Doctoral Thesis

Helium and neon in presolar silicon carbide grains and in relict chromite grains from fossil meteorites and micrometeorites as tracers of their origin

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HELIUM AND NEON IN PRESOLAR SILICON CARBIDE GRAINS AND IN RELICT CHROMITE GRAINS FROM FOSSIL METEORITES AND MICROMETEORITES AS TRACERS OF THEIR ORIGIN

A dissertation submitted to the

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presented by

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**Frontcover:**

*Upper left:* About 90% of all known presolar dust grains are thought to originate in late stages of low- to intermediate mass stars such as the Egg Nebula CRL 2688, a proto-planetary nebula in a distance of ~3000 light years. In this visible-light image (about 1 light year wide) taken with the Hubble Space Telescope several polarizing filters have been used to show how light is scattered by dust particles. The concentric dust shells can be explained with episodic mass-loss during the thermal pulses of the AGB phase. Image credit: NASA and The Hubble Heritage Team (STScI/AURA, W. Sparks (STScI) and R. Sahai (JPL)).

*Upper right:* SEM image of presolar silicon carbide grain SiC121 (size 1.4 x 1.8 µm) from the meteorite Murchison prior to ion-microprobe and noble-gas analysis. Image credit: Ph. Heck, K. Marhas, J. Huth.

*Lower left:* A 480 Myr old fossil meteorite recovered from the Thorsberg quarry in southern Sweden (size 6 x 8.5 cm). Although mineralogically the fossil meteorite has been completely altered (with the exception of microscopic chromite grains), the texture of mm-sized chondrules has been conserved. At that time a large asteroid collision occurred and resulted in an about 100 x higher flux of extraterrestrial material that rained down on Earth than today. Photo courtesy: B. Schmitz.

*Lower right:* SEM image of a 480 Myr old, well preserved extraterrestrial chromite grain (diameter ~200 µm, Hälekis quarry, Sweden) extracted from a fossil meteorite. Image credit: C. Alwmark and B. Schmitz.
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Acknowledgements

Curriculum Vitae
Abstract

This Ph.D. thesis is dedicated to the study of noble gases, in particular helium and neon, from dust-sized extraterrestrial samples, to gain insight on their provenance. The noble gas analyses were conducted with an ultra-high sensitivity noble gas mass spectrometer coupled with an infrared laser gas extraction system. The two main parts of this dissertation are devoted to noble gases in two different kinds of sample materials: presolar silicon carbide (SiC) stardust from primitive meteorites and relict chromite grains from fossil meteorites and micrometeorites.

The main goal of the first study was to improve our understanding of the stellar sources of presolar stardust grains. Helium and neon isotopes in submicron to micron-sized, single presolar SiC grains from primitive meteorites were investigated. The primary objective was to determine the fraction of grains containing nucleosynthetic noble gases detectable with an ultra-high sensitivity mass spectrometer. This was combined with NanoSIMS ion-microprobe analyses of silicon, carbon and nitrogen isotopes to constrain the origin of the presolar grains. About 40 percent of the samples studied contain nucleosynthetic noble gases. The majority of them formed as circumstellar condensates around evolved, late-stage, low-mass carbon stars (C-rich stars on the Asymptotic Giant Branch, AGB). A small fraction of the gas-rich grains might have originated in the winds of intermediate-mass AGB stars, other particular types of carbon stars (J-type carbon stars and born-again giants) and in the ejecta of supernova and arguably nova explosions.

The second major study is dedicated to noble gases in tiny chromite grains from fossil meteorites and sediment-dispersed extraterrestrial chromite grains from 480 Myr old (Ordovician) marine sediments from Sweden to constrain the delivery modes and times of extraterrestrial material from the asteroid belt to Earth.

An important result of this work are the unusually low cosmic-ray exposure ages (about 100 kyrs to 1 Myr) of a suite of fossil meteorites, determined from noble gas concentrations in relict chromite grains. Furthermore, the exposure ages of the meteorites increase in younger sediments. The exposure age difference between the meteorites found in the youngest sediments and the ones from oldest sediments is about 1 Myr and corresponds to the age difference of the host sediments. The short cosmic-ray exposure ages are in agreement with dynamical model predictions of space residence times of meteorites generated by a major asteroid collision close to regions where orbits are unstable due to resonances with Jupiter and Saturn. Such a region occurs for example where the orbital period of an object is a third of the one of Jupiter. The timing of one of the largest asteroid collisions in recent solar system history, the L chondrite parent body break-up event, coincides with the age of the meteorite-bearing sediments and
makes this event the most likely source for the Ordovician fossil meteorites. In particular, the low exposure ages indicate this major asteroid collision occurred near an important orbital resonance in the inner asteroid belt.

Surprisingly, extraterrestrial chromite grains dispersed in the same sediments as the fossil meteorites are very rich in solar noble gases. This prevented the determination of their cosmic-ray exposure ages. However, the solar gas-richness suggests they were produced as dust in the L chondrite parent body break-up and came to Earth as sub-mm sized micrometeorites. Their solar gas concentrations and compositions are similar to the values reported for gas-rich micrometeorites and gas-poor stratospheric interplanetary dust particles (IDPs).

In a pilot study, helium and neon isotopes in stratospheric IDPs were also analyzed. The aim was to test feasibility and to optimize experimental methods to IDP noble gas analyses, for possible future studies on “cluster IDPs”. For the latter, other research groups reported unusual helium isotopic ratios, which are difficult to explain. The IDPs studied in this thesis have solar noble gases comparable in concentration and composition to other, “non-cluster” IDPs collected in the stratosphere. The analytical methods developed here are therefore well suited to analyze different types of IDPs.
Zusammenfassung


Das Hauptziel der ersten Studie besteht darin, Ergebnisse von Laboranalysen präsolaren Sternenstaus mit theoretischen Sternmodellen zu vergleichen, um dadurch das Verständnis der verschiedenen Typen der Ursprungssterne der Staubkörner zu verbessern.


Die zweite Hauptstudie widmete sich den Edelgasen in Chromitkörnern, die aus fossilen Meteoriten aus etwa 480 Millionen Jahre alten, ordovizischen Meeressedimenten aus Schweden gewonnen wurden und von winzigen extraterrestrischen Chromitkörnern, die einzeln verteilt in denselben Sedimenten gefunden wurden. Das Ziel war in erster Linie die Dauer, sowie die Art und Weise des Transfers der Meteorite von ihrem Ursprungsasteroiden zur Erde mittels Edelgasen in Chromiten zu bestimmen.

Eine entscheidende Erkenntnis dieses Forschungsprojekts ist, dass die Transferzeiten (Bestrahlungsdauer im Weltraum) aller untersuchten fossilen Meteorite aussergewöhnlich kurz waren (etwa 100000 bis 1 Million Jahre). Ausserdem erhöhen sich die Transferzeiten

In einer Pilotstudie wurden ausserdem Helium- und Neonisotope in stratosphärischen IDPs gemessen. Das Ziel war die experimentellen Methoden auf Edelgasanalysen von IDPs zu optimieren. Dies im Hinblick auf zukünftige Untersuchungen an sog. „Cluster IDPs“. In letzteren haben andere Forschungsgruppen eine ungewöhnliche, schwer erklärbare Helium-isotopenzusammensetzung beobachtet. Die IDPs, die hier untersucht wurden, haben vergleichbare Edelgaskonzentrationen und -zusammensetzungen wie andere, nicht-cluster IDPs. Aus diesem Grund lässt sich festhalten, dass die in dieser Dissertation entwickelten analytischen Methoden sehr gut für das Studium von IDPs geeignet sind.
I. Introductory Chapter
1. Foreword

This Ph.D. thesis consists of two different laboratory studies on very small amounts of light noble gases in extraterrestrial materials. The analyses require an ultra-high sensitivity noble gas mass spectrometer and have been conducted under the direction of Rainer Wieler and Heinrich Baur from the Noble Gas Laboratory at the Institute for Isotope Geology and Mineral Resources of ETH Zürich. The first study is devoted to isotopic analyses of single presolar silicon carbide grains from meteorites to improve our understanding of their stellar sources. This work was done in collaboration with Peter Hoppe and Kuljeet K. Marhas from the Max-Planck Institute for Chemistry in Mainz, Germany. The second project is dedicated to noble gas analyses of tiny chromite grains from fossil meteorites and micrometeorites from 480 Myr old marine sediments from Sweden to constrain the delivery times of extraterrestrial material from the asteroid belt to Earth. This work was realized in collaboration with Birger Schmitz from the University of Lund in Sweden.

2. Outline of Thesis

The introductory chapter serves as an overview, gives the motivation for our studies and summarizes briefly the physical processes and cosmochemical concepts relevant to the understanding of this work. This chapter is followed by a description of the experimental and analytical methods.

Chapter 3, 4 and 5 are manuscripts of articles to be submitted to or already published in scientific journals: In chapter 3 we present a combined study on the noble gas isotopes of He and Ne and on C-, N-, and Si-isotopes in single presolar silicon carbide grains from the Murchison and Murray meteorites. This paper will be submitted to The Astrophysical Journal. In chapter 4 we report the discovery of unusually short transfer times of asteroidal material to Earth. In an article published in Nature we describe how we use fossil meteorites from 480 Myr old (Ordovician) marine sediments from southern Sweden to test theoretical predictions of meteorite delivery after a major asteroid collision. In chapter 5 we reveal the nature of sediment-dispersed extraterrestrial chromite grains found earlier by Schmitz et al. in the fossil meteorite bearing strata and present the first cosmic-ray exposure ages of the two fossil meteorites Gullhögen 001 and Brunflo from the Ordovician sediments in Sweden. This paper will be submitted to the journal Geochimica et Cosmochimica Acta. The references in these chapters are formatted in the style of the respective journal.
Preliminary experiments done on stratospheric interplanetary dust particles (IDPs) are presented in chapter 6; work of a collaboration started with Don Brownlee and David Joswiak from the University of Washington in Seattle, USA. References are given at the end of each chapter.

3. Introduction

In this introduction we will first address presolar dust grains and their stellar sources. A more detailed discussion on this is given in chapter 3. We then continue to briefly describe solar system evolution and the formation and delivery of meteorites and interplanetary dust. The delivery of meteorites and dust is treated in more detail in chapters 4 and 5, respectively.

3.1 Why Do We Study Presolar Dust Grains?

Presolar dust, such as carbonaceous dust (silicon carbide (SiC), graphite and nanodiamonds), forms as a high-temperature condensate in the ejecta of different types of evolved stars (Zinner 2004, Hoppe 2004, Clayton and Nittler 2004). Besides being composed of inherited matter, it incorporates freshly synthesized isotopes from its parent star. After passage through the interstellar medium (ISM) such grains became part of the solar nebula and a small fraction of this dust survived the formation and evolution of our Solar System inside small planetary bodies, such as comets and asteroids. These presolar grains are brought to the Earth by meteorites and they serve today as a direct sample for dust from a variety of extinct stars. Meteoritic stardust is recognized by large isotopic anomalies (compared to solar system matter) and these samples allow stellar nucleosynthetic models to be tested and constrained directly.

3.2 Why Helium and Neon?

Noble gases like helium and neon can be implanted by stellar winds into circumstellar dust grains. They are amongst the most important products of nuclear fusion reactions in the prominent hydrogen- and helium-burning shells of evolved stars. As will be outlined in the following sections, their abundance and isotopic composition are not only the result of specific nuclear reactions but also depend on the extent of mixing processes and accordingly let us probe physiochemical conditions deep inside evolved stars.
3.3 Circumstellar Dust

The greatest dust producers in our galaxy are low- to intermediate-mass stars (IMS) in their late stages of evolution (red giant branch (RGB) and asymptotic giant branch (AGB) stars, see below). They are in the mass range of 1 to 8 solar masses \((M_\odot)\). Only about 5% of all stars are thought to be more massive. Hence, late stage IMS are not only efficient dust producers but they are also very abundant.

3.4 Stellar Evolution and Nucleosynthesis

In the following section a rough sketch of stellar evolution and nucleosynthesis for a solar-mass star is given to facilitate accessibility of this work to the readers with no particular background in basic astrophysical concepts. The emphasis lies on issues relevant for the understanding of presolar dust grains. For a much more complete and in-depth presentation of stellar evolution and nucleosynthesis the reader is referred to excellent textbooks (e.g. Prialnik 2000; Kippenhahn & Weigert 1990) and review papers (e.g. Section 2: Theory of Nucleosynthesis and Stellar Evolution, in: Bernatowicz & Zinner 1997; Wallerstein et al. 1997 and the classic Burbidge, Burbidge, Fowler & Hoyle 1957).

As will be described in the following text, stars produce elements through nuclear reactions. Fusion reactions are mainly responsible for producing the elements up to iron. Basically, very high temperatures allow two nuclides to overcome their mutual electric repulsion, the Coulomb barrier, so that the nuclear strong force – which only gets important at very small distances – holds the two nuclides together. During the fusion process, part of the mass gets transformed into nuclear binding energy and radiation. The net product nuclides are therefore lighter than the sum of the input nuclei (e.g. \(m_{\text{\text{\text{\text{\text{\text{\text{He}}}}}} < 4 \times m_{\text{\text{\text{\text{\text{\text{He}}}}}}}\)). The binding energy attains a maximum at iron and therefore, a net energy output cannot be produced by fusion processes. Hence, fusion of nuclides more massive than iron is prevented. Most of these heavy nuclides are produced by neutron-capture processes in evolved, low to intermediate mass stars (see below). During slow neutron capture (s-process), a nucleus is bombarded with a neutron and a new, unstable nucleus is formed. Neutron densities are relatively low and the newly formed radioactive nucleus decays before a new neutron is captured, until a stable form is reached. This product is called an \(s\)-process nucleus. In case much higher neutron densities are achieved, such as in supernova explosions (see below), a neutron capture can be followed by subsequent ones before radioactive decay sets in and neutron-rich nuclei can be formed. This rapid neutron capture is called the \(r\)-process. Analogous to the \(s\)-process, the end products are called \(r\)-process nuclei. Further nuclear reactions important for stellar nucleosynthesis are known but will not be mentioned here (for an overview, see Wallerstein et al. 1997).
3.4.1 Big Bang Nucleosynthesis

The lightest elements hydrogen and helium were primarily produced during Big Bang nucleosynthesis (75% H, 25% He). Roughly 14 Gyr after the Big Bang, about 5% of the H has been converted inside stars mainly into He, and subsequently into heavier elements. The latter comprise about two percent of the total mass of baryonic matter, which accounts for only about 4% of the total energy density of the universe, the rest being essentially dark energy and a non-baryonic, yet unknown kind of dark matter. In the interstellar medium about a third to half of all heavy elements ("metals") are bound in dust particles.

3.4.2 The Main-Sequence Phase

Solar-mass stars spend most of their ~10 Gyr lifetime in the main-sequence phase when they burn hydrogen into helium in the core by the pp chain. The minimum temperature for hydrogen fusion to occur is ~4 · 10^6 K in minimum mass red dwarf stars (M_⊙ ≈ 0.08 M_⊙). The basic reaction is proton-fusion via deuterium (pp I),

\[ p(p,e^+\nu)^2\text{H} \]
\[ ^2\text{H}(p,\gamma)^3\text{He} \]
\[ ^3\text{He}(^3\text{He},2p)^4\text{He}. \]

Two other pp branches (II, III) are producing 4He simultaneously with pp I via capture and subsequent radioactive decay of ^7Be-^7Li and ^7Be-^8B-^8Be.

Stars with higher masses sustain higher core temperatures and the CNO reaction chain (Fig. 1) dominates over the pp process in stars having >1.5 M_⊙ resulting in T_{core} > 15 · 10^6 K:

Although C, N and O serve mainly as catalysts to produce 4He from protons, the CNO-cycle leads to an enrichment of ^13C and ^14N. Predicted equilibrium ratios are 12C/13C = 3.4 and 14N/15N = 20000 for T = 15 Mio. K. Solar ratios are 12C/13C = 89 and 14N/15N ~ 272 (air), i.e. 13C and 14N are enriched by factors of 26 and ~70, respectively. The O-isotopic ratios are also changed in a side branch of the main CNO cycle, leading to an enhanced 17O/16O ratio.

During the main sequence phase the core burning products are not mixed into the envelope and do not reach the stellar surface. The star is in hydrostatic equilibrium maintained by a balance between the gravitational force versus the force from radiation and gas pressure originating in the active core.
3.4.3 The Red Giant Phase

When about 10% of the total hydrogen has been transformed into He, H-burning ceases. The outward direct pressure force decreases and gravitational contraction heats the inner regions of the star, until the temperature is high enough for H-fusion to commence in a shell around the He-core. As more H is transformed into He the core-mass increases. Increase of core density and temperature lead to a larger outward directed pressure force, which expands the envelope until hydrostatic equilibrium is regained. The expanded atmosphere is cooler and therefore redder. The star has become a Red Giant. Only at this stage fusion products are being transported to the stellar surface by convection in the envelope (so-called first dredge-up). Addition of freshly produced He from the H-burning shell further increases the mass of the core and its temperature by the release of gravitational energy. At a certain mass threshold a core temperature of about 100 million K is reached and He burning sets in, which further raises the temperature and leads to explosive He burning, the He flash. The explosion is absorbed by the envelope and is probably not visible from outside the star (at least such an event has not been recognized up to now). Gradually, the He in the core is transformed into carbon by steady He-burning through the triple-alpha reaction via highly unstable beryllium $^8$Be.

$$^4\text{He} \rightleftharpoons (2\alpha,\gamma)^{12}\text{C}.$$  

Part of the C in the core can be converted by further alpha-captures to oxygen and neon. After
exhaustion of core He burning the star reaches the AGB and stars more massive than $\sim 4 \, M_\odot$ experience a second dredge-up of CNO processed matter.

3.4.4 The AGB Phase

Once He in the core is exhausted, He-burning continues in a shell around the now inert C-O core and burns alternately with a H-shell further out (Fig. 2).

The He-burning shell is the main source of $^{12}\text{C}$ (by the triple-alpha reaction) and of $^{22}\text{Ne}$ by alpha-capture on H-burning CNO product nitrogen $^{14}\text{N}$:

$$^{14}\text{N}(\alpha,\gamma)^{18}\text{F}(e^+\nu)^{18}\text{O}(\alpha,\gamma)^{22}\text{Ne}$$

$^{22}\text{Ne}$ destruction by alpha- and proton-capture is not important in IMS with comparatively low mass and gets only relevant for stars with $M > 5-6 \, M_\odot$ through the following reactions:

$$^{22}\text{Ne}(\alpha,n)^{25}\text{Mg}$$
$$^{22}\text{Ne}(\alpha,\gamma)^{26}\text{Mg}$$
$$^{22}\text{Ne}(p,\gamma)^{23}\text{Na}$$

Fig. 2. Schematic cut through an AGB star. An inert CO core, the product of He-core burning, is surrounded by a He-burning shell, which ignites explosively in a thermal pulse (“He-flash”) during which convection currents transport freshly synthesized material outward into the He-intershell. The pulse leads the star to expand and extinguishes the He- and H-burning shells. The convection currents in the extensive envelope then reach into the intershell region and dredges-up He-burning material to the surface (“3rd dredge up”). Contraction follows and allows H burning to set in until the next thermal pulse. During this interpulse phase, convection is limited to the H-rich envelope. Except in stars with $M > 5-6 \, M_\odot$ the convective envelope reaches to the base of the H-burning shell (“hot bottom burning (HBB)”) (after Lattanzio and Boothroyd 1997).
The $^{20}$Ne abundance is left almost unchanged in AGB stars.
Furthermore, heavier elements up to lead and bismuth can be formed by slow neutron capture reactions (s-process nuclides) on He-burning products.

The H- and He-shell products are transported to the stellar surface by convection currents in the stellar envelope by the so-called ‘third dredge-up’ events. Important mixing events in AGB stars are summarized in Tab. 1.

Table 1. Important mixing processes in late stage intermediate mass stars (after Lattanzio & Boothroyd 1997).

<table>
<thead>
<tr>
<th>Mixing event</th>
<th>Main characteristics</th>
<th>Surface enrichment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>first dredge-up</strong></td>
<td>after main sequence H-core burning</td>
<td>partial H-burning products:</td>
</tr>
<tr>
<td></td>
<td>during Red Giant phase</td>
<td>$^4$He, $^{14}$N, $^{13}$C, $^{17}$O</td>
</tr>
<tr>
<td><strong>second dredge-up</strong></td>
<td>on the early AGB in stars $M \geq 4 M_\odot$</td>
<td>H-burning products</td>
</tr>
<tr>
<td><strong>He-shell flash = thermal pulse</strong></td>
<td>usually repeated several dozen times</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>convection between He burning shell and He intershell</td>
<td></td>
</tr>
<tr>
<td><strong>third dredge-up (TDU)</strong></td>
<td>• After thermal pulses except the first few</td>
<td>increases C/O to $&gt; 1$</td>
</tr>
<tr>
<td></td>
<td>• responsible mixing event to convert the star to a carbon star ($C&gt;0$)</td>
<td>He-burning products: $^{12}$C, $^4$He, $^{16}$O, $^{22}$Ne</td>
</tr>
<tr>
<td></td>
<td></td>
<td>s-process products (heavy elements)</td>
</tr>
<tr>
<td><strong>hot bottom burning (HBB)</strong></td>
<td>convective envelope reaches into H-burning shell in stars $M \geq 4 M_\odot$</td>
<td>decreases C/O to $&lt; 1$</td>
</tr>
<tr>
<td></td>
<td>envelope mass loss shuts down HBB while TDU continues</td>
<td>strong N-enrichment due to C$\rightarrow$ N burning</td>
</tr>
<tr>
<td><strong>cool bottom processing (CBP)</strong></td>
<td>non-convective mixing: rotation and/or shear induced turbulence)</td>
<td>$^{16}$O depletion, $^{13}$C and $^{14}$N enrichments (Wasserburg et al. 1995)</td>
</tr>
<tr>
<td></td>
<td>One model: “conveyor belt” circulation from the relatively cool bottom of convective envelope into outer wing of H-burning shell</td>
<td></td>
</tr>
</tbody>
</table>
The star, which now has two nuclear burning shells, is thermally unstable and goes through many thermal pulses. Together with an increased radiation pressure, this leads to a further expansion of the envelope which becomes gravitationally less bound to the rest of the star and is experiencing high mass loss through strong stellar winds ($10^{-9}$ to $10^{-4}$ $\text{M}_\odot/\text{yr}$). This evolved stage of a star is called the thermally pulsing Asymptotic Giant Branch (AGB) phase. In view of the production of elements and their isotopes and ejection into interstellar space the AGB phase is the most important stage for most stars.

Astronomical observations of infrared and sub-millimeter radiation from evolved AGB stars revealed the existence of considerable amounts of circumstellar dust. Stars with very high mass loss might allow the condensation of dust grains in stellar winds. One of the best-studied evolved AGB stars with a circumstellar dust envelope is IRC+10216 (e.g. Skinner et al. 1998, Willacy & Cherneff 1998; see Fig. 3). The first solid inorganic circumstellar compounds detected were amorphous silicates around oxygen-rich AGB stars, they are very common and have been identified spectroscopically in more than 4000 stars. Around these stars most of the carbon is bound in the CO molecule. On the other hand, AGB stars with a C/O-ratio larger than unity (carbon stars) allow the formation of carbonaceous dust. The most prevalent form is

Fig. 3. Infrared image of IRC+10216 taken with the Hubble Space Telescope’s (HST) Wide Field and Planetary Camera 2 (WFPC2) equipped with broad-band filter centered at $\lambda=0.8269$ $\mu$m. Around the central (AGB) star a compact bipolar nebula is visible (fig. 1 in Skinner et al. 1998).
silicon carbide (SiC), which has been detected in 700 carbon stars by the characteristic infrared emission feature at 11.3 μm (Kwok 2004). The isotopic signatures of many elements measured in presolar SiC stardust grains extracted from meteorites suggest that about 90% originated from low- to intermediate-mass AGB stars (Hoppe & Zinner 2000).

3.4.5 The Planetary Nebula Phase

After several dozen thermal pulses so much material is being lost, that fusion eventually ceases and the hot stellar core is stripped of its envelope. Strong UV-radiation from the exposed core ionizes the detached expanding envelope, which then appears as a beautiful planetary nebula (PN, Fig. 4). Temperatures in the PN eventually become low enough to allow condensation of dust grains. These dust grains incorporate nuclear burning products from the AGB phase (e.g. He, C, N, O and Ne) but also inherited, unprocessed material from earlier generations of other stars (such as Si). Observations of planetary nebulae show these objects as important dust condensation sites (e.g. see review by Kwok 2004). Dust, which condensed already in the AGB and post-AGB phase is not strongly destroyed during the PN phase. Nebular abundance studies show a strong depletion of silicon and other refractory elements in the ionized nebular gas. This

Fig. 4. The Egg Nebula CRL 2688 is a proto-planetary nebula in a distance of ~3000 light years, the image is about 1 light year wide. In this visible-light image taken by the HST’s Advanced Camera for Surveys (ACS) several polarizing filters have been used to show how light is scattered by dust particles. Brighter areas represent higher dust densities. The concentric dust shells can be explained with episodic mass-loss during the thermal pulses of the AGB phase. Credit: NASA and The Hubble Heritage Team (STScI/AURA, W. Sparks (STScI) and R. Sahai (JPL)) For an interpretation of this image see Sahai et al. (1998) and Tartar et al. (2004, 2005).
implies the dust is far enough from the central star at the time the UV source turns on (Hans Martin Schmid, pers. comm.).

While the dense inert central star slowly cools and forms a compact white dwarf (average density \( \sim 10^{6} \text{ g/cm}^3 \)), the planetary nebula expands into the interstellar medium (ISM) and enriches it with the products of stellar nucleosynthesis. PNs are major contributors of dust to the ISM.

3.4.6 Massive Stars

*Luminous Blue Variables*

High velocity winds from hot stars have low densities and constitute no good dust condensation sites, except for certain Wolf-Rayet stars in binaries with colliding winds (see below). More prominent dust producers are luminous blue variables (LBVs) like eta Carinae (\( \eta \) Car). The LBV phase is run through by massive, luminous hot stars and characterized by strong stellar winds and major eruptions, which can form massive circumstellar nebulae. The probably >100 \( M_\odot \)-star \( \eta \) Car is a particularly nice example for the production of a dusty nebula with several solar masses. In the 19\textsuperscript{th} century for two decades \( \eta \) Car was one of the brightest stars of the southern sky. As Davidson & Humphreys (1997) note in their review paper, in the year 1847 John Herschel already considered \( \eta \) Car as perhaps the most interesting object in the sky which “unites more points of interest” than any other star. A major eruption in the mid-19\textsuperscript{th} century

---

Fig. 5. The very massive star \( \eta \) Car is surrounded by a nebula created in several outbursts (see text). The inner nebula consists of two bipolar gas and dust lobes and a thin equatorial disk and lies at a distance of about 8000 light-years. This image in visible light has been recorded with the HST WFPC2. Credit: Jon Morse (University of Colorado) and NASA.
made it the second brightest star in the sky for a short time. Together with several other outbursts which followed, it produced an obscuring dusty nebula making the star just barely visible for the following hundred years. Huge amounts of freshly condensed circumstellar dust absorb the strong UV radiation from the hot star and reemit it at IR wavelengths. Spectroscopic studies of the nebular gas show a strong depletion in C and O, while N is overabundant (Smith & Morse 2004). Although a N-enrichment at the expense of C and O is expected from equilibrium CNO burning (see above), nucleosynthesis alone cannot account for the observed depletions. It is suggested that much of the C and O is bound in dust grains (Smith 2005).

*Wolf-Rayet Stars*

Most stars more massive than ~25 $M_\odot$ pass through the so-called Wolf-Rayet (WR) phase. Radiation pressure is so high that the H-rich envelope is lost via a strong stellar wind. The exposed core is enriched in nuclear fusion products like He, C, N, O and Ne, depending on stage and sub-type. Dominating spectral emission lines change with the evolution of the WR star and form the basis of their classification. Although different evolutionary pathways are suggested by different models (Arnould et al. 1997), a WR star starts with a spectrum dominated by N-emission in the so-called WN phase due to surface enrichment of CNO burning products. This stage is followed by the WC phase, where partial He-burning products (like e.g. $^{12}$C, $^{16}$O and $^{22}$Ne) appear on the surface and C/O > 1. In this phase, the highest $^{22}$Ne enrichments relative to initial abundance are expected (>100×) by alpha capture on $^{14}$N (Meynet et al. 2001). This phase can be followed by the WO stage, where the star displays prominent O-emission line in

Fig. 6. Image of spiral dust around Wolf-Rayet star WR104. The spiral dust structure has a diameter of 160 AU. The spiral is a result of the orbital motion of the stars in this binary system. Dust is thought to form in the high-density region of the collision front of the two stellar winds. The infrared image has been recorded with the 10-m-Keck Telescope in Hawai‘i at a wavelength of 2.27 microns (Tuthill et al. 1999).
its spectrum. The WR star ends its life by exploding as a supernova of type Ib/Ic either directly after the WC or preceded by the WO stage (see also Hoppe et al. 1995, Chapter 5.1 and 5.22).

Some WR stars are thought to originate in close binary systems where the H-rich envelope is lost by mass transfer to the companion star. Despite intense UV radiation, dust is observed sometimes, in particular if the wind density is enhanced by collision with a wind of a companion star (see Fig. 6). Marchenko et al. (2002) estimate that ~20 % of WR grains survive the harsh circumstellar environment and become part of the ISM.

Core-Collapse Type II Supernovae

Nucleosynthesis does not go beyond the processes described in the previous section on the AGB phase in stars with less than three solar masses. However, the most massive stars (>30 M⊙) can produce isotopes up to 56Fe by nuclear fusion reactions. They develop an onion-like structure of different nuclear burning shells around a core, which eventually consists of iron (see Fig. 7).

In the following, I briefly describe the origin of the distinct shell-structure of a massive star,

---

Fig. 7. A schematic cut through the onion-skin structure of an evolved, massive star (25 M⊙) just before its explosion as a type II SN. The most abundant elements in the shells (not drawn to scale) are indicated and are products of nucleosynthetic reactions during the evolution of the star (see text). After the explosion a dense stellar remnant is left, either a neutron star or a black hole, indicated as the dark core in the schematic (after Meyer et al. 1995).
according to a model developed by Meyer, Weaver & Woosley (1995) based on Weaver & Woosley (1993). They chose a 25 Mₜₜ star for their model since the supernova frequency of such stars in conjunction with their nucleosynthetic output constitute an optimum regarding the enrichment of the interstellar medium.

After hydrogen in the core is transformed into ⁴He, the core He ignites and forms ¹²C and ¹⁶O. After He exhaustion, C-core burning follows to produce ²⁰Ne. Subsequently, part of the freshly produced core-²⁰Ne disintegrates to ¹⁶O while part of it is transformed into ²⁴Mg by α-capture. Simultaneously, C ignites in a shell surrounding the Ne-burning core. Next, the O-burning sets in and produces Si (see Fig. 8). This element is of particular importance in the context of this work as it is a major constituent of presolar SiC grains. The major isotope ²⁸Si is produced mainly by oxygen-burning (Wallerstein et al. 1997):

\[
^{16}\text{O}(^{16}\text{O},\alpha)^{28}\text{Si}
\]

or via ²⁴Mg:

\[
^{16}\text{O}(^{16}\text{O},2\alpha)^{24}\text{Mg}
\]

\[
^{12}\text{C}(^{12}\text{C},\gamma)^{24}\text{Mg}
\]

alpha-capture on Mg then produces Si

\[
^{24}\text{Mg}(\alpha,\gamma)^{28}\text{Si}
\]

²⁸Si gets destroyed by silicon burning in reactions like

\[
(\gamma,\alpha), (\gamma,p) \text{ and } (\gamma,n)
\]

and

\[
(\alpha,\gamma), (p,\gamma), (n,\gamma), (\alpha,p) \text{ and } (\alpha,n)
\]

to form heavier nuclides in later stages (Wallerstein et al. 1997).

The isotopes of Si can also be produced in the MgAl cycle

\[
^{27}\text{Al}(p,\gamma)^{28}\text{Si}
\]
Similarly to the Ne-burning core, the O-burning core is surrounded by a Ne-burning shell. In the last pre-supernova stage, the core Si burning commences and produces iron-core nuclei like Ni. Since convective currents are active in the shells, abundances are generally more or less uniform within each shell.

