Chondrule formation and accretion processes in the early solar nebula
Clues from noble gases in different constituents of unequilibrated chondrites

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Publication Date:
2003

Permanent Link:
https://doi.org/10.3929/ethz-a-004552563

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Chondrule formation and accretion processes in the early solar nebula – Clues from noble gases in different constituents of unequilibrated chondrites

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH
for the degree of
DOCTOR OF NATURAL SCIENCES

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Zürich 2003
# Content

Abstract ........................................................................................................................................... 11

Kurzfassung ........................................................................................................................................ 13

Chapter 1: Introduction ..................................................................................................................... 15
  1.1 Formation of the solar system ................................................................................................. 16
  1.2 Classification of chondrites ................................................................................................. 20
  1.3 Constituents of chondrites .................................................................................................... 21
    1.3.1 Chondrules .................................................................................................................. 22
    1.3.2 Metal-sulphide-rich rims and droplets ......................................................................... 24
    1.3.3 Calcium-aluminium-rich inclusions (CAIs) ................................................................. 25
    1.3.4 Matrix .......................................................................................................................... 27
  1.4 Noble gases in primitive meteorites ..................................................................................... 29
    1.4.1 In situ produced noble gas components ...................................................................... 30
    1.4.2 Trapped noble gas components ................................................................................. 32
  1.5 Objectives of this study ........................................................................................................ 36

Chapter 2: Samples and experimental procedures ..................................................................... 39
  2.1 Selection of suitable meteorites .......................................................................................... 40
    2.1.1 Allende (CV3\textsubscript{ex}) ....................................................................................... 41
    2.1.2 Leoville (CV3\textsubscript{red}) ....................................................................................... 42
    2.1.3 Renazzo (CR2) .......................................................................................................... 43
    2.1.4 Semarkona (LL3.0) .................................................................................................... 44
    2.1.5 Bishunpur (LL3.1) ..................................................................................................... 45
    2.1.6 Krymka (LL3.1) ........................................................................................................ 46
  2.2 Sample preparation ................................................................................................................ 47
  2.3 Noble gas extraction ............................................................................................................. 48
    2.3.1 The infrared-laser noble gas extraction line ................................................................. 48
    2.3.2 Sample gas extraction ............................................................................................... 50
    2.3.3 Cleaning of the gas and separation of the He/Ne- from the Ar-fraction ...................... 52
  2.4 Noble gas measurements and data reduction ..................................................................... 52
2.4.1 Mass spectrometry ................................................................. 52
2.4.2 Interferences ................................................................. 52
2.4.3 Blanks ............................................................................. 53
2.4.4 Calibrations and determination of noble gas concentrations and isotopic ratios .................................................................................. 57
2.4.5 Uncertainties ........................................................................ 59

Chapter 3: Tests of the IR-laser and the extraction line ......................... 61
3.1 First test on Allende ............................................................ 62
  3.1.1 Results and implications .................................................. 62
3.2 Reduction of the IR-laser focus width ...................................... 64
  3.2.1 Adjustment of the optical and IR-laser focal planes ............. 64
  3.2.2 Operating the laser in the single-mode? ...................... 65
3.3 Fractionation of noble gases during in situ sample gas extraction .......................................................... 66
  3.3.1 Tests on Admire olivines .................................................. 66
  3.3.2 Tests on Allende fine-grained material ......................... 69
3.4 Reduction of active gases ..................................................... 71
  3.4.1 Reduction of CO₂ and H₂O in the mass spectrometer .... 74
3.5 Summary and conclusion ...................................................... 75

Chapter 4: Microdistribution of primordial Ne and Ar in fine-grained Rims,
Matrices, and Dark Inclusions of unequilibrated Chondrites –Clues on Nebular Processes ................................................................. 79
4.1 Abstract ............................................................................... 80
4.2 Introduction ......................................................................... 81
4.3 Samples and Experimental Procedure .................................. 83
  4.3.1 Samples ......................................................................... 83
  4.3.2 Gas extraction and measurements ................................ 86
  4.3.3 Blanks and corrections for cosmogenic noble gases ....... 87
  4.3.4 Calibrations .................................................................... 88
  4.3.5 Uncertainties ................................................................... 88
4.4 Results ................................................................................. 89
  4.4.1 Isotopic ratios .............................................................. 89
Abstract
The microdistribution of primordial noble gases in unequilibrated chondrites provides information about accretion and alteration processes including melting in the early solar nebula. Therefore, He, Ne, and Ar were analysed in small samples of different constituents of the unequilibrated carbonaceous and ordinary chondrites Allende, Leoville, Renazzo, Semarkona, Bishunpur, and Krymka. The separated constituents were chondrules and associated metal-sulphide-rich phases, calcium-aluminium-rich inclusions, fine-grained rims around chondrules, dark inclusions, and structureless matrix.
In Leoville, Semarkona, Bishunpur and Krymka slight changes of the noble gas compositions from rims to matrix were observed, which reflect changes in the dust reservoirs from which the rims and subsequently the matrix accreted to the respective parent bodies. The changing noble gas composition of the dust is attributed to nebular mixing of dust reservoirs with different noble gas inventories. The dark inclusions have noble gas compositions mostly different from their respective fine-grained host material. Whereas Allende dark inclusions seem to have experienced different degrees of alteration compared to the host material, the noble gas compositions of Leoville and Krymka dark inclusions do not show any association to their respective host material. This indicates that the clasts were formed in different dust reservoirs and were later accreted to the Leoville and Krymka parent bodies, respectively. The Krymka dark inclusion contains unusually high primordial noble gas concentrations, suggesting – in agreement with literature - a very primitive nature of this object.
The chondrules of the studied meteorites mostly contain low but measurable concentrations of primordial Ar, and in some cases also primordial Ne. The primordial $^{36}\text{Ar}/^{20}\text{Ne}$ ratios are unusually low (HL-like) compared to the surrounding fine-grained materials indicating a preferential depletion of Ar carried by phase Q. Compatibly, some of the metal-sulphide-rich phases surrounding the chondrules of ordinary chondrites have higher primordial $^{36}\text{Ar}/^{20}\text{Ne}$ ratios than the respective fine-grained materials. This points to a siderophile behaviour of phase Q during the separation of the metal- from the silicate-melt, when the chondrules formed from a precursor material with ambient trapped noble gases. The results suggest local chondrule formation in a dust-rich environment and fast accretion to the respective parent bodies.
No primordial noble gases could be detected in Allende fluffy and compact CAIs. Their Ne and Ar signatures can be fully explained by cosmogenically pro-
duced noble gases. The main target materials for the Ne production were Na and Al; the cosmogenic Ar was mainly produced from Ca and Cl. The differences in the $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of fluffy and compact CAIs are attributed to different Ca and Cl concentrations in both CAI groups. The lack of primordial noble gases in CAIs is in agreement with their higher formation temperatures compared to those of chondrules.
KURZFASSUNG


Die meisten der untersuchten Chondren aus allen oben aufgeführten Meteoriten enthalten zwar kleine, aber durchaus messbare Mengen an primordialem Ar, und teilweise auch an primordialem Ne. Verglichen mit dem umgebenden feinkörnigen Material sind die primordiaalen Elementverhältnisse ³⁶Ar/²⁰Ne in diesen Fällen ungewöhnlich niedrig („HL-artig"), was auf eine bevorzugte Verarmung des primordiaalen Ar hindeutet, dessen Trägerphase die „Phase Q" ist. Hingegen enthalten einige der Metall-Sulfid-reichen Phasen, die manche Chondren in gewöhnlichen Chondriten ummanteln, höhere ³⁶Ar/²⁰Ne Verhältnisse als das je-

CHAPTER 1

INTRODUCTION
This thesis deals with noble gases in different constituents of unequilibrated chondrites, which represent the most pristine material available from the time of the formation of the solar system. The noble gases stored in these meteorites can give information about the conditions and processes ruling in the solar nebula, when the first micron sized particles started to accrete to larger objects. These are the primary building blocks of all bodies in the solar system, including the meteorites of this study. In the first part of this chapter an overview is given about the current knowledge of the formation of the solar system from a presolar molecular cloud. Following is a description of chondrites and the noble gas components relevant for the study.

1.1 Formation of the solar system

The proto-sun was born ~4.6 billion years ago, when a dense part of a giant molecular cloud (Fig. 1.1) became unstable and contracted under the influence of its own gravity. The rotation of the system forced infalling matter to concentrate in a flattening disk of gas and dust rotating around the central object, the proto-star (Fig. 1.1). From this nebular matter the planetary objects of the solar system formed by a hierarchical process, including sticking and coagulation of micron sized particles, and later collisions and gravitational attraction, which finally led to a runaway growth of few proto-planets. The masses of the inner planets were too low to hold nebular gas. In contrast, the outer planets Jupiter and Saturn obviously had achieved enough mass within a few Ma to accrete substantial amounts of nebular gas (Beckwith et al., 2000) before the solar nebula had dissipated (see below). However, also a much faster formation of Jupiter by gravitational instability in the early solar nebula instead of growth from a solid core is discussed. Based on gravitational instability, computer modelling suggests a possible accretion time as short as ~1000 years for Jupiter (Mayer et al., 2002). In both cases, the accretion of Jupiter was much faster than that of the inner planets, which was probably completed 30 to 100 Ma after the start of the solar system. Planetary accretion was probably only a minor mechanism to clear the solar nebula (Hollenbach et al., 2000). It is, e.g., proposed that the inner disk (<10 AU; see Fig. caption of Fig. 1.1) was mainly cleared by mass flow onto the central star, whereas in the outer regions (>10 AU) the matter was largely dispersed by photo-evaporation. Thereby the ultraviolet radiation from the central star or an external star heated and evaporated the outer disk matter. The authors point out that strong stellar winds (Fig. 1.1), which are commonly believed to have transported most of the solar nebula matter to the interstellar space, actually had a minor influence on disk dispersal. It probably took between 1 and 10 Ma until the dust
disk around the proto-sun was dispersed. This sets important time constraints on the formation of the planetesimals, which are the building blocks of the planets in the inner solar system: Their formation must have been largely finished before the solar nebula was dispersed (within \(~10\) Ma).

The “true birth” of the solar system, i.e., the start of the contraction of the proto-sun cannot currently be dated directly. However, the oldest available solar system materials, refractory inclusions in primitive meteorites (CAIs, see section 1.3.3) have ages of up to \(~4.57\) Ga (Allègre et al., 1995). Since their Ca-Al-rich chemistry resembles very much the first condensing material from a cooling nebula with solar composition, the contraction of the proto-sun cannot have started much earlier. This is further supported by the presence of decay products of short-lived nuclides in CAIs (MacPherson et al., 1995). A part of these was probably synthesized in one or more neighbouring stars in their final stages, just before the separation of the solar nebula (see section 1.3.3 for an alternative explanation). Further evidence for a fast evolution of the early solar system is provided by the ages of undifferentiated and differentiated meteorites, which were formed only \(~10\) and \(~20\) Ma, respectively, after the condensation of CAIs (e.g., Tilton, 1988).
The sun, which represents basically unfractionated solar nebula matter, consequently best represents the original chemical composition of the solar nebula. However, besides measurements of the solar wind, which in turn represents roughly the solar composition, no samples of the sun are available. The planetesimals of the inner solar system with diameters of roughly >500 km are differentiated into metallic cores and silicate-rich mantles. This was probably caused by heating due to the decay of relatively short-lived radionuclides and by gravitational energy released during accretion. Also the inner solar system planets are differentiated possibly due to the decay of long-lived nuclides and also gravitational energy. However, also their precursor planetesimals might have already been differentiated. This is supported by Hf-W studies, which revealed that core formation on the asteroid Vesta took place within the first 5-15 Ma (Lee and Halliday, 1997) or even faster, within the first 5 Ma (Kleine et al., 2002) of the solar system history.

Information about the original chemical composition of the solar nebula is very difficult to obtain from these differentiated objects. However, smaller bodies with diameters less than ~500 km did not experience these large-scale differenti-
tiation processes and parts of them even escaped severe thermal and/or aqueous alteration until today. A source for such "small" objects is the asteroid belt at ~2-3 AU between Mars and Jupiter. Gravitational disturbances of the nearby giant planet Jupiter probably inhibited the accretion of a larger planetary body from the planetesimals in this region.

Samples of undifferentiated material, the chondrites, display a chemical composition very close to that of the sun (except for the most volatile elements) and thus to the solar nebula itself. Therefore, these rocks are invaluable for science, since they still contain information about the processes and conditions in the solar nebula at the time of the birth of the solar system.

To decipher these processes, the noble gases helium, neon, argon, krypton, and xenon represent key elements for several reasons: They are chemically inert and occur in very low abundances in solid matter. Further, they have very different physical properties like condensation temperatures, (ion) radii, diffusion constants, solubility, or adsorption coefficients. Each of these properties is reflected in the specific composition of a given noble gas component, i.e., a "compositionally well defined and uniform reservoir" (Ozima and Podosek, 2002). Section 1.4 gives a description of different noble gas components relevant for this study. Despite the inertness of the noble gases, there are processes, which can fix them to so-called "carrier phases". This may happen, e.g., by adsorption of noble gases to reactive surfaces, or by implantation into mineral phases. A more detailed description of these processes and carrier phases is given in section 1.4.2. Noble gases, which were trapped in such carrier phases at the beginning of the solar system, were incorporated into solid objects accreting from the nebula. However, in contrast to the outer planets, the objects of the inner solar system were not massive enough to gravitationally capture noble gases residing in the gas phase of the solar nebula. Therefore the inner solar system is strongly depleted in noble gases ("rare" gases). The low abundance of noble gases in solids allows distinguishing different noble gas components in extraterrestrial samples in the laboratory. The noble gas components in turn help drawing conclusions on the processes in the early solar nebula like condensation, accretion, mixing, and alteration, which affected the primitive meteorites nearly 4.6 billion years ago.

The following section contains a short overview of the properties of the major mineral constituents found in unequilibrated chondrites. Also our best knowledge about their formation scenarios is given. In addition, a summary of the major noble gas components in unequilibrated chondrites is given. Also the origin of the noble gas components and their carrier phases are emphasised. However, a classification scheme for chondrites is presented first.
1.2 Classification of chondrites

Meteorites are basically divided into the undifferentiated meteorites, the chondrites, and the differentiated meteorites. The latter include achondrites, stony-iron-, and iron meteorites. Within the chondrites, different classes and groups are defined on the basis of their bulk chemistry, isotopic composition, oxidation state, and the relative abundance of the different constituents, which will be described in section 1.3.

![Chondrites classification](image)

**Fig. 1.2**: Classification of chondrite classes and groups. Numbers represent occurring petrologic types (see text for further explanation). The figure is modified from Brearley and Jones (1998).

The chondrites are divided into several chemical classes, which are the carbonaceous (C), ordinary (O), Enstatite (E), and Rumuruti (R) chondrites (Fig. 1.2). The carbonaceous chondrites are further subdivided into 7 groups, each with distinct bulk compositions and oxygen isotopic signatures. The letters refer to the name of the type specimen of the respective group except for the CH chondrites. The subdivision of the ordinary chondrites is performed on the basis of their total iron content and the fraction of metallic to oxidised iron. Thereby H and L indicate high and low total Fe contents, respectively. The LL chondrites show low total Fe as well as a low metallic to total Fe content. Also the enstatite chondrites are subdivided into two groups with high and low iron content, EH and EL, respectively. The specific chondrite groups generally contain meteorites of different petrographic types, i.e., with different degrees of aqueous or thermal alteration (Van Schmus and Wood, 1967). This is expressed as numbers added to the respective group classification (Figs. 1.2 and 1.3). Whereas type 3 represents the least altered (most “primitive”, unequilibrated) material, types 2 to 1 indicate increasing aqueous, types 4 to 6 increasing thermal alteration. The type 3 ordinary and CO chondrites can be further subdivided into 3.0 to 3.9, also indicating increasing aqueous and thermal processing.
1.3 Constituents of chondrites

This chapter summarises general information about chondrites as far as it is relevant for the present study, mainly based on the book “Meteorites and the early solar system” by Kerridge and Matthews (1988) and the chapter “Chondritic Meteorites” (Brearley and Jones, 1998) in the book “Planetary Materials” (Papike, 1998). Images of the single constituents of chondrites were mostly performed by scanning electron or optical microscopy of thick and thin sections of the meteorites studied in this work.

Chondritic meteorites are accretionary rocks containing a mixture of different constituents, which themselves had experienced a wide range of pre-accretionary processes. Fig. 1.4 shows the typical constituents of the carbonaceous chondrite Allende: matrix, chondrules, and calcium-aluminium-rich inclusions (CAIs).
1.3.1 Chondrules

The most outstanding (and common) constituents of chondrites are the name-giving chondrules, which comprise up to 80 vol% of the ordinary chondrites and more than 15 vol% of most carbonaceous chondrites (see, e.g., compilation in Brearley and Jones, 1998). Most of them are sub-millimetre sized spheroidal objects consisting predominantly of the silicate phases olivine, pyroxene and feldspar-normative glass (Fig. 1.5). Common opaque phases are troilite and kamacite (Grossman et al., 1988). The droplet shapes and igneous textures of chondrules prove an igneous origin. However, the chondrule precursor material and even more so the formation environment and heat source, the “chondrule forming process”, are far from being understood (e.g., Wood, 1996). At present, all chondrule formation models can be divided in two competing scenarios. In the first scenario chondrule formation is supposed to have taken place in the solar nebula. In contrast, the second scenario favours chondrule formation on planetary bodies. The latter scenario includes, e.g., chondrule formation during impact (e.g., Sears et al., 1996) or by ablation of molten droplets from planetary bodies in nebular shock waves (e.g., Genge, 2000). Most of the models supporting chondrule formation in the solar nebula imply small aggregates of matrix-like material (“dust-balls”) as chondrule precursors. These are molten in transient flash-heating events like, e.g., nebular lightning, magnetic reconnection flares and gas dynamic shock waves (see Rubin, 2000, and references therein for a comprehensive review).

**Fig. 1.4:** Specimen of the unequilibrated chondrite Allende. Spheroidal chondrules and an irregularly formed CAI are visible. Both constituents are embedded in a grey fine-grained groundmass, the matrix.
However, also a direct condensation of droplets, which subsequently coagulated to form chondrules, is under discussion (e.g., Blander, 1983; Zanda et al., 2002). Recently, much attention has been attracted by the so-called “X-wind model” proposed by Shu et al. (1997, 2001). In this model chondrules are melted from precursor dust by flares near the so-called reconnection region, which represents the part of the accretion disc directly connected to the magnetic field lines from the young stellar object. Subsequently, the chondrules are transported to asteroidal distances via the so-called X-wind, where accretion to the respective parent bodies takes place. However, this model fails to explain genetic relationships between chondrules and the fine-grained enveloping matrix material in single meteorites (Klerner and Palme, 2000; Kong and Palme, 1999).
1.3.2 Metal-sulphide-rich rims and droplets

Metal-sulphide-rich (MS-rich) material in chondrites often occurs as droplets within chondrules or isolated in the matrix, or as coatings around chondrules (Fig. 1.6). In contrast to the fine-grained matrix-like dust rims around chondrules, which are described in section 1.3.4), the formation of MS-rich material is genetically related to chondrule formation (e.g., Kong and Palme, 1999; Alexander, 1989; Connolly et al., 1994; Connolly et al., 2001; Kong and Ebihara, 1997): It seems that in the molten chondrules small metal droplets coagulated to larger
blebs due to liquid-liquid-separation of the silicate and the metal melt. The metal has either been present in the chondrule precursor dust (Grossman and Wasson, 1985; Kong and Palme, 1999; Zanda et al., 2002), or was formed during chondrule formation by reduction of FeO and NiO from the precursor silicate phases (Alexander, 1989; Connolly et al., 2001; Kong and Ebihara, 1997; Kong and Palme, 1999). The reducing agent may have been carbonaceous material present in the chondrule precursor (Connolly et al., 1994; Connolly et al., 2001). Also ambient nebular H or H2, phosphorus or sulphur as reducing agents have been discussed (Kong and Palme, 1999; Rambaldi and Wasson, 1981; Zanda et al., 2002). Due to surface tension forces and/or the spin of the chondrules the metal droplets moved to the chondrule margins (Connolly et al., 2001; Grossman and Wasson, 1987; Humayun et al., 2002; Kong et al., 1999; Kong and Palme, 1999). There, they either evaporated and recondensed onto the chondrules (“recondensed” MS-rich rim type) or the droplets solidified directly on the chondrule surfaces without precedent evaporation (“expelled” MS-rich rim type). However, some MS-rich droplets were also completely separated from their host chondrules and are now found as isolated blebs in the matrix of unequilibrated chondrites (e.g., Kong and Palme, 1999; Alexander, 1989; Connolly et al., 1994; Connolly et al., 2001; Kong and Ebihara, 1997).

**Fig. 1.6:** Backscattered electron (BSE) images of a) white metal-sulphide-rich droplets isolated in the matrix and in contact with chondrule silicates (e.g., droplet on the right hand side of the image) of Renazzo b) a thick irregular expelled-type metal-sulphide-rich rim around a chondrule of Krymka c) a thin layered recondensed metal-sulphide-rich rim around a chondrule of Bishunpur. Further metal-sulphide-rich droplets are visible within the chondrules in the images b) and c).

### 1.3.3 Calcium-aluminium-rich inclusions (CAIs)

Calcium-aluminium-rich inclusions (CAIs) are mainly found in carbonaceous chondrites, where they can make up to 13 vol% (Brearley and Jones, 1998). They are much less abundant (< 1 vol%) in ordinary chondrites. Their sizes vary from
<1mm to >1cm, and they display shapes from highly irregular (Fig. 1.7) to nearly spheroidal. The mineral assemblage in CAIs is extraordinarily refractory and consists mainly of oxides and silicates of Ca and Al with minor amounts of Ti and Mg, like corundum, hibonite, grossite, perovskite, anorthite, spinel, melilite, and fassaite (Brearley and Jones, 1998). These minerals remarkably resemble the first phases predicted to condense from a cooling gas of solar composition (see, MacPherson et al., 1988, and references therein). Allende CAIs also represent the oldest available solar system material with Pb/Pb ages between 4.568 and 4.565 Ga (Allègre et al., 1995). Furthermore, they contain decay products of various short-lived nuclides (e.g., MacPherson et al., 1995), which had possibly been synthesised in a nearby star and were injected into the forming solar system right before the formation of the CAIs. This would indicate that the CAIs were indeed formed very early in the history of the solar system. However, an alternative interpretation of the presence of short-lived nuclides is given below.

The formation of CAIs is not well constrained, mainly because multiple secondary processes obliterate primary signatures. Proposed mechanisms of CAI-formation (see MacPherson et al. (1988) for a comprehensive review) include, e.g., direct vapour-solid condensation from the hot solar nebula or condensation with an intermediate liquid phase. The molten texture of many CAIs (Fig. 1.7) could also point to a formation by intense fractional evaporation, which would lead to the observed enrichment of refractory phases. Again, the X-wind scenario is attractive, where CAIs are produced even closer to the sun than the chondrules (Shu et al., 2001). This would explain the more intense heating and evaporation and thus the more refractory chemistry of the CAIs compared to the chondrules (Gounelle et al., 2001; Shu et al., 2001). In the authors view, also the short-lived nuclides were formed by spallation reactions in CAIs close to the young sun. Indeed, many of these nuclides have been successfully modelled in the framework of an X-wind scenario (Gounelle et al., 2001; Leya et al., 2002; Russel et al., 2001).
1.3.4 Matrix

The most important constituent in unequilibrated chondrites besides chondrules and CAIs is the matrix, which makes up to 10-15 vol% in ordinary and distinctly higher percentages, 30-50% in the CR and ~40% in the CV chondrites (Scott et al., 1996). Although many definitions of matrix are available, this work follows the one of Scott et al. (1988). They define matrix in unequilibrated chondrites as “…fine-grained, predominantly silicate material, interstitial to macroscopic, whole or fragmented, entities such as chondrules, inclusions and large isolated mineral (i.e. silicate, metal, sulphide, and oxide) grains”. Although matrix is compositionally heterogeneous between different chondrites and even within one individual chondrite, it is in many chondrite groups composed of olivine with very variable contents of forsterite (Fo$_{90}$-Fo$_{99}$), pyroxene, augite, albite, Fe-Ni metal, troilite, magnetite, spinel, chromite, calcite and small amounts of carbonaceous material (Brearley, 1996). In some groups, e.g., the CI, CM, or CR chondrites phyllosilicates are dominant. The matrix is also the host for interstellar grains like diamonds, silicon carbides, and graphite (e.g., Alexander et al., 1990; Banhart et al., 1998; Huss et al., 1996). However, despite its unequilibrated character even matrix material of the most unequilibrated chondrites has suffered certain degrees of aqueous and/or thermal alteration in the solar nebula or later on a parent body. This resulted in the formation of hydrous phases and equilibration features within single minerals or between different mineral phases (Brearley and Jones, 1998).

There is much debate about the origin of matrix. However, it is accepted that it consists of a variety of different components with distinctly different origins:
These include presolar material like the interstellar grains and solar material, which is supposed to have condensed within the solar system from the solar nebula; also present is finely ground chondrule debris (Scott et al., 1988). However, the relative proportions of these components in the matrix are unclear and seem to vary substantially from chondrite to chondrite (e.g., Brearley et al., 1996). Matrix-like fine-grained material is also suggested to be the most probable chondrule precursor material (e.g., Connolly et al., 2001; Kong and Palme, 1999; Kong and Ebihara, 1997; Alexander et al., 1989; Scott et al., 1983). This emphasises on the one hand the primitive nature of matrix, which might still carry information about the solar nebula and the earliest stages of planetesimal accretion. On the other hand one might suggest multiple generations of chondrules, since chondrule debris might represent in some cases, e.g., in unequilibrated ordinary chondrites, even a substantial portion of matrix material (Alexander, 1989).

The matrix can be subdivided on the basis of textural criteria (Fig. 1.8). Its most common occurrence is as opaque texture-less groundmass or filling of interstices. In the following, only this material will be addressed as “matrix”. If all fine-grained material is addressed collectively, it is called “matrix-like material”. Furthermore, matrix-like material occurs as fine-grained concentric rims around chondrules or other larger objects, and as macroscopically distinct dark lumps and clasts, collectively addressed as "dark inclusions" (DIs). However, the genetic relationships between these different occurrences of matrix-like material are not yet clear.

**FIG. 1.8:** BSE images of different occurrences of matrix-like material. a) Thick concentric fine-grained rim around a porphyritic chondrule embedded in a fine-grained groundmass (“matrix”) in Allende. b) Thin concentric fine-grained rim around a porphyritic chondrule in Leoville. The surrounding matrix is slightly darker than the rim and much less abundant than in a). c) The large subrounded fragment represents a fine-grained dark inclusion in Leoville. In the upper left corner, an irregularly formed porphyritic chondrule surrounded with a concentric fine-grained rim is visible.
The fine-grained concentric rims around chondrules and other larger objects are common in many groups of carbonaceous chondrites, as, e.g., summarised in the comprehensive review of Metzler and Bischoff (1996). The formation of these rims probably occurred in the solar nebula by accretion of dust onto the surfaces of chondrules and other coarse components as they passed through dust-rich areas. The layering of fine-grained rims around Allende CAIs led MacPherson et al. (1985) to suggest that the rims might reflect a time-dependent nebular accretion sequence, with the structureless matrix representing the last accreted material. Nakamura et al. (1999b) found the highest concentrations of primordial noble gases in CM chondrites in the fine-grained around chondrules, which also supports rim formation directly from nebular dust. However, also rim accretion in a wet planetary regolith (e.g., Sears et al., 1993) or by aqueous alteration of chondrules themselves on a parent body (e.g., Sears et al., 1991) are discussed. The term “dark inclusions” comprises fine-grained matrix-like fragments with very variable textures reflecting their origins from different sources and complex secondary processing. Formation models include condensation directly from the solar nebula (Kurat et al., 1989), and the formation of fragments, which were later (re-)incorporated into parent bodies with various intermediate nebular and later parent body alteration stages (e.g., Johnson et al., 1990; Kojima and Tomeoka, 1997; Krot et al., 1997).

The formation of the different fine-grained constituents of chondrites and possible genetic relationships among them are discussed in chapter 4.

1.4 Noble gases in primitive meteorites

The noble gases extracted from a bulk primitive meteorite often represent mixtures of at least two or more noble gas components. For example, there exist noble gas components that were produced in situ in the meteorite, in particular radiogenically or cosmogenically produced noble gases. All other noble gas components are so-called “trapped” components, which are further subdivided. On the one hand these are “primordial” components, where the noble gases were bound to certain carrier phases very early in the history of the solar system or even in the parent molecular cloud. Among these components, the two most prominent ones are those of the so-called phase Q and noble gases carried by presolar diamonds. On the other hand, trapped noble gases also comprise those implanted into the minerals of a regolith on a parent body during irradiation of the regolith with solar wind much later in the history of the solar system. Also noble gases of the terrestrial atmosphere adsorbed on a sample might be significant.
The following section contains a description of the most common noble gas components that might be present in unequilibrated chondrites. Also possible sources of the noble gas components and/or their carrier phases are described. For recent comprehensive reviews see, e.g., Wieler (2002b), Wieler (2002a), Ott (2002), and Ozima and Podosek (2002). Isotopic and elemental compositions of the respective noble gas components are given in Tab. 1.1.

**Tab. 1.1.** He, Ne and Ar isotopic and elemental compositions of various noble gas components relevant for this study

<table>
<thead>
<tr>
<th>Component</th>
<th>$^3\text{He}/^4\text{He}$</th>
<th>$^{20}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{21}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{36}\text{Ar}/^{38}\text{Ar}$</th>
<th>$^{20}\text{Ne}/^{36}\text{Ar}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>1.23(2)</td>
<td>10.05(5) - 10.7(2)</td>
<td>0.0291(16) - 0.0294(10)</td>
<td>5.34(2)</td>
<td>14 - 84</td>
</tr>
<tr>
<td></td>
<td>{1}</td>
<td>{1}</td>
<td>{1}</td>
<td>{1}</td>
<td>{1}</td>
</tr>
<tr>
<td>HL</td>
<td>≤1.7×10^{-4}(1)</td>
<td>8.50(6)</td>
<td>0.036(1)</td>
<td>4.41(6)</td>
<td>0.103(142)</td>
</tr>
<tr>
<td></td>
<td>{2}</td>
<td>{2}</td>
<td>{2}</td>
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<td>{2}</td>
</tr>
<tr>
<td>SW</td>
<td>(4.18-4.63)×10^{-4}</td>
<td>13.8(1)</td>
<td>0.0328(5)</td>
<td>5.58(3)</td>
<td>~0.04</td>
</tr>
<tr>
<td></td>
<td>{3}</td>
<td>{3}</td>
<td>{3}</td>
<td>{3}</td>
<td>{3}</td>
</tr>
<tr>
<td>subsolar</td>
<td>1.80(6)×10^{-4}</td>
<td>11.7(3)</td>
<td>0.0294</td>
<td>5.48(6)</td>
<td>~26</td>
</tr>
<tr>
<td></td>
<td>{4}</td>
<td>{4}</td>
<td>{4}</td>
<td>{4}</td>
<td>{4}</td>
</tr>
<tr>
<td>GCR</td>
<td>5.2(3), 6.1(3)</td>
<td>0.70-0.93</td>
<td>0.80-0.95</td>
<td>0.65(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>{6}</td>
<td>{6}</td>
<td>{6}</td>
<td>{6}</td>
<td>{6}</td>
</tr>
<tr>
<td>Air</td>
<td>1.399(13)×10^{-6}</td>
<td>9.80(8)</td>
<td>0.0290(3)</td>
<td>5.32(1)</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>{9}</td>
<td>{7}</td>
<td>{7}</td>
<td>{8}</td>
<td>{9}</td>
</tr>
</tbody>
</table>

Numbers in parentheses represent uncertainties in units of the least significant digit. {1} Busemann et al., 2000; {2} Huss and Lewis, 1994a; {3} Benkert et al., 1993; {4} Busemann et al., 2002, trapped $^{20}\text{Ne}/^{22}\text{Ne}$ for an adopted $^{21}\text{Ne}/^{22}\text{Ne}$ of 0.0294; {5} Crabb and Anders, 1981; {6} Wieler, 2002a, and references therein. GCR: Galactic Cosmic Radiation. $^3\text{He}/^4\text{He}$ and $^{26}\text{Ar}/^{38}\text{Ar}$: for stony meteorites; $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$: for chondrites, {7} Eberhardt et al., 1965; {8} Nier, 1950; {9} Ozima and Podosek, 2002, and references therein.

### 1.4.1 In situ produced noble gas components

#### 1.4.1.1 Cosmogenic noble gases

Cosmogenic noble gases are produced by nuclear reactions of energetic particles from the galactic cosmic radiation (GCR) with meteoritic material. The mean attenuation length of GCR in solid material is ~150 g/cm$^2$. This is in the “pre-atmospheric” size range of many meteorites, which means the size of an object, before it loses a large part of its mass due to the passage through the Earth’s atmosphere. Although many nuclides are formed by these reactions, effects are detectable only for those, whose original abundance in the target material is extremely low. This is mainly the case for the noble gases and the radionuclides.
For example, in many meteorites $^3$He, $^{21}$Ne, and $^{38}$Ar are predominantly of cosmogenic origin. The production rate of a certain cosmogenic nuclide strongly depends on the chemistry of the target material. Ne is mainly produced from Mg, Al, and Si, whereas the main Ar-producing targets are Ca, Ti, Fe, and Ni (Leya et al., 2000). Helium is an exception, being produced in similar amounts from essentially all elements. Furthermore, the production rate depends on the shielding depth of a sample, which means the depth of a meteorite sample within the respective meteoroid (per definitionem the meteorite before its arrival on Earth). The shielding depth is a priori unknown, but can be estimated, e.g., via the cosmogenic $^{22}$Ne/$^{21}$Ne or the $^3$He/$^{21}$Ne ratios (see Wieler, 2002a). With the help of the production rate and the absolute amount of cosmogenic nuclides in a meteorite sample, it is possible to estimate its so-called "exposure age". This is the time span between the separation of a meteoroid from a parent body, where it was shielded from the GCR, and its arrival on Earth.

The cosmogenic isotopic ratios generally are much less variable than the absolute production rates. For a chondritic meteorite the cosmogenic $^{20}$Ne/$^{21}$Ne/$^{22}$Ne composition is roughly 0.8:0.9:1, but small variations occur due to differing sample chemistry and shielding depth (see, e.g., chapter 5). The cosmogenic $^{36}$Ar/$^{38}$Ar ratio of ~0.65 does not even significantly change between stony and iron meteorites due to similar production rate ratios from Ca and Fe (Leya et al., 2000; Wieler and Graf, 2000).

For the present study cosmogenic nuclides are basically a nuisance, since they obscure the trapped noble gas components of interest. Therefore the measured noble gas data have to be corrected for cosmogenic contributions. A correction is unproblematic as long as the cosmogenic noble gases do not contribute a substantial portion to the measured noble gases. This is the case for the matrix-like components of the primitive meteorites studied here (see chapter 4). However, the chondrules of this study have low trapped noble gas concentrations; thus, the cosmogenic component significantly contributes to the total noble gas amounts. In these cases a very precise knowledge of the amounts and isotopic compositions of the cosmogenic noble gases is necessary. This in turn would presume a detailed knowledge of the sample chemistry, the exposure age, and the shielding depth. However, an alternative methodology to precisely correct for cosmogenic contributions is described in detail in chapter 5.

1.4.1.2 Radiogenic and fissionogenic noble gases

Radiogenic and fissionogenic noble gases are produced by the decay and fission of radionuclides, respectively. For example, $^{235}$U, $^{238}$U, and $^{232}$Th are the main parent
nuclides for radiogenic \(^4\)He, and \(^{40}\)K decays in part to \(^{40}\)Ar. The relatively short-lived, now extinct, \(^{129}\)I was an important source for \(^{129}\)Xe in meteorites. The heavy isotopes of Kr and Xe are produced by neutron induced fission of \(^{235}\)U and by spontaneous fission of \(^{238}\)U and the extinct \(^{244}\)Pu (e.g., Swindle, 2002). With the help of radiogenic nuclides the absolute gas-retention age or, in the case of the relatively short-lived nuclides, a relative chronology can be established. However, also radiogenic noble gases may obscure other noble gas components like the trapped noble gases. Concerning this study, the major part of the measured \(^4\)He and \(^{40}\)Ar are of radiogenic origin. Even if detailed information about concentrations of the parent nuclides would have been available, it generally would not have been possible to correct for the large amounts of radiogenic \(^4\)He and \(^{40}\)Ar as precisely as it would have been necessary to determine any other \(^4\)He and \(^{40}\)Ar components. Further, the trapped \(^{40}\)Ar/\(^{36}\)Ar is very small (\((^{40}\)Ar/\(^{36}\)Ar)-Q: \(\sim 2.9 \times 10^{-4}\) (Göbel et al., 1978); \((^{40}\)Ar/\(^{36}\)Ar)-HL: \(< 0.8\) (Huss and Lewis, 1994a)). Thus, trapped \(^{40}\)Ar and \(^4\)He are not discussed in this study.

