

A big message from small grains:
Constraints for solar nebula conditions from primitive meteorites

H a b i l i t a t i o n s - S c h r i f t

zur Erlangung der

Venia Legendi

im Fach

Mineralogie

an der Mathematisch-Naturwissenschaftlichen Fakultät
der Universität zu Köln

vorgelegt von

Dominik C. Hezel

Institut für Geologie und Mineralogie
Universität zu Köln
Oktober 2014

For Lucia

Table of Contents

| | |
|---|-----------|
| 1 Introduction | 6 |
| 1.1 The Significance of Meteorites..... | 6 |
| 1.2 Chondrite Components and their Formation Environment..... | 8 |
| 1.3 Where we Find Meteorites..... | 10 |
| 1.4 Habilitation Objectives | 11 |
| 2 Constraints on Component Formation Conditions | 12 |
| 2.1 The Central Questions of Chondrite Component Formation..... | 12 |
| 2.2 Chondrule Precursor Grains | 12 |
| 2.3 Conditions of Chondrule Formation | 16 |
| 2.4 Formation Reservoir of Chondrules and Matrix | 21 |
| 2.5 Technical Developments..... | 24 |
| 2.6 Ca,Al-rich Inclusions (CAIs)..... | 25 |
| 3 Component Formation in the Early Solar System..... | 28 |
| 4 References | 31 |
| 5 Publications..... | 42 |
| 6 Curriculum Vitae..... | 44 |

5.1

Palme H, Spettel B and Hezel DC (2014) Siderophile Elements in Chondrules of CV-Chondrites. *Chemie der Erde – Geochemistry* 74:507–516.

5.2

Hezel DC, Friedrich J and Uesugi M (2013) Looking Inside: 3D Structures of Meteorites. *Geochimica et Cosmochimica Acta* 116:1-4.

5.3

Beitz E, Blum J, Mathieu R, Pack A, Hezel DC (2013) Experimental investigation of the nebular formation of chondrule rims and the formation of chondrite parent bodies. *Geochimica et Cosmochimica Acta* 116:41-51.

5.4

Hezel DC, Elangovan P, Viehmann S, Howard L, Abel RL and Armstrong R (2013) Visualisation and quantification of CV chondrite petrography using micro-tomography. *Geochimica et Cosmochimica Acta* 116:33-40.

5.5

Elangovan P, Hezel DC, Howard L, Armstrong R and Abel RL (2012) PhaseQuant: A Tool for Quantifying Tomographic Data Sets of Rock Specimens. *Computers & Geosciences* 48:323-329.

5.6

Griffin L, Elangovan P, Mundell A and Hezel DC (2012) Improved segmentation of chondrules from micro-CT images of meteorites using local histograms. *Computers & Geosciences* 39:129-134.

5.7

Hezel DC, Schlüter J., Kallweit H., Jull AJT, Al Fakeer OY, Al Shamsi M and Strekopytov S (2011) Meteorites from the United Arab Emirates: description, weathering and terrestrial ages. *Meteoritics & Planetary Sciences* 46:327–336.

5.8

Emmerton S, Muxworthy AR, Hezel DC and Bland PA (2011) Magnetic characteristics of CV chondrules with paleointensity implications. *Journal of Geophysical Review - Planets* 116:E12007.

5.9

Moynier F, Agranier A, Hezel DC, Bouvier A (2010) Sr stable isotope composition of Earth, the Moon, Mars, Vesta and meteorites. *Earth & Planetary Science Letters* 300:359–366.

5.10

Hezel DC and Kießwetter R (2010) Quantifying the error of 2D bulk chondrule analyses using a computer model to simulate chondrules (SIMCHON). *Meteoritics & Planetary Sciences* 45:555-571.

5.11

Hezel DC, Needham AW, Armytage R, Georg B, Abel R, Kurahashi E, Coles BJ, Rehkämper M and Russell SS (2010) A nebula setting as the origin for bulk chondrule Fe isotope variations in CV chondrites. *Earth & Planetary Science Letters* 296:423-433.

5.12

Hezel DC & Palme H (2010) The chemical relationship between chondrules and matrix and the chondrule-matrix complementarity. *Earth & Planetary Science Letters* 294:85-93.

5.13

Hezel DC, Russell SS, Ross AJ and Kearsley AT (2008) Modal abundances of CAIs: Implications for bulk chondrite element abundances and fractionations. *Meteoritics & Planetary Sciences* 43:1879-1894.

5.14

Hezel DC & Palme H (2008) Constraints for chondrule formation from Ca-Al distribution in carbonaceous chondrites. *Earth & Planetary Science Letters* 265:716-725.

5.15

Hezel DC, Dubrovinsky L, Nasdala L, Cauzid J, Simionovici A, Gellissen M and Schönbeck T (2008) In situ micro-Raman and X-ray diffraction study of diamonds and petrology of the new ureilite UAE 001 from the United Arab Emirates. *Meteoritics & Planetary Sciences* 43:1127-1136.

5.16

Hezel DC & Palme H (2007) The conditions of chondrule formation, Part I: Closed system. *Geochimica et Cosmochimica Acta* 71:4092-4107.

5.17

Hezel DC (2007) A model for calculating the errors of 2D bulk analysis relative to the true 3D bulk composition of an object, with application to chondrules. *Computers & Geosciences* 33:1162-1175.

5.18

Hezel DC, Palme H, Nasdala L and Brenker FE (2006) Origin of SiO₂-rich components in ordinary chondrites. *Geochimica et Cosmochimica Acta* 70:1548-1564.

6 Curriculum Vitae

1 Introduction

This chapter is a brief introduction to the field of meteoritics and what we learn from studying meteorites

1.1 The Significance of Meteorites

Meteorites are extraterrestrial rocks that originate mostly from asteroids, which orbit the sun in ~2 to 5 Astronomical Units distance (1 AU: distance Sun - Earth). Today, more than forty thousand meteorites are stored in collections worldwide, and of those only about two hundred are not from the asteroid belt, but instead are rocks from Mars and the Earth's Moon. Asteroids are the building blocks that formed the terrestrial planets by aggregational growth ('Aufklumpfung'). They maybe also served as embryos for the cores of the gas giants. Hence, almost all meteorites predate Earth and the Moon. In fact, the age of the Solar System is the age of the oldest material (Ca,Al-rich inclusions; e.g. MacPherson, 2014 and references therein) found in primitive meteorites. Meteoritics, the science of studying meteorites, allows us to investigate in detail the processes in the protoplanetary disk from which the Sun and all other planets formed.

Meteoritics revealed some general types of meteorites. The widest known grouping of meteorites is into three general types: (i) stony, (ii) stony-iron and (iii) iron. It is currently believed that iron meteorites represent the cores of differentiated asteroids, stony-iron meteorites are from the border zone of the mantle and the metallic core of differentiated asteroids and stony meteorites either originate from the mantle of differentiated asteroids or from undifferentiated asteroids. Although this classification is well known to the public, meteoriticists prefer a division into two groups: (a) undifferentiated and (b) differentiated meteorites. Of course, not the meteorite itself is (un)differentiated, but its parent body from which it originates.

Undifferentiated meteorites contain all the components that formed in the protoplanetary disk, generally sub- μm to cm sized rocky and metallic or sulphide particles that agglomerated into asteroids.

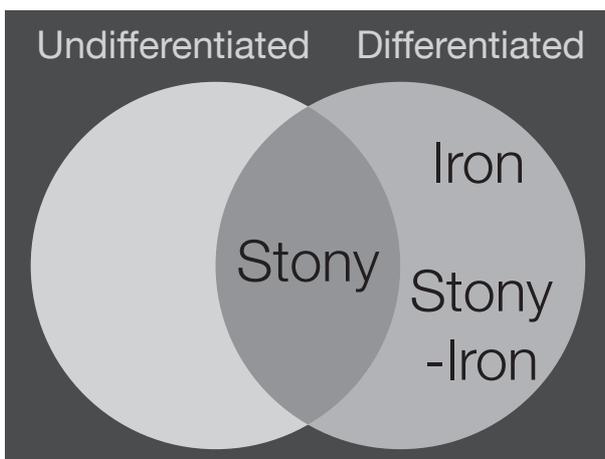


Figure 1: Relationship between the commonly known stony – stony-iron – iron meteorite classification scheme and the scheme undifferentiated – differentiated meteorites more commonly employed by meteoriticists.

Stony meteorites belong to either the undifferentiated or the differentiated meteorite subgroup. The classification scheme preferred by meteoriticists and its relationship to the more well known classification is displayed in Fig. 1. Further division of the meteorite groups into subclasses is displayed in Fig. 2.

The events in the early Solar System are best divided into 4 distinct epochs (Fig. 3). The discriminating criteria for each epoch is a distinct size of the grains or bodies. The transition from one epoch to the next is marked by a sudden increase in grain or body size. The first epoch is represented by the interstellar cloud that became

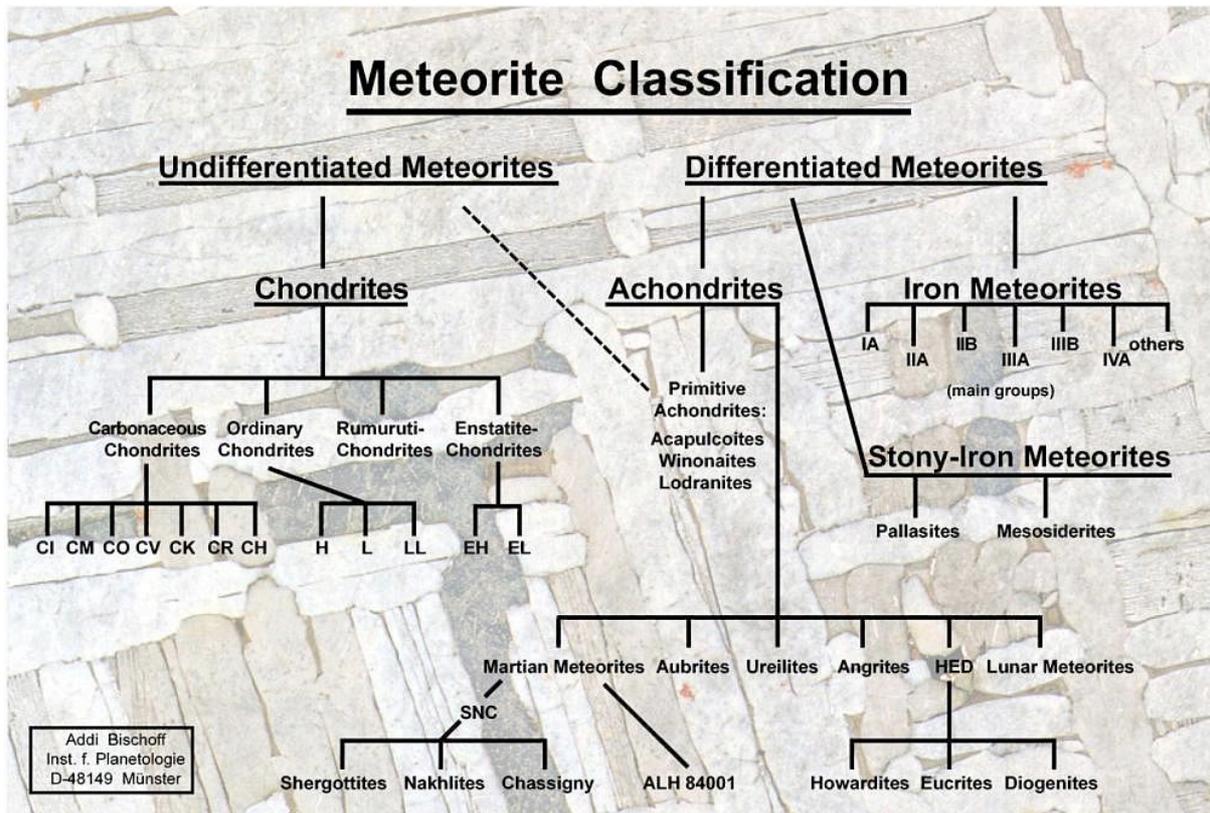


Figure 2: Meteoriticists meteorite classification scheme.

isolated from the interstellar medium (ISM). It was filled with interstellar grains in the sub-micrometer size range. About 95% of this material formed in-situ in the ISM in an evaporation ↔ re-condensation cycle. Only about 5% represented original stardust grains that formed in various stellar environments (e.g. Zinner, 2014). The famous phrase ‘We are all made from stardust’ is therefore not entirely true, as we are probably made up by only ~5% stardust, otherwise we are made of ISM.

The interstellar cloud collapsed and a swirling protoplanetary disk formed around the nascent sun. Processes and conditions that will be the focus of this habilitation lead to the formation of tens of μm to more than mm sized grains that are preserved until today in the so called primitive meteorites from undifferentiated asteroids (→ chondrites; e.g. Scott & Krot, 2014 and references therein). This second epoch is marked by a particle size increase of 2-6 orders of magnitude.

In the third epoch, the aforementioned grains agglomerated to form meter to kilometer sized asteroids, a size increase of up to 6 orders of magnitude. These are no longer small particles, but celestial bodies of which some few millions survived as asteroids in the asteroid belt. Despite this vast number, their combined mass is approximately only a third of the mass of our Moon. These asteroids are the major source of meteorites, and the latter most probably start their tens to hundreds of million years long travel to Earth after the collision of two asteroids (Herzog & Caffee, 2014).

In the final fourth epoch, the planetesimals collided to form the planets of our Solar System, which are up to 140,000 km in size. From down to 10 nm sized interstellar grains up to the present planets of our Solar System is a growth factor of almost 10²⁰. And the growth factor of the sun is even a few orders of magnitude larger, but its growth process is entirely different.

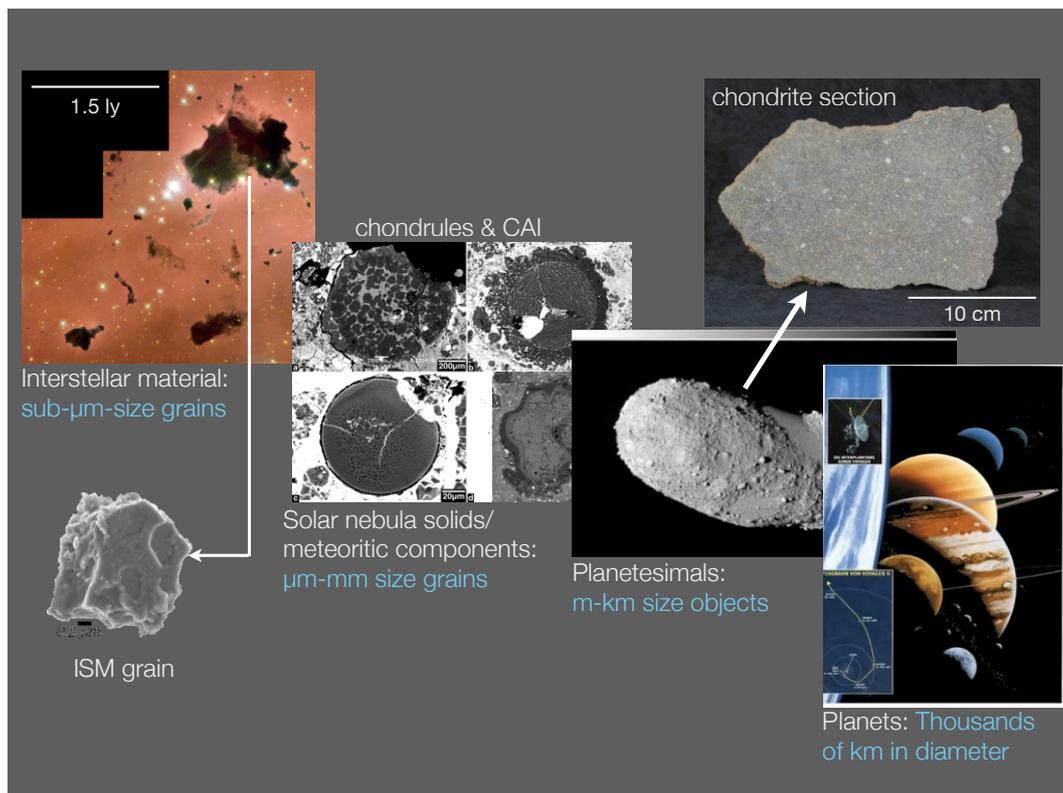


Figure 3: Four epochs represent the different events leading to the formation of the bodies of our Planetary System.

1.2 Chondrite Components and their Formation Environment

Primitive meteorites consist of two major, two minor, and a number of rare components (Fig. 4; e.g. Krot et al., 2014; Scott & Krot, 2014). Each of these components formed individually and were later aggregated into the meteorite parent body or asteroid. It is the goal of meteoritics to identify the origin and formation of these various components and form a coherent picture of the history of the first ~ 5 Ma years of our Solar System after the collapse of its parental ISM cloud.