Once fusion ceases, because the thermonuclear reactions cannot produce energy anymore, the pressure drops and the already dense core collapses followed by a collapse of the outer parts. The resulting temperature increase ignites unburned material explosively, leading to a powerful supernova explosion, which completely disrupts the massive star. During the violent explosion very high neutron densities lead to the formation of elements by rapid neutron capture (r-process). Other processes requiring extreme conditions, such as neutrino nucleosynthesis, are thought to be active during such a core-collapse supernova explosion (SN Type II). Only the dense central part survives as a neutron star or as a black hole if the mass is high enough. SN type II are expected to occur only in stars with masses >8 $M_\odot$.

Conditions in the expanding supernova remnant (SNR, Fig. 8) will eventually allow dust formation to take place from freshly produced nuclei. Dust has been observed to condense

Fig. 8. The SNR Cassiopeia A has been formed by a SN explosion observed around the year 1680. The orbiting X-ray observatory Chandra recorded X-rays from highly ionized silicon ions heated to about 15 million K. Krause et al. (2004) estimated a maximum of about 0.2 $M_\odot$ of dust have been produced in this SN. Image credit: NASA/CXC/GSFC/U.Hwang et al.; Hwang et al. 2004.
in the SNR of type II SN 1987A, which occurred in our satellite galaxy the Large Magellanic Cloud, more than a year after the explosion. IR and sub-mm observations of SNRs suggest that SN dust is a less important component of the ISM. In fact, many SNRs do not show any detectable signs of dust at all.

About 1% of presolar silicon carbide dust grains extracted from meteorites (see §3.6.2) are thought to have formed in SN (X grains) (Hoppe & Zinner 2000). The most convincing evidence stems from an excess in $^{28}\text{Si}$ and of the presence of radiogenic $^{44}\text{Ca}$ and $^{49}\text{Ti}$, the decay products of radioactive $^{44}\text{Ti}$ ($\tau_{1/2}=60$ yrs) and $^{49}\text{V}$ ($\tau_{1/2}=330$ days), respectively. $^{28}\text{Si}$, $^{44}\text{Ti}$, and $^{49}\text{V}$ are produced in the innermost zones of a type II supernova. $^{44}\text{Ti}$ and $^{49}\text{V}$ were incorporated in the condensing SiC grains and decayed in situ. Their short half-life is in accordance with observed timescales of dust condensation after a SN explosion (Amari et al. 1992; Hoppe & Besmehn 2002; Besmehn & Hoppe 2003). There are models for core-collapse (Type II) SNe, which are able to explain many isotopic characteristics of SiC X grains (Deneault, Clayton, Heger 2003; Hoppe et al. 2000). In the SN mixing calculation by Hoppe et al. (2000), which are based on the SN models by Woosley and Weaver (1995), it was shown that the best match between models and SiC X grain data can be achieved for 15 $M_{\odot}$ Type II SNe. However, it was also proposed that SN of Type Ia (white dwarf explosions in close binaries, see below) can produce many isotopic features observed in X grains (Clayton et al. 1997, Amari et al. 1998). Hence, it is not clear what fraction of X grains originate in core-collapse SNe and SNIa (the reader is referred to the discussion in chapter 3).

3.4.7 Binary Stars

More than half of all stars are thought to exist in binary or multiple systems. If their separation is large enough, they develop independently. In terms of stellar evolution and nucleosynthesis they can almost be considered as single stars. However, when they are close enough, mass transfer can occur and dramatically change their fate (Fig. 9). We will briefly address binary configurations leading to important nucleosynthetic events.

Novae

Novae can occur in close binary systems where H-rich matter is being transferred from a low-mass main sequence star onto the surface of its white dwarf (WD) companion. Once a critical density is achieved, thermonuclear fusion is ignited explosively and leads to the ejection of freshly synthesized isotopes from the WD surface into the ISM. IR and UV observations of
nova ejecta show dust to condense already about one to two months after the explosion. This timing is in good agreement with the discovery of radiogenic $^{22}\text{Ne}$ in presolar nova dust grains: Novae are believed to produce considerable amounts of radioactive sodium ($^{22}\text{Na}$, $\tau_{1/2} = 2.6$ yrs), by proton-capture on $^{20}\text{Ne}$ via unstable $^{21}\text{Na}$ which decays into $^{21}\text{Ne}$ and produces $^{22}\text{Na}$ by proton-capture. This sodium is incorporated into the condensing dust grains and decays in-situ into $^{22}\text{Ne}$:

$$^{22}\text{Na}(e^+ \nu)^{22}\text{Ne}$$

accompanied by a characteristic $\gamma$-ray emission. This emission has not been observed so far but is expected to be detectable from novae occurring in less than about 2000 light-years distance (Jenkins et al. 2004).

Matter produced during the nova outburst can be identified later by its very low carbon isotopic ratio ($^{12}\text{C}/^{13}\text{C} = \sim 0.3$ to 2; José et al. 1998) due to $^{12}\text{C}$ enrichment relative to initial composition at the expense of $^{13}\text{C}$ by the following reaction (hot H burning at $T > 100$ million K):

$$^{12}\text{C}(p,\gamma)^{13}\text{N}(\beta^+)^{13}\text{C}$$

The nature of the WD left by the progenitor star determines the peak temperature of the explosion and is decisive on the nucleosynthetic output. CO-rich WDs are produced by low-to intermediate-mass stars, while ONe-rich WDs are the end product of the evolution of more
massive stars. Nitrogen isotopic ratios (\(^{14}\text{N}/^{15}\text{N}\)) tend to decrease with increasing WD mass (José et al. 2004). The high peak temperatures allow an enrichment of \(^{15}\text{N}\) through 
\[ ^{14}\text{N}(p,\gamma)^{15}\text{O}(\beta^+)^{15}\text{N}. \]

In contrast to CO novae, unusually high \(^{20}\text{Ne}/^{22}\text{Ne}\)-ratios (~100 to 250) are expected in ONe nova ejecta, due to the high initial \(^{20}\text{Ne}\) abundance of the WD (José et al. 2004). Although nova dust seems to be highly distinctive in composition, it is only a minor dust component and it is estimated to constitute only about 3 % of the interstellar dust (Gehrz et al. 1998).

Si is formed in novae by p-capture reactions on \(^{20}\text{Ne}\) and \(^{24}\text{Mg}\) (Starrfield et al. 2001). The silicon isotopic composition during CO novae is not altered strongly and remains close to solar. However, ONe novae, particularly with larger WD masses, can produce large \(^{30}\text{Si}\) enrichments (José et al. 2004). Silicates, as well as carbonaceous dust (graphite or amorphous carbon) has been observed in nova ejecta (Smith et al. 1995).

To which extent nova dust contributes to the presolar grain inventory is still not well known. In general, presolar grains with low \(^{12}\text{C}/^{13}\text{C}\) and \(^{14}\text{N}/^{15}\text{N}\) ratios have been assumed to originate from novae (Amari et al. 2001). However, new isotopic analyses of presolar SiC grains suggest that, based on the detection of radiogenic \(^{44}\text{Ca}\) and \(^{49}\text{Ti}\) in some grains with low \(^{12}\text{C}/^{13}\text{C}\) and \(^{14}\text{N}/^{15}\text{N}\) ratios, part of the grains previously considered as nova grain candidates might actually have a SN origin (Nittler & Hoppe 2005).

**Type Ia SNe**

In close binaries with mass transfer a far more dramatic explosion can take place, when the white dwarf star is close to its upper mass limit at \(\sim 1.4 \, M_\odot\) (Chandrasekhar mass). When more mass is being added by its companion star, the electron pressure in the degenerate white dwarf cannot hold up against pressure of the accumulating matter anymore. The matter in the white dwarf (WD; mainly C, O and Ne) then gets transformed by explosive nuclear fusion to heavier elements up to iron and is ejected into the ISM leaving no stellar remnant (Whelan & Iben 1973, Hillebrandt & Niemeyer 2000). WD explosions (Type Ia SNe) are very important contributors of Fe and intermediate mass elements like Ne, Na, Mg, Si, S and Ca into the ISM. A part of the ISM enriching SNIa ejecta consists of unburned matter such as \(^{12}\text{C}, ^{16}\text{O}\) and \(^{22}\text{Ne}\), the major original constituents of the WD star. The latter isotope is predicted to make up several percent of the WD star (Travaglio et al. 2004).
Neutron Star Mergers

Other nucleosynthetic sources include neutron star mergers (NSM). The very high neutron fluxes during the merger are favorable for the production of large amounts of r-process nuclides. However, the frequency of NSM is quite low compared to SNe and their contribution to the enrichment of the ISM is therefore rather small compared to the sources described above (Argast et al. 2004).

For comprehensive reviews on the astrophysics of dust see the dust symposium proceedings by Bernatowitz & Zinner (1997) and Witt, Clayton & Draine (2004).

Mechanisms of grain formation are reviewed by Sedlmayr & Krüger (1997). The formation of circumstellar dust depends on the composition of the circumstellar matter, its temperature and density. Favourable dust condensation sites have low temperature and high density conditions and are usually several radii away from the star. The main factor determining the nature of the dust is the C/O ratio. Oxygen-rich circumstellar environments (C/O < 1) allow the formation of silicates, in amorphous and crystalline form. With C/O < 1 essentially all the carbon is bound in the CO molecule. Hence, in an expanding gas in thermal and chemical equilibrium a C/O ratio above unity is required for the formation of carbonaceous dust. Dust condensation generally occurs via the path from ions to neutral atoms, which form molecules to condense later as dust seeds. The condensation temperature depends on the C/O ratio and partial pressures of the main mineral constituents (Jura 1997). For typical AGB star atmosphere conditions (C/O = 1.05, p = 10^{-5} bar) the first dust particles to form are high temperature minerals like titanium carbide (TiC), which can start to condense at 1700 K, graphite (1600 K) and SiC, which typically condenses around 1500 K (Lodders and Fegley, 1995). Clayton et al (1999) proposed a model where conditions in SNe allow graphite to form even while O>C. Fast electrons, γ-rays form radioactive decays and highly reactive ions reduce the lifetime of the CO molecule dramatically, liberating C, which then is available for the growth of large graphite particles. Similarly, also SiC might form in SN ejecta even if C/O < 1. SN reverse shocks can increase densities about two orders of magnitude relative to the surroundings in certain zones with high Si and C densities, leading to the condensation of SiC within the SN just several days after explosion (Deneault, Clayton, Heger 2003).

Circumstellar dust species mentioned reveal themselves due to their characteristic infrared emission. Their presolar siblings have been extracted from primitive meteorites and can be studied in great detail in the laboratory (see section on presolar grains below and chapter 3).
3.5 Interstellar Journey

After their formation around evolved stars, dust grains are exposed to many perils in the interstellar medium. Among the most efficient dust destructors are SN shockwaves. The primary destruction mechanism is sputtering by collisions of the dust grains with gas of the shockwave. Additionally, grain-grain collisions lead to vaporization and fragmentation. These processes also occur less frequently in other regions of interstellar space. Furthermore, grains can be heated by interaction with high-energy photons (from extreme UV light to $\gamma$-rays), hot gas ($T \geq 10^6 \text{ K}$) and low-energy cosmic-ray particles. Thereby, many of them partially sublime or even get vaporized completely. The same interactions can lead to charging of the dust, which leads to ion loss through field emission and in the extreme case to explosion, when Coulomb forces exceed the tensile strength of the grain.

All these destruction mechanisms lead to smaller grain sizes in case of grain survival. Jones (2004) estimates the interstellar lifetime of small dust grains to be $\sim 5 \cdot 10^8$ yrs, for large dust grains to be $< 10^8$ yrs. Since the rate of grain destruction and fragmentation is higher than the supply of new grains from circumstellar environments and stellar explosions, the existence of larger grains in the ISM requires a re-formation mechanism. How dust can coagulate, re-condense or re-accrete efficiently in the ISM is not clear yet (Jones 2004).

A part of the stardust survives the destructive processes in the ISM and makes its way into the cores of molecular clouds where it gets incorporated into newly formed stars and planetary materials.

Before describing the concept of the formation of the solar system in §3.7, we will address the discovery of presolar grains with a particular focus on SiC.

3.6 Presolar Grains

3.6.1 Discovery of Presolar Grain

Presolar material in meteorites was first suspected after a highly anomalous noble gas component had been detected in primitive, unaltered meterorites, the carbonaceous chondrites (see Fig. 10 and 12). This Xe component which is highly enriched in the heaviest and lightest isotopes (Xe-HL) was found by Reynolds and Turner (1964). An overview of trapped noble gas components in meteorites is given by Ott (2002).
The first types of presolar grains discovered were refractory phases in unaltered, primitive meteorites. Their presolar nature was recognised mainly due to extreme isotopic compositions. The isotopic ratios in these grains can be several orders of magnitude different from any other solar system material. The grains are extracted from the dark, fine-grained matrix of chondrites, which is basically a sediment of the solar nebula (see Fig. 10).

Elaborate acid dissolution procedures were applied to carbonaceous chondrites to first isolate nanometer-sized presolar diamonds, the carrier of the highly anomalous Xe-HL gas (Lewis et al. 1987). The isolation of presolar silicon carbide (SiC) (Bernatowicz et al. 1987; Tang & Anders 1988) followed. Later, other presolar refractories, such as graphite (Amari et al. 1990), TiC (Bernatowicz et al. 1991), corundum (Hutcheon et al. 1994; Nittler et al. 1994), spinel (Nittler et al. 1994), silicon nitride (Nittler et al. 1995) and hibonite (Choi, Wasserburg & Huss 1999) were extracted. Although well known from astronomical observations of circumstellar environments of evolved O-rich stars, no presolar silicate grains were found in meteorites until recently (Tab. 2). This is because in the early days all presolar silicates were destroyed in the acid dissolution steps. New measurement techniques (NanoSIMS ion microprobe) makes it now possible to avoid the harsh chemical treatments and to extent isotopic analyses to much smaller scales. Use

Fig. 10. The carbonaceous chondrite Murchison is a source of presolar grains studied during in this thesis. They are extracted from the very dark, fine-grained matrix, the sediment of the solar nebula. All the other components visible are altered material, in particular the round mm-sized spherules, the chondrules, which are solidified melt droplets.
of the NanoSIMS has been essential for the detection of presolar silicates. The first presolar olivine and amorphous silicate (“GEMS”, glass with embedded metal and sulfides) grains were discovered in an interplanetary dust particle (IDP) in 2003 by Messenger et al. (2003). The first evidence of presolar silicates in meteorites was reported by Mostefaoui et al. (2003) in the same year. Subsequent ion microprobe work lead to the discovery of various presolar silicate phases in meteorites only known from astronomical observations so far (pyroxenes, olivines and GEMS) (Nguyen & Zinner 2004, Nagashima et al. 2004, Mostefaoui & Hoppe 2004).

Recent reviews on presolar grains were published by Zinner (2004), Hoppe (2004), and Clayton & Nittler (2004).

Table 2: Presolar grain types discovered today are listed with their typical size range and the discovery reference. We do not list abundances, since they are different in most meteorites and depend on parent-body metamorphosis.

<table>
<thead>
<tr>
<th>Presolar refractory phases</th>
<th>Size</th>
<th>Discovery reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>C</td>
<td>2-3 nm</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>SiC</td>
<td>~0.2 to 10 µm</td>
</tr>
<tr>
<td>Spinel</td>
<td>MgAl₂O₄</td>
<td>0.1 to 5 µm</td>
</tr>
<tr>
<td>Graphite</td>
<td>C</td>
<td>0.8 to 20 µm</td>
</tr>
<tr>
<td>Corundum</td>
<td>Al₂O₃</td>
<td>0.1 to 5 µm</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>Si₃N₄</td>
<td>~1 µm</td>
</tr>
<tr>
<td>Hibonite</td>
<td>CaAl₁₂O₁₉</td>
<td></td>
</tr>
</tbody>
</table>
Other carbides as subgrains of graphite

- TiC, ZrC, MoC

Bernatowicz et al. 1991, 1996

Presolar silicates

<table>
<thead>
<tr>
<th>Silicate Type</th>
<th>Composition</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous silicates</td>
<td>“GEMS”, glass with embedded metal and sulfides</td>
<td>IDP: Messenger et al. 2003; Mostefaouï &amp; Hoppe 2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 to 1 µm</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>Mg$_{1-x}$Fe$_x$SiO$_4$ (0 ≤ x ≤ 1)</td>
<td>Mostefaouï et al. 2003, Nguyen &amp; Zinner 2004, Mostefaouï &amp; Hoppe 2004</td>
</tr>
</tbody>
</table>

3.6.2 Silicon Carbide (SiC)

In this work we focus on the best-studied presolar mineral SiC. Differences in isotopic composition of the main elements, Si and C, the most abundant trace element N and the abundance of radiogenic $^{26}$Mg (from the decay of radioactive $^{26}$Al) allow a genetic classification (Hoppe & Ott 1997). 90% of all grains belong to the so-called mainstream population, the remainder is subdivided into type A, B, X, Y and Z grains according to characteristic isotopic composition (see Tab. 3). A few grains have a peculiar isotopic composition and cannot be assigned to one of these types (Hoppe 2004).
Table 3: Different populations of presolar SiC according to their isotopic composition (Hoppe & Ott 1997), isotope characteristics from Hoppe 2004). $M_\odot$ = Solar mass; $Z_\odot$ = Solar metallicity; GCE = Galactic Chemical Evolution; CBP = Cool bottom processing.

<table>
<thead>
<tr>
<th>Type</th>
<th>Abundance</th>
<th>$^{12}\text{C}/^{13}\text{C}$</th>
<th>$^{14}\text{N}/^{15}\text{N}$</th>
<th>Si-isotopes</th>
<th>Additional remark</th>
<th>Stellar source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar composition</td>
<td></td>
<td>89</td>
<td>272</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(for comparison)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mainstream</td>
<td>90%</td>
<td>40-80</td>
<td>50-5000</td>
<td>In Si-three-isotope</td>
<td>$^{12}\text{C}$ and $^{14}\text{N}$ excess as imprint of CNO cycle, s-process</td>
<td>AGBs, mainly carbon stars, different</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>data diagram data plots</td>
<td>nuclides like Kr, Xe, Ba, Nd, Sm, Sr, Zr, Mo</td>
<td>Z</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>along a line with a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>slope of 1.34.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Reflects GCE.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A/B</td>
<td>5%</td>
<td>&lt;10</td>
<td></td>
<td>Most &gt; solar, some &lt; solar</td>
<td></td>
<td>J-type C stars, born-again AGBs (e.g.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sakurai’s Object)</td>
</tr>
<tr>
<td>X</td>
<td>1%</td>
<td>Mostly &gt; solar (up to 80x solar)</td>
<td>&lt; solar, down to 0.05x solar</td>
<td>Enriched in $^{28}\text{Si}$</td>
<td>Large amounts of radiogenic $^{26}\text{Mg}$, $^{44}\text{Ca}$, $^{90}\text{Ti}$</td>
<td>Supernovae</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>up to 5x solar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>rare</td>
<td>&gt; 100</td>
<td></td>
<td>Si and N distinct from X</td>
<td></td>
<td>0.5 $Z_\odot$, 3-5 $M_\odot$, AGBs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>grains</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>rare</td>
<td>&lt; solar mostly &gt; solar</td>
<td>&lt; solar</td>
<td>$^{29}\text{Si}/^{28}\text{Si}$</td>
<td></td>
<td>0.3 $Z_\odot$, 1.5-3 $M_\odot$, AGBs with strong CBP</td>
</tr>
</tbody>
</table>
3.6.3 Helium and Neon in Presolar SiC

Noble gases in bulk separates of presolar SiC have been first studied by Zinner et al. (1987) and Lewis et al. (1990, 1994). The first He and Ne analyses in single presolar SiC have been carried out by Nichols et al. (1991, 1992 and Ph.D Thesis 1992). Presolar SiC is the carrier of the G noble gas component, formerly known as Ne-E because of its highly anomalous Ne isotopic composition. Characteristic for Ne-G is a very low $^{20}\text{Ne}/^{22}\text{Ne}$ ratio (see Tab 4.). Since most presolar SiC originates from AGB stars, the $^{22}\text{Ne}$ source is $\alpha$-capture on CNO product $^{14}\text{N}$ in the He-burning shell (see above). Since the $^{20}\text{Ne}$ abundance remains almost unaltered in low- to intermediate-mass stars, the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio decreases during the AGB phase. Ne-G is expected to be accompanied by $^4\text{He}$, a hydrogen burning product, since implantation into the circumstellar dust has been suggested to be a plausible trapping mechanism (Gallino et al. 1990).

Monoisotopic $^{22}\text{Ne}$ from the decay of $^{22}\text{Na}$ ($\tau_{1/2} = 2.6$ yr) has been observed in presolar graphite grains (Amari et al. 1995) and can also be expected in certain presolar SiC grains. Radioactive $^{22}\text{Na}$ is produced in large amounts in nova and supernova explosions and can get incorporated into dust grains condensing after the explosion. There it decays in situ to $^{22}\text{Ne}$. This radiogenic $^{22}\text{Ne}$ has been termed Ne-R by Amari et al. (1995).

Table 4. He and Ne of different composition in presolar SiC grains. Isotopic ratios for Ne-G are from Lewis et al. (1994) and for Ne-R from Amarie et al. (1995).

<table>
<thead>
<tr>
<th>Noble gas component</th>
<th>He</th>
<th>$^{20}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{21}\text{Ne}/^{22}\text{Ne}$</th>
<th>Origin</th>
<th>Trapping mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-G</td>
<td>$^4\text{He}$</td>
<td>&lt;0.1</td>
<td>0.0827</td>
<td>H-burning zone</td>
<td>implantation</td>
</tr>
<tr>
<td>He-G</td>
<td>accompanied by $^4\text{He}$</td>
<td>&lt;0.0015</td>
<td>0.00059</td>
<td>He-burning zone</td>
<td>implantation</td>
</tr>
<tr>
<td>Ne-G</td>
<td>-</td>
<td>&lt;0.01</td>
<td>&lt;0.0001</td>
<td>radiogenic from $^{22}\text{Na}$; mainly produced in novae and supernovae</td>
<td>in-situ decay product of radioactive $^{22}\text{Na}$ ($\tau_{1/2}=2.6$ yrs)</td>
</tr>
<tr>
<td>Ne-R</td>
<td>-</td>
<td>&lt;0.01</td>
<td>&lt;0.0001</td>
<td>in-situ decay product of radioactive $^{22}\text{Na}$ ($\tau_{1/2}=2.6$ yrs)</td>
<td>in-situ decay product of radioactive $^{22}\text{Na}$ ($\tau_{1/2}=2.6$ yrs)</td>
</tr>
</tbody>
</table>
3.7 Formation of the Solar System

3.7.1 The Solar Nebula

The solar system formed from a rotating gas and dust disk, the solar nebula. This concept was first introduced by the philosopher Immanuel Kant in 1755 on a qualitative description based on Newtonian physics. A few decades later, mathematician and astronomer Pierre-Simon Laplace presented a similar theory for the formation of the solar system. Today, new models developed from observations of star-forming regions, physical simulations and cosmochemical analyses basically confirm Kant’s original hypothesis.

Star-forming regions are observed with astronomical telescopes in various parts of our galaxy and also in other galaxies. Extensive regions in interstellar space, where large amounts of gas are present and where the density is clearly higher above average are termed molecular clouds. They are mainly composed of H and to a lesser extend of He, while heavier elements (“metals”) are much less abundant and are present in the form of molecules and dust. Particularly dense regions in cold molecular clouds are called cloud cores, and allow more dust condensation due to very low temperatures and high densities ($T \approx 10^{-10}$ K; $\rho \approx 10^3 – 10^6$ particles/cm$^3$). These cloud cores can undergo gravitational collapse and contract to form an even denser protostellar cloud. The conservation of initial angular momentum leads to a higher spin rate of the cloud core with advancing collapse. Matter in non-equatorial orbits loses its vertical velocity component by mutual collisions and settles in the equatorial plane. Gradually, a flattened and growing protoplanetary disk forms, in our case the solar nebula (Fig. 11). Most of the material in the disk flows into the central object, which evolves into a protostar, the protosun.

Fig. 11. This HST Near-Infrared Camera and Multi-Object Spectrometer (NICMOS) image shows the protoplanetary nebula IRAS 04302+2247 in the constellation Taurus. The protoplanetary disk itself is seen edge-on and is the dark band dividing the bright nebula, which is illuminated by the protostar (hidden from view by the optically thick disk). This protoplanetary nebula has a mass comparable to what is estimated for the solar nebula and has a diameter of ~900 AU. Credit: D. Padgett (IPAC/Caltech), W. Brandner (IPAC), K. Stapelfeldt (JPL) and NASA
heated due to transformation of gravitational energy into heat, long before the onset of nuclear fusion. This phase is called the T Tauri phase – named after the prototype variable star in the constellation Taurus. It took about 10 Myr of accretion and gravitational collapse until the core of the protosun became hot enough to ignite hydrogen burning, which gave birth to the Sun. By then, the planets must have started forming already: T Tauri stars emit strong radiation and eventually clear their surrounding disk of dust and gas. Therefore, it seems plausible that the first solids in the solar nebula formed before the nebula was blown away by the strong T-Tauri radiation. The first solids of the solar nebula are found today in very primitive meteorites as calcium-aluminum-rich inclusion (CAIs) and can be dated radiometrically. For cosmochemists their age defines the “start of the solar system”. The current value is $4567.2 \pm 0.6$ Myr, determined from lead isotopes of CAIs from the primitive meteorite Efremovka (Amelin et al. 2002).

3.7.2 The Formation of Asteroids and Planets

These first solar system solids formed from dust particles, which stuck together to form larger, cm-sized aggregates by physical processes not fully understood yet. These grains collided randomly and constructive collisions lead to meter-sized objects. By this process (accretion), larger, kilometer-sized objects – planetesimals – were formed. Planetesimals are the building blocks of the planets of our solar system. The largest of these objects evolve through accretion into planetary embryos, the last stage before the final planet. While these large objects accrete more and more planetesimals (runaway growth), to finally become planets, these impacts generate a considerable amount of heat, which leads to melting and isotopic equilibration. This destroys any remaining presolar isotopic signatures in the matter. However, planetesimals survived until today and the most primitive ones preserve almost unaltered presolar and solar-nebula matter. They survived in regions of the solar system, where gravitational influence of giant planets prevented the formation of larger planets, who could capture and accrete the planetesimals. Within Jupiter’s orbit they mainly populate the region between the planets Mars and Jupiter and are known as asteroids, in the outer solar system they are known as trans-neptunian objects (also known as Kuiper-Belt Objects) and, further out, might populate the hypothetical Oort cloud.

Back in time to the formation of the solar nebula, the protosun was responsible for a radial temperature gradient through the disk. While the inner part was very hot ($T > 500$ K) and no ices could persist, temperatures in the outer regions of the disk were low enough for ices ($T < 300$ K). This gradient determined what kind of material was available for the formation of planets and is reflected in the composition of the larger and minor planets observed today. The asteroids and the planets of the inner solar system are primarily composed of heavy elements,
while the outermost planetary objects mainly consist of ices (H$_2$O, CH$_4$, NH$_4$ etc.). In between these extremes we find the four giant planets. Jupiter and Saturn grew massive fast enough to capture essentially gas and dust from the solar nebula in its integral composition. Also Uranus and Neptune still have captured a considerable amount of solar nebula H and He. As mentioned above, the strong gravitational influence of the giant planets, allowed the survival of planetesimals. The small icy bodies of the large population of trans-neptunian objects are thought to have formed in the vicinity of Uranus and Neptune and later have been transported by gravitational interaction with them into their present region outside of Neptune’s orbit. Jupiter, which has grown to more than 300 Earth-masses to the most massive planet of our solar system, is not only responsible for the existence of the asteroid belt but also determines its fate today (Bottke et al. 2005). As we will outline in the following, the delivery of asteroidal material to Earth (meteorites) is closely related to the evolution of the asteroid belt due to Jupiter. Gravitational and non-gravitational perturbations move asteroids into orbital resonances with Jupiter. The resonances occur at orbits whose periods are integer multiples of Jupiter’s orbital period (e.g. 3:1, 5:2). Periodic transfer of momentum from Jupiter to an asteroid in such an orbit leads to a progressive change of the orbital elements of the latter. Eventually, the orbit is modified in such a way that the asteroid can fall into the inner solar system and collide with the Sun, a terrestrial planet, or even gets ejected out of the solar system. This process is responsible for preventing the accretion of a larger planetary body between Mars and Jupiter and for clearing out the asteroid belt. Still active today, this mechanism is mainly accountable for the supply of asteroidal material to Earth (see below and chapter 4 and 5).

3.8 Meteorites

3.8.1 The Origin of Meteorites

Asteroids, the parent bodies of most meteorites, are of different composition, depending primarily on their formation region. They have experienced different degrees of thermal alteration, mainly as a function of their size. Smaller planetary bodies have a large surface relative to their volume and therefore loose heat – generated from accretion and from the decay of radioactive isotopes – more quickly than larger bodies. They practically leave their original constituents unaltered. Mutual collisions between these small asteroids produce fragments, which can arrive on Earth as meteorites. These meteorites are of the unequilibrated chondrite class and are among the most copious archives of the early solar system for cosmochemists. The bulk of meteorites are chondrites. On the contrary, larger bodies have a smaller surface-to-volume ratio and retain accretionary and radiogenic heat better. Thermal metamorphism can occur and leads to recrystallization of minerals in the parent body, obliterating any pre-existing
presolar signature. The abundance of presolar minerals therefore generally decreases with increasing thermal metamorphism. Conversely, aqueous alteration does not affect presolar grain abundance very much. Meteorites which have experienced extensive aqueous alteration but were not heated above ~370 K such as the carbonaceous chondrites Orgueil (CI1), Murchison and Murray (both CM2) have the highest abundances of presolar carbonaceous grains (Huss 1997). Lower abundances of carbonaceous presolar grains are found in ordinary chondrites (which comprise 81% of all chondrites) but these meteorites turned out to be an important source for presolar oxide grains.

In larger planetary bodies partial melting occurs and heavy elements like iron and nickel segregate from lighter ones and sink to the center, forming a core, while lighter ones such as silicates rise by buoyancy and form a mantle. This process is called planetary differentiation and occurred in the largest asteroid and in all terrestrial planets. Differentiation almost completely resets earlier isotopic signatures. Meteorites from these differentiated parent bodies are classified as achondrites if they are from the crust or mantle, or as iron meteorites if they are fragments of the core. In rare cases stony-iron meteorites are found, they are thought to originate from the core-mantle boundary. Thus, meteorites are either from differentiated (achondrites, iron- and stony-iron meteorites) or undifferentiated parent bodies (chondrites). For studies of presolar grains, the carbonaceous and ordinary chondrites are the meteorites of primary interest. Ordinary chondrites are further subdivided into LL, L and H chondrites, according to their metal content (very low, low and high, respectively). The different types of chondrites are shown in Fig. 12.

![Extended meteorite classification system for chondrites after Van Schmus and Wood.](image)
3.8.2 Fossil Meteorites

Meteorites fallen during Earth’s history are preserved until today in rare cases as fossil meteorites. As with fossils from Earth’s fauna, most of the original constituents have been replaced during diagenesis. However, very resistant minerals, in particular chromite, can survive and can carry precious compositional information about the fossil meteorites (Schmitz et al. 2001). Well-preserved specimens of fossil meteorites show even textural information, such as chondrules (see Fig. 13). A relatively high abundance of fossil meteorites has been found in ~480 Myr old marine sediments from the Ordovician in southern Sweden (Schmitz et al. 2001). Together with the subsequent recovery of sediment-dispersed extraterrestrial chromite grains Schmitz et al. (2003) estimated the meteorite flux to have been about two orders of magnitude higher than today, during at least one million years. This period of elevated flux coincides with the break-up of the L chondrite parent body around 500 Myrs ago (see chapter 4 and 5). Other examples of similar correlations are the increased extraterrestrial flux about 36 Myrs ago, during the Late Eocene, which was even accompanied by impact cratering (Farley et al. 1998).