1.4.2 Trapped noble gas components

1.4.2.1 Solar wind noble gases

Solar wind (SW) noble gases are emitted from the chromosphere of the Sun. The particles have velocities between 300 - 800 km/s and are implanted into the outermost grain layers (several 10 nm (Mewaldt et al., 2001)) of material exposed to SW radiation, e.g. the fine-grained regolith surfaces of meteorite parent bodies or the moon. The lunar regoliths are, e.g., generally well mixed due to ongoing impacts; thus, almost all dust grains are at least once exposed to the solar wind to collect SW noble gases. SW noble gas implantation might also have been active in the very early history of the solar system, when infalling dust was directly exposed to SW radiation at the innermost part of the accretion disk (Okazaki et al., 2001b). Subsequent processing of this irradiated dust by heating or melting may have even produced specific meteorite noble gas components by mass fractionation of the SW noble gases, as, e.g., the subsolar noble gas component (see below).

SW noble gases contain high amounts of He and Ne compared to the heavier noble gases (see, e.g., Wieler, 2002b) as well as compared to the other meteoritic noble gas components shown in Fig. 1.9. Therefore, meteorite samples containing “regolithic” SW noble gases were excluded in this study since they would have obscured especially the light noble gas signatures of the primordial noble gas components, being the major topic of this work.
1.4.2.2 Subsolar noble gases

The subsolar noble gases are less elementally fractionated than the Q-gases relative to the solar composition (Fig. 1.9). The isotopic composition of subsolar noble gases is similar to SW (compare Tab. 1.1). Subsolar noble gases are predominantly found in enstatite chondrites of higher petrologic type, which are not included in this study. Nevertheless we introduce this component here since high concentrations of subsolar noble gases were found in the chondrules of an enstatite chondrite, whereas the matrix had a normal “Q-like” composition (Okazaki et al., 2001b). The authors suggested that the subsolar pattern evolved during the melting of dust heavily irradiated with SW noble gases in an X-wind environment (see chapter 5 for a detailed explanation). Assuming this as the predominant chondrule formation scenario, subsolar noble gases could be expected also in chondrules of other chondrite classes including those of this study, carbonaceous and ordinary chondrites.

However, in a recent noble gas study of the enstatite chondrite St. Marks by Busemann et al. (2003), the authors show that the isotopic and elemental compo-
sition of the subsolar noble gas component can be interpreted as a mixture of SW, meteoritic (Q), and atmospheric noble gases. It thus appears that the subsolar noble gas component in meteorites as a whole requires a thorough review since the SW-like noble gases might represent a primordial component.

1.4.2.3 Noble gases of phase Q

Most of the heavy trapped noble gases (Ar, Kr, Xe) in unequilibrated chondrites, which have not been irradiated by SW, reside in the carrier phase Q. The definition of phase Q is operational: It survives the treatment of a meteorite with hydrofluoric and hydrochloric acid together with the bulk of noble gases, but releases essentially all of the “Q-gases” during subsequent oxidation of the residue with HNO₃ (Lewis et al., 1975). Roughly 1% of a bulk chondrite survives the HF/HCl treatment, whereas the decrease in mass during the oxidation of the HF/HCl-residue is more variable, between 1 and 75% (Busemann, 1998). The variability is ascribed to different acids and etching times, as well as to the formation of solid chemical compounds during etching. Anyway, the carrier phase Q seems to have a minor mass only, and the noble gas concentrations of phase Q are apparently very high (on the order of 10⁻⁵ cm³STP/g ³⁶Ar; see, e.g., Busemann et al., 2000). However, it has not been possible to precisely define the nature of the carrier phase Q so far. Various mineral phases were suggested as the carriers of the Q-gases, among them also chromite and sulphide phases (Lewis et al., 1975), but it finally turned out that the carrier phase must be carbonaceous (e.g., Ott et al., 1981). This is supported by a recent high resolution transmission electron microscopy study of acid-resistant residues of CV chondrites (Vis et al., 2002). The authors report various carbon structures, which could all serve as potential carriers for Q-gases. However, Ar-X-ray signals from these structures were obtained in a few cases only.

Also the trapping mechanism of such large amounts of noble gases in the carrier phase Q is a topic of ongoing discussion. Due to the apparently small mass of the carrier it was, e.g., suggested that the noble gases are not incorporated in, but only reside on the inner surfaces of amorphous carbonaceous material (Wacker et al., 1985). If this were indeed the case, it would be complicated to understand the high release temperatures of the Q-gases during pyrolysis in the range of 1000–1800 °C (Huss et al., 1996) and its high resistance during thermal metamorphism. Both parameters even exceed those of the bulk of the extremely stable presolar diamonds (Huss et al., 1996). A recent model by Hohenberg et al. (2002) proposes the impingement of noble gases onto sticky growing films, where the noble gases are retained by anomalous adsorption long enough to be entrapped in the growing surfaces.
It is further unclear whether the Q gases were trapped within the solar system or earlier, e.g., in the parent molecular cloud. The Q-gases have a roughly “normal” isotopic composition, which means that it could have been derived by mass fractionation of noble gases having a solar origin (Ott, 2002). The elemental composition of phase Q shows a strong depletion of the light noble gases relative to the heavier ones as well as when compared to solar composition (Fig. 1.9). However, it is also possible that the carrier phase Q obtained its noble gas inventory already in the parent molecular cloud or even earlier in the interstellar space (Huss and Alexander, 1987; Ott, 2002) and was injected into the solar system as solid particles similar to the presolar diamonds (see below). This would, e.g., explain the widespread occurrence and roughly uniform noble gas signature of phase Q in many solar system objects.

1.4.2.4 Noble gases in presolar diamonds

The light noble gas inventory of unequilibrated chondrites (free of SW-gases) is dominated by He and Ne from presolar diamonds. These have sizes of up to a few nanometres. On the basis of different average release temperatures during pyrolysis it is possible to distinguish 3 isotopically different sub-components within the diamonds (P3, HL, P6), which are discussed in detail by Huss and Lewis (1994a): The major component is the so-called HL-component with a wide range of release temperatures between 1100 and 1600 °C. Helium and Ne in this component are correlated with smaller amounts of the heavier noble gases, of which Xe is the most important one. This so-called Xe-HL displays an exotic isotopic composition, which is characterised by the enrichment of the heavy \(^{134,136}\text{Xe}\) and of the light \(^{124,126}\text{Xe}\) isotopes compared to the median masses and the solar Xe isotopic composition. In contrast to a "normal", solar-like isotopic composition, stellar nucleosynthesis processes are required to explain an exotic noble gas composition. In the case of Xe-HL the light Xe isotopes are produced in p-, the heavy ones in r-processes, whereas the intermediate masses show contributions from the s-process (see Ott (2002) for a comprehensive review). This possibly indicates a supernova origin of the HL component and thus a presolar origin of its carrier phase. Therefore, also the associated He and Ne isotopes (He-HL, Ne-HL) are suggested to be of presolar origin despite their rather normal isotopic compositions (Tab. 1.1).

Furthermore, there exists the normal so-called P3 component, which releases its noble gases at lower temperatures (200-900 °C) during pyrolysis than the HL-gases. Therefore, P3 gases are already lost in chondrites, which had suffered mild thermal metamorphism. The so-called P6 noble gases, cannot be fully separated from the bulk of HL gases during pyrolysis, therefore, also the P6 composition is
somewhat uncertain. Huss and Lewis (1994a) propose a roughly normal isotopic composition of the P6 noble gases. However, despite the (probably) normal noble gas isotopic composition of the P3 and P6 carrying diamonds, the authors suggest a presolar origin for both components. The large range of noble gas release temperatures of the different sub-groups of presolar diamonds points to the presence of different populations of diamonds probably with different physical properties (e.g., Ott, 2002).

1.4.2.5 Siting of phase Q and presolar diamonds in unequilibrated chondrites

Both, phase Q and the presolar diamond noble gases in unequilibrated chondrites occur in variable concentrations in the fine-grained matrix-like material, which surrounds larger objects like chondrules and CAIs. Nakamura et al. (1999b) found in fine-grained rims around chondrules of CM chondrites an enrichment of presolar diamond and phase Q noble gases compared to chondrules and so-called PCP-rich areas. The latter are present in CM chondrites and consist of small generally micron-sized objects, “poorly characterised phases”, which are now known to be rich in serpentine and tochilinite (e.g., Metzler et al., 1992). The PCP-rich objects are rimmed like the chondrules with fine-grained matrix-like material. Another extraordinary enrichment of primordial noble gases was found in a fine-grained dark inclusion of Krymka (Lewis et al., 1979). However, the reasons for the variability of the noble gas concentrations in the different fine-grained materials within one meteorite as well as among different meteorites are not yet fully understood. Possible explanations may be, e.g., variable thermal or aqueous alteration, or different mixing proportions between noble gas carrying and noble gas free matter in the fine-grained materials. Also heterogeneous mixing of the two noble gas carriers phase Q and presolar diamonds in the solar nebula might serve as an explanation.

The chondrules and CAIs are strongly depleted in primordial noble gases of phase Q and presolar diamonds. The depletion is generally ascribed to the high-temperature event, during which chondrules and CAIs were formed, accompanied by a more or less complete degassing of the noble gas carrier phases.

1.5 Objectives of this study

So far, most noble gas studies on unequilibrated chondrites were performed on bulk samples or acid-resistant residues. The noble gases were extracted by combustion or pyrolysis, often in several temperature steps. The isotopic and elemental signatures of noble gases residing in different noble gas carrier phases could
then be determined on the basis of different gas release temperatures. Also on- or off-line etching of a bulk sample with different acids like HF, HCl or HNO₃ is suitable to separate different noble gas carrier phases (Signer et al., 1993). However, unequilibrated chondrites consist of very different constituents including presolar material, solar nebula condensates, and the high temperature objects chondrules and CAIs. The individual noble gas signatures of these constituents reflect their different formation and/or alteration histories. These include in particular, e.g., (i) mixing of material with different noble gas inventories, (ii) thermal and/or aqueous alteration including melting, which releases and fractionates the noble gases, and (iii) possibly irradiation with SW. It is even unclear, whether the noble gas carrier phases were originally homogeneously distributed throughout the solar nebula or displayed a heterogeneously distribution in the accretion regions of the meteorite parent bodies. Therefore, the goal of this work was to decipher the microdistribution of trapped noble gases in the different constituents of unequilibrated carbonaceous and ordinary chondrites. In contrast to etching or classical pyrolysis, this approach enables the correlation of a certain noble gas component with specific constituents of an unequilibrated chondrite. This allows deciphering the formation history of the particular constituent and in turn helps understanding the genetic relationships between the different constituents of a chondrite. Only few studies exist so far on the distribution of trapped noble gases among these constituents and possible implications on formation scenarios (e.g., Nakamura et al. (1999b), Okazaki et al. (2001b)). This is on the one hand certainly because of the inconvenience to separate pure, uncontaminated samples due to the small sizes of the constituents. On the other hand a major reason is also the difficulty to precisely analyse the small concentrations of noble gases released from the tiny samples, since the gas amounts are generally near the blank-levels and/or the detection limit of the mass spectrometer. During this study however, improved analytical techniques and a substantial blank reduction by laser heating made it possible to measure such low noble gas concentrations with sufficient precision. The first part of the study (chapter 4) addresses the formation and alteration histories of the different fine-grained constituents rims, matrix, and DI's of selected primitive meteorites. Also the genetic relationships among the constituents are emphasised. Therefore, the noble gas signatures of small samples of rims, matrix and DI's are compared. In the second part of the work noble gases in the high-temperature objects chondrules and CAIs (chapters 5 and 6, respectively) are analysed to draw conclusions on possible precursor materials and the environment, in which the objects were formed. In this context, the X-wind model proposed by Shu et al. (2001) is
discussed, in which chondrules and CAIs are supposed to be created near the young sun.
CHAPTER 2

SAMPLES

AND EXPERIMENTAL PROCEDURES
2.1 Selection of suitable meteorites

In order to decipher early solar nebula processes by means of noble gases in meteoritic samples, these have to be as pristine as possible. Since especially thermal (and to a lower degree also aqueous) alteration can change the noble gas signature of meteorites, we restricted our study to chondrites of the petrographic types 2 and 3. These types of meteorites are not very abundant and therefore usually not easy to obtain. Additionally, some restrictions had to be made concerning the petrography and the noble gas inventory of the samples.

The single constituents (matrix, rims, DIIs, chondrules, MS-rich rims, CAIs) have to be large enough to enable a proper separation under the binocular microscope without cross-contaminating the different constituents. This was especially important for the separation of chondrules CAIs, since these generally contain very low primordial gas concentrations (e.g., Smith et al., 1977; Nakamura et al., 1999b), whereas the surrounding fine-grained rim and matrix material is often the most gas-rich constituent of an primitive meteorite (e.g., Nakamura et al., 1999b).

Concerning the noble gas inventory of the samples, it was important to find chondrites, in which the primordial noble gas signatures were not compromised by additional noble gas components, i.e., SW and cosmogenic noble gases. Therefore, regolithic breccias were excluded from the study, because they may contain large amounts of SW noble gases. Also meteorites with high exposure ages and thus high cosmogenic noble gas concentrations should be avoided (see Tab. 2.1).

Below, basic information about the selected meteorites as well as descriptions of their particular characteristics are given. The information was taken from the catalogue of meteorites (Grady, 2000). Bulk noble gas data (compiled from Schultz and Franke, 2000) and estimated exposure ages are given in Tab. 2.1.
Tab. 2.1: Measured and trapped bulk $^{20}$Ne and $^{36}$Ar data and exposure ages of the selected samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Class</th>
<th>$^{20}$Ne$_{meas}$ $^1$ %</th>
<th>Cosmogenic contribution to $^{20}$Ne in % $^2$</th>
<th>$^{36}$Ar$_{meas}$ $^1$ %</th>
<th>Cosmogenic contribution to $^{36}$Ar in % $^2$</th>
<th>trapped $^{36}$Ar/$^{36}$Ne $^2$</th>
<th>Estimated exposure age [Ma] $^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
<td>CV3ox</td>
<td>6</td>
<td>26</td>
<td>17</td>
<td>0.5</td>
<td>4.3</td>
<td>5.1</td>
</tr>
<tr>
<td>Leoville</td>
<td>CV3red</td>
<td>12</td>
<td>22</td>
<td>226</td>
<td>0.0</td>
<td>24.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Renazzo</td>
<td>CR2</td>
<td>14</td>
<td>12</td>
<td>24</td>
<td>0.5</td>
<td>2.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Semarkona</td>
<td>LL3.0</td>
<td>8</td>
<td>33</td>
<td>59</td>
<td>0.4</td>
<td>11.3</td>
<td>9.1</td>
</tr>
<tr>
<td>Bishunpur</td>
<td>LL3.1</td>
<td>7</td>
<td>53</td>
<td>48</td>
<td>0.7</td>
<td>14.5</td>
<td>10.7</td>
</tr>
<tr>
<td>Krymka</td>
<td>LL3.1</td>
<td>11</td>
<td>77</td>
<td>48</td>
<td>1.4</td>
<td>15.6</td>
<td>26.3</td>
</tr>
</tbody>
</table>

Gas concentrations are given in units of $10^8$ cm$^3$STP/g.  
$^1$ Average measured bulk $^{20}$Ne and $^{36}$Ar concentrations from Schultz and Franke (2000).

$^2$ Trapped and cosmogenic gases were determined by two-component deconvolution (see chapter 4).

$^3$ Exposures ages were estimated on the basis of the bulk cosmogenic $^{21}$Ne concentrations. The $^{21}$Ne production rates of $3.19 \times 10^{-9}$ cm$^3$STP/gMa and $3.32 \times 10^{-9}$ cm$^3$STP/gMa for CV- and LL-chondrites, respectively, were calculated with the formula given in Eugster (1988) using a typical cosmogenic $^{22}$Ne/$^{21}$Ne of 1.11 (Wieler, 2002a).

2.1.1 Allende (CV3ox)

Allende fell as a meteorite shower in 1969 in Mexico. Altogether, roughly 2 tons of material was recovered, representing the second largest stony meteorite found on Earth. It is classified as a CV3 chondrite of the oxidised subgroup (see, e.g., Krot et al., 1995, and references therein). Due to the relatively large amount of sample material available, and the suitable characteristics of this meteorite (i.e., large size of constituents, easy separability of samples), most of the experimental procedure including gas extraction, gas cleaning, and the analytical routine (see chapter 3) were tested with Allende samples. The high proportion of large matrix-like constituents and large CAIs (e.g., Figs. 1.4 and 2.1) made Allende especially suitable for studies of these constituents. Allende is a very soft rock, which made the separation of small samples with stainless steel tools easy. However, this also increased the probability of contaminating chondrule samples with dust of fine-grained surrounding rim and matrix material, which continuously accrued during the separation. This caused indeed an overprint of several Allende chondrule noble gas signatures with a-matrix-like signature (see chapter 5). Several pieces of Allende were kindly provided by the Institute of Planetology, Münster. Others were taken from the meteorite collection of the Department of Earth Sciences at ETH Zürich.
Fig. 2.1: Composite BSE images of three thick sections of Allende, from which chondrules, matrix, fine-grained rims, and dark inclusions were separated. The dark inclusions (marked by dashed lines) are not well visible in the BSE image, because the chemistry of DIs and matrix is very similar. It is unclear, whether the area marked with a “?” represents the second part of the indicated DI in the middle thick section. In some cases fine-grained rims are visible as weak concentric textures around chondrules (arrows). Note the much higher abundance of matrix-like material and the lack of MS-rich rims around chondrules compared to the ordinary chondrite samples (see Figs. 2.4-2.6).

2.1.2 Leoville (CV3_red)

Two pieces of Leoville with a total mass of 8.1 kg were found in Kansas, USA, in 1961 or 1962. As Allende, Leoville was classified as a CV3 chondrite. However, due to its more reduced mineral assemblage, it was assigned to the reduced subgroup (see, e.g., Krot et al., 1995, and references therein). Leoville contains particularly large chondrules with diameters of up to several mm, which are mostly rimmed with fine-grained matrix-like material (Fig. 2.2). Structureless matrix is only present in small interstices between the rimmed chondrules. The chondrules are generally flattened and display a clear, even macroscopically visible linear orientation. This is probably due to shock compaction on the parent body (Nakamura et al., 1992). The compaction also seems to be the reason for the extreme hardness of the meteorite, which made the separation of the samples very difficult. Also the sample of Leoville was available from the in-house meteorite collection.
Fig. 2.2: Composite BSE-image of Leoville. Most of the dark chondrules and the dark inclusion (marked by a dashed line) are elongated and linearly oriented probably due to shock compaction (see text). The irregularly shaped, coarse area in the lower-left part of the DI is due to the separation of a sample from that region. Fractures are often filled with Fe-Ni oxides or hydroxides (light grey). Chondrules are surrounded by thin fine-grained rims (arrows), which are slightly brighter than the interstitial matrix. The two large light patches at the margin of the specimen are – as in the following images - conductive silver used to reduce the charging of the sample during the SEM-imaging.

2.1.3 Renazzo (CR2)

Several pieces of Renazzo fell in 1824 in Italy, three of which with a total mass of ~10 kg were recovered. The meteorite was classified as a CR chondrite of the petrographic type 2, since the fine-grained matrix-like material consists mostly of phyllosilicates indicating aqueous alteration (McSween, 1979). Renazzo contains a relatively high amount of metal (12 wt%, Kong and Palme, 1999) compared to most other carbonaceous chondrites. In our sample the metal occurs mainly as blebs either within the chondrules or isolated in the matrix (see Fig. 2.3). Some of these blebs were large enough for a proper separation. The sample of Renazzo (0.51 g) was kindly provided by the Muséum National d’Histoire Naturelle, Paris.
2.1.4 Semarkona (LL3.0)

Semarkona fell in 1940 in India. Two pieces with a total mass of only 691 g were recovered. Semarkona represents one of the rare LL3.0 chondrites (see, e.g., Anders and Zadnik, 1985; and Jarosewich and Dodd, 1981, and references therein). The classification (compare Fig. 1.3) takes into account the substantial aqueous alteration of the matrix, which is nearly entirely composed of phyllosilicates. Although ordinary chondrites generally contain only minor amounts of matrix-like material, it was possible to separate some fine-grained rims around chondrules and interstitial matrix. Furthermore, the sample contains well developed MS-rich rims around chondrules (Fig. 2.4). I thank the Smithsonian National Museum of Natural History, Washington DC, for providing 0.4 g of Semarkona.
Fig. 2.4: Composite BSE-image of Semarkona. In contrast to the CV chondrites the chondrules of Semarkona are tightly packed and matrix-like material occurs mainly in interstices or as thin and often incomplete rims around chondrules (arrows). Part of the MS-rich material occurs as coatings around chondrules (A). In some cases it is however unclear, whether the MS-rich material represents rim material or isolated patches in the matrix (B).

2.1.5 Bishunpur (LL3.1)

Four pieces of Bishunpur fell in 1895 in India; only two pieces of altogether 1039 g were recovered. Bishunpur is classified as an LL3.1 chondrite (see, e.g., Anders and Zadnik, 1985; and Jarosewich and Dodd, 1981, and references therein). This takes into account the less extensive aqueous alteration of the matrix-like material compared to e.g. that of Semarkona (LL3.0). The constituents of Bishunpur generally are slightly finer-grained than those of Semarkona and small metallic grains are distributed throughout the sample (see Fig. 2.5). Therefore a proper separation of pure fine-grained rims and matrix material was somehow limited. However, Bishunpur shows well developed different types of MS-rich rims around chondrules (see also Fig. 5.1). We thank the Natural History Museum, London, for providing 2 g of Bishunpur.
2.1.6 Krymka (LL3.1)

Krymka fell as a meteorite shower in 1946 in the Ukraine. Roughly 50 kg of the meteorite were recovered. Krymka itself is classified as an LL3.1 chondrite (see, e.g., Grady 2000; and Jarosewich and Dodd, 1981, and references therein), however, it also contains single DIs of probably carbonaceous chondrite material (Semenenko et al., 2001). In one piece of Krymka, Semenenko et al. (2001) observed a DI with unusually “cloudy” textures, suggesting a very primitive nature of this object. V. P. Semenenko kindly provided the counterpart of this piece of Krymka (see Fig. 2.6) containing the second half of the cloudy dark inclusion for noble gas analyses. Fortunately, the large concentrations of cosmogenic noble gases in Krymka (Tab. 2.1) did not substantially affect the determination of the

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**Fig. 2.5:** Composite BSE-image of the thick section of Bishunpur. Since well rounded chondrules of different sizes are closely packed, matrix-like material is restricted to interstices and thin fine-grained rims surrounding some chondrules (not visible in this overview). MS-rich material occurs as coatings around chondrules (A) and as small isolated patches in the matrix (B).
trapped noble gas component of the DI, since the trapped noble gas concentra-
tions of this inclusion were extremely high. To be able to relate the DI data to the
Krymka host meteorite, we also measured chondrules, matrix, and MS-rich rims.
As expected, the noble gas inventories of these constituents are in fact dominated
by cosmogenic contributions.

**FIG. 2.6:** Composite BSE-image of the Krymka thick section. As for the other ordinary chon-
drites of this study, matrix-like material is restricted to small interstices between and thin fine-
grained rims (arrows) around chondrules, which are variable in size. MS-rich material forms
coatings around chondrules (A) or is present as isolated patches in the matrix (B). Also visible is
the large homogeneous fine-grained DI (marked by a dashed line). High-resolution images of
this object displayed “cloudy” accretionary features (see text for further explanation and refer-
ence).

### 2.2 Sample preparation

The sample preparation for the noble gas analyses was generally based on com-
posite BSE-images of thick sections of the selected meteorites. Only in the case
of Leoville and Krymka some macroscopically visible samples were separated
from areas of the thick sections, which had not been previously imaged. For im-
aging by scanning electron microscopy the sample generally has to be well polished and coated with a thin layer of carbon to increase the conductivity of the sample. However, the selected samples for this study were polished only slightly in order to minimise contamination with silicon carbide from the polishing paste. We omitted also the carbon coating, except for the first sections of Allende, since remainders of conductive carbon could form CO₂ during a noble gas analysis and thus interfere with ²²Ne (see section 2.4.2). Consequently, the quality of the BSE-images was reduced because of these restrictions. The images of Allende shown in Fig. 2.1 were taken at the scanning electron microprobe (SEM) JEOL JSM 840-A at the Institute of Planetology at the University of Münster, Germany. The images of all other meteorite samples were taken with a CamScan CS44LB at the Institute of Solid State Physics at ETH Hönggerberg.

The samples for the noble gas analyses were removed from the thick sections with a stainless steel needle, paying special attention not to cross-contaminate the various constituents. One single sample, e.g., of one chondrule, consisted of up to ~6 pieces with a total mass between 20 and 900 μg. Few samples of metal grains and chondrules were cleaned with acetone and subsequently with demineralised water in an ultrasonic bath (1 min each) to remove possible remnants of matrix-like material. After weighing, each sample was filled into one of the nine storage holes of an aluminium sample holder. Each aluminium sample holder was used for one sample charge only.

The nomenclature of the samples is explained in detail, e.g., in section 4.3.

2.3 Noble gas extraction

2.3.1 The infrared-laser noble gas extraction line

The infrared (IR) - laser noble gas extraction line (Fig. 2.7) is the most recent part of a large noble gas extraction and measurement system, which is exclusively used for analysing extraterrestrial samples. For the noble gas analyses the mass spectrometer “Albatros” is used, which is especially suitable for measuring low noble gas concentrations. The whole system is kept under ultra-high-vacuum conditions (10⁻⁸ Torr in the extraction lines down to 10⁻¹⁰ Torr in the spectrometer) by several turbo molecular- and ion-pumps.

The major advantage of the laser line is its low blank, which does not significantly increase when applying the laser (see Tab. 2.2) and its small volume. Therefore, the laser line is especially suitable for extracting noble gases from very small and/or very gas-poor samples.
The Nd-YAG-laser has a wavelength of 1024 nm and can be operated in pulsed or continuous wave (CW) mode. For melting small sample grains the CW mode is most suitable (see chapter 3). The output power of the laser is variable with a maximum of ~60W. The laser beam can be focused to ~140 µm, which is ideal for melting grains in this size range. The melting procedure can be observed via a CCD camera attached to the laser system. The sample holder is illuminated through the same optical system used to focus the laser beam, so that both, the IR and the visible light beam are focused on the same spot. The laser system is further equipped with a timer, which allows to precisely reproduce melting times (e.g., for first and second extraction of a sample, see section 2.4.3.2). The laser light enters the sample chamber through a glass viewport transmitting light with wavelengths between 320 and 2700 nm (Varian®). The chamber can be moved in x, y and z direction by micrometer screws. The sample holder is water-cooled, which avoids significant heating of neighbouring samples, as tests have shown. The sample chamber is connected via two valves to a pumping system and to the extraction line, where the gas is cleaned and separated into a He/Ne and an Ar-fraction (Fig. 2.7). Between the sample chamber and the extraction line a U-shaped cold trap is mounted. During a sample extraction it is cooled.

**FIG. 2.7:** The IR-laser extraction line. Spec. = mass spectrometer ("Albatros"). The width of the area shown is ~1 m. See text for further explanation.
with liquid N$_2$ mainly to freeze out H$_2$O and CO$_2$, which are released in large amounts from chondritic samples (Fig. 2.8).

Experiments have shown that the noble gas fractions analysed in this study are not significantly frozen onto the cold trap. The extraction line itself consists of two getters filled with Ti/Zr pellets (Danielson®), which are operated at 280 °C to remove further reactive gases. Additionally, an activated charcoal finger at the temperature of boiling liquid N$_2$ (-196 °C) is used to separate the Ar- from the He/Ne-fraction.

### 2.3.2 Sample gas extraction

One analysis run generally lasts several days and comprises the measurements of all samples in one sample holder and associated blanks and calibrations. Before each analysis run atmospheric gases adsorbed on the samples and the sample chamber have to be removed. Therefore, after mounting the sample holder in the
chamber, the system is evacuated and the chamber is subsequently baked at 100 °C for 24 hours.

To extract the sample gases, the sample is heated very carefully by increasing the energy of the laser beam until the sample starts glowing and later forms a melt droplet. To ensure a complete gas extraction, the melt droplet and the recondensed material in the storage hole are heated repeatedly. The gas extraction generally takes between 2 and 4 minutes, depending on the size and chemistry of the sample. However, during this procedure it often happens that samples with a high volatile content “jump” out of the focus (in few cases even out of the storage hole), which requires careful re-adjustments of the sample. This increased the irradiation time in some cases to up to 8 minutes.

It might be possible that during the irradiation a part of the evaporated sample material condenses onto the viewport glass (Fig. 2.9), which could cause laser light to couple into the glass and to destroy the latter. Therefore, the sample chamber with its cold trap is completely separated from the rest of the system during the gas extraction phase.

**Fig. 2.9:** Viewport glass with condensed sample material (dark round areas). At the transmission points of the IR laser beam (centres of the dark areas) a part of the light had coupled into the glass and begun to melt it.
2.3.3 Cleaning of the gas and separation of the He/Ne- from the Ar-fraction

Most of the water and CO₂ is frozen out in the cold trap during the sample gas extraction phase. The noble gases and the remaining active gases are then expanded into the extraction line. There, the gases are further cleaned and the He/Ne-fraction is separated from the Ar-fraction, since ⁴⁰Ar interferes with ²⁰Ne (see section 2.4.2). While the Ar-fraction is trapped in the activated charcoal at -196 °C, the He/Ne-fraction remains in the gas phase and is cleaned by the two getters. After 10 minutes the He/Ne-fraction is expanded into the mass spectrometer, where an Al/Zr getter (SAES®) at 20 °C continuously removes H₂. The activated charcoal in the spectrometer held at -196 °C removes Ar, which is on the one hand continuously desorbed from the walls of the spectrometer. On the other hand Ar is removed from the walls by hitting ions from the sample gas (memory effect). During the measurement of the He/Ne-fraction, the charcoal of the laser extraction line is heated to ~50 °C to release the Ar-fraction, which is then cleaned for a second time. When the He/Ne measurement is finished, the spectrometer is pumped for several minutes. Subsequently, the Ar-fraction is expanded into the spectrometer and analysed.

2.4 Noble gas measurements and data reduction

2.4.1 Mass spectrometry

The noble gases were measured using the mass spectrometer “Albatros”. Albatros is a non-commercial mass spectrometer (90°, 21 cm radius) equipped with an electron multiplier operating in counting mode and a Faraday cup. The upper limit of the multiplier is set to 5×10⁵ Hz, which corresponds, e.g., to ~1.5×10⁻⁸ cm³ STP ²²Ne. Generally, most of the isotopes were analysed on the electron multiplier, except for ⁴He and ⁴⁰Ar, which were measured on the Faraday cup. In the He-Ne fraction, also the active gases H₂, H₂O, CO₂ and ⁴⁰Ar were continuously monitored; CH₄ was measured only at the beginning of each measurement. During the analysis of the Ar isotopes, ³⁵Cl and ³⁷Cl were continuously monitored because of the possible formation of H³⁵Cl and H³⁷Cl, which could interfere with ³⁶Ar and ³⁸Ar, respectively.

2.4.2 Interferences

The current mass resolution (M/ΔM of ~550) of the spectrometer is sufficient to resolve ³He from HD, and also ²⁰Ne is separated from H₂¹⁸O (see section 3.4 for a detailed discussion). However, doubly ionised CO₂ and ⁴⁰Ar interfere with ²²Ne
and $^{20}\text{Ne}$, respectively. In order to reduce the double ionisation of $\text{CO}_2$ and $^{40}\text{Ar}$ and thus to minimise the necessary corrections, the gas in the mass spectrometer is ionised with 45 eV electrons, only.

First, the $^{20}\text{Ne}$ and the $^{22}\text{Ne}$ signals are corrected for interferences from $^{40}\text{Ar}^{++}$ and $\text{CO}_2^{++}$. The $^{40}\text{Ar}^{++}/^{40}\text{Ar}$ is $0.0012 \pm 0.0006$ (Busemann, 1998). The doubly ionised $^{40}\text{Ar}$ portion is subtracted from the respective $^{20}\text{Ne}$ signal in all $\text{He}/\text{Ne}$ measurements. The contribution of $^{40}\text{Ar}^{++}$ to the sample $^{20}\text{Ne}$ was generally below 1%. The $\text{CO}_2^{++}/\text{CO}_2$ is determined via the isotopic ratio $^{20}\text{Ne}/^{22}\text{Ne}$ in so called “residuals”. Thereby, the noble gas signals in the “empty” spectrometer are measured. It is assumed that the $^{20}\text{Ne}/^{22}\text{Ne}$ ratios in the residuals are of atmospheric composition. Using the $^{40}\text{Ar}^{++}$-corrected $^{20}\text{Ne}$ signal of the residual, the air portion of $^{22}\text{Ne}$ is calculated. The measured $^{22}\text{Ne}$ signal is generally slightly higher, which is attributed to interfering $\text{CO}_2^{++}$. The resulting $\text{CO}_2^{++}/\text{CO}_2$ was constantly low, $(5\pm4)\times10^{-4}$, over 2 years. The portion of $\text{CO}_2^{++}$ on mass 22 was subtracted in all measurements. It contributed on average ~1% to the $^{22}\text{Ne}$ of the samples.

Since the $^{35}\text{Cl}$ and $^{37}\text{Cl}$ signals during the analyses of the Ar isotopes are very low and constant in blanks and samples, possible interferences of $^{35}\text{ClH}$ on $^{36}\text{Ar}$ and of $^{37}\text{ClH}$ on $^{38}\text{Ar}$, would be self-corrected by the blank subtraction. Therefore no particular correction was applied for these items.

### 2.4.3 Blanks

Below, the different types of blanks used for the correction of the samples and the calibrations are described. Average $^4\text{He}$, $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations for “cold”, “sample”, and “aluminium” blanks are given in Tab. 2.2. Especially for the chondrules, a precise blank determination and correction was important, since the noble gas concentrations of the chondrules are often only slightly above the blank levels. In chapter 5 the blank correction for these samples is described in detail.

#### 2.4.3.1 Cold Blanks

Cold blanks simulate a sample extraction without application of laser energy. They were always measured at the beginning and sometimes also within an analysis run. They served to check the noble gas background in the IR-laser extraction line and represent a measure for a possible variability of all three blank types. The slow calibrations (SCs, see below) were corrected using cold blanks. Fig. 2.10 shows the evolution of the $^4\text{He}$, $^{20}\text{Ne}$ and $^{36}\text{Ar}$ cold blanks over two
years, including their average concentrations (grey bars) and standard deviations (light grey areas). Compared to the respective average values, the blanks were relatively constant. However, $^{36}$Ar shows several single “peaks” (not included in the average value), which are not visible for $^{4}$He and $^{20}$Ne. In these cases the cold blank had been measured immediately (pumping duration ~30 min) after a SC, which contains high Ar-concentrations. This demonstrates that especially Ar is sensitive to memory effects.
Fig. 2.10: Evolution of the $^4$He (a), $^{20}$Ne (b), and $^{36}$Ar (c) cold blanks over two years. Given are the average blank concentrations and standard deviations, which are also indicated as grey bars and light grey areas, respectively. Data points in brackets were not used for the calculation of the average value and the standard deviation. See text for further explanations.
2.4.3.2 Sample and aluminium blanks

Sample blanks are analysed by applying the laser on already degassed samples. For this, extraction time and energy are similar to those of the previous sample extraction procedure. However, since the total sample volume had been significantly reduced due to evaporation during the main sample extraction step, the total energy per sample mass was higher during the second irradiation. Sample blanks served to check the completeness of the noble gas extraction of the main sample step. Sample blanks without discernible amounts of sample gas were used for the blank-correction of the samples.

The sample blanks were generally slightly higher than the cold blanks (see Tab. 2.2). This can be attributed to the application of the laser and the associated heating procedure during the sample blanks. However, it was sometimes difficult to decide whether the enhancement of the sample blank compared to a cold blank was due to the application of the laser or due to small amounts of sample gas. Therefore, additional “aluminium blanks” were performed by applying the laser onto the aluminium sample holder with the same irradiation parameters as for the sample but without heating any sample material. The obtained noble gas amounts served as reliable blank levels to decide whether a sample blank contained remnants of sample gas. If so, both, the gas of the sample blank and that of the sample were corrected with a suitable aluminium or cold blank before the nominal gas amounts of sample and sample blank were added. This was the case for 14% of the He-Ne fractions of all samples, and for 23% for all Ar-fractions.

