Doctoral Thesis

Zirconium isotope cosmochemistry

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„Zirconium isotope cosmochemistry”

A dissertation submitted to the
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Abstract

Radionuclides with half-lives of less than 100 million years were present when the solar system formed 4.56 Gyr ago. In the meantime, these nuclides have decayed and are now essentially extinct. The prior existence of these radionuclides can be inferred from variations in the relative abundances of their daughter isotopes in sufficiently old samples, such as meteorites. Due to their short half-life, they provide the best available isotopic constraints on the chronology of nebular and planetary events in the early solar system. They also offer insights into the nucleosynthetic processes that contributed to the presolar molecular cloud shortly before its collapse.

This study is an investigation of the extinct radionuclide $^{92}\text{Nb}$, which decays to $^{92}\text{Zr}$ with a half-life of 36 ± 3 million years. The initial abundance of $^{92}\text{Nb}$ (expressed as $^{92}\text{Nb}/^{93}\text{Nb}$) has been a matter of debate and current estimates range from about $10^{-5}$ to $10^{-3}$. In this study, internal Nb-Zr isochrons were determined for the ordinary chondrite Estacado, the eucrite Juvinas and a silicate clast of the mesosiderite Vaca Muerta. The isochrons for all three meteorites define an initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of about $10^{-5}$. This provides strong evidence that the solar system started with a $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of less than $3 \times 10^{-5}$. Zirconium isotopic data combined with Nb/Zr ratios for calcium-aluminium-rich inclusions (CAI) of Allende and bulk eucrites support such a low initial abundance of $^{92}\text{Nb}$.

Also investigated were eleven lunar basalts and internal Nb-Zr isochrons were determined for the two early highland rocks 60025 and 77215. No Zr isotopic variations were found and thus there is no evidence for the former existence of live $^{92}\text{Nb}$ on the moon. The most likely reason for the uniform Zr isotopic compositions of lunar samples is that there was only modest Nb/Zr fractionation, even in the ilmenite-rich source regions of high-Ti basalts. The Nb/Zr ratios of lunar ilmenites and bulk rock samples only vary by a factor of two to three relative to the chondritic value. This indicates that lunar reservoirs with strongly fractionated Nb/Zr did not form.

An initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of the solar system of < $3 \times 10^{-5}$ combined with a modest Nb-Zr fractionation greatly limits the utility of the $^{92}\text{Nb}$-$^{92}\text{Zr}$ decay system. The chronometer cannot be used to draw conclusions about the timing of the early differentiation history of the Earth and Moon. Furthermore, the low initial abundance of $^{92}\text{Nb}$ does not constrain the site of $p$-process nucleosynthesis, where $^{92}\text{Nb}$ was formed.
Precise Zr isotopic measurements were also performed for carbonaceous, ordinary and enstatite chondrites, eucrites, a mesosiderite and terrestrial samples to study the isotopic homogeneity of the solar nebula. All bulk rock samples yield isotopic compositions that are identical to the terrestrial standard. This provides evidence that the solar nebula was well mixed at the bulk rock and larger scale. However, there is evidence for heterogeneities at a smaller scale in carbonaceous chondrites. Some CAIs from Allende and certain metal-rich phases of Renazzo display small excesses of $r$-process $^{96}\text{Zr}$. This effect is even more pronounced in the first leachates that were obtained by the stepwise dissolution of the carbonaceous chondrites Allende, Murchison and Orgueil. Excess $^{96}\text{Zr}$ is most distinctive in the acetic acid fraction and this indicates the presence of $r$-process components in an unidentified carrier phase presumably of presolar origin that is easily leachable. In addition, the final dissolution steps of these experiments also revealed $s$-process components, which are characterised by depletion in $^{96}\text{Zr}$. Known varieties of presolar grains (graphite and SiC) could account for these anomalies, although other presolar or solar phases cannot be excluded.

These data imply that distinct nucleosynthetic components which survived the formation of the solar system were partially preserved in carbonaceous chondrites in easily soluble phases. This complements the in-situ isotopic data for acid-resistant presolar grains from previous studies. Taken together, these results provide evidence that the solar system was formed from a thoroughly homogenised mixture of cold material derived from various nucleosynthetic sources. The precursor material included $r$- and $s$-process components that were distributed homogeneously at a bulk rock or larger scale. Isotopic heterogeneity is only preserved at a smaller scale in primitive meteorites.
Zusammenfassung


