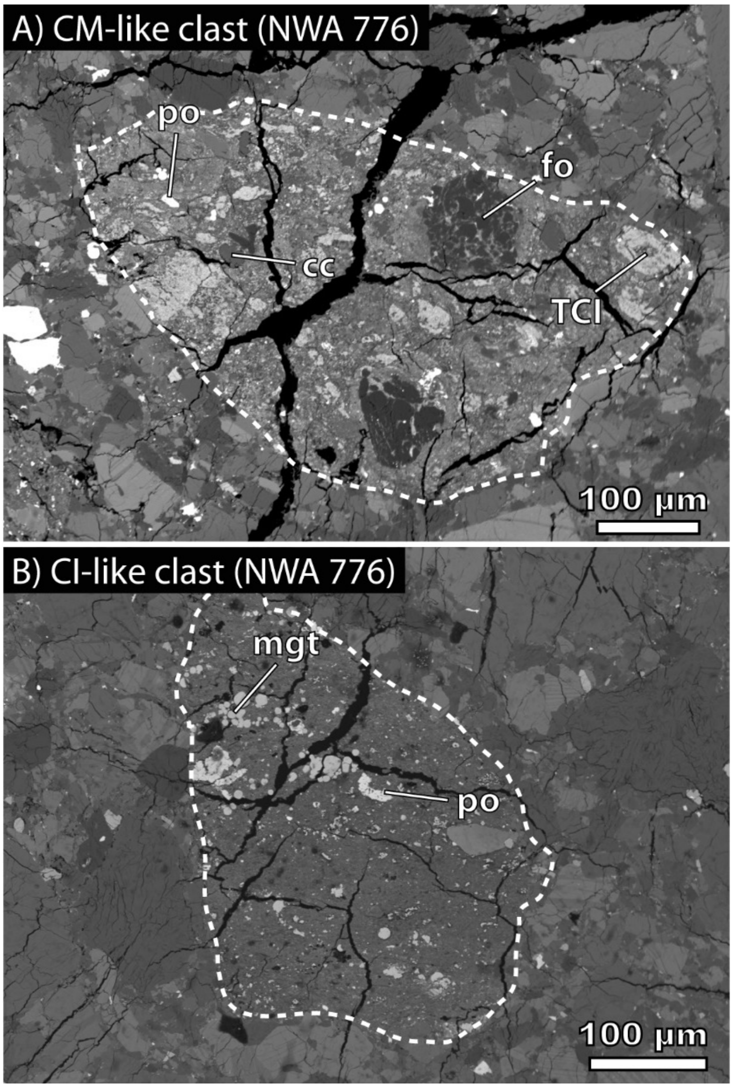

Fig. 1.3: Examples of a CM-like volatile-rich clast (A) and a CI-like volatile-rich clast both enclosed in the NWA 776 howardite. The CM-like clast has the typical mineralogy, with forsterite chondrules surrounded by an accretionary ring, TCI, carbonates, and sulfides. The CI-like clast contains magnetite, pyrrhotite and a fine grained phyllosilicate matrix.

1.5 Aim of the thesis

In this thesis I aim to present cumulative research which constrains formation environments and evolution processes of low-temperature hydrothermally altered parent bodies in the outer solar system. The thesis is divided into three chapters where the comparison of volatile-rich CI-like and CM-like clasts to CI and CM chondrites will be a recurring point of interest. Are volatile-rich clasts the same material as their analogue chondrites or are they in fact material that has not yet been found as bulk meteorites? Additionally, both volatile-rich clasts and chondrites will be used to better comprehend the thermal history of this material, to resolve the heating source, extent, and influence of heating on the mineral and isotope compositions. Sulfides are examined to obtain more information on the sulfide formation processes, the degree of equilibration within parent bodies, and the possibility of different S isotope reservoirs. Finally, I examine hydrothermal alteration to understand whether hydrothermal alteration was a relative simultaneous event among different parent bodies in the outer solar system with a single cause, or consisted of multiple different events.