In certain cases no sample blanks were measured: When (i) a sample displayed noble gas signals near the blank level, or (ii) much of the sample material had condensed on the glass viewport, so that the possibility existed to destroy the glass during a second irradiation of the sample (see Fig. 2.9). The blanks for the fine-grained matrix-like samples contributed on average 2% to the total $^{20}\text{Ne}$ signal and <1% to the total $^{36}\text{Ar}$ signal (see chapter 4). The blank contributions to the measured $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations of the chondrules were on average 4% and 16%, respectively. Only for some nearly gas-free chondrules, both blanks increased up to 100% (see chapter 5).


**Table 2.2: Average cold, aluminium, and sample blanks from all analysis runs.**

<table>
<thead>
<tr>
<th></th>
<th>$^4$He (10$^{-12}$ cm$^3$STP)</th>
<th>$^{20}$Ne (10$^{-13}$ cm$^3$STP)</th>
<th>$^{36}$Ar (10$^{-13}$ cm$^3$STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold blank$^1$</td>
<td>4.5±1.6</td>
<td>1.1±0.6</td>
<td>1.4±0.7</td>
</tr>
<tr>
<td>Aluminium blank$^1$</td>
<td>6.5±1.5</td>
<td>1.6±0.9</td>
<td>2.3±1.6</td>
</tr>
<tr>
<td>Sample blank$^1$</td>
<td>4.0±1.7</td>
<td>1.2±0.6</td>
<td>1.8±0.7</td>
</tr>
</tbody>
</table>

$^1$ The lowest gas concentrations are displayed by the cold blanks. Sample and aluminium blanks are slightly higher. See text for further explanation. Given uncertainties are the standard deviations of the respective blank values.

### 2.4.4 Calibrations and determination of noble gas concentrations and isotopic ratios

Calibrations are needed to determine the sensitivity of the spectrometer (see Tab. 2.3) and the mass fractionation. For this, standards with precisely known concentrations and isotopic compositions of high purity He-Ne and Ar are used. Known amounts of these standard gases were regularly expanded as Slow Calibrations (SCs) and Fast Calibrations (FCs) into the system. Whereas the Ar isotopic composition of the standard gas is atmospheric, Ne is slightly (5% per amu) enriched in the heavy isotopes compared to air (Wieler et al., 1989). Helium is enriched in $^3$He ($(^3$He/$^4$He)$_{FC} = 0.047; ($^3$He/$^4$He)$_{SC} = 0.06$).
Tab. 2.3: Sensitivities of the ion counter and the Faraday cup in the Albatros.

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity Counter (x10^{-14} cm^3 STP/Hz) (^1)</th>
<th>Sensitivity Faraday cup (x10^3 cm^3 STP/A) (^1)</th>
<th>Split factor (^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3)He</td>
<td>2.6</td>
<td></td>
<td>1.48</td>
</tr>
<tr>
<td>(^4)He</td>
<td></td>
<td>153</td>
<td></td>
</tr>
<tr>
<td>(^{20})Ne</td>
<td>2.0</td>
<td></td>
<td>1.46</td>
</tr>
<tr>
<td>(^{36})Ar</td>
<td>1.7</td>
<td></td>
<td>no split</td>
</tr>
<tr>
<td>(^{40})Ar</td>
<td></td>
<td>9.5</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Given are average sensitivities of the counter and the Faraday cup over 2 years. Standard deviations are <1.2% for He and Ne, and <2.5% for the Argon sensitivity. These uncertainties include daily sensitivity variations, which cancel out by using SC/FC and Sample/FC ratios. The corrected uncertainties are below 0.8% except for \(^{21}\)Ne with 1.4%. The latter is mainly due to the low gas concentrations in the FCs and SCs resulting in an increase of the statistical error of the \(^{21}\)Ne measurement. \(^2\) Since the He-Ne fractions of the samples were expanded in a \(-30\)% smaller volume than the SCs, the SC gas amounts were reduced by these \(-30\)% (division by split factor). Given sensitivities for He and Ne on counter and Faraday cup represent the reduced values. For the Ar-fraction no split factor is necessary (see text for explanation).

Sample gas is generally treated identical to the slow calibration gas in order to directly compare their gas amounts. However, it was not affordable to dilute the small sample gas amounts released by laser extraction into the larger volume needed to expand the SC gas into the mass spectrometer. Therefore, split factors were determined, which were used to reduce the standard concentrations of the He-Ne SC (Tab. 2.3). Since the Ar-fractions of SCs and samples are quantitatively trapped in the activated charcoal of the extraction line, and then re-expanded into identical volumes, no correction of the Ar-concentrations was necessary. Generally, one SC was measured at the end of every analysis run.

To correct for long-term variations of the mass spectrometer sensitivity, Fast Calibrations are analysed daily. Thereby the calibration gas is expanded from the reservoir directly to the spectrometer but not into the entire laser extraction line. The sensitivity of the spectrometer is quite stable; the standard deviation of the FC/SC ratios over a period of 2 years is <1.3% for all isotopes of He, Ne, and Ar.

Finally, the noble gas concentration of one reference isotope of He, Ne, and Ar, (generally \(^4\)He, \(^{20}\)Ne, \(^{36}\)Ar, respectively), is obtained by comparing the noble gas signals of the samples to those of the SC. The daily variability of the spectrometer sensitivity is corrected for by comparing (sample/FC) / (SC/FC) pairs.
The He, Ne and Ar isotopic ratios were directly determined from the blank-corrected signals. However, the isotopic ratios have to be corrected for mass discrimination since the sensitivity of the mass spectrometer varies slightly for the different isotopes of one element. The mass discrimination is determined by comparing the measured isotopic ratios of the FCs and SCs with their actual ratios. For example, if the measured $\frac{^{20}\text{Ne}}{^{22}\text{Ne}}$ ratio of a calibration is 9.65, which is slightly lower than the actual ratio of 9.72, the $\frac{^{20}\text{Ne}}{^{22}\text{Ne}}$ ratios of all samples have to be increased by the factor of $\sim1.01$. The mass discrimination of the He, Ne, and Ar isotopic ratios on the multiplier in counting mode is generally low, $<0.9\%/\text{amu}$.

2.4.5 Uncertainties

All reported uncertainties in this work are $1\sigma$. The uncertainties of the noble gas concentrations always include statistical errors, uncertainties from the blanks, splitting, and interferences. In some cases a substantial part of the uncertainty is also contributed by the uncertainty of the sample weight. Not included is the short-term variability of the spectrometer sensitivity between the measurement of a FC and a sample as well as the uncertainty from incorrect counting of the calibration gas volumes used. Comparisons of gas concentrations of identical samples measured in different laboratories revealed a $\sim3\%$ uncertainty in the determination of the absolute gas concentrations (Wieler et al., 1989). However, this uncertainty does not affect the comparison among our data, since all samples of this study were measured on the same mass spectrometer with the same calibration reservoirs. Thus, also this error is not included in the given uncertainties. The uncertainties of the isotopic ratios include statistical, interference and blank uncertainties, as well as uncertainties from the mass discrimination corrections.
CHAPTER 3

Tests of the IR-laser

and the extraction line
The initial objective of this work was to decipher the microdistribution of noble gases in different constituents of unequilibrated chondrites, e.g., in CM chondrites. The constituents (e.g., rims, matrix, chondrules) of this chondrite group are generally in the size range of several tens of microns. It was originally planned to analyse He and Ne \textit{in situ} in thick sections, which would allow a high throughput of samples. To test the applicability of the laser for this requirement and the degassing properties of a chondritic sample during \textit{in situ} studies, a first test on a thick section of Allende was performed. This test revealed three major problems:

1. The focus area of the IR-laser beam was too large for the desired application.
2. Large amounts of active gases were released, which compromised the measurements of noble gases.
3. It appeared possible that the released noble gases might be substantially mass fractionated.

By modifications of the set-up of the IR-laser and the extraction line a part of the problems could be solved. However, also an adaptation of the extraction technique was necessary. Below, the first tests and resulting modifications are presented.

\textbf{3.1 First test on Allende}

Several \textit{in situ} shots of the laser were performed on a thick section of Allende to determine the focus area of the IR-laser beam and to roughly estimate the amounts of noble and active gases released from a chondrite sample. The laser was operated in the energy-rich multi-mode with energies and irradiation times given in Tab. 3.1. The extracted gases were monitored and backscattered electron images of the laser pits were taken (Fig. 3.1).

\textbf{3.1.1 Results and implications}

The pits produced by the laser beam (Fig. 3.1) were irregularly funnel shaped and rimmed with material that had been ejected in the molten stage from the irradiated area.
The pits have diameters in the range of 260 and 360 μm (without taking into account the ejecta rims) (Tab. 3.1). These pit sizes and thus the focus areas of the IR-laser are distinctly too large to extract noble gases exclusively from a specific constituent in the size range of <100 μm without degassing surrounding material. Furthermore, the shape of the pits makes it difficult to determine the exact volume of extracted material, which is essential to deduce absolute gas concentrations.
Tab. 3.1: Laser application parameters and pit sizes.

<table>
<thead>
<tr>
<th>Laser pit</th>
<th>Applied energy [W]</th>
<th>Duration of irradiation [s]</th>
<th>Pit diameter [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser pit 1</td>
<td>~39</td>
<td>20</td>
<td>290</td>
</tr>
<tr>
<td>Laser pit 2</td>
<td>~46</td>
<td>60</td>
<td>260</td>
</tr>
<tr>
<td>Laser pits 3a, b</td>
<td>~46</td>
<td>30</td>
<td>320</td>
</tr>
<tr>
<td>Laser pit 4</td>
<td>~46</td>
<td>60</td>
<td>320</td>
</tr>
</tbody>
</table>

1 Identical laser application parameters were used for laser pits 3a and b (46 W and 30 s each). 2 The laser was operated in multi-mode. The given energies are estimated by assuming a roughly linear relationship between the adjustable output current of the laser lamps and the energy range (6–60 W) covered by the laser. 3 The pit sizes were determined from the inner funnel of the pit without taking into account the surrounding ejecta rims.

The test further revealed that, besides the noble gases from the sample, large amounts of active gases, e.g., CO₂, and H₂O (up to ~100 times above blank level) were extracted from the samples. These compromise the accuracy of the noble gas analyses, e.g., by mass interferences, ion scattering, and memory increase. The large amounts of active gases were probably extracted from a volume distinctly larger than the pit volume itself due to heating. It appeared also possible that, depending on their different masses and/or carrier phases, also the noble gases might have been extracted from variable volumes, which would cause isotopic and elemental fractionation.

Therefore, three major tests were performed to approach the specific problems described above (pit size, fractionation of noble gases, active gases). The tests, their results, and consequences are described below.

### 3.2 Reduction of the IR-laser focus width

#### 3.2.1 Adjustment of the optical and IR-laser focal planes

A sample is focused by moving the sample chamber in vertical (z) – direction until a sharp image is visible on the video-screen. The sample is illuminated by sending visible light through the same optical system used to focus the laser beam. To a first approximation the foci of the visible and the IR-laser light are identical. However, because the refractive indices of the lenses are wavelength dependent, it was presumed that the focus of the visible light (optical focus) might be slightly offset from the IR-laser focus. Thus, the large laser pits in the
preliminary inquiry would have been caused by a slightly defocused IR-laser beam.

To test this hypothesis, the laser was applied on an aluminium foil, which was fixed in a defined plane by using a special holder. Starting from the optical focus the foil was moved in 100 µm steps up- and downwards, each time applying the laser on the aluminium foil with identical irradiation parameters (see Fig. 3.2). The smallest pit diameters of ~140 µm were obtained 1.4 mm below the optical focus and increased rapidly slightly above and below the IR-laser focal plane. Thus, the video camera was re-adjusted in a way that the optical and the IR-laser foci were in the same focal plain.

Fig. 3.2: Aluminium foil with laser pits to determine the exact focus of the IR-laser beam. The laser was operated in multi-mode with an irradiation time of one second and power of ~56 W for each pit. See text for further explanations.

3.2.2 Operating the laser in the single-mode?

A further reduction of the size of the IR-laser focus can theoretically be achieved by operating the laser in the “single-mode” instead of the “multi-mode”, or by using apertures. However, in both cases the energy of the laser beam is reduced significantly. The multi-mode is generally used for all applications, which require high output energies, but no particularly small focus areas. Operating the laser in single-mode to obtain a smaller focus area, only one mode (T_{00}) is filtered out of the laser beam and leaves the resonator. This generally reduces the output energy (and the focus area) by a factor of
about 6, which corresponds to a maximum output energy of \( \sim 10 \) W in the single mode for the IR-laser used in this work. However, the minimum output energy necessary to produce a laser pit in a meteoritic sample with the \( \sim 140 \) \( \mu \)m focus in the multi-mode is about 14 W. Therefore, even the maximum output energy of the laser operated in the single-mode would not be sufficient to melt a meteoritic sample. Indeed, irradiations of aluminium foil and a meteoritic sample with the laser operated in single-mode with maximum output energy revealed no visible effects on both target materials. The same reduction of energy was to be expected by operating the laser in multi-mode and using an aperture to reduce the focus area of the IR-laser beam. In conclusion, a further reduction of the laser focus of presently \( \sim 140 \) \( \mu \)m by operating the laser in the single-mode or applying an aperture would have resulted in an associated maximum output energy too low to melt a meteoritic sample.

### 3.3 Fractionation of noble gases during in situ sample gas extraction

It is well known that during the in situ application of an IR-laser beam on a sample generally a volume larger than the respective pit volume itself is degassed (e.g., Nakamura et al., 1999b), which might cause fractionation. To determine the degree of fractionation, whole grain and in situ analyses of He and Ne were performed on a material with high amounts of homogeneously distributed noble gases. For this, large olivine crystals of the differentiated stony-iron meteorite Admire were chosen. Due to its long cosmic-ray exposure (\( \sim 90 \) Ma, estimated from Admire olivine Ne data given by Schultz and Franke (2000)), the olivines in Admire contain large quantities of cosmogenic noble gases, e.g., up to \( \sim 4 \times 10^{-7} \) cm\(^3\)/g \(^{20}\)Ne. The results of this test may not be directly transferable to samples containing mainly primordial noble gases due to different sitings of the cosmogenic and primordial noble gas components. Therefore, in a second test the same whole grain and in situ analyses were performed on chondritic target material containing primordial noble gases rather than cosmogenic ones. For this, fine-grained matrix and dark inclusion material of Allende was selected. For both, Admire and Allende tests, the absolute extracted noble gas amounts of the whole grain analyses were comparable to the respective gas amounts extracted in situ (see Tabs. A3.2, A3.3).

#### 3.3.1 Tests on Admire olivines

Several small, separated pieces of Admire olivines were totally extracted using the laser as described in section 2.3.2. These analyses served on the one hand to
deduce unfractionated elemental and isotopic ratios and were used on the other hand to check the homogeneity of the noble gas distribution among the olivines. In the second part of the test the noble gases were extracted in situ from large pieces of olivines. By comparing the He and Ne isotopic and elemental ratios of the whole grain and in situ analyses, the degree of fractionation during the in situ extraction were determined.

Fig. 3.3 shows some isotopic and elemental ratios of the whole grain (a) and in situ analyses (b). Absolute measured gas concentrations, as well as isotopic and elemental ratios are given in Tab. A3.1. The whole grain analyses of the olivines revealed fairly homogeneous noble gas concentrations, e.g., \( (4.0 \pm 0.2) \times 10^{-7} \, \text{cm}^3\text{STP/g} \, ^{20}\text{Ne} \). The same variability (standard deviation \( \sim 4\% \)) is displayed by the isotopic ratios \(^3\text{He}/^4\text{He}\) and \(^{20}\text{Ne}/^{22}\text{Ne}\) as well as by the elemental ratios \(^3\text{He}/^2\text{Ne}\) and \(^4\text{He}/^2\text{Ne}\) of the whole grain analyses. The scatter of the in situ isotopic ratios (standard deviations \( \leq 3\% \)) compares very well with the one of the whole grain analyses. However, the in situ elemental ratios \(^3\text{He}/^2\text{Ne}\) and \(^4\text{He}/^2\text{Ne}\) (not shown) were much more variable with standard deviations of 33% and 38%, respectively.

Fig. 3.3 also shows that the average in situ isotopic ratios are similar to the respective whole grain ratios. However, the in situ elemental ratio \(^3\text{He}/^2\text{Ne}\) is clearly fractionated, with a preferential release of the lighter isotope.

To check the fractionation in more detail, the mean values of isotopic and elemental ratios of the whole grain and in situ samples (without taking into account their respective uncertainties) are compared in Tab. A3.1. Fig. 3.4 shows the
mass fractionation as deviation in % of the *in situ* (is) ratios from the whole grain (wg) ratios defined as:

$$\left[ \frac{(m_1/m_2)_{is} - (m_1/m_2)_{wg}}{(m_1/m_2)_{wg}} \right] \times 100 \quad \text{(III.1.)}$$

The resulting values are plotted versus $\sqrt{\frac{m_1}{m_2}}$.

Fig. 3.4: Fractionation of isotopic and elemental ratios of *in situ* analysed Admire samples compared to whole grain analyses. The mass fractionation in % is defined by equation III.1. See text for further explanations.

As shown in Fig. 3.4, no fractionation effect is detected for the $^{21}\text{Ne}/^{22}\text{Ne}$ ratio due to the relatively low relative mass difference of only $\sim$5%. For the $^{3}\text{He}/^{4}\text{He}$ ratio with a relative mass difference of 25%, the average $^{3}\text{He}/^{4}\text{He}$ ratio of the *in situ* analyses deviates by $\sim$5% from that of the whole grains. In contrast, the fractionation increases up to $\sim$130% for the elemental ratios $^{4}\text{He}/^{20}\text{Ne}$ and $^{3}\text{He}/^{21}\text{Ne}$ with relative mass differences of 80% and 86%, respectively.

The tests on Admire olivines are not necessarily representative for chondritic material due to (i) possibly different degassing behaviours of single minerals and fine-grained mineral assemblages and (ii) differing noble gas inventories. For example, primordial noble gases residing in specific stable carrier phases cer-
tainly have release properties different from the cosmogenic noble gases, which are mostly sited in common mineral phases of the target material. Therefore, the test described above was repeated on chondritic material.

3.3.2 Tests on Allende fine-grained material

Allende contains lower noble gas concentrations than Admire (e.g., bulk $^{20}$Ne ~4x$10^{-8}$ cm$^3$STP/g) representing a mixture of cosmogenic and primordial noble gases. These are generally distributed heterogeneously among the different constituents of the meteorite. To minimise this heterogeneity, only fine-grained matrix and DI material was selected for the test. In the first part of the test, He and Ne were measured on four whole grain samples; in the second part, noble gases were extracted in situ from the thick section. The noble gas data are given in Tab. A3.2. Fig. 3.5 shows the isotopic and elemental ratios of the Allende whole grain (a) and in situ analyses (b). The whole grain ratios are fairly homogeneous, however, their standard deviations are higher than for the Admire whole grain data: roughly 8% and 13% for $^{3}$He/$^{4}$He and $^{20}$Ne/$^{22}$Ne, respectively, and 16% and 6% for the two elemental ratios $^{4}$He/$^{20}$Ne (not shown) and $^{3}$He/$^{21}$Ne, respectively. The lowest variability is displayed by the $^{3}$He/$^{21}$Ne ratio dominated by cosmogenic noble gases; thus, the major reason for the variability of the other ratios seems to be a heterogeneous distribution of the primordial noble gases. The Allende in situ isotopic and elemental ratios display in part a distinctly higher variability than those of the whole grain analyses, between ~5% standard deviation for the $^{3}$He/$^{4}$He ratio, ~55% for the $^{20}$Ne/$^{22}$Ne ratio, and 57% and 64% for the elemental ratios $^{4}$He/$^{20}$Ne (not shown) and $^{3}$He/$^{21}$Ne, respectively. Since the scatter of the in situ ratios is distinctly higher than the one of the whole grain analyses, it cannot be attributed exclusively to a heterogeneous distribution of primordial noble gases in the samples. It rather has to be attributed to a variable fractionation during each single extraction caused by slightly different physical properties of the respective irradiated material.
Fig. 3.5: Isotopic and elemental ratios analysed from whole grain (a) and *in situ* samples (b) of Allende. Compared to Admire (see Fig. 3.3), the ratios are distinctly more heterogeneous. See text for further explanations.

The noble gas fractionation in the Allende *in situ* samples, determined using equation III.1, are plotted in Fig 3.6. The data show a trend similar to the one discussed for the Admire samples: except for the $^{21}\text{Ne} / ^{22}\text{Ne}$ ratio, which is slightly below the “zero-fractionation” line in Fig 3.6, the respective light isotope is preferentially released. However, for the *in situ* samples of Allende the degree of fractionation is more variable. For example, the mean $^3\text{He} / ^4\text{He}$ ratio of the *in situ* Allende samples is nearly 40% larger than the respective whole grain value; the *in situ* $^4\text{He} / ^{20}\text{Ne}$ is more than twice as high as the respective whole grain ratio. The *in situ* $^3\text{He} / ^{21}\text{Ne}$ ratio is even more than three times higher than the whole grain $^3\text{He} / ^{21}\text{Ne}$ ratio. The variable fractionation among different Allende *in situ* samples as well as among the Allende and the Admire *in situ* samples is mainly attributed to different physical properties of the respective target materials, which led to variable heating of the irradiated area (and its surrounding) and therefore to variable degrees of degassing of each single isotope.
The results obtained from Admire olivines and Allende fine-grained material clearly show that it is not possible to correct the isotopic and elemental ratios for fractionation caused by the in situ noble gas extraction. Mainly due to this finding, it was finally decided to perform the study not with in situ measurements, but on carefully separated whole grain samples of the chondrite constituents of interest.

### 3.4 Reduction of active gases

Large amounts of active gases compared to blank levels were released while extracting the Allende whole grain and in situ samples. The gases compromised the noble gas analyses, e.g., due to mass interferences or ion scattering. It was not possible to remove these gases with the two getters originally used to clean the sample gas. Therefore, the active gases were expanded into the mass spectrometer together with the noble gases. This led, e.g., to a significant contribution of doubly charged CO$_2$ on $^{22}$Ne: $\sim$1% for the whole grain, and up to $\sim$10% for the in situ analyses (Fig. 3.7).
The used mass resolution $M/\Delta M$ of $\sim 550$ of the spectrometer is generally not sufficient to fully resolve water with mass 20 ($^{1}_2^{18}$O) and $^{20}$Ne. The natural ratio of $^{1}_2^{16}$O:$^{1}_2^{18}$O is $\sim 0.002$. Therefore the amount of water on mass 18 ($^{1}_2^{16}$O) is monitored throughout every He-Ne measurement, and 0.2% of it is routinely subtracted from the $^{20}$Ne signal to correct for the interference. The Allende whole grain and in situ analyses (see previous chapter) were first routinely corrected for this mass interference, which revealed an average contribution of ($^{1}_2^{18}$O) to the $^{20}$Ne signal of 7% for the whole grain, and up to 100% or even higher for the in situ analyses (Fig. 3.8).
This finding shows on the one hand that the contributions of the active gases to the corresponding noble gas signals were much higher in the \textit{in situ} than in the whole grain analyses. The most probable explanation for this is that during the \textit{in situ} analyses the active gases are released from a distinctly larger volume than the noble gases, because CO$_2$ and H$_2$O are easier released than the noble gases, which are bound to resistant carrier phases. On the other hand the nominal >100\% contribution of H$_2$O to the Ne signal indicates that this mass interference is – at least in some cases – distinctly overestimated. Therefore, the peak area of the Ne and H$_2$O peak was scanned in detail to reveal the relative locations of both peaks. First, the Ne peak area of a calibration with a high TS$_{le}$ signal was scanned. To make the H$_2$O peak visible the same area was scanned in a residual (representing the empty spectrometer), which generally displays only a small Ne signal of few counts/s. The peak of ~100 counts/s (see Fig. 3.9) in the residual thus represents the peak of H$_2$O. Fig. 3.9 is a composed image of the two peaks. During both scans the peak on H$_2^{16}$O was similar, around 5x10$^4$ counts/s. The image shows that the Ne and the H$_2^{18}$O peaks can indeed
be separated depending on the relative peak height differences and the accuracy of determining the precise peak centre of the $^{20}\text{Ne}$ peak. In these cases no interference corrections would be necessary. However, no particular “threshold” could be determined to unambiguously decide, in which cases an interference correction was necessary.

![Composite scan over mass 20 ± 0.1 masses in a residual without $^{20}\text{Ne}$ and in a calibration with a $^{20}\text{Ne}$ signal of ~1x10^5 counts/s.](image)

**Fig. 3.9:** Composite scan over mass 20 ± 0.1 masses in a residual without $^{20}\text{Ne}$ and in a calibration with a $^{20}\text{Ne}$ signal of ~1x10^5 counts/s. In both cases the water background on mass 18 was ~5x10^4 counts/s. The small peak of water in the right edge of $^{20}\text{Ne}$ peak generally does not significantly contribute to the $^{20}\text{Ne}$ signal as long as $^{20}\text{Ne}$ is properly centred and its concentration is distinctly higher than that of $^1\text{H}_2^{18}\text{O}$.

To solve this problem, the amount of water in the spectrometer and its variability had to be substantially reduced. This would on the one hand reduce the possibility of interference of the $^{20}\text{Ne}$ and $^1\text{H}_2^{18}\text{O}$ peaks, so that an interference correction would not be necessary in most cases. On the other hand, if the two peaks would nevertheless interfere, the nominal corrections would be so small that they would be easily corrected via the blank subtraction.

### 3.4.1 Reduction of CO₂ and H₂O in the mass spectrometer

The reduction of the active gases CO₂ and H₂O in the He-Ne fraction was achieved by mounting a U-shaped cold trap directly to the sample chamber (see
Fig. 2.8). By cooling the trap to −196 °C, the major part of CO₂ and H₂O is frozen out, without affecting the sample He, Ne, and Ar to a measurable degree. The application of the cold trap resulted in constantly low CO₂ and H₂O amounts in the mass spectrometer in the range of blank values, and with only a minor dependence on the type of the sample and the amount of material degassed. To ensure precise measurements of the signals on the ²⁰Ne peak, i.e., to resolve the ²⁰Ne from the ¹H²¹⁸O peak, the determination of the peak centre of ²⁰Ne was only performed when the ²⁰Ne/ ¹H²¹⁸O ratio was at least ~100. Using this improved set-up, the corrections of CO₂ on Ne were reduced on average to ~1% and even for very gas-poor samples never exceeded 12% (see Fig. 3.7). Also the ¹H²¹⁸O signals compared to the ones of ²⁰Ne were reduced substantially, on average to ~3% (see Fig. 3.8). However, still blank or residual measurements often showed distinctly lower ²⁰Ne signals than expected from the contribution of 0.2% of ¹H²¹⁸O, indicating that the two peaks were indeed resolved during the measurements. Therefore, generally no interference correction was performed for ¹H²¹⁸O on the ²⁰Ne signal. Since the ¹H²¹⁸O is very constant in the samples and their respective blanks, possible small interferences of the two signals would have been corrected for via the blank-correction.

3.5 Summary and conclusion

It was originally planned to analyse in situ the noble gas signatures of small constituents of unequilibrated chondrites. For the in situ sample gas extraction from thick sections an IR-laser was available. The tests reported in this chapter revealed several problems during the in situ analyses concerning

- the too large size of the IR-laser focus area,
- the undefined extracted sample volume,
- isotopic and especially elemental fractionation during in situ sample gas extractions,
- the release of large amounts of interfering active gases, which in part compromised the measurements of noble gases substantially.

By modifying the set-up of the IR-laser and the extraction line a part of these problems could be solved:

- The focus area could be significantly reduced by a very precise determination of the focal plane of the IR-laser beam and the respective adjustment of the sample. Further reduction of the focus area would have been possible by operating the laser in the single-mode or mounting an aperture into
the optical system. However, the associated loss of output energy was too high to allow the melting of a meteoritic sample.

- The active gases CO\textsubscript{2} and H\textsubscript{2}O could be substantially reduced by freezing them out with the help of a cold trap connected directly to the sample chamber. This is essential for precise Ne measurements, both during \textit{in situ} and whole grain analyses.

However, it was not possible to reduce or correct for the isotopic and especially the large elemental fractionations during the \textit{in situ} noble gas extractions, which vary with the physical properties of each single irradiated area. Therefore, it was finally decided to perform the planned study not by extracting the noble gases \textit{in situ} from the thick sections, but by separating small whole grain samples from the constituents of interest as described in chapter 2. Although this method significantly reduced the throughput of samples, it provides several important advantages compared to \textit{in situ} analyses: first of all, no fractionation occurs during the total extraction of a whole grain sample. Analysing whole grains further provides the possibility to control the complete degassing of a sample by performing re-extraction steps (sample blanks, see section 2.4.3.2). Finally, it is possible to determine precise sample masses before the noble gas analyses to obtain precise noble gas concentrations. Due to the ill-defined sample volume extracted during an \textit{in situ} noble gas analysis, noble gas concentrations would always have been more or less rough estimates. This would have inhibited a large part of this study (see, e.g., chapter 4).
**TAB. A3.1:** He and Ne isotopic and elemental composition of Admire olivines deduced from whole grain and *in situ* analyses.

<table>
<thead>
<tr>
<th>Admire samples</th>
<th>Sample weight</th>
<th>$^4$He $\times 10^{12}$[cm$^3$STP]</th>
<th>$^3$He $\times 10^{12}$[cm$^3$STP/g]</th>
<th>$^3$He/$^4$He</th>
<th>$^20$Ne $\times 10^{15}$[cm$^3$STP]</th>
<th>$^23$Ne $\times 10^6$[cm$^3$STP/g]</th>
<th>$^23$Ne/$^20$Ne</th>
<th>$^3$He/$^20$Ne</th>
<th>$^3$He/$^23$Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>whole grain 1B</td>
<td>7.227(7)</td>
<td>52(2)</td>
<td>724(21)</td>
<td>0.1538(6)</td>
<td>2.641(1)</td>
<td>36.6(2)</td>
<td>0.868(5)</td>
<td>1.00(1)</td>
<td>19.8(6)</td>
</tr>
<tr>
<td>whole grain 4A</td>
<td>8.958(9)</td>
<td>70(2)</td>
<td>778(23)</td>
<td>0.1467(6)</td>
<td>3.59(2)</td>
<td>40.1(2)</td>
<td>0.928(7)</td>
<td>1.01(1)</td>
<td>19.4(6)</td>
</tr>
<tr>
<td>whole grain 2C</td>
<td>9.037(9)</td>
<td>69(2)</td>
<td>767(23)</td>
<td>0.1566(6)</td>
<td>3.43(2)</td>
<td>37.9(2)</td>
<td>0.883(6)</td>
<td>1.00(1)</td>
<td>20.2(6)</td>
</tr>
<tr>
<td>whole grain 4B</td>
<td>14.80(2)</td>
<td>117(3)</td>
<td>787(23)</td>
<td>0.148(6)</td>
<td>5.82(3)</td>
<td>39.3(2)</td>
<td>0.891(5)</td>
<td>1.01(1)</td>
<td>20.0(6)</td>
</tr>
<tr>
<td>whole grain 3B</td>
<td>10.07(1)</td>
<td>82(2)</td>
<td>819(24)</td>
<td>0.140(7)</td>
<td>4.00(2)</td>
<td>39.8(2)</td>
<td>0.924(6)</td>
<td>1.01(1)</td>
<td>20.6(6)</td>
</tr>
<tr>
<td>whole grain 1C</td>
<td>19.46(2)</td>
<td>144(4)</td>
<td>738(22)</td>
<td>0.153(9)</td>
<td>7.24(3)</td>
<td>37.2(2)</td>
<td>0.871(5)</td>
<td>1.01(1)</td>
<td>19.8(6)</td>
</tr>
<tr>
<td>whole grain 3A</td>
<td>10.07(2)</td>
<td>149(4)</td>
<td>741(22)</td>
<td>0.152(6)</td>
<td>7.50(3)</td>
<td>37.4(2)</td>
<td>0.865(6)</td>
<td>1.01(1)</td>
<td>19.8(6)</td>
</tr>
<tr>
<td>whole grain 4C</td>
<td>20.21(2)</td>
<td>156(5)</td>
<td>773(23)</td>
<td>0.151(2)</td>
<td>7.88(4)</td>
<td>39.0(2)</td>
<td>0.878(6)</td>
<td>1.01(1)</td>
<td>19.8(6)</td>
</tr>
<tr>
<td>whole grain 2B</td>
<td>24.22(2)</td>
<td>181(8)</td>
<td>741(26)</td>
<td>0.163(3)</td>
<td>9.01(4)</td>
<td>36.9(2)</td>
<td>0.864(6)</td>
<td>1.01(1)</td>
<td>20.1(7)</td>
</tr>
<tr>
<td>average $^1$</td>
<td></td>
<td>763(30)</td>
<td>38(1)</td>
<td>0.152(6)</td>
<td>0.597(3)</td>
<td>1.00(1)</td>
<td>51(2)</td>
<td>6.9(2)</td>
<td>6.9(2)</td>
</tr>
</tbody>
</table>

1 Uncertainties represent the standard deviations of the values. Numbers in brackets represent 1σ uncertainties in units of the least significant digit. $^4$He and $^20$Ne are given as measured gas amounts and concentrations, respectively, to be able to compare the absolute gas amounts of whole grain and *in situ* measurements and on the other hand to compare the whole grain data to literature noble gas concentrations.
Tab. A3.2: He and Ne isotopic and elemental composition of Allende matrix and DIs deduced from whole grain and in situ analyses.

<table>
<thead>
<tr>
<th>Allende samples</th>
<th>Sample weight [g] * 10^-4</th>
<th>(^4\text{He} \times 10^{-5}) [cm(^3)STP]</th>
<th>(^4\text{He} \times 10^{-8}) [cm(^3)STP/g]</th>
<th>(^3\text{He} / ^4\text{He})</th>
<th>(^{20}\text{Ne} \times 10^{-10}) [cm(^3)STP]</th>
<th>(^{20}\text{Ne} \times 10^{-8}) [cm(^3)STP/g]</th>
<th>(^{20}\text{Ne} / ^{22}\text{Ne})</th>
<th>(^{21}\text{Ne} / ^{22}\text{Ne})</th>
<th>(^{4}\text{He} / ^{20}\text{Ne})</th>
<th>(^{3}\text{He} / ^{21}\text{Ne})</th>
</tr>
</thead>
<tbody>
<tr>
<td>whole grain DI2</td>
<td>1.65(2)</td>
<td>0.523(7)</td>
<td>3160(49)</td>
<td>0.00240(4)</td>
<td>0.178(4)</td>
<td>10.8(3)</td>
<td>4.1(2)</td>
<td>0.60(3)</td>
<td>293(7)</td>
<td>4.7(2)</td>
</tr>
<tr>
<td>whole grain Ma4</td>
<td>1.73(2)</td>
<td>0.575(5)</td>
<td>3344(50)</td>
<td>0.00210(3)</td>
<td>0.151(5)</td>
<td>8.7(3)</td>
<td>3.6(2)</td>
<td>0.61(2)</td>
<td>383(14)</td>
<td>4.7(1)</td>
</tr>
<tr>
<td>whole grain DI1</td>
<td>4.48(2)</td>
<td>1.16(1)</td>
<td>2584(26)</td>
<td>0.00243(2)</td>
<td>0.409(3)</td>
<td>9.13(7)</td>
<td>4.05(8)</td>
<td>0.58(1)</td>
<td>283(3)</td>
<td>4.80(8)</td>
</tr>
<tr>
<td>whole grain Ma5</td>
<td>4.80(2)</td>
<td>1.40(1)</td>
<td>2880(29)</td>
<td>0.00235(2)</td>
<td>0.361(3)</td>
<td>7.51(8)</td>
<td>3.11(6)</td>
<td>0.67(2)</td>
<td>383(5)</td>
<td>4.20(7)</td>
</tr>
<tr>
<td>Average</td>
<td>2992(332)</td>
<td>0.0023(2)</td>
<td>9(1)</td>
<td>3.7(5)</td>
<td>0.62(4)</td>
<td>335</td>
<td>4.6(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in situ DI, margin</td>
<td>0.869(5)</td>
<td>0.00301(3)</td>
<td>0.21(3)</td>
<td>4.3(2)</td>
<td>0.59(4)</td>
<td>414(6)</td>
<td>9.4(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in situ DI, cent-</td>
<td>5.84(6)</td>
<td>0.00349(3)</td>
<td>1(1)</td>
<td>3.8(4)</td>
<td>0.60(2)</td>
<td>454(47)</td>
<td>10.3(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in situ DI (1)</td>
<td>2.37(4)</td>
<td>0.00319(4)</td>
<td>0.20(2)</td>
<td>1.94(5)</td>
<td>0.76(2)</td>
<td>1168(22)</td>
<td>9.8(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in situ DI (3)</td>
<td>6.31(9)</td>
<td>0.00325(3)</td>
<td>2(1)</td>
<td>6.9(6)</td>
<td>0.34(1)</td>
<td>402(33)</td>
<td>27(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in situ DI (4)</td>
<td>1.89(3)</td>
<td>0.00327(4)</td>
<td>0.13(8)</td>
<td>1.9(1)</td>
<td>0.33(2)</td>
<td>1463(94)</td>
<td>28(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.0032(2)</td>
<td>4(2)</td>
<td>0.5(2)</td>
<td>780(500)</td>
<td>17(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Deviation of in situ from whole grain ratios

| Deviation (1) | 40 | -1 | 15 | -133 | -265 |

(1) Uncertainties represent the standard deviations of the values. Numbers in brackets represent 1σ uncertainties in units of the least significant digit. \(^4\text{He}\) and \(^{20}\text{Ne}\) are given as measured gas amounts and concentrations, respectively, to be able to compare the absolute gas amounts of whole grain and in situ measurements and on the other hand to compare the whole grain data to literature noble gas concentrations.
Chapter 4

Microdistribution of primordial Ne and Ar in fine-grained rims, matrices, and dark inclusions of unequilibrated chondrites – Clues on nebular processes
This chapter represents a reviewed manuscript by Nadia Vogel, Rainer Wieler, Addi Bischoff, and Heinrich Baur submitted to Meteoritics and Planetary Science in June 2002. In the text, we sometimes refer to chondrule data, which are so far published in abstracts (e.g., Vogel et al. 2001a, 2002). A comprehensive description and discussion of all measured chondrule data is given in chapter 5.