Diese Studie ist der Erforschung des kurzlebigen Radionuklides $^{92}$Nb gewidmet, welches mit einer Halbwertszeit von 36 ±3 Millionen Jahre zu $^{92}$Zr zerfällt. Die „initiale“ Häufigkeit von $^{92}$Nb (ausgedrückt in $^{92}$Nb/$^{93}$Nb) zu Beginn des Sonnensystems ist umstritten und aktuelle Schätzungen liegen im Bereich von $10^{-5}$ bis $10^{-3}$. In dieser Arbeit wurden interne Nb-Zr Isochronen für den gewöhnlichen Chondrit Estacado, für den Eukrit Juvinas und für einen silikatischen Klast des Mesosideriten Vaca Muerta bestimmt. Die Isochronen dieser drei Meteorite definieren ein initiales $^{92}$Nb/$^{93}$Nb-Verhältnis von ungefähr $10^{-5}$. Diese Beobachtung legt nahe, dass das Sonnensystem ein initiales $^{92}$Nb/$^{93}$Nb-Verhältnis von weniger als $3 \times 10^{-5}$ aufwies. Die Zr-Isotopenzusammensetzung und Nb/Zr-Verhältnisse für Kalzium-Aluminium-reiche Einschlüsse (CAI) des Meteoriten Allende sowie Gesamtgesteinsanalysen an Eukriten liefern weitere Hinweise für eine niedrige initiale Häufigkeit des Radionuklides $^{92}$Nb.

Ein initiales $^{92}$Nb/$^{93}$Nb-Verhältnis des Sonnensystems von weniger als $3 \times 10^{-5}$ und die geringe Nb-Zr Fraktionierung schränken die Anwendungsmöglichkeiten des $^{92}$Nb-$^{92}$Zr Zerfallssystems drastisch ein. Dieses chronometrische System kann nicht dafür benützt werden, Entwicklungen auf der frühen Erde und dem Mond zu datieren. Ausserdem erlaubt es die geringe initiale Häufigkeit von $^{92}$Nb nicht, Rückschlüsse auf den Ort zu ziehen, an dem die $p$-Prozess Nukleosynthese vom $^{92}$Nb stattfand.


Chapter 1

Introduction
1.1 Extinct radionuclides

The main part of this thesis is dedicated to investigation of the extinct radionuclide $^{92}\text{Nb}$, which decays to $^{92}\text{Zr}$ with a half-life of 36 Myr. Extinct radionuclides offer new and often unique insights into exciting topics such as stellar nucleosynthesis, solar nebula processes and the formation of the solar system. The characteristic feature of extinct radionuclides are their short half-lives, which range between about $10^5$ to $10^8$ Myr. This is long enough to survive the time interval between nucleosynthesis and the formation of solids in the solar system, but short enough to almost completely decay away such that they are now essentially extinct in the solar system.

The first evidence for the former existence of an extinct radionuclide in the solar system was provided by Reynolds (1960), who discovered excess $^{129}\text{Xe}$ in the Richardton meteorite. It was subsequently shown that this excess is correlated with the I/Xe ratios of the sample and this is indicative of the former presence of the short-lived radionuclide $^{129}\text{I}$. Later advances in analytical techniques and the sampling of more meteoritic materials have led to the discovery of more than 10 additional short-lived radionuclides that were alive in the early solar system (Table 1.1). Hints for the presence of formerly live $^{92}\text{Nb}$ were first reported by Harper (1996) for rutiles from the iron meteorite Toluca. Other studies confirmed the occurrence of $^{92}\text{Nb}$ in the early solar system based on the discovery of $^{92}\text{Zr}$ anomalies for calcium-aluminium-rich inclusions (CAI) and other samples (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000).

Extinct radionuclides are used to trace and date processes that occurred in the early solar system. These applications are discussed in the following sections and a brief overview of solar system formation is given. Subsequently, this chapter provides an introduction to stellar nucleosynthesis and it outlines how such processes can be studied with the help of extinct radionuclides.

<table>
<thead>
<tr>
<th>Table 1.1: Extinct radionuclides in early solar system materials</th>
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</thead>
<tbody>
<tr>
<td>Parent</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>$^{41}\text{Ca}$</td>
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<tr>
<td>$^{26}\text{Al}$</td>
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<tr>
<td>$^{60}\text{Fe}$</td>
</tr>
<tr>
<td>$^{10}\text{Be}$</td>
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<tr>
<td>$^{53}\text{Mn}$</td>
</tr>
<tr>
<td>$^{107}\text{Pd}$</td>
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<tr>
<td>$^{182}\text{Hf}$</td>
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<tr>
<td>$^{129}\text{I}$</td>
</tr>
<tr>
<td>$^{92}\text{Nb}$</td>
</tr>
<tr>
<td>$^{244}\text{Pu}$</td>
</tr>
<tr>
<td>$^{146}\text{Sm}$</td>
</tr>
</tbody>
</table>
1.2 Extinct radionuclides as chronometers

Since an extinct radionuclide cannot be measured directly today in solar system material, its former existence can only be inferred from suitable samples that display variations in the relative abundances of the radiogenic daughter isotope. Such variations must correlate with the parent/daughter elemental ratio, if the isotopic anomalies are indeed due to the decay of the parent nuclide in the early solar system. This is because variations in the relative abundance of an isotope can also be produced by processes other than the radioactive decay. They may be of nucleosynthetic origin, or they can be generated by exposure to cosmic rays. Anomalies may also be due to “cosmochemical memory” in a particular sample. For example, a presolar grain that forms in the vicinity of a star may incorporate live $^{26}\text{Al}$. The $^{26}\text{Al}$ is assumed to decay to $^{26}\text{Mg}$ before the grain becomes part of the solar nebula. If the grain survives the formation of the solar system, it will display an isotopic anomaly in $^{26}\text{Mg}$, that is not due to the presence of live $^{26}\text{Al}$ in the early solar system.