All (co-)authored manuscripts and conference abstracts with important results and conclusions regarding the mineralogy, bulk D/H isotopes, in situ and bulk O isotopes, and bulk Cr isotopes directly related to this thesis are listed in Appendix 1. All supplements indicated in the different chapters can be found in Appendix 3.

1.6 Scientific chapters

Chapter 2. Temperature constraints by Raman spectroscopy of organic matter in volatile-rich clasts and carbonaceous chondrites (Visser R., Menneken M., John T., Patzek M., Bischoff A. Published in *Geochimica et Cosmochimica Acta*, 2018)

This chapter focuses on the peak temperatures and thermal history of CI and CM chondrites and CM-like and CI-like clasts. The thermal histories or peak temperatures of CM and CI chondrites are so far not well constrained and the thermal histories for volatile-rich clasts have not yet been investigated. They are however, of great importance to further understand the source(s) and extent of heating as well as the influence of heating on other processes that occurred during the evolution of the parent bodies. To constrain the thermal history as well as determining whether clasts and chondrites experienced similar thermal histories, I use Raman carbon thermometry. This method estimates peak temperatures based on the irreversible transformation of the carbon structure with increasing temperature. The main advantage of this is that we estimate an upper limit of the main heating processes that played a significant role in the formation environments of these chondrites and clasts.

The study was designed and conducted by Robbin Visser and Timm John. Scanning electron microscope measurements (SEM), Electron probe micro-analyzer analyses (EPMA), and petrological microscopy were performed and described in Patzek et al. (2018). The Raman spectroscopy data was obtained by Robbin

Visser with help from Martina Menneken. Together with Johannes C. Vrijmoed, Robbin Visser produced a MatLab script that was capable of fitting the large amounts of Raman spectra. The manuscript was written by Robbin Visser and all others commented on the manuscript and were actively involved in scientific discussions. The samples were supplied by Addi Bischoff (*Westfälische Wilhelms Universität Münster*), Ansgar Greshake (*Museum für Naturkunde Berlin*), and Ludovic Ferriére (*Naturhistorisches Museum Wien*).

Chapter 3. Sulfur isotope study of sulfides in CI, CM, C2$_{\mathrm{ung}}$ chondrites and volatile-rich clasts - evidence for different generations and reservoirs of sulfide formation (Visser R., John T., Patzek M., Bischoff A., Whitehouse M. Published in *Geochimica et Cosmochimica Acta*, 2019)

The focus of this chapter is to resolve the origin and formation of sulfides in individual CI-like clasts, CI chondrites, CM-like clasts, and CM chondrites. Sulfides, which are abundant in these chondrites and clasts, can either be formed by solar nebula processes or during hydrothermal alteration in the parent body. By analyzing the S isotope compositions of sulfides in the volatile-rich clasts and CI and CM chondrites new insights into the similarities between the clasts and their analogue chondrites, the formation environments of these sulfides, and possible fractionation processes during the formation process can be resolved.

Robbin Visser, Timm John, Markus Patzek, and Addi Bischoff designed the study. The S isotope compositions were analyzed by Robbin Visser and Markus Patzek with technical assistance from Martin J. Whitehouse at the NordSIMS institute at the Natural History Museum in Stockholm, Sweden. Petrologic and mineralogic studies were performed by Markus Patzek and Robbin Visser and are described in further detail in Patzek et al. (2018). Robbin Visser wrote the manuscript. All others authors were involved in active discussions and finalizing of the manuscript. The samples were supplied by Addi Bischoff (*Westfälische Wilhelms Universität Münster*), Ansgar Greshake (*Museum für Naturkunde Berlin*), Ludovic Ferriére (*Naturhistorisches Museum Wien*), and Kevin Righter (*NASA Johnson Space Center).*

Chapter 4. A short-lived ^{26}Al induced hydrothermal alteration event in the outer solar system: Constraints from Mn/Cr ages of carbonates (Visser R., John T., Patzek M., Bischoff A., Whitehouse M. *In preparation for submission to Earth and Planetary Science Letters*)