4.1 Abstract

The low-temperature fine-grained material in unequilibrated chondrites, which occurs as matrix, rims, and dark inclusions, carries information about the solar nebula and the earliest stages of planetesimal accretion. The microdistribution of primordial noble gases among these components helps revealing their accretionary and alteration histories. We measured the Ne and Ar isotopic ratios and concentrations of small samples of matrix, rims and dark inclusions from the unequilibrated carbonaceous chondrites Allende (CV3), Leoville (CV3), and Renazzo (CR2), and from the ordinary chondrites Semarkona (LL3.0), Bishunpur (LL3.1), and Krymka (LL3.1) in order to rule on their genetic relationships. The primordial noble gas concentrations of Leoville, Semarkona, Bishunpur, and to a limited degree also of Allende decrease from rims to matrix. This indicates a progressive accretion of nebular dust from regions with decreasing noble gas contents, and cannot be explained by a formation of the rims on parent-bodies. The decrease is probably due to dilution of the noble-gas-carrying phases with noble-gas-poor material in the nebula. Krymka shows an increase of primordial noble gas concentrations from rims to matrix, indicating admixture of noble-gas-rich dust to the nebular region from which first rims and then matrix accreted. Larger clasts of the noble-gas-rich dust form macroscopic dark inclusions in this meteorite, which are supposed to be among the most pristine materials available to us. The noble gas signatures of Renazzo rims and matrix could be explained by both, rim formation by aqueous alteration of matrix, and by progressive admixture of noble-gas-rich dust to the reservoir from which the Renazzo constituents accreted.

The Leoville and Krymka dark inclusions as well as one of Allende show noble gas signatures different from those of the respective host meteorites. Whereas the Allende dark inclusions probably accreted from the same region as Allende rims and matrix, but suffered a higher degree of alteration, the Leoville and Krymka dark inclusions must have accreted from regions different from those of rims and matrix, respectively, and were later incorporated into their host meteorites. The noble gas data imply a heterogeneous reservoir with respect to its primordial noble gas content in the accretion region of the studied meteorites. Further studies
will have to decide, whether these differences are primary or evolved from an originally uniform reservoir.

4.2 Introduction

All groups of unequilibrated carbonaceous and ordinary chondrites (CCs and OCs, respectively) contain variable proportions of fine-grained opaque material that is interstitial to larger entities such as chondrules or inclusions. This "matrix-like" material is mainly composed of solar nebula condensates and reprocessed matter such as chondrule debris (Alexander, 1989; Brearley, 1996; Brenker et al., 2000; Buseck and Hua, 1993; Huss et al., 1981; Scott et al., 1988). Additionally, it contains presolar grains (Anders and Zinner, 1993; Huss and Lewis, 1995). The matrix-like material suffered various alteration processes both in the solar nebula and later on parent bodies (Bischoff, 1998; Brearley and Jones, 1998; Buseck and Hua, 1993). Only in type 3 chondrites it escaped severe aqueous or thermal alteration. Therefore, it still carries information about the solar nebula and the earliest stages of planetesimal accretion (e.g., Buseck and Hua, 1993).

The matrix-like material is the host for most of the primordial noble gases in unequilibrated chondrites (Huss et al., 1996; Smith et al., 1977). These reside in two main carrier phases: presolar diamonds containing the so-called HL component (Huss and Lewis, 1994a) and the enigmatic, carbonaceous “phase Q” (Busemann et al., 2000; Ott, 2002; Ott et al., 1981), which is the carrier of the “normal” primordial noble gas component (Lewis et al., 1975; Ott, 2002). Whereas presolar diamonds carry the bulk of the primordial He and Ne (Huss and Lewis, 1994a), the major part of the primordial heavier noble gases Ar, Kr, and Xe reside in phase Q (Lewis et al., 1975). The Ne and Ar isotopic and elemental noble gas compositions for Q and HL gases, as well as for other reservoirs relevant here, are given in Tab. 4.1.

Based on textural criteria, matrix-like material can be further subdivided (e.g., Brearley and Jones, 1998; Metzler et al., 1992; Scott et al., 1988; Semenenko et al., 2001; Weisberg and Prinz, 1998). Besides its most common occurrence as an opaque groundmass (termed “matrix” in the following), fine-grained rims (“rims”) around larger objects such as chondrules and inclusions are common (e.g., MacPherson et al., 1985; Metzler and Bischoff, 1989; Metzler et al., 1992). In CM chondrites the highest concentrations of primordial noble gases are found in this rim component (Nakamura et al., 1999b). The third occurrence of matrix is as macroscopically distinct dark lumps and clasts (Brearley and Jones, 1998; Endress et al., 1994; Scott et al., 1984) collectively termed “dark inclusions” (DIs).
The genetic relationships among these fine-grained components are not yet well understood.

In this paper we report the results of Ne and Ar analyses of matrix, rims, and several DI's from the type 2 and 3 CCs and OCs Allende (CV3), Leoville (CV3), Renazzo (CR2), Semarkona (LL3.0), Bishunpur (LL3.1), and Krymka (LL3.1). Apart from these “gas-rich” components we also analysed high-temperature objects like chondrules and refractory inclusions (CAIs) containing much lower concentrations of primordial noble gases. These data have been published so far in abstracts (Vogel et al., 2000, 2001a; Vogel et al., 2001b, 2002) and will be comprehensively discussed in a future paper).

The primordial noble gas concentrations and isotopic and elemental abundances of matrix, rims, and DI's provide information of the conditions and processes during the accretion of the meteorite parent bodies, such as mixing and thermal or aqueous alteration both in the solar nebula and on larger bodies. Furthermore, they hint on the genetic relationship between the above components.

Tab 4.1: Ne and Ar isotopic and elemental compositions of phase Q, presolar diamonds (HL), and other reservoirs relevant here.

<table>
<thead>
<tr>
<th></th>
<th>20Ne/22Ne</th>
<th>21Ne/22Ne</th>
<th>36Ar/38Ar</th>
<th>20Ne/36Ar</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>10.05(5)</td>
<td>0.0291(16)</td>
<td>5.34(2)</td>
<td>14 - 84</td>
<td>Busemann et al., 2000</td>
</tr>
<tr>
<td>HL</td>
<td>8.50(6)</td>
<td>0.036(1)</td>
<td>4.41(6)</td>
<td>0.103(42)</td>
<td>Huss and Lewis, 1994a</td>
</tr>
<tr>
<td>SW</td>
<td>13.8(1)</td>
<td>0.0328(5)</td>
<td>5.58(3)</td>
<td>~0.04</td>
<td>Benkert et al., 1993</td>
</tr>
<tr>
<td>Air</td>
<td>9.80(8)</td>
<td>0.0290(3)</td>
<td>5.32(1)</td>
<td>1.9</td>
<td>a) Eberhardt et al., 1965, b) Nier, 1950, c) Ozima and Podosek, 2002</td>
</tr>
<tr>
<td>GCR (typical ranges)</td>
<td>0.70-0.93</td>
<td>0.80-0.95</td>
<td>0.65(3)</td>
<td></td>
<td>Wieler, 2002a</td>
</tr>
</tbody>
</table>

1 Allende\textsubscript{cos} 0.83(2) 0.93(5)
1 Leoville\textsubscript{cos} 0.83(8) 0.93(2)
1 Renazzo\textsubscript{cos} 0.81(2) 0.87(6)
1 Semarkona\textsubscript{cos} 0.81(1) 0.87(4)
1 Bishunpur\textsubscript{cos} 0.82(4) 0.90(2)
1 Krymka\textsubscript{cos} 0.83(4) 0.92(1)

Numbers in brackets represent uncertainties in units of the least significant digit. 1 The cosmogenic 20Ne/22Ne and 21Ne/22Ne for each meteorite are average values determined in this work from chondrules of the respective meteorites. The uncertainties represent the standard deviations of the values.
4.3 Samples and Experimental Procedure

4.3.1 Samples

The samples had to meet the following requirements: (i) to ensure an only small degree of alteration, only type 2 and 3 chondrites were selected; (ii) the different components had to be large enough to enable a proper separation without cross-contamination with adjacent material, which precluded CM chondrites; (iii) the samples should not contain solar wind (SW) noble gases, since these would obscure the primordial gas components; (iv) the exposure ages of the samples should be short to minimise the contribution of cosmogenic noble gases. Krymka has an exposure age of ∼26 Ma and thus does not fulfil the latter requirement. Nevertheless, Krymka was included, since it is among the most unequilibrated chondrites, and the sample contains a DI with extraordinarily primitive textures (Semenenko et al., 2001). It turned out during the study that the DI contained extremely high primordial noble gas concentrations, which were not affected significantly by the cosmogenic contributions. However, the major proportion of the noble gases in the matrix and rims, which were measured for comparison, were indeed of cosmogenic origin.

Before sampling, most of the cut and polished meteorite chips were mapped by SEM (CamScan CS44LB with a four-quadrant BSE detector). In order to avoid contamination of the samples with carbon, the chips were not coated. Examples of the images with selected sample locations are given in Figs. 4.1-4.4.

From the chips small samples (~20 to ~600 µg) of matrix, rims, and DIs were carefully hand-separated under a binocular microscope. All samples were weighed and put into the storage holes of aluminium sample holders, each with the capacity to carry 9 samples.

Matrix and rim material was not always easy to separate from each other, since the transition between the two components is often blurred, especially for ordinary chondrites. Therefore the samples may not always represent the pure component, but can be cross-contaminated to some degree. Furthermore, the third dimension could not be monitored, which in a few cases may have even led to a substantial contamination of a sample.

The nomenclature of the samples is as follows: The first letter indicates the meteorite (A=Allende, L=Leoville, R=Renazzo, S=Semarkona, B=Bishunpur, K=Krymka). Next follows the specification of the component (Ma=fine-grained opaque matrix, Rim=fine-grained material displaying concentric structures around larger objects, DI=dark inclusion). The next letter (A-H) distinguishes the different samples of one component in the respective meteorite; numbers (1-9) attached to these letters indicate different analyses of the same object.
**Fig. 4.1:** Composite BSE image of Leoville showing the fine-grained dark inclusion L-DI-A. Also visible are typical fine-grained rims around chondrules and slightly darker interstitial matrix (not separated at this location).

**Fig. 4.2:** Composite BSE image of the studied chip of Renazzo with all sample locations. Rims and matrix were generally easy to separate.
**FIG. 4.3:** Composite BSE image of the studied chip of Semarkona with all sample locations. Note the small amount of fine-grained rim and interstitial matrix material, and the overall abundance of light-coloured metal-sulphide-rich rims and blebs.
4.3.2 Gas extraction and measurements

After a bake out in vacuum (~24 h at 100 °C) to remove atmospheric gases from the samples, the noble gases were extracted by melting the samples with an Nd-YAG-laser in CW-mode (\(\lambda = 1064 \text{ nm}\)). During melting of the samples, the output power of the laser was individually adjusted (20-30 W). The melting was observed on a video-monitor and generally took 60-300 s depending on the size of the sample and its volatile content. To avoid heating of adjacent samples, the sample holder was water-cooled. Shots on already degassed samples or on empty holes proved that no measurable amounts of noble gases from neighbouring samples were extracted.

The gas was purified with the help of a cold trap at the temperature of liquid N\(_2\) (-196°C) and two Ti/Zr getters. An activated charcoal trap cooled with liquid N\(_2\)
was used to separate the He-Ne- from the Ar-fraction. Noble gases were measured on a non-commercial mass spectrometer (90°, 21 cm radius) equipped with an ion counting electron multiplier and a Faraday cup. The gas was ionised by electrons with the energy of only 45 eV to reduce the double ionisation of ⁴⁰Ar and ⁴⁴CO₂. Thus, only ~0.1% of the measured ⁴⁰Ar (Busemann, 1998) and ~0.05% of the measured ⁴⁴CO₂ are doubly ionised and interfere with ²⁰Ne and ²²Ne, respectively. The interference correction generally accounts for less than 1% of the measured ²⁰Ne and ²²Ne in the samples. The mass resolution of the spectrometer is sufficient to resolve ³He and HD as well as ²⁰Ne and H₂¹⁸O. Therefore, no interference corrections for these background species are necessary. ³⁵,³⁷Cl signals were constantly low during the Ar analyses of samples and blanks. Therefore, possible small interferences of ³⁵ClH with ³⁶Ar and ClH with Ar would have been corrected for via the blank subtraction.

4.3.3 Blanks and corrections for cosmogenic noble gases

“Cold blanks” were determined by simulating a sample extraction procedure without laser beam. Average ²⁰Ne and ³⁶Ar cold blanks over 2 years are (1.1±0.6)×10⁻¹³ and (1.4±0.7)×10⁻¹³ cm³STP, respectively. Also measured were “s-blanks”, where an already extracted sample was re-heated. Thereby, extraction time and laser energy were identical to the respective values in adjacent sample runs, as blank signals significantly depend on these parameters. S-blanks served to verify the completeness of the noble gas extraction. Additional “a-blanks”, where the laser was applied on empty holes of the aluminium sample holder, served as reliable blank levels, since it was not always clear, whether the increase of an s-blank was due to small amounts of sample gas or simply due to the use of the laser. Typical ²⁰Ne and ³⁶Ar amounts of sample-gas-free s-blanks were only slightly higher than the cold blanks, (1.2±0.6)×10⁻¹³ and (1.8±0.7)×10⁻¹³ cm³STP, respectively. Generally, an “s-blank” was performed for every sample and was used for the blank-correction, unless in the cases where it still released discernible amounts of sample gas. These were added to the noble gas amounts of the nominal sample extraction steps, after both had been corrected with an a-blank. Despite the small sample amounts, the ²⁰Ne blanks contributed on average only 2% to the measured amounts of ²⁰Ne and never exceeded 17%. The ³⁶Ar blanks contributed on average 0.6% to the measured ³⁶Ar gas amounts and the maximum contribution was 8%.

The extracted gases represent mixtures of primordial and cosmogenic noble gases. To obtain the primordial ²⁰Ne and ³⁶Ar portions (²⁰Neₚrιm, ³⁶Arₚrιm), the measured gas amounts had to be corrected for cosmogenic contributions by two-component deconvolution. The respective endmember ratios are given in Tab.
4.1 To calculate the $^{20}\text{Ne}_{\text{prim}}$ a primordial $^{21}\text{Ne}/^{22}\text{Ne}$ of 0.03 and individual primordial $^{20}\text{Ne}/^{22}\text{Ne}$ ratios for every meteorite adopted from the regressions in the Ne-3-isotope-plots (Fig. 4.5) were used. The cosmogenic Ne isotopic composition varies significantly with the exposure depth of a given sample (Wieler, 2002a). Therefore we individually corrected the samples of each meteorite with the average cosmogenic $^{20}\text{Ne}/^{21}\text{Ne}$ ratio from chondrules of the same specimens, which did not contain significant amounts of primordial Ne. The average cosmogenic contribution to the measured $^{20}\text{Ne}$ was 19% and increased up to 65% for some very gas-poor Bishunpur and Krymka samples, resulting in larger uncertainties of the $^{20}\text{Ne}_{\text{prim}}$ concentrations of these samples (Tabs. A4.5, A4.6).

To calculate the $^{36}\text{Ar}_{\text{prim}}$ we used the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of phase Q, 5.34 (Busemann et al., 2000). All samples show measured $^{36}\text{Ar}/^{38}\text{Ar}$ ratios close to this value, indicating only a minor contribution (<2%) of cosmogenic Ar with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of 0.65 (Wieler, 2002a).

The blank contributions to the resulting $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations significantly increased only for those samples with relatively high cosmogenic contributions to the measured noble gas amounts (Tabs. A4.1-A4.6). We exclude the possibility that the primordial component in our samples is compromised by adsorbed air to any significant degree. Our average primordial $^{20}\text{Ne}/^{22}\text{Ne}$ of ~8.6 is in the range of HL-gases (Fig. 6), distinctly below the air value of 9.8 (Tab. 4.1). Also the ($^{36}\text{Ar}/^{20}\text{Ne}$)$_{\text{prim}}$ ratios all lie significantly higher than the air ratio of 1.9 (Tabs. 4.1, A4.1-A4.6) and are comparable to literature data of larger samples as far as available. Most importantly, we are able to measure primordial gas concentrations, e.g., in chondrules, which are much smaller than the values reported for the gas-rich components here (e.g., Vogel et al., 2002).

4.3.4 Calibrations

Sensitivity and mass discrimination of the spectrometer were determined by peak-height comparison using standard mixtures of high-purity Ne and Ar of atmospheric isotopic composition in amounts known to within ~1% (see also Wieler et al., 1989). All isotopic ratios were corrected for mass discrimination. The corrections for Ne and Ar on the ion counting electron multiplier are ~0.2 and 0.8%/amu, respectively.

4.3.5 Uncertainties

All given uncertainties are 1σ. The reported uncertainties of the isotope concentration data (Tabs. A4.1-A4.6) include statistical errors, uncertainties in sample weight, blanks, interferences, standard gas amounts, and, in the case of $^{20}\text{Ne}_{\text{prim}}$
and $^{36}$Ar$_{prim}$, uncertainties from the cosmogenic corrections. Not included are uncertainties due to short-term variations in spectrometer sensitivity between sample and calibration analyses, which are assumed to be <2%. Inter-laboratory comparisons revealed a ~3% uncertainty in the determination of the absolute gas concentrations (Wieler et al., 1989). However, this does not affect the comparison of gas concentrations reported here. The uncertainties of the isotopic ratios (Tabs. A4.1-A4.6) include statistical and blank uncertainties, as well as those from interference and mass discrimination corrections.

4.4 Results

4.4.1 Isotopic ratios

4.4.1.1 Neon
FIG. 4.5: Ne isotopic composition of rims (open circles), matrix (black solid circles) and dark inclusions (grey triangles) of Allende (a), Leoville (b), Renazzo (c), Semarkona (d), Bishunpur (e), and Krymka (f). The Ne composition of solar wind (SW), phase Q (Q), presolar diamonds (HL) and typical cosmogenic ratios are listed in Tab. 4.1. Numbers in boxes are the primordial $^{20}\text{Ne}/^{22}\text{Ne}$ composition (adopted $^{21}\text{Ne}/^{22}\text{Ne}$ ratio: 0.03) from the calculated mixing lines of all data points of each meteorite, respectively. The inserts are close-ups of the locations of the data points. See text for further explanations.

Fig. 4.5 shows the Ne isotopic composition of all samples for Allende (a), Leoville (b), Renazzo (c), Semarkona (d), Bishunpur (e), and Krymka (f). In
$^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$ plots the data points form mixing lines between the cosmogenic end-member in the lower right and the primordial end-members near the upper left corners (star symbols). Regression of these mixing lines (taking into account errors in $x$ and $y$ direction and forced through the cosmogenic end-members listed in Tab. 4.1) allows estimating the primordial $^{20}\text{Ne}/^{22}\text{Ne}$ ratios (numbers in boxes in Fig. 4.5), and hence the relative proportions of Ne-HL and Ne-Q for each meteorite. Due to the small database it was not possible to calculate single regressions for rims, matrix, and DIs of the respective meteorites. However, since most data points of each meteorite fall within error onto the respective mixing lines, similar mixing proportions of the two primordial Ne components Q and HL in all samples within one meteorite can be assumed. For Allende, Leoville, Renazzo, Bishunpur, and Semarkona the regressions lead to primordial $^{20}\text{Ne}/^{22}\text{Ne}$ ratios of 8.5-8.9 indicating that the Ne is mainly derived from presolar diamonds ($^{20}\text{Ne}/^{22}\text{Ne}$-HL ~8.5, Tab. 4.1) with only small - if any - contributions of Ne-Q. This is in accordance with Lewis et al. (1975) and Huss and Lewis (1995) who show that primordial He and Ne in primitive meteorites are clearly dominated by the HL-component with only a minor Q-contribution. The regression line through the Krymka samples yields a primordial $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of 9.2±0.2. This value is distinctly shifted toward the Ne-Q value of 10.1-10.7 (Busemann et al., 2000), indicating some 15-60% of Ne-Q. The slope of the regression line is dominated by the data points of the Krymka DI, which show also an extraordinarily high $^{36}\text{Ar}_{\text{prim}}$ concentration (see below). Therefore, it is assumed that mainly the DI carries the unusual enrichment of Ne-Q.

4.4.1.2 Argon

Only $^{36}\text{Ar}$ and $^{38}\text{Ar}$ are useful to characterise different primordial noble gas reservoirs, since $^{40}\text{Ar}$ is mainly produced by the decay of radioactive $^{40}\text{K}$. Furthermore, different trapped noble gas components show less variable $^{36}\text{Ar}/^{38}\text{Ar}$ than $^{20}\text{Ne}/^{22}\text{Ne}$ ratios. Only the $(^{36}\text{Ar}/^{38}\text{Ar})_{\text{HL}}$ value of 4.41 and the cosmogenic component of ~0.65 (Tab. 4.1) are distinctly different from the $^{36}\text{Ar}/^{38}\text{Ar}$ ratios for Q, SW and air, which all lie in the range of ~5.3 (Tab. 4.1). The relative cosmogenic contribution to the measured Ar is generally much lower than for Ne due to smaller cosmogenic production rates and higher primordial Ar concentrations. Most of the samples show $^{36}\text{Ar}/^{38}\text{Ar}$ ratios around 5.2 (Tabs. A4.1-A4.6), clearly indicating that essentially all primordial Ar is derived from phase Q with only minor - if any - contributions of Ar-HL. This result is in agreement with that of Huss et al. (1996) who showed that ~90% of the Ar in acid resistant residues resides in phase Q. Only the Leoville DI and the Krymka rims K-Rim-C and K-Rim-H show slightly lower $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of ~4.8. This can be attributed in all
probability to the lower $^{36}\text{Ar}_{\text{prim}}$ concentrations in these samples compared to all other samples causing a relative increase of the respective cosmogenic $^{36}\text{Ar}$ portion, and does not necessarily indicate the presence of significant amounts of Ar-HL. Since the exact primordial $^{36}\text{Ar}/^{38}\text{Ar}$ ratio can hardly be determined, we used the ($^{36}\text{Ar}/^{38}\text{Ar})_{Q}$ ratio of Busemann et al. (2000) (Tab. 4.1) to correct the measured $^{36}\text{Ar}$ for cosmogenic contributions. Because this correction is very minor (0-2%), slightly different primordial Ar compositions would hardly affect the inferred primordial $^{36}\text{Ar}$ concentrations.

4.4.2 Primordial gas concentrations and the elemental ratio ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$

Below, the $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations and the elemental ratios ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ of all samples (Tabs. A4.1-A4.6) are presented in plots ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ vs. $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ (Figs. 4.6-4.11), respectively. Two samples, L-Ma-C1 and L-Rim-C1, were discarded from the discussion due to substantial cross-contamination of rim and matrix material already noted during the sample separation. However, for both samples pure aliquots existed. Two further samples, A-Rim-A1 and B-Rim-D, were discarded on the basis of their ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios, which were in the range of bulk values of the respective meteorites or even distinctly lower. This indicates substantial contamination with chondrule material poor in primordial noble gases. Also for A-Rim-A1 a pure aliquot existed. The discarded samples are shown in brackets in the plots and marked by italics in Tabs. A4.1-A4.6.
Allende

**Fig. 4.6:** $\left( ^{36}\text{Ar}/^{20}\text{Ne}\right)_{\text{prim}}$ vs. $^{36}\text{Ar}_{\text{prim}}$ and $^{20}\text{Ne}_{\text{prim}}$ of Allende rims (open circles), matrix (black solid circles), and DIs (grey triangles), respectively. Discarded data points in brackets. The light grey and grey boxes contain all rim and all matrix samples, respectively. See text for further explanations.

Fig. 4.6 shows the $\left( ^{36}\text{Ar}/^{20}\text{Ne}\right)_{\text{prim}}$ ratios vs. the $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations of rims (open circles), matrix (black solid circles) and DIs (grey triangles) in comparison, respectively. The dark grey and light grey boxes comprise all matrix and rim data points, respectively. The presentation will be the same for all meteorites (Figs. 4.6-4.11). The box areas in Fig. 4.6 nearly fully overlap, and no differences of the primordial Ne and Ar concentrations or the elemental ratios can be detected between matrix and rim samples. All but one sample have $^{20}\text{Ne}_{\text{prim}}$ concentrations between $5 \times 10^{-8}$ and $8 \times 10^{-8}$ cm$^3$STP/g, and $^{36}\text{Ar}_{\text{prim}}$ concentrations of $11 \times 10^{-8}$ to $27 \times 10^{-8}$ cm$^3$STP/g. A-Rim-D (marked with an arrow in Fig. 4.6), which was taken from a rim around an Allende CAI, is an exception with distinctly higher $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations; $13 \times 10^{-8}$ and $41 \times 10^{-8}$ cm$^3$STP/g, respectively. The $\left( ^{36}\text{Ar}/^{20}\text{Ne}\right)_{\text{prim}}$ for rims and the matrix are identical within uncertainties and scatter between values of 3 and 4. Also the three Allende DIs are within the range of $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations given for rims and matrix. However, whereas A-DI-B and A-DI-C also show the same $\left( ^{36}\text{Ar}/^{20}\text{Ne}\right)_{\text{prim}}$ ratios as rims and matrix, that of A-DI-B ($\left( ^{36}\text{Ar}/^{20}\text{Ne}\right)_{\text{prim}} \sim 5$) is the highest ratio of all Allende samples.
4.4.2.2 Leoville

Fig. 4.7: \( \frac{^{36}\text{Ar}^{20}\text{Ne}}{^{20}\text{Ne}} \) vs. \( ^{36}\text{Ar} \) and \( ^{20}\text{Ne} \) of Leoville rims (open circles), matrix (black solid circles), and DIs (grey triangles), respectively. Discarded data points are in brackets. The light grey and grey boxes contain all rim and all matrix samples, respectively. See text for further explanations.

Fig. 4.7 shows that the Leoville rims contain distinctly higher \( ^{20}\text{Ne} \) (29\times10^{-8} to 34\times10^{-8} cm\text{cm}^{3}\text{STP/g}) and \( ^{36}\text{Ar} \) (650\times10^{-8} to 813\times10^{-8} cm\text{cm}^{3}\text{STP/g}) concentrations than the matrix \( ^{20}\text{Ne} \) (12\times10^{-8} to 29\times10^{-8} cm\text{cm}^{3}\text{STP/g}; \( ^{36}\text{Ar} \) 311\times10^{-8} to 580\times10^{-8} cm\text{cm}^{3}\text{STP/g}). The \( \frac{^{36}\text{Ar}^{20}\text{Ne}}{^{20}\text{Ne}} \) ratios are identical within errors for rims and matrix and scatter between 22 and 27. The Leoville DI (Fig. 4.1, marked with arrows) shows the lowest primordial gas concentrations of all Leoville samples. Its \( ^{20}\text{Ne} \) is ~2 times and the \( ^{36}\text{Ar} \) 24 times lower than the respective matrix value. Therefore the \( \frac{^{36}\text{Ar}^{20}\text{Ne}}{^{20}\text{Ne}} \) ratio of the DI of ~2.5 is roughly one order of magnitude lower than the average \( \frac{^{36}\text{Ar}^{20}\text{Ne}}{^{20}\text{Ne}} \) ratio of the matrix. The noble gas signature of the Leoville DI is very different from the values of rims and matrix. This suggests a separate origin of the Leoville DI from the one of rims and matrix.
4.4.2.3 Renazzo

The Renazzo rims (Fig. 4.8) show clearly lower $^{36}\text{Ar}_{\text{prim}}$ concentrations between $50\times10^{-8}$ and $64\times10^{-8}$ cm$^3$STP/g than the matrix with $72\times10^{-8}$ to $91\times10^{-8}$ cm$^3$STP/g. Also the $^{20}\text{Ne}_{\text{prim}}$ concentrations tend to be lower for the rims ($13\times10^{-8}$ to $16\times10^{-8}$ cm$^3$STP/g) than for the matrix ($16\times10^{-8}$ to $23\times10^{-8}$ cm$^3$STP/g). However, a significant overlap between the two boxes - taking in account the uncertainties - exists for the $^{20}\text{Ne}_{\text{prim}}$. This is probably due to the higher uncertainty of the correction for cosmogenic Ne than Ar. The ($^{36}\text{Ar}/^{20}\text{Ne}$)$_{\text{prim}}$ ratios are identical for rims and matrix scattering around a value of ~4.

The ordinary chondrites Semarkona, Bishunpur, and Krymka

The ordinary chondrites generally contain much less fine-grained material (at maximum 15 vol%; Brearley, 1996) than the CV chondrites (~40 vol%; Scott et al., 1996), which makes the separation of rims and matrix more difficult (compare, e.g., Figs. 2.1-2.3). Therefore, in some cases only few samples of rims and matrix could be obtained.
Fig. 4.9: \((^{36}\text{Ar} / {^{20}\text{Ne}})_{\text{prim}}\) vs. \(^{36}\text{Ar}_{\text{prim}}\) and \(^{20}\text{Ne}_{\text{prim}}\) of Semarkona rims (open circles) and matrix (black solid circles), respectively. The light grey and grey boxes contain all rim and all matrix samples, respectively. See text for further explanations.

Fig. 4.9 shows that the Semarkona rims contain on average twice as high \(^{20}\text{Ne}_{\text{prim}}\) and \(^{36}\text{Ar}_{\text{prim}}\) concentrations than the matrix. The rims have \(^{20}\text{Ne}_{\text{prim}}\) concentrations of \(20 \times 10^{-8}\) to \(24 \times 10^{-8}\) cm\(^3\)STP/g and \(^{36}\text{Ar}_{\text{prim}}\) concentrations between \(266 \times 10^{-8}\) and \(361 \times 10^{-8}\) cm\(^3\)STP/g. The matrix has \(^{20}\text{Ne}_{\text{prim}}\) concentrations of \(10 \times 10^{-8}\) to \(15 \times 10^{-8}\) cm\(^3\)STP/g and \(^{36}\text{Ar}_{\text{prim}}\) concentrations between \(131 \times 10^{-8}\) and \(221 \times 10^{-8}\) cm\(^3\)STP/g. Again, the \((^{36}\text{Ar} / {^{20}\text{Ne}})_{\text{prim}}\) ratios of rims and matrix are identical within uncertainties.
4.4.2.5 Bishunpur

**FIG. 4.10:** $(^{36}\text{Ar}^{20}\text{Ne})_{\text{prim}}$ vs. $^{36}\text{Ar}_{\text{prim}}$ and $^{20}\text{Ne}_{\text{prim}}$ of Bishunpur rims (open circles) and matrix (black solid circles), respectively. The light grey and grey boxes contain all rim and all matrix samples, respectively. Most probably due to contamination with chondrule material one rim sample (in brackets) lies in the range of bulk $^{36}\text{Ar}$ and $^{20}\text{Ne}$ concentrations. See text for further explanations.

Only few Bishunpur rim and matrix samples could be separated from the thick section. The three matrix data points in Fig. 4.10 show $^{20}\text{Ne}_{\text{prim}}$ concentrations between $4 \times 10^{-8}$ and $6 \times 10^{-8}$ cm$^3$STP/g and $^{36}\text{Ar}_{\text{prim}}$ concentrations between $85 \times 10^{-8}$ and $143 \times 10^{-8}$ cm$^3$STP/g. The two rim samples have very different noble gas signatures: B-Rim-G shows higher $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations of $8 \times 10^{-8}$ and $183 \times 10^{-8}$ cm$^3$STP/g than the matrix, however, B-Rim-D has a primordial noble gas signature in the range of Bishunpur bulk. This indicates a substantial contamination with noble-gas-poor chondrule material, and led us to discard this sample. We are aware of the fact that no differences in the primordial noble gas concentrations of rims and matrix could be stated if B-Rim-D was not discarded. However, without taking into account this sample, the Bishunpur rim has higher $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations than the matrix, whereas no differences in the $(^{36}\text{Ar}^{20}\text{Ne})_{\text{prim}}$ ratios of rims and matrix are visible.
4.4.2.6 Krymka

The Krymka rims show distinctly lower $^{20}\text{Ne}_{\text{prim}}$ ($3 \times 10^{-8}$ to $4 \times 10^{-8}$ cm$^3$/STP/g) and $^{36}\text{Ar}_{\text{prim}}$ ($60 \times 10^{-8}$ to $68 \times 10^{-8}$ cm$^3$/STP/g) concentrations than the matrix (Fig. 4.11). The matrix contains $6 \times 10^{-8}$ to $7 \times 10^{-7}$ cm$^3$/STP/g $^{20}\text{Ne}_{\text{prim}}$ and $142 \times 10^{-8}$ to $199 \times 10^{-8}$ cm$^3$/STP/g $^{36}\text{Ar}_{\text{prim}}$. Also the $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios are smaller for the rims than for the matrix. Taking into account the respective uncertainties, the $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios of the rims range from 15-21, those of the matrix from 21 to 30.

The Krymka DI (Fig. 4.4) shows the highest primordial noble gas concentrations of all samples presented here with $\sim 37 \times 10^{-8}$ cm$^3$/STP/g $^{20}\text{Ne}_{\text{prim}}$ and even $\sim 1637 \times 10^{-8}$ cm$^3$/STP/g $^{36}\text{Ar}_{\text{prim}}$. The $^{36}\text{Ar}_{\text{prim}}$ is enriched relative to matrix values by an order of magnitude and is comparable to $^{36}\text{Ar}_{\text{prim}}$ concentrations in bulk acid resistant residues, where the carrier phase Q has been chemically enriched (e.g., Busemann et al., 2000). Also its $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratio of $\sim 45$ is very different from all other samples presented here, further emphasising the extraordinary nature of this object.

4.5 Discussion

In the previous sections we have shown that the Ne isotopic composition of nearly all samples is dominated by Ne-HL. Only the Krymka DI shows a significant contribution of Ne-Q. The Ar isotopic signature is always dominated by Ar of phase Q. Clear differences in the $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations between rims and matrix could be detected in Semarkona, Krymka, and Renazzo (here...
mainly in the $^{36}\text{Ar}_{\text{prim}}$ concentration). The same is basically true for Leoville and Bishunpur rims and matrix. However, in both cases some cross-contaminated samples were discarded, which would have changed the results. Allende rims and matrix show uniform $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations except for A-Rim-D with distinctly higher primordial Ne and Ar concentrations. Except for Krymka, the $^{36}\text{Ar}/^{20}\text{Ne}_{\text{prim}}$ ratios of rims and matrix in the respective meteorites are identical within uncertainties. The Leoville and Krymka DIs as well as one of the Allende DIs display noble gas signatures different from their respective host rim and matrix material, indicating separated formation and/or alteration histories.