The most reliable evidence for the former existence of an extinct radionuclide in the solar system is provided by internal isochrons. The determination of such an isochron requires a sample with a co-genetic suite of mineral phases that have remained undisturbed since their formation. Furthermore, the phases must display variation in the parent/daughter elemental ratios. If this is the case, the mineral phases will plot on a single straight line or “isochron” in the diagram of isotope versus elemental ratio (Fig. 1.1). The equation of the isochron for the extinct decay system of $^{92}\text{Nb}-^{92}\text{Zr}$ is:

$$\left(\frac{^{92}\text{Zr}}{^{90}\text{Zr}}\right)_{\text{meas}} = \left(\frac{^{92}\text{Zr}}{^{90}\text{Zr}}\right)_{\text{ini}} + \left(\frac{^{92}\text{Nb}}{^{93}\text{Nb}}\right)_{\text{ini}} \times \left(\frac{^{93}\text{Nb}}{^{90}\text{Zr}}\right)$$

where “meas” indicates the measured ratio and “ini” denotes the initial ratios of the sample. The slope of the isochron yields the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of the sample. If the sample formed very early, this initial ratio will also be close to the initial abundance of the radionuclide of the solar system. The comparison of the slope of an isochron for one object with that of another object yields a relative formation age. However, this is only the case if both objects formed from an identical homogeneous reservoir. It is difficult to show that a reservoir was indeed homogeneous, because for any short-lived decay system the parent isotope is now extinct. Inhomogeneities in the abundance of the parent, therefore, manifest themselves only indirectly as anomalies in the isotopic composition of the daughter element. Furthermore, if there are
indications for an inhomogeneous distribution, it is not obvious whether it is the daughter element or the parent nuclide, which is isotopically anomalous. There are ongoing discussions as to whether both $^{26}$Al and $^{53}$Mn were distributed inhomogenously in the solar system (MacPherson et al., 1995; Shukolyukov and Lugmair, 2000).

1.3 Extinct radionuclides and solar system evolution

Solar system evolution usually is defined as starting with the collapse of a cold molecular cloud about 4.6 billion years ago. The cloud became unstable and contracted under the influence of its own gravity. A centrally condensed proto-star was born, surrounded by a rotating ring of gas and dust. From this dusty nebular matter the planetary objects of the solar system formed. Initially, this happened because micron sized objects stuck together and coagulated. At a later stage, larger objects formed through collisions and gravitational attraction, and this finally led to the runaway growth of a few large proto-planets. Planetesimals with a diameter of $> 500$ km and the planets of the inner solar system differentiated into metallic cores and silicates-rich mantles. Differentiation requires large-scale melting and the heat for this was probably provided by the gravitational energy released during accretion and the decay of radionuclides.

Meteorites are the oldest witnesses of early solar system history. They can be divided into two main groups, namely the chondrites which are primitive and undifferentiated and another group of more evolved, differentiated meteorites including the achondrites and iron meteorites (see Table 1.2). Only chondritic meteorites have preserved presolar material from the solar nebula and hence they are most suited for the study of nucleosynthetic and solar nebula processes. Furthermore, they contain calcium-aluminium rich inclusions (CAI), which are generally believed to be the first condensates of the solar nebula (Grossman, 1972). Most chondrites were subsequently affected by secondary processes such as aqueous alteration and thermal metamorphism, which occurred within parent planetesimals. Nevertheless, their chemical composition was not significantly altered and it is
similar to that of our sun. Carbonaceous chondrites, in particular, are considered to reflect the chemical composition of unprocessed solar system material that has not been significantly fractionated by volatile loss, metal fractionation or silicate melting. Differentiated meteorites, in contrast, have a chemical composition distinct from unprocessed solar system material. Achondrites, for example, are silicate-rich, mafic or ultramafic objects of igneous origin, while many iron meteorites are considered to be the remains of metallic cores of small asteroidal bodies.

Processes that took place in the early solar system can be dated using radionuclides. The absolute age of the solar system, which is about 4600 Myr, is based on studies that applied long-lived decay systems such as the U-Pb, Rb-Sr or Sm-Nd to meteorites. Extinct radiometric systems cannot provide absolute ages but superior relative chronological information with a resolution of about ±1 Myr, for processes that occurred in the early solar system. Only the relatively short half-life of the still extant $^{235}$U ($t_{1/2}=704$ Myr) allows the U-Pb system to achieve a similar resolution. Because extinct radionuclides do not provide absolute ages they need to be calibrated relative to an absolute time-scale. This can be done by linking the relative age information provided by extinct nuclides to an absolute U-Pb age. However, it has to be considered that different decay systems do not necessarily date the same event. On one hand, this complicates
the linking and comparison of different chronometers. On the other hand, this provides an opportunity to date different events that occurred in the early solar system such as accretion, differentiation and parent-body processes including alteration and metamorphism.