In this chapter, Mn-Cr chronology of carbonates in volatile-rich clasts as well as CM and CI chondrites is used to constrain hydrothermal alteration in the outer solar system. The Mn/Cr system is a short-lived, robust method to date processes in the first ~20 Ma of the solar system. Moreover, Mn/Cr chronology is a particularly useful method to obtain information about the low temperature hydrothermally altered chondrites and clasts, dominated by small, delicate minerals. Differences in S, H, O, and Cr isotope systems in C1 (previously CI-like clasts) and CI chondrites suggest that they originate from different parent bodies. The Mn/Cr ages from carbonates can therefore not only be used to determine if the differences observed in S, H, O, and Cr isotopic systems are caused by related hydrothermal alteration processes, but also to constrain the source and timing of hydrothermal alteration and resolve whether hydrothermal alteration was a near-contemporaneous event among different parent bodies in the outer solar system, or whether it consisted of multiple different events.

This study was designed and carried out by Robbin Visser and Timm John, in collaboration with Markus Patzek and Addi Bischoff. All the Mn-Cr data were obtained processed by Robbin Visser with assistance from Martin J. Whitehouse and technical assistant Heejin Jeon at the NordSIMS institute at the Natural History Museum in Stockholm, Sweden. The petrology and mineralogy were determined by Markus Patzek and Robbin Visser (described in Patzek et al. 2018). The manuscript was written by Robbin Visser and all other authors were involved in active discussions and finalizing the manuscript. The samples were provided by Addi Bischoff (*Westfälische Wilhelms Universität Münster*), Ansgar Greshake (*Museum für Naturkunde Berlin*), Ludovic Ferriére (*Naturhistorisches Museum Wien*), Mike Zolensky (*NASA Johnson Space Center)*, and Kevin Righter (*NASA Johnson Space Center)*.

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Chapter 2

Temperature constraints by Raman spectroscopy of organic matter in volatile-rich clasts and carbonaceous chondrites

Published as:

Visser R., Menneken M., John T., Patzek M., Bischoff A (2018). Temperature constraints by Raman spectroscopy of organic matter in volatile-rich clasts and carbonaceous chondrites. *Geochim. Cosmochim. Acta*, **241**, 38-55.

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Chapter 3

Sulfur isotope study of sulfides in CI, CM, C2$_{ung}$ chondrites and volatile-rich clasts - evidence for different generations and reservoirs of sulfide formation

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Chapter 4

A short-lived ^{26}Al induced hydrothermal alteration event in the outer solar system: Constraints from Mn/Cr ages of carbonates

Submitted as:

Visser R., John T., Whitehouse M. J., Patzek M., Bischoff A. (2019). A short-lived ^{26}Al induced hydrothermal alteration event in the outer solar system: Constraints from Mn/Cr ages of carbonates. *Submitted to Earth Planet. Sci. Lett.*

Chapter 5

Conclusions

In this thesis and the whole B5 subproject of the 'TRR 170 Late Accretion onto Terrestrial Planets' collaborative research program, new elaborate data about volatile-rich clasts as well as formation processes and environments are presented. Significant conclusions can be made after the mineralogical, analytical, and isotopic analyses of a large dataset of volatile-rich clasts and carbonaceous chondrite. The main conclusions presented here are a cumulative product from the chapters discussed in this thesis, as well as the (co-) authored manuscripts and conference abstracts in the publication list (Appendix 1).

Mineralogy of volatile-rich clasts compared to CI and CM chondrites

Based on the mineralogy the volatile-rich clasts can be subdivided into two main types. The mineral composition of CM-like clasts is very similar to CM chondrites. These CM-like type clasts contain similar textures of which accretionary rims are representative examples. Further, the overall mineral compositions between CM-like clasts and CM chondrites are also very similar. Small differences, however, do exist between clasts in terms of their specific mineral abundances, density of the TCI, and the amount of chondrules and fragments. These differences are similar to what studies find in the often brecciated CM chondrites and can be contributed to slight differences in the degree of alteration at the thin section scale, for example, in LON 94101. The CI-like clasts are, based on their mineralogy and microstructures, very similar to CI chondrites. Again, differences in mineral abundances of magnetite, Fe/Ni sulfides, but also carbonates between multiple volatile-rich clasts can be detected. This, however, can also be observed in CI chondrites themselves, which are often heavily brecciated meteorites that differ in mineral abundances on the centimeter scale.