The two major components – chondrules and matrix – constitute ~ 95 vol.% of chondrites in various proportions (e.g. Brearley & Jones, 1998). The word chondrule has its roots in the greek ‘chondros’ (it is sort of geek to also provide its greek transcript $\chi\omicron\nu\delta\rho\omicron\varsigma$) and is commonly falsely translated as ‘roundish’. The dictionary translates it as ‘cartilaginous’, and this describes the 3D appearance of chondrules in most cases much better than simply ‘roundish’. Although occasionally chondrules have neat, round shapes. Chondrules are believed to have formed during brief (minutes to hours) high-temperature events in the protoplanetary disk. The ambient temperature of the disk in the chondrule forming region is only vaguely known, and believed to be in the range of 600 ± 200 K. The temperature during the chondrule forming event in cases exceeded the liquidus temperature of the chondrules of ca. >1700 K, depending on composition, and was probably only buffered by the H_2 dissociation temperature at about 2200 K. The presence of chondrules in most of the primitive meteorites lead to their designation ‘chondrites’. The first letter ‘C’ is used in the naming conven-

tion for carbonaceous chondrites and consequently abbreviated with ‘C’. Then the first letter of the type meteorite for a certain group follows, e.g. is Ivuna the type meteorite for the important chondrite group CI. This is, however, only part of the naming scheme, and e.g. the most abundant chondrite group, the ordinary chondrites, are subdivided into L-, LL- and H-chondrites, without any ‘C’ (cf. Fig. 2). Further naming schemes exist, but their details are not relevant here and can be studied elsewhere (e.g. Van Schmus & Wood, 1967; Krot et al., 2014; Sears & Dodd, 1988).

Formation conditions and/or origin of the matrix is controversial and rather speculative. The fine grained nature of the matrix is a challenge for most analytical approaches and our knowledge is limited (e.g. Abreu & Brearley, 2010). Interpretations range from primitive ISM that was altered on the meteorite parent body to material that condensed from a gas either during or contemporary to chondrule formation. Transmission electron microscope studies of matrix identified local alteration processes on the parent body. No large scale element redistribution, i.e. the range of meters to tens of meters and more could be unequivocally identified. Some alteration features in matrix minerals might have formed in the protoplanetary disk (Brearley, 2014). A concentrated and focused effort to study chondrite matrix is required to understand this still highly enigmatic component much better.

A minor component are the opaque phases metal and sulphide, commonly contributing between 0 and 10 vol.% (e.g. Brearley & Jones 1998). Opaques occur in chondrules and matrix. The relationship between opaque phases in chondrules and matrix is rather poorly studied and not well known (e.g. Connolly et al., 2001; Ebel et al., 2008; Uesugi et al., 2008; Palme et al., 2014). Some hypotheses place their origin inside chondrules, and interpret them as reduction of silicates; other hypotheses regard opaques as direct condensates.

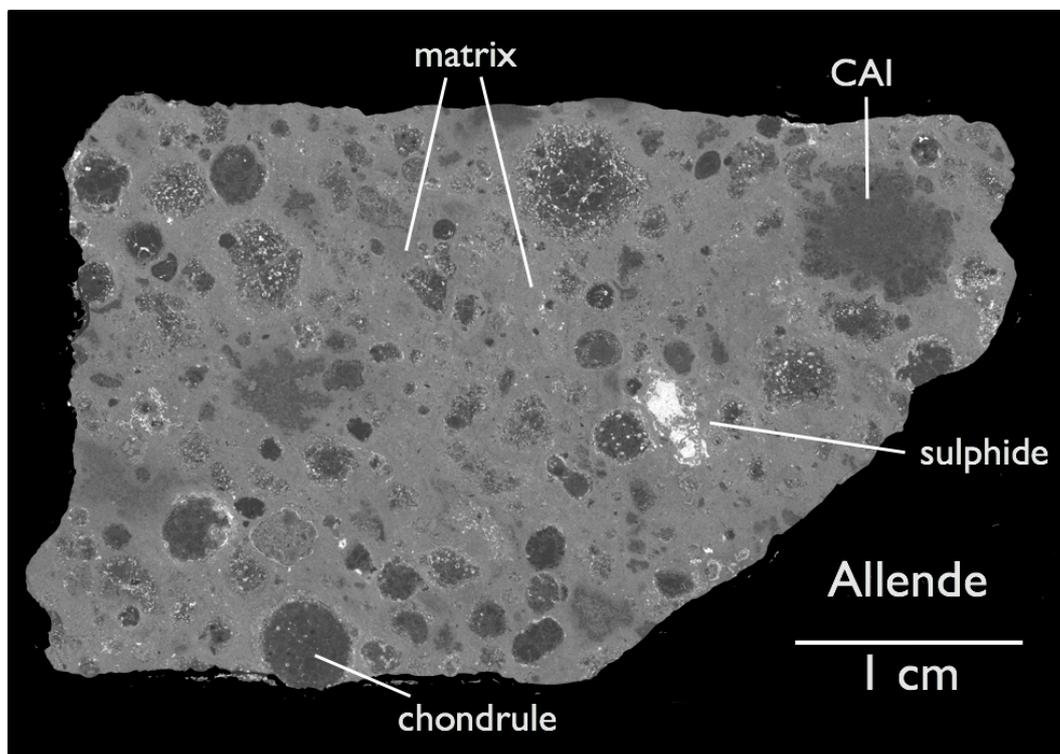


Figure 4: Back Scattered Electron (BSE) image of the CV chondrite Allende.

A second minor component are Ca,Al-rich inclusions (CAIs). These have been found to be the oldest components in our Solar System (e.g. Burkhardt et al. 2008; Davis & MacPherson, 2014) and, hence, are the reference for the age of our Solar System. Their concentric structure of high temperature to low temperature minerals from core to rim is a testimony of condensation processes of a once hot, i.e. up to >2000 K hot solar nebula. Their occurrence represent a significant reservoir of refractory elements. The CAI abundances differ significantly among the chondrite groups, from almost 0 to a maximum of about 3-4 vol.% (Hezel et al., 2008¹; Ebel et al., 2009).

1.3 Where we Find Meteorites

Meteoriticists only rarely search for meteorites themselves. Although more than 40 t of extraterrestrial material rains down to Earth mainly in the form of micro-meteorites every day, only few large meteorites collide with Earth. On average, two meteorites the size of a tennis ball fall on the area of Germany each year. The dense vegetation of Germany prohibits the find of most of these falls. Only sufficient observations of a single fall by many witnesses allow to triangulate the fall ellipse of a meteorite. This lead, for example, to the first fall recovered in this way by Wegener (1917). More

recent falls are the Neuschwanstein meteorite that fell in 2002 (Oberst et al., 2004); and in Russia, of course, Chelyabinsk that fell in February, 2013.



Figure 5: The 26 meteorites found during the field campaign in 2009 together with Jochen Schlüter, Heiko Kallweit and about ten UAE rangers that supplied us in the field and found the majority of meteorites.

Hot and cold deserts, on the other hand, do not weather away meteorites quickly and their mostly black fusion crust that formed during atmospheric entry makes them an easy spot on bright surfaces such as antarctic ice shields or white, calcic desert planes. Meteoriticists are – unsurprisingly – primarily interested in the scientifically most meaningful meteorites. Unfortunately, most meteorites belong to scientifically rather uninteresting groups such as L5 or H6. I was very interested in the effort of finding meteorites – which requires careful field trip preparation, establishing mandatory contacts with the government of the country as meteorites represent a special natural heritage (cf. ethics code of the Meteoritical Society), etc. – and sheer luck. The most successful search campaign I attended was to the United Arab Emirates in 2009 where we found 26 meteorites in 10 days – a good

¹All blue coloured references are part of this habilitation and presented in chapter 5. Consequently, these references are not listed in chapter 4 *References*.

yield (Fig. 5). Unfortunately, all were of the ‘boring’ sort. However, since then I started appreciating even this boring sort, and started projects on these meteorites (see below). This has the additional advantage that these samples are much easier to obtain than many other meteorites of ‘high’ scientific value, which are often rare and

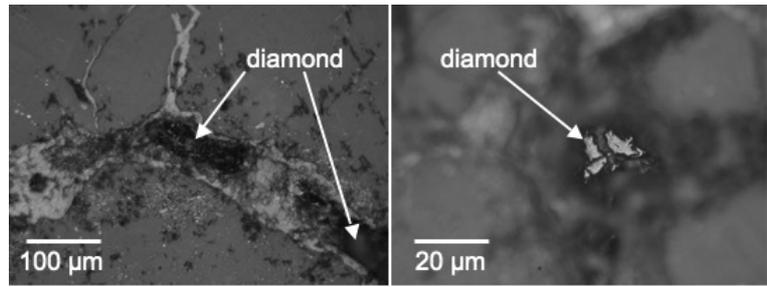


Figure 6: Reflected light images showing typical diamond in the ureilite UAE 001.

difficult to obtain. The findings of the just mentioned 2009 field campaign to the United Arab Emirates are published in [Hezel et al. \(2011\)](#). The emphasis of this publication is on terrestrial ages of the meteorites and general effects of terrestrial weathering on meteorites.

The motivation to search for meteorites in the UAE for the first time came from a meteorite find by an archeologist (Heiko Kallweit), who sent us the sample. This turned out to be a rare ureilite. This unusual meteorite group contains diamonds of still controversial origin (Fig. 6). I studied the diamonds in this ureilite – and named it, UAE 001 (following the restrictive and rather technical, but mandatory Meteoritical Society naming scheme) – and concluded that the diamonds most probably formed during a shock event, probably during excavation of the meteorite after the collision of its parent body with another asteroid. These findings are published in [Hezel et al. \(2008\)](#).

1.4 Habilitation Objectives

Meteoritics, unlike e.g. geochemistry or biology, lack a basic framework to interpret and understand data. In geochemistry, plate tectonics serves as the fundamental framework to interpret data of terrestrial rocks. In biology, evolution is the all encompassing framework to understand plant and animal relationships or genetic genealogies. No such basic framework exists for meteoritics. The reason for this absence might be that we are still missing some key information, or that we in fact still miss the all-connecting idea. In this habilitation I will make an attempt and propose a fundamental framework for meteoritics. I developed this framework during the past decade from my own and my colleagues research. I have to note, however, not all of my colleagues will necessarily agree with this.

2 Constraints on Component Formation Conditions

This chapter presents a synopsis of my research – the full results are presented as reprints in chapter 5

2.1 The Central Questions of Chondrite Component Formation

Meteoritics primarily focuses on the second and the transition from the first to the second epoch introduced in chapter 1.1. These epochs encompass the formation of the sub-mm to cm sized grains found today in chondrites. The most long standing and central question in meteoritics is no doubt: *how did chondrules form?* Many processes have been suggested – shock waves, planetesimal collision, lightning, etc. (cf. Ciesla, 2005) – but none is unequivocally proven. One problem might be that the chondrule formation *process* is the wrong focus. I therefore suggest to re-phrase the question slightly to: What are the key *constraints* for chondrule formation? Answering this will allow unequivocal dismissal or support for one or more of the suggested chondrule formation processes, and any chondrule formation process possibly suggested in the future.

An important question directly related to chondrule formation is about the nature of their precursor material. Intriguingly, no such material has so far been clearly identified. It appears almost all precursor material was transformed to other material, mainly chondrules and matrix. It is, however, possible to obtain indirect information on the precursor material of chondrules, and possibly also matrix.

Another highly important question is the origin of the matrix and its formation relationship to chondrules. Many chondrule formation hypothesis rely on a certain formation configuration of chondrules and matrix, e.g. that both components either formed in separate or in the same parental reservoir. It is a fundamental constraint to know whether chondrules and matrix must or must not have formed from the same reservoir.

It is essential to learn which processes occurred in the protoplanetary disk and which on the parent body. A parent body process mistaken for a protoplanetary disk process or vice versa would obviously render all interpretations on e.g. chondrule formation obsolete.

This is the canvas on which I will present the results of my research of the past years. In addition, I will briefly cover the origin of CAIs and discuss analytical developments. And, as mentioned earlier, I will make an attempt to put all this in a concise framework of component formation in the early Solar System.

2.2 Chondrule Precursor Grains

Chondrules are often studied as individual objects. I study them rather as populations within chondrites. They then provide various information, the first I will discuss is about their precursor grains. It has been reported in numerous studies that chondrules in all types of chondrites show large scatter in chemical and oxygen isotope compositions (e.g., Clayton, 1983; Clayton, 1993; Jones et al.,

2005; Russell et al., 2005; Scott & Krot, 2005; Hezel et al., 2006; Mullane et al., 2005; Hezel et al., 2010). The range of oxygen isotopes is even so large that any given OC chondrule cannot be assigned to a single OC group with a well defined bulk oxygen isotopic composition. Figure 7 displays the elemental variation for 132 ordinary chondrite (OC) chondrules. Four major hypotheses surfaced to explain this scatter: (i) *closed system*: chondrules inherited their compositional scatter from heterogeneous precursor grains (e.g., Clayton, 1983; Grossman & Wasson, 1983a; Alexander, 1994; Uesugi et al., 2003; Ciesla, 2005; Hezel et al., 2006); (ii) *open system*: chondrules exchanged material with the surrounding gas, thereby altering their composition (e.g., Sears et al., 1996; Alexander, 2004; Davis et al., 2005; Jones et al., 2005; Huss et al., 2005; Cuzzi & Alexander, 2006; Hezel et al., 2010); (iii) *fractional condensation*: Nagahara et al. (2005) and in a series of papers Blander et al. (1976), Blander (1983), and Blander et al. (2001,2004) proposed chondrules being liquid condensates. They suggest that fractionation during condensation caused the observed scat-

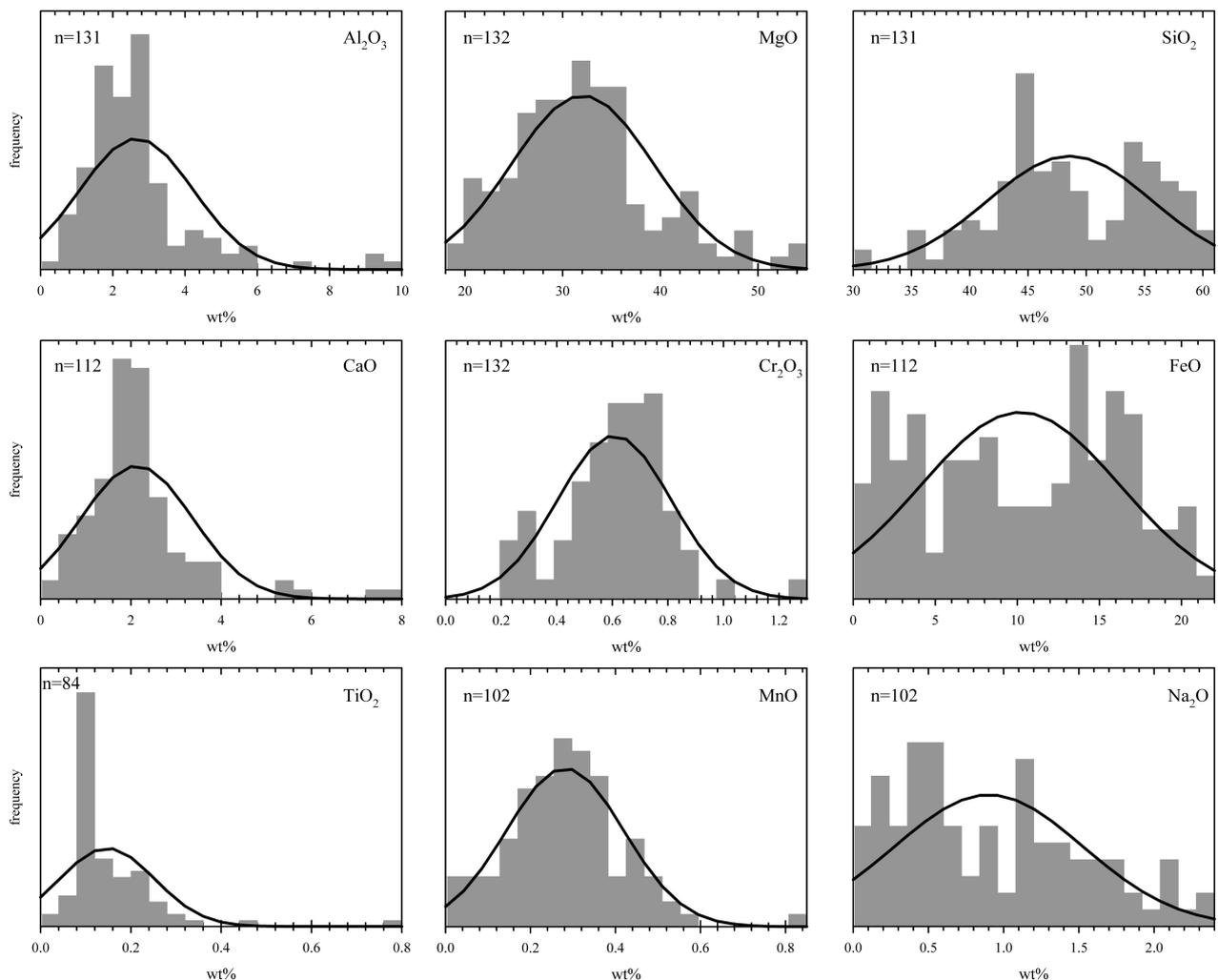


Figure 7: Compositional variation of ordinary chondrite chondrules. Solid lines are calculated Gaussian probability density functions. n: number of used bulk chondrule compositions. Data taken from Tachibana et al. (2003); Dodd (1978); Rubin and Pernicka (1989); Grossman and Wasson (1983b); Huang et al. (1996); Jones (1990); Jones (1994); Jones (1996a); Matsunami et al. (1993); McCoy et al. (1991); Kimura and Yagi (1980).

ter; (iv) *parent body processes*: Some workers invoke magmatic processes on parent bodies to explain the scatter (e.g., Hutchison et al., 2005; Sanders & Taylor, 2005; Sanders & Scott, 2012).

It is a still widely accepted hypothesis that chondrules inherited their bulk compositional variation from heterogeneous precursor grains. If this were true, each chondrule could have only formed from few precursor grains, as otherwise all chondrules would have the average composition of the reservoir. This consequence is briefly noted in publications by Grossman & Wasson (1983a) and Alexander (1994). However, the tight limitations accompanying this hypothesis, like the maximum number of precursor grains contributing to a single chondrule before the population becomes uniform, or the size of the precursor grains have not been considered.