The oldest available solar system materials are CAIs, which have Pb-Pb ages of 4568.0 ± 0.4 Myr (Amelin et al., 2002). The contraction of the proto-sun cannot have started much earlier, since CAIs have a refractory chemistry similar to that expected for the first material that condenses from a cooling nebula of solar system composition. The early formation of CAIs is further supported by the presence of 26Mg from the decay of the short-lived radionuclide 26Al, which has a half-life of only 0.7 Myr (see MacPherson et al., 1995 for review).

Evidence for fast evolution of the early solar system is provided by extinct radionuclides in general. Age data for many different meteorites indicates that planetesimal differentiation was well underway within 2-10 Myr of the condensation of the first solids from the nebula (Carlson and Lugmair, 2000). While formation and differentiation of the planets was ongoing or perhaps even finished, another major event took place in the early solar system: the birth of the Earth’s moon. The most widely accepted model for the formation of the moon is a giant impact. This theory proposes that there was a collision between the Earth and a body of at least the size of Mars during the later stages of terrestrial accretion (Stevenson, 1987; Cameron and Benz, 1991). This collision generated hot debris from which the moon formed. According to various interpretations of isotopic data for the extinct 182Hf-182W decay system, this event took place between 30 and 60 Myr after the formation of the solar system (Lee et al., 2002; Kleine et al., 2003), although the exact age is the subject of current dispute (Halliday et al., 2003; Kleine et al., 2003).

1.4 Stellar nucleosynthesis

Extinct radionuclides are not only useful as early solar system chronometers, they also provide important constraints on stellar nucleosynthesis and the formation of the solar system. Since the Big Bang, the chemical elements have been produced either within stars during different episodes of their evolution or by spallation reactions in the interstellar medium and around stars. The light elements with atomic masses < 11 amu were predominately formed either just moments after the Big Bang (4He, 7Li) or later by spallation (7Li, 9Be, 10B and 11B). Elements with atomic masses between 12 and 56 amu are generated by nucleosynthetic reactions occurring at different
stages of stellar evolution. The mechanisms change with increasing stellar temperatures. The
evolution starts with hydrogen burning, but given a sufficient size of a star, it will develop through
a sequence of C-, Ne-, O- and Si burning cycles. However, elements with atomic masses >56 amu
cannot be generated by these fusion reactions because the nuclear binding energy per nucleon
reaches a maximum for $^{56}$Fe. For the formation of elements heavier than Fe, three additional
processes are required:

(1) The $s$-process involves neutron capture in a stellar environment with relatively low neutron
fluxes. Therefore, if the neutron irradiation produces isotopes with short half-lifes, they will
decay by $\beta$ emission before other neutrons are captured. This limits the nuclides that can be
produced by the $s$-process to the most stable isotopes of heavier elements and it terminates
with $^{205}$Tl and $^{206}$Pb. The $s$-process is thought to occur predominantly in AGB (Asymptotic
Giant Branch) stars. These are massive stars, advanced in their evolution, that lie on the
asymptotic giant branch in the Hertzsprung-Russell diagram (surface temperature of stars
against luminosity, e.g. Pagel (1997)).

(2) The $r$-process occurs at higher neutron fluxes. As a consequence, slightly unstable nuclei
do not have the time to $\beta$ decay before further neutron capture. Neutron-rich nuclei are thus
produced during this rapid process, which is believed to take place in some types of super-
nova. However, in the past decade alternative sites have been suggested, such as a neutrino-
heated atmosphere surrounding newly formed neutron stars (Wallerstein et al., 1997).

(3) The $p$-process produces nuclides that cannot be formed by neutron capture. They lie on the
proton-rich side of the $s$-process path and include, for example, the short-lived radionuclides
$^{92}$Nb and $^{146}$Sm. The existence of these nuclei are explained either by proton-irradiation or
by photo-disintegration of neutrons at high temperatures ($> 2 \times 10^9$ K) in the outer regions
of a supernova explosion.

One additional process exists, the $e$-process. It takes place just prior to a supernova explosion and
it enhances the abundance of Fe and the neighbouring transition metals (Wallerstein et al., 1997).
The isotopes of Zr are predominantly formed by either the $s$-process or $r$-process. This
feature renders Zr isotopes particularly useful for tracing nucleosynthetic material formed by these
processes and to study mixing processes that took place prior to, or during, the formation of the solar system (see chapters 5 and 6).