Fig. 13. A fossil meteorite recovered from the Thorsberg quarry in southern Sweden (size 6 x 8.5 cm). Although mineralogically the fossil meteorite has been completely altered (with the exception of microscopic chromite grains), the texture of mm-sized chondrules has been conserved. The meteorite fell into an epicontinental sea about 480 Myrs ago and has been found embedded in marine limestone along with marine organisms such as the nautiloid located at right. Photo courtesy: B. Schmitz.
The transfer times of meteorites from their parent bodies to Earth can be determined with cosmic-ray exposure age dating (Wieler 2002). This can be applied to meteorites that reached Earth recently, but also to fossil meteorites, to study the transfer times of (Heck et al. 2004). Every object in interplanetary space is exposed to cosmic rays. The latter consist primarily of protons (~87%), alpha-particles (~12%) and to a smaller degree of heavier nuclei (Simpson 1983). Interaction of solid matter with cosmic-rays causes nuclear reactions (spallation), which produce new cosmogenic nuclei. High-energy cosmic-rays originate outside of our solar system far away in our galaxy and can acquire part of their high energies at their – yet unknown – source, might get accelerated further by supernova shock waves and are transported by interstellar magnetic fields (reviews by Heber 2001 and Gaisser 2003). They can penetrate solid rock up to 1-2 m and have a mean penetration depth of ~0.5 m. Low-energy cosmic rays are generated in solar flares and enter solid matter only a few Å to mm. Additionally, the continuously sun-outward streaming solar wind (SW) and solar energetic particles (SEP) are implanted into surfaces of interplanetary objects. Smaller objects like IDPs having high surface-to-volume ratios show a more prominent contribution of solar cosmic ray (SCR)-produced nuclides but most importantly have high concentrations of implanted SW and SEP, overshadowing cosmogenic nuclides (see chapter 5). On the other hand, for meter-sized objects like meteoroids only galactic cosmic rays (GCRs) are of importance and surface-correlated SW and SCR products can be neglected. GCR-produced cosmogenic nuclides like stable $^3$He and $^{21}$Ne can be used to determine the exposure age of a meteorite. While residing deep in its parent asteroid, the potential meteoroid is shielded from GCR and no cosmogenic nuclides are produced. When a collision disrupts the parent asteroid into many fragments, the ones reaching escape velocity can get inserted into a solar orbit. Immediately after the collision, meter-sized fragments get exposed to cosmic rays leading to the production of cosmogenic nuclides, like $^3$He$_{\text{cos}}$ and $^{21}$Ne$_{\text{cos}}$. Once the orbit becomes Earth-crossing, the meteoroid can collide with our planet and after survival of the atmospheric passage, rest on Earth’s surface as a meteorite. At that time, Earth’s atmosphere shields the meteorite from primary cosmic rays and essentially no cosmogenic nuclides are being produced. Actually, secondary cosmic-rays still reach the terrestrial surface, but they produce orders of magnitudes less cosmogenic nuclides than the GCRs in space, thus their contribution can be neglected in most cases. Cosmogenic noble gases are favorable to measure since they are very rare in original, non-radiated meteoritic matter. By measuring the $^{21}$Ne$_{\text{cos}}$ concentration in the meteorite, its exposure age can be determined once a production rate of $^{21}$Ne$_{\text{cos}}$ is known. The latter depends on several factors like the composition of the meteorite, the sample depth, the preatmospheric size of the meteoroid and the GCR flux.
The GCR flux is considered to be more or less constant over time scales of millions of years. Production rates are determined by irradiating targets of different compositions in accelerators and incorporating the experimental data into physical models (e.g. Leya et al. 2000) as well as by measuring pairs of radionuclides and stable isotopes.

Exposure ages for chondrites are on the order of several million to several dozen million years. Only very few meteorites have exposure ages < 1 Myr (see chapter 4). Exposure ages of different meteorites are distributed in clusters. This suggests that only few collisions are responsible for the meteorite collection we have on our planet and that the meteorites presently available are only a limited collection of asteroidal samples (see review by Wieler 2002).

3.9 Dust in the Solar System

Long before the discovery of presolar dust grains, extraterrestrial dust was observed by humans as dark dust clouds in the Milky Way, comet dust tails and zodiacal light. The faint glow of cone-shaped zodiacal light can be marveled at in moonless nights far from sources of light pollution (see Fig. 14).

The observation of Zodiacal light from Earth was already mentioned by the Iranian poet,
astronomer and mathematician Omar Khayyam (1048-1123). He referred to the phenomenon as *Subhi Kazib*, the ‘false dawn’ in his famous collection of poems, the Rubaiyat (English translation by Fitzgerald 1889). (One should not be fooled by the dawn-like light of the zodiacal light and not to stop take the pre-dawn breakfast (Suhur) during the daylight fasting month of Ramadan.) Giovanni Domenico Cassini (1625-1712) observed the zodiacal light from Europe and interpreted the light correctly as a flattened cloud of dust in the plane of the solar equator.

All the dust from the solar nebula, the primordial nebula from which the solar system formed 4.5 Gyrs ago, was incorporated into planetary materials, fell into the sun or left our solar system (see above). The dynamical lifetime of small dust particles in the solar system is only a few thousand to about one million years. It is mainly a function of grain size, composition and distance from the sun. Hence, no primordial dust survived, unless it was incorporated in small solar system bodies, which did not suffer from thermal alteration. In chapter five, solar system dust production and dynamics will be discussed in more detail. The zodiacal light therefore stems from sunlight reflected and scattered on fresh dust from comets and from asteroidal collisions. Similar circumstellar dust discs are observed around other main-sequence stars (see Fig. 15). Their presence implies the existence of dust-producing comets and asteroids. Only a small part of today’s interplanetary dust has an interstellar origin. The first interstellar grains in interplanetary space were detected by the Ulysses spacecraft (Grün et al. 1993). Several spacecraft are equipped with dust detectors and mass spectrometers for in-situ experiments. But much more detailed analyses can be made in the laboratory. Therefore, sample return is highly

Fig. 15. HST ACS image in visible light of the circumstellar dust disk around sun-like star HD 107146. The amount of dust in this debris disk is estimated to be 3-4 magnitudes higher than in our solar system. This star is very similar to but younger than our sun, it is estimated to be only 30-250 million years old. The star light illuminates the dust disk but itself is artificially hidden from view to allow exposure of the faint debris disk. Credit: NASA, ESA, D.R. Ardila (JHU), D.A. Golimowski (JHU), J.E. Krist (STScI/JPL), M. Clampin (NASA/GSFC), J.P. Williams (UH/IfA), J.P. Blakeslee (JHU), H.C. Ford (JHU), G.F. Hartig (STScI), G.D. Illingworth (UCO-Lick) and the ACS Science Team.
desirable. Interplanetary dust particles (IDPs) were routinely collected in the stratosphere by high-flying aircraft (see chapter 6), during manned space-missions in low Earth-orbit and with the specially designated Stardust spacecraft. Stardust is scheduled to return to Earth in January 2006 with primarily cometary dust from comet Wild-2 but also interstellar dust grains.

For studies of recent solar system history to presolar stellar astrophysics, noble gas cosmochemistry represents a very useful tool to improve our understanding of physical processes and conditions.

References


II. Methods
1. Introduction

Noble gas analyses on all samples were carried out at the Noble Gas Laboratory of the Department of Earth Sciences of ETH Zürich, Switzerland. Presolar SiC grain extraction, selection and analysis were conducted with Kuljeet Marhas and Peter Hoppe at the Max-Planck Institute for Chemistry in Mainz, Germany, using SEM/EDX and a NanoSIMS ion-microprobe. Murchson SiCs were analyzed in two runs. One measurement run has been accomplished by Kuljeet Marhas, while the other NanoSIMS-analyses were conducted together with the author. Recovery, extraction and SEM/EDX analyses of relict chromite grains from fossil meteorites and micrometeorites was done by Birger Schmitz at the Department of Geology of the University of Lund, Sweden and at the Department of Marine Geology at the University of Göteborg, Sweden. This chapter describes the noble gas methods, which were developed during the work for this thesis. Therefore, the details of the noble gas analyses slightly vary in different samples studied. The sample-specific methods, as well as the other laboratory techniques and methods used, are described in the methods section of the respective chapters of this thesis.

2. Noble Gas Laboratory Methods

2.1 Experimental Setup

The mass spectrometer was developed and built by Heinrich Baur together with the highly skilled mechanical and electronic workshop staff of the Institute of Isotope Geology and Mineral Resources at ETH Zürich. The low-blank laser-extraction line – designed by Nadia Vogel and Heinrich Baur – was assembled and tested during this work.

The experimental setup consists of an infrared-laser gas extraction line connected to an ultra-high sensitivity mass spectrometer. A schematic view is shown in Fig. 1, the individual components and analysis steps are explained in the following sections.

2.2 Laser Extraction of Noble Gases

Gases were released by melting the sample in ultra-high vacuum (UHV) with a focused Nd-YAG Spectron SL902TQ infrared laser (now GSI Lumonics). The laser radiation is at a wavelength of 1064 nm. The laser was operated in continuous wave mode with a maximum output of 16 W in low-energy mode \((\text{TEM}_{00})\) and 65 W in high-energy mode (multi-mode). Beam-width was adjusted with a selectable aperture, which determines the energy mode (\(\text{TEM}_{00}\) or multi-mode)
Laser light then passed through a beam expander/zoom-optics and via a 45° mirror into the sample chamber. Because the small, micron- to submicron-sized SiC grains were quite densely distributed on the sample holder, a small beam size was desirable in order to prevent melting of adjacent samples. The smallest beam size we obtained in the focus using our smallest aperture (ø 1.3 mm) was 50 µm with the available optics. The simple optics were actually conceived for material processing applications and the smallest focused spot size is fairly large. On the other hand, we used the full aperture to obtain a larger laser beam size with a higher energy, for the analyses of batches of a few, larger chromite grains (ø 80-100 µm). This is needed to entirely melt these large samples. Depending on sample size, laser irradiation time was varied from 1 minute (for SiC grains) to 3 minutes (for batches of chromite grains). The melt residues of several large SiC and of all chromite samples were laser-heated in a second measurement to verify if the grains had degassed completely. In all of these cases complete degassing was achieved already in the first shot.

Beam position was monitored by a CCD camera video system looking through the viewport, transmissive for light with a wavelength between 320 to 2700 nm. The water-cooled sample chamber is mounted on a manually operated X-Y-Z micro-positioning stage.

Fig. 1. Schematic representation of the low-blank infrared-laser gas extraction line connected to the ultra-high sensitivity mass spectrometer equipped with a compressor source. See text for explanations.
2.3 Gas Cleaning Procedure

Before letting the gas into the mass spectrometer, unwanted components need to be removed. To obtain a useful signal of the sample gas, potential isobaric interferences on isotopes of interest (see Tab. 1) have to be minimized. In the following section these steps are described. The extraction line is illustrated schematically in Fig. 1.

Table 1. We list measured items with their isobaric interferences, the method to trap interfering species and the correction applied to the measured items to remove interfering signals. In order to perform interference correction we monitored masses of 18, 40 and 44 during all measurements.

<table>
<thead>
<tr>
<th>Mass (charge) Item</th>
<th>Interference on</th>
<th>Trapping method</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass 3 (+): HD</td>
<td>Mass 3:</td>
<td>H₂ gettering with Zr-Al pellets at room temperature (SAES St-101)</td>
<td>Mass resolution of the mass spectrometer allows the achieved HD peak to be separated from ³He</td>
</tr>
<tr>
<td></td>
<td>³He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass 20 (+): (H₂¹⁸O)⁺</td>
<td>Mass 20:</td>
<td>Liquid N₂-cooled horseshoe trap and activated charcoal filters (cold traps)</td>
<td>H₂¹⁸O / H₂¹⁶O = 2.00485·10⁻³</td>
</tr>
<tr>
<td></td>
<td>²⁰Ne⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass 40 (++): ⁴⁰Ar⁺⁺</td>
<td>Mass 20:</td>
<td>Cold traps</td>
<td>⁴⁰Ar⁺⁺ / ⁴⁰Ar⁺ = 4.5·10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>²⁰Ne⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass 44 (++): (¹²C¹⁶O₂)⁺⁺</td>
<td>Mass 22:</td>
<td>Ti/Zr Getter</td>
<td>(¹²C¹⁶O₂)⁺⁺ / (¹²C¹⁴O₂)⁺⁺ = 1.6·10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>²²Ne⁺</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In a first cleaning step the gas was led through a cooled horseshoe bend tube immersed in boiling liquid $N_2$ ($T \approx 77$ K) to trap mainly $H_2O$ and $CO_2$. After that, several gas purification getters were used to remove active gases. Getter materials are highly porous and have a large surface area. The gas was forced through a permanently heated vessel ($T \approx 570$ K) filled with getter pellets from the company Danielson and subsequently got in contact with a second “appendix” getter filled with identical pellets. The composition of this getter material is unknown to us due to company policy, but the pellets behave like Zr-V-Fe alloy pellets from SAES (eg. St 707 with 70% Zr, 24.6% V and 5.4% Fe). If heated to an optimal activation temperature to remove the passive surface layer they trap active gases like CO, $CO_2$, $N_2$ and $O_2$ by sorption. On the pellet surface, the molecules are dissociated and form heat-resistant oxides, carbides and nitrides with the getter material. Since noble gases are chemically inert they do not get captured in the getter.

It is necessary to trap the noble gas argon, since $^{40}Ar^{++}$ interferes with $^{20}Ne^+$. Additionally, we cannot measure Ar with this mass spectrometer due to ion pumping effects (see below for explanation). We therefore trapped Ar by exposing it to a liquid $N_2$ cooled activated charcoal filter ($T \approx 77$ K).

In a next step the gas got exposed to another getter (Zr-Al alloy) at room temperature ($T \approx 293$ K) to remove $H_2$. Hydrogen gas diffuses into the getter material and gets trapped there at low temperatures. In stand-by mode overnight, the getter was heated to release and pump away the trapped $H_2$ to restore full getter capacity for the next day. The remaining argon was frozen with another cooled ($N_2(l)$ at $T\approx 77$ K) activated charcoal finger.

2.4 Mass Spectrometry

After several stages of purification the gas entered the mass spectrometer. The heart of the mass spectrometer is a special ion source, equipped with a “compressor”, i.e. an inverse turbo molecular drag pump which concentrates the gas into a small ionization volume (Fig. 2; Baur 1999). The ion source is a 0.5× linear-scaled version of the Baur-Signer source (Baur 1980). An electron impact acceleration voltage of 40 eV was used to minimize double-charged, interfering $^{44}CO_2$ and $^{40}Ar$ ions. The compression of the gas into a small ionization chamber leads to a sensitivity increase of two orders of magnitudes for He and Ne compared to the sensitivity without the compressor. Due to the higher ionization cross-section for the heavier noble gases Ar, Kr and Xe, the latter are pumped away quickly and their residence time in the spectrometer does not allow them to be measured. Therefore, this mass spectrometer is best suited for the light noble gases He and Ne.
$^4$He ions were detected with a faraday cup while all other ions as well as $^4$He during SiC measurements were detected with an electron multiplier in ion counting mode. A special Y-shaped alignment of the detectors allows $^3$He and $^4$He ions to be detected simultaneously and results in an abundance sensitivity increase. This enables to measure extreme He isotopic ratios such as He from terrestrial samples with $^3$He/$^4$He ratios $> 10^8$.

A memory signal results from gases released by ion-impacts into the interior surfaces of the mass spectrometer. However, we can compensate for this partly with a newly developed method for data reduction.

![Fig. 2. Schematic view of ion source, equipped with a compressor (from Baur 1999). The compressor consists of a magnetically levitated rotor, spinning at 1500 Hz, which forces the gas along spiral grooves (thick arrows) in the inner wall of the stator. The neutral gas then enters the ionization volume and gets accelerated to the left towards the mass selector and ion detectors. The rotor itself is not shown. Image courtesy: H. Baur.](image-url)
2.5 Data Reduction

2.5.1 General Treatment of Data

We developed an experimental procedure to minimize the effects of mass spectrometer memory, to be able to measure extremely small amounts of gas expected from our dust-sized samples.

To compensate for the memory signal, we monitored the signal before, during, and after sample gas inlet. By extrapolating the signal intensity to the time of gas inlet, from data obtained before and after inlet, we obtain two signals, which we can subtract from one another (see Fig. 3). The difference gives the amount of gas released from the sample.

The sample gas obtained is then corrected for interferences as described above. We applied the same procedure to all masses measured, including masses used for interference corrections. The same method was used for sample and blank measurements. Deconvolution into different noble gas components allows further interpretation of the data.

![Graph showing 22Ne signal vs. time during presolar grain analysis. The first four data points show the increase of the spectrometer memory. The time of gas inlet is indicated with a vertical line crossing the time axis. After gas inlet, the signal intensity increased according to the gas amount of the sample. A linear regression through the data points before and after gas inlet, respectively, allows the signal intensity at the time of gas inlet to be extrapolated from both sides. The difference between these two values, indicated with a vertical arrow, corresponds to the gas amount in the sample.](image)

Fig. 3. $^{22}$Ne signal vs. time during presolar grain analysis. We use gas-rich presolar Murchison grain SiC 070 as an example. The first four data points show the increase of the spectrometer memory. The time of gas inlet into the spectrometer is indicated with a vertical line crossing the time axis. After gas inlet, the signal intensity increased according to the gas amount of the sample. A linear regression through the data points before and after gas inlet, respectively, allows the signal intensity at the time of gas inlet to be extrapolated from both sides. The difference between these two values, indicated with a vertical arrow, corresponds to the gas amount in the sample.
Fig. 4. $^4$He signal of blanks and presolar SiC for Murchison. The measurements have been done in two successive sessions. While the first one shows a large scatter of the blanks, the second one has a clearly lower blank scatter. Scatter of the blanks is indicated as the shaded region, representing the 2σ standard deviation of the blanks. We also show the 3σ scatter of blanks. The average blank value is represented by the central horizontal line running through the shaded box. SiC grains containing nucleosynthetic $^4$He are located above the upper border of the shaded region (detection limit). Error bars of sample and blank data points are 1σ and represent analytical errors.
2.6.2 Determination of Detection Limits

We need to determine and define the detection limits clearly in order to recognize also grains with only very small amounts of noble gases. Due to very small sample size (submicron to micron range) presolar grains are expected to contain even less gas than the other small samples we analyzed. Previous studies (Nichols 1992) and preliminary experiments showed that signals of single presolar grains can be expected to be only little above blank signals. Our detection limit of He and Ne isotopes depends not only on the sensitivity of the spectrometer but also critically on the size and the stability of the blank signal. We use the standard deviation (σ) of the blanks to quantify the scatter of the blanks. We define our detection limit as the 2σ-scatter of all blanks during one measurement session. The detection limits obtained this way are shown in Table 2. By using the same definition of the detection limit as Nichols (1992) we can compare our results with his pioneering work on single presolar SiC grain analyses.

The stability of the blanks depends primarily on the quality of the vacuum and secondarily on the measurement procedure applied. This is illustrated in the following: We used two different procedures: In the first one, we opened the valve connecting the mass spectrometer to the extraction line after laser gas extraction and gas cleaning (used for Murchison runs and first session of Murray run). In the second one, this valve is already opened after closing the vacuum pumps and the gas extraction and cleaning volume stays in contact with the mass spectrometer volume during the entire analysis (used for second Murray run). Despite the same procedure has been used during the entire Murchison run, we see a pronounced decrease of the $^4$He-blank scatter in the second session compared to the first one (Fig. 4). Extended vacuum pumping resulted in a better vacuum and reduced gas residence times in the extraction line by shortening gas cleaning to the minimum necessary. This effect is less dramatic for $^{22}$Ne (Fig. 5a). The difference of the two sessions in the Murray run (Fig. 5b) is caused by the use of a new method: Immediately before gas extraction, valves between the mass spectrometer and the extraction line were opened and valves to the vacuum pumps were closed. The advantage not to operate any valves after pumping stopped, resulted in a lower blank, as expected. The manipulation of UHV-valves releases measurable amounts of gas into the system, mainly by quenching and de-quenching of the UHV-copper seal.
Fig. 5. $^{22}$Ne signal of blanks and presolar SiC grains for Murchison (a) and Murray (b). The measurement runs for samples from both meteorites runs consist of two sessions per meteorite. The first sessions show higher average blank values and larger blank scatter than the second ones. Blank scatter during one entire session is indicated by the shaded region, which represents the 2$\sigma$ standard variation of all blank values. Dashed lines are the 3$\sigma$ of blank scatter. Samples lying above the shaded 2$\sigma$-region are considered to be gas-rich. Error bars of sample and blank data points are 1$\sigma$ and represent analytical errors.
Table 2. Detection limits during Murchison and Murray measurement runs on the ultra high-sensitivity noble gas mass spectrometer. Detection limit are given in units of cm$^3$ of gas at standard temperature and pressure (STP). Differences between the four measurement sessions are explained in the text. See also Figs. 4 and 5.

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References


III. Presolar Silicon Carbide Grains
Presolar He and Ne Isotopes in Single Circumstellar SiC Grains
Short title: He and Ne isotopes in circumstellar grains

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Abstract

Noble gas isotopes in presolar silicon carbide (SiC) dust grains from primitive meteorites provide, together with major element isotopic compositions, insight into the nucleosynthetic output of different types of evolved stars >4.5 Gyrs ago. We report here new results from helium and neon isotopic analyses of single presolar SiC grains with sizes between 0.6 and 6.3 µm using an ultra-high sensitivity mass spectrometer. These noble gas studies were complemented by an ion microprobe study (NanoSIMS) of Si-, C- and N-isotopic compositions of the same grains. About 40 percent, or 46 of the 110 grains analyzed, contain nucleosynthetic Ne-22 and/or He-4 from their parent stars above our detection limit. We discuss the possible stellar sources using isotopic ratios as constraints combined with model predictions. Among the considered stellar sources are asymptotic giant branch (AGB) stars, Wolf-Rayet stars, supernovae and novae. We argue that most grains are of the mainstream type and originate in low-mass AGB stars. We find a higher than expected percentage of A/B type grains, with some containing Ne-22 and/or He-4. Additionally, one noble gas-rich nova grain candidate is evaluated, one supernova grain (X type grain), and one Ne-22-rich X or Z type grain candidate is discussed.

Subject headings: dust, extinction --- circumstellar matter --- methods: laboratory --- methods: analytical --- nuclear reactions, nucleosynthesis, abundances

Online material: color figures

1. Introduction

This study focuses on the finding of nucleosynthetically-produced helium and neon in the parent stars of presolar silicon carbide (SiC) grains from primitive meteorites. Helium and neon are among the most prominent elements produced in the H- and He-burning shell of late stage stars. Presolar dust originated in the outflows and ejecta of evolved stars and incorporated stellar nucleosynthetic products. C-rich asymptotic giant branch (AGB)-stars, the carbon stars, are major dust producers in our Galaxy. In their circumstellar environment, a considerable fraction of the matter expelled by stellar winds condenses as high-temperature minerals, such as silicon carbide (SiC), and elements remaining in the gas phase such as the noble gases can get implanted into the newly formed grains. Other potential stellar sources of presolar grains are discussed below and include supernovae, Wolf-Rayet stars and novae. Presolar grains arrive on Earth within meteorites or interplanetary dust particles (IDPs), from which they can be extracted for laboratory analyses. Comparisons of their isotopic compositions for various elements with
predictions from models of stellar nucleosynthesis allow the latter to be tested and constrained (for a recent review on presolar grains see Clayton & Nittler 2004; Hoppe 2004; Zinner 2004).

In the 1960s noble gas studies of primitive meteorites revealed a component with highly anomalous Xe-isotopic composition, which was attributed to a presolar carrier phase (e.g. Reynolds and Turner 1964). Some 20 years later, nanodiamonds were isolated as the carrier of this anomalous Xe component (Lewis et al. 1987). The noble gases played also a key role for the isolation of presolar SiC and graphite from the Murray and Murchison meteorites (Bernatowicz et al. 1987; Amari et al. 1990). Nichols et al. (1991, 1992) were the first to study He- and Ne-isotopic compositions in single presolar SiC and graphite grains from the Murchison meteorite. They found that only about 6% of the single SiC grains (~1.5 to 4 µm diameter) contained detectable amounts of nucleosynthetic Ne (Ne-G, also known as Ne-E(H)) which was always accompanied by $^4$He. A considerably larger fraction of presolar graphite grains (~30%) was reported to contain isotopically anomalous Ne (Ne-E(L)) above the detection limit, in this case without any accompanying $^4$He. The gas-rich grains accounted for >90% of the gas concentration measured in bulk samples in the case of SiC and 100% in the case of graphite.

There are two nucleosynthetic Ne-components, Ne-G and Ne-R, which are strongly enriched in $^{22}$Ne relative to solar composition. Ne-G, formerly known as Ne-E(H), is highly enriched in $^{22}$Ne relative to $^{20}$Ne and the theoretically expected $^{20}$Ne/$^{22}$Ne-ratio of this component, derived from the AGB star He shell, is 0.0827 (Lewis, Amari, & Anders 1994). $^{20}$Ne in Earth’s atmosphere is two orders of magnitudes more abundant than $^{20}$Ne-G. Therefore, the latter is difficult to measure in the laboratory, even at ultra-high vacuum conditions, and only an upper limit of the ($^{20}$Ne/$^{22}$Ne)-G ratio has been determined (experimental value: $^{20}$Ne/$^{22}$Ne < 0.1; Lewis et al. 1994). The ratio of ($^{21}$Ne/$^{22}$Ne)-G is even smaller with an experimentally determined upper limit of 0.0015 and a theoretical value of 0.00059 (Lewis et al. 1994). $^{22}$Ne-G is predicted to be produced by $\alpha$-capture on the hydrogen burning, carbon-, nitrogen-, oxygen-cycle (CNO) product $^{14}$N in the He-burning shell of low- to intermediate-mass (1-8 $M_\odot$) AGB stars by $^{14}$N($\alpha,\gamma$)$^{18}$F(e$^+$+ν)$^{18}$O($\alpha,\gamma$)$^{22}$Ne. Continuous dredge-up of matter from the He shell in the thermally pulsing-(TP)-AGB phase strongly enhances the $^{22}$Ne abundance in the star’s envelope. On the other hand, the $^{20}$Ne abundance is almost left unaltered during the AGB phase (e.g. Karakas & Lattanzio 2003). The accompanying $^4$He is the main H-burning product by pp and CNO reactions and it is brought to the stellar surface along with $^{22}$Ne by deep convection currents (third dredge-up events). From there they are expelled by stellar winds into the circumstellar environment before getting implanted into newly formed dust grains (Gallino et al. 1990). It is estimated that AGB stars produce about half of the $^{22}$Ne abundance in our Galaxy (Gallino et al. 1998).
The other Ne-component with a very low $^{20}\text{Ne}/^{22}\text{Ne}$-ratio is Ne-R (Amari, Lewis, & Anders 1995). Ne-R, pure $^{22}\text{Ne}$, is believed to be of radiogenic origin from the decay of short-lived radioactive $^{22}\text{Na}$ ($\tau_{1/2} = 2.6$ yrs). It has been observed in presolar graphite grains. Actually, many graphite grains show Ne-R as well as Ne-G, which has been subsumed as Ne-E(L) (Amari et al. 1995), while the most gas-rich ones seem to contain Ne-R only (Amari, Zinner, & Lewis 2005).

The $^{20}\text{Ne}/^{22}\text{Ne}$-ratio of Ne-G is higher than for Ne-R. To distinguish between Ne-R and Ne-G one needs to determine the upper limit of the $^{20}\text{Ne}/^{22}\text{Ne}$-ratio ($^{20}\text{Ne}/^{22}\text{Ne}$ of Ne-R < 0.01, Amari et al. 1995; and Ne-G < 0.1, Lewis et al. 1994). Large amounts of $^{22}\text{Na}$ are produced in nova and supernova explosions and condense with carbonaceous material to form dust grains in the expanding ejecta. There, it decays in situ to $^{22}\text{Ne}$ (Ne-R). To explain the coexistent occurrence of the G component, the same grains need to get exposed to $^4\text{He}$, $^{20}\text{Ne}$ and He-shell $^{22}\text{Ne}$. Only ~1% of all presolar SiC are attributed to have a supernova origin (e.g., Hoppe et al. 2000) and only a handful of grains might originate from novae (Amari et al. 2001a). On the other hand, graphite grains from supernovae and novae seem to be more common, as deduced from the presence of Ne-R. Ne-R, together with a low $^{12}\text{C}/^{13}\text{C}$-ratio indicates a nova origin, while Ne-R with above solar $^{12}\text{C}/^{13}\text{C}$-ratios tends toward a supernova origin.

In this work we analyzed He and Ne isotopes in single presolar SiC grains from the carbonaceous meteorites Murchison and Murray. Using a unique noble-gas mass spectrometer equipped with a molecular drag pump we achieve detection limits by factors of up to ~11 ($^4\text{He}$) and ~8 ($^{22}\text{Ne}$) lower than those attained by Nichols et al. (1992). The absolute detection limits of our ultra-high sensitivity mass spectrometer are $(0.9$ to $14) \times 10^{-13}$ cm$^3$ STP (1 cm$^3$ STP = $2.6868 \times 10^{19}$ atoms) for $^4\text{He}$ and $(2.2$ to $7.0) \times 10^{-15}$ cm$^3$ STP to for $^{22}\text{Ne}$.

Our primary objectives were to determine if this higher sensitivity would make the measurement of smaller grains (submicrometer in size) possible and whether a higher percentage of grains contains measurable amounts of nucleosynthetic noble gases from their stellar sources than was determined in previous studies. Also, we wanted to verify whether nucleosynthetic $^{22}\text{Ne}$ is always accompanied by $^4\text{He}$. Furthermore, we measured the Si-, C- and N-isotopic compositions of the same grains with the NanoSIMS ion microprobe to classify the grains after Hoppe & Ott (1997).

2. Samples and Experimental

We have investigated 110 presolar SiC grains from the Murchison and Murray carbonaceous chondrites of type CM2. Meteorites of type CM2 experienced only minimal (aqueous) alteration on their asteroid parent body and therefore conserved presolar minerals in their interior during the entire history of the Solar System (Huss 1997).
2.1 Sample Preparation and Selection

Using the procedure of Ott & Merchel (2000), SiC grains were extracted from the Murchison meteorite. SiC from Murray was extracted by a procedure described by Amari, Lewis, & Anders (1994). The extracted SiC grains were transferred to ultra-clean Au foils in an isopropanol/water suspension. Special care was taken to have a sparse grain distribution on the sample mount, in order to prevent heating of neighboring grains during laser-induced noble gas extraction. The minimum grain separation distance was aimed to be larger than the laser spot size, which was about 50 µm. Single SiC grains were identified by SEM/EDX and selected only if the distance to neighboring grains was >50 µm. Detailed maps of the grain mounts were made and coordinates of selected grains were recorded for the subsequent noble gas and NanoSIMS studies.

2.2 NanoSIMS Ion Microprobe Analyses

The C-, N-, and Si-isotopic compositions of the Murchison SiC grains were measured after noble gas extraction, on the remaining grain melt resulting from laser heating. The opposite sequence of measurements was chosen for the Murray grains. Here, in order to save material for the following noble gas measurements, N-isotopic compositions were not measured. Negative secondary ions of $^{12}\text{C}$, $^{13}\text{C}$, $^{28}\text{Si}$, $^{29}\text{Si}$, and $^{30}\text{Si}$ and of $^{12}\text{C}$, $^{13}\text{C}$, $^{12}\text{C}^{14}\text{N}$, and $^{12}\text{C}^{15}\text{N}$ were measured in multi-collection in two different runs using a defocused Cs$^+$ primary ion beam (<1 pA). Instrumental mass fractionation was determined by measuring a big synthetic SiC crystal (C and Si analyses) and a powdered synthetic SiC standard doped with N (C and N analyses). Reproducibility of $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$, $^{28}\text{Si}/^{29}\text{Si}$, and $^{30}\text{Si}/^{28}\text{Si}$ ratios between different spots on the standards was 3 ‰, 5 ‰, 6 ‰, and 3 ‰, respectively, and is included in the errors given in Table 2. In most cases the $^{12}\text{C}/^{13}\text{C}$ ratios from the C- and Si-measurement series agree within 2σ errors with those from the C- and N-measurement series. For 3 grains we observed differences in the $^{12}\text{C}/^{13}\text{C}$ ratio and in these cases the more anomalous value is listed in Table 2. Out of 20 gas-rich Murchison grains, 16 were studied for C-, N-, and Si-isotopic compositions. For Murray, we measured some 50 SiC grains for C- and Si-isotopic compositions, 24 of which turned out to be gas-rich. In Table 2 C, N, and Si data are given for the gas-rich grains. In addition 2 gas poor-grains from rare SiC populations are listed: One from Murchison, which was originally classified as gas-rich and one grain from Murray.