In Hezel & Palme (2007) we performed statistical calculations to study in detail the case that the compositional bulk chondrule variation is the result of heterogeneous precursor grains. Figure 8 displays a simplified cartoon of the implemented Monte Carlo simulation. Different precursor types and compositions were used to account for different chondrule types (e.g. Al-rich chondrules) and to simulate elemental and isotopic variations. The most typical chondrule composition was represented by five different precursor types: orthopyroxene (63%), olivine (24%), anorthite (9%), clinopyroxene (3%) and albite (1%). The modal abundances of the precursor types given in the brackets correspond to modal abundances of these minerals at 1200 K during equilibrium condensation (Davis & Richter, 2003). The chemical compositions of the precursor types were assumed to be small ranges (Fig. 9, top plates) to account for compositional variations within the minerals. The size was assumed to be the same for all precursor types. Different sizes affect the results only minor. The total number of precursor grains was 60,000.

Only 5 to maybe 20 precursor grains are sufficient to produce a chondrule population that has

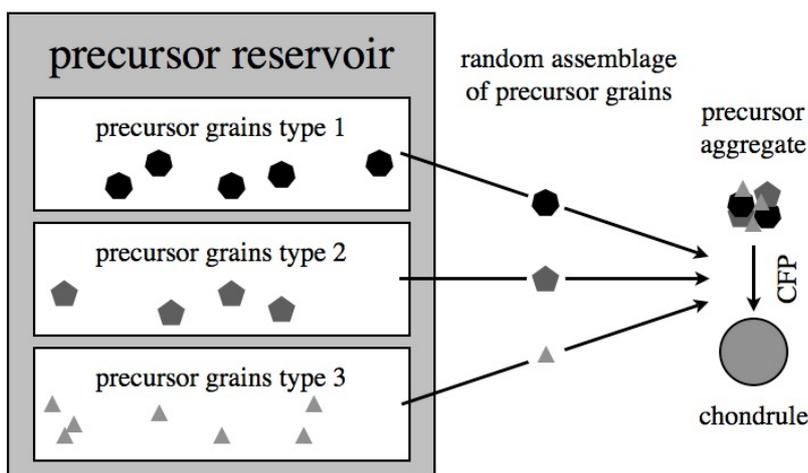


Figure 8: Cartoon outlining the model used in this study. A precursor reservoir consists of different precursor types. Each precursor type consists of precursor grains. Precursor grains of all precursor types of the precursor reservoir are randomly mixed to form the precursor aggregate. The precursor aggregate is transformed into the chondrule during the chondrule forming process (CFP). Precursor aggregate and chondrule are chemically equivalent.

almost uniform bulk compositions. The MgO bulk compositional variation of the 132 chondrules displayed in Fig. 7 ranges from about 20 to nearly 50 wt.%. In the simulation results presented in Fig. 9 a chondrule population in which each chondrule is made from 20 precursor grains would have a bulk compositional range from only about 40 to 50 wt.%, much smaller than the observed population (Fig. 7).

The diameters of typical chondrules range from about 100 to about 1000 μm . If individual

chondrules were formed from less than 20 precursor grains, these grains must have had sizes of 100 to a few 100 μm . This result does not change significantly if a large portion (e.g. 50 vol.%) of fine-grained, e.g. matrix material was part of the chondrule precursor aggregate. No current hypothesis promotes the formation or existence of large chondrule precursor grains. On the contrary, chondrule precursor grains are commonly assumed to be small (e.g. Alexander, 1994; Ciesla, 2005; Libourel & Chaussidon, 2011). Hence, chondrules most certainly did not form from large, heterogeneous precursor grains.

Alexander (1994) suggested chondrules were their own precursors that formed from destruction and re-assembly of a previous chondrule population. This could allow for large chondrule precursor grains. In a second set of calculations we evaluated this hypothesis. The scenario would be possible, if chondrules disaggregated in heterogeneous fragments of olivine, pyroxene and mesostasis and if such recycling occurred only once or twice. As chondrule fragments are usually rather mixtures of olivine, pyroxene and mesostasis, this hypothesis seems rather unlikely.

Of course, so far the assumption was that chondrules formed from the same reservoir. If chondrules formed in different reservoirs of different compositions (e.g. Zanda et al., 2006), a mixture of chondrules from these different reservoirs would result in a non-uniform bulk compositional chondrule population. However, in this case a multi-modal distribution should be expected and not a continuous distribution as is obvious for chondrule populations from Fig. 7. I will provide even more supportive evidence for the formation of chondrule populations of individual meteorites from the same reservoir in subsequent sections.

The first hypothesis mentioned above, in which chondrules were *closed systems* does not satisfactorily explain bulk chondrule compositional variations. The second hypothesis, in which chondrules are *open systems* will be discussed in detail in the subsequent section. The third hypothesis

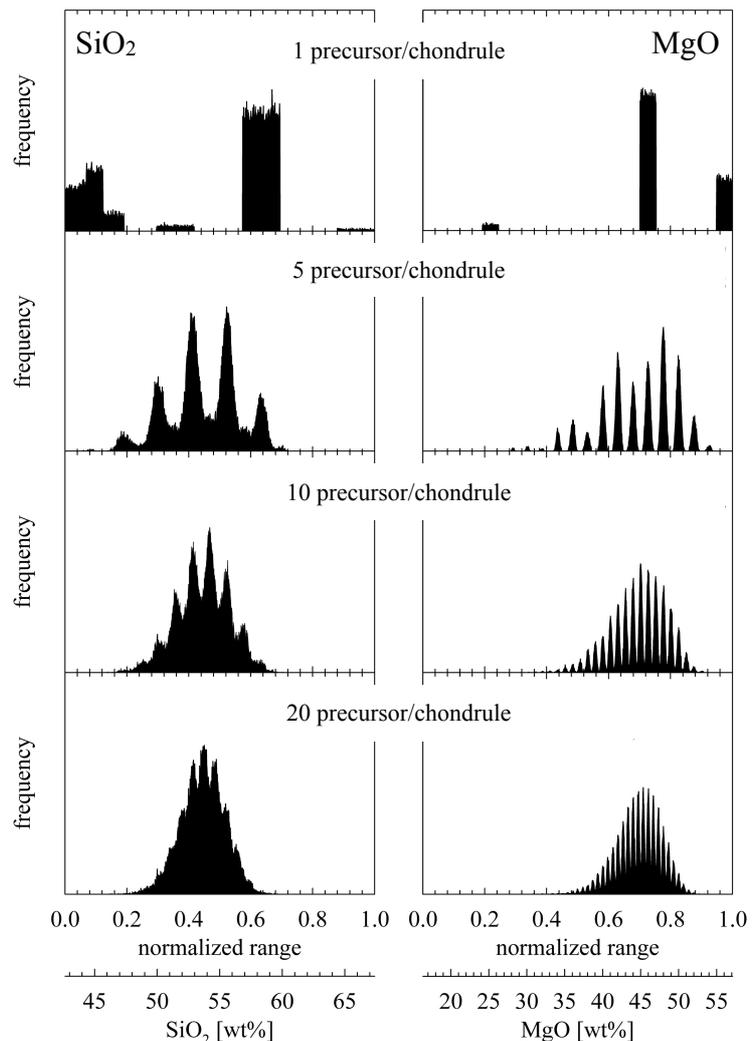


Figure 9: The development of bulk chondrule compositions of a chondrule population in a single meteorite for two elements and a starting composition of 63% orthopyroxene, 24% olivine, 9% anorthite, 3% clinopyroxene and 1% albite.

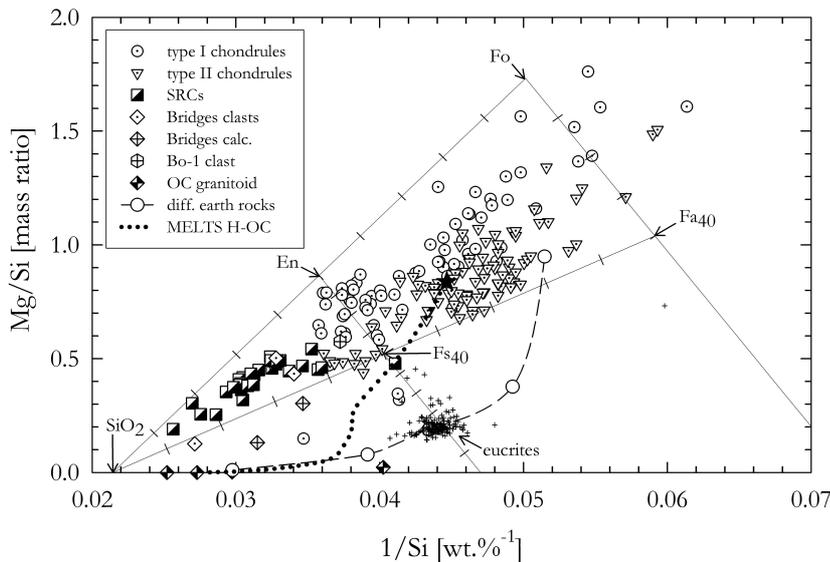


Figure 10: Bulk chondrule compositions in OC. Fo: forsterite; En: enstatite; Fa: fayalite; Fs: ferrosilite; Bridges clasts: three clasts from Parnallee (Bridges et al., 1995); Bo-1: clast from Bovedy (Ruzicka et al., 1995). Bridges calc: calculations from Bridges et al. (1995); OC granitoid: granitoid clast in Adzhi Bogdo (Bischoff et al., 1993); Star: H-chondrite starting composition (Mason, 1965) for the MELTS fractional crystallization sequence; diff. earth rocks: terrestrial rocks in order of increasing SiO₂ (=decreasing 1/Si): komatiitic peridotite–basanite–tholeiitic basalt–andesite–granite (taken from Hughes (1982)). Bulk chondrule data are from: Dodd (1978); Grossman and Wasson (1983b); Olsen (1983); Sears et al. (1984); Rubin and Pernicka (1989); Jones (1990, 1994, 1996); McCoy et al. (1991); Matsunami et al. (1993); Bridges et al. (1995); Ruzicka et al. (1995); Huang et al. (1996); Tachibana et al. (2003).

from bulk chondrule compositions (Fig. 10). In particular, SiO₂-rich chondrules plot far away from the calculated magmatic trend. On the other hand, meteorites and clasts found in meteorites for which a magmatic origin is widely accepted (e.g. eucrites, granitoid clasts, e.g. Mittlefehldt, 2014) fall on a magmatic trend. Further, REE element patterns of chondrules are flat, but could be expected to be fractionated if chondrules are the result of melt evolution. It is therefore highly unlikely that chondrules formed in a magmatic setting on a parent body.

These studies on bulk chondrule compositional variations of chondrule populations in individual chondrites lead to the conclusion that open system processes, i.e. the exchange of material between the chondrule and the surrounding gas is the most likely or at least the dominant process responsible for bulk chondrule compositional variations.

2.3 Conditions of Chondrule Formation

The past 10-15 years are marked by an increasing amount of evidence that chondrules indeed behaved as open systems (e.g. Tissandier et al., 2002; Hezel et al., 2003; Krot et al., 2004; Huss et al., 2005; Libourel et al., 2006). However, the extent of material exchanged between chondrules and surrounding gas remains controversial and not all agree that for example the entire range of bulk

that explains bulk chondrule compositional variations by *fractional condensation* of molten chondrules requires many hypothetical constraints, as outlined in e.g. Blander et al. (2001, 2004) and is therefore rather unlikely and not discussed further. The forth hypothesis, *parent body processes* is discussed now.

The bulk compositional variation of chondrules extends to highly SiO₂-rich compositions as Hezel et al. (2003, 2006 and references therein) demonstrated. In Hezel et al. (2006) we modelled the melt evolution of an H-chondrite parent body using the MELTS program from Ghiorso and Sack (1995). The resulting trend is very different

chondrule compositions can solely be explained by evaporation, re-condensation and/or exchange of material with the surrounding gas (e.g., Cuzzi and Alexander, 2006). It is, for example, puzzling that the isotope compositions of bulk chondrules deviate only minor from the solar, i.e. CI chondritic value. It is commonly assumed that chondrules formed in low pressure environments of 0.1 to 10 Pa. Evaporation at such low pressures should result in isotope fractionations of a few tens of per mill (e.g. Davis & Richter, 2014). Yet, only isotope compositions of a few per mill deviation from CI are observed, at most, except for oxygen. For example, the typical range for the volatile element K is -3 to +5‰, with only a few chondrules going down to -15.5‰ and up to +17.8‰ of $\delta^{41/39}\text{K}$ (Humayun & Clayton, 1995; Alexander et al., 2000; Alexander & Grossman, 2005). Typical deviations from a standard of about solar values for major elements range from -1.33 to +1.21‰ for $\delta^{56/54}\text{Fe}$ (Alexander & Wang, 2001; Zhu et al., 2001; Kehm et al., 2003; Mullane et al., 2005; Poitrasson et al., 2005; Needham et al., 2009), -1.73‰ to +0.13‰ for $\delta^{88/86}\text{Sr}$ (Moynier et al., 2010) and from -0.69 to +0.47‰ for $\delta^{29/28}\text{Si}$ (Molini-Velsko et al., 1986; Clayton et al., 1991; Georg et al., 2007; Fitoussi et al., 2009). Data for Mg isotopes are inconsistent, as different workers used different standards. The reported maximum range of fractionation is 1.7‰ (Galy et al., 2000; Nguyen et al., 2001; Young et al., 2002; Bouvier et al., 2009).

The small extent of these deviations becomes even more clear when compared to CAIs or cosmic spherules. CAIs have deviations of up to +12‰ in $\delta^{29}\text{Si}$ and +8.5‰ in $\delta^{25}\text{Mg}$ (Young et al., 2002; Richter et al., 2007; Knight et al., 2009) and are explained by high temperature evaporation processes in the protoplanetary disk. Cosmic spherules are small (up to a few 100 μm at maximum) commonly glassy objects and formed during atmospheric entry, and have large isotope compositions of up to +51.1‰ in $\delta^{57}\text{Fe}$, +8.8‰ in $\delta^{29}\text{Si}$, +8.0‰ in $\delta^{25}\text{Mg}$ and +183‰ in $\delta^{41}\text{K}$, which is close to what is expected from Rayleigh fractionation (Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005). However, tektites, which are solidified melts that formed in the aftermath of giant impacts on Earth, have no fractionations of K ($\sim 0\%$ $\delta^{41/39}\text{K}$, Humayun & Koeberl, 2004; Herzog et al., 2008) and minor to significant fractionations in Cd (-0.7 to +7.6 $\epsilon\text{Cd}/\text{amu}$, Wombacher et al., 2003), Zn (+0.17 to +2.49‰ of $\delta^{66/64}\text{Zn}$ Moynier et al., 2009) and Cu (+1.99 to +6.98‰ $\delta^{65/63}\text{Cu}$, Moynier et al., 2010). A simple Rayleigh fractionation explanation does not apply to the tektite data.

Krot et al. (1995) and Krot et al. (1998) describe a series of alteration processes that affected chondrules in CV chondrites. It has therefore been suggested that the bulk chondrule isotope composition of e.g. Fe is not the result of open system behaviour of chondrules during their formation, but rather the result of element re-distribution on the parent body. Yet, Fe is a particularly interesting element in chondrules, as it occurs not only in chondrule silicates, but also in metal, sulphide and occasionally magnetite contained in chondrules. As such, it serves as a tool to decide whether the Fe isotope composition of chondrules is the result of open system behaviour during chondrule formation or of element re-distribution on the parent body.

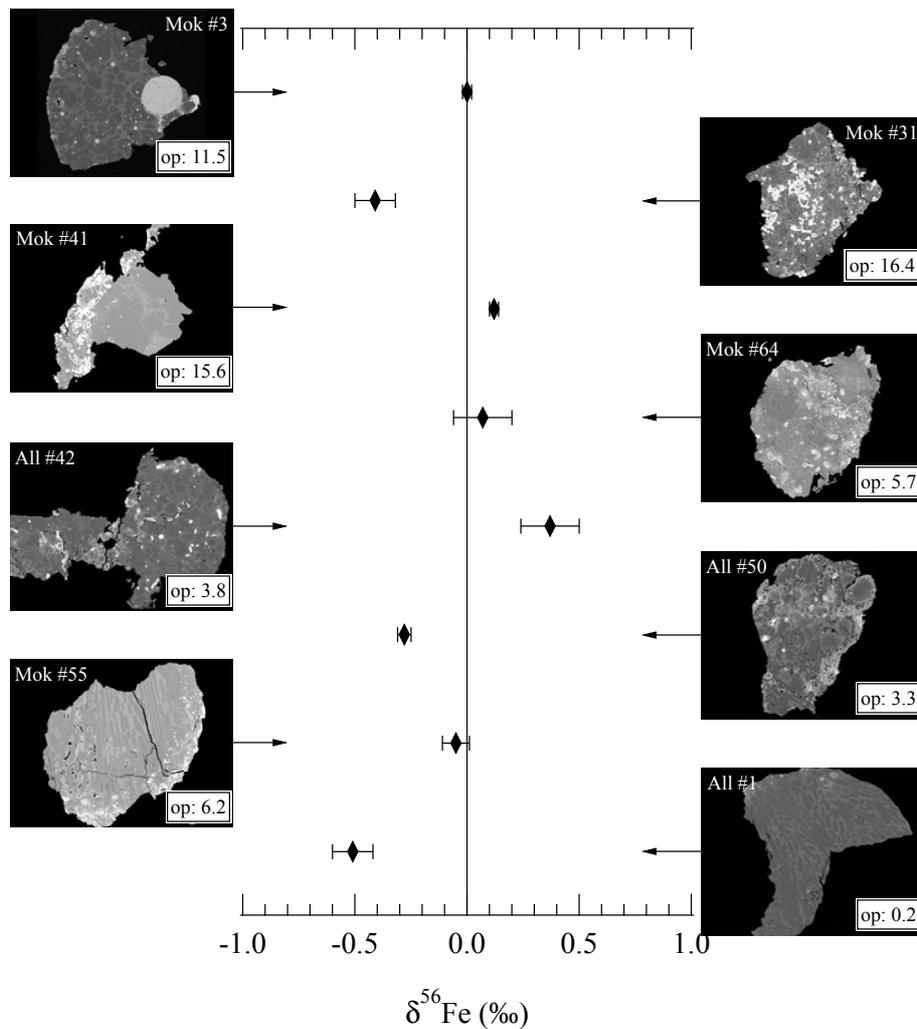


Figure 11: All but one chondrules displayed have large amounts of opaque phases (white) and, hence, their bulk Fe concentrations are dominated by the opaque phases. The exception is the BO chondrule at the bottom right. The chondrules span nearly the entire range of measured $\delta^{56}\text{Fe}$ values, i.e. chondrules with high opaque phase abundances do not have a particular isotope composition. Likewise, there is no correlation between petrographic type and isotope composition. This is especially obvious for the two BO chondrules: Mokoia #55 is unfractionated, whereas Allende #1 has a very light composition. op: opaque phase modal abundance in area%.