1.5 Interval between final nucleosynthesis and condensation

By means of nucleosynthetic models, it is possible to calculate the abundances of nuclides produced by one particular process. The initial abundance of a radioactive nuclide can be used to test these models (chapter 3). For this purpose, the time interval, called free decay interval, between the isolation from the nucleosynthetic source and the incorporation into the solids of the solar system has to be estimated. Inversely, once a model is established, the initial abundance can be used to constrain the free decay interval.

The first two extinct radionuclides I and Pu, which were discovered are both r-process nuclides. Both require a free decay interval of about 100 Myr. Hence, it was concluded that this was the time during which the presolar material that formed the solar system was isolated from inputs of fresh nucleosynthetic products. However, the discovery of other short-lived radionuclides with shorter half-lives, such as 26Al, led to the conclusion that this time interval had to be shorter. Otherwise, 26Al could not have been present in the solar system. This discrepancy can be explained if different nucleosynthetic events contributed to the inventory of short-lived radionuclides in the early solar system. Furthermore, it is probable that many stars contributed toward the solar system inventory of longer-lived radionuclides (\( t_{1/2} > 128 \) T), whereas shorter-lived isotopes (e.g. 182Hf, 107Pd, 53Mn and 26Al) originated from only a few, or perhaps a single, nucleosynthetic event.

Lee et al. (1976) suggested that the occurrence of 26Al in the solar system can be explained by late addition of freshly synthesised material from a nearby supernova explosion. Cameron and Truran (1977) pointed out that such an explosion in the vicinity of the solar nebula is likely to trigger its collapse. In contrast, Wasserburg et al. (1994) suggested that the abundances of most short-lived radionuclides, except 53Mn, can be explained by late injection of material from an AGB star. In summary, it can be concluded that the last injection of freshly synthesised material took place only a few million years or less before the formation of the first solids in the solar system.

Some of the extinct radionuclides could also have been formed by spallation reactions close to the early sun (X-wind model; Shu et al., 1997). The initial abundances of 10Be, 26Al, 41Ca and
53Mn have been successfully modelled in the frame work of the X-wind scenario (Gounelle et al., 2001; Russell et al., 2001; Leya et al., 2002). However, this model cannot explain the initial abundances of ⁶⁰Fe and it is a unlikely source for heavy radionuclides such as ²⁴⁴Pu. Therefore, additional nucleosynthetic sources than the irradiation of the early sun are required to explain the initial abundances of certain extinct radionuclides.

1.6 Objectives of this study

The goal of this thesis was to develop the short-lived ⁹²Nb-⁹²Zr decay system for the use as an early solar system chronometer. Its aim was furthermore to investigate, if Zr isotope abundances can be used to trace different nucleosynthetic components in the solar system. To this end, the following investigations were performed in this study:

a) A new technique was developed for the precise and accurate determination of Zr isotopic compositions and Nb/Zr ratios in geological samples (chapter 2).

b) Internal isochrons were determined for early equilibrated meteorites to define the initial ⁹²Nb/⁹²⁸Nb ratio of the solar system (chapters 3 and 7).

c) Two internal isochrons of lunar highland rocks and a number of lunar basalts samples were analysed to study the early differentiation history of the moon. Such chronology may provide new constraints for the age of the moon (chapter 4).

d) The Zr isotopic compositions of a wide range of samples were determined to search for isotopic heterogeneities. The samples include calcium-aluminium-rich inclusions (CAI) and leachates of carbonaceous chondrites, bulk carbonaceous, ordinary and enstatite chondrites, eucrites and mesosiderites, as well as terrestrial and lunar samples (chapters 5 and 6).
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Chapter 2

Ion Exchange Chromatography and High Precision Isotopic Measurements of Zirconium by MC-ICPMS

* accepted for publication in The Analyst: Schönbächler M., Rehkämper M., Lee, D.-C., Halliday, A. N. Ion exchange chromatography and high precision isotopic measurements of zirconium by MC-ICPMS.
Abstract

This paper presents a technique for the precise and accurate determination of Zr isotopic composition in geological samples. The method includes a two-stage anion-exchange procedure for the chemical separation and Zr isotopic analysis by MC-ICPMS. A long-term reproducibility of ± 39 ppm for \( ^{91}\text{Zr}/^{90}\text{Zr} \), ± 25 ppm for \( ^{92}\text{Zr}/^{90}\text{Zr} \), and ± 82 ppm for \( ^{96}\text{Zr}/^{90}\text{Zr} \) was obtained on < 100 nanograms Zr from replicate dissolutions of the carbonaceous chondrite Allende. The method has been successfully applied to terrestrial igneous rocks, meteorites and mineral separates including samples with high Ti contents.