Using SEM imaging we distinguished between SiC grain aggregates and single grains. Only the latter where selected for further studies. Visual inspection of SEM images of Murray SiC did
not always allow to distinguish unambiguously between single grains and grain aggregates (see Fig. 1). About 20% of the Murray grains fall into this category of ambiguous grains. Therefore, high-resolution ion images of two representative ambiguous grains were recorded with the NanoSIMS (see Fig. 2). Two observations led us to assume that we observe single grains: First, the distribution of $^{13}$C/$^{12}$C ratios on the grain surface is matched by the Gaussian distribution of ratios on the basis of counting statistics. Spots with high $^{13}$C/$^{12}$C ratios (> 0.03) are clearly underabundant compared to previous SiC studies (e.g., ~10 % in Hoppe et al 1994, 1996); only one spot, which accounts for about 1 % of the visible grain area, exhibits this isotopic signature ($^{13}$C/$^{12}$C = 0.035; Fig. 2) and this ~300 nm-sized grain might just stick to the surface of the larger host grain. Second, the average $^{13}$C/$^{12}$C ratios of these grains ($^{13}$C/$^{12}$C = 0.016) differs clearly from the average ratio ($^{13}$C/$^{12}$C ≈ 0.03; Hoppe et al. 1996) one would obtain in a random sample from a mixture of all types of SiC grains in the right proportions.

We dismiss the possibility that heating of SiC grains from Murray with the ion beam in the NanoSIMS causes considerable elemental fractionation, namely, preferential He-loss. As will be outlined later, our $^4$He/$^{22}$Ne of the most gas-rich grains are comparable with previously measured ratios.

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Fig. 1.- SEM image of grain SiC205 from the Murray meteorite. Visual appearance of this grain does not un-ambiguously allow to identify it as a single grain or grain aggregate. About 20% of all Murray grains fall into this category.

Fig. 2.- High resolution map (a) of the surface $^{13}$C/$^{12}$C-ratio of Murray grain SiC205 recorded with the NanoSIMS using a focused Cs+ ion beam (100 nm beam diameter). Field of view is 7x7 μm². The ion image is subdivided into 10×10 pixel areas (~300 nm, the typical size of single particles) and the $^{13}$C/$^{12}$C ratios are plotted in a histogram. The curve represents the distribution of ratios expected on the basis from counting statistics. The average ratio ($^{13}$C/$^{12}$C=0.016) is lower than the ratio we would expect from a bulk SiC mixture ($^{13}$C/$^{12}$C=0.03; see text). Despite its ambiguous visual appearance, these observations point to a single grain. The bright spot in the ion image might represent a tiny SiC grain with $^{13}$C/$^{12}$C = 0.035 that sticks to the surface of the larger host grain. Based on these observations and conclusions for two similar Murray grains, where it is difficult to determine from visual inspection of SEM images if they are single grains and agglomerates, all 20% of the Murray grains, which fall into the same category, are believed to be single grains.
data from bulk and single grains as well as with theoretically expected values. Furthermore we will show that grains in which the noble gases were extracted prior to ion microprobe analyses (Murchison) have comparable $^{4}$He/$^{22}$Ne ratios to those from Murray.

2.3 Noble Gas Analyses

During melting with IR laser light, we could see the grain glowing for a few seconds in case the contrast in the CCD image was high enough. All analyzed samples were imaged in the SEM to verify complete melting of the grain. In all cases complete melting has been achieved, although some material remained on the gold foil, which, in case of the Murchison SiC grains, was used to measure C-, N-, and Si-isotopic compositions with the NanoSIMS.

Due to the very small sample size (0.6 to 6.3 µm grain-diameter), extremely low gas amounts are expected. This requires the use of an ultra-high sensitivity mass spectrometer (Baur 1999) and an extremely low-blank extraction line. Previous work done using the same experimental setup proved to be successful in detecting very small gas amounts from chromite grains from fossil meteorites (Heck et al. 2004). Gases were extracted in ultra-high vacuum by completely melting the single SiC grains for one minute with a continuous-wave Nd-YAG IR laser. H$_2$O, Ar and active gases were removed by letting the gas flow through a liquid-nitrogen-cooled U-tube and activated charcoal traps, and by exposure to several types of adsorption getters. After cleaning, an inverse turbomolecular drag pump concentrates the gas into a very small chamber where it is further gettered and subsequently ionized by electron impacts with a 2x scaled-down version of a Baur-Signer source (Baur 1999). This compressor source results in a sensitivity increase of about two orders of magnitude compared to the same mass spectrometer equipped with a conventional Baur-Signer source. Ions are detected with an electron multiplier in ion counting mode.

A standard correction by simply subtracting a “blank” from the sample signal would prevent us to detect very small gas amounts. We therefore used a more sophisticated method. Memory gas and background signals were monitored before, during and after sample gas admission. Memory gas is produced by ion-impacts into the interior surfaces of the UHV tubes, is a function of pressure and increases with time since pumping has stopped. After sample gas inlet, the sample signal adds up to the memory and background signal in a step-like increase (see Fig. 3). To resolve the sample signal we need to determine the amplitude of the step. We therefore determine the signal $I_1$ for the moment of gas inlet by extrapolation from data points before inlet. Determination of the signal $I_2$ at the moment after the step-like signal increase was done by extrapolation from data points after gas inlet. By subtracting the two signals we obtain the
amplitude of the step

\[ \Delta I = I_2 - I_1. \]

Subsequently, we need to correct \( \Delta I \) for interferences (\(^{44}\text{CO}_2^{2+}\) interferes with \(^{22}\text{Ne}^{+}\); \(^{40}\text{Ar}^{2+}\) and \(\text{H}_2^{18}\text{O}^{+}\) with \(^{20}\text{Ne}^{-}\)). To minimize the production of double-charged ions an electron acceleration voltage of 40 eV was used. Interferences were usually less than 1%. Ion signals were calibrated using gas from standard air reservoirs, amounts believed to be known to better than 3%.

As mentioned above, \(^{20}\text{Ne}-\text{G}\) is very difficult to measure since it is by about two orders of magnitude less abundant than atmospheric \(^{20}\text{Ne} \) ((\(^{20}\text{Ne}/^{22}\text{Ne})_{\text{G}} = 0.0827 < (^{20}\text{Ne}/^{22}\text{Ne})_{\text{atmospheric}} = 9.8\) and \(^{20}\text{Ne}_{\text{measured}} \approx ^{20}\text{Ne}_{\text{air}} \gg ^{20}\text{Ne}-\text{G}\)). Our detection limit for \(^{20}\text{Ne} \) is \((4.1\) to \(6.9) \times 10^{-14}\) cm\(^3\) STP. In case \(^{20}\text{Ne}_{\text{sample}} \) is identical to \(^{20}\text{Ne}_{\text{blank}} \) within 2σ-analytical error, we can assume all \(^{20}\text{Ne}_{\text{sample}} \) is blank and \(^{20}\text{Ne}-\text{G}\) is far below detection limit and “drowns” in the 2σ-error of the blank. In fact, the \(^{20}\text{Ne}\)-signals of all samples are indistinguishable from the blank signals.

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Fig. 3.- \(^{22}\text{Ne}\) signal vs. time during presolar grain analysis. We use gas-rich presolar Murchison grain SiC 070 as an example. The first four data points show the increase of spectrometer memory. The time of gas inlet into the spectrometer is indicated with a vertical line crossing the time axis. After gas inlet the signal intensity increased according to the gas amount of the sample. A linear regression through the data points before and after gas inlet, respectively, allows the signal intensity at the time of gas inlet to be extrapolated from both sides. The difference between these two values, indicated with a vertical arrow, corresponds to the gas amount in the sample (see text for further explanations).
21Ne-G is even rarer than 20Ne-G and more than two orders of magnitudes less abundant, with a theoretical value for 21Ne/22Ne=0.00059 and an experimentally determined upper limit of 21Ne/22Ne<0.0015 (Lewis et al. 1994). Our detection limit for 21Ne is (2.3 to 3.5) × 10^{-16} cm³ STP. With this detection limit, we do not expect to be able to measure 21Ne-G. As for 20Ne, the 21Ne-signals of our samples are not distinguishable from blanks. We therefore concentrate on the most abundant Ne isotope in the G-component, 22Ne. To obtain the fraction of nucleosynthetic 22Ne-G we subtract the amount of blank signal from the total amount of interference-corrected 22Ne:

\[ 22\text{Ne-G} = 22\text{Ne}_{\text{sample}} - 22\text{Ne}_{\text{average blank}} \]

We only consider this gas amount as significant above blank if the following condition is fulfilled. We define that a grain contains detectable amounts of 22Ne-G if it has a positive amount of gas above the 2σ-scatter of all blanks in one session:

\[ 22\text{Ne}_{\text{sample}} - 22\text{Ne}_{\text{average blank}} - 2\sigma_{\text{average blank}} > 0 \]

This is illustrated for Murray samples in Figure 4. To obtain the amount of nucleosynthetic 4He-G we proceeded likewise. We basically applied the same criteria as Nichols (1992, Ph.D. thesis). This allows us to compare our data with these previous analyses.

Gas concentrations were calculated as a first approximation by assuming spherical grains with a density of 3 g·cm⁻³, using the average of the semi-major and semi-minor axis of each grain. Compared to a cubic volume approximation we obtain ~2 × higher concentrations (V_{cube}/V_{sphere} = 2). Nichols et al. (1992, 1993) used cubic volume approximation, this has to be taken into account when comparing concentrations from these two studies.

3. Results

3.1 Murchison SiC

We analyzed 65 single presolar SiC grains extracted from the meteorite Murchison. Nine grains, representing 14% of all grains, contain 4He and 22Ne gas above our detection limit, attributable to a stellar nucleosynthetic source (Fig. 5, Table 1). A similar number of the grains (11 of 65 grains; 17%) contain 4He only, without any detectable 22Ne (Table 1). Only 2 grains (3%) contain 22Ne only, without any detectable 4He. Nichols et al. (1992) found only 9 (6%) of their 153 analyzed SiC grains from Murchison to contain nucleosynthetic 22Ne above their detection limit.
Fig. 4. $^4$He signal of blanks and presolar SiC for Murchison. The measurements have been done in two successive sessions. While the first one shows a large scatter of the blanks, the second one has a clearly lower blank scatter. Scatter of the blanks is indicated as the shaded region, representing the $2\sigma$ standard deviation of the blanks. We also show the $3\sigma$ scatter of blanks. The average blank value is represented by the central horizontal line running through the shaded box. SiC grains containing nucleosynthetic $^4$He are located above the upper border of the shaded region (detection limit). Error bars of sample and blank data points are $1\sigma$ and represent analytical errors.
limit, always being accompanied by $^4\text{He}$.

$^4\text{He}/^{22}\text{Ne}$ ratios are in the range of 25±1 to 299±94 with an arithmetic mean of 87. Single Murchison KJG grains analyzed by Nichols et al. (1992) have a $^4\text{He}/^{22}\text{Ne}$ range from about 100 to 500, KJH grains have $^4\text{He}/^{22}\text{Ne}$≈100-2000. Bulk sample $^4\text{He}/^{22}\text{Ne}$ ratios measured by Lewis et al. (1990) are in the range 240-940, predictions for the He-shell in AGB stars lie between 179 and 422 (Gallino et al. 1990). Our single grain $^4\text{He}/^{22}\text{Ne}$ ratios are lower than the ratios found in previous analyses and predicted by nucleosynthetic AGB star models and only overlap their lower range. Gas amounts for $^{22}\text{Ne}$ range from (0.31±0.29) to (11.5±0.3) $\times$ 10$^{-14}$ cm$^3$ at standard temperature and pressure (STP) and for $^4\text{He}$ from (9.8±3.4) to (681.2±2.9) $\times$ 10$^{-14}$ cm$^3$ STP. Approximate gas concentrations for $^{22}\text{Ne}$ range from (0.08±0.01) to (14.9±0.5) $\times$ 10$^{-3}$ cm$^3$ STP $\times$ g$^{-1}$ and for $^4\text{He}$ from (8.8±1.3) to (628.1±7.7) $\times$ 10$^{-3}$ cm$^3$ STP $\times$ g$^{-1}$, compared to Nichols et al. (1992) measurements for $^{22}\text{Ne}$-concentrations from (0.14±0.02) to (28.1±0.3) $\times$ 10$^{-3}$ cm$^3$ STP $\times$ g$^{-1}$ and for $^4\text{He}$-concentrations from (92±2) to (2206±8) $\times$ 10$^{-3}$ cm$^3$ STP $\times$ g$^{-1}$ of single grains from the KJG- and KJH-fraction of Murchison SiC, using spherical volume approximation (2× concentration for cubic volume approximation; see above). We find similar concentrations as Nichols et al. (1992), however our grains with smallest concentrations are about 50% lower for $^{22}\text{Ne}$ and about 95% lower for $^4\text{He}$. On the other hand, Nichols et al.’s most gas-rich grains have concentrations almost twice as high (Ne) and more than 3× as high (He) as our gas-rich ones.

NanoSIMS analyses were conducted on 15 grains containing either $^4\text{He}$ or $^{22}\text{Ne}$ gas, or both isotopes, and one grain containing no detectable noble gases. Si-, C- and N-isotopic compositions indicate that 11 out of 16 (~70%) of our analyzed samples are mainstream grains (Table 2; Figs. 6, 7). One of the gas-rich grains (SiC096) is classified as an X grain. It has a large $^{28}\text{Si}$ excess (δ$^{29}\text{Si}$=-346‰, δ$^{30}\text{Si}$=-274‰), and enrichments in $^{12}\text{C}$ and $^{15}\text{N}$ ($^{12}\text{C}^{13}\text{C}$=101, $^{14}\text{N}^{15}\text{N}$=45). Unfortunately, in this particular case we cannot exclude that the $^{22}\text{Ne}$ and $^4\text{He}$ gas stems from other, close-by SiC grains. Contrary to all other samples selected, some grains were located in within 50 µm distance to SiC096. During gas extraction by laser heating, we saw these neighboring grains glow. Hence, heating must have occurred and we cannot exclude that the $^4\text{He}$ and $^{22}\text{Ne}$ we see during analyses of X grain SiC 096 is actually from these neighboring grains. We like to note here that for all other samples analyzed, we can exclude heating and gas loss of neighboring grains, mainly because the distance separating them from other grains was much larger.

Four grains can be classified as type A/B grains owing to their particularly low $^{12}\text{C}^{13}\text{C}$ ratios (3.4, 9.9, 11.1, 11.4), Gas-rich grains SiC070 ($^4\text{He}$ and $^{22}\text{Ne}$), SiC136 and SiC004 (both $^4\text{He}$ only), and gas-poor grain SiC019, respectively. The first two grains have a $^{12}\text{C}^{13}\text{C} < 10$, characteristic for type A/B grains. However, we will also consider SiC019 and SiC004 to be of this type because
Fig. 5.- Nucleosynthetic $^{22}\text{Ne}$ against $^4\text{He}$ gas amounts (a) and concentrations (b) for presolar SiC grains from Murchison and Murray with gas $>2\sigma$ above detection limit. Errors are $1\sigma$. Error bars for KJH and KJG grains are smaller than the symbol size. Inset: $1\sigma$-errors of KJG grains appear as boxes.
Fig. 6.- Silicon isotope ratios given as permil deviation from the solar ratios (horizontal and vertical lines) for presolar SiC grains from Murchison (a) and Murray (b). The dotted line represents the Si mainstream line with a slope of 1.3 (Hoppe & Ott 1997). Errors are 1σ and are shown if larger than symbol size.
small amounts of contamination might have shifted their $^{12}\text{C}/^{13}\text{C}$ ratios above the value of 10. A source for C contamination is, e.g., addition of terrestrial carbon during particle transfer, SEM/EDX analysis, and laser heating. The A/B type grain SiC070 is the sample richest in $^4\text{He}$ and $^{22}\text{Ne}$. Since the measured $^{20}\text{Ne}$ and $^{21}\text{Ne}$ amounts in all samples are not different from blank values, we use the most gas-rich grain (SiC070) and the detection limit (upper limit of 2σ blank scatter) to determine the upper limit of our Ne isotope ratios ($^{20}\text{Ne}/^{22}\text{Ne} < 0.36$, $^{21}\text{Ne}/^{22}\text{Ne} < 0.0025$).

### 3.2 Murray SiC

Nine Murray SiC grains out of 45 grains analyzed for the noble gases contain nucleosynthetic $^4\text{He}$ and $^{22}\text{Ne}$ from their stellar source above our detection limit (Fig. 5). This is a higher fraction (20%) as for Murchison grains (14%). $^4\text{He}$ only, without any detectable $^{22}\text{Ne}$, is found in 5 grains (11%), while 10 grains (22%) contain $^{22}\text{Ne}$ without any $^4\text{He}$ above detection limit (Table 1). $^4\text{He}/^{22}\text{Ne}$-ratios of grains with detectable amounts of He and Ne lie between 42±14 and 246±181 with an arithmetic mean of 134. Two-thirds of the samples have $^4\text{He}/^{22}\text{Ne}$-ratios >100, in contrast to ~20% of the Murchison samples. The most gas-rich Murray sample is mainstream...
grain SiC210, it contains both $^4$He ($(4.6\pm0.5) \times 10^{-12}$ cm$^3$ STP) and $^{22}$Ne ($(4.1\pm0.2) \times 10^{-14}$ cm$^3$ STP). The lowest gas amount has been measured in mainstream grains SiC260 $(0.23\pm0.19) \times 10^{-14}$ cm$^3$ STP $^{22}$Ne and SiC271 $(70\pm35) \times 10^{-14}$ cm$^3$ STP $^4$He. The most gas-rich grains contain only about 50% of the amount of $^{22}$Ne and 60% of the $^4$He amount found in the most gas-rich Murchison SiC in our study. Approximated gas concentrations for $^{22}$Ne range from $(0.22\pm0.11)$ to $(27.1\pm1.4) \times 10^{-3}$ cm$^3$ STP × g$^{-1}$ and for $^4$He from $(70\pm35)$ to $(2049 \pm 1017) \times 10^{-3}$ cm$^3$ STP × g$^{-1}$ comparable to the concentrations found in our Murchison samples but closer to Nichols et al.’s Murchison grains.

In contrast to the Murchison samples, Si- and C-isotopic compositions were analyzed with the NanoSIMS ion probe prior to noble gas extraction (Table 2; Fig. 6). From the 49 single SiC grains analyzed with NanoSIMS, 47 grains (96%) are mainstream grains, including all but one (SiC254) $^{22}$Ne-bearing grain from Murray (Tables 2, 3). This fraction of mainstream grains is more representative than our Murchison fraction (~70%), since from Murray also gas-poor grains were analyzed. From a much larger number of grains, about 90% of all grains are expected to be of the mainstream type (Hoppe and Zinner 2000). Two non-mainstream grains were found in the Murray sample: The first one, SiC254, contains $^4$He without any detectable $^{22}$Ne. Its Si- and C-isotopic ratios indicate that it is either an X grain, i.e. having a SN origin, or a Z grain, i.e. originating from a low-metallicity AGB star. In the second non-mainstream grain (SiC213) from Murray, unfortunately no noble gases have been detected. This grain has by far the lowest $^{12}$C/$^{13}$C-ratio (13.7) of our Murray samples. While its $^{12}$C/$^{13}$C ratio still lies in the range of mainstream grains, it is close to the range expected for A/B grains ($^{12}$C/$^{13}$C < 10, see remark in §3.1) and taking the possibility of C contamination into account it might actually belong to this rare population of presolar SiC grains.

3.3 Relationship Between Grain Size and Gas Concentration

We see a relationship between grain size and noble gas concentration in the samples from both meteorites (Fig. 8). The highest concentrations are found in small grains and decrease with increasing grain size. This is expected if the noble gases have been implanted into the surface of the grains: Smaller grains have a higher surface-to-volume ratio than the larger ones. If the noble gases were indeed surface-correlated we would expect to see concentrations to vary with $r^4$. Part or even all of the grain-size-concentration relationship is apparently biased due to a sample selection: First, small grains contain smaller gas amounts and only high-concentration-grains are detectable. Second, only a few large grains have been analyzed and it cannot be excluded that also large grains have higher concentrations than those observed. Clearly, a larger number of samples would be required to reduce this bias and to draw definite conclusions. Bulk
analyses of size-sorted SiC grains (Lewis et al. 1994) and ion-implantation models (Verchovsky, Wright, & Pillinger 2004) show also a grain-size dependency of He- and Ne-G concentrations. In their model Verchovsky et al. (2004) assume an implantation range of 0.8 µm and obtain a concentration maximum in grains with diameters between 1 and 2 µm. Smaller grains have lower concentrations since their size falls below the stopping distance of the ions and the latter fly through the grains. Because of the sparsity of grains with sizes < 1 µm, our data cannot be used to test this model.

4. Discussion

In the following section we will focus on possible stellar sources for our presolar SiC grain samples. In particular, we will discuss stellar sources known to produce SiC dust with a characteristic noble gas composition, which can be used, in conjunction with Si-, C- and N-isotopes, to constrain the origin of presolar SiC. In view of planned future laboratory studies of presolar grains, we also include stellar sources in our discussion, which are less likely to have produced the selection of 110 grains we analyzed.

In the SiC separates from both meteorites Murchison and Murray we detected 14-20% of grains containing detectable amounts of $^{22}\text{Ne}$ accompanied by $^4\text{He}$ which we attribute to be nucleosynthetically produced Ne- and He-G. We note that the most gas-rich ~4% of the grains always contain both nucleosynthetic $^4\text{He}$ and $^{22}\text{Ne}$ and contain about 30-60% of the total gas measured, whereas Nichols et al.’s (1992) ~4% gas-rich grains accounted for >90% of the total sample gas. Another fraction of the grains (20-33%) contains measurable amounts of either $^4\text{He}$ or $^{22}\text{Ne}$ only. If the non-detected isotope in the grains of this subset would be close to the detection limit, the $^4\text{He}/^{22}\text{Ne}$ ratio would then be in the range of observed ratios of grains containing observable amounts in both isotopes. The total fraction of grains with nucleosynthetic He and Ne in this study is about 6 times higher than reported earlier (Nichols et al. 1991, 1992). Our observations confirm that in the grains richest in gas the G-component $^{22}\text{Ne}$ is always accompanied by $^4\text{He}$. At least for the grains containing both $^4\text{He}$ and $^{22}\text{Ne}$ a likely trapping mechanism is gas implantation in the circumstellar environment by stellar winds, as already proposed by Gallino et al. (1990).
Fig. 8. $^4$He and $^{22}$Ne concentrations vs. grain size for single presolar SiC grains from the Murchison (a) and Murray (b) meteorites. Grain size represents the arithmetic mean of the major and minor axis of the grain. Errors are 1σ.
4.1 Grains from AGB stars

4.1.1 Mainstream Grains with $^4$He and $^{22}$Ne Gas

From their Si- and C-isotopic compositions (Figs. 5 and 6) most of the grains are mainstream grains, which are thought to originate from low-mass ($1-3 \, M_\odot$) AGB stars of solar metallicity. $^{12}$C/$^{13}$C ratios of typical mainstream grains range from 40 to 80, $^{14}$N/$^{15}$N ratios are between 1000 to 10000, and in a Si-three-isotope representation the grains plot along a line with slope $\sim 1.3$ (Hoppe & Zinner 2000). The $^{14}$N/$^{15}$N ratios of the mainstream grains of this study are lower than expected, probably caused by contamination of the laser-heated grain remnants with terrestrial N.

4.1.2 Mainstream Grains with $^4$He only

In the 16 mainstream grains where only $^4$He without any accompanying $^{22}$Ne has been detected, we could explain the non-detection of $^{22}$Ne with a gas amount being just below our detection limit. However, if we consider these grains have $^4$He/$^{22}$Ne-ratios in the range of the lowest ratios found in grains where He and Ne has been detected, we would expect detectable amounts of $^{22}$Ne in 3 grains. Therefore, we cannot exclude that some grains have unusually high $^4$He/$^{22}$Ne ratios. This would imply that these SiC grains originated in circumstellar environments with low $^{22}$Ne abundances. A depletion of $^{22}$Ne is expected in more massive AGB stars around 5-6 $M_\odot$ where $^{22}$Ne gets destroyed by $\alpha$-capture, $^{22}$Ne($\alpha,n$)$^{25}$Mg and $^{22}$Ne($\alpha,\gamma$)$^{26}$Mg (Karakas & Lattanzio 2003), and by p-capture, $^{22}$Ne(p,$\gamma$)$^{23}$Na (Ventura & D’Antona 2005). The latter can reduce the $^{22}$Ne abundance by up to an order of magnitude in low-metallicity ($Z=0.001$) stars. Do we still expect SiC dust to form in the circumstellar environments of such stars? In these 5-6 $M_\odot$ AGB stars the extensive convective envelope reaches into the H-burning shell and destroys C by conversion into N via the CNO cycle (Lattanzio, Forestini, & Charbonnel 2000). This so-called hot bottom burning (HBB) thus leads to a decrease of the C/O-ratio, which would prevent the formation of circumstellar SiC while C/O<1. However, with advancing AGB evolution, the envelope experiences strong mass loss and eventually the temperature at the base of the envelope gets too low and shuts down HBB. Model calculations (Lattanzio et al. 2000) show third dredge-up (TDU) is still active at the time after HBB shut-down and transports He-shell carbon to the surface. TDU can bring the C/O ratio to above unity and turns the star into a carbon star, a prerequisite for SiC condensation under thermal and chemical equilibrium conditions.
4.1.3 Mainstream Grains with $^{22}$Ne only

Twelve grains fall into this category. Only two of these grains are from Murchison while the remaining 10 of them are from Murray. Analogous as for grains with $^4$He only, we can explain the detection of $^{22}$Ne without any measurable amounts of $^4$He, with a $^4$He amount just below detection limit. However, two grains (SiC205 and SiC254) clearly require a $^4$He/$^{22}$Ne-ratio below the range found in grains bearing both He and Ne. We can explain a low $^4$He/$^{22}$Ne-ratio by diffusive loss of $^4$He. Alternatively, a simple astrophysical explanation in this case would be that the $^{22}$Ne of these grains stems from $\sim 3 ~M_\odot$ AGB stars. According to stellar models by Karakas & Lattanzio (2003) these stars show the highest $^{22}$Ne enrichments relative to initial abundance, almost two orders of magnitude for low-metallicity ($Z = 0.008$) and about 80 times for solar-metallicity ($Z_\odot = 0.02$). Although grains showing $^{22}$Ne only are not richest in $^{22}$Ne, they might have the highest $^{22}$Ne enrichment relative to $^4$He.

4.1.4 Type A/B Grains

Presolar SiC with particularly low $^{12}$C/$^{13}$C ratios are classified as A/B type grains. With consideration of possible C contamination 5 grains of this study belong to this group (SiC 004, 019, 070, 136 and 213). Hoppe et al. (1994, 1996) suggested that J-type carbon stars are likely to be the source of many A/B type grains. J-type C stars are a sub-group of the cooler N-type C stars ($T_{\text{Photosphere}} < 3000$ K) and are characterized by circumstellar SiC dust envelopes, detected by IR emission at 11.3 $\mu$m, and low $^{12}$C/$^{13}$C ratios (mainly $\sim 3-5$, maximum 32) produced by CNO-cycle burning (Lodders and Fegley 1995). Born-again giant stars, typified by Sakurai’s object, are other possible sources for the type A/B grains, in particular for those with enhanced s-process element abundances (Amari et al. 2001b). Born-again giants are post-AGB stars, central stars of planetary nebulae (PN), on their way to become a white dwarf, which experience a very late He-flash. They are characterized by low $^{12}$C/$^{13}$C-ratios and enrichments in s-process elements (Amari et al. 2001b). Up to 25 % of PN central stars are estimated to experience this very late thermal pulse (Renzini 1982; Iben 1984).

Among the gas-rich grains from Murchison are 3 A/B type grains, representing about 14 % of all gas-rich grains. This fraction is somewhat higher than the abundance of type A/B grains among presolar SiC (~5 %; Hoppe et al. 1994, 1996). In particular, at least one gas-rich grain (SiC070) has nucleosynthetic $^{22}$Ne with $^4$He, which suggests gas implantation to be a plausible trapping mechanism. Its $^4$He/$^{22}$Ne-ratio is 60±1. The two other gas-rich A/B type grains have detectable amounts of $^4$He only. Whereas SiC004 has a $^4$He-concentration ($(225\pm10) \times 10^{-3}$ cm$^3$ STP), which is comparable to the average of all gas-rich Murchison grains $(226 \times 10^{-3}$ cm$^3$ STP).
cm$^3$ STP) and $\sim 3 \times$ higher than for SiC136. As for the mainstream grains, we can also assume here, that the nucleosynthetic $^{22}\text{Ne}$ is below our detection limit and escapes from our grasp. Unfortunately, no data on s-process element abundances exist for these gas-rich grains. It is not unrealistic to assume that the grains with $^4\text{He}$ and $^{22}\text{Ne}$ might also have enhanced s-process element abundances which would make born-again giant stars the most likely sources for those grains (Amari et al. 2001b). Only two of our type A/B grains do not show any detectable $^4\text{He}$ and $^{22}\text{Ne}$. Assuming that this observation implies also low s-process element abundances, this grain may originate from a J-type carbon star (Amari et al. 2001b).

4.1.5 Type Z Grains

In the Si three-isotope diagram, grains that have lower than solar $^{29}\text{Si}/^{28}\text{Si}$ and plot to the $^{30}\text{Si}$-rich side of the mainstream line are classified as Z type grains. Z grains most likely originate from low-mass ($< 2.3 \, M_\odot$), low-metallicity AGB stars, which are expected to enrich the envelope with s-processed Si ($^{28}\text{Si}$ and also $^{29}\text{Si}$, with an initial Si-isotopic composition on the extension of the mainstream line to negative $\delta^{29,30}\text{Si}$ values), dredged-up from the He-shell (Hoppe et al. 1997). Lower metallicities allow higher He-shell temperatures and more efficient slow neutron capture, leading to larger enhancements of the heavy Si isotopes (Gallino, Busso, & Lugaro 1997).

Murray grain SiC254 might be a Z grain, although the possibility that it is an X grain cannot completely ruled out. We find measurable amounts of $^{22}\text{Ne}$ without any detectable $^4\text{He}$. The amount of $^{22}\text{Ne}$ ($(0.65\pm0.12) \times 10^{-14}$ cm$^3$ STP) is rather at the lower end of the range observed in our other samples ($(0.23$ to $11) \times 10^{-14}$ cm$^3$ STP). This strengthens the suspicion that we can attribute the non-detection of $^4\text{He}$ to our spectrometer limits. In this case a Z grain classification is favoured, where the noble gases can be well explained by implantation by a stellar wind into the circumstellar dust grain. We will discuss in the next section (§4.2), that $^{22}\text{Ne}$ and $^4\text{He}$ implantation into grains forming in supernova environments is difficult to achieve. However, we have to consider that the $^{22}\text{Ne}$ might stem from the decay of radioactive $^{22}\text{Na}$ (Ne-R), which is not expected to occur in AGB star environments.

4.2 Grains from Supernovae

Do X grains generally contain similar amounts of $^4\text{He}$ and $^{22}\text{Ne}$ as mainstream grains? Can $^{22}\text{Ne}$ in X grains be explained as radiogenic Ne-R? Unfortunately, we have found only one and possibly two SiC grains, which can be classified as X grains and the data basis for further
conclusions on He and Ne in X grains is too small. However, both grains have detectable amounts of noble gases, one grain (SiC254) with $^{22}\text{Ne}$ only (without any $^4\text{He}$ above our detection limit) and another one (SiC096), which could have $^4\text{He}$ and $^{22}\text{Ne}$. We will therefore discuss the possibility of noble gas implantation into supernova grains as well as the production of Ne-R in supernovae in the following section.