Constraints on the thermal histories of mineralogically similar clasts and chondrites

The estimated peak temperatures of the volatile-rich CM-like and C1 clasts agree with those of CM and CI chondrites. All the CM and CI materials fall into a similar range between 50-100 °C, apart from one exception that has not only proved to be different in temperature but also shows considerable differences in texture compared to the ‘normal’ CI and CM material. The temperatures of CM and CI chondrites have already been estimated in the literature with various methods, however, our temperatures are considerably better constrained compared to previous estimated temperature ranges estimated in literature.

The peak temperatures themselves indicate an overall low-temperature history experienced during hydrothermal alteration triggered by ^{26}Al decay in the first ~5 Ma after CAI formation. This decay provided heat to melt ice and produce fluids that resulted in the prominent secondary mineral formation. I also conclude that the volatile-rich clasts were incorporated into their host rocks (that formed at high temperature), after the host rocks had already cooled which limits the possibility of interaction between host and clast. We cannot completely rule out that the clasts but also CM and CI chondrites were heated by impacts, however, this additional heating source is improbable considering the low peak temperatures and overall porous nature of the material.

Isotopic signatures of S isotopes - first hints for different CI-like parent bodies

The results of this thesis also advocate a correlation between S isotope compositions of sulfides in CM, CI, CR, and C_{ung} carbonaceous chondrites and the degree of alteration previously suggested in the literature. This correlation demonstrates heavier S isotope composition with an increasing degree of hydrothermal alteration. The C1 clasts, nevertheless, show considerably different S isotope compositions compared to CI chondrites even though, both materials experienced similar hydrothermal alteration histories derived from their mineralogy and peak temperatures. Furthermore, this dichotomy in S isotope composition cannot be observed while comparing S isotope compositions of CM-like clasts to those of CM chondrites. This may therefore provide a first hint that C1 clasts originate from different parent bodies, that sampled different S isotope reservoirs, compared to CI chondrites. The dichotomy between C1 clasts and CI chondrites is not exclusively observed in S isotopes but also reoccurs in multiple other isotope systems, such as, O, H, and Cr (Appendix 1). I therefore propose that C1 clasts represent material which originates from different parent bodies that are comparable to CI chondrites in mineralogy and thermal history, but are different in isotope compositions. Hence, they can better be referred to as C1 clasts rather than the previously used term CI-like clasts. CM-like clasts, on the contrary, are similar to CM chondrites in isotopic composition, mineralogy, and thermal history. For that reason, I conclude that the CM-like clasts are the same material as the CM chondrites.

Source and timing of hydrothermal alteration among parent bodies in the outer solar system

The Mn/Cr ages of carbonates in various different chondrites (CI, CM, CR, and $C2_{ung}$) as well as those in C1 and CM clasts, show coherent ages between 2-6 Ma after CAI formation. The formation age of these carbonates is consistent with a model where carbonates in these low-temperature carbonaceous chondrites are hydrothermally formed by a fluid, that formed as a result of heat produced through ^{26}Al decay in the first ~5 Ma after CAI formation. Furthermore, from the similar Mn/Cr ages of multiple different meteorites and clasts, I can conclude that hydrothermal alteration was a near-contemporaneous event among parent bodies in the outer solar system. The similarity of Mn/Cr ages of C1 clasts and CI chondrites suggests that the isotopic (S, O, H, and Cr) differences are not caused by related hydrothermal alteration processes and are thus most likely caused by spatially different reservoirs in the outer solar system.

Impact on 'Late Accretion'

The observations of volatile-rich carbonaceous chondrite-like clasts in many achondritic and chondritic meteorites suggest that more volatile-rich material has been added to the terrestrial planets than previously assumed. The systematic difference between the C1 clasts and the CI chondrites also suggests that there are volatile-rich parent bodies in the solar system that are still unaccounted for and could have made a significant contribution to the Earth's volatile budget in the late stage of Late Accretion.