2.1. Introduction

The element Zr is of special cosmochemical interest, mainly because of the production of \( ^{92}\text{Zr} \) from the decay of the now-extinct radionuclide \( ^{92}\text{Nb} \), which has a half-life of 36 Myr (Nethaway et al., 1978). With such a long half-life, the \( ^{92}\text{Nb}-^{92}\text{Zr} \) system could be used to study early solar system development provided that at the start of the solar system, the abundance of \( ^{92}\text{Nb} \) was high and there were processes that fractionated Nb/Zr. Moreover, Zr isotopes offer the opportunity to study nucleosynthetic processes (Schönbächler et al., 2003a), because they have different production mechanisms. The nuclide \( ^{96}\text{Zr} \) is primarily produced by the \( r \)-process, which is thought to take place in a supernova environment. All other Zr isotopes (\( ^{89}\text{Zr}, ^{91}\text{Zr}, ^{92}\text{Zr}, ^{94}\text{Zr} \)) are predominately formed by the \( s \)-process, presumably in an AGB star.

With special focus on determining the initial abundance of \( ^{92}\text{Nb} \) in the solar system, diverse efforts have been made to measure Zr isotopic compositions accurately and precisely during the past twenty years (Minster and Ricard, 1981; Minster and Allègre, 1982; Nomura et al., 1983; Harper, 1996; Sahoo and Masuda, 1997; Hirata and Yamaguchi, 1999; Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000; Hirata, 2001). The early studies, which were performed by thermal ionisation mass spectrometry (TIMS), were hampered by the high first ionisation potential of Zr. This problem was overcome by the development of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS). The ICP ion source of these instruments produces ionisation yields of > 90% for most elements of the periodic table (Jarvis et al., 1992). This instrumental advance has renewed the search for anomalies in Zr isotopic compositions from the decay of extinct \( ^{92}\text{Nb} \). Although some studies found hints for formerly live \( ^{92}\text{Nb} \) (Harper, 1996; Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000), the most reliable
evidence for its existence in the early solar system was still missing: the acquisition of an internal isochron from a meteorite containing a co-genetic suite of phases that remained undisturbed after their formation. Therefore, we developed a new analytical procedure for the determination of Zr isotopic compositions at high precision for various geological materials, with the ultimate aim of producing internal meteorite isochrons. This method includes, first, a selective dissolution procedure that is used in conjunction with conventional physical methods to obtain the required mineral separates. Second, we developed an optimised chemical separation procedure for Zr. It efficiently isolates Zr from matrix elements for different types of sample, including chromite, ilmenite, terrestrial igneous whole rocks and stony meteorites. A clean separation of Zr from abundant elements such as Ti, Cr and Fe is particularly important for the MC-ICPMS analyses, because these elements form argides that interfere with the Zr isotopes. Third, we developed protocols for the precise and accurate determination of Zr isotopic compositions by MC-ICPMS. A separate method that utilises quadrupole ICPMS was designed to determine Nb/Zr ratios, which are required for Nb-Zr chronology (Hattendorf et al., 2001). These analyses were made with sample aliquots that did not undergo chemical separation in order to avoid any chemical fractionation of Nb from Zr during processing. Spectral interferences were minimised by using dynamic reaction cell technology with hydrogen as reactive gas.

2.2. Sample preparation

2.2.1 Reagents and materials

All acids are purified once or twice (HF) by sub-boiling distillation in quartz or Teflon stills, except for the H2SO4, where Merck ultrapure sulfuric acid (96%) is employed. Reagent grade H2O2, CS2 and 18 MΩ-grade water from a Millipore system is used. Saturated bromine water, which is required for sulfide digestion, is prepared by the equilibration of approximately 5 ml of high-purity bromine (99.998%, Alfa-Aesar) with 100 ml of purified water in a 250 ml Teflon bottle.

2.2.2 Dissolution of whole rocks and mineral separates

Whole rock samples of stony meteorites are crushed in a boron carbide mortar under a laminar flow of filtered air to avoid contamination. The terrestrial samples are processed in the same way, but in a different clean environment. Terrestrial and meteorite whole rock samples of
up to 150 mg are digested in 16 ml Savillex vials placed inside a 125 ml Parr bomb. A mixture of 3 ml concentrated HF and 700 ml concentrated HNO₃ is used for digestion during 4 ½ days at a temperature of 180°C. Subsequently, the samples are dried down and completely re-dissolved in 6 ml 6 M HCl on a hot plate for 1 day. Instead of HCl, 4 ml of aqua regia is used, if the sample contains carbonaceous material. Traces of HF are added after this dissolution step. This ensures that all Zr and Nb is in solution and avoids possible fractionation between these two elements.

Mineral separates of pyroxene, olivine and feldspar are obtained using a Frantz magnetic separator. Up to 1.5 g of these mineral separates are dissolved on a hotplate, first in 15 ml of concentrated HF and HNO₃ (2:1), followed by 25 ml 7 M HNO₃ and as a last step in 30 ml 6 M HCl and traces of HF. The samples are dried down between each step. For feldspar, some minor Ca and Mg precipitate may not completely dissolve in the last HCl step. However, this does not reduce the yield of the ion-exchange separation or fractionate Nb from Zr.