$^{22}\text{Ne}$-only Murray grain SiC254, could be a Z or an X grain, its Si- and C-isotopic composition is ambiguous (see §3.2). Above (§4.1.5.) we make the point for a Z type classification. But, as we already mentioned, the $^{22}\text{Ne}$ from SiC254 might actually be Ne-R, the decay product of radioactive $^{22}\text{Na}$ ($T_{1/2} = 2.6\text{ y}$). Supernova models (Woosley & Weaver 1995) predict important amounts of $^{22}\text{Na}$ are synthesized during the explosion and enrich the ejecta. This $^{22}\text{Na}$ can be incorporated into condensing SN dust and decays there in situ to $^{22}\text{Ne}$ (Amari et al. 1995). This is the simplest explanation for the $^{22}\text{Ne}$ observed in SiC254 and would not need to invoke invisible $^4\text{He}$, and hence, strengthen the case of an X type grain. This view is supported by the fact that this grain requires a particularly low $^4\text{He}/^{22}\text{Ne}$-ratio (< 28) to explain the non-detection of $^4\text{He}$.

The X type case for Murchison grain SiC096 (Fig. 9), which might be gas-rich, is clear: The Si-, C- and N-isotopic compositions of SiC096 are that of X type grains, which most likely have a supernova origin. X grains have $^{12}\text{C}/^{13}\text{C}$ ratios that in most cases are higher than solar (89), they show an enrichment of $^{28}\text{Si}$, and have lower than solar $^{14}\text{N}/^{15}\text{N}$ (272). These isotopic signatures, together with other evidence like the presence of now extinct supernova-produced short-lived radionuclides (e.g. $^{44}\text{Ti}$, $\tau_{1/2} = 60\text{ yrs}$), have been taken as proof for a supernova origin (Amari & Zinner 1997). However, as explained in §3.1, only in this particular case we have to keep in mind that the $^4\text{He}$ and $^{22}\text{Ne}$ gas detected during analysis of SiC096 might come from neighbouring grains. Nevertheless, we subsequently discuss the possibility of a $^4\text{He}$- and $^{22}\text{Ne}$-rich X grain. We note that the $^4\text{He}$ and $^{22}\text{Ne}$ amounts detected are comparable to the amounts and ratios of the more gas-rich mainstream grains, while the $^4\text{He}/^{22}\text{Ne}$-ratio (105±9) is among the highest for Murchison samples (see Table 1).

In case our analysis method misses the $^4\text{He}$-G from $^{22}\text{Ne}$-rich X grain candidate SiC254, and if the $^{22}\text{Ne}$ and $^4\text{He}$ from grain SiC096 are indeed intrinsic, these isotopes are likely to have been implanted into the X grains. Many of the isotopic signatures of X grains can be explained by heterogeneous mixing of matter in the ejecta from a 15 M$_\odot$ Type II SN (Hoppe et al. 2000). Pure condensation of matter from such mixtures, however, cannot account for the presence of noble gases and other scenarios must be considered. Deneault, Clayton, & Heger (2003, hereafter DCH 2003) proposed a core-collapse SN model where SiC condenses within a SN. Their one-dimensional simulation, based on a 25 M$_\odot$ Type II SN model by Woosley, Heger, &
Weaver (2002) produces a reverse shock when the expanding shock experiences deceleration while moving through the hydrogen envelope about 10 days after the explosion. This creates a dense shell of C and Si atoms where SiC might form despite high-temperature and O>C. Under equilibrium conditions, when O is more abundant than C, all the C is bound in the CO molecule. However, in this harsh environment with non-equilibrium conditions, CO gets destroyed by fast electrons, \( \gamma \)-rays from radioactive decays and reactive species like He\(^+\) (Clayton, Liu, & Dalgarno 1999). Similarly, the SiO molecule gets disintegrated and liberates Si (Clayton 1999).

In the predicted high-density zone formed by the reverse shock, where Si is about \( \geq 10 \times \) more abundant than C, condensation of SiC is possible. This zone has the right abundances to explain the enhancement of \(^{28}\)Si and \(^{15}\)N seen in X grains. Later, two reverse shocks are predicted by the model (DCH 2003): The dust grains – condensed in the first reverse shock within the SN – move at high speed through the decelerated gas and implant atoms from this gas. These newly acquired nuclides change the isotopic composition of minor elements in the grain and could in principle explain \(^4\)He and \(^{22}\)Ne gas in SiC X grains by implantation. To account for \(^{22}\)Ne/\(^{20}\)Ne ratios larger than 10 (as observed for our grains) strong constraints on the SN zones from which He and Ne has to be implanted have to be applied. Mixing over the whole ejecta of a 25 M\(_\odot\) Type II SN yields \(^{22}\)Ne/\(^{20}\)Ne = 0.07 (Meyer, Weaver, & Woosely 1995). A closer inspection of the 25 M\(_\odot\) Type II SN data table of Meyer et al. (1995) shows that only matter from the He/C zone has \(^{22}\)Ne/\(^{20}\)Ne \( \sim 10 \), and \(^4\)He/\(^{22}\)Ne = 300, a signature that is qualitatively consistent with the data of grain SiC096. It is worth noting that implantation of noble gases from only a single SN zone is an adhoc scenario in view of the turbulences expected in the SN ejecta several years after the explosion. These fundamental problems emphasize the possibility that the noble gases attributed to grain SiC096 might stem from nearby mainstream grains and that the \(^{22}\)Ne in SiC254 is actually Ne-R, if the grain is not a Z grain after all.

Can noble gases serve as diagnostic tools to specify which supernova types are responsible to produce X grains? Although core-collapse SN models like DCH 2003 can successfully explain many characteristics of SiC X grains, it is not yet clear, which fraction of the X grain population originates from Type II SNe. Models of white dwarf explosions in close binary systems (SN Type Ia) explain many isotopic characteristics of X grains (Clayton et al. 1997), too. Although both Type Ia and Type II SN models have problems to fully account for the observed isotopic signatures of X grains, type II SNe models seem to be more promising to overcome the existing problems (Hoppe et al. 2000). With respect to the noble gases the Type Ia SN model of Clayton et al. (1997) predicts a low \(^{22}\)Ne/\(^{20}\)Ne (0.02 for zones 1-8 and consideration of radioactive \(^{22}\)Na) and a high \(^4\)He/\(^{22}\)Ne (>10000) ratio in the ejecta, clearly distinct from the data for grain SiC096 and SiC254. The carbon deflagration Type Ia SN model of Thielemann, Nomoto, & Yokoi (1986) predicts a higher \(^{22}\)Ne/\(^{20}\)Ne ratio of \( \sim 1 \) in the ejecta, which, however, is still too low to match the Ne data of the grains. This makes also a Type Ia SN an unlikely source for the noble
gases in our grains, underlining the possibility that the noble gases of SiC096 are not intrinsic and that the $^{22}$Ne from SiC254 is Ne-R.

4.3 Alternative Stellar Sources

All our SiC samples can be explained by the stellar sources already discussed in this chapter. To consolidate our allocation of samples to these sources and in anticipation of future noble gas studies on single presolar grains, we will discuss interesting alternatives, which have been proposed for the origin of presolar SiC. These stellar sources are less abundant in the galaxy than AGB stars but are known as (1) prolific dust producers and (2) anticipated sites for efficient nucleosynthesis of the isotopes addressed in this study.

4.3.1 Wolf-Rayet Stars

Wolf-Rayet (W-R) stars have been proposed as parent stars for the highly anomalous noble gas composition in presolar grains (Maeder 1983). How diagnostic is the He and Ne isotopic composition? Since W-R stars are much less abundant than AGB stars, they are expected to contribute only a small fraction of the presolar grain population. Most stars $>25M_\odot$ pass through this phase (which is subdivided into the WN-WC-WO phases, according to N, C, and O enhancements at the surface), which is characterized by high mass-loss by fast stellar winds.
Despite the very high temperatures, $T_{\text{photosphere}} \approx 30'000$ K (Schmutz, Leitherer, & Gruenwald 1992), conditions in high-density regions can allow the condensation of dust in the circumstellar environment of W-R stars (e.g. Cherchneff et al. 2000). In principle, SiC can condense during the WN-WC transition and WC phase (Prantzos et al. 1986; Maeder 1987), that is when the products of core He burning are exposed to the surface. Particularly $^{22}\text{Ne}$ gets enriched in He burning by $\alpha$-capture on $^{14}\text{N}$. This leads to $^{20}\text{Ne}/^{22}\text{Ne}$-ratios of between 0.03 and 10 (compared to $^{20}\text{Ne}/^{22}\text{Ne}=0.08$ of the G-component; Lewis et al. 1994) and the mean $^{22}\text{Ne}$ abundance increases by a factor of >100x relative to the initial abundance (Meynet et al. 2001). The $^{22}\text{Ne}$ enhancement is such that it represents the most abundant isotope after $^4\text{He}$, $^{12}\text{C}$ and $^{16}\text{O}$ (if $^{20}\text{Ne}/^{22}\text{Ne} < 1$) (Smith & Houck 2005). Maeder (1983) proposed W-R stars as a source for Ne-E because of their low $^{20}\text{Ne}/^{22}\text{Ne}$ ratio in their stellar winds. The mean $^4\text{He}/^{22}\text{Ne}$ ratio ($\sim 165$) is comparable to the value expected from AGB star He-shell (Maeder 1983). Models predict a $^{12}\text{C}$ enrichment while the $^{13}\text{C}$ abundance remains almost unaltered, resulting in a high $^{12}\text{C}/^{13}\text{C}$ ratio ($>> 100$). This seems to exclude W-R stars as sources of any of the SiC grains studied here. Other isotope systems are less diagnostic in order to distinguish W-R star grains from AGB star grains: E.g., slight enrichments in the heavy Si isotopes are predicted during the C-rich phases in W-R stars, i.e., when SiC may form (Meynet et al. 2001), similar to AGB stars.

4.3.2 Novae

Novae – thermonuclear runaway explosions on white dwarf (WD) stars – are important nucleosynthetic sites of Ne. We discuss in this section how the Ne isotopic composition can be used in conjunction with other isotopes, to state a nova origin for presolar grains. We note here, that nova grains are quite rare, it is estimated that they comprise only about 3‰ of the interstellar dust (Gehrz et al. 1998). Novae produce – among other, more abundant nuclides - significant amounts of radioactive $^{22}\text{Na}$ ($T_{1/2} = 2.6$ yrs), which get ejected and incorporated into condensing dust grains such as SiC (Starrfield, Gehrz, & Truran 1997) within a few months after the explosion. Within the newly formed grains it decays into $^{22}\text{Ne}$, representing the monoisotopic Ne-R (Amari et al. 1995). Depending on the initial WD composition (CO-rich from <8 M$_\odot$ progenitors or ONe-rich from more massive progenitors) different $^{20}\text{Ne}/^{22}\text{Ne}$ ratios are predicted. CO novae lead to low $^{20}\text{Ne}/^{22}\text{Ne}$ ratios of 0.07 to 0.7, which would be in agreement with our observations ($^{20}\text{Ne}/^{22}\text{Ne} < 0.36$), while ONe novae lead to very high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios ranging from ~100 to 250, due to the high initial Ne abundance of the WD. In the 110 grains studied here, none of the samples has such a high $^{20}\text{Ne}/^{22}\text{Ne}$ ratio, therefore we can reject ONe novae as a possible source for any of our grains. ONe nova models tend to produce large $^{30}\text{Si}/^{28}\text{Si}$ enrichments and $^{29}\text{Si}/^{28}\text{Si}$ depletions relative to solar, while CO novae models produce close to solar values for Si-isotopic ratios (e.g. Starrfield et al. 1997).
is large, model-dependent spread in $^{14}\text{N}/^{15}\text{N}$ ratios. In most cases $^{15}\text{N}$ is heavily enriched with $^{14}\text{N}/^{15}\text{N}$ ratios generally increasing with decreasing WD mass (José et al. 2004). Unanimously, different models predict strong enrichments of $^{13}\text{C}$ by proton-capture on $^{12}\text{C}$, resulting in very low $^{12}\text{C}/^{13}\text{C}$-ratios (~0.2 to 3) (José et al. 2004).

In our data set we have one grain (SiC070) whose C-isotopic composition ($^{12}\text{C}/^{13}\text{C}=3.4$) comes close to the expected $^{12}\text{C}/^{13}\text{C}$-ratio ($\leq 3.2$) for a 1.35 $M_\odot$ ONe WD nova (José et al. 2004), which has the highest $^{12}\text{C}/^{13}\text{C}$-ratio of all models. Its $^{14}\text{N}/^{15}\text{N}$ ratio (317) and Ne-isotopic composition ($^{22}\text{Ne} >> ^{20}\text{Ne}$), however, are clearly incompatible with a ONe nova origin. On the other hand, CO novae of masses $< 1 M_\odot$ are predicted to have $^{12}\text{C}/^{13}\text{C} = 0.5-2$, $^{14}\text{N}/^{15}\text{N} = 100-1400$, and $^{20}\text{Ne}/^{22}\text{Ne} = 0.18-0.53$ (José et al. 2004), which is at least qualitatively consistent with the data for grain SiC070, classified originally as a type A/B grain. In view of existing uncertainties in the model predictions and the possibility of C and N contamination affecting the NanoSIMS analyses we consider a CO nova origin of grain SiC070 a realistic possibility, even if condensation calculations do not predict formation of SiC in the ejecta of CO novae (José et al. 2004). For the other grains of type A/B, the $^{12}\text{C}/^{13}\text{C}$ ratios are too high and fail to account for a nova origin. We could attribute this partly to contamination of sample surfaces from isotopically normal carbon, but for (type A/B) grains SiC004, SiC019, SiC136 and SiC213 the absence of $^{22}\text{Ne}$ together with the Si-isotopic signatures seem to rule out a nova origin. So far, only a few presolar grains have been discovered that might be associated with novae (Amari et al. 2001a; Amari 2002). Some grains previously proposed to have a nova origin, are now shown to have supernova-produced nucleosynthetic signatures. This rules out a nova origin for these particular samples (Nittler & Hoppe 2005). It remains to be seen whether this applies to all nova grain candidates known so far. To follow up on this problem, we plan to search systematically for grains with low $^{12}\text{C}/^{13}\text{C}$ ratios by fully automated imaging techniques with the NanoSIMS, which subsequently will be studied for diagnostic isotopic signatures such as presence of radiogenic $^{44}\text{Ca}$ and enhancements in $^{15}\text{N}$ and $^{22}\text{Ne}$.

5. Summary and Conclusions

1. We have applied a new laser-induced noble gas (He, Ne) extraction method to 110 presolar SiC grains from the Murchison and Murray carbonaceous meteorites. Detection limits are improved by a factor of ~10 compared to previous studies. This permits analysis of submicrometer-sized grains as well as lower gas-concentrations to be detected.

2. About 30-50 % of presolar SiC grains from both meteorites contain nucleosynthetic $^{22}\text{Ne}$ and/or $^4\text{He}$. 14-20 % of all samples contain nucleosynthetic $^{22}\text{Ne}$, which is always accompanied by $^4\text{He}$. This suggests noble gas implantation into freshly condensed dust grains in the
circumstellar AGB- and post-AGB-star environment as the most plausible trapping mechanism for these grains. Another fraction of SiC grains (20% for Murchison, 33% for Murray) has either nucleosynthetic $^{22}\text{Ne}$ or $^4\text{He}$ above our detection limit.

3. Compared to the results obtained in previous studies, we find $7-10\times$ more presolar SiC grains to contain nucleosynthetic $^4\text{He}$ and/or $^{22}\text{Ne}$. This can be attributed to the better detection limit of our ultra-high sensitivity mass spectrometer with its compressor-ion source. Most of the gas-rich grains are in around 1 $\mu$m in diameter.

4. The isotopic compositions of He, Ne, C, N and Si indicate most presolar SiC grains are of mainstream type and suggest low-mass (1-3 $M_\odot$) AGB stars to be the most probable stellar sources. A small fraction of the mainstream population might have formed in the winds of intermediate-mass (3 and 5-6 $M_\odot$) AGB stars, as indicated by unusually high or low $^4\text{He}/^{22}\text{Ne}$ ratios.

5. Three out of 5 A/B type grains have nucleosynthetic $^4\text{He}$ and $^{22}\text{Ne}$, or $^4\text{He}$ only. Those grains might originate from born-again giant stars while for the gas-poor type A/B grains formation in the winds of J-type carbon stars is favored.

6. There is a realistic possibility that one grain, with particularly low $^{12}\text{C}/^{13}\text{C}$ ratio and rich in $^{22}\text{Ne}$ (and $^4\text{He}$), has formed in the ejecta of a CO novae (instead of a born-again giant).

7. The noble gas measurement of one SiC X grain, which is attributed to originate from a SN, revealed $^4\text{He}$ and $^{22}\text{Ne}$. Current SN models fail to account for this observation and it is likely that the observed noble gases stem from nearby SiC mainstream grains.

8. A SN origin for one X grain candidate is corroborated by the presence of $^{22}\text{Ne}$ only, which can be interpreted as radiogenic Ne-R. However, the same grain could as well be a Z type grain originating from a low-mass, low-metallicity AGB star, if a very low $^4\text{He}/^{22}\text{Ne}$ ratio is assumed.

9. We find a dependency of $^4\text{He}$ and $^{22}\text{Ne}$ isotope concentrations from grain size. The highest concentrations are found in the smallest grains and decrease with increasing grain size. This supports the view that for most samples the noble gases were implanted into the surface of the grains. We note however, that a sampling bias is partly responsible for the correlation because small, low-concentration-grains were excluded from our measurements.
### TABLE 1

$^4$He and $^{22}$Ne amounts, concentrations and ratios of single SiC from Murchison and Murray

<table>
<thead>
<tr>
<th>Grain Type</th>
<th>Grain</th>
<th>Size (µm)</th>
<th>$^{22}$Ne (10$^{14}$ cm$^3$ STP)</th>
<th>$[^{22}$Ne]/$^{4}$He (10$^{14}$ cm$^3$ STP/g)</th>
<th>$^{4}$He (10$^{14}$ cm$^3$ STP)</th>
<th>$[^{4}$He]/$^{22}$Ne (10$^{14}$ cm$^3$ STP/g)</th>
<th>$^{4}$He/$^{22}$Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Murchison</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SiC102</td>
<td>ms</td>
<td>1.3</td>
<td>0.72 ± 0.23</td>
<td>2.10 ± 0.66</td>
<td>216.8 ± 2.7</td>
<td>628.1 ± 7.7</td>
<td>299 ± 94</td>
</tr>
<tr>
<td>SiC128</td>
<td>ms</td>
<td>0.9</td>
<td>1.78 ± 0.21</td>
<td>15.5 ± 1.9</td>
<td>91.1 ± 3.1</td>
<td>796 ± 27</td>
<td>51 ± 6</td>
</tr>
<tr>
<td>SiC138</td>
<td>ms</td>
<td>1.6</td>
<td>0.98 ± 0.12</td>
<td>1.52 ± 0.18</td>
<td>58.1 ± 1.5</td>
<td>90.3 ± 2.3</td>
<td>59 ± 7</td>
</tr>
<tr>
<td>SiC166</td>
<td>ms</td>
<td>1.4</td>
<td>6.41 ± 0.21</td>
<td>14.86 ± 0.48</td>
<td>160.9 ± 3.0</td>
<td>373.2 ± 7.1</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>SiC070</td>
<td>A/B</td>
<td>5.3</td>
<td>11.45 ± 0.27</td>
<td>0.489 ± 0.012</td>
<td>681.2 ± 2.9</td>
<td>29.13 ± 0.13</td>
<td>60 ± 1</td>
</tr>
<tr>
<td>SiC096</td>
<td>X</td>
<td>1.1</td>
<td>2.74 ± 0.22</td>
<td>13.1 ± 1.1</td>
<td>288.2 ± 2.8</td>
<td>1379 ± 13</td>
<td>105 ± 9</td>
</tr>
<tr>
<td>SiC097</td>
<td>u.</td>
<td>6.3</td>
<td>0.329 ± 0.21</td>
<td>0.0837 ± 0.0053</td>
<td>297.7 ± 3.8</td>
<td>7.579 ± 0.098</td>
<td>91 ± 6</td>
</tr>
<tr>
<td>SiC133</td>
<td>u.</td>
<td>1.0</td>
<td>2.12 ± 0.17</td>
<td>13.5 ± 1.1</td>
<td>123.0 ± 3.7</td>
<td>783 ± 23</td>
<td>58 ± 5</td>
</tr>
<tr>
<td>SiC168</td>
<td>u.</td>
<td>2.5</td>
<td>0.57 ± 0.20</td>
<td>0.230 ± 0.080</td>
<td>21.5 ± 3.3</td>
<td>8.8 ± 1.3</td>
<td>38 ± 14</td>
</tr>
<tr>
<td>SiC071</td>
<td>u.</td>
<td>0.9</td>
<td>0.31 ± 0.29</td>
<td>2.7 ± 2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC162</td>
<td>u.</td>
<td>1.0</td>
<td>0.39 ± 0.18</td>
<td>2.5 ± 1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC014</td>
<td>ms</td>
<td>3.4</td>
<td></td>
<td></td>
<td>404.4 ± 9.3</td>
<td>65.5 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>SiC068</td>
<td>ms</td>
<td>2.8</td>
<td></td>
<td></td>
<td>34.7 ± 3.8</td>
<td>10.1 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>SiC087</td>
<td>ms</td>
<td>0.9</td>
<td></td>
<td></td>
<td>17.6 ± 2.3</td>
<td>154 ± 21</td>
<td></td>
</tr>
<tr>
<td>SiC105</td>
<td>ms</td>
<td>2.2</td>
<td></td>
<td></td>
<td>31.5 ± 2.7</td>
<td>18.8 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>SiC110</td>
<td>ms</td>
<td>1.9</td>
<td></td>
<td></td>
<td>115.1 ± 2.4</td>
<td>106.9 ± 2.3</td>
<td></td>
</tr>
<tr>
<td>SiC121</td>
<td>ms</td>
<td>1.6</td>
<td></td>
<td></td>
<td>13.4 ± 3.4</td>
<td>20.9 ± 5.3</td>
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</tr>
<tr>
<td>SiC134</td>
<td>ms</td>
<td>0.9</td>
<td></td>
<td></td>
<td>15.4 ± 2.9</td>
<td>134 ± 25</td>
<td></td>
</tr>
<tr>
<td>SiC136</td>
<td>A/B</td>
<td>1.2</td>
<td></td>
<td></td>
<td>17.6 ± 2.4</td>
<td>64.9 ± 8.9</td>
<td></td>
</tr>
<tr>
<td>SiC004</td>
<td>A/B</td>
<td>1.9</td>
<td></td>
<td></td>
<td>224.6 ± 9.8</td>
<td>208.5 ± 9.1</td>
<td></td>
</tr>
<tr>
<td>SiC144</td>
<td>u.</td>
<td>1.4</td>
<td></td>
<td></td>
<td>14.7 ± 2.4</td>
<td>34.1 ± 5.6</td>
<td></td>
</tr>
<tr>
<td>SiC154</td>
<td>u.</td>
<td>1.3</td>
<td></td>
<td></td>
<td>9.8 ± 3.4</td>
<td>28.3 ± 9.9</td>
<td></td>
</tr>
<tr>
<td><strong>Murray</strong></td>
<td></td>
<td></td>
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<tr>
<td>SiC207</td>
<td>ms</td>
<td>1.0</td>
<td>0.88 ± 0.14</td>
<td>5.60 ± 0.89</td>
<td>163 ± 15</td>
<td>1036 ± 96</td>
<td>185 ± 34</td>
</tr>
<tr>
<td>SiC210</td>
<td>ms</td>
<td>1.4</td>
<td>4.13 ± 0.19</td>
<td>9.59 ± 0.45</td>
<td>459 ± 54</td>
<td>1065 ± 127</td>
<td>111 ± 14</td>
</tr>
<tr>
<td>SiC211</td>
<td>ms</td>
<td>1.1</td>
<td>1.05 ± 0.18</td>
<td>5.04 ± 0.87</td>
<td>72 ± 20</td>
<td>346 ± 93</td>
<td>69 ± 22</td>
</tr>
<tr>
<td>SiC219</td>
<td>ms</td>
<td>1.1</td>
<td>0.79 ± 0.14</td>
<td>3.75 ± 0.66</td>
<td>112 ± 27</td>
<td>536 ± 130</td>
<td>143 ± 43</td>
</tr>
<tr>
<td>SiC242</td>
<td>ms</td>
<td>0.8</td>
<td>2.18 ± 0.11</td>
<td>27.1 ± 1.4</td>
<td>92 ± 31</td>
<td>1144 ± 387</td>
<td>42 ± 14</td>
</tr>
<tr>
<td>SiC252</td>
<td>ms</td>
<td>1.0</td>
<td>1.53 ± 0.18</td>
<td>9.8 ± 1.2</td>
<td>130 ± 25</td>
<td>828 ± 158</td>
<td>85 ± 19</td>
</tr>
<tr>
<td>SiC</td>
<td>ms/u.</td>
<td>Size ± Error</td>
<td>Ne ± Error</td>
<td>He ± Error</td>
<td>主要集中radius ± Error</td>
<td>Mass ± Error</td>
<td>Size ± Error</td>
</tr>
<tr>
<td>-----</td>
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</tr>
<tr>
<td>SiC271 ms</td>
<td>0.6</td>
<td>0.28 ± 0.15</td>
<td>8.3 ± 4.5</td>
<td>70 ± 35</td>
<td>2049 ± 1017</td>
<td>246 ± 181</td>
<td></td>
</tr>
<tr>
<td>SiC250/1 u.</td>
<td>1.1</td>
<td>1.17 ± 0.12</td>
<td>5.6 ± 0.6</td>
<td>139 ± 14</td>
<td>663 ± 68</td>
<td>119 ± 18</td>
<td></td>
</tr>
<tr>
<td>SiC261 u.</td>
<td>0.8</td>
<td>0.39 ± 0.14</td>
<td>4.8 ± 1.8</td>
<td>80 ± 18</td>
<td>992 ± 220</td>
<td>207 ± 89</td>
<td></td>
</tr>
<tr>
<td>SiC240 ms</td>
<td>1</td>
<td>0.42 ± 0.20</td>
<td>2.6 ± 1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC233 ms</td>
<td>0.7</td>
<td>0.30 ± 0.14</td>
<td>5.5 ± 2.5</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SiC260 ms</td>
<td>1.8</td>
<td>0.23 ± 0.19</td>
<td>0.25 ± 0.20</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SiC262 ms</td>
<td>1.6</td>
<td>0.36 ± 0.16</td>
<td>0.56 ± 0.24</td>
<td></td>
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<tr>
<td>SiC263 ms</td>
<td>0.9</td>
<td>0.25 ± 0.22</td>
<td>2.18 ± 1.94</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SiC202 u.</td>
<td>1.6</td>
<td>0.45 ± 0.10</td>
<td>0.70 ± 0.16</td>
<td></td>
<td></td>
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<tr>
<td>SiC203 u.</td>
<td>2</td>
<td>0.27 ± 0.14</td>
<td>0.22 ± 0.11</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SiC244 u.</td>
<td>1.6</td>
<td>0.34 ± 0.16</td>
<td>0.53 ± 0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC205 u. (ms. from C)</td>
<td>3.6</td>
<td>1.78 ± 0.14</td>
<td>0.243 ± 0.019</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC254 X, Z</td>
<td>0.8</td>
<td>0.65 ± 0.12</td>
<td>8.0 ± 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC215 ms</td>
<td>0.7</td>
<td>76 ± 15</td>
<td>1403 ± 273</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC228 ms</td>
<td>0.8</td>
<td>85 ± 31</td>
<td>1062 ± 380</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC229 ms</td>
<td>1.1</td>
<td>74 ± 25</td>
<td>354 ± 121</td>
<td></td>
<td></td>
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<tr>
<td>SiC235 ms</td>
<td>0.8</td>
<td>108 ± 24</td>
<td>1342 ± 299</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC247 ms</td>
<td>0.8</td>
<td>82 ± 32</td>
<td>1015 ± 396</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTE.**—Only grains containing detectable amounts of $^{22}$Ne and/or $^4$He are listed.