The CV chondrites Allende (Fig. 4) and Mokoia contain nearly 40 vol.% chondrules and about 55 vol.% interstitial material that is here collectively called matrix (Hezel et al., 2013; Ebel et al., 2009). Silicates in the majority of chondrules are FeO-poor (mostly <1-5 wt.%), whereas the matrix contains up to 40 wt.% FeO (e.g. Palme et al. re-submitted and references therein), which means that matrix and chondrule silicates are in stark thermodynamic disequilibrium. The bulk chondrule Fe composition is a combination of silicate FeO and opaque phase Fe. The chondrule bulk Fe is dominated by the opaque phases if the bulk chondrule silicate contains 2.5 wt.% FeO, and only about 0.3 vol.% metal or about 2 vol.% sulphide are present in the chondrule. The bulk Fe content of most of the chondrules displayed in Fig. 11 are dominated by the high abundance of opaque phases. We measured opaque abundances in 7 Allende and 10 Mokoia chondrules using tomography and found that in many chondrules the opaque phases dominate the Fe content of the chondrule, with individual chondrules having more than 10 vol.% opaques. This is in agreement

with bulk chondrule measurements using INAA of Jones and Schilk (2009), who found a continuous range in Fe concentrations from about 2 to 30 wt.%. This can only be explained by mostly high opaque abundances within the FeO-poor silicates, as is obvious from Fig. 11. The comparatively small and most probably secondary magnetite in some chondrule mesostases (glassy to fine-grained material interstitial to larger chondrule silicates such as olivine and pyroxene) is insufficient to account for the large range of bulk chondrule Fe concentrations found by Jones and Schilk (2009)².

We measured the $\delta^{56/54}\text{Fe}$ isotope compositions of 35 bulk chondrules from the three CV chondrites Allende, Mokoia and Grosnaja (Figs. 11,12) and found a range from -0.82 to +0.37‰ (Hezel et al., 2010). Figure 11 illustrates that chondrules in which opaques dominate the bulk chondrule Fe concentration show the almost full range of Fe isotope variation. Hence, it must be the opaques that carry the variable Fe isotope compositions, not the silicates. Chondrules in these meteorites experienced limited alteration, as mentioned earlier and as we demonstrated in a magnetic study of chondrules in these meteorites (Emmert et al., 2011). This limited alteration was insufficient to exchange significant amounts of Fe and Mg between chondrules and matrix, and it is hence similarly implausible that significant amounts of Fe were exchanged between chondrule and matrix opaques. Secondary magnetite is a minor phase in chondrules and does not contribute significantly to the bulk chondrule Fe. The bulk chondrule Fe isotope composition is therefore not carried by magnetite. This is also obvious from a mass balance perspective: the matrix has the same Fe isotope composition as the bulk chondrite, while bulk chondrules have lighter and heavier Fe isotope composition. However, bulk chondrules must have the bulk chondrite Fe isotope composition.

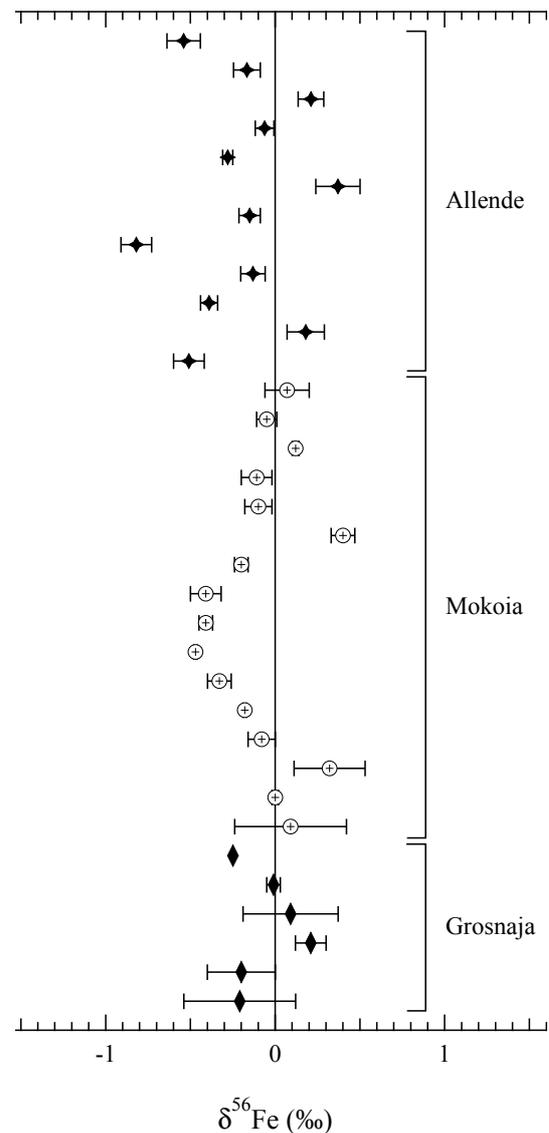


Figure 12: Variation of bulk chondrule Fe isotope compositions in three different CV chondrites.

²I add the discussion of the Jones and Schilk (2009) data as we reported lower average opaque phase modal abundances of chondrules in Allende (1.1 vol.%) and Mokoia (1.3 vol.%) in Hezel et al. (2013). I therefore do not want to base the dominating effect of opaques on the bulk chondrule Fe content solely on our tomographic finds reported in Hezel et al. (2009). In my opinion, the difference in the reported values is based on two effects: (i) In Hezel et al. (2009) we use only a small number of chondrules and the result might be biased to chondrules with higher opaque abundances. (ii) In Hezel et al. (2013) we report average opaque abundances, which make no statement about individual chondrules or the distribution of opaques in the chondrule population. Further, the automated approach we use in this study might underestimate the reported value. Having said that, detailed tomographic studies are required to resolve and address this issue, which is also highly important to understand the so far rather poorly understood relationship between chondrule and matrix opaques.

tions, as bulk and matrix are similar. Any significant redistribution of Fe isotopes between matrix and chondrules should therefore change the matrix composition, which is not observed. Keeping matrix and bulk chondrite at the same Fe isotope value, while changing chondrules to lighter *and* heavier Fe isotope compositions, is almost impossible to explain by magnetite formation in chondrules. The bulk chondrule isotope composition is hence unlikely to be an effect of parent body element exchange or secondary magnetite formation in chondrules.

Opaques often occur as abundant tiny blebs in chondrules and using the argument from the previous section, heterogeneous precursor grains – in this case opaques – seem unlikely to explain the isotope variation. The currently remaining and hence most likely explanation is exchange of material, i.e. evaporation and re-condensation during the molten stage of chondrule formation. Hence, chondrules acted as open systems.

It was recently proposed by Cuzzi & Alexander (2006) and Alexander et al. (2008) that high dust/gas ratios can explain the small isotope fractionations in chondrules. High pressure environments can indeed suppress large isotope fractionations, as we recently demonstrated from meteorite fusion crusts in Hezel et al. (in revision). Hence, we consider our results as evidence for this suggested scenario. There is, however, currently no known setting for such a high dust/gas ratio. Johansen et al. (2007) proposed that planetesimals formed in gravitational instabilities. The dust/gas ratio constantly increases during such a collapse until the final planetesimal is formed. We suggest it might be possible that chondrule formation and the isotopic exchange occurred during such a collapse phase.

The bulk chondrule Fe isotope composition is a continuous distribution similar to the elemental bulk chondrule compositions discussed above. Open system behaviour of chondrules and the

exchange of material between chondrule and surrounding gas was probably the cause for both, the elemental and isotope variations observed in bulk chondrules.

We currently study the most abundant chondrule types in meteorites, FeO-poor, porphyritic, so called type I chondrules (Hezel et al., 2014a,b). It appears these chondrules are typically zoned with olivine in the centre and low-Ca pyroxene at the rim (Fig. 13). This zonation has been mentioned before, but was never systematically studied. We find this zonation is typical in chondrules, and not an ex-

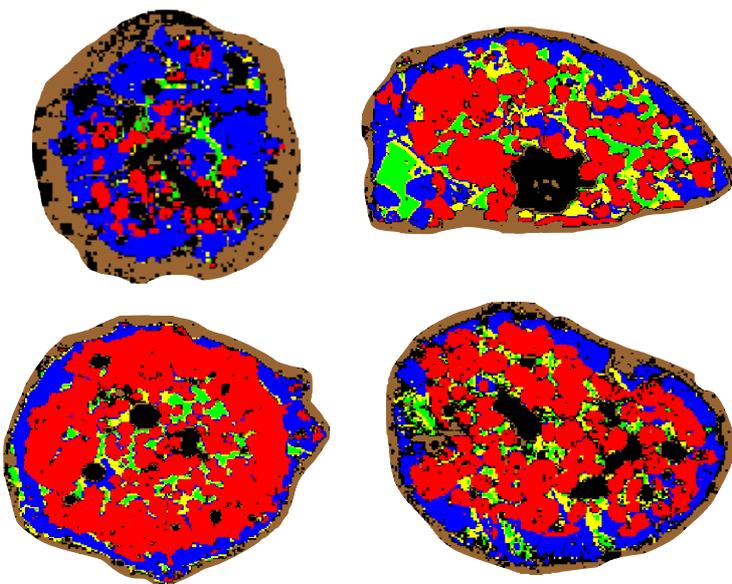


Figure 13: Phase maps of four zoned chondrules from the CO chondrite A-881632. Red: olivine; Blue: low-Ca pyroxene; Green & Yellow: mesostasis.

ception as it is often perceived, probably because the low-Ca rim can be thin and is difficult to spot in BSE images. Only few studies exist on this zonation for only a limited number of meteorite classes (e.g. Krot et al., 2004; Hezel et al., 2003; Libourel et al., 2009). All these studies attribute this zonation to open system behaviour of chondrules and the reaction olivine + SiO(g) → pyroxene, i.e. chondrule olivine reacts with the gaseous species of Si (SiO) to low-Ca pyroxene (cf. Tissandier et al., 2002). This is further evidence for the open system behaviour of chondrules during their formation and I will use this zonation as a key for my proposed model of component formation in the early Solar System presented in chapter 3.

2.4 Formation Reservoir of Chondrules and Matrix

Chondrules and matrix are the two voluminous most important components, together often constituting >95 vol.% of the meteorite. In carbonaceous chondrites (CC), chondrules and matrix often occur in approximately equal amounts. Possible chondrule formation processes might be broadly divided in single reservoir models and multiple reservoir models („2-component models“). In the

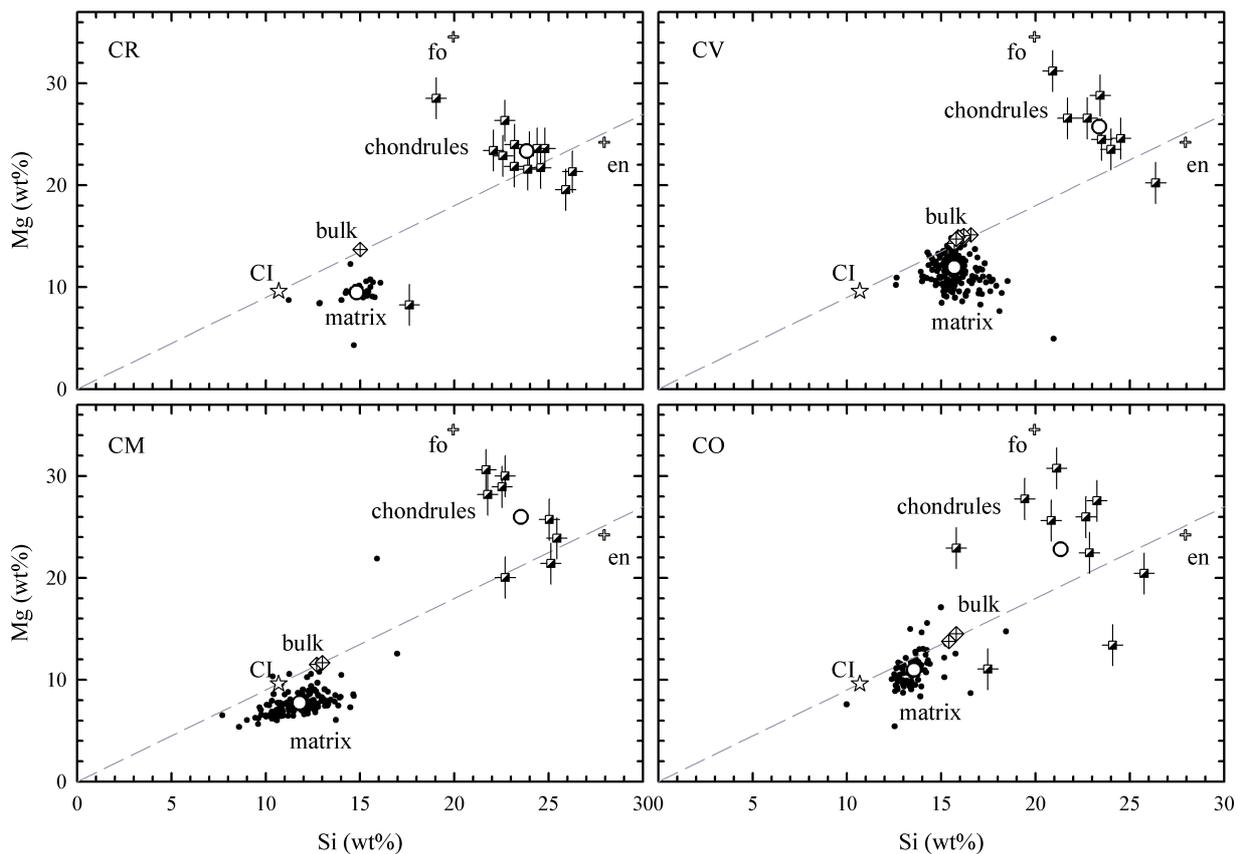


Figure 14: Chondrule and matrix compositions of four different carbonaceous chondrites. In principle, average chondrules, matrix and bulk chondrite must plot on a tie line (average chondrules and matrix are represented by large open circles). This is not always observed for a series of analytical reasons: we did not include metal and sulphide in bulk chondrule analyses, broad beam matrix analyses include metal and sulphide that are not fully accounted for, and bulk chondrite analyses usually contain minor elements such as S that are not included in chondrule and matrix analyses. These analytical differences would decrease the absolute concentrations of bulk chondrule and matrix analyses, while keeping the bulk chondrite analyses the same. A shift to lower Mg- and Si- concentrations of average bulk chondrules and matrix will position the bulk chondrite analyses more in between the two components, as should be expected. Error bars for chondrules are the error from the analysed 2D bulk chondrule relative to the true 3D chondrule (cf. section 2.5).

first scenario, chondrules and matrix form from the same parental reservoir. In the second scenario, chondrules and matrix form from separate, maybe even multiple parental reservoirs. Most of the so far suggested chondrule forming processes either require the formation of chondrules and matrix from the same or from separate parental reservoirs. The genetic relationship between chondrules and matrix in chondrites, hence, holds a clue to pivotal constraints for the chondrule forming process.

Chondrules and matrix have different average compositions for many elements,

but also isotopes. Here I will focus on the different elemental compositions. I will discuss element ratios rather than absolute concentrations, as element ratios are independent from absolute element concentrations. As a first example, Fig. 14 illustrates differences in the Mg/Si ratios between chondrules and matrix (Hezel & Palme, 2010). The slope of the dashed line represents the CI chondritic or solar Mg/Si ratio. Chondrules plot above this line and have higher than CI chondritic Mg/Si ratios. Matrix plots below this line and has lower than CI chondritic Mg/Si ratios. Magnesium and Si are nearly entirely contained in chondrules and matrix, as CAIs contain comparatively small amounts of Mg and Si and opaques contain basically none of these two elements. Further, CAIs and opaques are only minor components in chondrites. The bulk chondrite composition is then defined by the combination of chondrules and matrix, and, depending on modal abundances of the two components, must plot anywhere on the mixing line between chondrules and matrix, as illustrated in Fig. 15. Possible bulk compositions on the mixing line are indicated by question marks on the figure. However, the Mg and Si bulk composition of CC does not plot just somewhere on the mixing line, but in all cases almost exactly on the CI chondritic Mg/Si ratio (Fig. 14).