2.2.3 Selective dissolution

The determination of Nb-Zr isochrons requires mineral separates with different Nb/Zr ratios. However, most minerals do not significantly fractionate Nb from Zr. The most important exceptions are rutile, zircon and ilmenite. Minerals such as ilmenite, however, are not easily separated by conventional methods (Frantz magnetic separator and heavy liquids) from bulk ordinary chondrites and, to a lesser extent, from eucrites. The separation is hampered by abundant inclusions, which render the magnetic separation ineffective, and by high contents of chromite and troilite with similar densities as ilmenite. Selective dissolution offers the possibility to overcome these problems.

After crushing the meteorite sample in a boron carbide mortar, it is washed and sieved under a laminar flow of filtered air. The metal is separated with a hand magnet, followed by a heavy liquid separation with Clerici solution. The metal needs to be removed prior to the heavy liquid separation to avoid corrosion of the metal. The extracted heavy mineral fraction consists mainly of troilite, chromite, ilmenite and possibly some zircons. This fraction is further cleaned by hand-picking and sequentially treated with a series of reagents to selectively dissolve troilite, ilmenite and chromite.

In the first step, 2 M HNO₃ and 25% bromine water are added to the heavy mineral fraction in a Savillex vial to digest troilite. This needs to be done with caution due to the formation of toxic
H₂S. After 2½ hours on a hot plate at ~100°C, the supernatant is decanted. The remaining grains and precipitated sulfur (from the oxidation of sulfide) are washed with water (which is combined with the decanted acid) and distilled ethanol. Then CS₂ is added and the solution is left to stand for 1 hour to dissolve precipitated sulfur. The residue is washed again with distilled ethanol and all steps starting with the addition of 2 M HNO₃ and 25% bromine water are repeated.

This procedure leaves ilmenite and chromite unaltered, as was verified by optical examination under the binocular microscope and by weighing ilmenite and chromite before and after the procedure. Nevertheless, some leaching of the grain surfaces can not be excluded. Exposure of the minerals to the HNO₃ - bromine water mixture for one to several days on the hotplate, leads to etching of the ilmenite surfaces while chromite appears unaffected. Minor amounts of sulfur precipitate may remain with the chromite and ilmenite.

In the second step, ilmenite is dissolved by adding concentrated HCl and HF (1:1). After 3 hours on a hot plate (~130°C), the ilmenite is completely dissolved. The supernatant is decanted and the residual chromite grains are washed with water. This fraction is also checked for the presence of zircons under a binocular microscope.

The third step comprises the digestion of chromite in concentrated HCl. Complete dissolution of the chromite is achieved after three days in a Savillex vial placed inside a Parr bomb at 180°C.

2.3. Ion-exchange chromatography

The two-stage procedure for Zr separation (Table 2.1) applies anion exchange chromatography with Bio-Rad AG1-X8 resin (200-400 mesh, chloride form). The first step is adapted from the primary column of the Hf chemistry developed by Salters and Hart (Salters and Hart, 1991). The same method was previously used for the separation of W (Lee and Halliday, 1997), but on a different scale. After the digestion, the sample solution is dried down at 100°C. 2 ml of 4 M HF is added and allowed to sit for at least 2 hours. Depending on the composition of the sample, some insoluble fluorides (mainly Ca-Mg fluorides) may form. This occurs for terrestrial and chondritic whole rock samples and mineral separates of chromite, feldspar and pyroxene. If fluorides precipitate, the sample is treated in an ultrasonic bath, centrifuged and decanted; the residue is subsequently treated twice with 1.5 ml 4 M HF, such that a total of 5 ml of acid is collected. This washing procedure enhances the total Zr yield by up to 7 % for chromite.
Table 2.1: Zr ion-exchange chromatography

<table>
<thead>
<tr>
<th>1. Column</th>
<th>2. Column</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step</strong></td>
<td><strong>Volume</strong></td>
</tr>
<tr>
<td>cleaning</td>
<td>8 ml</td>
</tr>
<tr>
<td>5 ml</td>
<td>6 M HCl - 1 M HF</td>
</tr>
<tr>
<td>5 ml</td>
<td>H2O</td>
</tr>
<tr>
<td>preconditioning</td>
<td>6 ml</td>
</tr>
<tr>
<td>load sample</td>
<td>1 - 5 ml</td>
</tr>
<tr>
<td>rinse matrix</td>
<td>8 ml</td>
</tr>
<tr>
<td>Zr</td>
<td>2 ml</td>
</tr>
<tr>
<td>W</td>
<td>3 ml</td>
</tr>
</tbody>
</table>

Ilmenite samples do not produce precipitates of Ca-Mg fluorides in HF and are directly loaded with 1 ml of 4 M HF. Ilmenite contains high amounts of Ti, which are adsorbed onto the resin in 4 M HF. Thus, each column is loaded with a maximum of ~10 mg ilmenite to avoid overloading. For other sample types (whole rocks, silicates), the column has sufficient capacity to process about 130 mg of material.