* ms = mainstream SiC; u. = unclassified SiC

$^b$ size = (major axis + minor axis)/2

$^c$ $\sigma$-errors

$^d$ concentrations based on spherical volume approximation and SiC density

$^e$ g/cm$^3$
### TABLE 2

$^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ ratios, and $\delta^{28}\text{Si}/^{29}\text{Si}$ and $\delta^{30}\text{Si}/^{28}\text{Si}$ values of single presolar SiC grains from Murchison and Murray

<table>
<thead>
<tr>
<th>Grain</th>
<th>Type</th>
<th>Gas rich?</th>
<th>Size (µm)</th>
<th>$^{12}\text{C}/^{13}\text{C}$</th>
<th>$^{14}\text{N}/^{15}\text{N}$</th>
<th>$\delta^{28}\text{Si}/^{29}\text{Si}$ (%)</th>
<th>$\delta^{30}\text{Si}/^{28}\text{Si}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murchison</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC102</td>
<td>ms</td>
<td>He, $^{22}\text{Ne}$</td>
<td>1.3</td>
<td>72.7 ± 0.5</td>
<td>430 ± 23</td>
<td>48 ± 9</td>
<td>52 ± 8</td>
</tr>
<tr>
<td>SiC128</td>
<td>ms</td>
<td>He, $^{22}\text{Ne}$</td>
<td>0.9</td>
<td>47.0 ± 0.2</td>
<td>252 ± 7</td>
<td>128 ± 6</td>
<td>113 ± 6</td>
</tr>
<tr>
<td>SiC138</td>
<td>ms</td>
<td>He, $^{22}\text{Ne}$</td>
<td>1.6</td>
<td>51.3 ± 0.2</td>
<td>263 ± 8</td>
<td>-18 ± 9</td>
<td>14 ± 9</td>
</tr>
<tr>
<td>SiC166</td>
<td>ms</td>
<td>He, $^{22}\text{Ne}$</td>
<td>1.4</td>
<td>60.9 ± 0.2</td>
<td>320 ± 8</td>
<td>59 ± 10</td>
<td>80 ± 9</td>
</tr>
<tr>
<td>SiC070</td>
<td>A,B</td>
<td>He, $^{22}\text{Ne}$</td>
<td>5.3</td>
<td>3.4 ± 0.1</td>
<td>317 ± 18</td>
<td>-97 ± 38</td>
<td>-72 ± 49</td>
</tr>
<tr>
<td>SiC096</td>
<td>X</td>
<td>He, $^{22}\text{Ne}$</td>
<td>1.1</td>
<td>10.10 ± 1.7</td>
<td>45 ± 1</td>
<td>-346 ± 8</td>
<td>-274 ± 9</td>
</tr>
<tr>
<td>SiC014</td>
<td>ms</td>
<td>He</td>
<td>3.4</td>
<td>90.0 ± 1.5</td>
<td>256 ± 21</td>
<td>-10 ± 15</td>
<td>-36 ± 16</td>
</tr>
<tr>
<td>SiC068</td>
<td>ms</td>
<td>He</td>
<td>2.8</td>
<td>56.4 ± 0.3</td>
<td>705 ± 29</td>
<td>80 ± 7</td>
<td>77 ± 4</td>
</tr>
<tr>
<td>SiC087</td>
<td>ms</td>
<td>He</td>
<td>0.9</td>
<td>19.3 ± 0.1</td>
<td>370 ± 26</td>
<td>38 ± 7</td>
<td>55 ± 11</td>
</tr>
<tr>
<td>SiC105</td>
<td>ms</td>
<td>He</td>
<td>2.2</td>
<td>57.7 ± 0.6</td>
<td>244 ± 12</td>
<td>-11 ± 11</td>
<td>-14 ± 13</td>
</tr>
<tr>
<td>SiC110</td>
<td>ms</td>
<td>He</td>
<td>1.9</td>
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<td>307 ± 10</td>
<td>45 ± 9</td>
<td>48 ± 8</td>
</tr>
<tr>
<td>SiC121</td>
<td>ms</td>
<td>He</td>
<td>1.6</td>
<td>67.4 ± 0.2</td>
<td>332 ± 8</td>
<td>62 ± 21</td>
<td>58 ± 27</td>
</tr>
<tr>
<td>SiC134</td>
<td>ms</td>
<td>He</td>
<td>0.9</td>
<td>69.4 ± 5.7</td>
<td>314 ± 10</td>
<td>104 ± 97</td>
<td>135 ± 122</td>
</tr>
<tr>
<td>SiC004</td>
<td>A,B</td>
<td>He</td>
<td>1.9</td>
<td>11.4 ± 0.1</td>
<td>648 ± 34</td>
<td>47 ± 9</td>
<td>29 ± 7</td>
</tr>
<tr>
<td>SiC136</td>
<td>A,B</td>
<td>He</td>
<td>1.2</td>
<td>9.9 ± 0.1</td>
<td>502 ± 41</td>
<td>21 ± 7</td>
<td>54 ± 11</td>
</tr>
<tr>
<td>SiC019</td>
<td>A,B</td>
<td>-</td>
<td>1.5</td>
<td>11.1 ± 0.1</td>
<td>516 ± 22</td>
<td>18 ± 7</td>
<td>46 ± 4</td>
</tr>
</tbody>
</table>

<p>| Murray |
|--------|------|-----------|-----------|-----------------|-----------------|-----------------|-----------------|
| SiC207 | ms | He, $^{22}\text{Ne}$ | 1.0 | 58.0 ± 0.6 | 12 ± 8 | 42 ± 11 |
| SiC210 | ms | He, $^{22}\text{Ne}$ | 1.4 | 70.7 ± 0.7 | 33 ± 8 | 49 ± 11 |
| SiC211 | ms | He, $^{22}\text{Ne}$ | 1.1 | 59.2 ± 0.5 | 9 ± 8 | 47 ± 11 |
| SiC219 | ms | He, $^{22}\text{Ne}$ | 1.1 | 85.9 ± 1.2 | -64 ± 12 | -56 ± 16 |
| SiC242 | ms | He, $^{22}\text{Ne}$ | 0.8 | 39.6 ± 0.5 | 30 ± 11 | 48 ± 14 |
| SiC252 | ms | He, $^{22}\text{Ne}$ | 1.0 | 69.3 ± 1.3 | -28 ± 14 | -22 ± 17 |
| SiC271 | ms | He, $^{22}\text{Ne}$ | 0.6 | 78.4 ± 1.5 | -10 ± 21 | 8 ± 26 |</p>
<table>
<thead>
<tr>
<th>Grain ID</th>
<th>Type</th>
<th>Neutron Ratio</th>
<th>Ne Ratio</th>
<th>C Ratio</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC205</td>
<td>ms</td>
<td>3.6</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC240</td>
<td>ms</td>
<td>1.0</td>
<td>73.5 ± 1.2</td>
<td>12 ± 12</td>
<td>56 ± 15</td>
</tr>
<tr>
<td>SiC253</td>
<td>ms</td>
<td>0.7</td>
<td>113.0 ± 2.3</td>
<td>-23 ± 11</td>
<td>12 ± 14</td>
</tr>
<tr>
<td>SiC260</td>
<td>ms</td>
<td>1.8</td>
<td>77.9 ± 0.8</td>
<td>32 ± 14</td>
<td>35 ± 17</td>
</tr>
<tr>
<td>SiC262</td>
<td>ms</td>
<td>1.6</td>
<td>63.7 ± 0.6</td>
<td>43 ± 7</td>
<td>40 ± 10</td>
</tr>
<tr>
<td>SiC263</td>
<td>ms</td>
<td>0.9</td>
<td>60.3 ± 0.9</td>
<td>11 ± 12</td>
<td>10 ± 15</td>
</tr>
<tr>
<td>SiC254</td>
<td>Z, X</td>
<td>0.8</td>
<td>89.6 ± 1.2</td>
<td>-242 ± 16</td>
<td>-6 ± 24</td>
</tr>
<tr>
<td>SiC215</td>
<td>ms</td>
<td>0.7</td>
<td>101.6 ± 1.4</td>
<td>-29 ± 10</td>
<td>30 ± 14</td>
</tr>
<tr>
<td>SiC228</td>
<td>ms</td>
<td>0.8</td>
<td>58.4 ± 0.9</td>
<td>8 ± 23</td>
<td>-12 ± 28</td>
</tr>
<tr>
<td>SiC229</td>
<td>ms</td>
<td>1.1</td>
<td>54.7 ± 0.6</td>
<td>29 ± 11</td>
<td>45 ± 14</td>
</tr>
<tr>
<td>SiC235</td>
<td>ms</td>
<td>0.8</td>
<td>53.2 ± 0.9</td>
<td>73 ± 12</td>
<td>49 ± 15</td>
</tr>
<tr>
<td>SiC247</td>
<td>ms</td>
<td>0.8</td>
<td>60.0 ± 1.0</td>
<td>17 ± 20</td>
<td>13 ± 24</td>
</tr>
<tr>
<td>SiC213</td>
<td>A/B</td>
<td>0.8</td>
<td>13.7 ± 0.1</td>
<td>9 ± 11</td>
<td>38 ± 14</td>
</tr>
</tbody>
</table>

**NOTE.**—With the exception of A/B type grain SiC 019 only gas-rich grains from Murchison have been measured. From Murray, only gas-rich grains and non-mainstream grains (SiC213) are listed. SiC205 has been classified as a mainstream grain only from its average $^{12}$C/$^{13}$C-ratio calculated from a high-resolution isotope map (see Fig. 2). No whole-grain isotopic ratio and no Si-isotopes were measured for SiC205. SiC254 can be classified either as a Z type or X type grain. Murray grains not shown here are mainstream grains and do not contain detectable amounts of noble gases, they are listed in Table 3. Two runs of C-isotopic measurements were performed. If the $^{12}$C/$^{13}$C-ratios of the two runs were different, we list the more anomalous value, and reject the one close to solar-terrestrial composition, which we attribute to dilution by contamination in the laboratory.

* ms = mainstream SiC
  
  * size = (major axis + minor axis)/2
  
  1σ-errors
### TABLE 3
12C/13C RATIOS, AND δ(28Si/28Si) AND δ(30Si/28Si) VALUES OF SINGLE PRESOLAR SiC GRAINS FROM MURRAY WITH NO DETECTABLE NOBLE GASES

<table>
<thead>
<tr>
<th>Grain</th>
<th>Typea</th>
<th>Sizeb (µm)</th>
<th>12C/13Cc</th>
<th>δ (28Si/28Si)c (%o)</th>
<th>δ (30Si/28Si)c (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC201</td>
<td>ms</td>
<td>1.6</td>
<td>60.7 ± 0.6</td>
<td>47 ± 8</td>
<td>64 ± 11</td>
</tr>
<tr>
<td>SiC204</td>
<td>ms</td>
<td>1.1</td>
<td>68.9 ± 0.7</td>
<td>-19 ± 7</td>
<td>6 ± 10</td>
</tr>
<tr>
<td>SiC212</td>
<td>ms</td>
<td>1.7</td>
<td>49.4 ± 0.4</td>
<td>-1 ± 8</td>
<td>17 ± 11</td>
</tr>
<tr>
<td>SiC213</td>
<td>A/B</td>
<td>0.8</td>
<td>13.7 ± 0.1</td>
<td>9 ± 11</td>
<td>38 ± 14</td>
</tr>
<tr>
<td>SiC214</td>
<td>ms</td>
<td>0.7</td>
<td>62.0 ± 1.3</td>
<td>10 ± 21</td>
<td>6 ± 25</td>
</tr>
<tr>
<td>SiC216</td>
<td>ms</td>
<td>0.8</td>
<td>47.4 ± 0.7</td>
<td>29 ± 18</td>
<td>23 ± 22</td>
</tr>
<tr>
<td>SiC221</td>
<td>ms</td>
<td>1.3</td>
<td>60.3 ± 0.6</td>
<td>76 ± 7</td>
<td>77 ± 10</td>
</tr>
<tr>
<td>SiC222</td>
<td>ms</td>
<td>1.4</td>
<td>60.0 ± 0.6</td>
<td>60 ± 18</td>
<td>29 ± 23</td>
</tr>
<tr>
<td>SiC223</td>
<td>ms</td>
<td>1.6</td>
<td>35.7 ± 0.3</td>
<td>-2 ± 7</td>
<td>16 ± 10</td>
</tr>
<tr>
<td>SiC224</td>
<td>ms</td>
<td>0.9</td>
<td>68.0 ± 0.8</td>
<td>40 ± 9</td>
<td>42 ± 12</td>
</tr>
<tr>
<td>SiC225</td>
<td>ms</td>
<td>1.3</td>
<td>80.9 ± 1.3</td>
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<td>8 ± 21</td>
</tr>
<tr>
<td>SiC226</td>
<td>ms</td>
<td>1.3</td>
<td>73.1 ± 0.9</td>
<td>55 ± 17</td>
<td>9 ± 21</td>
</tr>
<tr>
<td>SiC227</td>
<td>ms</td>
<td>2.5</td>
<td>61.8 ± 0.6</td>
<td>2 ± 8</td>
<td>23 ± 11</td>
</tr>
<tr>
<td>SiC228</td>
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<td>1.0</td>
<td>71.5 ± 1.0</td>
<td>30 ± 15</td>
<td>19 ± 19</td>
</tr>
<tr>
<td>SiC229</td>
<td>ms</td>
<td>1.3</td>
<td>62.2 ± 0.8</td>
<td>16 ± 16</td>
<td>25 ± 20</td>
</tr>
<tr>
<td>SiC230</td>
<td>ms</td>
<td>4.2</td>
<td>74.4 ± 0.5</td>
<td>27 ± 5</td>
<td>30 ± 8</td>
</tr>
<tr>
<td>SiC231</td>
<td>ms</td>
<td>1.4</td>
<td>55.9 ± 0.4</td>
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<td>71 ± 9</td>
</tr>
<tr>
<td>SiC232</td>
<td>ms</td>
<td>1.1</td>
<td>75.8 ± 0.9</td>
<td>-7 ± 10</td>
<td>26 ± 13</td>
</tr>
<tr>
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<td>1.3</td>
<td>53.3 ± 0.5</td>
<td>79 ± 7</td>
<td>85 ± 10</td>
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<tr>
<td>SiC234</td>
<td>ms</td>
<td>0.9</td>
<td>69.4 ± 0.9</td>
<td>-44 ± 12</td>
<td>31 ± 16</td>
</tr>
<tr>
<td>SiC235</td>
<td>ms</td>
<td>1.5</td>
<td>45.7 ± 0.4</td>
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<td>44 ± 11</td>
</tr>
<tr>
<td>SiC236</td>
<td>ms</td>
<td>1.4</td>
<td>77.6 ± 0.9</td>
<td>-20 ± 11</td>
<td>21 ± 14</td>
</tr>
<tr>
<td>SiC237</td>
<td>ms</td>
<td>1.2</td>
<td>54.8 ± 0.6</td>
<td>17 ± 11</td>
<td>51 ± 14</td>
</tr>
<tr>
<td>SiC238</td>
<td>ms</td>
<td>1.5</td>
<td>62.3 ± 0.5</td>
<td>17 ± 5</td>
<td>33 ± 8</td>
</tr>
<tr>
<td>Sample</td>
<td>Size</td>
<td>( \frac{^{12}C}{^{13}C} )</td>
<td>Size</td>
<td>( \frac{^{12}C}{^{13}C} )</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>----------------</td>
<td>------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>SiC258 ms</td>
<td>1.7</td>
<td>42.5 ± 0.4</td>
<td>25 ± 7</td>
<td>63 ± 10</td>
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</tr>
<tr>
<td>SiC259 ms</td>
<td>1.8</td>
<td>59.8 ± 0.5</td>
<td>24 ± 11</td>
<td>41 ± 14</td>
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</tr>
<tr>
<td>SiC266 ms</td>
<td>0.8</td>
<td>51.6 ± 0.7</td>
<td>47 ± 16</td>
<td>11 ± 20</td>
<td></td>
</tr>
<tr>
<td>SiC267 ms</td>
<td>1.7</td>
<td>59.4 ± 0.6</td>
<td>20 ± 8</td>
<td>34 ± 11</td>
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<td>62 ± 18</td>
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<tr>
<td>SiC269 ms</td>
<td>1.0</td>
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<td>19 ± 13</td>
<td>37 ± 17</td>
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</tr>
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<td>59.9 ± 0.6</td>
<td>7 ± 9</td>
<td>52 ± 12</td>
<td></td>
</tr>
<tr>
<td>SiC272 ms</td>
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<td>48.5 ± 0.4</td>
<td>140 ± 7</td>
<td>111 ± 9</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE.**– Murray grains shown here do not contain detectable amounts of noble gases. Two runs of C-isotopic measurements were performed. If the \( \frac{^{12}C}{^{13}C} \)-ratios of the two runs were different, we list the more anomalous value, and reject the one close to solar-terrestrial composition, which we attribute to dilution by contamination in the laboratory.

\(^{a}\) ms = mainstream SiC

\(^{b}\) Size = (major axis + minor axis)/2

\(^{c}\) 1σ-errors
Acknowledgements

We thank S. Merchel and U. Ott for preparing the Murchison residue for SiC, J. Huth for his help with SEM and E. Gröner for technical assistance with the NanoSIMS in Mainz. ETH Zürich partly funded this project.

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IV. Chromites From Fossil Meteorites of the Thorsberg Quarry, Sweden
Fast delivery of meteorites to Earth after a major asteroid collision

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Very large collisions in the asteroid belt could lead temporarily to a substantial increase in the rate of impacts of meteorites on Earth. Orbital simulations predict that fragments from such events may arrive considerably faster than the typical transit times of meteorites falling today, because in some large impacts part of the debris is transferred directly into a resonant orbit with Jupiter\(^1\)\(^-\)\(^2\). Such an efficient meteorite delivery track, however, has not been verified. Here we report high-sensitivity measurements of noble gases produced by cosmic rays in chromite grains from a unique suite of fossil meteorites\(^3\) preserved in 480 million year old sediments. The transfer times deduced from the noble gases are as short as \(10^5\) years, and they increase with stratigraphic height in agreement with the estimated duration of sedimentation. These data provide powerful evidence that this unusual meteorite occurrence was the result of a long-lasting rain of meteorites following the destruction of an asteroid, and show that at least one strong resonance in the main asteroid belt can deliver material into the inner Solar System within the short timescales suggested by dynamical models.

One of the best-documented large asteroid collisions in the meteorite record disrupted a parent body of the L chondrites, one of the two most abundant meteorite classes. Many L chondrites show signs of severe shock and were degassed about 500 million years (Myr) ago, as demonstrated by their K-Ar gas retention ages\(^4\)\(^-\)\(^5\). The L chondrites from this event that are falling today were delivered to Earth by later collisions mostly some 3–60 Myr ago, as measured by the amounts of noble gases produced by cosmic rays (cosmogenic noble gases). Evidence that this event also delivered many meteorite-sized fragments shortly after the original collision has been found in the form of an unexpectedly high abundance of fossil meteorites in 480 Myr old sediments in southern Sweden\(^3\). The meteorite flux recorded in these sediments was two orders of magnitude
higher than today. Apart from tiny relict chromite grains, the minerals in the fossil meteorites are almost completely replaced by diagenetic pseudomorphs. The chemical composition of the chromite grains matches that of modern L (or LL) chondrites, providing strong evidence that the fossil meteorites originate from the same major collision as the one recorded in the low gas retention ages of L chondrites. This conclusion has been corroborated by the finding of extraterrestrial chromite grains of L (or LL) chondrite composition dispersed in 480 Myr old sediments in other locations in southern Sweden.

Extraterrestrial $^3$He is present in bulk samples of the fossil meteorites, but the very low concentrations indicate a nearly complete loss during diagenesis. We therefore have measured He and Ne isotopes in chromite grains from nine fossil meteorites from six different sediment beds with the high sensitivity compressor source noble gas mass spectrometer at ETH. Figure 1 shows the positions of the meteorites in the sediment column. The total deposition time from the lowermost Arkeologen (Ark) bed to the uppermost Glaskarten (Gla) bed is probably between 1

![Figure 1](image1.png)

**Figure 1** Limestone beds in the Thorsberg quarry in southern Sweden where the fossil meteorites were deposited in the Ordovician 480 Myr ago. Total sedimentation time was 1–2 Myr, estimated by conodont biochronology and average sedimentation rates. The number of meteorites analysed per quarry bed is indicated. Each meteorite had a size of between 2 and 9 cm. Reddish-brown limestones are shown shaded dark, grey sediments are shaded light grey.
and 2 Myr (ref. 9), with the true value probably being closer to the low end of this interval.

He and Ne data are shown in Table 1 and Supplementary Table 1. All grain batches have retained cosmogenic \(^{3}\)He and \(^{21}\)Ne acquired during the journey of their parent meteorite to Earth (minor corrections for non-cosmogenic contributions on these isotopes are explained in Methods and Supplementary Discussion). Table 1 also shows nominal cosmic-ray exposure ages (the time a meteorite spends as a small object in space) deduced from both \(^{3}\)He and \(^{21}\)Ne. For all six samples of Golvsten 001 (Gol 001), \(^{21}\)Ne ages as well as \(^{3}\)He ages agree within uncertainties, and the mean \(^{3}\)He age agrees with the mean \(^{21}\)Ne age within the estimated error of the production rate ratio \(P(\^{3}\text{He})/P(\^{21}\text{Ne})\) in chromite (Methods). This indicates that these grains cannot have lost a considerable fraction of their \(^{3}\)He, in agreement with their excellent state of preservation (Supplementary Fig. 1). However, the less well-preserved grains from most other meteorites must have lost a major fraction of their \(^{3}\)He, as nominal \(^{3}\)He ages in Table 1 are often considerably below the respective \(^{21}\)Ne ages. We therefore base our arguments on the \(^{21}\)Ne ages only. These are shown in Fig. 2.

The \(^{21}\)Ne ages of different samples from the same meteorite always agree within error limits, providing evidence that the chromite grains have been retentive. Figure 2 shows three additional notable features. First, excluding Ark 007, there is agreement between the mean exposure ages of samples from different meteorites from the same bed, confirming the integrity of the data. Second, exposure ages are all close to or less than a million years. This is at the very low end of ages typical for L chondrites falling at present, which mostly range between 3 and 60 Myr (refs 10, 11). Third, exposure ages generally increase according to their position in the sediment column, and the difference between the highest and lowest ages is consistent with the total deposition time of the sediments of 1–2 Myr. The only exceptions are Ark 007 and Gla 001, discussed below.

These observations provide strong additional support for the conclusion\(^2\) that all fossil meteorites derive from one large collision in the asteroid belt. However, the low nominal exposure ages first require critical assessment of their validity. Ages that are too low could be the result of overestimated production rates or losses of cosmogenic Ne. The overall data pattern is inconsistent with both possibilities. The first would require that all fossil meteorites were interior fragments from unusually large pre-atmospheric bodies of perhaps several metres size. The age progression in Fig. 2 and the similar nominal ages of different meteorites from the same bed would then be a pure coincidence, because production rates in very large bodies strongly depend on the sample position. The regular data pattern is also inconsistent with very substantial gas losses of the order of 90% or more—such losses are required if the true exposure ages of the fossil meteorites were in the range of those of most L chondrites falling today.
As noted, two meteorites do not perfectly fit the overall pattern. The two analyses of Ark 007 yield higher nominal exposure ages than all five samples from two other meteorites from the same bed, and these analyses also display the largest relative age difference of any two samples from the same meteorite. As explained in the Supplementary Discussion, the most likely reason for this is a large contribution of nucleogenic $^{21}\text{Ne}$ (from the reaction $^{18}\text{O}(n,\gamma)^{21}\text{Ne}$) in these two samples which show the highest $^4\text{He}$ concentrations, that is, the highest fluence of $^\alpha$-particles. Therefore, the Ark 007 results can reasonably be dismissed. The nominal exposure age of sample Gla 001 is somewhat lower than would be expected from its position at the top of the studied sediment column. A larger than average meteorite size is a viable explanation in this case, as argued in the Supplementary Discussion, although $^{21}\text{Ne}$ loss of the order of 40–50% cannot firmly be excluded. Note that it is very unlikely that either Ark 007 or Gla 001 are unrelated to the collision that produced the other meteorites, for two reasons: first, their atypically low exposure ages compared to modern falls would then be a coincidence; and second, it is a priori unlikely that we sampled a meteorite from the normal background population, which represents only 1% of the fossil meteorites.

Figure 2 Distribution of $^{21}\text{Ne}$ exposure ages. Meteorites from oldest sediments are shown on the left-hand side. Ark 007 samples have large nucleogenic neon corrections and are therefore discarded (Supplementary Discussion). Ages of Gla 001 may be too low owing to unusually large meteorite size or moderate losses of cosmogenic Ne (see main text). Error bars are 1, and include weighing uncertainties, ion statistics, and blanks. Open circles are averaged $^{21}\text{Ne}$ exposure ages of all analyses from the same quarry bed. Ark, Arkeologen; Gol, Golvsten; Gla, Glaskarten; Sex, Sextummen; Tre, Tredje Karten; Goda, Goda Lagret.
We conclude that the low nominal $^{21}$Ne exposure ages in Fig. 2 are essentially correct. Losses of $^{21}$Ne—if any—must be minor. The exposure age progression of meteorites from bottom to top of the sediment column, which inversely matches the relative sediment ages to within better than a factor of two, yields strong independent support for the hypothesis that the fossil meteorites are all derived from one single very large asteroid collision. This event was probably the same event that reset the K-Ar clocks of many L chondrites some 500 Myr ago. Therefore, the chromite grains in the fossil meteorites allow us to deduce transport times to Earth of fragments from a large asteroid collision. This work demonstrates that the first fragments from the L-chondrite parent body break-up event arrived on Earth only 100,000 to 200,000 yr after the impact (the $^{21}$Ne ages of the Arkeologen meteorites). The low exposure ages of the Arkeologen meteorites are also consistent with the conclusion that the asteroid disruption occurred shortly before the deposition of the Arkeologen bed. This conclusion is based on the distribution of extraterrestrial chromite grains dispersed in sediment layers.

Numerical simulations of asteroid and meteorite delivery from the main asteroid belt into the inner Solar System predict that a body which has moved into an orbit in resonance with that of a planet or the Solar System’s natural frequencies typically will collide with the Sun (or rarely a terrestrial planet) within a very few million years. The fact that exposure ages of stony meteorites typically are an order of magnitude longer is explained by a slow drift of a meteorite freshly ejected from its parent body into a resonance by the so-called Yarkovsky effect, which is a momentum transfer due to re-radiation of solar energy at infrared wavelengths. Hence, very short total exposure ages are only to be expected if meteorites are directly injected into an orbital resonance from a nearby impact. The most probable candidates are very large collisions creating families of asteroids with similar orbital elements.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Helium and neon concentrations and $^{21}$Ne ($T_f$) and $^{36}$Ar ($T_M$) exposure ages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>$^{40}$He ($10^{-9}$ cm$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>Gla 001 C6.1</td>
<td>44.1 ± 4.8</td>
</tr>
<tr>
<td>Gla 001 C5.9</td>
<td>54.3 ± 5.0</td>
</tr>
<tr>
<td>Gla 001 C6.5</td>
<td>23.1 ± 4.7</td>
</tr>
<tr>
<td>Gla 001 C3.6</td>
<td>16.2 ± 1.6</td>
</tr>
<tr>
<td>Tre 002 C6.9</td>
<td>30.3 ± 4.2</td>
</tr>
<tr>
<td>Zek 002 C3.1</td>
<td>20.6 ± 1.5</td>
</tr>
<tr>
<td>Zek 002 C2.9</td>
<td>34.5 ± 3.5</td>
</tr>
<tr>
<td>Zek 002 C2.3</td>
<td>30.6 ± 3.5</td>
</tr>
<tr>
<td>Zek 001 C4.3</td>
<td>37.6 ± 1.5</td>
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<tr>
<td>Zek 001 C2.6</td>
<td>35.4 ± 5.6</td>
</tr>
<tr>
<td>Zek 001 C2.7</td>
<td>29.2 ± 6.4</td>
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<tr>
<td>Zek 001 C3.9</td>
<td>34.3 ± 4.5</td>
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<tr>
<td>Ark 002 C3.7</td>
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<tr>
<td>Ark 002 C3.6</td>
<td>22.1 ± 2.3</td>
</tr>
<tr>
<td>Ark 002 C3.9</td>
<td>65.1 ± 2.1</td>
</tr>
<tr>
<td>Ark 002 C3.7</td>
<td>36.5 ± 1.8</td>
</tr>
<tr>
<td>Ark 002 C3.6</td>
<td>50.9 ± 7.7</td>
</tr>
<tr>
<td>Ark 003 C4.4</td>
<td>11.6 ± 1.3</td>
</tr>
<tr>
<td>Ark 003 C4.7</td>
<td>9.12 ± 1.7</td>
</tr>
</tbody>
</table>

Data for all samples from the main asteroid belt. All values assumed to be cosmogenic (except for Ark 002 and Ark 003, Supplementary Discussion). Cosmogenic $^{40}$He ($^{36}$Ar) calculated by subtracting trapped and nucleogenic $^{40}$He concentrations. Production rates used in calculations are for $^{40}$He ($^{36}$Ar) in the Martian environment (see Supplementary Discussion). Uncertainties (1σ) include weighing errors, ion statistics, and blank corrections. Complete noble gas data given in Supplementary Table 1.
The exposure ages of the fossil meteorites confirm the dynamical models to the extent that they show that at least one strong orbital resonance in the main asteroid belt is capable of delivering material to Earth within the short timescales suggested by the models. The data also show that an L chondrite parent body was located close enough to a powerful resonance that collisional ejecta could directly reach a resonant orbit. The two most prolific resonances are situated in the inner main belt\textsuperscript{14, 15}. This is consistent with the hypothesis\textsuperscript{16, 17} that L chondrites and other ordinary chondrites come from the S(IV) subset of the S asteroids, the most abundant spectroscopic class in the inner belt\textsuperscript{18}. The fossil meteorites in southern Sweden thus probably originate in the inner main asteroid belt. A viable parent body is the precursor of the Flora family near 2.2 astronomical units from the Sun\textsuperscript{19}.

**Methods**

**Samples and analytical methods** We analysed a total of 23 batches of one to a few chromite grains (average grain size 80–100 µm; mass of each batch 4–40 µg). Chromite grains were separated from bulk fossil meteorites\textsuperscript{3}. Major element composition was determined using SEM/EDAX. Most of the grains studied have compositions very similar to the average composition of chromites from 26 fossil meteorites analysed by Schmitz et al.\textsuperscript{3}. Only the grains from Tre 002 have about twice as much MgO (5%) as chromites from the other meteorites.

Gases were extracted by melting grains with a Nd-YAG CW laser. Samples were heated for 3–4 min. Gases were cleaned with several liquid nitrogen cold traps and ZrAl ‘getters’ to remove active gases. Helium and Ne were separated before analysis by a cryotrap in order to measure He and Ne isotopes with the appropriate mass resolution. The mass spectrometer is equipped with a molecular drag pump compressing the sample gas into the ion-source, resulting for He and Ne in a sensitivity increase of about two orders of magnitude compared to conventional noble gas mass spectrometers\textsuperscript{8}. The sensitivity of the mass spectrometer is about $7.2 \times 10^{14}$ Hz cm\textsuperscript{-3} STP for He and $2.8 \times 10^{15}$ Hz cm\textsuperscript{-3} STP for Ne, respectively, yielding count rates for samples of the order of 10–100 Hz for $^3$He and $^{21}$Ne. Spectrometer noble gas memory was monitored before and after gas inlet, and signals were corrected accordingly. Gas amounts were calibrated using gas from a standard air reservoir, believed to be known to better than 3%.

**Production rates** Because no information on pre-atmospheric meteorite size and sample depth can be deduced from our data, we have to assume nuclide production rates typical for ‘average-sized’ meteorites. Elemental production rates\textsuperscript{20} of cosmogenic $^3$He and $^{21}$Ne by galactic cosmic rays were calculated assuming a typical meteorite radius of 25 cm and a sample position about 10 cm below the surface. Since the atomic mass difference between Fe and Ni, and between Cr and Fe, both are 2 mass units, we assume the production rate differences between $P_{21Ne}(Cr)$ and $P_{21Ne}(Fe)$ to be similar to the difference between $P_{21Ne}(Fe)$ and $P_{21Ne}(Ni)$. Overall uncertainties
of production rates are estimated to be about 40%, including uncertainties due to unknown meteorite sizes and sample positions (unless pre-atmospheric sizes of the fossil meteorites would have been considerably larger than typical values of present day meteorites, see main text).

Relevant target elements for cosmogenic $^3$He production are O, Cr, Fe, Al and Mg (in the order of decreasing contribution). Cosmogenic $^{21}$Ne is mainly produced by spallation on Mg, Al, Cr and Fe. Although Cr and Fe are the major compositional constituents of chromite besides oxygen, much of the total $^{21}$Ne production is from Mg and Al (on average 43% from Mg, 34% from Al, 16% from Cr and 7% from Fe).

Production rates (calculated from elemental production rates and major element composition) are on average $1.23 \times 10^{-8} \text{ cm}^3 \text{ STP g}^{-1} \text{ Myr}^{-1}$ for $^3$He and in the range $(4.7–7.2) \times 10^{-10} \text{ cm}^3 \text{ STP g}^{-1} \text{ Myr}^{-1}$ for $^{21}$Ne.

**Corrections for non-cosmogenic noble gases** Trapped Ne has been corrected for by assuming atmospheric composition for all samples except Ark 002, for which solar wind composition was assumed (Supplementary Fig. 2). Nucleogenic $^{21}$Ne produced when $^{18}$O captures -particles from U/Th decay was calculated by assuming all $^4$He to be radiogenic and a ratio $^{21}\text{Ne}_{\text{nucl}}/^{4}\text{He}_{\text{rad}} = 2.8 \times 10^{-8}$ for a mean O concentration of the chromites of 33.6% (ref. 3). Corrections for $^{21}\text{Ne}_{\text{nucl}}$ are between 0.2% and 3.3% only, except for Ark 007 (up to 39%, Supplementary Discussion). A correction for nucleogenic $^3$He produced through the reaction $^6$Li$(n,p)\text{He}$ is not possible, since Li concentrations in the grains are unknown. They are expected to be very low, however. Furthermore, $^3$He/$^4$He ratios in the chromites are mostly much higher than typical crustal radiogenic production ratios of $10^{-7}$–$10^{-8}$, indicating that nucleogenic $^3$He is negligible. We therefore assume that the $^3$He in the chromites is entirely cosmogenic. (Two exceptions, Ark 007 and Ark 002, are discussed in the Supplementary Discussion).

In some grains, the $^{21}$Ne excesses are several times higher than what would have been produced during 480-Myr exposure on the very surface of the Earth at the present day altitude (a completely unrealistic scenario). Since the meteorites fell into an epicontinental sea and were later shielded by at least several 10 m of sediments essentially until their recovery, cosmogenic nuclide production on Earth fails by many orders of magnitude to explain the observed excesses.

**Supplementary information** accompanies this paper.

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**Competing interests statement.** The authors declare that they have no competing financial interests.
Figure 1. Preservation state of chromite grains based on corrosion plotted against ZnO (wt%) content. Well-preserved grains have large smooth, shiny black surfaces like black glass or flint (index 1), whereas badly preserved grains have uneven surfaces with many cracks (index 5). The latter are usually rare and small. Another indicator of the preservation state is the ZnO content of the grains. The higher ZnO concentration the more Cr and Fe have been replaced. The figure shows that the two indices correlate roughly with each other. Quantitative retention of cosmogenic $^3$He and $^{21}$Ne in the Gol 001 grains (see main text) is consistent with their excellent preservation. Nominal $^3$He ages of other samples are often several times lower than the $^{21}$Ne ages, indicating loss of cosmogenic $^3$He. This is particularly pronounced in both samples from Gla 001 and in some of the Sex 003 samples. These grains were quite severely altered.
Supplementary Figure 2

Figure 2. Neon three-isotope plot showing all data with their 1σ errors. Most data points lie on the mixing line between atmospheric (air) and galactic cosmic-ray (GCR) composition. Therefore, trapped Ne is assumed to be of atmospheric composition for all samples except Ark 002 for which solar wind composition (SW) was assumed. No ³He age can be given for these samples due to probable additions of SW ³He. Larger analytical errors for Gol 001 samples are due to the fact that these samples were analyzed at an early stage and our analytical protocol has subsequently been improved.
Supplementary Discussion

**Corrections for non-cosmogenic $^{21}\text{Ne}$ and $^{3}\text{He}$:** As mentioned in the main text, cosmogenic $^{21}\text{Ne}$ ($^{21}\text{Ne}_{\text{cos}}$) is determined by correcting measured $^{21}\text{Ne}$ for trapped and nucleogenic $^{21}\text{Ne}$. As Supplementary Figure 2 shows, trapped Ne has an atmospheric composition in all meteorites except the three samples of Ark 002. For this meteorite all data points cluster around the point representing solar wind Ne. It is well known that a few percent of all L chondrites contain Ne implanted by the solar wind in the surface dust layer of their parent body. Obviously, the chromite grains of Ark 002 have not only retained cosmogenic $^{21}\text{Ne}$ in the volume of their grains but even solar Ne on the grain surfaces during 480 Ma of storage on Earth.