**4.5.1 Relationship between rims and matrix**

**4.5.1.1 Formation models of rims and matrix**

Basically two contrasting ideas about rim formation have been discussed in the literature. These are on the one hand rim formation by various processes on parent bodies, and on the other hand rim formation by accretion in the nebula. After a brief introduction of some models we will discuss them in the context of our noble gas data for rims and matrix.

In the framework of rim formation on parent bodies Sears et al. (1991, 1993) suggested that chondrule rims of the CM chondrite Murchison were formed by aqueous alteration of the host chondrule material in situ. Bunch et al. (1991) postulated the formation of granular and opaque rims around chondrules in some ordinary chondrites during impact processes partly accompanied by melting and fragmentation of the outer margins of the host chondrules. Tomeoka and Tanimura (2000) proposed the formation of phyllosilicate-rich chondrule rims in the CV chondrite Vigarano by aqueous alteration of matrix around chondrules on the Vigarano parent body. Subsequently the rock was brecciated and clasts composed of one chondrule plus surrounding matrix were rounded. The rounded clasts were finally transported to anhydrous regions of the Vigarano regolith.

„Nebular models” postulate that fine-grained dust sticks to the surfaces of chondrules and other objects to form accretionary rims in the solar nebula before these rimmed objects are incorporated into parent bodies (e.g., Hua et al., 2002; Metzler and Bischoff, 1996; Metzler et al., 1992 and references therein; Nakamura et al., 1999b). The latter authors, who found the highest primordial noble gas concentrations in the rim components of two CM chondrites also postulate an accretionary origin for these rims. MacPherson et al. (1985) conclude that rims
and matrix in Allende reflect time-dependent nebular accretion sequences, with the rims being accreted prior to the matrix.

4.5.1.2 Behaviour of primordial noble gases during alteration processes

The abundance of primordial noble gases in chondrites decreases with increasing metamorphic grade (Heyman and Mazor, 1968; Sears et al., 1980; Huss et al., 1996; Marti, 1967). Furthermore, Huss et al. (1996) found that the abundance of Q-gases ("PI" in their notation) decreases more slowly with increasing petrographic subtype than the abundance of HL-gases from presolar grains. The authors concluded that the Q-carrier is more resistant to metamorphism than the HL-carrier. Nakamura et al. (1999a) reported an inverse correlation of the abundance of heavy primordial noble gases and the degree of aqueous alteration in CM chondrites. In accordance with these results are recent laboratory experiments by Nakasyo et al. (2000) who found that artificial aqueous alteration of Allende at elevated temperatures led to a faster loss of Xe-HL than of Xe-Q, also indicating that the HL-carrier is less resistant to aqueous alteration than phase Q. Since the $^{20}\text{Ne}_{\text{prim}}$ of our samples is dominated by HL-gases and the $^{36}\text{Ar}_{\text{prim}}$ is carried by phase Q, thermal or aqueous alteration of a given sample would lead to a decrease of the primordial noble gas concentrations and a simultaneous increase of the $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratio due to the preferential susceptibility of the Ne-carrying presolar diamonds to alteration.

4.5.1.3 Formation of rims by alteration processes?

Formation of rims by aqueous alteration of matrix on a parent body as proposed by Tomeoka and Tanimura (2000) should result in lower primordial noble gas concentrations in the rims than in the matrix accompanied by higher $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios. In the case of rim formation from chondrules, which contain only very low primordial noble gas concentrations (Nakamura et al., 1999b; Vogel et al., 2000, 2001a; Vogel et al., 2001b), the rims should contain substantially lower primordial noble gas concentrations than the matrix. Further, the rims could also have lower $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios than the matrix, since chondrules may have distinctly lower $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios than the surrounding matrix (e.g., Vogel et al., 2001a, 2002).

The $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ concentrations of Allende, Leoville, Semarkona, and Bishunpur do not decrease from matrix to rims. Thus, for these samples rim formation by aqueous alteration of matrix in a parent body environment can be excluded. However, Renazzo and Krymka rims have lower primordial Ne and Ar
concentrations than the matrix, therefore, rim formation by alteration of matrix would be principally possible. In fact, Renazzo rims and matrix show identical \((^{36}\text{Ar} / ^{20}\text{Ne})_{\text{prim}}\) ratios, which does not match the alteration scenarios described above. However, small differences in the \((^{36}\text{Ar} / ^{20}\text{Ne})_{\text{prim}}\) ratios between rims and matrix may have remained undetected due to the relatively large uncertainties of the ratios. The Krymka rims with lower primordial noble gas concentrations and lower \((^{36}\text{Ar} / ^{20}\text{Ne})_{\text{prim}}\) ratios than the matrix, could theoretically point to a rim formation by alteration of chondrule margins. However, the absolute \(^{20}\text{Ne}_{\text{prim}}\) and especially \(^{36}\text{Ar}_{\text{prim}}\) concentrations of the rims are too high to be formed from chondrules (compare Vogel et al. 2001a, 2002). Taking into account also the noble gas signature of the Krymka DI, a nebular formation scenario can consistently explain the noble gas signatures of Krymka rims, matrix and the DI (see below).

4.5.1.4 Nebular formation of rims and matrix?

In the context of nebular rim and matrix formation the noble gas carriers would have accreted together with the fine-grained silicate dust onto chondrules and other objects before the latter were incorporated into a parent body. The decrease of primordial noble gas concentrations from rims to matrix could then reflect a time-dependent decrease of the primordial noble gas abundance in the nebular region, in which progressive accretion took place. There are several possible scenarios to explain such a decrease:

1. Progressive thermal or aqueous alteration of the nebular dust itself would lead to a decrease of the primordial noble gas concentration from rims to matrix. The \((^{36}\text{Ar} / ^{20}\text{Ne})_{\text{prim}}\) would increase simultaneously due to the preferential attack of the Ne carrier during alteration.

2. Also progressive dilution of the noble gas carrying dust with noble gas poor chondrule debris would lead to a decrease of the primordial noble gas concentrations from rims to matrix. The \((^{36}\text{Ar} / ^{20}\text{Ne})_{\text{prim}}\) ratios are also expected to decrease due to the low \((^{36}\text{Ar} / ^{20}\text{Ne})_{\text{prim}}\) ratios found in chondrules (Vogel et al., 2002). It is well known that variable amounts of chondrule debris are present in the fine-grained portions of unequilibrated chondrites (Alexander, 1989; Brearley, 1996), and, e.g., Housley and Cirlin (1983) suggested that also the Allende matrix is predominantly composed of altered chondrule material.

3. Since phase Q is very refractory (Huss et al., 1996) and possibly even presolar like the HL-carrier (Busemann et al., 2001; Huss and Alexander, 1987), it can be assumed that both, phase Q and presolar diamonds, have been among the first solids in the solar nebula. Therefore, it can be expected that later condensation of the bulk of the nebular dust being free of primordial noble gases progressively
diluted the primordial noble gas concentration in the solid matter but leaves the \( (^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}} \) roughly constant. The decrease of the primordial noble gas concentrations from rims to matrix would in this case reflect a dilution due to progressive condensation.

The primordial noble gas concentrations decrease from rims to matrix in Leoville, Semarkona, and Bishunpur, which indicates a nebular rim and matrix formation. This is in accordance with the results of Metzler et al. (1992), Metzler and Bischoff (1996), and MacPherson et al. (1985), who propose rim and matrix formation by progressive accretion from slightly changing dust reservoirs. No systematic differences in the \( (^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}} \) ratios between rims and matrix could be detected, therefore, the third scenario, dilution by condensing material, would best match our results. However, the second conclusion is not unambiguous, since, again, possible small systematic variations of the \( (^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}} \) ratios between rims and matrix might have remained undetected due to the relatively large uncertainties of the \( (^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}} \) ratios.

Allende rims and matrix do basically not show differences in their primordial noble gas signatures. However, A-Rim-D alone shows nearly twice as high \( ^{20}\text{Ne}_{\text{prim}} \) and \( ^{36}\text{Ar}_{\text{prim}} \) concentrations than the other rim and matrix samples, associated with a similar \( (^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}} \) ratio. This would in principle also match the third nebular scenario as for Leoville, Bishunpur, and Semarkona. However, it is unclear, why the other Allende rims do not show this enhanced primordial noble gas concentrations. Either, the particular location of A-Rim-D in a pocket of a fluffy CAI protected this sample from later aqueous and/or thermal alteration on the parent body, which led to a decrease of the primordial noble gas concentrations of the other rims and the matrix. A more probable possibility however is that most of the rims and matrix accreted very fast to the Allende parent body, thus the time-span between accretion of rims and matrix was too short for establishing any differences in the respective noble gas signatures. The CAI could have collected its accretionary rim somewhat earlier or from a slightly differing reservoir.

4.5.1.5 Alternative formation scenarios for Krymka and Renazzo rims and matrices

The primordial noble gas concentrations and the \( (^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}} \) ratios increase distinctly from Krymka rims to matrix. None of the alteration scenarios can consistently explain these noble gas signatures. However, the data can be explained by progressive admixture of material with high primordial noble gas concentra-
tions and high \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) ratios to the region, from which first the rims and then the matrix accreted. Evidence for the presence of such material in the Krymka accretion region comes from the Krymka DI, which exactly matches the requirements stated above. Another Krymka DI with a similar noble gas inventory had already been reported by Lewis et al. (1979), showing that the Krymka parent body trapped more material with noble gas signatures very different from those of Krymka rims and matrix. Just about ~7% of DI-like material admixed to the rim material could well explain the \(^{20}\text{Ne}_{\text{prim}}\) and \(^{36}\text{Ar}_{\text{prim}}\) concentrations of the Krymka matrix. Thus, we suggest that after the accretion of fine-grained rims on Krymka chondrules, material from a different region with a noble gas signature similar to that of the Krymka DI was admixed to the original dust reservoir. The added dust led to increasing primordial noble gas concentrations and \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) ratios of the progressively accreting Krymka matrix. Macroscopic clasts of the added material form the present-day DIs in Krymka.

It is highly unlikely that the higher primordial gas concentrations of the Krymka matrix samples is an artefact due to admixture of DI-dust during sewing and polishing of the sample chip. First, the amount of 7% of DI-admixture to the matrix samples is very high taking into account that the DI occupies less than 5% of the overall surface area of the sample chip. Second, in this case we would not expect the clear difference between rim and matrix noble gas patterns, but rather homogeneous patterns for all rim and matrix samples.

The Krymka data generally show that not only rim formation by aqueous alteration of matrix can explain a decrease of the primordial noble gas concentrations from matrix to rims. Also admixture of noble-gas-rich material to a reservoir from which first rims and subsequently matrix accreted to a parent body is possible. Therefore, also the higher \(^{20}\text{Ne}_{\text{prim}}\) and \(^{36}\text{Ar}_{\text{prim}}\) concentrations in Renazzo matrix compared to rims could be explained this way, although we do not have particular evidence for the presence of a gas-rich component as in the case of Krymka. The Renazzo noble gas data do not allow a final conclusion about the formation of its rims and matrix, either by aqueous alteration or by nebular mixing processes.

### 4.5.2 Relationship between dark inclusions and rims and matrix

Studies of dark inclusions in chondrites revealed a considerable diversity in their textures, indicating multiple sources and/or complex formation or alteration histories of the DIs (Brearley and Jones, 1998). Most formation scenarios for DIs presented in the literature include the accretion of nebular dust to small or larger precursor bodies. Subsequently, these bodies are destroyed or single fragments of them are released by impacts to the nebular reservoir, from where the final accre-
tion of the cm-sized objects to the present-day host meteorites took place (Bischoff, 1989; Bischoff et al., 1988; Kurat et al., 1989; Grady et al., 1999; Johnson et al., 1990; Semenenko et al., 2001). The degrees of precursor body-, nebular-, and parent body alteration of the DI are highly variable in these scenarios (e.g., Buchanan et al., 1996; Kojima and Tomeoka, 1997; Tomeoka and Kojima, 1998).

Based on mineralogical observations, Semenenko et al. (2001) describe in detail the evolution of the Krymka dark inclusion “fragment BK13”, which is from the same DI as the Krymka DI studied here: dust particles first accreted to small porous spherules and then to fine-grained “accretionary rocks”. After mild thermal metamorphism, these were destroyed by impacts, and the fragments were transported into the nebular formation region of Krymka, where they were admixed to the Krymka host meteorite.

We will discuss the genetic relationships between the DI and their respective host meteorites based on the behaviour of the primordial Ne and Ar during alteration as described above.

Of each studied DI at least two measurements exist, which mostly are identical within uncertainties (see Figs. 4.6, 4.7, and 4.11). This shows that the primordial noble gases are distributed homogeneously throughout the respective DI. Differences in the noble gas signatures among the different DI thus cannot be attributed to a heterogeneous distribution of primordial noble gases within the objects. The Allende DI A-DI-B and A-DI-C are similar to each other and to Allende rims and matrix in their primordial Ne and Ar concentrations and \( \frac{^{36}Ar}{^{20}Ne} \) prim ratios. However, A-DI-A contains less \( ^{20}Ne \) prim and \( ^{36}Ar \) prim and a higher \( \frac{^{36}Ar}{^{20}Ne} \) prim ratio than the other DI. Taking into account the experiments of Nakasyo et al. (2000), this indicates a higher degree of alteration of A-DI-A compared to A-DI-B and A-DI-C. Since all studied Allende DI were located within an area of \(-10 \times 10 \text{ cm}^2\), parent body alteration should have affected all of them in a similar way. Therefore, it appears likely that A-DI-A obtained the differing noble gas signature due to a higher degree of alteration before it was incorporated at its final location in the Allende parent body. The more gas-rich DI A-DI-B and A-DI-C may have well formed by accretion of small lumps of dusty material from the same nebular region and simultaneously to Allende rims and matrix. They also might represent fragments of Allende itself, released and redistributed during smaller impact events on the Allende parent body. The altered A-DI-A instead could represent a fragment from a larger hydrous precursor body that accreted in the same nebular region as Allende, or from a distant water-rich region of the Allende parent body itself, from where fragments were redistributed to their present locations by impacts, as proposed, e.g., by Johnson et al. (1990).
The Leoville DI shows by far the lowest noble gas concentrations of all Leoville components studied here, with a \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) ratio one order of magnitude lower than the rim and matrix values. A decrease of the noble gas concentrations by thermal or aqueous alteration is generally accompanied by an increase of the \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) ratio, and thus cannot explain the noble gas signature of the DI as an alteration product from the same material as the Leoville rims and matrix. In agreement with Kracher et al. (1982), we propose that this clast originated from a different precursor with the required noble gas signatures, and was later added to the Leoville parent body.

The Krymka DI contains extraordinarily high primordial noble gas concentrations and also the highest elemental ratio \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) of all our samples. Since no secondary process is known, which increases the primordial noble gas concentration in a fine-grained low-temperature object, we exclude the possibility that Krymka rims and matrix are a precursor material for the DI. On the other hand, a decrease of the primordial noble gas concentrations by alteration should be accompanied by an increasing \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) ratio as stated above. Thus, the DI cannot have served as a precursor material for Krymka rims and matrix either. In agreement with Semenenko et al. (2001), we conclude that the Krymka DI ("BK 13" in the notation of Semenenko et al., 2001) originated from a different precursor, which accreted in a region with distinctly different noble gas signatures than the one that delivered Krymka rims and matrix. Further evidence for such a "Krymka DI precursor rock" is provided by a trace element and noble gas study on another DI in Krymka (Lewis et al., 1979). This sample also has a relatively high \(^{20}\text{Ne}/^{22}\text{Ne}\) of ~9.1, contains even more \(^{20}\text{Ne}_{\text{prim}}\) than ours, and has a lower \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) of ~15. Despite this difference, the extraordinarily high gas concentrations in both DIs argue for a common origin. Although Lewis et al. (1979) could not explain the particular noble gas signature of the DI, they concluded that it was a new type of primitive meteorite similar to C-chondrites. They suggested that it represents a late condensate that collected large amounts of volatiles like Ag, Bi, Tl left behind by earlier generations of meteorites. We do not expect, however, that such a mechanism can explain the high primordial noble gas concentration of the DI. This is because the noble gases reside in refractory or even presolar carriers (phase Q, presolar diamonds), which are supposed to be among the first solids in the condensing nebula and thus should somewhat be depleted in the last condensates. We rather suggest that the Krymka DIs may have been among the earliest accreted rocks in the solar nebula available to us so far. The higher \((^{36}\text{Ar}/^{20}\text{Ne})_{\text{prim}}\) and slightly lower gas concentrations in our DI compared to the one studied by Lewis et al. (1979) indicates variable degrees of mild aqueous or thermal alteration of this precursor rock.
In summary, the Allende DIs probably accreted from the same region as Allende rims and matrix, but especially A-DI-A suffered a higher degree of alteration than the others. In contrast, the DIs of Leoville and Krymka have noble gas signatures differing substantially from those of their respective host meteorites, indicating an accretion from different regions in the solar nebula, respectively. Thus, the nebular reservoir in the accretion area of the meteorites must have been heterogeneous on a large scale with respect to its noble gas signatures. However, we agree with Nakamura et al. (1999b) that on a small scale (e.g., within one DI) phase Q and the presolar diamonds seem to be well mixed. Individual present-day chondrites must have sampled material from different regions in continuously changing proportions.

4.6 Conclusions

In this study we used the primordial $^{20}$Ne and $^{36}$Ar signatures of fine-grained rims, matrices and dark inclusions of six unequilibrated chondrites to reveal genetic relationships among these components and draw conclusions on accretionary and alteration processes in the solar nebula. Differences of the $^{20}$Ne$_{\text{prim}}$ and $^{36}$Ar$_{\text{prim}}$ concentrations between rims and matrix could be detected in all studied meteorites, although in the case of Allende only for one rim sample (A-Rim-D). The differing noble gas signatures can mostly be explained in the framework of a time-dependent nebular accretion sequence of rims and subsequently matrix. The rims of Leoville, Semarkona, Bishunpur, and Allende A-Rim-D contain higher primordial Ne and Ar concentrations than the respective matrices, but constant ($^{36}$Ar/$^{20}$Ne)$_{\text{prim}}$ ratios. This is explained by a progressive accretion of fine-grained nebular dust from a reservoir with decreasing primordial noble gas content. The decrease is most probably due to a continuous dilution of the carrier phases of HL- and Q-gases with noble-gas-free condensing material. However, also the admixture of chondrule debris is possible. Underlying is the assumption that both, phase Q and the presolar diamonds, are among the first solids in the cooling solar nebula. It is unclear, why the other Allende rims and the matrix do not show differences in their primordial noble gas concentrations. A possible explanation would be that most of the fine-grained material accreted very fast to the Allende parent body, so that no measurable differences in the noble gas signatures of rims and matrix could be established. In contrast, A-Rim-D accreted to its enclosed CAI somewhat earlier or from a slightly differing reservoir. The Krymka primordial Ne and Ar concentrations and the ($^{36}$Ar/$^{20}$Ne)$_{\text{prim}}$ ratio increase from rims to matrix, indicating an admixture of primordial noble-gas-rich dust to the region, from which first Krymka rims and then matrix progres-
sively accreted. Larger clasts of such extremely gas-rich material were incorporated as DIIs into the Krymka parent body.

Renazzo also shows higher primordial Ne and Ar concentrations in the matrix than in the rims, but constant $({^{36}}\text{Ar}/^{20}\text{Ne})_{\text{prim}}$ ratios. This could be either explained by formation of the rims from matrix by thermal or aqueous alteration, or, similar to Krymka, by admixture of dust with higher primordial noble gas concentrations to the reservoir, from which first rims and subsequently the matrix accreted to the Renazzo parent body.

The Allende DIIs probably accreted from the same nebular region as Allende rims and matrix, but one DI (A-DI-A) suffered a higher degree of alteration before it was incorporated into its final location in the parent body. The DIIs of Leoville and Krymka have noble gas signatures very different from those of their respective host meteorites, indicating accretion from different nebular regions than their respective rims and matrices.

Our noble gas data imply a heterogeneous dust reservoir in the accretion region of the meteorites. This is not only due to the different noble gas signatures among the different meteorites studied, but also because of the differences of the noble gas signatures among the different fine-grained constituents within one meteorite. Further studies are needed to decide whether the heterogeneity of the nebula is primary due to variable mixing of the primordial noble gas carrier phases of HL- and Q-gases with primordial noble-gas-free matter. Alternatively, an originally uniform noble gas signature of the solar dust reservoir could have been later fractionated to various degrees in different regions of the solar nebula.

4.7 Acknowledgements

We are grateful to A. Patzer and an anonymous reviewer, whose thorough reviews considerably improved the quality of the manuscript. We further thank H. Busemann for a very helpful review of the manuscript. We thank the Muséum National d’Histoire Naturelle (Paris) and the Smithsonian National Museum of Natural History (Washington, DC) for providing samples of Renazzo and Semarkona (USNM 1805), respectively. We further thank the Natural History Museum (London) and the SSC of Environmental Radiochemistry (Kyiv) for providing samples of Bishunpur and Krymka, respectively. For assistance with SEM work we are grateful to T. Grund, A. Baarnholm and K. Kunze. This work was supported by the Swiss National Science Foundation.
**Tab. A4.1**: Ne and Ar isotopic, elemental, and primordial composition of Allende rims, matrix, and dark inclusions. Also given are the contributions of blanks to $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ and the portion of cosmogenic gases at the measured $^{20}\text{Ne}$ ($^{20}\text{Ne}_{\text{meas}}$) in %.

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<thead>
<tr>
<th>Name</th>
<th>weight [g] $\times 10^{-4}$</th>
<th>$^{20}\text{Ne}_{\text{meas}}$</th>
<th>$^{36}\text{Ar}_{\text{meas}}$</th>
<th>$^{20}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{21}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{36}\text{Ar}/^{38}\text{Ar}$</th>
<th>$^{20}\text{Ne}_{\text{prim}}$</th>
<th>blank contr. to $^{20}\text{Ne}_{\text{prim}}$</th>
<th>cosmogenic contr. to $^{20}\text{Ne}_{\text{meas}}$</th>
<th>$^{36}\text{Ar}_{\text{prim}}$</th>
<th>blank contr. to $^{36}\text{Ar}<em>{\text{prim}}$ $(^{36}\text{Ar}/^{20}\text{Ne})</em>{\text{prim}}$</th>
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<td>5.0(2)</td>
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<td>7.6</td>
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<tr>
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<td>9.8(5)</td>
<td>28(1)</td>
<td>3.5(4)</td>
<td>0.60(7)</td>
<td>5.3(1)</td>
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Gas concentrations are given in units of $[10^{-5} \text{cm}^3 \text{STP/g}]$. The correction of the measured $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations for cosmogenic contributions is explained in the text. *Italics* indicate samples that are discarded from the discussion of primordial noble gas systematics. See text for further explanation.
**TAB. A4.2:** Ne and Ar isotopic, elemental, and primordial composition of Leoville rims, matrix, and a dark inclusion. Also given are the contributions of blanks to 20Ne_{prim} and 36Ar_{prim} and the portion of cosmogenic gases at the measured 20Ne (20Ne_{meas}) in %.

<table>
<thead>
<tr>
<th>Name</th>
<th>weight [g]</th>
<th>20Ne_{meas}</th>
<th>36Ar_{meas}</th>
<th>20Ne/22Ne</th>
<th>21Ne/22Ne</th>
<th>36Ar/38Ar</th>
<th>20Ne blank contr to 20Ne_{prim}</th>
<th>cosmogenic contr to 20Ne_{meas}</th>
<th>36Ar_{prim}</th>
<th>blank contr to 36Ar_{prim}</th>
<th>(36Ar/20Ne)_{prim}</th>
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<td>10.8(6)</td>
<td>21.2(5)</td>
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<td>4.87(7)</td>
<td>7.5(9)</td>
<td>3.6</td>
<td>31.0</td>
<td>21.0</td>
<td>17.5(5)</td>
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<tr>
<td>L-Ma-B</td>
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<td>497(25)</td>
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<td>18.0</td>
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<tr>
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Gas concentrations are given in units of 10^{-4} cm^3 STP/g. The correction of the measured 20Ne and 36Ar concentrations for cosmogenic contributions is explained in the text. *Italics* indicate samples that are discarded from the discussion of primordial noble gas systematics. See text for further explanation.
<table>
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<tr>
<th>Name</th>
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<th>36Ar_meas</th>
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<th>21Ne/22Ne</th>
<th>36Ar/38Ar</th>
<th>20Ne blank contr to Ne_pnm</th>
<th>blank contr to Ne_pnm</th>
<th>36Ar_prim</th>
<th>cosmogenic contr. to Ne_meas</th>
<th>36Ar_pnm</th>
<th>blank contr. to 36Ar_pnm</th>
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Gas concentrations are given in units of [10^-18 cm^3 STP/g]. The correction of the measured 20Ne and 36Ar concentrations for cosmogenic contributions is explained in the text.
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<th>$^{21}\text{Ne}$/$^{22}\text{Ne}$</th>
<th>$^{36}\text{Ar}$/$^{38}\text{Ar}$</th>
<th>$^{20}\text{Ne}<em>{\text{blank}}$ contr to $^{20}\text{Ne}</em>{\text{prim}}$</th>
<th>$^{36}\text{Ar}<em>{\text{prim}}$ contr to $^{36}\text{Ar}</em>{\text{prim}}$</th>
<th>($^{36}\text{Ar}$/$^{20}\text{Ne}$)$_{\text{prim}}$</th>
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<td>S-Rim-D</td>
<td>0.495(4)</td>
<td>24.8(7)</td>
<td>338(4)</td>
<td>6.0(3)</td>
<td>0.34(2)</td>
<td>5.36(6)</td>
<td>23(2)</td>
<td>1.1</td>
<td>5</td>
</tr>
<tr>
<td>S-Rim-E</td>
<td>0.176(7)</td>
<td>26(1)</td>
<td>362(15)</td>
<td>6.2(6)</td>
<td>0.44(5)</td>
<td>5.34(5)</td>
<td>24(2)</td>
<td>1.5</td>
<td>6</td>
</tr>
</tbody>
</table>

Gas concentrations are given in units of $[10^{-4} \text{ cm}^3 \text{ STP/g}]$. The correction of the measured $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations for cosmogenic contributions is explained in the text.
**Tab. A4.5:** Ne and Ar isotopic, elemental, and primordial composition of Bishunpur rims and matrix. Also given are the contributions of blanks to $^{20}\text{Ne}_{\text{prim}}$ and $^{36}\text{Ar}_{\text{prim}}$ and the portion of cosmogenic gases at the measured $^{20}\text{Ne}$ ($^{20}\text{Ne}_{\text{meas}}$) in %.

<table>
<thead>
<tr>
<th>Name</th>
<th>weight [g] x$10^{-4}$</th>
<th>$^{20}\text{Ne}_{\text{meas}}$</th>
<th>$^{36}\text{Ar}_{\text{meas}}$</th>
<th>$^{20}\text{Ne}^{22}\text{Ne}$</th>
<th>$^{21}\text{Ne}^{22}\text{Ne}$</th>
<th>$^{36}\text{Ar}^{38}\text{Ar}$</th>
<th>$^{20}\text{Ne}_{\text{prim}}$</th>
<th>blank contr. to $^{20}\text{Ne}_{\text{prim}}$</th>
<th>cosmogenic contr. to $^{20}\text{Ne}_{\text{meas}}$</th>
<th>$^{36}\text{Ar}_{\text{prim}}$</th>
<th>blank contr. to $^{36}\text{Ar}_{\text{prim}}$</th>
<th>$(^{36}\text{Ar}^{20}\text{Ne})_{\text{prim}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-Ma-A</td>
<td>4.88(1)</td>
<td>7.9(1)</td>
<td>110.9(6)</td>
<td>2.46(6)</td>
<td>0.70(2)</td>
<td>5.29(3)</td>
<td>5.9(6)</td>
<td>0.8</td>
<td>25</td>
<td>110.9(8)</td>
<td>0.0</td>
<td>19(2)</td>
</tr>
<tr>
<td>B-Ma-B</td>
<td>1.44(1)</td>
<td>9.1(2)</td>
<td>143(1)</td>
<td>2.3(1)</td>
<td>0.74(3)</td>
<td>5.29(4)</td>
<td>6.5(9)</td>
<td>2.6</td>
<td>29</td>
<td>143(1)</td>
<td>0.0</td>
<td>22(3)</td>
</tr>
<tr>
<td>B-Ma-E</td>
<td>0.710(7)</td>
<td>6.2(2)</td>
<td>85(1)</td>
<td>1.8(1)</td>
<td>0.82(4)</td>
<td>5.35(4)</td>
<td>3.6(6)</td>
<td>3.2</td>
<td>42</td>
<td>85(1)</td>
<td>0.3</td>
<td>23(4)</td>
</tr>
<tr>
<td>B-Rim-D</td>
<td>0.47(2)</td>
<td>4.4(3)</td>
<td>39(2)</td>
<td>1.6(1)</td>
<td>0.89(7)</td>
<td>5.23(6)</td>
<td>2.2(4)</td>
<td>8.9</td>
<td>51</td>
<td>39(2)</td>
<td>1.2</td>
<td>18(3)</td>
</tr>
<tr>
<td>B-Rim-G</td>
<td>0.602(6)</td>
<td>10.4(3)</td>
<td>184(2)</td>
<td>3.4(2)</td>
<td>0.74(5)</td>
<td>5.30(4)</td>
<td>8(1)</td>
<td>2.0</td>
<td>20</td>
<td>183(2)</td>
<td>0.2</td>
<td>22(3)</td>
</tr>
</tbody>
</table>

Gas concentrations are given in units of $[10^{-14} \text{ cm STP/g}]$. The correction of the measured $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations for cosmogenic contributions is explained in the text. Italics indicate samples that are discarded from the discussion of primordial noble gas systematics. See text for further explanation.
**Tab. A4.6:** Ne and Ar isotopic, elemental, and primordial composition of Krymka rims, matrix, and a dark inclusion. Also given are the contributions of blanks to \(^{20}\text{Ne}_{\text{prim}}\) and \(^{36}\text{Ar}_{\text{prim}}\) and the portion of cosmogenic gases at the measured \(^{20}\text{Ne} (^{20}\text{Ne}_{\text{meas}})\) in \%.

<table>
<thead>
<tr>
<th>Name</th>
<th>weight [g] (\times 10^{-4})</th>
<th>(^{20}\text{Ne}_{\text{meas}})</th>
<th>(^{36}\text{Ar}_{\text{meas}})</th>
<th>(^{20}\text{Ne}/^{22}\text{Ne})</th>
<th>(^{21}\text{Ne}/^{22}\text{Ne})</th>
<th>(^{36}\text{Ar}/^{38}\text{Ar})</th>
<th>(^{20}\text{Ne}_{\text{prim}})</th>
<th>blank contr. to (^{20}\text{Ne}_{\text{prim}})</th>
<th>cosmogenic contr. to (^{20}\text{Ne}_{\text{meas}})</th>
<th>(^{36}\text{Ar}_{\text{prim}})</th>
<th>blank contr. to (^{36}\text{Ar}_{\text{prim}})</th>
<th>(^{36}\text{Ar}/^{20}\text{Ne}_{\text{prim}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Di-A3</td>
<td>0.316(5)</td>
<td>45(1)</td>
<td>1643(26)</td>
<td>3.51(8)</td>
<td>0.61(2)</td>
<td>5.33(4)</td>
<td>38(2)</td>
<td>1.1</td>
<td>16</td>
<td>1641(27)</td>
<td>0.0</td>
<td>43(2)</td>
</tr>
<tr>
<td>K-Di-A4</td>
<td>0.119(5)</td>
<td>43(2)</td>
<td>1619(68)</td>
<td>3.7(2)</td>
<td>0.71(5)</td>
<td>5.36(4)</td>
<td>35(3)</td>
<td>3.7</td>
<td>17</td>
<td>1620(69)</td>
<td>0.1</td>
<td>46(3)</td>
</tr>
<tr>
<td>K-Di-A5</td>
<td>0.170(5)</td>
<td>44(1)</td>
<td>1680(50)</td>
<td>3.5(1)</td>
<td>0.61(3)</td>
<td>5.37(4)</td>
<td>37(2)</td>
<td>2.1</td>
<td>15</td>
<td>1680(51)</td>
<td>0.0</td>
<td>45(2)</td>
</tr>
<tr>
<td>K-Di-A6</td>
<td>0.50(3)</td>
<td>45(3)</td>
<td>1660(100)</td>
<td>3.45(8)</td>
<td>0.62(2)</td>
<td>5.36(4)</td>
<td>38(3)</td>
<td>0.5</td>
<td>15</td>
<td>1658(100)</td>
<td>0.0</td>
<td>43(2)</td>
</tr>
<tr>
<td>K-Di-A7</td>
<td>0.618(5)</td>
<td>43.6(8)</td>
<td>1658(34)</td>
<td>3.6(1)</td>
<td>0.64(2)</td>
<td>5.4(1)</td>
<td>37(2)</td>
<td>0.5</td>
<td>15</td>
<td>1658(39)</td>
<td>0.0</td>
<td>45(2)</td>
</tr>
<tr>
<td>K-Di-A8</td>
<td>0.96(6)</td>
<td>42(3)</td>
<td>1596(104)</td>
<td>3.63(8)</td>
<td>0.64(2)</td>
<td>5.4(1)</td>
<td>36(3)</td>
<td>0.4</td>
<td>15</td>
<td>1598(106)</td>
<td>0.0</td>
<td>45(2)</td>
</tr>
<tr>
<td>K-Di-A9</td>
<td>1.31(3)</td>
<td>41(1)</td>
<td>1599(48)</td>
<td>3.73(6)</td>
<td>0.61(1)</td>
<td>5.4(1)</td>
<td>35(2)</td>
<td>0.3</td>
<td>15</td>
<td>1602(52)</td>
<td>0.0</td>
<td>46(2)</td>
</tr>
<tr>
<td>K-Ma-B</td>
<td>1.039(7)</td>
<td>13.8(3)</td>
<td>200(1)</td>
<td>1.51(4)</td>
<td>0.81(2)</td>
<td>5.21(5)</td>
<td>7.2(5)</td>
<td>1.0</td>
<td>48</td>
<td>199(2)</td>
<td>0.1</td>
<td>28(2)</td>
</tr>
<tr>
<td>K-Ma-C</td>
<td>0.737(7)</td>
<td>12.5(2)</td>
<td>143(1)</td>
<td>1.42(5)</td>
<td>0.80(3)</td>
<td>5.15(6)</td>
<td>6.2(5)</td>
<td>1.5</td>
<td>51</td>
<td>142(2)</td>
<td>0.1</td>
<td>23(2)</td>
</tr>
<tr>
<td>K-Rim-C</td>
<td>1.435(5)</td>
<td>9.5(1)</td>
<td>68.8(4)</td>
<td>1.26(2)</td>
<td>0.85(2)</td>
<td>4.96(4)</td>
<td>3.7(3)</td>
<td>5.7</td>
<td>61</td>
<td>68.0(5)</td>
<td>0.1</td>
<td>18(2)</td>
</tr>
<tr>
<td>K-Rim-H</td>
<td>0.27(1)</td>
<td>9.5(5)</td>
<td>60(3)</td>
<td>1.21(5)</td>
<td>0.87(4)</td>
<td>4.92(7)</td>
<td>3.3(6)</td>
<td>12.1</td>
<td>65</td>
<td>60.3</td>
<td>1.8</td>
<td>19(3)</td>
</tr>
</tbody>
</table>

Gas concentrations are given in units of \([10^8 \text{ cm}^3\text{STP/g}]\). The correction of the measured \(^{20}\text{Ne}\) and \(^{36}\text{Ar}\) concentrations for cosmogenic contributions is explained in the text.
CHAPTER 5

NOBLE GASES IN CHONDRULES AND ASSOCIATED METAL–SULPHIDE–RICH SAMPLES: CLUES ON CHONDRULE FORMATION AND THE BEHAVIOUR OF NOBLE GAS CARRIER PHASES
This chapter basically represents a manuscript by Nadia Vogel, Rainer Wieler, Addi Bischoff, and Heinrich Baur, which will be submitted to Meteoritics and Planetary Science. The chondrule data are related to their respective surrounding rim and matrix material discussed in the previous chapter. This is referred as “Vogel et al., 2003”.