Chapter 6

Outlook

The conclusions indicate that brecciated material may contain materials that are currently not available as bulk meteorites such as volatile-rich clasts. In terms of peak temperature, mineralogy, and degree of alteration, CM-like and C1 clasts proved to be similar to CM chondrites and CI chondrites, respectively. C1 clasts however, contain isotopic characteristics different from CI chondrites, which may indicates the presence of unrepresented hydrothermally altered parent bodies in the outer solar system, that sampled different isotopic reservoirs.

Apart from the characterization and isotopic analyses done so far (S, O, H, Cr), future investigation on volatile-rich clasts is still strongly encouraged. Especially, the study of elements bearing nucleosynthetic anomalies (i.e. Mo and Ru) of C1 clast and their chemical bulk composition are of great interest for the further investigation with respect to the heritage and classification of this material. Volatile-rich clasts may turn out to contribute to solving the problem of a missing component, which is needed to explain the isotopic characteristic of the bulk silicate Earth (BSE) and the nature of the late accreted material on Earth.

The characterization of volatile-rich clasts led to an additional asset for constraining hydrothermal parent body processes, with respect to the timing, sources, and extent of hydrothermal alteration. The peak temperatures, timing, and mineralogical evidence obtained in this thesis may benefit future parent body studies. Moreover, the increased accuracy of the experienced peak temperatures in combination with the age evidence obtained for the hydrothermal alteration, may allow models to better understand processes in the parent body, such as; (i) the degree of equilibrium (ii) formation of localized domains and scale of fluid flow (iii) heat transport and the ability to retain heat. For this reason, I also support additional research on uncharacterized material in brecciated meteorites, because this material may also represent material that is so far unavailable as bulk meteorites and may help to improve our understanding of the early Solar System.

Appendix 1

Thesis-related publications

Additional information:

In this supplementary publication list, all published first and co-authored journal papers and conference abstracts that are directly related to the results and conclusions of this thesis are documented in chronological order.

Peer reviewed journal papers

Patzek, M., Bischoff, A., Visser, R., John, T. (2019). Hydrogen isotopic composition of CI- and CM-like clasts from meteorite breccias - sampling unknown sources of carbonaceous chondrite materials. *Geochim. Cosmochim. Acta* **(in review)**.

Visser R., John T., Patzek M., Bischoff A., Whitehouse M. J. (2019) Sulfur isotope study of sulfides in CI, CM, C2ung chondrites and volatile-rich clasts – Evidence for different generations and reservoirs of sulfide formation. *Geochim.Cosmochim. Acta* **261**, 210-223.

Visser R., John T., Menneken M., Patzek M., Bischoff A. (2018) Temperature constraints by Raman spectroscopy of organic matter in volatile-rich clasts and carbonaceous chondrites. *Geochim.Cosmochim. Acta* **241**, 38-55.

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Appendix 2

Meteorite list

Additional information:

In this supplementary meteorite list, all meteorite samples used in this dissertation are catalogued in alphabetical order. Meteorite samples that have not been analyzed in this dissertation, but originate from cited literature and have been used in figures are stressed with an asterisk (*). The list contains 45 meteorites and provides general information on the type of meteorites, whether it was a find or fall, collected mass, location of recovery, date of recovery, where it has been published, and if applicable from which institution it was loaned.

Acfer 182: CH3 chondrite, 166 g was recovered from Tamanghasset, Algeria (1990), *Meteoritical Bulletin* No. **72** (1992); *Meteoritics* **27**, 109-117 (1992), loan from the Museum für Naturkunde Berlin, Germany.

Alais: CI chondrite, ~6 kg was recovered after the observed fall in Occitanie, France (1806). *Never published in Meteoritical Bulletin*, loan from the Westfälische Wilhelms Universität Münster, Germany.