From the amounts of solar wind Ne, the Ark 002 samples are also expected to contain sizeable amounts of trapped solar wind $^{3}\text{He}$ in addition to cosmogenic $^{3}\text{He}$. The measured ratio $^{3}\text{He}/^{20}\text{Ne}$ of ~0.03-0.06 (Supplementary Table 1) is comparable to values measured in other meteorites rich in solar gases. Therefore, probably a major fraction of the total $^{3}\text{He}$ in Ark 002 is from the solar wind and hence we are unable to report the concentrations of cosmogenic $^{3}\text{He}$ in these samples. In all other samples, trapped (atmospheric) $^{3}\text{He}$ is negligible, since $^{3}\text{He}/^{4}\text{He}$ ratios are much higher than the atmospheric value of $1.40 \cdot 10^{-6}$, while $^{4}\text{He}/^{20}\text{Ne}$ ratios show that in most grains essentially all $^{4}\text{He}$ must be radiogenic rather than atmospheric anyway.

Nucleogenic $^{21}\text{Ne}$ ($^{21}\text{Ne}_{\text{nuc}}$) has been calculated from $^{4}\text{He}$ as explained in the Methods section in the main text. Supplementary Table 1 shows that this correction is only between 0.2 and 3.3%, except for Ark 007. Hence, even if $^{4}\text{He}$ should not have been completely retained in some samples, it is not expected that the corresponding uncertainty in nucleogenic Ne would substantially affect calculated $^{21}\text{Ne}$ exposure ages. This is confirmed by the regular exposure age pattern. In Ark 007, however, the corrections for $^{21}\text{Ne}_{\text{nuc}}$ are much larger, up to 39%. This meteorite also shows the highest concentrations of radiogenic $^{4}\text{He}$, presumably because it took up much more U and Th on Earth than the other meteorites. In particular, $^{4}\text{He}$ in Ark 007 is roughly two orders of magnitude higher than in the other Ark meteorites. Most of the radiogenic $^{4}\text{He}$ in the chromites presumably was implanted by recoil from $\alpha$-decay of U/Th incorporated into diagenetically altered adjacent minerals, as the recoil length of the $\alpha$-particles (~40 µm) is comparable to the size of the chromites. Therefore, corrections for nucleogenic $^{21}\text{Ne}$ were very substantial for the Ark 007 samples and it is most likely that the uncertainties on these corrections are the reason for their relatively high and somewhat inconsistent apparent ages.
As discussed in the Methods section in the main text, nucleogenic $^3$He is thought to be negligible. A probable exception is again Ark 007, which contains large amounts of nucleogenic $^{21}$Ne, hence large amounts of U-Th (see above).

The relatively low age of Gla 001: We note in the main text that the somewhat lower than expected age of Gla 001 might basically be due to a modest (40-50%) loss of cosmogenic $^{21}$Ne or a relatively large pre-atmospheric size of this meteorite, which would lead to a $^{21}$Ne production rate lower than the assumed value typical for “average-sized” meteorites (see Methods). Although the chromites from this meteorite were among the least well preserved of all studied here (Supplementary Figure 1), the former explanation is perhaps less likely, because both grain batches yield similar nominal ages. On the other hand, a sample from, say, near the centre of a meteorite with 120 cm radius would have had a production rate low enough to explain the somewhat short nominal exposure age$^3$. Such large pre-atmospheric meteorites are not very uncommon.


V. Chromites From Fossil Micrometeorites And Fossil Meteorites From Different Locations
**Noble Gases in Fossil Micrometeorites and Meteorites from 480 Myr old Sediments from Southern Sweden and new Evidence for the L Chondrite Parent Body Break-Up Event**

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**Abstract**

We present new noble gas analyses of sediment-dispersed chromite grains and of relict chromites in fossil meteorites recovered from ~480 Myr old sediments at different locations in southern Sweden. We find that all samples studied are related to the same major asteroid collision (the L chondrite parent body break-up event), which generated the suite of fossil meteorites from Thorsberg quarry studied earlier. The fossil meteorites we investigate (Brunflo and Gullhögen 001) have very low cosmic-ray exposure ages (< 1 Myr), comparable to the fossil meteorites from Thorsberg. Copious amounts of solar noble gases in the sediment-dispersed chromite grains prevents the determination of their exposure ages, but let us conclude that these grains are micrometeorites rather than fragments of larger meteorites.

**1. Introduction**

Schmitz et al. (1996) discovered a high concentration of fossil meteorites in a quarry of 480 Myr old marine limestone in Southern Sweden (Thorsberg quarry). Although the mineralogy of the meteorites has been altered during sediment diagenesis, the very resistant mineral chromite remained virtually preserved in its original composition and allowed these meteorites to be classified as L (or LL) chondrites (Schmitz et al. 2001). Furthermore, chromite proved to be retentive for cosmogenic (and in one case also for solar) noble gases (Heck et al. 2003, 2004). Transfer times of the fossil L chondrites from their parent body to Earth, measured by cosmogenic noble gases, proved to be unusually short, only between 0.1-1 Myrs, and ages increase with decreasing sediment age (see fig. 1; Heck et al. 2004). The observed short transfer times are in agreement with dynamical models of debris produced in large asteroid collisions occurring close to important orbital resonances in the inner asteroid belt (Gladman et al. 1997, Zappalà et
The suite of fossil L chondrites is thought to have been produced in the break-up of the L chondrite parent-body (Schmitz et al. 2003, Heck et al. 2004). This event is well-documented by a clustering of K-Ar gas retention ages around 500 Myr in recently fallen L chondrites, which also show signs of shock (Keil et al. 1994, Bogard 1995). The high fossil meteorite density and their L chondrite composition (Schmitz et al. 2001), their low exposure ages and the exposure age gradient, in accordance with theoretical predictions for a major asteroid breakup, confirm that the fossil meteorites are debris of the L chondrite parent-body break-up event near an important orbital resonance in the inner asteroid belt (Heck et al. 2004).

Since such an event should have produced a global increase in the flux of extraterrestrial material, it would be desirable to recover fossil meteorites from other locations in the same Ordovician stratigraphic sequences. The first and only fossil meteorite found to date in the same sediment beds at another location (Gullhögen quarry at Billingen, southern Sweden) proved also to be an L chondrite (Tassinari et al. 2004). In strata about 5 Myrs younger the first fossil meteorite Brunflo was reported already in 1981 by Thorslund and Wickmann. The meteorite was originally classified as an H chondrite (Thorslund and Wickman, 1981), but recent studies indicate it may be an L3 or L4 meteorite (B. Schmitz, in prep.). In this work we present the cosmic-ray exposure ages of these two meteorites.

The chance to find fossil meteorites, even in meteorite-rich strata, is very small. Only in active quarries with workers trained for meteorite identification, systematic recoveries were reported (Schmitz et al. 2001). Accidental finds such as Österplana 001 (Nyström et al. 1988), Brunflo and Gullhögen 001 are rare. A much more promising method is to look for meteorite relict minerals in bulk sediment samples. By this approach sediment-dispersed extraterrestrial chromite grains were found at various locations in southern Sweden in the same sediments beds as the fossil meteorites (Schmitz et al. 2003). It was suggested that these grains are remnants of disintegrated small meteorites of 0.1 to 1 cm diameter (Schmitz et al. 2003). They allowed to determine the flux of extraterrestrial (ET) matter to Earth: During the sediment deposition period in the Ordovician the ET flux was about two orders of magnitude higher than today (Schmitz et al. 2003). Chemical analyses indicated a chemical composition that matches L chondrites (Schmitz et al. 2001). The main purpose of this work is to determine if the cosmic-ray exposure ages of these two meteorites can be determined.

In an auxiliary study we determined cosmic-ray production rates of He and Ne in chromite. Due to a lack of measured cross-section data for Cr, a major target element in chromite (FeCr$_2$O$_4$), production rates for cosmogenic $^3$He and $^{21}$Ne in chromite $P(^3$He, $^{21}$Ne) were based on physical model calculations (Heck et al. 2004). By comparing measured cosmogenic noble gas concentrations in chromite separates from ordinary chondrites with $^3$He and $^{21}$Ne from bulk meteorite samples, adjacent to those from which the chromites have been extracted, we
determined $P(^3\text{He}, ^{21}\text{Ne})$ in chromite directly.

2. Samples & Experimental

2.1 Chromite Grains

The Orthoceratite Limestone samples containing the extraterrestrial chromites are collected from different sediment beds in the Hälleks and the Thorsberg quarries in southern Sweden (Table 1), formed in an epicontinental sea during the middle Ordovician about 480 Myr ago (see map, fig. 1 in Schmitz et al. 2003; Lindström 1971). Sediment sample sizes range between 10-30 kg. Chromite grains (Fig. 1) were extracted by dissolving the limestone with hydrochloric and hydrofluoric acids. The maximum yields were ca. 3 grains per kg of rock in the Arkeologen bed (Schmitz et al. 2003) leading to an accumulation density of about 3000 grains per m². Relict chromite grains from the two fossil meteorites Brunflo and Gullhögen 001 were extracted as described in Schmitz et al. (2001). Chromite grains from recent ordinary chondrites were extracted by HF acid dissolution only.

Fig. 1. SEM image of a well preserved relict meteoritic chromite grain (Hälleks quarry, Sweden). Although chromite is one of the most resistant mineral phases in ordinary chondrites, different stages of alteration can be observed by inspecting surface morphology and ZnO content. The preservation state is also a measure of $^3\text{He}$ retentivity (Heck et al. 2004). Image credit: Carl Alwmark and Birger Schmitz.
Tab. 1. Location and description of sediment or fossil meteorite samples, from where relict chromite grains have been recovered. The samples are arranged according to time of deposition as determined by their stratigraphic position. Arkeologen samples are the oldest ones, while the Brunflo meteorite has been found in the youngest sediments. The samples are chromite grains extracted from fossil meteorites or directly from sedimentary rock (SD grains = sediment-dispersed grains).

Grains were selected under the light microscope and picked with a fine brush. Chemical composition of each grain was determined with SEM/EDS to identify them as extraterrestrial. As with previous studies of ET chromite (Schmitz et al. 2003) the grains have L (or LL) chondrite chemical composition. Batches of 4-8 µg of 4-6 single relict chromite grains (average grain-size 80-100 µm) of the same sample location were weighted with a micro-balance to an accuracy of ~10%.

Four batches of 3-12 µg of 4-6 single chromite grains from Brunflo and 2 batches of 6 and 14

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quarry</th>
<th>Position</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brunflo</td>
<td>Rödbrottet (Jämtland, central Sweden)</td>
<td>Sediment beds ~5 Myrs younger than Arkeologen</td>
<td>Fossil meteorite, probably L chondrite, ~10 cm diameter</td>
<td>Thorslund &amp; Wickman 1981; B. Schmitz, in. prep.</td>
</tr>
<tr>
<td>Hällekis 5.50</td>
<td>Hällekis, at Kinnekulle (4 km NW of Thorsberg)</td>
<td>5.50 m above Arkeologen base</td>
<td>SD grains, L chondrite composition</td>
<td>-</td>
</tr>
<tr>
<td>Hällekis 3.57</td>
<td>Hällekis</td>
<td>3.57 m above Arkeologen base</td>
<td>SD grains, L chondrite composition</td>
<td>-</td>
</tr>
<tr>
<td>Gullhögen 001</td>
<td>Gullhögen, at Billingen mountain (35 km SE of Thorsberg)</td>
<td>Yangtze-placognathus crassus conodont Zone; equivalent to the Tredje Karten and Sextummen beds in the Thorsberg quarry</td>
<td>Fossil meteorite, L chondrite, ~1 cm diameter</td>
<td>Tassinari et al. 2004</td>
</tr>
<tr>
<td>Arkeologen</td>
<td>Thorsberg, at Kinnekulle</td>
<td>Upper part of Arkeologen bed</td>
<td>SD grains, L chondrite composition</td>
<td>Schmitz et al. 2003</td>
</tr>
</tbody>
</table>

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µg consisting of 5 and 6 single grains were prepared for analyses. Nine batches of chromites from five recent meteorites in the same size range with a batch mass range of 4-23 µg were prepared. The five meteorites are ordinary chondrites of type L, LL and H, with well-known, relatively high cosmic-ray exposure ages (~15-60 Myr) and average shielding, indicated by \(^{22}\text{Ne}/^{21}\text{Ne} \approx 1.11\): Mt. Tazerzait (L5), Harleton (L6), St. Severin (LL6), Eva (H5) and Hessle (H5).

The extremely low gas amounts expected in chromites require the use of an ultra-high sensitivity mass spectrometer (Baur 1999) in conjunction with an extremely low-blank extraction line: Gases were extracted by complete melting of chromite samples for ~3-4 minutes with a CW Nd-YAG laser (1064 nm) in ultra-high vacuum (UHV). Exposure to liquid-nitrogen-cooled stainless-steel trap and activated charcoal traps, and to several types of adsorption getters removes Ar, H\(_2\)O and active gases from the sample gas. After cleaning, an inverse turbomolecular drag pump (“compressor”) concentrates the gas into a very small ionization volume. In order to minimize the production of double-charged interfering species, such as Ar and CO\(_2\), in the ion source, an electron voltage of 40 eV was used. This mass spectrometer results in a about two orders of magnitude higher sensitivity compared to the same mass spectrometer equipped with a conventional ion source without a compressor (Baur 1999). "He can be resolved from HD, as the mass resolution of the instrument is ~650. Ions are detected simultaneously with an electron multiplier in ion counting mode and with a Faraday cup (for \(^{4}\text{He}\)). Because of the very small gas amounts, spectrometer memory and background signals were monitored before, during and after sample gas admission and sample signals were corrected.

2.2 Bulk Meteorite Samples

The larger gas amounts expected in bulk meteorite samples do not require the use of the ultra-high sensitivity mass spectrometer used for chromites. Therefore, we used a mass spectrometer equipped with a conventional (Baur-Signer) ion source (Baur 1980), without compressor. We measured helium and neon isotopes in ~100 mg bulk samples of four of the five recent ordinary chondrites mentioned above. Gases from the ~100 mg bulk meteorite samples were extracted in a furnace by total fusion at T \(\approx 2000\) K in UHV and subsequently cleaned using liquid-nitrogen-cooled activated charcoal traps and heated getters. Ionization was achieved by 45 eV-electron-impacts. This electron energy minimizes the amount of double-charged \(^{40}\text{Ar}\) which interferences with \(^{20}\text{Ne}^+\). He and Ne isotopes as well as masses needed for interference corrections were measured. The mass resolution of the instrument (M/\(\Delta M \approx 550\)) allows \(^3\text{He}\) and \(^{20}\text{Ne}\) to be separated from HD and H\(_2\)\(^{18}\text{O}\), respectively. Ion detection was done using an electron multiplier in counting mode and a Faraday cup.
2.3 Data Reduction

Gas amounts of bulk meteorite samples were corrected by subtracting blank measurements and corrected for remaining interferences. Ion signals in both spectrometers were calibrated using gas from standard air reservoirs, which amounts are believed to be known to better than 3%. We assume the $^3$He amount is entirely cosmogenic. Cosmogenic $^{21}$Ne from bulk meteorite samples has been slightly corrected for atmospheric Ne.

3. Results

3.1 Cosmogenic Noble Gas Production Rates in Chromite

Concentrations of cosmogenic $^3$He and $^{21}$Ne in chromites from modern ordinary chondrites correlate well with cosmogenic $^3$He and $^{21}$Ne from bulk samples of their respective host meteorite. Aliquots always agree within $2\sigma$ analytical error. In Figure 2 we plot the adopted exposure age, calculated using our bulk meteorite noble gas data with models by Eugster (1988) and Leya et al. (2001) using the $^{22}$Ne/$^{21}$Ne ratio for shielding correction, against the measured concentrations in batches of chromite grains. Measured concentrations correlate linearly with adopted CRE. The slope of the best linear fit forced through the origin therefore gives the production rate of $^3$He and $^{21}$Ne, respectively (Table 2).

Our new $^{21}$Ne production rate, $P(^{21}\text{Ne}) = (7.04 \pm 0.65) \cdot 10^{-10}$ STP g$^{-1}$ Myr$^{-1}$, falls in the range of previously used values (see Tab. 2). This result confirms the low exposure age range found for fossil meteorite exposure ages by Heck et al. (2004). We therefore adopt the newly determined values for $P(^{21}\text{Ne})$. The new $^3$He production rate, $P(^3\text{He}) = (1.99 \pm 0.17) \cdot 10^{-8}$ STP g$^{-1}$ Myr$^{-1}$, is $\sim 50\%$ higher than the previous value. The new, higher $P(^3\text{He})$ is of no concern, since $^3$He is lost by diffusion from chromites of fossil meteorites. We therefore base our ages on the more reliable cosmogenic $^{21}$Ne concentration. We adopt the new $P(^3\text{He})$ instead of the value from model predictions. $^3$He loss is expected for increasing grain alteration. Different stages of chromite grain alteration can be observed by inspecting surface-morphology in the SEM and by measuring ZnO content. With advancing alteration, mainly Fe is being replaced by Zn and ZnO concentrations increase.
Production rates for chromites based on
measured bulk data predictions\textsuperscript{a} using model\textsuperscript{b}

<table>
<thead>
<tr>
<th></th>
<th>P(\textsuperscript{3}He) $10^{-8}$ STP g\textsuperscript{-1} Myr\textsuperscript{-1}</th>
<th>P(\textsuperscript{21}Ne) $10^{-10}$ STP g\textsuperscript{-1} Myr\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.99 ± 0.17</td>
<td>7.04 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>1.23 ± 0.49</td>
<td>4.7 - 7.2</td>
</tr>
</tbody>
</table>

Tab. 2. Comparison of experimentally determined \textsuperscript{3}He and \textsuperscript{21}Ne production rates in chromites based on measured bulk meteorite data and measured noble gas concentrations in chromites. Values for \textsuperscript{21}Ne in the last column vary mainly due to variable Mg concentrations (a target element for incoming cosmic-ray particles) in relict chromite grains from fossil meteorites. \textsuperscript{a}Heck et al. (2004); \textsuperscript{b}Leya et al. (2001).
Table 3. Helium and neon concentrations and ratios for batches of relict chromite grains extracted from fossil meteorites and sediment dispersed extraterrestrial chromite grains. Uncertainties (2\(\sigma\)) include weighing errors, ion statistics, and blank corrections. In the column for \(^{21}\text{Ne}\) the cosmogenic component is given for samples from fossil meteorites (Brunflo and Gullhögen 001), while for sediment-dispersed grains the interference-corrected, measured value is given. Brun, Brunflo; Gull, Gullhögen 001; Ark, Arkeologen; H-Kis, Hälleks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>µg</th>
<th>(^{3}\text{He}) ((10^{-10} \text{cm}^3 \text{g}^{-1}))</th>
<th>(^{4}\text{He}) ((10^{-5} \text{cm}^3 \text{g}^{-1}))</th>
<th>(^{20}\text{Ne}) ((10^{-8} \text{cm}^3 \text{g}^{-1}))</th>
<th>(^{21}\text{Ne}) ((10^{-10} \text{cm}^3 \text{g}^{-1}))</th>
<th>(^{4}\text{He}/^{21}\text{Ne})</th>
<th>(^{20}\text{Ne}/^{22}\text{Ne})</th>
<th>(^{4}\text{He}/^{22}\text{Ne})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chromites from fossil meteorites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brun 1</td>
<td>12</td>
<td>29.4 ± 3.0</td>
<td>16.1 ± 1.6</td>
<td>1.93 ± 0.21</td>
<td>1.22 ± 0.18</td>
<td>2.09 ± 0.23</td>
<td>1.82 ± 0.05</td>
<td>9.26 ± 0.53</td>
</tr>
<tr>
<td>Brun 2</td>
<td>3.5</td>
<td>105 ± 11</td>
<td>45.3 ± 4.5</td>
<td>8.17 ± 0.85</td>
<td>5.16 ± 0.74</td>
<td>8.96 ± 1.04</td>
<td>2.31 ± 0.05</td>
<td>9.12 ± 0.60</td>
</tr>
<tr>
<td>Brun 3</td>
<td>8.0</td>
<td>50.9 ± 5.2</td>
<td>22.6 ± 2.3</td>
<td>6.33 ± 0.64</td>
<td>2.04 ± 0.30</td>
<td>6.33 ± 0.66</td>
<td>2.26 ± 0.05</td>
<td>10.0 ± 0.34</td>
</tr>
<tr>
<td>Brun 4</td>
<td>8.0</td>
<td>90.8 ± 9.2</td>
<td>77.5 ± 7.7</td>
<td>9.17 ± 0.92</td>
<td>4.95 ± 0.61</td>
<td>9.94 ± 1.02</td>
<td>1.17 ± 0.02</td>
<td>9.22 ± 0.23</td>
</tr>
<tr>
<td>Gull 001-1</td>
<td>6.0</td>
<td>85.1 ± 8.7</td>
<td>2.95 ± 0.30</td>
<td>4.55 ± 0.49</td>
<td>5.13 ± 0.66</td>
<td>5.60 ± 0.64</td>
<td>28.8 ± 0.6</td>
<td>8.12 ± 0.53</td>
</tr>
<tr>
<td>Gull 001-2</td>
<td>14</td>
<td>116 ± 12</td>
<td>4.26 ± 0.43</td>
<td>4.46 ± 0.45</td>
<td>7.25 ± 0.77</td>
<td>5.61 ± 0.57</td>
<td>27.3 ± 0.4</td>
<td>7.95 ± 0.15</td>
</tr>
<tr>
<td><strong>Sediment-dispersed chromite grains</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ark 1-1</td>
<td>5.0</td>
<td>12526 ± 1253</td>
<td>551.7 ± 55.2</td>
<td>2352 ± 235</td>
<td>7708 ± 771</td>
<td>22.7 ± 0.03</td>
<td>7.16 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Ark 1-2</td>
<td>4.0</td>
<td>11743 ± 1174</td>
<td>649.2 ± 64.9</td>
<td>2093 ± 209</td>
<td>6818 ± 682</td>
<td>18.1 ± 0.03</td>
<td>9.52 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Ark 2</td>
<td>8.0</td>
<td>10063 ± 1006</td>
<td>488.1 ± 48.8</td>
<td>1977 ± 198</td>
<td>6520 ± 652</td>
<td>20.6 ± 0.03</td>
<td>7.49 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>H-Kis 5.50-1</td>
<td>4.0</td>
<td>13171 ± 1317</td>
<td>515.4 ± 51.5</td>
<td>2770 ± 277</td>
<td>9046 ± 905</td>
<td>25.6 ± 0.05</td>
<td>5.70 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>H-Kis 5.50-2</td>
<td>7.0</td>
<td>5134 ± 514</td>
<td>222.3 ± 22.2</td>
<td>2573 ± 257</td>
<td>8441 ± 844</td>
<td>23.1 ± 0.05</td>
<td>2.63 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>H-Kis 5.50-4</td>
<td>7.0</td>
<td>22258 ± 2226</td>
<td>941.5 ± 94.1</td>
<td>16974 ± 1698</td>
<td>23.6 ± 0.03</td>
<td>5.55 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-Kis 3.57-1</td>
<td>4.5</td>
<td>2925 ± 293</td>
<td>135.6 ± 13.6</td>
<td>5748 ± 575</td>
<td>1493 ± 149</td>
<td>4887 ± 489</td>
<td>21.6 ± 0.09</td>
<td>11.8 ± 0.05</td>
</tr>
<tr>
<td>H-Kis 3.57-2</td>
<td>6.0</td>
<td>18231 ± 1823</td>
<td>739.3 ± 73.9</td>
<td>2598 ± 260</td>
<td>8609 ± 861</td>
<td>24.7 ± 0.04</td>
<td>8.59 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Fossil meteorites Gullhögen 001 and Brunflo

Noble gas concentrations measured in chromites from the fossil meteorites Gullhögen 001 and Brunflo are given in Table 3. Two batches of relict chromite grains from the meteorite Gullhögen 001 contained cosmogenic noble gases in comparable concentrations as chromites from the suite of fossil meteorites found at the nearby Thorsberg quarry (Table 3). The exposure age \( T_{21} \) of Gullhögen 001 is with 0.7-1.0 Myrs unusually low and similar to the CRE of the Thorsberg meteorites (Fig. 3). The age based on cosmogenic \(^3\)He \((T_3)\) is at the lower end or below the range of \( T_{21} \) (Table 4). This indicates He loss, as observed for other fossil meteorites (Heck et al. 2004) and \( T_3 \) is therefore dismissed.

We measured noble gases in four batches of chromite grains from the meteorite Brunflo (Table 3). Concentrations were similar to samples from Gullhögen 001. We find a cosmic ray exposure age for Brunflo of 0.3 - 1.1 Myrs. Helium and neon ages, \( T_3 \) and \( T_{21} \) respectively, agree within 2\( \sigma \)-error. There is a positive correlation between cosmogenic \(^3\)He and \(^{21}\)Ne. The large spread in cosmogenic noble gas concentrations for different Brunflo aliquots has not been observed in the fossil meteorites from the Thorsberg quarry. This makes Brunflo special compared to other fossil meteorites. However, the very low exposure age for Brunflo is comparable to the CRE of the fossil L chondrites found in \(~5\) Myr older sediments (Table 4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_3 ) (10(^5) yrs)</th>
<th>( T_{21} ) (10(^5) yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brun1</td>
<td>2.3 ± 0.2</td>
<td>2.6 ± 0.4</td>
</tr>
<tr>
<td>Brun2</td>
<td>8.2 ± 0.8</td>
<td>11.1 ± 1.6</td>
</tr>
<tr>
<td>Brun3</td>
<td>4.0 ± 0.4</td>
<td>4.4 ± 0.6</td>
</tr>
<tr>
<td>Brun4</td>
<td>7.1 ± 0.7</td>
<td>10.6 ± 1.3</td>
</tr>
<tr>
<td>Gull 001-1</td>
<td>4.3 ± 0.4</td>
<td>7.3 ± 0.9</td>
</tr>
<tr>
<td>Gull 001-2</td>
<td>5.8 ± 0.6</td>
<td>10.3 ± 1.1</td>
</tr>
</tbody>
</table>

Table 4. Cosmic-ray exposure ages of relict chromite grains from the fossil H chondrite Brunflo (Brun) and the fossil L chondrite Gullhögen 001 (Gull) in 10\(^5\) yrs. Errors are given as 1\( \sigma \) and include weighing uncertainties, ion statistics, and blanks.
3.3 Sediment Dispersed Grains

Rather surprisingly, the sediment-dispersed chromite grains contain very high concentrations of trapped He and Ne (Table 3). Unfortunately, this inhibits one of our original goals, the determination of a cosmic-ray exposure age. However, trapped gas provides interesting clues about the provenance of chromites. Because of the very high trapped gas amounts $^{20}$Ne could only be measured in one sample. In the other grains $^{20}$Ne gas amounts were above the detection threshold of the ion counter (>1 MHz). This one grain (H-Kis 3.57-1) has a $^{20}$Ne/$^{22}$Ne-ratio of 11.8 - close to the neon isotopic composition of solar energetic particles (SEP, 11.2) and lies in a Ne three-isotope plot, on the mixing line from SEP to solar wind (SW, 13.8) composition. Furthermore, the $^3$He/$^4$He ratio of all grain batches is close to Solar Energetic Particle (SEP) composition. The element ratio $^4$He/$^{22}$Ne lies between air and solar. The isotopic composition of He and Ne in our chromite grains is clearly consistent with solar composition. As we will see in the discussion section, the solar noble gases clearly indicate the sediment dispersed chromite grains were small particles in interplanetary space and came to Earth as micrometeorites.

Several research groups measured solar noble gases in micrometeorites. Amari and Ozima (1985, 1988) measured He, Ne and Ar in bulk samples of micrometeorites extracted from deep-sea sediments. They found the Ne has solar composition (SEP and SW) with a minor contribution of cosmogenic nuclides. Olinger et al. (1990) extracted Ne with a similar composition in individual micrometeorites ($\phi ~0.1$ to 1 mm) from meltwater lakes on the Greenland ice sheet. The sediment-dispersed relict chromite grains studied here have a comparable noble gas composition (see discussion).

4. Discussion

As it turned out, chromites from the fossil meteorites analyzed here tell a different story than sediment-dispersed chromites, because their cosmogenic noble gases could be detected. We start with the two fossil meteorites and then pass into discussion of the sediment dispersed grains.

4.1 Gullhögen 001 and Brunflo

The short exposure age of the Gullhögen 001 meteorite is comparable to the unusually young ages of the suite of fossil meteorites found in the Ordovician sediments of southern Sweden. Remarkably, it fits smoothly into the age gradient determined from fossil meteorites of the
Fig. 3. $^{21}\text{Ne}$ exposure ages for fossil meteorites from the Gullhögen quarry at Billingens mountain (filled bars) and the Thorsberg quarry (empty bars). Ages of Gla 001 may be too low due to an unusually large preatmospheric size or moderate losses of cosmogenic Ne (see Heck et al. 2004 for discussion). Error bars are 1σ, and include weighing uncertainties, ion statistics, and blanks. Open circles are averaged $^{21}\text{Ne}$ exposure ages of all analyses from the same quarry bed. Ark, Arkeologen; Gol, Golvsten; Gla, Glaskarten; Sex, Sextummen; Tre, Tredje Karten; Gull, Gullhögen; Goda, Goda Lagret.
Thorsberg quarry (Fig. 3). Gullhögen 001 has been recovered from sediments belonging to the *Yangtzeplacognathus crassus* conodont Zone in the Gullhögen quarry, which encompasses the Tredje Karten and Sextummen sediment beds in the Thorsberg quarry. Its $^{21}\text{Ne}$-exposure age ($T_{\text{21}} = 0.88 \pm 0.10 \text{ Myrs}$) is similar to the one of fossil meteorite Tredje Karten 002 ($T_{\text{21}} = 0.86 \pm 0.09 \text{ Myrs}$) from Thorsberg (Heck et al. 2004). The age of the sediments from which Gullhögen 001 was recovered is therefore consistent with the sediment age of Tredje Karten. Exposure ages of the Sextummen meteorites recovered from the same conodont zone (but below Tredje Karten) are ~0.2 to 0.4 Myrs lower.

This is an additional confirmation for the progression of cosmic-ray exposure ages found in the Thorsberg sediment column and strongly suggests that the Ordovician sediments on the Gullhögen quarry also contain (many) meteorites from the L chondrite parent body break-up event ~480 Myrs ago.

The low exposure age of Brunflo (0.26 - 1.1 Myrs) is quite surprising for two reasons. First, if Brunflo is also of L chondrite composition and is therefore probably also a product of the L chondrite parent body event, one would expect *a priori* a ~5 Myr exposure age. Second, the large spread of cosmogenic noble gas concentrations of a factor 4 is much higher than for all other meteorites studied. Several facts suggest that Brunflo ages are doubtful. Diffusive loss is not very likely, because He- and Ne-ages correlate very well. We note, however, that much higher ZnO content (up to 12 wt%), compared to the fossil meteorites from the Thorsberg quarry (Schmitz et al. 2001), suggest much higher diagenetic alteration. Would this imply that some grains would have lost most of their cosmogenic He and Ne (although we do not see a correlation of cosmogenic gas content and ZnO concentration)? Whether the Brunflo chromite with the 1.1 Myr exposure age can have lost ~80% of its gas is unclear. An alternative explanation would be that Brunflo actually is a later fragment of the collisional cascade following the initial asteroid destruction event (W. Bottke, pers. comm.). If this would be the case indeed, it would mean that the age progression observed in Thorsberg would not be nicely continued in younger sediments, but the progression would be disturbed by secondary cascade material.