It is highly unlikely that chondrules and matrix from different parental reservoirs (→ 2-component model) are in all cases mixed in the exact right proportions, so the bulk chondrite is CI chondritic (Fig. 15). An exception would be, if chondrules and matrix had different parental reservoirs, which had the same elemental compositions. In this case, chondrules and matrix could have been mixed together and the complementary element ratio was established on the parent body by elemental exchange between chondrules and matrix. For Mg and Si this would most plausibly require the exchange of Mg and Fe between chondrules and matrix. Such an exchange would produce chondrule and matrix silicates of similar composition. It is not possible that such an exchange can produce forsteritic olivine in chondrules and fayalitic olivine in matrix. However, this is exactly what is observed in CC. An even more unlikely re-distribution would be the loss of Si from chon-

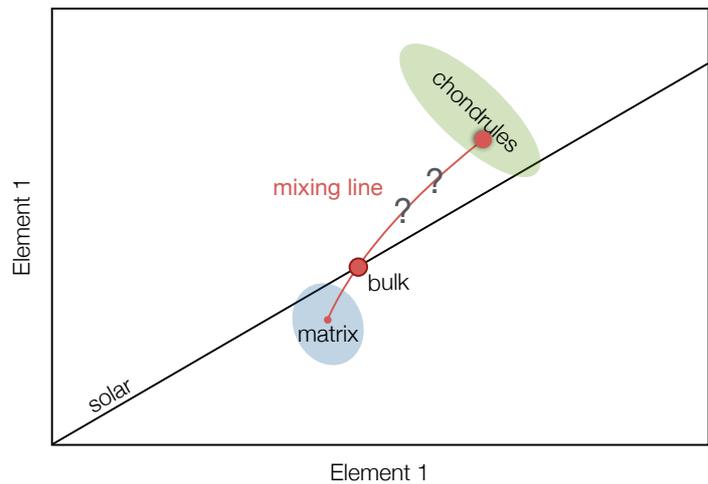


Figure 15: The sketch illustrates that a chondrite bulk composition should plot somewhere between the matrix and chondrule composition (indicated by question marks). Bulk chondrites, however, always plots very close or often directly on the CI chondrite (solar) composition.

drules to matrix. Even if this would have occurred, we calculated this re-distribution could not move sufficient amounts of Si from chondrules into the matrix to produce the observed Mg/Si complementarity between chondrules and matrix.

Complementary relationships are not only found for Mg and Si. A particular interesting case are the two refractory elements Ca and Al (Hezel & Palme, 2008). In the CV chondrite Allende, Ca/Al ratios are sub-chondritic in chondrules and super-chondritic in the matrix. The Y-86751 meteorite is also a CV chondrite of the Allende type, yet its Ca/Al ratios are super-chondritic in chondrules and sub-chondritic in the matrix – opposite to the Ca/Al complementary in Allende (Fig. 16). The Ca/Al bulk of both meteorites is CI chondritic.

It is not possible to explain this opposite complementarity by any volatility related process in the protoplanetary disk. On the parent body, Ca can be mobile, but it is unreasonable that Ca is re-distributed from chondrules to matrix in one meteorite and from matrix to chondrules in the other meteorite. Further, Ca is not primarily re-

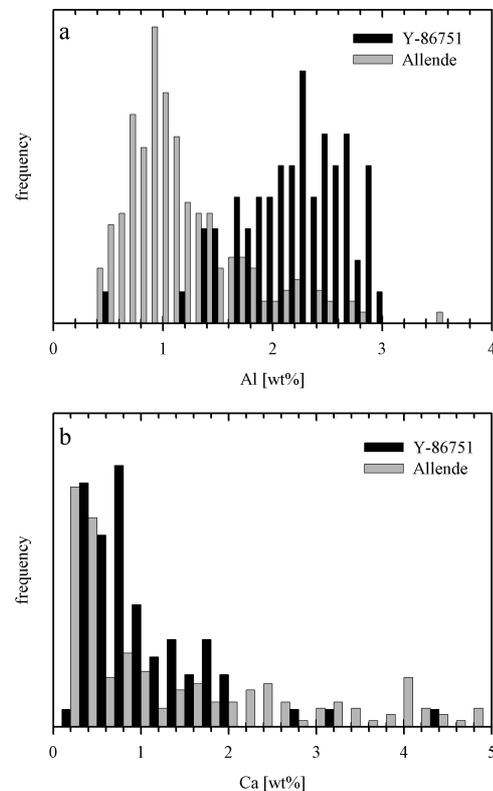


Figure 17: Histograms of (a) Al and (b) Ca in Allende and Y-86751 matrix.

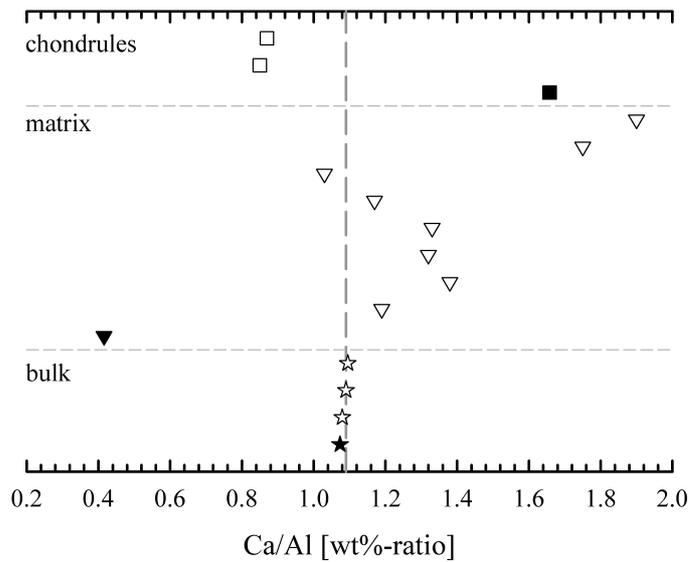


Figure 16: Compilation of Ca/Al-ratios. Empty symbols represent Allende and filled symbols Y-86751. Vertical long dashed line represents the CI chondritic ratio.

ponsible for the complementarity, but Al, as can be seen from Fig. 17. The Ca/Al sub-chondritic matrix of Y-86751 contains numerous Al-rich spinel grains (Kimura & Ikeda 1998). These are not seen in the Allende matrix. It appears likely that spinel grains in case of Y-86751 ended up in the matrix. In Allende, spinel grains ended up in chondrules and were either dissolved in the chondrule melt, or are hard to discover in the 2D section of the 3D chondrule (see below).

The Ca/Al complementarity in these two CV chondrites provide further evidence for a single parental reservoir for chondrules and matrix, and a further strong argument against any parent body element re-distribution hypotheses. The findings also hint at the process of complementarity, which is the selective incorporation of element carrier phases such as spinel (Al-carrier) in chondrules and matrix during chondrule formation.

We identified a number of other element complementarities (e.g, Becker et al., 2013; Table 1), including

in Rumurutiites, a different group than CC (Friend et al., 2014). Other researchers even start reporting complementarities in OC (Lobo et al., 2014). It appears, complementarity might be a typical characteristic across all chondrite groups.

Similar arguments can be made for complementary isotope compositions. In consequence, only chondrule forming processes in which chondrules and matrix share the same parental reservoir are possible. This result supports the shock wave model (e.g. Desch & Connolly, 2002; Desch et al., 2005) and excludes asteroid impact models (e.g. Asphaug et al., 2011; Sanders & Scott, 2012) and the X-wind model (Shu et al., 1996).

| | Mg/Si | Ca/Al | Al/Ti | Fe/Mg | Cr/Fe | Hf/W | ... |
|-----|-------|-------|-------|-------|-------|------|-----|
| CV | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ... |
| CR | ✓ | n.d. | ✓ | n.d. | n.d. | n.d. | ... |
| CO | ✓ | n.d. | n.d. | n.d. | n.d. | n.d. | ... |
| CM | ✓ | n.d. | n.d. | n.d. | n.d. | n.d. | ... |
| R | ✓ | ✓ | ✓ | ✓ | n.d. | n.d. | ... |
| ... | ... | ... | ... | ... | ... | ... | ... |

Table 1: Compilation of element pairs and chondrite classes, for which complementary element ratios between chondrules and matrix have been found. n.d.: not determined.

2.5 Technical Developments

Studying chondrule-matrix complementarities or bulk chondrule compositional variations as in section 2.2 depends critically on reliable bulk chondrule data. The number of such data is unfortunately limited, as mentioned earlier. Ideally, bulk chondrule data are obtained from entire chondrules as done by e.g. Jones & Schilk (2009). However, their INAA technique lacks the important major element Si. As an alternative, chondrule bulk compositions are often measured in meteorite sections (e.g. Jones 1990,1994,1996; Hezel et al., 2006; Hezel & Palme, 2008,2010; Ebel et al., 2009). It is then, however, unclear whether the obtained 2D bulk composition is representative of the full 3D chondrule. I developed a routine to quantify this problem and it is now possible to assign errors to 2D bulk chondrule data (Hezel, 2007; Hezel & Kießwetter, 2010). For example, the data presented in Fig. 14 have typical errors of about 1-2 wt.% in both, Si and Mg. The extent of the errors depend primarily on the type of chondrule (porphyritic, barred, etc.), element concentrations and carrier phases.

A number of important petrographic and petrologic characteristics have so far usually been studied from 2D sections, for example chondrule,

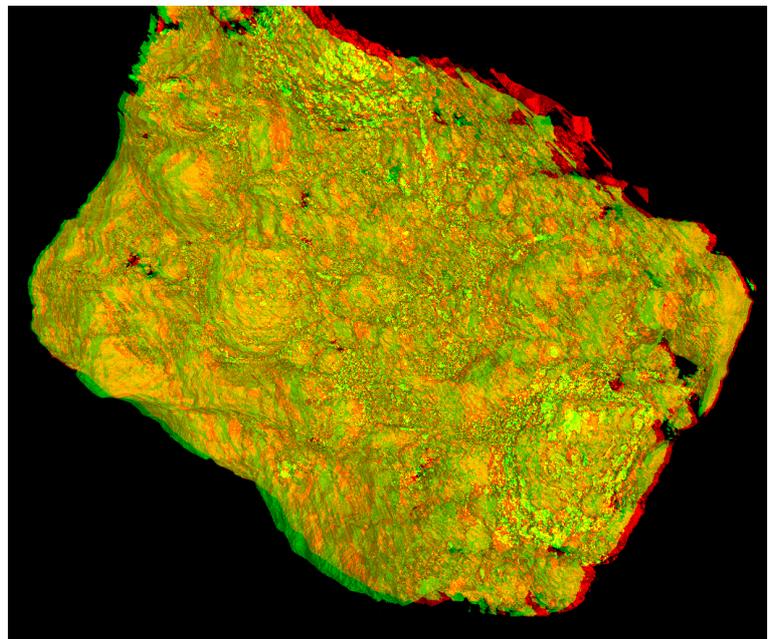


Figure 18: Stereographic image of Allende (red/green glasses required for 3D effect, supplied on the last page of the printed version; red over left eye). Shown are chondrules/CAs and opaques. Opaques are slightly more light yellow. The empty space is matrix. An opaque-layered chondrule can be seen in the central upper part.

matrix, CAI, etc. abundances and size distributions, occurrence of opaques in matrix and chondrules, etc. I recently started using X-ray micro-tomography to study and quantify these structural characteristics in detail (Hezel et al., 2013a,b; Griffin et al., 2012; Elangovan et al., 2012). Some of the results have been used to quantify opaque abundances in chondrules as described in section 2.2. One of the most intriguing results are two groups of so far unrecognised chondrules in Allende: one with only few opaques in them, and the other having abundant opaques that form multiple onion shell like layers (Fig. 18). This is an ongoing study and it is yet unclear how to best explain these two chondrule types. First results were published in Hezel et al. (2013b).

2.6 Ca,Al-rich Inclusions (CAIs)

Ca,Al-rich inclusions are the focus of many studies, mostly for two reasons: (i) these are the oldest objects in our Solar System, and (ii) a certain share of CAIs have irregular outlines with a zoned structure that is clear indication of a condensation origin (e.g. Davis & McKeegan, 2014). These CAIs serve as important witnesses of hot regions in the protoplanetary disk (>1800 K) that gradually cooled through a condensation sequence (e.g. Davis & Richter, 2014; Petaev et al., 1998).

Despite their importance for several problems in cosmochemistry such as age of the solar system, condensation processes or their influence on bulk chondrite compositions, no compilation of CAI modal abundances in chondrites existed until our report in Hezel et al. (2008). Several publications report CAI modal abundances, however, the values were inconclusive as they spread over a large range for individual chondrite groups (McSween 1977a, 1977b, 1979; Simon & Haggerty 1979; Kornacki & Wood 1984; Rubin et al. 1985; Kallemeyn et al. 1991; Noguchi 1993; Scott et al. 1996; Russell et al. 1998; Rubin 1998; May et al. 1999; Aléon et al. 2002; Krot et al. 2002; Norton & McSween, 2007). We demonstrate that this spread is the result of a Poisson distribution of the CAIs within their host chondrites. A Poisson distribution represents the spatial distribution of a small number of particles that is randomly mixed with a larger number of particles, as is the case for CAIs within a chondrite. A characteristic feature of Poisson distributions is that some areas of the chondrite contain only few and others many CAIs. This feature is more pronounced with smaller areas studied and vanishes with larger areas (Fig. 19). We provided a new set of CAI modal abundances that we obtained for all CC except for CH and CI chondrites, and further calculated recommended minimum sizes of areas that need to be studied to obtain CAI modal abundances with small errors (ideally >1000 mm², depending on CAI abundance). It is independent from this approach possible to calculate CAI abundances from either bulk chondrite element concentrations or element concentrations of individual chondrite components. I will review here only the first possibility.

CAIs are dominated by refractory elements, such as Ca and Al. We used only one element for the calculation, and arbitrarily choose Al. We assumed that all chondrites start with the same and CI chondritic bulk chondrite Al concentration. A higher than CI chondritic Al abundance in a chondrite is regarded as ‘excess Al’. The theoretical CAI abundance is calculated from this excess Al and a bulk CAI Al concentration taken from the literature (Simon & Grossman, 2004). In case the bulk

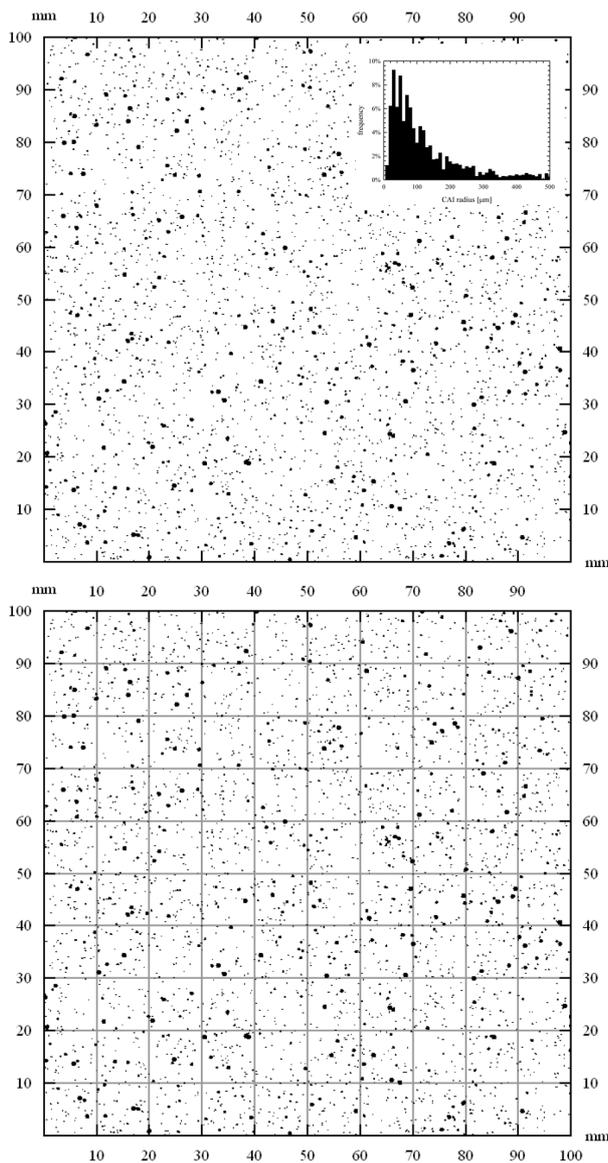


Figure 19: Screenshots of the computer model simulating the CAI distribution in a meteorite. The CAIs (black dots) have been randomly placed in this 100 × 100 mm sized square. CAI sizes follow a log-normal distribution with a maximum radius of 500 μm resulting in an average radius of 113 μm. The inset displays the CAI size distribution used for this figure. The modal abundance is 2.61 area%. The grid in (b) illustrates the non-homogeneous distribution of CAIs, which in fact follow a Poisson distribution and demonstrates why some thin sections are likely to have much more or much fewer CAIs than average.

elements are then due to different additions of CAIs, not because of possible differences in their element reservoirs. This is an important results, as it means, most probably the entire chondrite forming region was depleted in refractory elements. The studied CK chondrites show significant parent body metamorphism, and refractory elements from a potential CAI population are now probably present in e.g. feldspars. The measured CAI modal abundance of CK chondrites is therefore smaller than the calculated CAI modal abundance.

chondrite does not have excess Al, but rather ‘deficit Al’, i.e. the bulk chondrite Al concentration is lower than in CI chondrites, basically a negative CAI abundances is calculated. This probably means, a refractory component has been lost from the chondrite, whereas in case of excess Al, CAIs were added to the chondrite. The results from counting CAIs and the calculations are in very good agreement.