ALH 81002*: CM2, 14 g was recovered during an Antarctic find expedition, in Allan Hills, Antarctica (1981). *Antarctic Meteorite Newsletter* **6** (1983); *Meteoritical Bulletin* **76** (1994); *Meteoritics.* **29**, 100-143 (1994).

ALH 83100*: CM1/2, 3.02 kg was recovered during an Antarctic find expedition, in Allan Hills, Antarctica (1983). *Antarctic Meteorite Newsletter* **7** (1984); *Meteoritical Bulletin* **76** (1994); *Meteoritics.* **29**, 100-143 (1994).

ALH 88045*: CM2, 18 g was recovered during an Antarctic find expedition, in Allan Hills, Antarctica (1988). *Meteoritical Bulletin* **69** (1990); *Meteoritics.* **25**, 237-239 (1990).

Allende: CV3 chondrite, ~2 t was recovered after the observed fall in Allende, Mexico (1969). *Meteoritical bulletin No.* ***45*** *(1969); Meteoritics.* ***5****, 85-109 (1970)*, loan from the Museum für Naturkunde Berlin, Germany.

Banten: CM2 chondrite, 639 g was recovered after the observed fall in Java, Indonesia (1980). *Meteoritical bulletin No.* ***57*** *(1980); Meteoritics* ***15****, 19-104 (1980)*, loan from the Museum für Naturkunde Berlin, Germany.

Bells: $C2_{ung}$ chondrite, 375 g was recovered after the observed fall in Texas, USA (1961). *Meteoritical bulletin No.* ***25*** *(1962)*, loan from the Westfälische Wilhelms Universität Münster, Germany.

Cold Bokkeveld*: CM2 chondrite, 5.2 kg was recovered after the observed fall in Western Cape, South Africa (1838). *Never published in Meteoritical Bulletin.*

DaG 164: Polymict ureilite, 57 g was recovered from the Al Jufrah desert, Libya (1996), *Meteoritical Bulletin* No. **81** (1997); *Meteorit. Planet. Sci.* **32**, A159-A166 (1997), loan from the Westfälische Wilhelms Universität Münster, Germany.

DaG 319: Polymict ureilite, 740 g was recovered from the Al Jufrah desert, Libya (1997), *Meteoritical Bulletin* No. **82** (1998); *Meteorit. Planet. Sci.* **33**, A221-A240 (1998), loan from the Westfälische Wilhelms Universität Münster, Germany.

DaG 976: Polymict ureilite, 32 g was recovered from the Al Jufrah desert, Libya (1999), *Meteoritical Bulletin* No. **87** (2003); *Meteorit. Planet. Sci.* **38**, A189-A248 (2003), loan from the Museum für Naturkunde Berlin, Germany.

DaG 999: Polymict ureilite, 17.9 kg was recovered from the Al Jufrah desert, Libya (2000), *Meteoritical Bulletin* No. **87** (2003); *Meteorit. Planet. Sci.* **38**, A189-A248 (2003), loan from the Museum für Naturkunde Berlin, Germany.

DaG 1000: Polymict ureilite, 2.1 kg was recovered from the Al Jufrah desert, Libya (1997), *Meteoritical Bulletin* No. **87** (2003); *Meteorit. Planet. Sci.* **38**, A189-A248 (2003), loan from the Museum für Naturkunde Berlin, Germany.

Efremovka*: CV3 chondrite, 21 kg was recovered after the observed fall in Pavlodar, Kazachstan (1962). *Meteoritical bulletin No.* ***25*** *(1962).*

Essebi: C2$_{ung}$ chondrite, 500 g was recovered after the observed fall in Province Oriental, Congo Democratic Republic (1957). *Meteoritical bulletin* No. **27** (1963), loan from the Westfälische Wilhelms Universität Münster, Germany.

GRO 95577.69*: CR1, 106.2 g was recovered during an Antarctic find expedition, in Grosvenor Mountain, Antarctica (1995). *Antarctic Meteorite Newsletter* **20** (1997); *Meteoritical Bulletin* **82** (1998); *Meteorit. Planet. Sci.* **33**, A221-A240 (1998).