However, the fact that Brunflo is a special case does not affect conclusions drawn from the fossil meteorites of the Thorsberg quarry. The relatively constancy of the $^{3}\text{He}/^{21}\text{Ne}$ argues against gas loss by diffusion, where we would see preferential loss of light $^{3}\text{He}$. However large ZnO concentration of up to 12 weight-% would imply strong alteration.
4.2 Sediment-Dispersed Chromite Grains

4.2.1 Solar Noble Gases

Rather surprisingly, the sediment-dispersed extraterrestrial (ET) chromite grains are rich in solar gases. Unfortunately, this prevented us from achieving one of the primary goals of this study, the determination of cosmic-ray exposure ages of the sediment-dispersed grains. In a future study, this might be attempted by analyzing chromites whose outermost solar-gas bearing layers would have been etched off, such that only the cosmic-ray induced He and Ne component would remain. However, the solar noble gases by themselves tell an interesting story.

We discuss two possibilities for the origin of the solar-gas-rich grains. First, the grains could have acquired their solar noble gas as small particles in space. Alternatively, the grains could have been meteoritic regolith breccias, fragments of asteroidal or lunar regolith with high abundances of solar noble gases (Suess 1964). While residing on the planetary surface they acquire their solar noble gases by ion implantation from SW and SEP events. However, meteorites like this are rare – only about 3% of L chondrites (5.5% of LL chondrites) are regolith breccias (Bischoff & Schultz 2004). Thus, it would be unlikely that all analyzed SD grains from different sediment beds were fragments of L chondrite parent body regolith.

We therefore favor the first explanation that the grains, came to Earth as small, gas-rich particles and at least partially retained solar gases during ~480 Myr in marine sediments. Our observation that all our SD chromites contain solar noble gases is a confirmation that they are primary particles, e.g. in contrast to secondary particles as fragments from larger meteorites. The fact that HF acid has been used to isolate the chromites can well explain that their noble gas isotopic composition is closer to SEP than to the SW value. Since SW particles are less energetic than SEPs, they are only implanted in the outermost surface to a depth of about 30 nm (Tamhane & Argrowal 1979). Subsequently, we can suspect surface etching with HF acid released the SW prior to noble gas analysis. On the other hand, the more energetic SEPs have been implanted deeper into the grains – to a nominal depth of 30 µm (Wieler et al. 1986) – and are therefore better protected from surface etching and from erosional processes on the seafloor and in the sediment.

An important fraction of interplanetary dust particles (IDPs) collected from the stratosphere (e.g. Nier 1994) and micrometeorites (e.g. Olinger et al. 1990) contain solar noble gases. Therefore, we compare gas concentrations in our SD chromite grains with data from micrometeorites and IDPs from other studies (see Fig. 4).

Noble gas concentrations of our samples (Fig. 4) are much higher compared with concentrations measured in micrometeorites from Greenland (up to 100× for Ne; Olinger et al. 1990) and in
Fig. 4. $^{21}$Ne vs. $^{22}$Ne concentrations. (a) Our sediment-dispersed chromite grains have clearly higher gas concentrations than most of the micrometeorites (in the same mass-range as our chromites) retrieved from Greenland melt-water lakes by Olinger et al. (1990) with the exception of two samples from mount MMWU-1, which are comparable to our sample with the lowest concentration (H-Kis 5.50). In the lower panel (b) we show the same plot with a double-logarithmic scale to include samples from other studies having much lower and higher concentrations. At the lower end are measurements from magnetically separated bulk fractions from Quaternary Pacific deep-sea sediments by Amari & Ozima (1988). At the higher end are stratospheric IDPs analyzed by Nier & Schlutter (1990). See main text for explanations. Air and solar wind (SW) compositions are given as straight lines. All errors are 1σ and include analytical and mass uncertainties.
Pacific deep-sea sediments (up to ~300× for He, up to ~1000× for Ne; Amari & Ozima 1988). Our gas poorest chromites have comparable concentrations as the most gas-rich micrometeorites from Greenland (Olinger et al. 1990). Higher concentrations than in our samples have been measured in most stratospheric IDPs (up to 30× for He, up to ~100× for Ne; Nier & Schlutter 1990). Although, 3 IDPs from collector W7013 (Nier & Schlutter 1990) have lower 4He- and similar 20Ne concentrations compared to our SD chromites.

The micrometeorites from Greenland are retrieved from seasonal meltwater lakes (“Blue Lakes”) on the inland ice sheet, where they occur embedded in cryoconite, cocoons of blue-green algae (Olinger et al. 1990). While the most gas-rich of these samples are comparable to our gas-poorest samples, we can explain the up to two orders of magnitude lower gas-concentrations of the other samples by weathering of the particles in the ice and in the lakes and also by dilution through surface contamination of the particles with terrestrial material (Olinger et al. 1990). Moreover, their larger grain-size (ø 100 µm to 1 mm) results in a lower surface-to-volume ratio and is responsible for an already lower concentration of (surface-implanted) solar noble gases before atmospheric entry, than for our chromite grains (ø 80 to 100 µm). Dust particles in space experience a surface-correlated implantation of solar noble gases, therefore smaller particles contain higher concentrations than larger ones (concentration correlates with grain size with 1/r).

Extraterrestrial noble gases from Quaternary Pacific deep-sea sediments were extracted from a magnetically separated bulk fraction (Amari & Ozima 1988). The up to three orders of magnitude lower gas concentrations can be explained partly by gas loss through alteration of the noble gas carriers and diffusion of noble gases during sediment residence time (Amari & Ozima 1988). It is also reasonable to assume, that non-chromite noble gas carriers are more prone to alteration and consequential gas loss. Another reason for the lower concentrations compared is the fact that the magnetically separated fractions contained terrestrial particles (Amari & Ozima 1988) which diluted the extraterrestrial signal. The particle size (50 to 100 µm) was comparable to our chromites.

The higher noble gas concentrations found in stratospheric IDPs are not unexpected. Dust particles can be altered during atmospheric entry and during residence on Earth. Although, IDPs experience some gas loss during atmospheric entry heating (Flynn 1994) and possibly during impact with silicon-oil covered collector flags on airplanes, but they are spared from terrestrial alteration effects. They therefore retain a much higher fraction of solar noble gases than micrometeorites found on Earth’s surface.

As mentioned already, our SD chromite grains have a similar noble gas isotope composition than most of the Greenland micrometeorites, the Pacific deep-sea sediment noble gases and IDPs (Fig. 5). Their 4He/22Ne-ratios lie on a mixing line between solar and air composition. The 3He/4He-ratios of our chromites and of the samples used for comparison (except IDP U2015 B3 from Nier & Schlutter 1990) are lower than expected for pure mixing of solar and air
Fig. 5. (a) $^4\text{He}/^{22}\text{Ne}$- vs. $^3\text{He}/^4\text{He}$-ratios. Comparison of isotopic composition of our sediment dispersed chromite grains with micrometeoritic material measured by Olinger et al. (1990) and Amari & Ozima (1988), and with stratospheric IDPs studied by Nier & Schlutter (1990). The reason for samples located below the mixing line (dashed) of air and solar wind (SW) composition is most probably more pronounced $^3\text{He}$-loss by diffusion compared to $^4\text{He}$. (b) Comparison of $^{22}\text{Ne}$- vs. $^4\text{He}$-concentrations of the same samples. See main text for explanations. All errors are 1σ and include analytical and mass uncertainties.
components (Fig. 5a). The most probable reason is preferential loss of $^3$He probably during atmospheric entry heating, since a deviation from the air-SW mixing line has been observed for all samples by comparable amounts.

Davis et al. postulated already in 1979 that major collisions among asteroids produce large amounts of dust along with much larger collisional fragments. Model calculations by Dermott et al. (2002) predict a disruption of a large rubble-pile asteroid produces such a large amount of dust that Earth’s ET mass-accretion rate would be increased by two orders of magnitude over the average background. Their model prediction is matched by the high flux estimate for the Ordovician based on distributions of ET chromites.

4.2.2 Dynamical Constraints on the Lifetime of Dust from the Asteroid Break-Up

Do we expect similar delivery times for impact-generated dust particles as for meteoroid-size debris? We analyzed SD chromite grains with solar noble gases in the interval starting at the Arkeologen beds and ending in the ~ >2 Myr younger sediments 5.5 m above the Arkeologen bed. The base of the Arkeologen bed contains the first L chondritic chromite grains extracted from fossil meteorites and arrived on Earth just about a few hundred thousand years after being generated in the L chondrite parent-body break-up (Heck et al. 2004). Such a fast delivery for meteorites is expected if the asteroid collision occurred close to an important orbital resonance in the inner asteroid belt (Gladman et al. 1997, Zappalà et al. 1998). Two of the most important resonances are the 3:1 orbital resonance with Jupiter at about 2.5 AU and the nu6-resonance with Saturn and Jupiter which is a function of inclination and is located at 2 AU for orbits in the plane of the ecliptic and lies at 2.5 AU for orbits with ~20 degrees inclination (Farinella et al. 1993).

The life-time of dust particles in interplanetary space depends on several factors. Poynting-Robertson (P-R) light drag is of particular importance in delivering particles < 500 µm from the asteroid belt into the inner solar system (Dermott et al. 2002). The cratering record of the Long Duration Exposure Facility (LDEF) satellite experiment (Love and Brownlee 1993) suggest that large dust particles in the size range of ~100 to 200 µm with a peak at 140 µm dominate the dust population at the Earth’s orbit at 1 AU, comparable to the average grain-size of our SD chromite grains (ø 80-100 µm). The cause for this is the relatively long lifetime of these particles, which allows their orbits to be modified by gravitational resonances of giant planets and gravitational scattering by terrestrial planets (Dermott et al. 2002).
Using the following equation (eq. 50; Burns et al. 1979) we can roughly estimate the orbital decay time by P-R drag to be about 0.6 to 1 Myrs for chromite grains with 100 µm diameter:

$$T_{PR} = 400 \cdot \frac{R^2}{\beta}$$

Where the ratio between solar radiation pressure to gravity $\beta$ is

$$\beta = 0.57 \cdot \frac{Q_{PR}}{(p \cdot s)}$$

with $Q_{PR} \approx 1$ for particles with $>1$ µm radius, spherical particle radius $s \approx 50$ µm, density of particles $\rho_{Chromite} \approx 4.6$ g/cm³ and heliocentric distance $R$ in AU. We assume the heliocentric distance of the dust generation event is the location of the 3:1 and nu6-resonance ($R = 2.0-2.5$ AU).

Consequently, using this rough estimate of $T_{PR}$ of 0.6 to 1 Myrs, we do not expect to find 100 µm-sized dust from the L chondrite parent body events in sediments younger than 1 Myr relative to the Arkeologen beds where the first collisional debris have been deposited. However, we have to keep in mind that the extraterrestrial sedimentary record after the large asteroid collision depends on the nature of the event and the collisional cascade produced by it. There could be several second, third, or higher generation particles produced by collisions among larger bodies that would reach Earth some time after the first wave of debris has arrived. Hence, collisional debris – dust and larger meteorite-sized fragments – could be found in sediments conceivably younger than 1 Myr relative to Arkeologen (W. Bottke, pers. comm.).

We can also evaluate a solar wind exposure age and compare it to estimates of dynamical lifetimes. The dust grains were exposed to solar wind between 1 and 2 AU. Using our measured gas concentrations and assuming present-day solar wind flux (latest value from the Genesis space probe; A. Grimberg, pers. comm.) and composition (from Apollo SWC experiments; Geiss et al. 2004), our gas concentrations would lead to nominal solar wind exposure ages in the order of month and years. This is a very low nominal exposure age compared to dynamical lifetime estimates and suggests considerable gas loss – most probably due to atmospheric entry heating and alteration effects during terrestrial residence. Hence, the SW exposure age for our chromite grains does not set constraints on delivery times.
4.2.3 $^3$He Flux Signal in the Ordovician Bulk Sediments

Patterson et al. (1998) measured ET $^3$He in bulk samples from the 480 Myr old Ordovician limestones from the Thorsberg quarry. They did not detect an elevated ET $^3$He signal in the same chromite-bearing bulk sediments and determined the $^3$He flux to be indistinguishable from the average Cenozoic flux and.

This observation is not necessarily in conflict with the observation of a two orders of magnitude higher flux determined from fossil meteorites and SD chromite grains (Schmitz et al. 2001, 2003). We propose two reasons for these findings and discuss an explanation based on dynamical arguments. First, the chances to find ET $^3$He carrying chromite grains in small volume bulk sediment samples are low. Second, sedimentary processes have been responsible of removing small, usually more abundant, ET $^3$He carrying dust particles. Third, due to the short interplanetary lifetime of these smaller dust particles, the remaining ones would mainly concentrate at the base and are missing in the entire meteorite bearing sediment column.

Farley et al. 1998 attribute the bulk of the $^4$He carrier in marine sediments to be small (~7 µm) IDPs, in contrast to the relatively large 80-100 µm ET chromite grains studied here. All SD chromites analyzed in our present study contain copious amounts of solar noble gases including $^3$He. The chromite-richest strata, the base of the Arkeologen bed, contains about two chromite grains per kg of rock, leaving Patterson et al. only a 4 - 6 ‰ chance to include a chromite in their 2 - 3 g sediment samples. Since all other ET minerals have been altered during diagenesis (Schmitz et al. 2001), it is also expected that minerals in the suggested small, $^3$He-carrying IDPs have been completely replaced by pseudomorphs, loosing its ET gases. Very low concentrations of ET $^3$He in bulk fossil meteorites indeed points out to severe gas loss during diagenesis (Patterson et al. 1998). However, ET $^3$He has been detected in these bulk sediment samples corresponding to the concentration expected from the Cenozoic background flux. It would be a coincidence if the gas loss would (a) reduce the $^3$He concentration to exactly match the one expected produced by background dust accretion (Patterson et al. 1998) or (b) only affect the $^3$He carriers originating in the asteroid break-up event. It would also be unlikely if the asteroid collision did produce only dust particles above a size threshold of several dozen microns. The near-absence of the most fine-grained fraction of IDPs is explained by sedimentary processes. Because of prevailing currents in the water column only coarse-grained (> 1 mm) (terrestrial as well as extraterrestrial) material settled on the sea floor, leading to the condensed sediments found at Thorsberg. Weak currents that have sufficient hydrodynamic energy to remove 70-90% of all particles smaller than 5 µm, but only a small fraction of the particles in the size range of micrometeorites, and none of the macroscopic meteorites (>1 cm), a biased size distribution of ET matter at the sea floor is obtained.

An explanation for “missing” $^3$He in Ordovician sediments based on dynamical arguments would be that very fine-grained dust produced in the parent body break-up near an important
orbital resonance entered Earth’s atmosphere with an unfavorable angle and/or velocity, leading to preferential heating and degassing of small particles. Hence, not more small $^3$He-bearing IDPs than usual would have been deposited on Earth. This explanation would be supported by the prediction that during an asteroid collision, dust particles can be accelerated to higher velocities than larger fragments (Nesvorny et al. 2003). Additionally, the shorter dynamical lifetimes of small dust particles (on the order of tens of kyr; $T_{pr} \approx 25$ to 40 kyr for particles with $\sigma = 7$ µm and $\rho = 2.5$ g/cm$^3$ particles using eq. 50, from Burns et al. 1979, see above) would lead to a shorter period of deposition than for larger particles with a longer lifetime ($T_{pr} \approx 0.6$ to 1 Myr for $\sim 100$ µm-ø particles, $\rho = 4.6$ g/cm$^3$). Assuming an estimated average sedimentation rate of $\sim 2$ mm/kyr (Schmitz et al. 1996) we estimate the small IDPs would have been only deposited in a less than dm-thick section at the base of the Arkeologen bed, where the first arrivers after the collisions have been found. In younger sediments, most of the $^3$He seems to be contained in the larger ($\sigma \geq 80-100$ µm) chromite grains, which have a much smaller sampling probability when using bulk sediment samples.

In a similar study, Farley et al. (1998) found in much younger, $\sim 36$ Myr old, late Eocene sediment samples of similar mass ($\sim 2.5$ g), a $\sim 5 \times$ increase of the $^3$He-flux during $\sim 2.5$ Myr, coeval with the formation of the two large impact craters Popigai, Siberia and Chesapeake Bay, USA. They argued for an impulsive comet shower based on dynamical constraints on asteroidal dust delivery. However, new dynamical dust models (Nesvorny et al. 2003), and geochemical evidence from the Popigai impact ejecta (Kyte et al. 2004) and impactor (Tagle & Claeys 2005) convincingly points to an asteroid shower of L-chondrite composition. The cause for this ET flux increase was most probably a much less dramatic asteroid collision than in the Ordovician, since only few L chondrites show (parent body-) impact ages of less than 100 Myrs B.P. (Bogard 1995).

Many L chondrites have cosmic-ray exposure ages of $\sim 40$ Myr (Marti and Graf 1992, Wieler 2002), dating their release as meter-sized fragments into interplanetary space. A transfer time of $\sim 4$ Myr from the asteroid belt to Earth would be in the normal range for meteorites and hence could explain the formation of late Eocene impact craters by larger fragments. However, the short dynamical lifetime of small dust particles ($T_{pr} < 50$ kyr) due to Poynting-Robertson drag would speak against generation of dust $\sim 4$ Myr before its deposition on Earth. On the other hand, a smaller asteroid collision near an orbital resonance in the inner asteroid belt could explain the simultaneous delivery of dust and larger fragments to Earth (Dermott et al. 2002) for the late Eocene event, analogous to the large asteroid break-up in the Ordovician.
5. Conclusions

1. New cosmogenic helium and neon production rates in chromite have been determined experimentally and essentially confirm the low cosmic-ray exposure ages of fossil meteorites found in Ordovician sediments of southern Sweden.

2. The meteorite Gullhögen 001 has a very low cosmic-ray exposure age, which falls in line with the ages of other fossil L chondrites recovered from the same sediment strata in southern Sweden. This meteorite is most likely also a fragment of the major asteroid collision which disrupted the L chondrite parent body ~480 Myrs ago.

3. The meteorite Brunflo has also a comparably low exposure age and gives highly variable results, making it a special case. This does not affect conclusions drawn from the other fossil meteorites.

4. The sediment-dispersed ET chromite grains found in Ordovician sediments in Southern Sweden are rich in solar gases and were generated as dust in the L chondrite parent body break-up event.

5. The solar noble gases have been partially retained in ET chromite grains embedded in ~480 Myr old limestone and survived diagenetic processes. The gas concentrations are comparable to the most gas-rich micrometeorites from Greenland melt-water lakes and to the most gas-poor stratospheric IDPs.

7. GCR-produced noble gases were not detectable in the sediment-dispersed ET chromites due to copious amounts of solar noble gases. Sediment dispersed chromites can therefore not be used for cosmic-ray exposure age dating using the same method used for chromites from fossil meteorites.

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References


VI. Helium and Neon in Interplanetary Dust Particles
Helium and Neon in Stratospheric Interplanetary Dust Particles from Collector W7030B

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Abstract

We present helium and neon concentrations and compositions of six stratospheric interplanetary dust particles (IDPs). This is a preliminary study in preparation of a project to investigate “cluster IDPs” to gain a better understanding of their unusual helium isotopic composition found in previous studies. Our preliminary experiments show that the six non-cluster IDPs we analyzed have comparable noble gas compositions and concentrations to non-cluster IDPs reported in the literature. We show that our experimental approach is well suited to study He and Ne isotopes in single IDPs.

1. Introduction

In a preliminary study we measured helium and neon isotopes in six individual stratospheric interplanetary dust particles (IDPs) at the Noble Gas Laboratory of ETH Zurich. The particular interest in IDPs stems from the fact, that part of them originates from comets. Because the latter formed as small objects in the cooler regions of the solar nebula (see chapter 1, §3.7.2 ), they incorporated more volatile elements than the asteroids which formed in hotter regions. Comets are also thought to have experienced less alteration after their formation. Cometary IDPs therefore represent the most primitive solar system material available to study in the laboratory (Brownlee 1985; Zolensky et al. 1994; Rietmeijer 1998) and have the potential to serve as archives for early solar system events (e.g. Pepin et al. 2000). Noble gases in IDPs have among the highest known concentrations of all solid samples and are primarily solar wind (SW) implanted helium and neon. The SW-like composition of the noble gases extracted from IDPs has been used to demonstrate their extraterrestrial origin.

The analyses presented below served mainly as a pilot study for noble gas analyses of so-called cluster IDPs with anomalously high $^{3}\text{He}/^{4}\text{He}$ ratios. Cluster IDPs are considered to be fragments of large IDPs, which shattered upon impact onto the stratospheric dust collector plates. Two unusual and interesting observations deserve further investigation. First, very
elevated $^3$He/$^4$He ratios (> 40× higher than solar wind) have been measured in a suite of cluster IDPs, in particular from collector L2011, by Nier & Schlutter (1993) and are difficult to explain. Second, most of these cluster IDPs have unusually low $^4$He concentrations. The low $^4$He content found in most cluster IDPs has been attributed to a short exposure to the solar wind. Since the exposure of collector L2011 coincided with the arrival of dust from Comet Schwassmann-Wachmann-3, Messenger and Walker (1998) suggested, that these low-$^4$He-IDPs actually originate from this particular comet (see also Kehm et al. 1999). This suggestion was also supported by dynamical arguments. The first observation is more difficult to explain. The $^3$He excess in cluster IDPs cannot be explained by cosmic-ray produced $^3$He, since the required exposure time to obtain the measured concentrations would by far exceed the maximal dynamical lifetime of IDPs (Pepin et al. 2001). These authors therefore proposed that the excess $^3$He might have been acquired from an intense low-energy $^3$He-rich radiation in the solar nebula or in the presolar molecular cloud.

From a noble gas perspective, cluster particles may thus be the most interesting IDPs to study. As Messenger and Walker (1998) and Pepin et al. (2001) stated, their hypotheses require further investigation, mainly by the extension of the database on cluster IDP noble gases. We planned to analyze cluster IDPs from the same collectors in order to reproduce the findings by Nier & Schlutter (1993). Our main objective would be the determination of cosmic-ray produced $^{21}$Ne in these IDPs, which can precisely measured with our ultra-high sensitivity mass spectrometer (Baur 1999) and would allow to estimate the amount of cosmogenic $^3$He. This would enable us to assess the cosmogenic contribution to the observed $^3$He excess.

To test feasibility and to optimize our analytical procedure to IDPs, we measured six non-cluster IDPs from another collector surface (W7030B). Unfortunately, due to time constraints on thesis submission, we were not able to continue this exciting project for the time being.

2. Samples & Experimental

The IDPs for our study were collected with high-flying NASA aircraft in about 20 km altitude using collection devices coated with high-viscosity silicone oil (Warren & Zolensky 1994). The silicon layer served as the impact medium. The IDPs were prepared at the University of Washington in Seattle. To remove residual silicon oil, the particles were washed with ultra-pure hexane. Using a micromanipulator they were mounted onto a gold foil placed on an Al sample holder. Masses were estimated at the University of Washington. Prior to noble gas analysis they were inspected in Seattle and Zurich with SEM/EDX. The SEM images shown in Fig. 1 were acquired at the Institute of Particle Physics of ETH Zürich.

To analyze He and Ne isotopes in single IDPs, we used the ultra-high sensitivity mass
spectrometer (Baur 1999) at ETH Zurich in conjunction with IR laser extraction of noble gases, as described in the “methods” chapter. Due to the generally volatile-element-rich nature of IDPs, special care needs to be taken to only gently increase laser energy for heating, in order to prevent explosive release of gases, which would propel the grains away before completely degassing them. Despite the special care taken, one grain (WHeA-1) jetted away during laser heating and most probably degassed only partially.

Table 1. Identification, size and mass of the six IDPs studied.

<table>
<thead>
<tr>
<th>Particle Name</th>
<th>Collector flag and particle ID</th>
<th>Size (µm)</th>
<th>Mass (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHeA-1</td>
<td>W7030B-2D</td>
<td>10 × 7</td>
<td>0.8</td>
</tr>
<tr>
<td>WHeA-2</td>
<td>W7030B-4A</td>
<td>11 × 9</td>
<td>1.2</td>
</tr>
<tr>
<td>WHeA-3</td>
<td>W7030B-4C</td>
<td>9 × 5</td>
<td>0.53</td>
</tr>
<tr>
<td>WHeA-4</td>
<td>W7030B-4G</td>
<td>12 × 10</td>
<td>0.50</td>
</tr>
<tr>
<td>WHeA-5</td>
<td>W7030B-4J</td>
<td>12 × 10</td>
<td>0.99</td>
</tr>
<tr>
<td>WHeA-6</td>
<td>W7030B-5B</td>
<td>5 × 5</td>
<td>0.32</td>
</tr>
</tbody>
</table>

3. Results & Discussion

Both, He and Ne isotopes from our W7030B IDPs were analyzed, except for WHeA-1, which jetted away before complete melting and only He was released in sufficient amounts to be detectable (results are shown in Tab. 2). Gas amounts measured were clearly above blanks, up to two orders of magnitude for He. Isotopic ratios for the five completely degassed grains indicate the measured He and Ne is primarily solar. In particular, as can seen in Fig. 2a, the Ne is a mixture between the solar and atmospheric Ne, whereby the solar Ne itself may be a mixture of the surface-implanted SEP and SW, as expected. The cosmogenic component (GCR) is basically negligible. The He isotopic composition is between SW and SEP composition with no recognizable dilution by air for all samples expect for WHeA-1 (Fig. 2b). The latter, partially degassed sample shows contamination by air He.

Helium concentrations range from $(0.0005$ to $0.096) \times 10^{-3}$ cm$^3$ STP g$^{-1}$ for $^3$He and from $(2.6$ to $342) \times 10^{-3}$ cm$^3$ STP g$^{-1}$ for $^4$He. The $^3$He/$^4$He ratios of all of our 5 fully degassed samples are in the range of $(2.8$ to $5.0) \times 10^{-4}$ (Tab. 2). The ratios and concentrations are in a similar range.
Fig. 1. SEM images of the small IDPs analyzed from collector surface W7030B. Image quality is limited due to charging of the samples during SEM imaging.
Fig. 2. (a) Neon three-isotope plot for the 5 IDPs from collector W7030B where we measured Ne (HeA2 to HeA6). For comparison, we plot IDPs from collectors W7013 and U2015 measured by Nier & Schlutter 1990. Reference compositions are plotted for solar wind (SW; Geiss et al. 2004), solar energetic particle (SEP; Benkert et al. 1993) and Earth’s atmosphere (Air; Eberhardt et al. 1965). (b) Log-log plot of $^4$He vs. $^3$He concentration for all 6 IDPs from collector W7030B we studied. Four of our samples are located between the dashed line indicating solar wind composition (SW) and the dotted line showing solar energetic particle (SEP) composition. WHeA-1 jetted away during heating and only partially degassed. We compare our data with previous studies of 2 IDPs from collector W7013, 4 IDPs from U2015 and 1 IDP from W7069 (Nier & Schlutter 1990). In addition we show data of 12 cluster IDPs from collector L2011, which have unusually high $^3$He/$^4$He ratios (Nier & Schlutter 1993). All errors are 1σ and include analytical uncertainties.
as values reported for stratospheric IDPs studied by Nier & Schlutter (1990) from collectors W7013, U2015 and W7069, where only one of their grains (U2015 A5) has unusually high $^3\text{He}/^4\text{He}$ ratio due to its relatively high $^3\text{He}$ concentration (see Fig. 2b). By contrast, our samples have higher $^4\text{He}$ concentrations than most of the cluster IDPs from collector L2011, which have been analyzed by Nier & Schlutter (1993). The latter mostly have unusually high $^3\text{He}/^4\text{He}$ ratios, with the maximum ratio $40\times$ above our highest one (see also “The Excess Helium-3 Problem” in Pepin et al. 2000).

Neon concentration of our samples range from $(0.4$ to $3.1) \times 10^{-3}$ cm$^3$ STP $^{20}\text{Ne}$ g$^{-1}$ and fall in the range of concentrations found in Nier & Schlutter’s (1990) W7013, U2015 and W7069 particles $(0.06$ to $5.7) \times 10^{-3}$ cm$^3$ STP $^{20}\text{Ne}$ g$^{-1}$. Our samples have clearly more Ne than the excess-$^3\text{He}$-cluster IDPs from L2011 $(0.05$ to $0.2) \times 10^{-3}$ cm$^3$ STP $^{20}\text{Ne}$ g$^{-1}$ (Nier & Schlutter 1993).

Table 2. Masses, gas concentrations and isotopic ratios measured in the IDPs from collector W7030B.

<table>
<thead>
<tr>
<th>Particle name</th>
<th>Mass (ng)</th>
<th>$[^4\text{He}]$ (cm$^3$ STP g$^{-1}$)</th>
<th>$[^3\text{He}/^4\text{He}]$ (10$^{-4}$)</th>
<th>$[^{20}\text{Ne}]$ (10$^{-3}$ cm$^3$ STP g$^{-1}$)</th>
<th>$[^{20}\text{Ne}/^{22}\text{Ne}]$</th>
<th>$[^{21}\text{Ne}/^{22}\text{Ne}]$ (10$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHeA-1</td>
<td>0.8</td>
<td>8.03 ± 0.78</td>
<td>0.67 ± 0.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WHeA-2</td>
<td>1.2</td>
<td>4.76 ± 0.53</td>
<td>4.98 ± 0.69</td>
<td>0.64 ± 0.01</td>
<td>11.57 ± 0.34</td>
<td>3.38 ± 0.20</td>
</tr>
<tr>
<td>WHeA-3</td>
<td>0.53</td>
<td>11.7 ± 1.5</td>
<td>2.87 ± 0.48</td>
<td>0.87 ± 0.02</td>
<td>9.83 ± 0.28</td>
<td>2.83 ± 0.26</td>
</tr>
<tr>
<td>WHeA-4</td>
<td>0.5</td>
<td>81.8 ± 1.8</td>
<td>3.64 ± 0.19</td>
<td>0.81 ± 0.03</td>
<td>9.82 ± 0.44</td>
<td>3.30 ± 0.32</td>
</tr>
<tr>
<td>WHeA-5</td>
<td>0.99</td>
<td>2.60 ± 0.54</td>
<td>3.9 ± 1.0</td>
<td>0.40 ± 0.01</td>
<td>10.47 ± 0.39</td>
<td>2.62 ± 0.31</td>
</tr>
<tr>
<td>WHeA-6</td>
<td>0.32</td>
<td>342.1 ± 1.7</td>
<td>2.81 ± 0.11</td>
<td>3.05 ± 0.05</td>
<td>10.91 ± 0.27</td>
<td>2.91 ± 0.11</td>
</tr>
</tbody>
</table>

4. Conclusions

We show that single grain IDP analysis is feasible with the experimental methods used in our laboratory. The composition of the noble gases from the W7030B IDPs are comparable to compositions found in previous studies on stratospheric IDPs and indicate noble gas implantation by SW and SEP is the most probable trapping mechanism. It is highly desirable to continue this study with cluster IDPs, to gain a better understanding of the “Excess Helium-3 Problem”. Our
observations prove, that promising samples such as precious cluster IDPs or dust that will be returned to Earth from space probes such as with NASA’s Stardust mission can potentially be successfully analyzed with the methods described in this thesis.

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References


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* * *

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## Curriculum Vitae

**Philipp Reza Heck**

<table>
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<tr>
<th>Date</th>
<th>Event Description</th>
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<tbody>
<tr>
<td>1980 – 1986</td>
<td>Primary school in Zollikerberg, Switzerland</td>
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<tr>
<td>1987 – 1989</td>
<td>Secondary school (Sekundarschule) in Zürich, Switzerland</td>
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<tr>
<td>1989 – 1995</td>
<td>High School (Gymnasium) in Zürich with Matura (Abitur) of Type E</td>
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<td>1995 – 1996</td>
<td>Studies of Physics at the Université de Genève, Switzerland</td>
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<tr>
<td>1996 – 2001</td>
<td>Studies of Earth Sciences at ETH Zürich; Diploma in Natural Sciences (Dipl. Natw. ETH; M.Sc.)</td>
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<td></td>
<td>Diploma/Master thesis at the Geology Institute, ETH Zürich, under supervision of Prof. Dr. Flavio Anselmetti and Prof. Dr. Judith McKenzie: <em>Surface and Sub-Surface Sediments and Ferromanganese Crusts from Marion Plateau (North-East Australian Margin)</em></td>
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<tr>
<td>2002 – 2005</td>
<td>Doctoral work under the direction of Prof. Dr. Rainer Wieler at the Institute of Isotope Geology and Mineral Resources, ETH Zürich</td>
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