The first important result of this study revealed much smaller CAI modal abundances than previously thought (e.g. Sunshine et al., 2008; Hezel & Russell, 2008). Secondly, the measured CAI modal abundances are larger than the calculated CAI modal abundances for CV, CM and CO chondrites (Fig. 20).

CAIs are generally regarded to be xenolithic components in all chondrites (e.g. MacPherson et al., 2005; MacPherson, 2014 and references therein), i.e. they add to the refractory element inventory of their host chondrite. If chondrites started with a CI chondritic composition, all super-chondritic refractory element concentrations (e.g. Al) must have been delivered by CAIs. As CV, CM and CO chondrites have higher measured than calculated CAI modal abundances, the chondrite must have started with sub-chondritic refractory bulk element concentrations. If this is correct, the element reservoir from which carbonaceous chondrites formed had similar refractory element concentrations as the element reservoirs from which other chondrite groups, such as ordinary chondrites, formed. Differences in refractory elements

Two further important constraints are that CAIs added to carbonaceous chondrites deliver only a minor amount of the carbonaceous chondrite bulk Al contents (usually 10 rel.% and 25 rel.% in case of CVs) and cannot have been the major source of large amounts of ^{26}Al that substantially contributed to heat the chondrite parent body, even if they contained live ^{26}Al on accretion. This is even more true for ordinary, enstatite, R- and K-chondrites, which all have Al deficits. Secondly, the CAI size distributions of nearly all CCs contain at least two different populations, of which one is small consisting of large CAIs, probably indicating that CAIs in a single chondrite group had multiple sources.

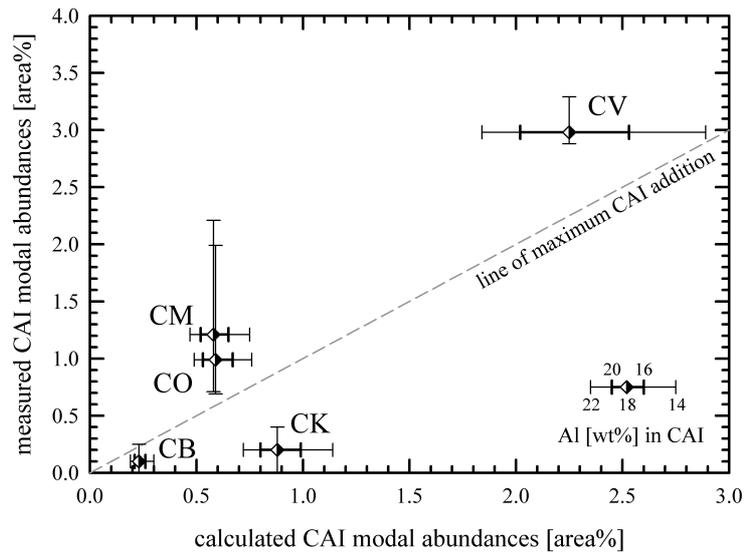


Figure 20: Calculated versus measured CAI modal abundances. Chondrites plot on the 'line of maximum CAI addition' if the Al excess in a chondrite equals the Al contributed by CAIs. If chondrites plot above the line, their initial bulk Al concentration must have been lower than the CI-chondritic value and vice versa. Two horizontal error bars represent calculated CAI modal abundances using 14 and 22 (thin bar) and 16 and 20 (bold bar) wt% Al in bulk CAIs. Vertical error bars are errors with respect to the studied section size.

3 Component Formation in the Early Solar System

In this chapter I propose a framework in which the processes in the early Solar System can be understood

Figure 21 is a graphical representation of the framework I propose to understand chondrite component formation in the early Solar System. I currently develop this yet unpublished hypothesis. The x-axis is a time line, running from 0 to about 5 Ma. Time 0 represents CAI condensation from a hot gas. CAIs are then stored separately for a few million years before being incorporated into their parent bodies together with other components. This prolonged storage is one of the problems in meteoritics, as disk dynamics should spiral CAIs into the young sun within a much shorter time span. Maybe the CAI population we find today is only a tiny fraction of survivors, maybe there is an unknown process that allows for this storage.

The chondrule-matrix complementarity (e.g. Mg/Si, Ca/Al; cf. section 2.4) requires the formation of these two components from the same parental reservoir. First, a chondrule precursor aggregate forms from μm -sized grains. This aggregate was comparatively rich in forsteritic olivine and refractory material, leaving an SiO(g) enriched reservoir during its formation. The temperature during chondrule precursor aggregate formation is unknown. The aggregate is flash-heated in the actual chondrule forming process to temperatures up to 2000 K. The molten chondrules were open

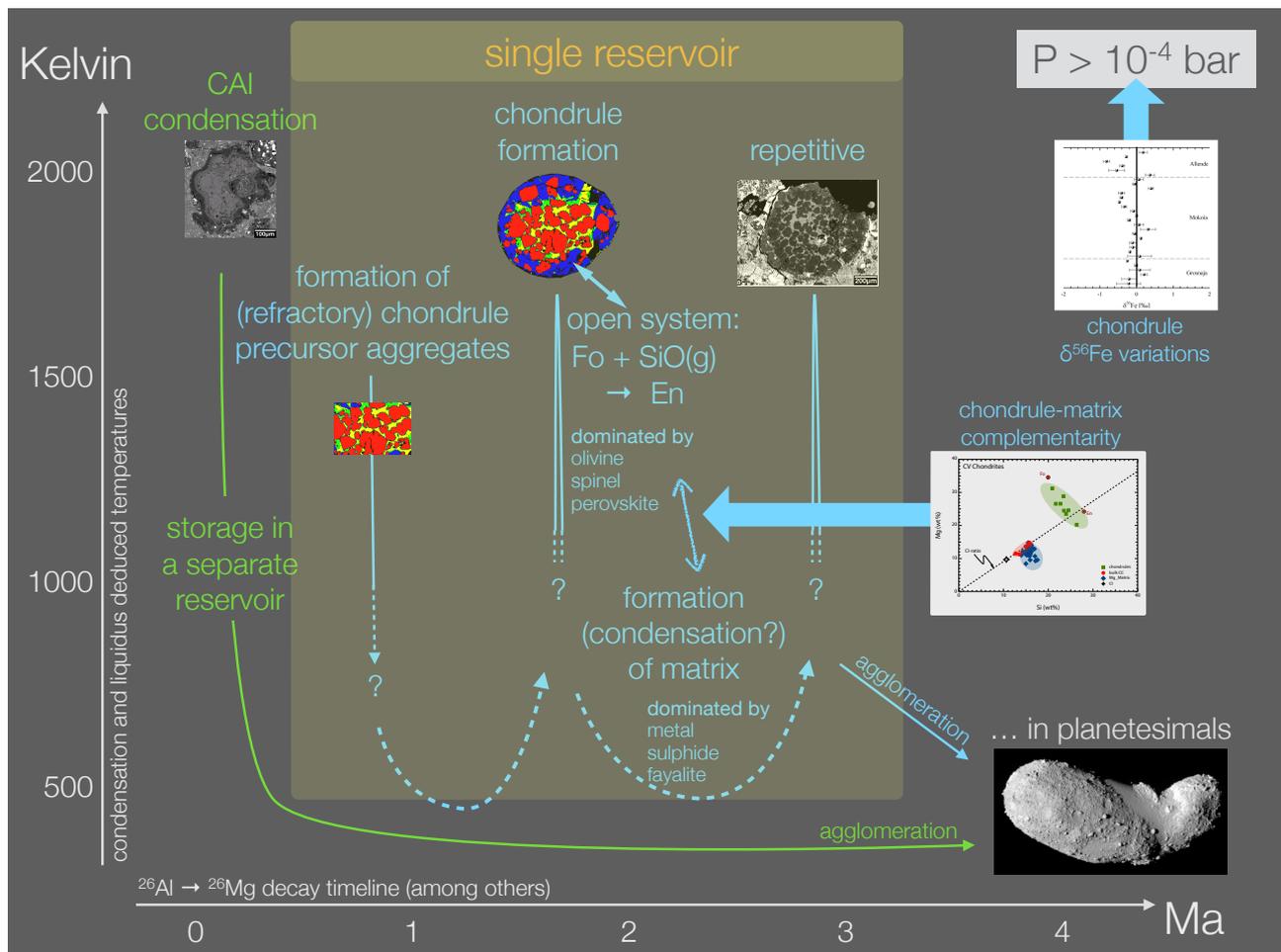


Figure 21: Proposed framework of chondrite component formation in the early Solar System.

systems during cooling and exchanged material with their surrounding, leading to elemental and isotopic variations among chondrules in a single chondrite. Further, the reaction of chondrule olivine with SiO(g) from the surrounding gas-phase produced low-Ca pyroxene rims. Alternatively, or in addition, condensed low-Ca pyroxene might have agglomerated directly onto chondrules. The addition of fine-grained material onto chondrules is well known from fine-grained rims around chondrules, as e.g. we studied in [Beitz et al. \(2013\)](#), and references therein). Selective incorporation of minerals such as spinel or perovskite in chondrules produced additional element complementarities between chondrules and matrix and at the same time attributed to bulk chondrule variations in individual chondrites.

In a recent study I model this pivotal phase in chondrite component formation. Although the model is highly simplified, it readily re-produces many of the observed characteristics. Figure 22

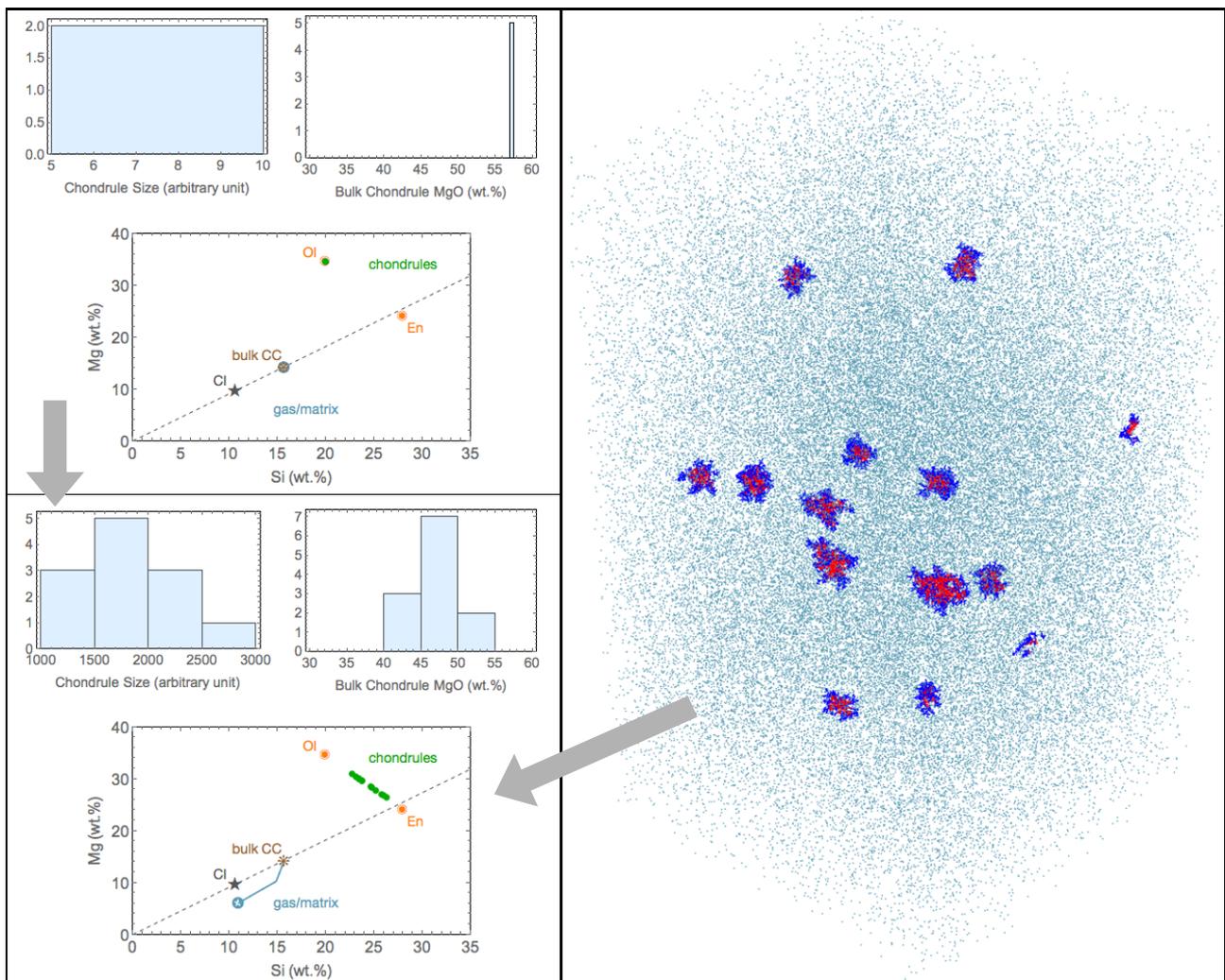


Figure 22: Screenshots of the model that re-produces chondrule size distribution, bulk chondrule compositional variation, chondrule-matrix complementarity, zoned chondrules and chondrule as well as matrix modal abundances in a chondrite from a single process. Small variations in model parameters may account for differences among chondrite classes. Upper left plate represents the start of the model, lower left plate the model after about 40% of the material was converted to chondrules (green in the Mg-Si plot). The path of the remaining gas is in turquoise in the Mg-Si plot and is interpreted as matrix that finally condenses from this gas. Right plate is the 3D model of turquoise particles and aggregates with olivine (red) in the core, surrounded by low-Ca pyroxene (blue).

displays screenshots of this model. The right plate displays the 3D box model with periodic boundary conditions and 100,000 particles following a random walk. First, a forsterite core forms when particles collide with nuclei that themselves form in short succession. At a set time, further aggregating particles have enstatite composition. The random walk and asynchronous as well as spatial random occurrence of nuclei produce object (hereafter: chondrule) size distributions similar to chondrites (Fig. 22, 'Chondrule Size' plots in left plates). The different surface to volume ratios of the differently sized chondrules produce variable forsterite to enstatite ratios, leading to (i) variations in the bulk compositions in the chondrule population (Fig., 22, 'Bulk Chondrule MgO' plots in left plates) and (ii) the chondrule matrix complementarity (Fig., 22, Mg-Si plots in left plates) – when the remaining particles are interpreted as the material from which matrix forms. Finally, the modal zonation of chondrules with olivine in the core and low-Ca pyroxene at the rim forms, as this is almost an intrinsic and the key parameter of the model. This model, although at an early stage of development and, hence, rather simple, requires only one single process to explain many characteristics that were previously explained by different processes. For example, (a) chondrule size distributions are often explained by chondrule size sorting in e.g. vortices (e.g. Cuzzi et al., 1996,2001); (b) the bulk chondrule elemental and isotopic variations by heterogeneous precursor grains (an explanation flawed in itself, e.g. Hezel & Palme, 2007); and (c) complementarity by the formation of chondrules and matrix in spatially separate elemental reservoirs (e.g. Zanda et al., 2006). The suggested model replaces all these different explanations by only one – while explaining even more of the observed characteristics. Opaques are not yet part of the model, but as for example CR chondrites contain chondrules that have metal with high Ni/Co in their center and metal with low Ni/Co at their rim, opaques might have formed and were incorporated at different temperatures in chondrules. Possibly, early formed opaques aggregated together with the initial forsterite-rich chondrule precursor aggregate, and later formed opaques were added to the rim together with enstatite. This is a rather general explanation and opaque formation would deserve a much more detailed discussion.

Continuing with the suggested model of Fig. 21, chondrule formation was repetitive, as is clear from relict chondrule grains in chondrules (e.g. Jones et al., 1996b; Jones, 2012). Variations in radiogenic ^{26}Mg in chondrules from single chondrites suggest chondrules formed over approximately 1-2 Ma; however there is still much dispute to whether these variations rather reflect ^{26}Al heterogeneities and, hence, provide only limited or even no age information (e.g. Tachibana et al., 2003; Mostefaoui et al., 2002; Thrane et al., 2006; Kurahashi et al., 2008; Villeneuve, 2009,2011; Larsen et al., 2011; Davis & McKeegan 2014). The ambient pressure was most likely elevated to prevent substantial isotope fractionation and retain volatile elements such as Na in chondrules (e.g. Alexander et al., 2008). Finally, all components agglomerated into the parent body. Variable degrees of fluid-assisted and/or thermal metamorphism overprinted the initial assemblage into the final rock we today study in the lab.