5.1 Abstract

Chondrules represent solidified melt droplets of a probably matrix-like precursor material. They are generally believed to have lost most or all of their trapped noble gases due to the melting event, during which the chondrules were created. However, Okazaki et al. (2001b) recently reported high amounts of “subsolar” noble gases in chondrules of the enstatite chondrite Y-791790 and concluded from this that the chondrules were formed from irradiated precursor dust close to the young sun, as proposed in the X-wind model by Shu et al. (2001). To verify whether also chondrules of other chondrite classes contain a solar-like signature and thus possibly formed near the young sun, He Ne and Ar were measured in chondrules of the 6 unequilibrated chondrites Allende (CV3), Leoville (CV3), Renazzo (CR2), Semarkona (LL3.0), Bishunpur (LL3.1), and Krymka (LL3.1). Additionally, we measured metal-sulphide-rich coatings of chondrules, which formed during chondrule formation from chondrule metal. The data revealed low primordial $^{20}\text{Ne}$ concentrations in some, and low primordial $^{36}\text{Ar}$ concentrations in most of the chondrules besides cosmogenic noble gases. Those chondrules containing both, primordial $^{20}\text{Ne}$ and $^{36}\text{Ar}$, show low presolar-diamond like primordial $^{36}\text{Ar}/^{20}\text{Ne}$ ratios. In contrast, the metal-sulphide-rich rims show higher, Q-like primordial $^{36}\text{Ar}/^{20}\text{Ne}$ ratios. It is concluded that during metal-silicate fractionation in the course of chondrule formation the Ar-carrying phase Q acted “siderophile” and thus got enriched in the metal-sulphide-rich rims around chondrules. In the silicate chondrule interior, only the most stable Ne-carrying presolar diamonds survived the melting event leading to the low observed $^{36}\text{Ar}/^{20}\text{Ne}$ ratios. In neither chondrule a solar-like signature was detected.

5.2 Introduction

Chondrules are generally sub-millimetre-sized silicate spherules in primitive meteorites, which show evidence for a once molten stage. Although they are among the most common constituents in all chondrite groups, except for the CI chondrites (e.g., Brearley and Jones, 1998), their formation mechanism(s) and environment(s) are still under debate. The two main theories are (i) nebular chondrule
formation by melting of dust-ball precursors and (ii) chondrule formation in a planetary environment (e.g., Brearley and Jones, 1998; Rubin, 2000). Models about the heating mechanisms and associated energy sources are numerous (see Rubin, 2000, and references therein for a comprehensive review).

Previous noble gas studies on chondrules revealed low to zero noble gas concentrations apart from cosmogenic gases (Kim and Marti, 1994; Miura and Nagao, 1996; Nakamura et al., 1999b; Okazaki et al., 2001a; Smith et al., 1977). This is generally attributed to an extensive gas-loss due to the melting event that formed the chondrules from a more gas-rich precursor (Alexander, 1989; Connolly et al., 2001; Kong and Ebihara, 1997; Kong and Palme, 1999; Scott and Taylor, 1983). However, Okazaki et al. (2001b) recently reported high noble gas concentrations (e.g., up to $7 \times 10^{-6}$ cm$^3$STP/g $^{36}$Ar) of “subsol” composition in chondrules of the enstatite chondrite Yamato 791790, whereas the surrounding matrix contained lower gas concentrations (on average $\sim 4 \times 10^{-7}$ cm$^3$STP/g $^{36}$Ar) with a normal “phase Q”-composition (see next chapter for a brief description of the noble gas reservoirs that are relevant here). The authors explain the high subsolar noble gas concentrations by irradiation of the chondrule precursor material with solar wind (SW) noble gases from the young sun. The noble gases of originally SW composition were successively fractionated towards a subsolar composition during melting of the irradiated precursor dust. Then, the chondrules were transported to distant shielded nebular regions, where they accreted to the enstatite parent body. However, a recent study by Busemann et al. (2003) revealed that the “subsol” noble gas composition is most probably a mixture of phase Q noble gases, atmospheric gases and small amounts of solar wind noble gases. In this case, a thorough review of the interpretation of “subsol” noble gases in general and also of the data of Okazaki et al. (2001b) would be necessary. The latter authors argue that their finding has important implications on the chondrule formation region and heat source, since it supports the “X-wind-model” proposed by Shu et al. (1997, 2001). In this model chondrules are formed by melting induced by flares near the connection region of the inner part of the accretion disc and the magnetic field lines from the young stellar object. Subsequently, the chondrules are transported to asteroidal distances via the so-called X-wind. If chondrule formation in the X-region around the young sun was indeed a major chondrule formation mechanism, solar-type noble gases, or at least remnants thereof, could also be expected in other chondrules independent of their host meteorite class. However, it is also possible that several independent chondrule formation mechanisms and/or precursor materials led to different noble gas signatures in chondrules of different meteorite classes.

To test these hypotheses, we performed a systematic study of the noble gases He, Ne and Ar in chondrules of the six unequilibrated carbonaceous and ordinary
chondrites Allende (CV3_ox), Leoville (CV3_red), Semarkona (LL3.0), Bishunpur (LL3.1), Krymka (LL3.1), and Renazzo (CR2). The \(^3\)He and \(^4\)He are mainly of cosmogenic and radiogenic origins, respectively, and thus are not discussed here. Kr and Xe concentrations in the samples were indistinguishable from blank values, and therefore not measured routinely. The study also includes metal-sulphide-rich (MS-rich) droplets within chondrules and in the matrix, and MS-rich coatings of chondrules, since these constituents are thought to be genetically related to chondrules (Alexander, 1989; Connolly et al., 2001; Kong and Palme, 1999; Kong and Ebihara, 1997; Connolly et al., 1994). It is assumed that during chondrule formation small droplets of metal-sulphides (MS) segregated from the silicate melt and coalesced to form larger droplets. Due to surface tension or the spin of the chondrules the MS-droplets moved to the chondrule margins and were eventually expelled (e.g., Connolly et al., 2001; Kong and Palme, 1999). Expelled droplets formed coatings (rims) around chondrules or were completely separated from their host chondrules and are now present as isolated MS-rich patches within the matrix of unequilibrated chondrites. It is also possible that MS evaporated from, and subsequently recondensed back onto the chondrule margins (e.g., Connolly et al., 2001). A comparison of noble gas data from chondrules and MS is crucial to understand the noble gas signatures of both constituents. The data will also be related to samples of rims and matrix (called “matrix-like material” in the following) of the respective meteorites (Vogel et al., 2003) to draw conclusions on possible chondrule precursor materials and to understand the behaviour of the noble gas carrier phases during chondrule formation.

5.3 Noble gas reservoirs, samples and experimental procedure

5.3.1 Noble gases in unequilibrated chondrites

The bulk noble gas composition of a primitive meteorite generally represents a mixture of two or more different noble gas components. These were either trapped (e.g., phase Q, SW, subsolar noble gases, or gases in presolar grains) in the accreting bodies of the solar system, or later produced in situ (radiogenic, cosmogenic noble gases). We will later discuss, which of these components dominate the noble gas composition of the chondrules. Therefore we will introduce the components in some detail in the following.

Two of the major trapped noble gas components reside in specific carrier phases, which are mainly found in the matrices of unequilibrated chondrites (Huss et al., 1996; Smith et al., 1977). Presolar diamonds carry mainly He and Ne, but also contain the isotopically “anomalous” Xe-HL component (Huss and Lewis,
1994a). The carbonaceous phase Q (Lewis et al., 1975; Ott et al., 1981; Busemann et al., 2000) is less depleted in Ar, Kr, and Xe than in He and Ne, compared to solar composition. Q-gases show "normal" isotopic compositions (Lewis et al., 1975; Ott, 2002). Solar wind noble gases are implanted into the outermost grain layers of material exposed to SW radiation, e.g., at the surfaces of asteroids or the moon (Wieler, 1998). These regolithic SW noble gases are generally trapped later than phase Q and presolar diamond noble gases, the latter are therefore called "primordial" noble gases. Subsolar noble gases are elementally less fractionated than Q-gases relative to SW composition. They are found in particular in enstatite chondrites, but no distinct carrier phase for these gases could be firmly determined yet (Busemann et al., 2001; Crabb and Anders, 1981; Ott, 2002; Patzer and Schultz, 2002). Recently, Busemann et al. (2003) however showed that the subsolar noble gas component is a mixture of SW, phase Q, and atmospheric noble gases.

The in situ produced noble gases have either a radiogenic or a cosmogenic origin. Radiogenic gases, e.g., $^4$He and $^{40}$Ar, result from the decay of the long-lived radionuclides $^{235,238}$U, $^{232}$Th and $^{40}$K, whereas cosmogenic noble gases are produced by nuclear reactions induced by galactic cosmic radiation on meteoritic target material.

The Ne and Ar isotopic and elemental ratios for the described components and the terrestrial atmosphere are given in Tab. 5.1. They are used here to determine the origins of the measured noble gases in this work.

Tab. 5.1: Ne and Ar isotopic and elemental compositions of various noble gas reservoirs relevant in this study.

<table>
<thead>
<tr>
<th></th>
<th>$^{20}$Ne/$^{22}$Ne</th>
<th>$^{21}$Ne/$^{22}$Ne</th>
<th>$^{36}$Ar/$^{38}$Ar</th>
<th>$^{36}$Ar/$^{20}$Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>10.05(5)-10.7(2)</td>
<td>0.0291(16)-0.0294(10)</td>
<td>5.34(2)</td>
<td>14-84(1)</td>
</tr>
<tr>
<td></td>
<td>(1)</td>
<td>(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HL</td>
<td>8.50(6) (2)</td>
<td>0.0361(1) (2)</td>
<td>4.41(6) (2)</td>
<td>0.103(42) (2)</td>
</tr>
<tr>
<td>SW</td>
<td>13.8(1) (3)</td>
<td>0.0328(5) (3)</td>
<td>5.58(3) (3)</td>
<td>~0.04 (3)</td>
</tr>
<tr>
<td>&quot;subsolar&quot;</td>
<td>11.7(3) (4)</td>
<td>(0.0294) (4)</td>
<td>5.48(6) (5)</td>
<td>&gt;26 (4,5)</td>
</tr>
<tr>
<td>GCR</td>
<td>0.70-0.93 (6)</td>
<td>0.80-0.95 (6)</td>
<td>0.65(3) (6)</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>9.80(8) (7)</td>
<td>0.0290(3) (7)</td>
<td>5.32(1) (8)</td>
<td>1.9 (9)</td>
</tr>
</tbody>
</table>

Numbers in parentheses represent uncertainties in units of the least significant digit. {1} Busemann et al., 2000; {2} Huss and Lewis, 1994a; {3} Benkert et al., 1993; {4} Busemann et al., 2002, trapped $^{20}$Ne/$^{22}$Ne for an adopted $^{21}$Ne/$^{22}$Ne of 0.0294. The "subsolar" Ne and Ar signatures are given to enable a comparison of our data with those of Okazaki et al. (2001b), as, e.g., in Fig. 5.5; however, Busemann et al. (2003) recently reviewed the origin of this "component" as described in the text; {5} Crabb and Anders, 1981; {6} Wieler, 2002a, Galactic Cosmic Radiation (chondritic); {7} Eberhardt et al., 1965; {8} Nier, 1950; {9} Ozima and Podosek, 2002.
5.3.2 Sample selection

The meteorites used in our study had to fulfill several requirements: Only type 2 and 3 chondrites were selected to minimise losses or the redistribution of trapped noble gases due to secondary thermal alteration. Regolithic breccias were excluded, since the implanted SW could have obscured possible early “solar-type” signature in the chondrules. To minimise cosmogenic contributions, the exposure ages of the samples had to be as short as possible. This requirement is not fulfilled by Krymka with an exposure age of ~25 Ma. However, we included Krymka, because it is among the most unequilibrated chondrites available, and it is mineralogically/petrographically well investigated (Huang et al., 1996; Rambaldi and Wasson, 1984; Semenenko et al., 2001). Finally, the chondrules had to be large enough to enable a proper hand-separation. This precluded CM chondrites.

Before the sample separation, most of the cut and polished meteorite chips were mapped (e.g., Fig. 5.1) with a CamScan CS44LB SEM equipped with a four-quadrant BSE detector. To avoid contamination of the samples with carbon, the chips were not coated. Then, small (20-800 µg) chondrule and MS-rich samples (rims and droplets) were carefully separated from the chips under a binocular microscope. Special attention was paid to avoid cross-contamination of the chondrule samples with surrounding fine-grained rim and matrix material containing generally much higher gas concentrations (Nakamura et al., 1999b; Vogel et al., 2003). Note that the MS-rich rims generally contain a certain degree of intimately mixed matrix-like silicate material (see, e.g., dark lumps in the MS-rich rim sample “B-MSRim-A” in Fig. 5.1d; or, e.g., Alexander et al., 1989). The samples were weighted and stored in the holes of aluminium sample holders, each with a capacity to carry 9 samples.

The samples are labelled as follows: The first letter indicates the meteorite (A=Allende, L=Leoville, S=Semarkona, B=Bishunpur, K=Krymka, R=Renazzo), followed by the specification of the component (Ch=Chondrule, MSDrop=metal-sulphide droplet, MSRim= metal-sulphide-rich rim, MS= metal-sulphide-rich sample, where a specification was not possible on the basis of the SEM image, see Fig. 5.1c). The next capital letter (A-K) distinguishes different samples of one constituent within a meteorite; numbers (1-7) attached to these letters indicate different analyses of the same object.
Fig. 5.1: Backscattered electron images of the chondrites Allende (CV3, oxidised subgroup) (a), Leoville (CV3, reduced subgroup) (b), Semarkona (LL3.0) (c), Bishunpur (LL3.1) (d), Krymka (LL3.1) (e), and Renazzo (CR2) (f). Selected sample locations are indicated with arrows. Roundish chondrules are embedded in fine-grained matrix for Allende, Leoville, and Renazzo. The matrix of the ordinary chondrites is restricted to interstices between chondrules and fine-grained rims around them. Studied chondrules of Allende and Leoville do not contain metal-sulphide-rich coatings, whereas chondrules of the ordinary chondrites are often surrounded by metal-sulphide-rich rims (bright chondrule coatings). Metal-sulphide in Renazzo often occurs as large droplets within chondrules or isolated in the matrix. The length of the bars is always 1 mm.
5.3.3 Gas extraction, measurements, data reduction

For a detailed description of the noble gas extraction technique with a Nd-YAG-laser, as well as the gas purification, spectrometer settings, interference corrections, and the calibration procedure we refer to Vogel et al. (2003). Since the noble gas concentrations measured in chondrules were generally low, special attention was paid to a precise blank determination and correction, which will be described in the following.

5.3.4 Blank correction

"Cold blanks" were measured by simulating a sample extraction procedure without laser beam. They were used to determine the variability of the blanks during one run, which generally lasted for several days. The Ne and Ar cold blanks have roughly atmospheric composition. The average long-term $^{20}\text{Ne}$ and $^{36}\text{Ar}$ cold blanks are $(1.1\pm0.6)\times10^{-13}$ and $(1.4\pm0.7)\times10^{-13} \text{ cm}^3\text{STP}$, respectively, indicating a variability of ~50%. However, the variability for both, $^{20}\text{Ne}$ and $^{36}\text{Ar}$ blanks, within one run are considerably lower, generally in the range of 15%.

The statistical uncertainties of the single $^{20}\text{Ne}$ blanks were roughly in the same range as their variability within one run, mainly because of signals close to the detection limit of the counting system. Therefore, the $^{20}\text{Ne}$ blanks were used with their respective statistical uncertainties for the blank corrections. However, the statistical uncertainty of a single $^{36}\text{Ar}$ blank was in the range of a few % only, distinctly lower than the variability within one run. To consider the latter, we adopted for all $^{36}\text{Ar}$ blanks a 15% uncertainty instead of the respective statistical errors of the single $^{36}\text{Ar}$ blanks.

To verify the completeness of a sample gas extraction “sample blanks” were measured by re-heating an already degassed sample with extraction times and laser energies similar to the values of the respective sample run. However, it was unclear whether the slight enhancements of the sample blanks compared to cold blanks could be explained by remnants of sample gas or simply by the fact that the laser was fired. Therefore we measured “aluminium blanks” by firing the laser on empty holes of the sample holder. Compared to the cold blanks these were enhanced by up to 40% due to gas release from the sample holder. Some sample blanks exceeded comparable aluminium blanks indicating the presence of remnant sample Ne and/or Ar. These additional gases were added to the noble gas amounts of the respective sample extraction step, after both had been corrected with a suitable blank. The $^{20}\text{Ne}$ and $^{36}\text{Ar}$ blanks contribute on average ~4% and


5.4 Results: Chondrules

Tab. 5.1 shows the blank-corrected Ne and Ar isotopic and elemental compositions of the chondrules. Also given are their noble gas concentrations and elemental ratios corrected for cosmogenic contributions ($^{20}\text{Ne}_{\text{tr}}$, $^{36}\text{Ar}_{\text{tr}}$, ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{tr}}$), as well as the contributions of the $^{20}\text{Ne}$ and $^{36}\text{Ar}$ blanks to the non-cosmogenic noble gas concentrations. The correction of the measured $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations for cosmogenic contributions is described in the following. The resulting $^{20}\text{Ne}_{\text{ncos}}$ and $^{36}\text{Ar}_{\text{ncos}}$ concentrations, and ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{ncos}}$ enable discussing the origin of these noble gases.

5.4.1 Correction of the measured $^{20}\text{Ne}$ for cosmogenic contributions

For typical chondritic material the cosmogenic $^{20}\text{Ne}/^{21}\text{Ne}$ ratio is in the range of 0.88-0.98, depending on the chemistry and the exposure depth of a given sample (Leya et al., 2001; Wieler, 2002a). The addition of even low non-cosmogenic noble gas amounts shifts this ratio to distinctly higher values. Therefore, it is difficult to decide, whether a small shift to higher ratios in a chondrule sample indicates a small non-cosmogenic contribution or is due to variations of the cosmogenic $^{20}\text{Ne}/^{21}\text{Ne}$ because of variable sample chemistry or shielding depth. This is illustrated in Fig. 5.2, where we plotted the ratios $^{22}\text{Ne}/^{21}\text{Ne}$ vs. $^{20}\text{Ne}/^{21}\text{Ne}$ of our chondrules (black symbols) and bulk ordinary chondrites (grey symbols) of high petrographic types (5 and 6), simple exposure histories, and exposure ages > 30Ma (data from Schultz and Franke (2000)). These samples are expected to contain a very low proportion of non-cosmogenic Neon most of the ordinary chondrite data plot in the range for chondritic cosmogenic Neon (compare Tab. 5.1: $^{20}\text{Ne}/^{21}\text{Ne}$ 0.74-1.16, $^{22}\text{Ne}/^{21}\text{Ne}$ 1.05-1.25). There is no well-defined upper limit for the $^{20}\text{Ne}/^{21}\text{Ne}$ ratios of the ordinary chondrite data, which is ascribed to variable small amounts of trapped noble gases in some samples shifting the data points to higher $^{20}\text{Ne}/^{21}\text{Ne}$ ratios. However, the data display a clear-cut left hand margin, which can be described as a straight line. This line represents the cosmogenic Neon component for ordinary chondrites, the "OCNL" (ordinary chondrite cosmogenic Neon line). The $^{20}\text{Ne}/^{21}\text{Ne}$ ratios described by the line increase slightly with increasing $^{22}\text{Ne}/^{21}\text{Ne}$ ratios, which reflects the dependence of the isotopic composition of cosmogenic Neon from the shielding depth and chemistry of a sample. The cosmogenic Neon production ratios in bulk ordinary chondrites and chondrules are
similar due to comparable bulk Mg/Si and Al/Si ratios, which are the main Ne-producing targets (data from Leya et al., 2000, and references therein; and McSween et al., 1983): mean Mg/Si ratios for ordinary chondrites and chondrules range between 0.81 and 0.87, respectively. The mean Al/Si ratios are similarly low for both, in the range of 0.06. Therefore, Al contributes only very minor to the cosmogenic Ne production. Thus, the OCNL can be applied to the chondrule data as well and represents the composition of cosmogenic Ne for all meteoritic material with chondritic Mg/Si and Al/Si ratios. Most of the chondrule samples plot on the right hand side of the OCNL indicating the presence of small amounts of non-cosmogenic noble gases, even though for many data points the deviation from the OCNL is smaller than their 1σ uncertainty. Few samples plot on the left hand side of the OCNL, however also overlapping it within 1σ uncertainties except for one sample of Krymka. We calculated the amounts of non-cosmogenic 20Ne by deducing a cosmogenic 20Ne/21Ne ratio for every individual chondrule. These were determined as the intersection of the OCNL with the straight line defined by the data point of the respective chondrule and a trapped end-member (see Fig. 5.2a). As trapped end-member we adopted the Ne isotopic composition of presolar diamonds (Tab. 5.1), but this assumption is not crucial.
Chondrules Allende

Regression line of A-Ch-B and trapped end-member to trapped end-member

Intersection: individual cos. \(^{20}\text{Ne}/^{21}\text{Ne}\) to correct A-Ch-B for cos. contributions.

Chondrules Leoville

Chondrules Semarkona
**Fig. 5.2:** Measured $^{22}\text{Ne}/^{21}\text{Ne}$ vs. $^{20}\text{Ne}/^{21}\text{Ne}$ of the chondrules of Allende (a), Leoville (b), Semarkona (c), Bishunpur (d), Krymka (e), and Renazzo (f) (black symbols). Also plotted are bulk ordinary chondrite data (grey symbols) with very low trapped and high cosmogenic noble gas concentrations (see text for explanation). Their left hand envelope defines the ordinary chondrite cosmogenic Ne isotopic composition (OCNL), taking into account the variability of the sample chemistry but mainly of the shielding depth. Most of the chondrules lie at the right hand side of the OCNL indicating the presence of non-cosmogenic $^{20}\text{Ne}$. The chondrules were corrected for cosmogenic contributions with individual $^{20}\text{Ne}/^{21}\text{Ne}$ ratios obtained by calculating the intersection of the OCNL with an extended regression line between the respective chondrule and the trapped end-member (see diagram 5.2a). Data points lying at the left hand side of the OCNL display nominally negative corrected $^{20}\text{Ne}$ concentrations (see Tab. A5.1) and were not considered in the discussion. Error bars are 1σ.

**5.4.2 Non-cosmogenic $^{20}\text{Ne}$**

As stated above, many of the chondrules fall on the right hand side of the OCNL, indicating indeed the presence of discernible amounts of $^{20}\text{Ne}_{\text{n-cos}}$. The deduced $^{20}\text{Ne}_{\text{n-cos}}$ concentrations are generally low ($\leq 2 \times 10^{-8}$ cm$^3$ STP/g) and within error limits often overlap zero (Tab. A5.1). It is notable, however, that only very few chondrules fall on the left hand side of the OCNL (but also mostly overlap the OCNL within 1σ uncertainties), resulting in nominally negative $^{20}\text{Ne}_{\text{n-cos}}$ values. These data were not considered in the discussion.

We need to ask whether these small $^{20}\text{Ne}_{\text{n-cos}}$ concentrations indeed represent trapped Ne released from the samples. It might be that our blank correction was underestimated in some cases, although we do not consider this to be likely in view of our careful blank experiments, which included re-extraction of our samples (see above). Nevertheless, we discard all samples for which the $^{20}\text{Ne}$ blank contribution to the $^{20}\text{Ne}_{\text{n-cos}}$ concentrations is higher than ~50% (Tab. A5.1, values in italics), which is the case for 19 of the 50 chondrule samples. This is a conservative approach taking into account the variability of the $^{20}\text{Ne}$ blank within one run of ~15%. For the remaining 31 samples we still need to consider the $^{20}\text{Ne}_{\text{n-cos}}$ being affected by adsorbed atmospheric Ne, which was not removed from the samples during the bake-out, or by contamination with small amounts of matrix-like material. Both issues are excluded on the basis of the ($^{36}\text{Ar}/^{20}\text{Ne})_{\text{n-cos}}$ in section 5.4.5.

**5.4.3 Correction of the measured $^{36}\text{Ar}$ for cosmogenic contributions**

In contrast to Ne where three isotopes are available, only the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio can be used to correct for cosmogenic Ar, since $^{40}\text{Ar}$ is mainly produced by the decay of $^{40}\text{K}$. Fortunately, the cosmogenic $^{36}\text{Ar}/^{38}\text{Ar}$ ratio is hardly chemistry-dependent, because the cosmogenic $^{36}\text{Ar}/^{38}\text{Ar}$ ratios are nearly identical for Ca
and Fe (Wieler, 2002a). Therefore, for all chondrules a uniform cosmogenic $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of 0.65±0.03 could be adopted (Tab. 5.1). Fig. 5.3 shows the $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of all chondrules. Within their 1σ uncertainties, most of the data points lie above the maximum cosmogenic $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of 0.68, indicating the presence of $^{36}\text{Ar}_{\text{n-cos}}$. The samples were corrected for cosmogenic contributions by a two-component deconvolution. As the non-cosmogenic end-member we adopted the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of phase Q (5.34±0.02, Tab. 5.1), which is the major Ar-carrier phase in unequilibrated chondrites. Other conceivable compositions for the trapped end-member, e.g., Ar-HL in presolar diamonds with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of 4.41 (Tab. 5.1) would only slightly change the $^{36}\text{Ar}_{\text{n-cos}}$ concentrations, but not the general noble gas pattern shown in Figs. 4 and 5.

**Fig. 5.3:** Plotted are the measured $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of all chondrules. All but two Bishunpur chondrules lie above the cosmogenic $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of 0.65±0.03 indicating the presence of non-cosmogenic $^{36}\text{Ar}$. Most of the data points scatter between the $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of cosmogenic and presolar diamond compositions. Two Semarkona chondrules in the range of $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of phase Q are contaminated with matrix material (see Fig. 5.5). We cannot explain the unusually high and low $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of two Bishunpur samples, respectively. For the cosmogenic correction of $^{36}\text{Ar}$ the cosmogenic $^{36}\text{Ar}/^{38}\text{Ar}$ ratio given above and the trapped end-member of phase Q with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of 5.34±0.02 (see Tab. 1) were used. Error bars are 1σ.
Besides the spallogenic production of $^{36}\text{Ar}$ from Ca and Fe there might be also some cosmogenic production of $^{36}\text{Ar}$ via the neutron-capture on $^{35}\text{Cl}$ with subsequent $\beta^{-}$ decay. This neutron-capture contribution ($^{36}\text{Ar}_{\text{nc}}$) strongly depends on the size of the meteoroid and the shielding depth of the sample. Due to small Cl-concentrations and generally moderate shielding conditions in bulk unequilibrated chondrites the $^{36}\text{Ar}_{\text{nc}}$ is generally small compared to $^{36}\text{Ar}_{\text{tr}}$ (e.g., <1% for bulk Semarkona (Tab. 2.1) assuming the produced amounts of $^{36}\text{Ar}_{\text{nc}}$ given in Tab. 5.2). However, in chondrules the $^{36}\text{Ar}_{\text{nc}}$ might contribute considerably to the small amounts of measured $^{36}\text{Ar}$ concentrations. Tab. 5.2 contains the maximum estimated $^{36}\text{Ar}_{\text{nc}}$ concentrations for our samples as well as the shielding parameters and Cl-concentrations used for the estimate. Explanations are given in the table caption.

**Tab 5.2:** Maximum estimated shielding depth, exposure age, and $^{36}\text{Ar}_{\text{nc}}$ concentrations for Allende, Leoville, Renazzo, Semarkona, Bishunpur, and Krymka.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average chondrule ($^{22}\text{Ne}/^{21}\text{Ne}$)$_{\text{cos}}$</th>
<th>$^{1}$ Estimated max. shielding depth</th>
<th>$^{2}$ Estimated exposure age</th>
<th>$^{3}$ Average bulk Cl concentration [ppm]</th>
<th>$^{4}$ Max. produced $^{36}\text{Ar}_{\text{nc}}$</th>
<th>$^{5}$ Max. contribution of $^{36}\text{Ar}<em>{\text{nc}}$ to $^{36}\text{Ar}</em>{\text{cos}}$ [%] in chondrules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
<td>1.06</td>
<td>$\geq$60</td>
<td>5.1</td>
<td>270</td>
<td>7.41E-09</td>
<td>19-74</td>
</tr>
<tr>
<td>Leoville</td>
<td>1.08</td>
<td>50</td>
<td>9.7</td>
<td>270</td>
<td>1.28E-08</td>
<td></td>
</tr>
<tr>
<td>Renazzo</td>
<td>1.15</td>
<td>10</td>
<td>6.1</td>
<td>270</td>
<td>2.01E-09</td>
<td>20-59</td>
</tr>
<tr>
<td>Semarkona</td>
<td>1.15</td>
<td>10</td>
<td>9.1</td>
<td>130</td>
<td>1.45E-09</td>
<td>3-44</td>
</tr>
<tr>
<td>Bishunpur</td>
<td>1.11</td>
<td>25</td>
<td>10.7</td>
<td>130</td>
<td>4.08E-09</td>
<td>27</td>
</tr>
<tr>
<td>Krymka</td>
<td>1.09</td>
<td>50</td>
<td>26.3</td>
<td>130</td>
<td>1.67E-08</td>
<td></td>
</tr>
</tbody>
</table>

$^{1}$ Maximum shielding depths were estimated on the basis of the average ($^{22}\text{Ne}/^{21}\text{Ne}$)$_{\text{cos}}$ ratios of the chondrules of each sample and Fig. 14 in Leya et al., 2000. $^{2}$ Thereby it is assumed that the ($^{22}\text{Ne}/^{21}\text{Ne}$)$_{\text{cos}}$ ratios are mainly shielding and only minor chemistry dependent. The ratios are similar to cosmogenic ($^{22}\text{Ne}/^{21}\text{Ne}$) ratios calculated from bulk Ne data of the respective meteorites (Schultz and Franke, 2000) by two-component deconvolution supporting the above assumption. Exposure ages of the samples were estimated via their bulk $^{21}\text{Ne}_{\text{cos}}$ concentrations (data source (Schultz and Franke, 2000)). $^{3}$ We used average bulk carbonaceous and ordinary chondrite Cl concentrations of Mason (1979) since bulk chondrule Cl concentrations were not available. $^{4}$ Exposure-depth-dependent $^{36}\text{Cl}$ production rates: pers. comm. I. Leya. $^{5}$ The maximum $^{36}\text{Ar}_{\text{nc}}$ proportions at the $^{36}\text{Ar}_{\text{nc}}$ of all chondrules vary between 0 and over 100%. Given in the table are only the maximum $^{36}\text{Ar}_{\text{nc}}$ portions for those chondrules, which display an unequivocally positive ($^{36}\text{Ar}/^{36}\text{Ne}$)$_{\text{cos}}$ ratio in Fig. 5.5.

Especially for the chondrules of Allende, Leoville, and Krymka the maximum $^{36}\text{Ar}_{\text{nc}}$ concentrations are in the range of the $^{36}\text{Ar}_{\text{nc}}$ values. However, the $^{36}\text{Ar}_{\text{nc}}$ concentrations are distinctly overestimated, because (i) we used bulk Cl-concentrations of unequilibrated chondrites, which should be generally higher than those for volatile-depleted chondrules (ii) we always chose the maximum
possible shielding depth of all measured samples. Therefore, the $^{36}$Ar$_{nc}$ concentrations often exceed the $^{36}$Ar$_{n-cos}$ concentrations substantially. However, for the important chondrule samples of Semarkona, Bishunpur, and Renazzo shown in Fig. 5.5, even correcting with the maximum estimated $^{36}$Ar$_{nc}$ concentrations would not change the general pattern. Although we do not correct our chondrule data for $^{36}$Ar$_{nc}$, we are aware of the fact that the $^{36}$Ar$_{n-cos}$ concentrations of Allende, Leoville, and Krymka chondrules might be compromised to a significant degree by $^{36}$Ar$_{nc}$.

5.4.4 Non-cosmogenic $^{36}$Ar

Most of the chondrules have $^{36}$Ar$_{n-cos}$ concentrations clearly above zero by more than 1σ and up to $5 \times 10^{-8}$ cm$^3$/STP/g. Exceptions are two Semarkona chondrules (S-Ch-H1, S-Ch-G) with $^{36}$Ar$_{n-cos}$ concentrations in the range of $10^{-7}$ cm$^3$/STP/g, which most probably result from contamination with matrix or MS-rich material (see below). Again, a possible source of small extra amounts of $^{36}$Ar$_{n-cos}$ in the samples might be an underestimated $^{36}$Ar blank as discussed for the $^{20}$Ne$_{n-cos}$. Therefore we exclude all samples, for which the $^{36}$Ar-blank contributed ≥50% to the $^{36}$Ar$_{n-cos}$ concentrations (Tab. A5.1, values in italics). This is the case for only 6 of the 46 measured chondrule samples. The possibility of the $^{36}$Ar$_{n-cos}$ concentrations being derived from adsorbed air on the samples or from contamination with matrix-like material is discussed below on the basis of the ($^{36}$Ar/$^{20}$Ne)$_{n-cos}$.

5.4.5 The $^{36}$Ar/$^{20}$Ne ratios of the non-cosmogenic component in chondrules

Fig. 5.4 shows the ($^{36}$Ar/$^{20}$Ne)$_{n-cos}$ ratios of the chondrule samples with $^{36}$Ar$_{n-cos}$ and $^{20}$Ne$_{n-cos}$ above blank levels.
Due to the correction for cosmogenic contributions especially for the $^{20}\text{Ne}$, the uncertainties are often quite high: 14 samples have uncertainties above 100%, and two samples show nominally negative $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{h-cos}}$ ratios (open symbols). However, 13 samples lie unequivocally above zero and have $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{h-cos}}$ ratios ranging from 0.3 to 29 (solid symbols). Only these chondrule data points are shown in Fig. 5.5. Note that the chondrule data points with higher uncertainties would plot in the same area as the 13 points shown. Fig. 5.5 also shows data of matrix-like material (open symbols) of the respective meteorites published in Vogel et al. (2003).
Fine-grained matrix-like material is a probable chondrule precursor material (e.g., Connolly, 2001; Kong and Palme, 1999; Kong and Ebihara; 1997; Alexander, 1989; Scott, 1983), but also represents a possible source for contamination of the chondrule samples. Compared to these gas-rich samples, the major part of the chondrules shows low $^{36}\text{Ar}/^{20}\text{Ne}$$_{h\text{-cos}}$ ratios as well as low $^{36}\text{Ar}_{t\text{-cos}}$ concentrations. These low $^{36}\text{Ar}/^{20}\text{Ne}$$_{h\text{-cos}}$ ratios in the chondrules could indicate variable mixtures between precursor matrix-like noble gases with a noble gas component with a distinctly lower $^{36}\text{Ar}/^{20}\text{Ne}$ ratio, such as HL- or SW noble gases. Also pure HL or SW noble gases, which were fractionated by alteration processes, may be possible.
However, before discussing these possibilities we have to discard on the basis of their $^{36}\text{Ar}^{20}\text{Ne}$ ratios those chondrule samples, which were substantially contaminated with matrix-like material during the sample separation. Subsequently, we will exclude that adsorbed air is the reason for the low $^{36}\text{Ar}^{20}\text{Ne}$ ratios of many chondrule samples.

If the non-cosmogenic noble gas concentration of a chondrule sample would be mainly influenced by contaminating matrix-like material, the $(^{36}\text{Ar}^{20}\text{Ne})_{\text{n-cos}}$ ratio of the chondrules would have to be ~identical to that of the respective surrounding matrix-like material. This is the case for five chondrule samples in Fig. 5.5, which have $(^{36}\text{Ar}^{20}\text{Ne})_{\text{n-cos}}$ ratios in the range of their respective matrix-like material (data points in brackets). In these cases a substantial contamination of the chondrules with rim and matrix material cannot be excluded, thus they are not considered any further. The $^{36}\text{Ar}_{\text{tr}}$ concentrations of the matrix-like material are generally distinctly higher than the $^{20}\text{Ne}_{\text{tr}}$ concentrations (compare Vogel et al. 2003). Thus, a minor contamination of a chondrule sample could also result in measurable $^{36}\text{Ar}_{\text{tr}}$ concentrations, but $^{20}\text{Ne}_{\text{tr}}$ concentrations in the range of blank values. This would lead to theoretical $(^{36}\text{Ar}^{20}\text{Ne})_{\text{tr}}$ ratios of the contaminated chondrule, which are higher than those of the contaminating matrix-like material. This is not observed in Fig. 5.5. In any case, it is not possible to explain the $(^{36}\text{Ar}^{20}\text{Ne})_{\text{n-cos}}$ ratios of the chondrules distinctly below those of the respective matrix-like material by contamination with matrix-like material.