Isheyevo*: CH/CBb chondrite, 16 kg was found in Bashkortostan, Russia (2003). *Meteoritical Bulletin* No. **89** (2005); *Meteorit. Planet. Sci.* **40**, A201-A263 (2005).

Ivuna: CI chondrite, 705 g was recovered after the observed fall in Ivuna, Tanzania (1938). *Never published in Meteoritical Bulletin,* loan from the Museum für Naturkunde Berlin, Germany.

Kaidun: C$_{ung}$ chondrite, 2 kg was recovered after the observed fall on Khuraybah, Yemen (1980). *Meteoritical Bulletin* **60** (1982); *Meteoritics* **17**, 93-97 (1982), loan from the NASA Johnson Space Center, USA.

Kainsaz: CO3.2 chondrite, 200 kg was recovered after the observed fall in Tatarstan, Russia (1937). *Never published in Meteoritical Bulletin*, loan from the Museum für Naturkunde Berlin, Germany.

LON 94101: CM2 chondrite, 2.8 kg was recovered during an Antarctic find expedition, Lonewolf Nunataks, Antarctica (1994). *Antarctic Meteorite Newsletter* **18** (1995); *Meteoritical Bulletin* **79** (1996); *Meteorit. Planet. Sci.* **31**, A167-A174 (1996), loan from the Westfälische Wilhelms Universität Münster, Germany.

MAC 02666: Howardite, 20.3 g was recovered during an Antarctic find expedition, in MacAlpine Hills, Antarctica (2002). *Antarctic Meteorite Newsletter* **26** (2003); *Meteoritical Bulletin* **88** (2004); *Meteorit. Planet. Sci.* **39**, A215-A272 (2004), loan from the Westfälische Wilhelms Universität Münster, Germany.

Mighei*: CM2 chondrite, 8 kg was recovered after the observed fall in Nikolayev, Ukraine (1889). *Never published in Meteoritical Bulletin.*

Murray: CM2 chondrite, 12.6 kg was recovered after the observed fall in Kentucky, USA (1950). *Meteoritical Bulletin* **8** (1958), loan from the Museum für Naturkunde Berlin, Germany.

Murchison: CM2 chondrite, 100 kg was recovered after the observed fall in Victoria, Australia (1969). *Meteoritical Bulletin* **48** (1969); *Meteoritics* **5**, 85-109 (1970), loan from the Museum für Naturkunde Berlin, Germany.

NWA 776: Howardite, 49 g was recovered from the desert in Morocco, North West Africa (2000), *Meteoritical Bulletin* No. **85** (2001); *Meteorit. Planet. Sci.* **36**, A293-A322 (2001), loan from the Naturhistorisches Museum Wien, Austria.

NWA 4894: Polymict eucrite, 20.5 g was recovered from the desert in North West Africa (2007), *Meteoritical Bulletin* No. **106** (2015); *Meteorit. Planet. Sci.* **54** (in press), loan from the Museum für Naturkunde Berlin, Germany.

NWA 6301: Polymict eucrite, 253 g was recovered from the desert in North West Africa (2009), *Meteoritical Bulletin* No. **102** (2015); *Meteorit. Planet. Sci.* **50**, 1662 (2015), loan from the Museum für Naturkunde Berlin, Germany.

NWA 6536: H6 chondrite, 40 g was recovered from the desert in North West Africa (2009), *Meteoritical Bulletin* No. **100** (2014); *Meteorit. Planet. Sci.* **49**, E1-E101 (2014), loan from the Westfälische Wilhelms Universität Münster, Germany.

NWA 7225: Polymict ureilite, 24 g was recovered from the desert in North West Africa (2010), *Meteoritical Bulletin* No. **102** (2015); *Meteorit. Planet. Sci.* **50**, 1662 (2015), loan from the Museum für Naturkunde Berlin, Germany.

NWA 7229: Polymict eucrite, 125 g was recovered from the desert in North West Africa (2011), *Meteoritical Bulletin* No. **102** (2015); *Meteorit. Planet. Sci.* **50**, 1662 (2015), loan from the Museum für Naturkunde Berlin, Germany.