4 References

Excluding those being part of the habilitation and presented in chapter 5

- Abreu, N. A., and Brearley, A. J., 2010. Early solar system processes recorded in the matrices of two highly pristine CR3 carbonaceous chondrites, MET 00426 and QUE 99177. *Geochimica et Cosmochimica Acta* 74, 1146–1171.
- Aléon, J., Krot, A. N., and McKeegan, K. D., 2002. Calcium-aluminum-rich inclusions and amoeboid olivine aggregates from the CR carbonaceous chondrites. *Meteoritics & Planetary Science* 37, 1729–1755.
- Alexander, C. M. O'D., 1994. Trace element distributions within ordinary chondrite chondrules: implications for chondrule formation conditions and precursors. *Geochimica et Cosmochimica Acta* 58, 3451–3467.
- Alexander, C. M. O'D., 2004. Chemical equilibrium and kinetic constraints for chondrule and CAI formation conditions. *Geochimica et Cosmochimica Acta* 68, 3943–3969.
- Alexander, C. M. O'D., and Wang, J., 2001. Iron isotopes in chondrules: implications for the role of evaporation during chondrule formation. *Meteoritics & Planetary Science* 36, 419–428.
- Alexander, C. M. O'D., and Grossman, J.N., 2005. Alkali elemental and potassium isotopic compositions of Semarkona chondrules. *Meteoritics & Planetary Science* 40, 541–556.
- Alexander, C. M. O'D., Grossman, J. N., Wang, J., Zanda, B., Bourot-Denise, M., and Hewins, R. H., 2000. The lack of potassium-isotopic fractionation in Bishunpur chondrules. *Meteoritics & Planetary Science* 35, 859–868.
- Alexander, C. M. O'D., Taylor, S., Delaney, J. S., Ma, P., Herzog, G. F., 2002. Mass-dependent fractionation of Mg, Si, and Fe isotopes in five stony cosmic spherules. *Geochimica et Cosmochimica Acta* 66, 173–183.
- Alexander, C. M. O'D., Grossman, J. N., Ebel, D. S., and Ciesla, F. J., 2008. The formation conditions of chondrules and chondrites. *Science* 320, 1617–1619.
- Asphaug, E., Jutzi, M., and Movshovitz, M., 2011. Chondrule formation during planetesimal accretion. *Earth and Planetary Science Letters* 308, 369–379.
- Becker, M., Krahner, K., Hezel, D. C., Schulz, T., and Münker, C., 2013. Component specific Hf-W dating of the Allende and Vigarano chondrites (CV3) including chondrule and matrix separates. *Goldschmidt Conference*.
- Bischoff, A., Geiger, T., Palme, H., Spettel, B., Schultz, L., Scherer, P., Schlüter, J., and Lkham-suren, J., 1993. Mineralogy, chemistry, and noble gas contents of Adzhi-Bogdo—an LL3-6 chondritic breccia with L- chondritic and granitoidal clasts. *Meteoritics* 28, 570–578.
- Blander, M., 1983. Condensation of chondrules. In: *Chondrules and Their Origins* (ed. E. A. King). Lunar and Planetary Institute, Houston, pp. 1–9.

- Blander, M., Planner, H. N., Keil, K., Nelson, L. S., and Richardson N. L. 1976. The origin of chondrules—experimental investigation of metastable liquids in the system Mg₂SiO₄–SiO₂. *Geochimica et Cosmochimica Acta* 40, 889–896.
- Blander, M., Unger, L., Pelton, A., and Ericksson, G., 2001. Nucleation constraints lead to molten chondrule precursors in the early Solar System. *The Journal of Physical Chemistry B* 105, 11823–11827.
- Blander, M., Pelton, A. D., Jung, I.-H., and Weber, R., 2004. Non-equilibrium concepts lead to a unified explanation of the formation of chondrules and chondrites. *Meteoritics & Planetary Science* 39, 1897–1910.
- Bouvier, A., Wadhwa, M., Simon, S. B., and Grossman, L., 2009. Magnesium isotope compositions of chondrules from the Murchison and Murray carbonaceous chondrites. 40. *Lunar and Planetary Science Conference*. #2193 (abstract).
- Brearely, A. J., 2014. Nebular Versus Parent Body Processing. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 309-334.
- Brearely, A. J., and Jones, R. H., 1998. Chondritic meteorites. In: *Reviews in Mineralogy: Planetary Materials*, vol. 36 (ed. J. J. Papike). Mineralogical Society of America, Washington, DC, p. 398.
- Bridges, J. C., Franchi, I. A., Hutchinson, R., Morse, A. D., Long, J. V. P., and Pillinger, C.T., 1995. Cristobalite- and tridymite-bearing clasts in Parnallee (LL3) and Farmington (L5). *Meteoritics* 30, 715–727.
- Ciesla, F. J., 2005. Chondrule-forming processes – An overview. In: Krot AN, Scott ERD, and Reipurth B (eds.) *Chondrites and the Protoplanetary Disk*, Astronomical Society of the Pacific Conference Series, vol. 341, 811–820.
- Clayton, D. D., 1983. Chemical state of pre-solar matter. In: *Chondrules and Their Origins* (ed. E. A. King). Lunar and Planetary Institute, Houston, pp. 26–36.
- Clayton, R. N., 1993. Oxygen isotopes in meteorites. *Annual Review of Earth and Planetary Sciences* 21, 115–149.
- Clayton, R. N., Mayeda, T. K., Goswami, J. N., and Olsen, E. J., 1991. Oxygen isotope studies of ordinary chondrites. *Geochimica et Cosmochimica Acta* 55, 2317–2337.
- Connolly, H. C., Huss, G. R., and Wasserburg, G. J. 2001. On the formation of Fe–Ni metal in Renazzo-like carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 65, 4567–4588.
- Cuzzi, J. N., and Alexander, C. M. O'D. 2006. Chondrule formation in particle-rich nebular regions at least hundreds of kilometres across. *Nature* 441, 483–485.
- Cuzzi, J. N., Dobrovolskis, A. R., and Hogan, R. C., 1996. Turbulence, chondrules, and planetesimals. In: *Chondrules and the protoplanetary disk*, edited by Hewins R. H., Jones R. H., and Scott E. R. D. Cambridge: Cambridge University Press. pp. 35– 44.

- Cuzzi, J. N., Hogan, R. C., Paque, J. M., and Dobrovolskis, A. R., 2001. Size-selective concentration of chondrules and other small particles in protoplanetary nebula turbulence. *The Astrophysical Journal* 546, 496–508.
- Davis, A. M., and Richter, F. M., 2014. Condensation and evaporation of solar system materials. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 335–360.
- Davis, A. M., and McKeegan, K. D., 2014. Short-Lived Radionuclides and Early Solar System Chronology. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 361–395.
- Davis, A. M., Alexander, C. M. O'D., Nagahara, H., and Richter, F. M., 2005. Evaporation and condensation during CAI and chondrule formation. In: *Chondrites and the Protoplanetary Disk*, vol. 341 (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). Astronomical Society of the Pacific, pp. 432–455.
- Desch, S. J., and Connolly, H. C. Jr., 2002. A model of the thermal processing of particles in solar nebula shocks: Application to the cooling rates of chondrules. *Meteoritics and Planetary Science* 37, 183–207.
- Desch, S. J., Ciesla, F. J., Hood, L. L., and Nakamoto, T. 2005. Heating of chondritic materials in solar nebula shocks. In: Krot AN, Scott ERD, and Reipurth B (eds.) *Chondrites and the Protoplanetary Disk*, Astronomical Society of the Pacific Conference Series, vol. 341, 849–872.
- Dodd, R. T., 1978. The composition and origin of large microporphyritic chondrules in the Manyash /L-3/chondrite. *Earth and Planetary Science Letters* 39, 52–66.
- Ebel, D. S., Weisberg, M. K., Hertz, J., and Campbell, A. J., 2008. Shape, metal abundance, chemistry, and origin of chondrules in the Renazzo (CR) chondrite. *Meteoritics & Planetary Science* 43, 1725–1740.
- Ebel, D. S., Leftwich, K., Brunner, C. E., and Weisberg M. K. 2009. Abundance and size distribution of inclusions in CV3 chondrites by X-ray image analysis. *40th Lunar and Planetary Science Conference*. #2065 (abstr.).
- Engrand, C., McKeegan, K., Leshin, L., Herzog, G., Schnabel, C., Nyquist, L., and Brownlee, D., 2005. Isotopic compositions of oxygen, iron, chromium, and nickel in cosmic spherules: toward a better comprehension of atmospheric entry heating effects. *Geochimica et Cosmochimica Acta* 69, 5365–5385.
- Fitoussi, C., Bourdon, B., Kleine, T., Oberli, F., and Reynolds, B. C., 2009. Si isotope systematics of meteorites and terrestrial peridotites: implications for Mg/Si fractionation in the solar nebula and for Si in the Earth's core. *Earth and Planetary Science Letters* 287, 77–85.
- Friend, P., Hezel, D. C., Palme H., and Bischoff, A., 2014. Elemental Complementarities in Rumuruti Chondrite NWA 753. *Tagung der Deutschen Mineralogische Gesellschaft* (abstract).
- Galy, A., Young, E. D., Ash, R. D., and O'Nions, R. K., 2000. The formation of chondrules at high gas pressures in the solar nebula. *Science* 290, 1751–1753.

- Georg, R. B., Halliday, A. N., Schauble, E. A., and Reynolds, B. C., 2007. Silicon in the Earth's core. *Nature* 447, 1102–1106.
- Ghiorso, M. S., and Sack, R. O., 1995. Chemical mass transfer in magmatic processes. IV. a revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid–solid equilibria in magmatic systems at elevated temperatures and pressures. *Contributions to Mineralogy and Petrology* 119, 197–212.
- Grossman, J. N., and Wasson, J. T., 1983a. The compositions of chondrules in unequilibrated chondrites: an evaluation of models for the formation of chondrules and their precursor materials. In: King, E.A. (Ed.), *Chondrules and their Origins*. Lunar and Planetary Institute, Houston, pp. 88–121.
- Grossman, J. N., and Wasson, J. T., 1983b. Refractory precursor components of Semarkona chondrules and the fractionation of refractory elements among chondrites. *Geochimica et Cosmochimica Acta* 47, 759–771.
- Herzog, G. F., and Caffee, M. W., 2014. Cosmic-Ray Exposure Ages of Meteorites. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 419–453.
- Herzog, G. F., Alexander, C. M. O'D., Berger, E. L., Delaney, J. S., and Glass, B. P., 2008. Potassium isotope abundances in Australasian tektites and microtektites. *Meteoritics & Planetary Science* 43, 1641–1657.
- Hezel, D. C., and Russell, S. S. 2008. Comment on “Ancient Asteroids Enriched in Refractory Inclusions”. *Science* 322, 1050a.
- Hezel, D. C., Poole, G., Hoyes, J., Coles, B. J., Unsworth, C., Albrecht, N., Smith, C., Rehkämper, M., Pack, A., Genge, M., and Russell, S. S. 2014. Fe and O isotope composition of meteorite fusion crusts: possible natural analogues to chondrule formation? *Meteoritics & Planetary Science* (in revisions)
- Hezel, D. C., Palme, H., Brenker, F. E., and Nasdala, L. 2003. Evidence for fractional condensation and reprocessing at high temperatures in CH-chondrites. *Meteoritics & Planetary Science* 38, 1199-1216.
- Hezel, D. C., Mucerschi, D., Friend, P., and Palme, H., 2014a. Chondrule Zonation in Carbonaceous Chondrites. *Meteoritics & Planetary Science* (abstract).
- Hezel, D. C., Mucerschi, D., Friend, P., and Palme, H., 2014b Almost all chondrules in carbonaceous chondrites are zoned. *Tagung der Deutschen Mineralogische Gesellschaft* (abstract).
- Huang, S., Lu, J., Prinz, M., Weisberg, M. K., Benoit, P. H., and Sears, D. W. G. (1996) Chondrules: their diversity and the role of open-system processes during their formation. *Icarus* 122, 316–346.
- Hughes, C. J., 1982. Igneous petrology. Series *Developments in Petrology* 7, 551 p.

- Humayun, M., and Clayton, R. N., 1995. Potassium isotope cosmochemistry: genetic implications of volatile element depletion. *Geochimica et Cosmochimica Acta* 59, 2131–2148.
- Humayun, M., and Koeberl, C., 2004. Potassium isotopic composition of Australasian tektites. *Meteoritics & Planetary Science* 39, 1509–1516.
- Huss, G. R., Alexander, C. M. O'D., Palme, H., Bland, P. A., and Wasson J. T., 2005. Genetic relationships between chondrules, fine-grained rims, and interchondrule matrix. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 701–731.
- Hutchison, R., Bridges, J. C., and Gilmour, J. D., 2005. Chondrules: chemical, petrographic and chronologic clues to their origin by impact. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 933–950.
- Johansen, A., Oishi, J. S., Low, M-M. M., Klahr, H., Henning, T., and Youdin, A., 2007. Rapid planetesimal formation in turbulent circumstellar disks. *Nature* 448, 1022–1025.
- Jones, R. H., 1990 Petrology and mineralogy of Type II, FeO-rich chondrules in Semarkona (LL3.0) —origin by closed-system fractional crystallization, with evidence for supercooling. *Geochimica et Cosmochimica Acta* 54, 1785–1802.
- Jones, R. H., 1994. Petrology of FeO-poor, porphyritic pyroxene chondrules in the Semarkona chondrite. *Geochimica et Cosmochimica Acta* 58, 5325–5340.
- Jones, R. H., 1996a. FeO-rich, porphyritic pyroxene chondrules in unequilibrated ordinary chondrites. *Geochimica et Cosmochimica Acta* 60, 3115–3117.
- Jones, R. H., 1996b Relict grains in chondrules: evidence for chondrule recycling. In: *Chondrules and the Protoplanetary Disk* (eds. R. Hewins, R. Jones and E. Scott), pp. 163–172.
- Jones, R. H., and Schilk, A. J. 2009. Chemistry, petrology and bulk oxygen isotope compositions of chondrules from the Mokoia CV3 carbonaceous chondrite. *Geochimica et Cosmochimica Acta* 73, 5854–5883.
- Jones, R. H., Grossman, J. N., and Rubin, A. E., 2005. Chemical, mineralogical and isotopic properties of chondrules: clues to their origin. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 251–285.
- Jones, R. H., 2012. Petrographic constraints on the diversity of chondrule reservoirs in the protoplanetary disk. *Meteoritics & Planetary Science* 47:1176–1190.
- Kallemeyn, G. W., Rubin, A. E., and Wasson, J. T., 1991. The compositionally classification of chondrites: V. The Karoonda (CK) group of carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 55, 881–892.
- Kehm, K., Hauri, E. H., Alexander, C. M. O'D., and Carlson, R. W., 2003. High precision iron isotope measurements of meteoritic material by cold plasma ICP–MS. *Geochimica et Cosmochimica Acta* 67, 2879–2891.

- Kimura, M., and Yagi, K. 1980. Crystallization of chondrules in ordinary chondrites. *Geochimica et Cosmochimica Acta* 44, 589–595.
- Kimura, M., and Ikeda, Y., 1998. Hydrous and anhydrous alteration of chondrules in Kaba and Mokoia CV chondrites. *Meteoritics & Planetary Science* 33, 1139–1146.
- Knight, K. B., Kita, N. T., Davis, A. M., Richter, F. M., and Mendybaev, R. A., 2009. Mg and Si isotope fractionations within three type B Ca–Al-rich inclusions. 40. *Lunar and Planetary Science Conference*. #2360 (abstract).
- Kornacki, A. S., and Wood, J. A., 1984. Petrography and classification of Ca, Al-rich and olivine-rich inclusions in the Allende CV3 chondrite. *Journal of Geophysical Research* 89, B573–B587.
- Krot, A. N., Scott, E. R. D., and Zolensky, M. E., 1995. Mineralogical and chemical modification of components in CV3 chondrites: nebular or asteroidal processing? *Meteoritics* 30, 748–775.
- Krot, A. N., Petaev, M. I., Scott, E. R. D., Choi, B.-G., Zolensky, M. E., and Keil, K., 1998. Progressive alteration in CV3 chondrites: more evidence for asteroidal alteration. *Meteoritics & Planetary Science* 33, 1065–1085.
- Krot, A. N., Aléon J., and McKeegan K. D., 2002. Mineralogy, petrography and oxygen-isotopic compositions of Ca,Al-rich inclusions and moeboid olivine aggregates in the CR carbonaceous chondrites (abstract). 33rd *Lunar and Planetary Science Conference*. (abstract)
- Krot, A. N., Libourel, G., Goodrich, C., Petaev, M. I., 2004. Silica-igneous rims around magnesian chondrules in CR carbonaceous chondrites: evidence for fractional condensation during chondrule formation. *Meteoritics & Planetary Science* 39, 1931–1955.
- Krot, A. N., Keil, K., Scott, E. R. D., Goodrich, C. A., and Weisberg, M.K., 2014. Classification of Meteorites and Their Genetic Relationships. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 1–52.
- Kurahashi, E., Kita, N. T., Nagahara, H., and Morishita, Y. (2008). 26Al – 26Mg systematics of chondrules in a primitive CO chondrite. *Geochimica et Cosmochimica Acta*, 72, 3865–3882.
- Larsen, K. K., Trinquier, A., Paton, C., Schiller, M., Wielandt, D., Ivanova, M. A., Connelly J. N., Nordlund, A., Krot, A. N. and Bizzarro, M., 2011. Evidence for Magnesium Isotope Heterogeneity in the Solar Protoplanetary Disk. *The Astrophysical Journal Letters* 735, L37.
- Libourel, G., Krot, A. N., and Tissandier, L., 2006 Role of gas-melt interaction during chondrule formation. *Earth and Planetary Science Letters* 251, 232–240.
- Libourel, G., and Chaussidon, M., 2011. Oxygen isotopic constraints on the origin of Mg-rich olivines from chondritic meteorites. *Earth and Planetary Science Letters* 301, 9–21.
- Lobo, A., Wallace, S.W., Ebel, D. S., 2014. Modal abundances, chemistry, and sizes of clasts in the semarkona (LL3.0) chondrite by X-ray map analysis. 45. *Lunar and Planetary Science Conference*. #1423 (abstract).