We noted above the possibility that adsorbed air might not have been completely removed from the chondrule samples by the bake-out. Adsorbed air is expected to have a distinctly higher $^{36}\text{Ar}^{20}\text{Ne}$ than the atmospheric value of 1.9 (Tab. 5.1), since Ar sticks better to a sample than Ne. However, the chondrules have $(^{36}\text{Ar}^{20}\text{Ne})_{\text{n-cos}}$ ratios in the range of or even distinctly lower than the value of 1.9. Therefore fractionated air is excluded as a reason for the $(^{36}\text{Ar}^{20}\text{Ne})_{\text{n-cos}}$ of the chondrules. Furthermore, the bulk values of Semarkona, Bishunpur and Renazzo shown in Fig. 5.5 (partly filled symbols) have slightly lower $^{36}\text{Ar}^{20}\text{Ne}$ ratios than the respective matrix-like samples. Apart from the chondrules there is no major constituent with low $^{36}\text{Ar}^{20}\text{Ne}$ ratios, which could account for the lower $^{36}\text{Ar}^{20}\text{Ne}$ ratios of the bulk samples compared to the respective matrix-like material. A mixture of roughly 80% chondrules with a $^{36}\text{Ar}^{20}\text{Ne}$ of ~3 and 20% matrix $(^{36}\text{Ar}^{20}\text{Ne} \sim 14)$ can explain, e.g., the bulk $^{36}\text{Ar}^{20}\text{Ne}$ ratio (~11) of Semarkona. This is in accordance with average chondrule and matrix proportions of ordinary chondrites (e.g., Brearley and Jones, 1998).

Since neither air nor blank, but clearly a trapped component is the reason for the low $^{36}\text{Ar}^{20}\text{Ne}$ ratios of the chondrules, we will henceforth use the subscript “tr” instead of “n-cos” for the non-cosmogenic noble gas concentrations and elemental ratios henceforth.
Simple heating of matrix-like precursor material with a given $({\text{Ar}}/{\text{Ne}})_{tr}$ ratio would lead to a fractionation of the noble gases resulting in higher $({\text{Ar}}/{\text{Ne}})_{tr}$ ratios. Studies on primitive meteorites of different metamorphic stages, and heating experiments showed that the major Ne-carrier (presolar diamonds) degasses at slightly lower temperatures than the major Ar-carrier (phase Q) (Heyman and Mazor, 1968; Huss et al., 1996; Nakasyo et al., 2000; Sears et al., 1980). Therefore, the $\text{Ar}/\text{Ne}$ ratio is expected to increase with decreasing noble gas concentrations. Also diffusive losses would alter the $\text{Ar}/\text{Ne}$ ratios in a way opposite to the one observed because Ne diffuses faster than Ar.

Due to the above reasons, we conclude that the low chondrule $({\text{Ar}}/{\text{Ne}})_{tr}$ ratios are neither artefacts due to adsorbed air, nor can be explained by simple heating of matrix-like chondrule precursor material. Thus, the low $({\text{Ar}}/{\text{Ne}})_{tr}$ ratios indicate the presence of HL noble gases with a $\text{Ar}/\text{Ne}$ ratio of ~0.1 or SW noble gases with a $\text{Ar}/\text{Ne}$ ratio of ~0.04 (see Tab. 5.1). Both could be slightly mass fractionated or mixed with very small amounts of matrix-like noble gases. During the study it turned out that the more gas-rich MS-rich samples, which are genetically related to chondrules, have to be taken into account to decide whether HL or SW noble gases represent the main noble gas component in chondrules.

5.5 Results: Metal-sulphide-rich samples

5.5.1 Ne and Ar isotopic composition of MS-rich samples and the correction for the cosmogenic component

We separated 13 MS-rich samples from Semarkona, Bishunpur, Krymka, and Renazzo. No such samples were available from Allende and Leoville. The measured $\text{Ne}$ and $\text{Ar}$ concentrations and isotopic compositions of the MS-rich samples are given in Tab. A5.2. The cosmogenic correction of the measured $\text{Ne}$ and $\text{Ar}$ is less delicate than that of the chondrules due to generally higher concentrations of trapped noble gases. Iron meteorites with exposure ages $\gg$100 Ma, and thus a clear cosmogenic noble gas signature, show a mean cosmogenic $\text{Ne}/\text{Ne}$ ratio of ~0.93 (Lavielle et al., 1999), identical to typical chondritic cosmogenic $\text{Ne}/\text{Ne}$ ratios (compare Tab. 5.1) within uncertainties. It is unclear however, what the proportion of sulphides in the iron meteorites studied by Lavielle et al. (1999) is compared to our MS-rich samples, and how the S would influence the $\text{Ne}/\text{Ne}$ ratios in sulphide bearing constituents, since no production rate ratios of Ne from S exist so far. Nevertheless we assume similar cosmogenic production rate ratios of Ne from S, silicates and iron due to a mass of S intermediate between Si and Fe. Also the cosmogenic $\text{Ar}/\text{Ar}$
ratios of iron meteorites and chondritic material (see above) are basically identical. Since no Ar is cosmogenically produced from S, the proportion of sulphides in the samples is not crucial. Therefore uniform cosmogenic isotopic ratios were used for the correction of both, matrix-like and MS-rich samples. As trapped Ne end-members we used individual primordial $^{20}\text{Ne}/^{21}\text{Ne}$ ratios of the respective meteorites deduced from regression lines in Ne-3-isotope plots (see Fig. 4.5), since generally also the MS-rich samples plot on these lines. As the trapped Ar end-member we adopted the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of phase Q (Tab. 5.1). The $^{20}\text{Ne}_{\text{n-cos}}$ and $^{36}\text{Ar}_{\text{n-cos}}$ concentrations of the MS-rich samples are calculated in the same way as the chondrules. The data are given in Tab. A5.2. The $^{20}\text{Ne}_{\text{n-cos}}$ and $^{36}\text{Ar}_{\text{n-cos}}$ concentrations of most of the MS-rich samples are roughly in the range defined by the matrix-like samples (Fig. 5.6). Also the $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{n-cos}}$ ratios are similar to but in several cases somewhat higher than the respective values of the matrix-like samples (Fig. 5.7). Only the $^{20}\text{Ne}_{\text{n-cos}}$ and $^{36}\text{Ar}_{\text{n-cos}}$ concentrations of the three Renazzo MS-rich samples and the lower limit of one MS-rich rim of Krymka (K-MSRim-E, see below) lie in the range of chondrule values (data points marked with arrows in Figs. 5.6 and 5.7).
FIG. 5.6: Matrix-like samples (open symbols) and metal-sulphide-rich samples (solid symbols) of Semarkona (a), Bishunpur (b), Krymka (c), and Renazzo (d) in plots $^{20}\text{Ne}_r$ vs. $^{36}\text{Ar}_r$. Numbers in boxes are the average $(^{36}\text{Ar}/^{20}\text{Ne})_r$ ratios of the shown matrix-like samples. Many metal-sulphide-rich samples show noble gas concentrations comparable to those of matrix-like samples. The metal-sulphide-rich samples are partly enriched in $^{36}\text{Ar}$ relative to $^{20}\text{Ne}$ compared to the fine-grained material, lying at the right hand side of the best fit line of all fine-grained samples. Few metal-sulphide-rich samples (indicated with arrows) have $^{20}\text{Ne}$ and $^{36}\text{Ar}$ concentrations in the range of chondrule values. Given uncertainties are 1σ.

A blank- or air-origin of the deduced $^{20}\text{Ne}_\text{n-cos}$ and $^{36}\text{Ar}_\text{n-cos}$ concentrations of the MS-rich samples can be excluded, since gas concentrations are much higher than those of the chondrules and their $(^{36}\text{Ar}/^{20}\text{Ne})_\text{n-cos}$ ratios are in the range of values for trapped meteoritic noble gases (see below). Thus, henceforth we will use the subscript “tr” (trapped) for the non-cosmogenic noble gas concentrations and elemental ratios.

5.5.1.1 Elemental ratio $(^{36}\text{Ar}/^{20}\text{Ne})_\text{tr}$ of metal-sulphide-rich samples

Fig. 5.7 shows the $(^{36}\text{Ar}/^{20}\text{Ne})_\text{tr}$ ratio vs. the $^{36}\text{Ar}_\text{tr}$ concentration of MS-rich samples. Again, the respective rim and matrix data are plotted for comparison. For sample K-MSRim-E we can give an upper limit for its $^{20}\text{Ne}_\text{tr}$ concentration and
hence a lower limit of $\sim 4$ (1σ) for its $^{36}\text{Ar}/^{20}\text{Ne}_{\text{tr}}$ ratio only. In contrast to the chondrules, the $^{36}\text{Ar}/^{20}\text{Ne}_{\text{tr}}$ ratios of many of the MS-rich samples in Fig. 5.7 plot within the range defined by their respective rim and matrix values. In more detail, some MS-rich samples display a general trend of increasing $^{36}\text{Ar}_{\text{tr}}/^{20}\text{Ne}_{\text{tr}}$ ratios with increasing $^{36}\text{Ar}_{\text{tr}}$ concentrations (indicated by arrows in Fig. 5.7) compared to their respective matrix-like samples. This may be interpreted as a variable mixture of an hypothetical “MS-endmember” with high $^{36}\text{Ar}/^{20}\text{Ne}_{\text{tr}}$ ratios and $^{36}\text{Ar}_{\text{tr}}$ concentrations and matrix-like material with lower $^{36}\text{Ar}/^{20}\text{Ne}_{\text{tr}}$ ratios and $^{36}\text{Ar}_{\text{tr}}$ concentrations.

**Fig. 5.7:** $^{36}\text{Ar}/^{20}\text{Ne}_{\text{tr}}$ ratios vs. $^{36}\text{Ar}$ concentrations of the metal-sulphide-rich samples of Semarkona (a), Bishunpur (b), Krymka (c), and Renazzo (d) (solid symbols). Compared to the respective matrix-like data (open symbols without error bars), many of the metal-sulphide-rich samples are enriched in $^{36}\text{Ar}_{\text{tr}}$ relative to the $^{20}\text{Ne}_{\text{tr}}$, resulting in the upward trends marked with grey arrows. The three metal-sulphide-rich samples of Renazzo (black arrow) have low $^{36}\text{Ar}_{\text{tr}}/^{20}\text{Ne}_{\text{tr}}$ ratios and $^{36}\text{Ar}$ concentrations similar to chondrules (see Fig. 5.5). If the lower limit of the $^{36}\text{Ar}_{\text{tr}}/^{20}\text{Ne}_{\text{tr}}$ of K-MSRim-E (black arrow) is reasonable, the noble gas signature of this sample would follow the trend of the metal-sulphide-rich samples of Renazzo. Error bars are $\pm 1\sigma$. 

139
The two Bishunpur MS-rich rims (B-MSRim-A, B-MSRim-F, see Fig. 1d) have quite differing noble gas signatures. Whereas B-MSRim-A shows the high \((^{36}\text{Ar}/^{20}\text{Ne})_{tr}\) ratios and \(^{36}\text{Ar}_{tr}\) concentrations described above, B-MSRim-F plots in the range of its matrix-like samples (Fig. 5.7d). This is correlated with different textures of the two samples and allows conclusions about the establishment of the noble gas signatures in MS-rich rims in general, which is discussed in detail below. The MS-rich samples of Renazzo (two droplets associated with chondrules and one MS-rich rim) are obviously different from Semarkona and Bishunpur MS-rich samples, since they have distinctly lower \((^{36}\text{Ar}/^{20}\text{Ne})_{tr}\) ratios and \(^{36}\text{Ar}_{tr}\) concentrations than Renazzo rims and matrix. In Fig. 5.7d they plot in the range of the chondrule samples. At the moment we have no straightforward explanation for the chondrule-like noble gas signature in these samples. The formation of these samples from precursor material already depleted in \(^{36}\text{Ar}_{tr}\) is discussed below. The noble gas signature of the Krymka MSRim-E shown in Fig. 5.7c is similar to those of the Renazzo MS-rich samples. However, the \((^{36}\text{Ar}/^{20}\text{Ne})_{tr}\) ratio of K-MSRim-E of this sample represents a lower limit only.

5.6 Discussion

During this study we found small but measurable amounts of trapped \(^{20}\text{Ne}\) and/or \(^{36}\text{Ar}\) in chondrules of unequilibrated CV, CR, and LL chondrites. In the following we discuss the origin of these trapped noble gases in the chondrules and the associated MS-rich samples. The \((^{36}\text{Ar}/^{20}\text{Ne})_{tr}\) ratios in the chondrules between 0 and ~7 are generally lower than those of their respective matrix-like host material. As noted above, the low ratios could be explained by the presence of HL or SW noble gases in the chondrules (Fig. 5.5). These two possibilities would imply different chondrule formation scenarios and are discussed in the following.

5.6.1 A solar-like noble gas signature in chondrules?

Remnants of SW noble gases in the chondrules of meteorites, which do not contain such gases in their surrounding matrix, would support a direct exposure of the chondrules or their precursor material to SW before their incorporation into a parent body. This scenario is postulated by Okazaki et al. (2001b) to explain the high amounts of subsolar noble gases in chondrules of the enstatite chondrite Y-791790. However, this explanation cannot straightforwardly account for the noble gas data of our chondrules: They have \((^{36}\text{Ar}/^{20}\text{Ne})_{tr}\) ratios much lower than subsolar (Tab. 5.1, Fig. 5.5) and \(^{36}\text{Ar}\) concentrations 2-3 orders of magnitude below those of the chondrules measured by Okazaki et al. (2001b). If the irradiation
process postulated by these authors would had similarly worked on the precursor material of our chondrules, they subsequently would have to have been degassed considerably more intense than the chondrules of the enstatite chondrite to explain the much lower $^{36}\text{Ar}_\text{T}$ concentrations. The fractionation thereby should have produced an unambiguously subsolar signature (e.g., $^{36}\text{Ar}/^{20}\text{Ne} \geq 26$, see Tab. 5.1) in our chondrules, which is actually not the case. However, the precursor dust of our chondrules could have been much less intensely irradiated than the precursor of the “Okazaki-chondrules”. This could explain the remarkable difference in the $^{36}\text{Ar}$ concentrations of the Okazaki-chondrules and ours despite roughly similar heating conditions. In this case also a less pronounced fractionation of the SW noble gases than adopted above would be reasonable and could explain the fact that the $^{36}(\text{Ar}/^{20}\text{Ne})_\text{T}$ ratios in our chondrules are much lower than the subsolar value.

Although in the following we handle the interpretation of Okazaki et al. (2001b) as valid, we point out again that Busemann et al. (2003) convincingly show that the so-called “subsolar” component can be straightforwardly explained by a mixture of phase Q, SW and atmospheric noble gases. The finding of Busemann et al. (2003) basically challenges the interpretation of the chondrule noble gas data of Okazaki et al. (2001b) and might finally lead to a different interpretation of the data, which probably do not allow a proposition about a SW irradiation of the chondrules or their precursors close to the young sun prior to their incorporation into the enstatite parent body.

Any explanation for the noble gas signature of the chondrules should also include the noble gas signatures of their MS-rich coatings, since both constituents were created by the same melting event (see below). In a scenario as proposed by Okazaki et al. (2001b) the MS-rich rims would have been necessarily created during the melting of the irradiated dust precursor close to the young sun. As described above, the MS-rich coatings are often intimately mixed with matrix-like material, which seems to have been accreted onto the molten MS (Alexander, 1989; Grossman and Wasson, 1987). This implies that the chondrule melting occurred in a dust-rich environment, as it is proposed for chondrule formation in transient “flash-heating” events caused by lightning or friction due to shock events passing through dust rich areas (see, e.g., Scott et al., 1996). In the model of Okazaki et al. (2001b) this dust would have to represent the non-molten portion of the SW irradiated chondrule precursor. Thus, we would expect well measurable amounts of noble gases with a low SW-like $^{36}\text{Ar}/^{20}\text{Ne}$ ratio in the MS-rich samples since the noble gas signature of the MS-rich rims is influenced by that of the matrix-like portion in these samples. In fact, except for Renazzo (and K-MSRim-E), the MS-rich rims show $^{36}\text{Ar}/^{20}\text{Ne}$ ratios between 20 and 40. These values are in the range of phase Q and in part even above the values of the
surrounding matrix-like material. Thus, it is difficult to straightforwardly explain the noble gas signature of the chondrules and the MS-rich samples by chondrule formation near the young sun as it is proposed by Okazaki et al. (2001b) for the chondrules of the enstatite chondrite Y-791790. The Renazzo MS-rich samples (and the lower limit of K-MSRim-E) show lower \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratios, but also very low trapped Ne and Ar concentrations, which would not be expected in the case of a SW irradiated material.

### 5.6.2 Primordial noble gas signatures in chondrules and associated MS-rich phases

We think that the noble gas signatures in our chondrules and MS-rich samples can better be explained as remnants of matrix-like noble gases, which are dominated by primordial noble gases of phase Q and presolar diamonds. Simple heating of matrix-like material would produce a high \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratio in the chondrules, which is in contrast to our observation. Therefore a fractionation mechanism is necessary, which actively separates the \(^{20}\text{Ne}\)-rich HL-component from the \(^{36}\text{Ar}\)-carrying phase Q to explain the low, more HL-like \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratios in the chondrules and the higher, more Q-like \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratios in the MS-rich rims. We propose that the metal-silicate separation during chondrule formation represents such a fractionation mechanism: metal-sulphides are often associated with carbonaceous material, which entered the metal-phase during chondrule formation (Kong and Ebihara, 1997; Kong et al., 1999; Mostefaoui and Perron, 1994). Since the \(^{36}\text{Ar}\)-carrier phase Q is carbonaceous as well (Ott et al., 1981), we suggest that also phase Q got associated to the metal-phase during melting. This could simultaneously explain the depletion of \(^{36}\text{Ar}\) relative to \(^{20}\text{Ne}\) in the chondrules and the \(^{36}\text{Ar}\) enrichment in surrounding MS-rich rims compared to the respective matrix-like material.

To corroborate this model, the next section represents a literature overview about the formation of MS and the role of carbonaceous material during chondrule formation. We will also present cases, where a relationship between meteoritic metal, carbonaceous material and \(^{36}\text{Ar}\) seems to exist. Based on this background, we will finally discuss our model, in which the HL- and Q-carrier phases are fractionated by metal-silicate separation during chondrule formation.
5.6.2.1 The origin of metal-sulphides and the role of carbon during chondrule formation

The relationship between MS and chondrules in enstatite, ordinary and CR chondrites has been extensively studied (Kong et al. 1999; Connolly et al., 2001; Kong and Palme, 1999; Rambaldi and Wasson, 1981, 1984; Kong and Ebihara, 1996, 1997; Grossman and Wasson, 1985, 1987; Mostefaoui and Perron, 1994; Zanda et al., 1994). The MS was either created during chondrule formation by the reduction of a matrix-like precursor (Alexander, 1989; Connolly et al., 2001; Kong and Ebihara, 1996; Kong and Palme, 1999), or it has already been present in the precursor (Grossman and Wasson, 1985; Kong and Palme, 1999; Zanda et al., 2002). In both scenarios liquid metal droplets were separated from the silicate melt during chondrule formation. Due to surface tension forces and/or the spin of the chondrules, the droplets eventually moved to the chondrule margins (Connolly et al., 2001; Grossman and Wasson, 1987; Humayun et al., 2002; Kong et al., 1999; Kong and Palme, 1999). Some MS droplets solidified while being expelled from chondrules and formed compact MS-rich coatings (“expelled” rims) (Alexander, 1989). Others were completely separated from their host chondrules and may be found as isolated blebs within chondrite matrices (Connolly et al., 2001; Humayun et al., 2002; Mostefaoui and Perron, 1994). In other cases MS evaporated from molten chondrules and recondensed onto their surfaces (“recondensed” rims) (Alexander, 1989; Connolly et al., 2001; Kong and Palme, 1999). Recondensation probably occurred on pre-existing (expelled) metal-nuclei at the chondrule surfaces (Campbell et al., 2002), which make up 10-30% of the recondensed-type rims (pers. comm. M. Humayun 2002).

Metallic phases in unequilibrated chondrites are often associated with carbonaceous material (e.g., Kong and Ebihara (1997), Kong et al. (1999), Mostefaoui and Perron (1994), and references therein). During chondrule melting organic material was possibly decomposed, dissolved into the metal and later released to form thin layers around metal grains of CR, enstatite, and ordinary chondrites (Kong et al., 1999, and references therein). Carbonaceous material in the chondrule precursor possibly played a major role in the metal formation during chondrule melting. Connolly et al. (2001) estimated that 2-4 wt% of C, which is in the range carbon concentrations in CM and CI chondrite matrices, are needed to entirely reduce precursor FeO and NiO. Excess carbon forms graphite grains associated with the metal (Connolly et al., 1994).

In some differentiated meteorites a relationship between metal, carbonaceous material, and the $^{36}$Ar concentration exists. The IAB iron meteorite Bohumilitz contains in its metallic matrix graphite inclusions containing $^{36}$Ar-Q (Maruoka et al., 2001). In the achondrite Lodran high $^{36}$Ar concentrations of up to 85×10$^{-8}$
cm$^3$STP/g were found in FeNi-separates (Busemann and Eugster, 2000; Weigel, 1996). Retrapping of the noble gases in bubbles (Busemann and Eugster, 2000) or, e.g., graphite inclusions as possible carrier phases of the noble gases (Weigel, 1996) are discussed. In conclusion, metallic phases in unequilibrated chondrites were probably created during chondrule formation and are often associated with carbonaceous material. Metal, carbonaceous material, and $^{36}$Ar-Q seem to be correlated in some differentiated meteorites. Since the $^{36}$Ar carrier phase Q is also carbonaceous, we explain the enrichment of $^{36}$Ar in some of our MS-rich samples by the association of metal and carbonaceous material.

5.6.2.2 Fractionation of phase Q and presolar diamond noble gases during chondrule formation

Chondrules of different chondrite groups formed most probably from primitive matrix-like precursor material (Alexander, 1989; Connolly et al., 2001; Kong and Ebihara, 1997; Kong and Palme, 1999; Scott and Taylor, 1983), which hosts the most important carriers for primordial noble gases, phase Q, and presolar diamonds (Huss et al., 1996; Smith et al., 1977). Based on the observation that Q-gases occur correlated with carbonaceous material in the metal-phases of differentiated meteorites, a similar behaviour of phase Q during chondrule formation can be expected. Due to differences in the physical-chemical properties, phase Q could have a higher affinity to MS than the presolar diamonds. Since both carriers are well mixed in the most unequilibrated chondrites, a mechanism must exist that is able to fractionate phase Q and the presolar diamonds to explain the Q-like noble gas signature in metal-phases of differentiated meteorites (see above). Therefore, we propose the following model to explain the noble gas signatures of chondrules and their MS-rich rims: the chondrules were formed in transient flash-heating events in a dust-rich environment. During the melting of the matrix-like precursor material phase Q entered the MS more efficiently than the presolar diamonds. The MS-droplets moved outwards and solidified quickly at the chondrule margins. Either phase Q (and its Ar-rich noble gas inventory) survived this high-temperature event encapsulated in the metal phase, or the noble gases were released and immediately re-trapped in the solidifying MS. The melting point of iron, nickel, and iron-sulphide phases is in the range of roughly 1200 to 1500°C. The liquidus temperatures experienced by chondrules is in the range of 1350 to 1800°C (Cohen et al., 2000, and references therein). The average liquidus temperatures of chondrules and MS phases are thus below the maximum release temperatures of noble gases of phase Q (1100 - $\geq$1800°C, Huss et al.,
and support the possibility that phase Q could partly survive, at least for a short time, in a molten metallic phase. The degree of $^{36}$Ar enrichment in the MS-rich rims would be a function of the peak temperature and cooling rate of the chondrules and their MS-rich coatings.

Simultaneously, fine-grained matrix-like dust accreted onto the solidifying MS coating the chondrules (see, e.g., dark lumps in B-MSRim-A, Fig. 1d) and added variable amounts of noble gases with a matrix-like signature to the rims. Thus, the final noble gas signature of the expelled MS-rich rims is a mixture of the $^{36}$Ar-rich MS and the matrix-like noble gas signature of the accreted dust. Thus, the MS-rich samples have higher ($^{36}$Ar/$^{20}$Ne)$_\text{r}$ ratios than the respective pure rim and matrix material. While phase Q was extracted, the $^{20}$Ne-carrying presolar diamonds remained predominantly in the molten chondrule interior. Thereby, most of the diamonds broke down and released their noble gases. In fact, the diamonds have a relatively large range of release temperatures between roughly 1100–1600 °C, which points to variably stable sub-groups (Huss and Lewis, 1994a; Huss and Lewis, 1994b). We suggest that the most resistant presolar diamonds survived the heating within the chondrules. Only due to the removal of the Q-gases the HL-like noble gas signature of these presolar diamonds became recognisable.

Theoretically, the noble gas signature of the MS-rich samples could also have been controlled by the ambient nebular gas but not by the noble gases of the chondrule precursor. In this case, the major part of the primordial noble gases could have been lost from the chondrules during melting except for the gases in the most resistant presolar diamonds. The MS moved to the chondrule margins, where it could equilibrate with the ambient nebular gas. Thus, nebular $^{36}$Ar could have been dissolved into the MS coating the chondrules. The simultaneous accretion of matrix-like material would have led to the same result as described above. However, the two Bishunpur MS-rich rims argue against this scenario: B-MSRim-A is a thick compact rim directly coating a chondrule, which is typical for expelled MS (e.g., Alexander et al., 1989). This compact MS-rim clearly shows an enhanced ($^{36}$Ar/$^{20}$Ne)$_\text{r}$ relative to the matrix-like material. In contrast, B-MSRim-F is a recondensed rim with a layered structure, and it is separated from the chondrule by a thin fine-grained clastic rim (not visible in Fig. 1d). This recondensed MS-rich rim does not show a $^{36}$Ar$_\text{r}$-enrichment but a ($^{36}$Ar/$^{20}$Ne)$_\text{r}$ ratio in the range of the surrounding matrix-like material. In this case the MS evaporated from the chondrule margins, thereby releasing the entrapped Q-gases. During recondensation of the noble-gas-free MS back onto the chondrule, matrix-like dust accreted simultaneously, which exclusively determined the final noble gas signature of the recondensed MS-rich rim. If the enhancement of the ($^{36}$Ar/$^{20}$Ne)$_\text{r}$ ratio in a MS-rich rim compared to the respective matrix-like mate-

145
rial would have been caused by reaction of the MS with the nebular gas, we would expect a higher \((^{36}\text{Ar}/^{20}\text{Ne})_r\) in the recondensed MS-rich rim than in the expelled MS-rich rim of Bishunpur, which is contradictory to our results. Therefore, we conclude that the noble gas signatures of the MS-rich rims were not determined by the ambient nebular gas.

Also the recondensed MS-rich rims can contain certain portions of the "expelled" MS (Campbell et al., 2002; pers. comm. M. Humayun 2002). Thus a certain increase of the \((^{36}\text{Ar}/^{20}\text{Ne})_r\) relative to the respective rim and matrix material would not contradict our results.

A MS-droplet of the interior of a Renazzo chondrule has the same unusually low \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratio as the MS-rich rim and MS-droplets within the Renazzo matrix. This also proves the genetic relationship between chondrule, rim, and matrix metal, and further rules out the possibility that the noble gas signatures of rim and matrix metal were controlled by the ambient nebular gas. However, it is difficult to straightforwardly explain the low \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratios of these MS samples, which are in the range of chondrule values. Possibly, the chondrule precursor has been already depleted in phase Q noble gases compared to those of the presolar diamonds. Hints for the presence of such material come, e.g., from the low \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratios of the Renazzo matrix-like material. A chondrule precursor already depleted in volatiles is also proposed by Humayun et al. (2002) to explain the net depletion of volatiles in Renazzo.

5.6.2.2 Implications on chondrule formation scenarios

According to literature chondrules and their associated MS-rich rims are genetically related. This is supported by our noble gas data, which show complementary noble gas signatures of chondrules and some of the studied MS-rich rims. The general similarity of the \((^{36}\text{Ar}/^{20}\text{Ne})_r\) ratios of the MS-rich samples of Semarkona, Bishunpur, and Krymka and the fine-grained matrix-like material of the respective meteorites implies on the one hand a genetic relationship between the meteorite matrices and the matrix-like portions within the MS-rich samples. To explain the simultaneous chondrule melting and accretion of matrix-like material onto their MS-rich rims, chondrule formation during transient high temperature events in a dust-rich environment is required. On the other hand the similarity further requires an immediate accretion of all constituents to avoid that large scale mixing processes separate the chondrules from their enveloping dust volumes. This finding is in accordance with the results of Klerner, (2001) and Kong and Palme (1999), who postulate a close relationship between chondrules and matrix in carbonaceous chondrites on the basis of main and trace element distributions between both constituents.
Our findings do not support chondrule formation close to the young sun as proposed for the chondrules of the enstatite chondrite Y-791790 (Okazaki et al., 2001b). In this case we would expect a SW or fractionated SW signature in our chondrules and their MS-rich coatings. Furthermore, in this scenario the chondrules need to be transported to asteroidal distances via the X-wind (Shu et al. 2001), where they accrete to the different parent bodies. This large-scale transport would fail to explain the similarity of the noble gas signatures in the MS-rich coatings of the chondrules and the matrix-like material of the respective meteorites studied here.

5.7 Conclusion

In this study we found in the chondrules of the primitive CV, CR and LL chondrites Allende, Leoville, Renazzo, Semarkona, Bishunpur, and Krymka low but discernable concentrations of trapped $^{20}\text{Ne}$ and/or $^{36}\text{Ar}$. Their $^{36}\text{Ar}/^{20}\text{Ne}$ ratios are unexpectedly low compared to the $^{36}\text{Ar}/^{20}\text{Ne}$ ratios of the respective matrix-like material. We also measured samples of metal-sulphide-rich material occurring within chondrules, as MS-rich rims around chondrules, and as isolated patches in the matrix. These generally show $^{36}\text{Ar}/^{20}\text{Ne}$ ratios in the range of, or slightly higher than, matrix-like material of the respective chondrites. Since chondrules and the MS-rich phases are genetically related, any model explaining the noble gas signature of the chondrules must also include the MS-rich samples. We explain the low $^{36}\text{Ar}/^{20}\text{Ne}$ ratios of the chondrules by fractionation of phase Q and presolar diamonds during chondrule formation from a matrix-like precursor. The fractionation occurred during metal-silicate separation in the molten chondrules and can simultaneously explain the low $^{36}\text{Ar}/^{20}\text{Ne}$ ratios in the chondrules and the high $^{36}\text{Ar}/^{20}\text{Ne}$ ratios of some MS-rich rims compared to surrounding matrix-like material: the carbonaceous phase Q was preferentially enriched in the metallic phase, which moved to the chondrule margins and formed coatings around the chondrules. Within the chondrules only the most resistant presolar diamonds survived the heating and display a HL-like noble gas signature. The general similarity of the noble gas signatures of the MS-rich rims and the surrounding matrix-like material of the respective meteorites implies that the chondrule formation took place in the same region as the subsequent accretion to parent bodies: matrix-like material had to accrete directly onto the solidifying MS-rich chondrule rims, to explain the intimate mixture of these two phases. Then, the coated chondrules and the remaining dust needed to accrete immediately to the respective meteorite parent bodies without large-scale trans-
portation, which would probably have destroyed the similarity between the fine-grained portion of the MS-rich material and the matrix-like constituents.

Our data cannot be explained by chondrule formation close to the young sun as proposed for the chondrules of the enstatite chondrite Y-791790 (Okazaki et al., 2001b), since no SW or fractionated SW noble gases were found in our chondrules and the MS-rich rims. Chondrule formation near the young sun and later accretion with matrix-like material to the respective parent bodies at asteroidal distances would further fail to explain the genetic relationship of the noble gas signatures of MS-coated chondrules and the respective matrix-like material of the meteorites studied here. However, there does not necessarily need to exist only one single way to form chondrules. Taking into account the results of Okazaki et al. (2001b), it seems well possible that different chondrule formation mechanisms were active simultaneously in different regions of the solar system.

5.8 Acknowledgements

We thank the following institutions for providing sample material: the Muséum National d’Histoire Naturelle (Paris) for Renazzo, the Smithsonian National Museum of Natural History (Washington, DC) for Semarkona, the Natural History Museum (London) for Bishunpur, and the SSC of Environmental Radiochemistry (Kyiv) for Krymka. We further like to thank T. Grund, A. Baarnholm, and K. Kunze for competent assistance with SEM work. This work was supported by the Swiss National Science Foundation.
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**Tab. A5.1:** Ne and Ar isotopic and elemental compositions, 20Ne, 36Ar concentrations, and (36Ar/20Ne)tr ratios of Allende, Leoville, Semarkona, Bishunpur, Krymka, and Renazzo chondrules. Also given are blank contributions to 20Netr and 36Artr concentrations [%].
<table>
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<th>^20Ne/^22Ne</th>
<th>^21Ne/^22Ne</th>
<th>^36Ar</th>
<th>^36Ar/^38Ar</th>
<th>^20Ne_tr</th>
<th>^36Ar_tr</th>
<th>(^36Ar/ ^20Ne_tr)</th>
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<th>blank contr. to ^36Ar_tr</th>
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Gas concentrations are given in units of $10^{-8}$ cm$^3$STP/g. Numbers in parentheses represent uncertainties (1σ) in units of the least significant digit. The cosmogenic correction of the measured $^{20}$Ne and $^{36}$Ar ($^{20}$Ne$_{cos}$, $^{36}$Ar$_{cos}$) is explained in the text. For values in italics an origin of the $^{20}$Ne$_{cos}$, $^{36}$Ar$_{cos}$ due to inaccurate blank correction cannot be excluded. For numbers in {} contamination with matrix material during sample separation cannot be excluded. n.m. = not measured.
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<th>20Ne/22Ne</th>
<th>21Ne/22Ne</th>
<th>36Ar</th>
<th>36Ar/38Ar</th>
<th>20Netr</th>
<th>36Artr</th>
<th>(36Ar/20Ne)tr blank contr. to 20Netr</th>
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<td>0.9(2)</td>
<td>0.24(5)</td>
<td>6.4(5)</td>
</tr>
<tr>
<td>R-MSDrop-C</td>
<td>2.344(8)</td>
<td>1.37(3)</td>
<td>4.4(4)</td>
<td>0.52(6)</td>
<td>1.53(2)</td>
<td>1.98(4)</td>
<td>1.22(9)</td>
<td>1.17(3)</td>
<td>0.96(7)</td>
<td>2.5(7)</td>
</tr>
<tr>
<td>S-MS-A</td>
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<td>3.4(2)</td>
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<td>230(4)</td>
<td>5.35(6)</td>
<td>7.6(7)</td>
<td>229(5)</td>
<td>30(1)</td>
<td>4.1(1)</td>
</tr>
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<td>8.6</td>
<td>3.5(3)</td>
<td>0.51(5)</td>
<td>144(5)</td>
<td>5.32(6)</td>
<td>7.4(8)</td>
<td>144(7)</td>
<td>19(1)</td>
<td>5.3(1)</td>
</tr>
<tr>
<td>S-MSRim-A</td>
<td>1.36(2)</td>
<td>6.4</td>
<td>2.49(7)</td>
<td>0.65(2)</td>
<td>122(2)</td>
<td>5.30(4)</td>
<td>4.8(5)</td>
<td>122(3)</td>
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</tr>
<tr>
<td>B-MSRim-A</td>
<td>1.42(2)</td>
<td>5.4</td>
<td>2.3(1)</td>
<td>0.70(3)</td>
<td>160(2)</td>
<td>5.32(4)</td>
<td>3.8(7)</td>
<td>159(2)</td>
<td>41(6)</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>B-MSRim-F</td>
<td>1.96(6)</td>
<td>7.4</td>
<td>2.50(7)</td>
<td>0.75(2)</td>
<td>99(3)</td>
<td>5.26(4)</td>
<td>5.1(5)</td>
<td>98(4)</td>
<td>19(2)</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>K-MSRim-B</td>
<td>0.861(5)</td>
<td>8.9</td>
<td>1.31(4)</td>
<td>0.80(2)</td>
<td>146(1)</td>
<td>5.17(4)</td>
<td>3.7(9)</td>
<td>145(1)</td>
<td>38(4)</td>
<td>7.1(4)</td>
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<tr>
<td>K-MSRim-D</td>
<td>0.466(5)</td>
<td>12.3</td>
<td>1.33(5)</td>
<td>0.86(3)</td>
<td>127(1)</td>
<td>5.12(4)</td>
<td>5.1(5)</td>
<td>126(2)</td>
<td>25(3)</td>
<td>6.0(3)</td>
</tr>
<tr>
<td>K-MSRim-E</td>
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<td>7.4</td>
<td>0.66(3)</td>
<td>0.93(2)</td>
<td>4.7(2)</td>
<td>2.49(6)</td>
<td>0(1)</td>
<td>3.9(3)</td>
<td>85(820)</td>
<td>76.7(7)</td>
</tr>
<tr>
<td>K-MSRim-F</td>
<td>0.32(2)</td>
<td>9.7</td>
<td>1.65(7)</td>
<td>0.87(4)</td>
<td>199(11)</td>
<td>5.17(6)</td>
<td>5(1)</td>
<td>198(15)</td>
<td>39(4)</td>
<td>6.0(5)</td>
</tr>
<tr>
<td>K-MSRim-G</td>
<td>0.54(2)</td>
<td>12.1</td>
<td>1.63(6)</td>
<td>0.85(3)</td>
<td>188(5)</td>
<td>5.14(5)</td>
<td>6.1(1)</td>
<td>187(7)</td>
<td>29(3)</td>
<td>1.0(1)</td>
</tr>
</tbody>
</table>

Gas concentrations are given in units of 10^-5 cm³ STP/g. Numbers in parentheses represent uncertainties (1σ) in units of the least significant digit. The cosmogenic correction of the measured 20Ne and 36Ar (20Netr 36Artr) is explained in the text. For value in italics an origin of the 20Netr 36Artr due to an inaccurate blank correction cannot be excluded.
CHAPTER 6

NOBLE GASES IN ALLENDE CAIs
6.1 Introduction

With ages of up to 4.57 Ga (Allègre et al., 1995) Allende CAIs represent the oldest material found so far in the solar system. The extraordinarily refractory chemistry of CAIs reflects their particular high-temperature origin. As described in section 1.3.3, CAIs can be interpreted as the first condensates from a cooling nebula of solar composition, or as the most refractory residues left over from an intense fractional evaporation process, which might have taken place in the context of the X-wind scenario (Shu et al., 2001). In the framework of the X-wind model, the CAIs are supposed to have formed closer to the sun than the chondrules in order to explain the more refractory chemistry of the CAIs. However, the X-wind model does not explain the different textural types of CAIs (MacPherson et al., 1988): on the one hand there are irregularly formed fine-grained (“fluffy”) CAIs, whose texture points to a condensation origin. On the other hand, the droplet-shaped, more coarse-grained (“compact”) CAIs might have formed by evaporation. It is also suggested that compact CAIs might have formed by the melting of fluffy CAIs (MacPherson et al., 1988).