NWA 7234: Polymict eucrite, 131 g was recovered from the desert in North West Africa (2010), *Meteoritical Bulletin* No. **102** (2015); *Meteorit. Planet. Sci.* **50**, 1662 (2015), loan from the Museum für Naturkunde Berlin, Germany.

NWA 7542: Polymict eucrite, 107 g was recovered from the desert in North West Africa (2012), *Meteoritical Bulletin* No. **102** (2015); *Meteorit. Planet. Sci.* **50**, 1662 (2015), loan from the Westfälische Wilhelms Universität Münster, Germany.

NWA 8431: Polymict eucrite, 2 kg was recovered from the desert in North West Africa (2013), *Meteoritical Bulletin* No. **103** (2017); *Meteorit. Planet. Sci.* **52**, 1014 (2017), loan from the Museum für Naturkunde Berlin, Germany.

Orgueil: CI chondrite, 14 kg was recovered after the observed fall in Montauban, France (1864). *Never published in Meteoritical Bulletin*, loan from the Westfälische Wilhelms Universität Münster, Germany.

PRA 04401: Howardite, 55 g was recovered during an Antarctic find expedition, in Mount Pratt, Antarctica (2004). *Antarctic Meteorite Newsletter* **30** (2007); *Meteoritical Bulletin* **92** (2007); *Meteorit. Planet. Sci.* **42**, 1647-1694 (2007), loan from the NASA Johnson Space Center, USA.

PRA 04402: Howardite, 37.8 g was recovered during an Antarctic find expedition, in Mount Pratt, Antarctica (2004). *Antarctic Meteorite Newsletter* **30** (2007); *Meteoritical Bulletin* **92** (2007); *Meteorit. Planet. Sci.* **42**, 1647-1694 (2007), loan from the NASA Johnson Space Center, USA.

Renazzo: CR2 chondrite, 1000 g was recovered after the observed fall in Emilia-Romagna, Italy (1824). *Never published in Meteoritical Bulletin*, loan from the Naturhistorisches Museum Wien, Austria.

Sahara 98645: H3 chondrite, 51 g was recovered from the Sahara Desert, Africa (1998), *Meteoritical Bulletin* No. **84** (2000); *Meteorit. Planet. Sci.* **35**, A199-A225 (2000), loan from the Westfälische Wilhelms Universität Münster, Germany.

Sayama*: CM2 chondrite, 430 g was recovered after the observed fall in Sayama, Japan (1986). *Meteoritical bulletin No.* ***85*** *(2001); Meteorit. Planet. Sci.* **36**, A293-A322 (2001).

Sutter's Mill*: CM2 chondrite, 993 g was recovered after the observed fall in California, USA (2012). *Meteoritical Bulletin* **100** (2014); *Meteorit. Planet. Sci.* **49**, E1-E101 (2014).

Tagish Lake: $C2_{ung}$ chondrite, 10 kg was recovered after the observed fall on Tagish Lake, Canada (2000). *Meteoritical Bulletin* **84** (2000); *Meteorit. Planet. Sci.* **35**, A199-A225 (2000), loan from the Westfälische Wilhelms Universität Münster, Germany.

Vigarano*: CV3 chondrite, 15 kg was recovered after the observed fall in Emilia-Romagna, Italy (1910). *Never published in Meteoritical Bulletin*.

Y 791198*: CM2, 179.8 g was recovered during an Antarctic find expedition, in Yamato, Antarctica (1979). *Never published in the Meteoritical Bulletin.*

Y 980115*: CI1, 772 g was recovered during an Antarctic find expedition, in Yamato, Antarctica (1998). *Never published in the Meteoritical Bulletin.*

Appendix 3

Supplement tables and figures

Additional information:

In this appendix, all the supplementary tables and figures of the scientific chapters are presented. The data is subdivided based on the three different chapters in the thesis and contain raw data, figure data, and supplementary figures.

Curriculum Vitae

The Currivulum Vitae is not included in the online-version due to data protection

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