- MacPherson, G. J., 2014. Calcium–Aluminum-Rich Inclusions in Chondritic Meteorites. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 139–179.
- MacPherson, G. J., Simon, S. B., Davis, A. M., Grossman, L., and Krot, A. N. 2005. Calcium-aluminum-rich inclusions: Major unanswered questions. In: *Chondrites and the protoplanetary disk*, edited by Krot A. N., Scott E. R. D., and Reipurth B. ASP Conference Series, vol. 341. San Francisco: Astronomical Society of the Pacific. 1029 p.
- Mason, B., 1965. The chemical composition of olivine-bronzite and olivine hypersthene chondrites. *American Museum Novitates No.*, 2223.
- Matsunami, S., Ninagawa, K., Nishimura, S., Kubono, N., Yamamoto, I., Kohata, M., Wada, T., Yamashita, Y., Lu, J., Sears, D. W. G., and Nishimura H., 1993. Thermoluminescence and compositional zoning in the mesostasis of a Semarkona group A1 chondrule and new insights into the chondrule-forming process. *Geochimica et Cosmochimica Acta* 57, 2101–2110.
- May, C., Russell, S. S., and Grady, M. M. 1999. Analysis of chondrule and CAI size and abundance in CO3 and CV3 chondrites: A preliminary study. *30th Lunar and Planetary Science Conference* (abstract).
- McCoy, T. J., Scott, E. R. D., Jones, R. H., Keil, K., and Taylor, G. J., 1991. Composition of chondrule silicates in LL3-5 chondrites and implications for their nebular history and parent body metamorphism. *Geochimica et Cosmochimica Acta* 55, 601–619.
- Mittlefehldt, D. W. 2014. Achondrites. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 235–266.
- Molini-Velsko, C., Mayeda, T. K., and Clayton, R. N., 1986. Isotopic composition of silicon in meteorites. *Geochimica et Cosmochimica Acta* 50, 2719–2726.
- Mostefaoui, S., Kita, N. T., Togashi, S., Tachibana, S., Nagahara, H., and Morishita, Y., 2002. The relative formation ages of ferromagnesian chondrules inferred from their initial aluminum-26/aluminum-27 ratios. *Meteoritics & Planetary Science* 37, 421–438.
- Moynier, F., Beck, P., Fred, J., Qing-Zhu, Y., Uwe, R., and Christian, K., 2009. Isotopic fractionation of zinc in tektites. *Earth and Planetary Science Letters* 277, 482–489.
- Moynier, F., Koeberl, C., Beck, P., Jourdan, F., and Telouk, P., 2010. Isotopic fractionation of Cu in tektites. *Geochimica et Cosmochimica Acta* 74, 799–807.
- McSween, H. Y. Jr., 1977a. Carbonaceous chondrites of the Ornans type: A metamorphic sequence. *Geochimica et Cosmochimica Acta* 41, 477–491.
- McSween, H. Y. Jr., 1977b. Petrographic variations among Modal abundances of CAIs carbonaceous chondrites of the Vigarano type. *Geochimica et Cosmochimica Acta* 41, 1777–1790.
- McSween, H. Y. Jr., 1979. Matrix variations in CM chondrites. *10th Lunar and Planetary Science Conference* (abstract) pp. 810–812.

- Mullane, E., Russell, S. S., Gounelle, M., 2005. Nebular and asteroidal modification of the iron isotope composition. *Earth and Planetary Science Letters* 239, 203–218.
- Nagahara, H., Ozawa, K., and Tomomura, S., 2005. Kinetic condensation of silicate melt and its role in the chemical diversity of chondrules. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 456–468.
- Needham, A. W., Porcelli, D., and Russell, S. S., 2009. An Fe isotope study of ordinary chondrites. *Geochimica et Cosmochimica Acta* 73, 7399–7413.
- Nguyen, L.-A., Alexander, C. M. O'D., and Carlson, R. W., 2001. Mg isotope variation in bulk meteorites and chondrules. *31. Lunar and Planetary Science Conference*. #1841 (abstract).
- Noguchi, T., 1993. Petrology and mineralogy of CK chondrites: Implications for the metamorphism of the CK chondrite parent body. *Proceedings of the NIPR Symposium on Antarctic Meteorites* 6, 204–233.
- Norton, M. B., and McSween, H. Y. Jr., 2007. Quantifying the volumetric abundances of the components of the Murray CM chondrite: A preliminary investigation. *38th Lunar and Planetary Science Conference* (abstract)
- Oberst, J., Heinlein, D., Köhler, U., and Spurny, P., 2004. The multiple meteorite fall of Neuschwanstein: Circumstances of the event and meteorite search campaigns. *Meteoritics & Planetary Science* 39, 1627–1641.
- Olsen, E. J., 1983. SiO₂-bearing chondrules in the Murchison (C2) meteorite. In: King, E.A. (Ed.), *Chondrules and their Origins*. Lunar and Planetary Institute, Houston, pp. 223–234.
- Palme, H., Hezel, D. C., and Ebel, D. S. 2014. Matrix Chondrule Relationship and the Origin of Chondrules. *Earth & Planetary Science Letters* (re-submitted).
- Petaev, M. I., and Wood, J. A., 1998. The condensation with partial isolation (CWPI) model of condensation in the solar nebula. *Meteoritics & Planetary Science* 33, 1123–1137.
- Richter, F. M., Janney, P. E., Mendybaev, R. A., Davis, A. M., and Wadhwa, M., 2007. Elemental and isotopic fractionation of Type B CAI-like liquids by evaporation. *Geochimica et Cosmochimica Acta* 71, 5544–5564.
- Poitrasson, F., Levasseur, S., and Teutsch, N., 2005. Significance of iron isotope mineral fractionation in pallasites and iron meteorites for the core–mantle differentiation of terrestrial planets. *Earth and Planetary Science Letters* 234, 151–164.
- Rubin, A. E., and Pernicka, E., 1989. Chondrules in the Sharps H3 chondrite—evidence for intergroup compositional differences among ordinary chondrite chondrules. *Geochimica et Cosmochimica Acta* 53, 187–195.
- Rubin, A. E., James J. A., Keck B. D., Weeks K. S., Sears D. W. G., and Jarosewich, E., 1985. The Colony meteorite and variations in CO3 chondrite properties. *Meteoritics* 20:175–196.

- Russell, S. S., Huss, G. R., Fahey, A. J., Greenwood, R. C., Hutchison, R., and Wasserburg, G., 1998. An isotopic and petrologic study of calcium-aluminium inclusion from CO3 meteorites. *Geochimica et Cosmochimica Acta* 62, 689–714.
- Russell, S. S., Krot, A. N., Huss, G. R., Keil, K., Itoh, S., Yurimoto, H., and MacPherson, G. J., 2005. The genetic relationship between refractory inclusions and chondrules. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 317–350.
- Ruzicka, A., Kring, D. A., Hill, D. H., Boynton, W. V., Clayton, R. N., and Mayeda, T. K., 1995. Silica-rich orthopyroxenite in the Bovedy chondrite. *Meteoritics* 30, 57–70.
- Sanders, I. S., and Taylor, G. J., 2005. Implications of ²⁶Al in nebular dust: formation of chondrules by disruption of molten planetesimals. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 915–932.
- Sanders, I. S., Scott, E. R. D., 2012. The origin of chondrules and chondrites: debris from low-velocity impacts between molten planetesimals? *Meteoritics & Planetary Science* 47, 2170-2192.
- Scott, E. R. D., and Krot, A. N., 2005. Chondritic meteorites and the high-temperature nebular origins of their components. In: *Chondrites and the Protoplanetary Disk* (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). ASP Conference Series, vol. 341, pp. 15–53.
- Scott, E. R. D., and Krot, A. N., 2014. Chondrites and Their Components. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 65–137.
- Scott, E. R. D., Love, S. G., and Krot, A. N., 1996. Formation of chondrules and chondrites in the protoplanetary nebula. In: *Chondrules and the Protoplanetary disk*, edited by Hewins R. H., Jones R. H., and Scott E. R. D. Cambridge: Cambridge University Press. pp. 87–96.
- Sears, D. W. G., Sparks, M. H., Rubin, A. E., 1984. Chemical and physical studies of type 3 chondrites. III chondrules from the Dhajala H3.8 chondrite. *Geochimica et Cosmochimica Acta* 48, 1189–1200.
- Sears, D. W. G., and Dodd, R. T. 1988. Overview and classification of meteorites. In: Kerridge JF and Matthews MS (eds.) *Meteorites and the Early Solar System*, pp. 3–31. Tucson, AZ: University of Arizona Press.
- Sears, D. W. G., Huang, S., and Benoit, P. H., 1996. Open-system behavior during chondrule formation. In: *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones and E. R. D. Scott). Cambridge University Press, pp. 221–232.
- Shu, F. H., Shang, H., and Lee, T., 1996. Toward an astrophysical theory of chondrites. *Science* 271, 1545–1552.
- Simon, S. B., and Haggerty, S., 1979. Petrography and olivine mineral chemistry of chondrules and inclusions in the Allende meteorite. *10th Lunar and Planetary Science Conference*. pp. 1119–1121. (abstract)

- Simon, S. B., and Grossman, L., 2004. A preferred method for the determination of bulk compositions of coarse-grained refractory inclusions and some implications of the results. *Geochimica et Cosmochimica Acta* 68, 4237–4248.
- Sunshine, J. M., Connolly, Jr. H. C., McCoy, T. J., Bus, S. J., La Croix, L. M., 2008. Ancient Asteroids Enriched in Refractory Inclusions. *Science* 320, 514-517.
- Tachibana, S., Nagahara, H., Mostefaoui, S., and Kita, N. T., 2003. Correlation between relative ages inferred from ²⁶Al and bulk compositions of ferromagnesian chondrules in least equilibrated ordinary chondrites. *Meteoritics & Planetary Science* 38, 939–962.
- Taylor, S., Alexander, C. M. O'D., Delaney, J., Ma, P., Herzog, G. F., Engrand, C., 2005. Isotopic fractionation of iron, potassium, and oxygen in stony cosmic spherules: implications for heating histories and sources. *Geochimica et Cosmochimica Acta* 69, 2647–2662.
- Thrane, K., Bizzarro, M., and Baker, J. A. 2006.. Extremely Brief Formation Interval for Refractory Inclusions and Uniform Distribution of ²⁶Al in the Early Solar System. *The Astrophysical Journal* 646, L159–L162.
- Tissandier, L., Libourel, G., and Robert, F., 2002. Gas-melt interactions and their bearing on chondrule formation. *Meteoritics & Planetary Science* 37, 1377– 1389.
- Uesugi, M., Sekiya, M., and Nakamoto, T., 2003. Deformation and internal flow of a chondrule-precursor molten sphere in a shocked nebular gas. *Earth, Planets and Space* 55, 493–507.
- Uesugi, M., Sekiya, M., and Nakamura, T., 2008. Kinetic stability of a melted iron globule during chondrule formation: I. Non- rotating model. *Meteoritics & Planetary Science* 43, 717–730.
- Van Schmus, W. R., and Wood, J. A., 1967. A chemical-petrologic classification for the chondritic meteorites. *Geochimica et Cosmochimica* 31, 747–754.
- Villeneuve, J., Chaussidon, M., and Libourel, G., 2009. Homogeneous distribution of ²⁶Al in the solar system from the Mg isotopic composition of chondrules. *Science* 325, 985–988.
- Villeneuve, J., Chaussidon, M., and Libourel, G., 2011. Magnesium isotopes constraints on the origin of Mg-rich olivines from the Allende chondrite: Nebular versus planetary? *Earth and Planetary Science Letters* 301, 107–116.
- Wegener, A., 1917 Das detonierende Meteor vom 3. April 1916, 3 1/2 Uhr nachmittags in Kurhessen. *Nachdruck*: Elwert, Marburg 2001.
- Wombacher, F., Rehkämper, M., Mezger, K., and Münker, C., 2003. Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. *Geochimica et Cosmochimica Acta* 67, 4639–4664.
- Young, E. D., Ash, R. D., Galy, A., and Belshaw, N. S., 2002. Mg isotope heterogeneity in the Allende meteorite measured by UV laser ablation–MC–ICP–MS and comparisons with O isotopes. *Geochimica et Cosmochimica Acta* 66, 683–698.

- Zanda, B., Hewins, R. H., Bourot-Denise, M., Bland, P. A., and Albarède, F., 2006. Formation of solar nebula reservoirs by mixing chondritic components. *Earth and Planetary Science Letters* 248, 650–660.
- Zhu, X. K., Guo, Y., O'Nions, R. K., Young, E. D., and Ash, R. D., 2001. Isotopic homogeneity of iron in the early solar nebula. *Nature* 412, 311–313.
- Zinner E 2014. Presolar Grains. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, vol. 1, second ed. Elsevier, Oxford, pp. 181–213.

5 Publications

The publications are only given here together with their doi numbers as the copyrights belong to the journals.

- Palme H, Spettel B and Hezel DC (2014) Siderophile Elements in Chondrules of CV-Chondrites. *Chemie der Erde – Geochemistry* 74:507–516.
[doi: 10.1016/j.chemer.2014.06.003]
- Hezel DC, Friedrich J and Uesugi M (2013) Looking Inside: 3D Structures of Meteorites. *Geochimica et Cosmochimica Acta* 116:1-4.
[doi: 10.1016/j.gca.2013.01.012]
- Beitz E, Blum J, Mathieu R, Pack A, Hezel DC (2013) Experimental investigation of the nebular formation of chondrule rims and the formation of chondrite parent bodies. *Geochimica et Cosmochimica Acta* 116:41-51.
[doi: 10.1016/j.gca.2012.04.059]
- Hezel DC, Elangovan P, Viehmann S, Howard L, Abel RL and Armstrong R (2013) Visualisation and quantification of CV chondrite petrography using micro-tomography. *Geochimica et Cosmochimica Acta* 116:33-40.
[doi: 10.1016/j.gca.2012.03.015]
- Elangovan P, Hezel DC, Howard L, Armstrong R and Abel RL (2012) PhaseQuant: A Tool for Quantifying Tomographic Data Sets of Rock Specimens. *Computers & Geosciences* 48:323-329.
[doi: 10.1016/j.cageo.2012.01.014]
- Griffin L, Elangovan P, Mundell A and Hezel DC (2012) Improved segmentation of chondrules from micro-CT images of meteorites using local histograms. *Computers & Geosciences* 39:129-134.
[doi: 10.1016/j.cageo.2011.07.002]
- Hezel DC, Schlüter J., Kallweit H., Jull AJT, Al Fakeer OY, Al Shamsi M and Strekopytov S (2011) Meteorites from the United Arab Emirates: description, weathering and terrestrial ages. *Meteoritics & Planetary Sciences* 46:327–336.
[doi: 10.1111/j.1945-5100.2010.01165.x]
- Emmerton S, Muxworthy AR, Hezel DC and Bland PA (2011) Magnetic characteristics of CV chondrules with paleointensity implications. *Journal of Geophysical Research - Planets* 116:E12007.
[doi: 10.1029/2011JE003856]
- Moynier F, Agranier A, Hezel DC, Bouvier A (2010) Sr stable isotope composition of Earth, the Moon, Mars, Vesta and meteorites. *Earth & Planetary Science Letters* 300:359–366.
[doi: 10.1016/j.epsl.2010.10.017]

- Hezel DC and Kießwetter R (2010) Quantifying the error of 2D bulk chondrule analyses using a computer model to simulate chondrules (SIMCHON). *Meteoritics & Planetary Sciences* 45:555-571.
[doi: 10.1111/j.1945-5100.2010.01040.x]
- Hezel DC, Needham AW, Armytage R, Georg B, Abel R, Kurahashi E, Coles BJ, Rehkämper M and Russell SS (2010) A nebula setting as the origin for bulk chondrule Fe isotope variations in CV chondrites. *Earth & Planetary Science Letters* 296:423-433.
[doi: 10.1016/j.epsl.2010.05.029]
- Hezel DC & Palme H (2010) The chemical relationship between chondrules and matrix and the chondrule-matrix complementarity. *Earth & Planetary Science Letters* 294:85-93.
[doi: 10.1016/j.epsl.2010.03.008]
- Hezel DC, Russell SS, Ross AJ and Kearsley AT (2008) Modal abundances of CAIs: Implications for bulk chondrite element abundances and fractionations. *Meteoritics & Planetary Sciences* 43:1879-1894.
[doi: 10.1111/j.1945-5100.2008.tb00649.x]
- Hezel DC & Palme H (2008) Constraints for chondrule formation from Ca-Al distribution in carbonaceous chondrites. *Earth & Planetary Science Letters* 265:716-725.
[doi: 10.1016/j.epsl.2007.11.003]
- Hezel DC, Dubrovinsky L, Nasdala L, Cauzid J, Simionovici A, Gellissen M and Schönbeck T (2008) In situ micro-Raman and X-ray diffraction study of diamonds and petrology of the new ureilite UAE 001 from the United Arab Emirates. *Meteoritics & Planetary Sciences* 43:1127-1136.
[doi: 10.1111/j.1945-5100.2008.tb01117.x]
- Hezel DC & Palme H (2007) The conditions of chondrule formation, Part I: Closed system. *Geochimica et Cosmochimica Acta* 71:4092-4107.
[doi: 10.1016/j.gca.2007.06.035]
- Hezel DC (2007) A model for calculating the errors of 2D bulk analysis relative to the true 3D bulk composition of an object, with application to chondrules. *Computers & Geosciences* 33:1162-1175.
[doi: 10.1016/j.cageo.2007.01.003]
- Hezel DC, Palme H, Nasdala L and Brenker FE (2006) Origin of SiO₂-rich components in ordinary chondrites. *Geochimica et Cosmochimica Acta* 70:1548-1564.
[doi: 10.1016/j.gca.2005.11.026]

6 Curriculum Vitae

An up to date version of my curriculum vitae can be found on the website of my current institution.