Only few noble gas studies on CAIs exist so far. For example, in a study on different Allende constituents Smith et al. (1977) found in CAIs Ne and Ar produced in part cosmogenically from Na and Cl, respectively. In volatile-rich CAIs, the authors further reported significant amounts of up to ~4x10^8 cm³STP/g of trapped ²⁰Ne. These concentrations are already in the range of Allende matrix-like material (see chapter 4). However, it was not possible to ascribe the trapped ²⁰Ne to a particular noble gas component. Russel et al. (1998) interpreted the ²²Ne overabundance in some temperature steps of a Vigarano (CV3) CAI as contributions of Ne-E consisting of nearly pure ²²Ne (Black and Pepin, 1969). Shukolyukov et al. (2001) reported primordial Ne (Ne-A in their notation) and a heterogeneous Ar isotopic composition in Efremovka CAIs, which they attributed to variable mixtures of cosmogenic, atmospheric, and solar Ar.

Significant amounts of trapped primordial noble gases would be quite unexpected in a high-temperature constituent – especially when considering the data of the chondrules (chapter 5). However, the presence of a solar-like trapped component in the CAIs would support their formation near the young sun as proposed, e.g., by Shu et al. (2001) and Gounelle et al. (2001). Therefore, a noble gas study on separates of fluffy and compact CAIs of Allende was performed to re-examine the presence of a trapped noble gas component (²⁰Ne) besides the cosmogenic gases with improved analytical techniques. Analyses of the chondrule samples (chapter 5) demonstrated that the analytical precision is sufficient to resolve the different noble gas components. In addition, the noble gas signa-
tures of the chondrules prove that it is possible to separate uncontaminated samples with the applied separation technique. The study of fluffy and compact CAIs should further help drawing conclusions on their different proposed formation histories and their possible genetic relationship.

6.2 Samples

Twenty-two samples of four compact and five fluffy Allende CAIs were separated. The CAIs labelled A-E (see Tab. 6.1) were separated from thick sections (Fig. 6.1) using the method described in chapter 2.2.

![compact CAI](image1)

**Fig. 6.1**: Examples of a coarse-grained compact CAI (a) and a fine-grained fluffy CAI (b) of Allende. The samples A-CAI-1,2 were separated from the compact CAI; the samples A-CAI-D1-3 were separated from the fluffy CAI.

To obtain the CAI samples F-I a larger piece of Allende was gently crushed so that small pieces containing CAI material could be picked out. As the samples separated from thick sections, the crushed CAI samples were classified as fluffy or compact by their outline shapes, and the grain sizes of the mineral assemblages (Tab. A6.1). Finally, adhering grey matrix material was carefully removed.
from the samples under the binocular microscope. The analytical procedure and the data reduction were performed as described in chapter 2.

6.3 Results and Discussion

6.3.1 Ne isotopic composition

Fig. 6.2 shows the Ne isotopic composition of the CAI samples (solid black and open symbols). Matrix-like samples of Allende (grey triangles) are plotted for comparison.

**Fig. 6.2**: Ne isotopic composition of fluffy (open symbols) and compact (black solid symbols) CAIs. For comparison, matrix-like samples of Allende (grey triangles) are also plotted (see chapter 4). The crosses represent calculated cosmogenic Ne-isotopic compositions of various minerals common in CAIs and of pure Na and Al (in circles). The ratios were calculated from cosmogenic production rates given by Leya et al. (2000) for a body of 50 cm radius and a mean shielding depth of ~25 cm. Slight changes in the body radius or shielding depth do not significantly affect the ratios. Fas= fassaite, Spi= spinel, Mel= melilite, An=anorthite, Gr=grossite, Co=corundum, Hi= hibonite, Nep= nepheline, Sod=sodalite. See text for further explanation.
Whereas matrix-like samples scatter around a mixing line between chondritic cosmogenic Ne and trapped Ne-HL, all CAIs plot on a regression line pointing from the chondritic cosmogenic Ne to smaller $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios. In accordance with the interpretation of Rüssel et al. (1998) the trend could indicate the presence of so-called Ne-E in the CAIs, which consists of nearly pure $^{25}\text{Ne}$ carried by presolar SiC and graphite (see, e.g., Ott, 2002, for a comprehensive review). However, the trend displayed by the CAIs in Fig. 6.2 can be explained more straightforwardly by the refractory CAI chemistry, which leads to cosmogenic Ne isotopic ratios different from those of a matrix-like sample. The crosses in Fig. 6.2 represent calculated cosmogenic Ne-isotopic ratios of different mineral phases common in CAIs (see Tab. 6.1) (Leya et al., 2000). They plot almost exactly on the line defined by the CAIs themselves. Aluminium and in particular Na, which is present in the secondary phases (e.g., Nepheline, Sodalite) of Allende CAIs (see, e.g., Brearley and Jones, 1998), shift the Ne isotopic ratios towards lower $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios. For an unequivocal identification of Ne-E, $^{21}\text{Ne}/^{22}\text{Ne}$ ratios below the cosmogenic $^{21}\text{Ne}/^{22}\text{Ne}$ ratio for sodalite ($<\sim0.5$) would have to be measured. None of our data points plots significantly above the "CAI$_{\text{cosm}}$-trend-line" (see Fig. 6.2), or even shows a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio above $>1$. This is in contrast to the data of Smith et al. (1977), who claimed to have detected trapped Ne because of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios $>1$ in some temperature steps. On the basis of our Ne isotopic data, however, the presence of any trapped component can be firmly excluded.

In conclusion, the Ne isotopic data of the Allende CAIs do in principal not contradict the presence of Ne-E as proposed by Rüssel et al. (1998). However, the CAI-trend in Fig. 6.2 can be more readily explained by cosmogenic produced Ne in the different refractory mineral phases. The presence of any further trapped component like Ne-Q, Ne-HL or solar-like Ne in the studied Allende CAIs can be firmly excluded. No differences could be detected in the Ne isotopic compositions of fluffy and compact CAIs.

157
**Tab. 6.1**: Structural formulas of common mineral phases in CAIs. Generally, the Al- and Na-rich endmembers of the minerals were taken to model the cosmogenic Ne isotopic ratios.

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Hibonite</td>
<td>Ca₃Al₂O₁₉</td>
</tr>
<tr>
<td>Grossite</td>
<td>Ca₆Al₂O₁₇</td>
</tr>
<tr>
<td>Perovskite</td>
<td>Ca₃TiO₃</td>
</tr>
<tr>
<td>Anorthite</td>
<td>Ca₃Al₂Si₂O₈</td>
</tr>
<tr>
<td>Spinel</td>
<td>Mg₃Al₂O₄</td>
</tr>
<tr>
<td>Melilit</td>
<td>Ca₂Al₂SiO₇ - Ca₂MgSi₂O₇</td>
</tr>
<tr>
<td>Fassaite</td>
<td>Ca(Mg,Al₂,Fe)(Si₂Al₂,Ti)O₆</td>
</tr>
<tr>
<td>Nepheline</td>
<td>(Na,K)Al₃SiO₄</td>
</tr>
<tr>
<td>Sodalite</td>
<td>Na₄Al₂Si₃O₁₂Cl</td>
</tr>
</tbody>
</table>

**6.3.2 Ar isotopic composition**

In Fig. 6.3 are plotted the $^{36}\text{Ar}^{38}\text{Ar}$ ratios of all CAIs vs. their measured $^{36}\text{Ar}$ concentrations ($^{36}\text{Ar}_{\text{meas}}$). In contrast to the Ne data, the fluffy and compact CAIs show a clear dichotomy in their $^{36}\text{Ar}^{38}\text{Ar}$ ratios. The compact CAIs show a mean $^{36}\text{Ar}^{38}\text{Ar}$ ratio of ~1.2, whereas the mean $^{36}\text{Ar}^{38}\text{Ar}$ ratio of the fluffy CAIs is distinctly higher, around 3.3 (Tab. A6.1). However, the ranges of the $^{36}\text{Ar}_{\text{meas}}$ concentrations are fairly similar for both groups, (1-5)×10⁻⁸ cm³STP/g.
At first glance, the enhanced $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of fluffy CAIs (open symbols) compared to the $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of the compact ones (solid symbols) might indicate the presence of well-discernible amounts of non-cosmogenic, e.g., trapped Ar as proposed by Shukolyukov et al. (2001). The concentrations would be up to $\sim4\times10^{-8}$ cm$^3$STP/g $^{36}\text{Ar}_\text{t}$, i.e., in the range of $^{36}\text{Ar}_\text{t}$ concentrations in chondrules (Tab. A5.1). This would support a formation of the compact CAIs by melting of fluffy CAIs accompanied by the loss of $^{36}\text{Ar}_\text{t}$.

However, also possible systematic differences in the chemistry of fluffy and compact CAIs might have had significant effects on the cosmogenic Ar production rates and isotopic ratios, and could thus be responsible for the differences in the Ar signatures of both CAI groups. This possibility is discussed in detail in the following.

6.3.2.1 Cosmogenic production of Ar from Ca in CAIs

The main target material for the cosmogenic production of Ar in CAIs is Ca (see Wieler, 2002a) with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of $\sim0.65$ identical to the “typical” chondritic
cosmogenic ratio (see Tab. 1.1). Thus, if Ar produced from Ca (Ar_{Ca}) was the only source of Ar in the studied CAIs, all samples should have the same $^{36}\text{Ar}/^{38}\text{Ar}$ ratio (0.65). Variable concentrations of Ca and thus of Ar_{Ca} in the samples would merely shift the data points along the x-axis in Fig. 6.3 without affecting the isotopic ratios.

However, the measured $^{36}\text{Ar}/^{38}\text{Ar}$ ratios in all CAIs scatter roughly between 0.7 and 5. This indicates the presence of a second Ar component with a higher $^{36}\text{Ar}/^{38}\text{Ar}$ ratio, which seems to be more prominent in the fluffy CAIs than in the compact ones. The most probable among several possible components is cosmogenic Ar produced by neutron capture and subsequent $\beta^-$ decay (Ar_{nc}) from Cl with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of ~100. This is discussed in detail in the next section.

Assuming that both groups of CAIs have similar Ca concentrations (i.e., similar Ar_{Ca} concentrations), the higher $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of the fluffy CAIs would have to be correlated with higher total $^{36}\text{Ar}$ concentrations in the fluffy CAIs compared to the compact CAIs due to the addition of $^{36}\text{Ar}$ from the second component. However, the range of total $^{36}\text{Ar}$ concentrations is fairly similar in both groups. Therefore, the amount of Ar_{Ca}, and thus the concentration of Ca must be systematically lower in the fluffy CAIs than in the compact ones. The additional $^{36}\text{Ar}_{\text{nc}}$ on average just seems to roughly compensate the "missing" $^{36}\text{Ar}_{\text{Ca}}$ in the fluffy CAIs. A somewhat more quantitative estimate can be made by assuming identical $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of the second endmember for both groups of CAIs and calculating the relative contribution from each component for both, compact and fluffy CAIs: the relative contribution of Ar_{Ca} to the total Ar is on average 3-4 times higher in the compact CAIs than in the fluffy ones. This can be translated to 3-4 times higher Ca concentrations in the compact CAIs compared to the fluffy ones. This result is supported by Ca concentrations in Allende CAIs determined by Grossman (1976 a,b). The author defined two CAI groups, coarse- and fine-grained CAIs, which basically represent the coarse-grained compact and the fine-grained fluffy CAIs of this study. The author analysed between 1 and 12% Ca in the fine-grained (fluffy) CAIs and 9 to 26% Ca in the coarse-grained (compact) CAIs, i.e. on average 3 times higher Ca concentrations in the compact CAIs. This is in agreement with the above estimate of the different relative portions of Ar_{Ca} in the two groups of CAIs and enables explaining the spread in the $^{36}\text{Ar}$ concentrations within each single group.

In conclusion, a systematically higher Ca-concentration in the compact CAIs compared to the fluffy CAIs correlated with a relatively higher proportion of Ar_{nc} in the fluffy CAIs (see next section) can explain the clear dichotomy in the Ar isotopic composition of both groups.
As already discussed above, principally several components with $^{36}\text{Ar}/^{38}\text{Ar}$ ratios above the cosmogenic ratio of 0.65 are possible to explain the higher ratios especially of the fluffy CAIs in Fig. 6.3. These could be trapped components like Ar-HL or Ar-Q with $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of 4.41 and 5.34, respectively (see, e.g., Tab. 5.1). However, more probable is Ar$_{nc}$ produced by neutron capture on Cl with subsequent $\beta$-decay with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of ~100. Ar$_{nc}$ might significantly contribute to the Ar inventory of the CAIs because of the large pre-atmospheric size of Allende and thus high production rates of Ar$_{nc}$, if Cl was present (see section 5.4.3).

Unfortunately, analyses of chlorine in meteorites are generally rare. However, Grossman and Ganapathy (1975) reported Cl concentrations in the two groups of Allende CAIs (fine- and coarse-grained). Whereas the authors did not detect Cl in the CAIs of the coarse grained (compact) group, the fine-grained (fluffy) CAIs contained up to 1.7% Cl, which is ~6 times higher than the value for bulk Allende (see Tab. 5.2). This exactly matches the requirement presented above, that the Ca and Cl concentrations in the two groups of CAIs should be anticorrelated: Indeed, the compact CAIs with higher Ca concentrations do not contain measurable concentrations of Cl, whereas the fluffy CAIs with lower Ca concentrations contain the high concentrations of Cl. Using the parameters given in Tab. 5.2, up to ~5x10$^{-8}$ cm$^3$STP/g $^{36}\text{Ar}_{nc}$ could have been produced theoretically in fluffy Allende CAIs during the 5.1 Ma of irradiation with GCR. Thus, it is probable that a part of the measured $^{36}\text{Ar}$ in the fluffy CAIs is cosmogenic Ar produced by neutron capture on Cl with subsequent $\beta$-decay shifting the $^{36}\text{Ar}/^{38}\text{Ar}$ ratios to higher values than the "normal" ($^{36}\text{Ar}/^{38}\text{Ar}$)$_{Ca}$ ratios of 0.65 (Fig. 6.3).

In conclusion, based on this semiquantitative estimate, the Ar isotopic signature of fluffy and compact CAIs can be explained by the cosmogenic production of Ar$_{Ca}$ and Ar$_{nc}$, but the estimate is not precise enough to allow excluding a small trapped Ar component in the CAIs.

A more quantitative approach would be to calculate the expected concentrations of Ar produced from Ca and Cl during the GCR exposure of Allende. However, the production rates of Ar from Ca and Cl are quite uncertain due to the lack of experimentally determined cross-section data (Leya et al., 2000), and no chemical analyses were performed on the studied CAIs. Therefore, an accurate calculation of the amounts of cosmogenic Ar and thus of possible further trapped contributions is not yet possible.

Na and Cl are present in the same secondary mineral phases in CAIs as, e.g., in sodalite (see Tab. 6.1). Therefore it is somewhat astonishing to find the clear dif-
ferences in the Ar isotopic compositions of fluffy and compact CAIs, but not in the Ne isotopic compositions. A possible explanation might be that the differences of the Ne-production from Na and Al ($^{21}\text{Ne}/^{22}\text{Ne} \sim 0.4$ and $\sim 0.7$, respectively) is much smaller than the differences of the Ar-production from Ca and Cl ($^{36}\text{Ar}/^{38}\text{Ar} \sim 0.65$ and $\sim 100$, respectively). Furthermore, there is no anticorrelation of the two main Ne producing targets Na and Al, as it is observed for the two main Ar producing elements Ca and Cl. This might further inhibit the establishment of clear differences in the $^{21}\text{Ne}/^{22}\text{Ne}$ ratios of fluffy and compact CAIs. To address this question detailed chemical analyses and modelled Ne and Ar production rates and ratios should be combined with Ne and Ar measurements for the respective fluffy and compact CAIs.

6.4 Conclusion

The Ne isotopic signature of the CAIs can be consistently explained by cosmogenic Ne production mainly from Al- and Na-rich phases. Ne-E as the reason for the low $^{20}\text{Ne}/^{22}\text{Ne}$ ratios in the Allende CAIs, as suggested by Russel et al. (1998) for a Vigarano CAI, is much less probable than the cosmogenic Ne production. In contradiction to the results presented by Smith et al. (1977), in none of the studied CAIs could any trapped Ne be detected. No differences in the Ne isotopic composition of fluffy and compact CAIs were observed.

The $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of fluffy and compact CAIs are clearly different: the fluffy CAIs have higher ratios than the compact ones. However, the measured $^{36}\text{Ar}$ concentrations are all in a similar range. This is most probably due to an anticorrelation of the Ca and Cl content in the two groups of CAIs, leading to differing cosmogenic Ar production rates. The Ar signature of the compact CAIs is influenced mainly by cosmogenic Ar produced from Ca, whereas the Ar signature of the fluffy CAIs with lower Ca, but higher Cl concentrations is shifted towards higher $^{36}\text{Ar}/^{38}\text{Ar}$ ratios of the cosmogenic Ar produced from neutron capture on Cl. Although the data are consistently explained by cosmogenic Ar production, a small additional trapped Ar component cannot be fully excluded. To verify the presence or absence of a trapped Ar component in CAIs, those from a distinctly smaller chondrite, e.g., the CV chondrite Axtell, should be studied, in which the cosmogenic production of $^{36}\text{Ar}$ from Cl is minor.

The lack of trapped Ne and probably also trapped Ar in CAIs is in contrast to the noble gas signatures of chondrules (discussed in chapter 5). These often still contain measurable amounts of trapped, probably HL-like Ne and mostly significant concentrations of trapped Ar. Thus, the noble gas data support the mineralogical-chemical evidence that the chondrules were less intensely heated than the CAIs.

162
Due to the more intense heating of the CAI precursor material, all trapped noble gases, which might have been present, were released, so that the condensing material or evaporation residue was basically free of any trapped noble gases. If the CAIs were formed close to the young sun, any solar-like signature was either lost from the material during heating, and/or no measurable amounts of solar-like Ne and Ar could be dissolved in the molten CAIs. Since no experimental or model data exist about the trapping of noble gases in constituents during high temperature processing, the lack of solar-like noble gases in Allende CAIs does not necessarily contradict CAI formation in the framework of the X-wind scenario (Shu et al., 2001).
**Tab. A6.1:** He, Ne and Ar isotopic ratios and concentrations of compact and fluffy CAIs of Allende.

<table>
<thead>
<tr>
<th>Allende CAIs</th>
<th>class</th>
<th>weight [g] x10^{-4}</th>
<th>20Ne blank contr. to 20Ne [%]</th>
<th>20Ne/22Ne</th>
<th>21Ne/22Ne</th>
<th>36Ar blank contr. to 36Ar [%]</th>
<th>36Ar/38Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-CAI-C1</td>
<td>c</td>
<td>3.21(3)</td>
<td>1.01(5)</td>
<td>2.3</td>
<td>0.89(6)</td>
<td>0.83(3)</td>
<td>2.42(3)</td>
</tr>
<tr>
<td>A-CAI-C2</td>
<td>c</td>
<td>9.48(1)</td>
<td>0.99(2)</td>
<td>0.6</td>
<td>0.79(2)</td>
<td>0.82(2)</td>
<td>2.32(1)</td>
</tr>
<tr>
<td>A-CAI-F</td>
<td>c</td>
<td>6.83(3)</td>
<td>2.69(5)</td>
<td>0.8</td>
<td>0.86(2)</td>
<td>0.93(1)</td>
<td>0.79(1)</td>
</tr>
<tr>
<td>A-CAI-H1</td>
<td>c</td>
<td>7.36(2)</td>
<td>0.99(3)</td>
<td>1.8</td>
<td>0.75(3)</td>
<td>0.83(2)</td>
<td>1.69(1)</td>
</tr>
<tr>
<td>A-CAI-H2</td>
<td>c</td>
<td>8.78(2)</td>
<td>1.23(2)</td>
<td>1.3</td>
<td>0.75(1)</td>
<td>0.77(1)</td>
<td>2.89(2)</td>
</tr>
<tr>
<td>A-CAI-H3</td>
<td>c</td>
<td>3.06(1)</td>
<td>1.17(4)</td>
<td>3.8</td>
<td>0.81(4)</td>
<td>0.81(3)</td>
<td>3.67(5)</td>
</tr>
<tr>
<td>A-CAI-H4</td>
<td>c</td>
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<td>1.04(4)</td>
<td>1.2</td>
<td>0.76(4)</td>
<td>0.79(3)</td>
<td>2.03(2)</td>
</tr>
<tr>
<td>A-CAI-G1</td>
<td>c</td>
<td>6.289(1)</td>
<td>1.25(4)</td>
<td>1.4</td>
<td>0.65(2)</td>
<td>0.72(1)</td>
<td>1.37(2)</td>
</tr>
<tr>
<td>A-CAI-G2</td>
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<td>11.246(9)</td>
<td>1.17(3)</td>
<td>0.9</td>
<td>0.64(2)</td>
<td>0.72(1)</td>
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<tr>
<td>A-CAI-G3</td>
<td>c</td>
<td>4.85(1)</td>
<td>1.34(4)</td>
<td>1.2</td>
<td>0.68(2)</td>
<td>0.73(1)</td>
<td>1.44(2)</td>
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<tr>
<td>average</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td>11.5(5)</td>
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<td></td>
<td>0.75(8)</td>
<td>0.78(6)</td>
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<td>A-CAI-A1</td>
<td>f</td>
<td>1.821(5)</td>
<td>1.18(4)</td>
<td>3.5</td>
<td>0.67(4)</td>
<td>0.72(4)</td>
<td>3.07(5)</td>
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<td>4.690(5)</td>
<td>1.27(4)</td>
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<td>0.71(2)</td>
<td>0.74(2)</td>
<td>4.31(5)</td>
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<tr>
<td>A-CAI-A4</td>
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<td>1.36(8)</td>
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<td>0.75(6)</td>
<td>0.77(5)</td>
<td>4.55(7)</td>
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<tr>
<td>A-CAI-B1</td>
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<td>1.58(6)</td>
<td>1.2</td>
<td>0.75(3)</td>
<td>0.81(3)</td>
<td>2.28(4)</td>
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<tr>
<td>A-CAI-B2</td>
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<td>3.588(5)</td>
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<td>0.85(2)</td>
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<td>6.089(1)</td>
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<td>0.77(2)</td>
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<td>0.78(3)</td>
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<td>0.82(3)</td>
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<td>8.537(3)</td>
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<tr>
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<td>2.03(6)</td>
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<td>0.95(3)</td>
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<td>0.80(2)</td>
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<td>1.5(3)</td>
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<td>0.75(7)</td>
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</table>

Gas concentrations are given in units of 10^{-8} cm³ STP/g. Uncertainties represent the standard deviations of the respective values. "c" = compact, "f" = fluffy. Numbers in brackets are 1σ uncertainties in units of the least significant digit. CAI data in italics: ~10% of matrix-contamination during separation, thus, the values were excluded from the averages.
CHAPTER 7

SUMMARY AND OUTLOOK
In this PhD thesis the microdistribution of trapped noble gases in different constituents of unequilibrated chondrites was studied. Unequilibrated chondrites are “cosmic sediments” basically consisting of two different types of constituents. These are on the one hand chondrules and CAIs, both being formed during particular high-temperature events. On the other hand, there are different fine-grained materials like fine-grained rims, dark inclusions, or matrix, which are rather low-temperature constituents. The distribution of trapped noble gases among the constituents enables deciphering variable processes like accretion, melting or evaporation, and alteration in the early solar nebula, and their relative timing. This is crucial for understanding the accretion of the larger bodies of the solar system.

For the study, the six unequilibrated carbonaceous and ordinary chondrites Allende, Leoville, Renazzo, Semarkona, Bishunpur, and Krymka were selected. Their constituents are large enough for a proper separation; furthermore, the primordial noble gas inventory is not obscured by SW noble gases. Their exposure ages range from 5 to 26 Ma, which sometimes led to substantial contributions from cosmogenic noble gases.

The thick sections were imaged by SEM before the sample separation under a binocular microscope. The weighted samples were extracted by an IR-laser and the sample gas was cleaned and separated in a low-blank extraction line especially designed to remove large amounts of active gases abundant in chondrites. He, Ne, and Ar analyses were performed on a mass spectrometer, which is suited to measure small amounts of noble gases.

Analyses of noble gases in fine-grained rims, matrix, and single dark inclusions allowed conclusions about accretion and alteration processes in the solar nebula. The primordial noble gas concentrations decreased from rims to matrix in Leoville, Semarkona, Bishunpur, and – less so – also Allende. In contrast, Krymka and Renazzo show an increase of the primordial noble gas concentrations from rims to matrix. This indicates subsequent accretion of nebular dust with decreasing and increasing noble gas content, respectively. The preferred explanation for these features is admixture either of noble-gas-poor or –rich dust to the reservoirs, from which the rims and subsequently the matrix accreted to the respective parent bodies. However, for Renazzo also rim formation by alteration of matrix cannot be excluded. The analysed dark inclusions have noble gas compositions different from their respective host meteorites, further pointing to mixing processes also of larger clasts in the solar nebula. However, it is unclear whether the heterogeneous distribution of trapped noble gases in the solar nebula was primary, or had evolved from an originally homogeneous nebula by alteration processes.
Despite their high-temperature origin, the studied chondrules generally contain measurable primordial Ar concentrations and for some of the chondrules in Renazzo, Semarkona, and Bishunpur, also primordial Ne. These show unusually low $^{36}\text{Ar}/^{20}\text{Ne}$ ratios compared to their surrounding matrix-like material. In contrast, metal-sulphide-rich rims around chondrules, which formed during chondrule formation by separation of the metal phase from the silicate melt droplets, show $^{36}\text{Ar}/^{20}\text{Ne}$ ratios in part above the respective surrounding matrix-like material. It is inferred that during chondrule formation the Ar carrier phase Q preferentially moved into the metal phase and thus is enriched in the metal-sulphide-rich rims around chondrules. The silicate chondrule interiors show a preferential depletion of Ar, and thus a more HL-like Ne-isotopic signature. The data support chondrule formation in a local dust-rich environment and subsequent fast accretion to the respective parent bodies rather than chondrule formation in an X-wind scenario. Taking into account literature results, more than one chondrule formation process seems to have worked more or less simultaneously in the solar nebula.

The studied Allende fluffy and compact CAIs show clear cosmogenic Ne and Ar signatures without a detectable trapped component. The Ne isotopic signature is uniform for both groups of CAIs and was mainly produced by interaction of galactic cosmic radiation with the main Ne-producing phases in CAIs, Al- and Na-rich phases. The $^{36}\text{Ar}/^{38}\text{Ar}$ ratios are distinctly higher for the fluffy CAIs than for the compact ones. This can be explained by lower Ca- and higher Cl-concentration in the fluffy CAIs compared to the compact ones, which led to different cosmogenic production ratios. No solar-like noble gases were detected, which would strongly have supported CAI formation in the framework of the X-wind scenario.

The very different noble gas compositions in the constituents of unequilibrated chondrites show the wealth of information stored within them concerning the processes and conditions in the solar nebula. Part of this information can be deciphered by studying the microdistribution of noble gases within the chondrites. However, the study also revealed some limitations of the method: To detect differences in the noble gas composition of the different constituents, a proper sample separation is crucial. However, the transitions are often blurred, e.g., between fine-grained rims and matrix. Therefore, in some cases a substantial cross-contamination of the different entities and their noble gas inventories occurred. This limits the method to unequilibrated chondrites with large constituents. Chondrite groups like CM chondrites, in which, e.g., fine-grained rims
around chondrules are very abundant, cannot be studied with the present method. For these, in situ analyses with an UV-laser, which mostly avoids fractionation effects, would be more suitable.

Especially for the chondrules the low noble gas concentrations were a limiting factor. Despite in part relatively large sample amounts compared to the matrix-like constituents, the extracted noble gas amounts were not far above the blank level. This caused in part a significant uncertainty in the analysed noble gas concentrations of the gas-poor chondrule samples.

From the present noble gas study also some questions especially concerning the formation of chondrules and their associated metal-sulphide-rich phases emerged:

The finding of low primordial noble gas concentrations in the chondrules of CV, CR, and LL chondrites points to a similar chondrule formation process and probably also similar precursor materials for the chondrules of these chondrite types. However, as discussed in chapter 5, chondrules of an enstatite chondrite showed high amounts of the subsolar noble gases, which were interpreted to support chondrule formation in the X-wind scenario. However, these analyses were performed in situ with an IR-laser, possibly causing systematic fractionation of the noble gases. Furthermore, the “subsolar” noble gas component possibly represents a mixture of trapped and atmospheric gases. A logical extension of the noble gas study on chondrules would be to perform whole grain analyses from chondrules of enstatite chondrites to find out whether their unusual noble gas signature can be confirmed or must be ascribed to artifacts due to atmospheric noble gases, fractionation processes, and/or matrix-contamination due to the in situ analyses.

The metal-sulphide-rich phases associated to chondrules revealed a preferential fractionation of the carrier phase Q into the metal phase. The different groups of carbonaceous chondrites also show a correlation of their average primordial Ar concentrations and their relative metal contents. It is certainly instructive to analyse the noble gas composition of pure (etched) metal separates of different chondrite groups and classes in order to better understand the nature of phase Q and its behaviour during thermal metamorphism.
REFERENCES


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Title of the diploma thesis: Systematic K/Ar age determinations on fine-fractions of middle-Devonian tuffs, siltstones, and sandstones derived from the Eastern part of the Rheinisches Schiefergebirge.

1999-2003 PhD. student at the Institute for Isotope Geology and Mineral Resources, ETH Zürich / Switzerland
DANK

Wahrscheinlich kann man sich hier auf den letzten Metern noch völlig disqualifizieren, ist doch die Danksagung der mithin am häufigsten und kritischsten gelesene Abschnitt einer solchen Arbeit. Trotzdem versuche auch ich hier das Unmögliche, nämlich, mich bei allen zu bedanken, die mir in den letzten vier Jahren während meiner Diss-Zeit lebens- und/oder arbeitstechnisch zur Seite gestanden haben:

Zu allererst möchte ich mich bei meinen Betreuer Rainer Wieler für die Vergabe des Projekts und die grossartige Betreuung bedanken. Er ist auf jeden Fall die Schlüsselfigur im Unternehmen „Diss“: Rainer ist immer und sofort zur Stelle, wenn es Probleme gibt und man Betreuung braucht („...kommst du rasch hinter, dann können wir das diskutieren...“), lässt einem aber auch immer genug Freiheit „herumzuforschen“. Ausserdem spielt er sich NIENENIE als „Chef“ auf, was eine unglaublich entspannte und motivierende Arbeitsatmosphäre schafft. Schade, kann ich ihn nicht mitnehmen....


Allerdings hätte das alles nichts genutzt, hätte sich nicht Addi Bischoff dazu bereit erklärt, mich in die Geheimnisse der Meteoritenforschung einzuweihen. So hat er stundenlanges Sitzen vor dem SEM oder dem Mikroskop und die ewige Fragerei meinerseits klaglos über sich ergehen lassen. Für all das und die Übernahme des Korreferats möchte ich mich ganz herzlich bedanken.

Alex Halliday verbreitet eine sehr motivierende, „geschäftige“ Atmosphäre um sich herum, und die vielen Laborbesichtigungen („be around and look busy“) geben einem das Gefühl, an einem besonderen Institut zu arbeiten. Für alles, und die Übernahme des Korreferates vielen herzlichen Dank.

Ein riesengrosses Dankeschön geht an meine Langzeit-Zimmerkollegin Veronika Heber, die mir den „first contact“ zum Institut, dem Labor und der Schweizer Bürokratie enorm erleichterte. Im Laufe der Jahre haben sich neben täglichen Diskussionen über wissenschaftliches („sind wir nun zu blöd oder nicht?“) unzählige schöne Treppen-Kaffees, Letten-Badi-Besuche, gemeinsame Konferenzen (plus die Sommerschule im


Bei Vronis „Nachfolger“ Philipp Heck muss ich mich vor allem für seine Hilfe in allen möglichen Computerfragen bedanken, und das, obwohl er PCs ja eigentlich zutiefst verabscheut. Ausserdem sollte man unter allen Umständen versuchen, bei ihm zum Essen (meist mit Kinovorführung) eingeladen zu werden, denn seine persischen Kochkünste sind sensationell!


Bei Britt Meyer möchte ich mich für die stetige und geduldige Unterstützung in allen kleinen und grossen Fragen des Papierkriegs mit der ETH und sonstigen bürokratischen Institutionen bedanken. Sie setzt sich wie sonst niemand für die Belange der Doktoranden ein, und hat neben dem Riesenberg an Arbeit sogar immer noch Zeit für Nicht-Instituts-Gespräche; vielen herzlichen Dank für alles!

Weiterhin möchte ich mich bei allen anderen Doktorandinnen und Doktoranden (Jörg, Maria, Manuela, Bettina, Zhou, Tomas, Morten, Sune, Veronika B., Marcus, Majka, Ansgar, und Benjamin; sowie dem Feuerwehrmann, Chris, Iris, Andreas und Frank in Münster), Postdocs, Oberassistenten und Mitarbeitern der Institute in Zürich und in Münster für das jeweils gemütliche Betriebsklima danken – es war eine wunderschöne Zeit!!!

Ein besonderer Dank gebührt Det Rost, der massgeblich daran beteilig war, dass alle meine Münster-Aufenthalte wunderschön (und immer lustig) waren – Danke!

Ein extra Dankeschön geht an Hemer Busemann, der, trotzdem ich ihm den Schreibtisch weggeklaut habe, fleissig Fernbetreuung betrieben und sich viel Zeit für Manuskriptkorrekturen und das eine oder andere Bier genommen hat. Merci!

Marco hat mich die ganze Diss-Zeit über mit österreichischer Fröhlichkeit, selbstgebastelten CDs, Adventskalendern etc. beiLaune gehalten. Hierfür gebührt ihm mein ganz besonderer Dank.

An dieser Stelle geht auch ein dickes Dankeschön an den ASWZ, der durch sein reichhaltiges Sportangebot entscheidend zu meinem Wohlbefinden, besonders in der Schlussphase beigetragen hat.

Wie ich mich bei Andi für die wunderbare Zeit bedanken soll, weiss ich leider nicht. Nichts von alledem wäre so möglich gewesen ohne ihn.

Ebenso unabdingbar waren und sind meine Eltern und Geschwister, die mir zu jeder Zeit Rückhalt und Unterstützung geboten haben, auch wenn ich viel zu selten zu Hause war. Danke für alles.