The first column with 0.7 ml of resin is preconditioned with 6 ml 4 M HF (Table 2.1). After loading of the sample dissolved in 1 - 5 ml 4 M HF, the matrix is eluted with 8 ml 4 M HF, while Zr, Hf, Ti, Mo, Te and W remain on the column. This behaviour is expected from the distribution coefficient for these elements (Faix et al., 1981). Zirconium is stripped from the column with 2 ml 6 M HCl - 1 M HF together with Ti and Hf (Nelson et al., 1960). Addition of further 3 ml 6 M HCl - 1 M HF elutes W. There may be some minor W (< 10% of the total W) in the Zr fraction, but this can be recovered in the following step.

The second separation step is based on the methods of Barovich et al. (1995) for the isolation of Hf from Ti-rich matrices. It was scaled down for use with 0.7 ml of resin and slightly modified to achieve a better separation of Ti from Zr. This separation is very important for Zr isotopic measurements because of the formation of Ti-argides, which may produce interferences for some Zr isotopes (Table 2.2). This is particularly true for ilmenite, which is an important mineral for Nb-Zr chronometry. Ilmenite can consist of more than 50 wt.% TiO2 and therefore, a reliable separation procedure, which can deal with high Ti contents, is required. The Zr fraction obtained from the first column is evaporated and taken up in 1.5 ml of freshly prepared 0.25 M H2SO4 - 1% H2O2. This solution is loaded onto the second column, which was previously
preconditioned with 6 ml of 0.25 M H$_2$SO$_4$ - 1% H$_2$O$_2$. Titanium is stripped from the column with 8 ml 0.25 M H$_2$SO$_4$ - 1% H$_2$O$_2$, followed by the elution of Zr and Hf with 2 ml 6 M HCl - 1 M HF. The separation of Ti is efficient, such that only traces of Ti elute in the Zr fraction, which displays Ti/Zr $\ll$ 1. A further separation of Zr from Hf is not necessary prior to the MC-ICPMS measurements. Tungsten can be eluted, if this is desired, by addition of 3 ml 6 M HCl - 1 M HF.

The yields for the two-stage procedure have been measured semi-quantitatively. The sample solutions and Zr standards of known concentration were spiked with $^{84}$Sr, followed by the comparison of the Zr/$^{84}$Sr ratios obtained for samples and the Zr standards. The yields are estimated to be between 70 and 100%. Total procedural chemistry blanks, including sample dissolution and ion exchange separation are typically < 150 pg. If Teflon bombs are used for the digestion of the sample, the blanks can be as high as 1000 pg.

2.4. Mass Spectrometry

2.4.1 Instrumentation and data collection protocols

All measurements have been performed with a Nu Plasma MC-ICPMS at ETH Zürich. A characteristic feature of the Nu Plasma is the combination of fixed Faraday collectors with variable dispersion zoom optics. The instrument is used in conjunction with a Cetac MCN 6000 desolvating nebuliser at uptake rates between 80 and 120 ml per minute. The masses from 90 to 97 amu are measured with Faraday cups and $10^{11}$ Ω resistors in a single cycle. A second cycle, which immediately follows the first, is required for the measurement of mass 99, which is needed for the Ru correction. The zoom optics and the laminated magnet of the Nu Plasma allow for fast switching between two different collector configurations. The Ru correction is only applied if necessary. This is checked on a small sample aliquot prior to the actual Zr isotopic measurement.

In each measurement, 80 ratios (5 s integrations) are collected in blocks of 20. On-peak baselines are measured for 15 s prior to each block, while the ion beam is deflected by the electrostatic analyser. A measurement that includes one cycle requires ~10 minutes and consumes 100 ng Zr for a Zr solution of 100 ppb. Such solutions yield total ion beams intensities of $4 \times 10^{11}$ - $6 \times 10^{11}$ amps. Before analysing samples, the performance of the instrument is checked with several runs of Zr standard solutions. The samples are always measured interspersed between
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Table 2.2: Important interferences on Zr isotopes for MC-ICPMS measurements

<table>
<thead>
<tr>
<th>Isotope</th>
<th>90Zr</th>
<th>91Zr</th>
<th>92Zr</th>
<th>94Zr</th>
<th>96Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interference:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobaric</td>
<td></td>
<td>92Mo</td>
<td>94Mo</td>
<td>96Mo</td>
<td></td>
</tr>
<tr>
<td>Double Charge</td>
<td></td>
<td>180Hf++</td>
<td>185W++</td>
<td>184W++</td>
<td></td>
</tr>
<tr>
<td>Argides</td>
<td>50Ti40Ar</td>
<td>51V40Ar</td>
<td>52Cr40Ar</td>
<td>54Fe40Ar</td>
<td>56Fe40Ar</td>
</tr>
<tr>
<td></td>
<td>40Ar214N</td>
<td>40Ar216O</td>
<td>56Fe40Ar</td>
<td>58Fe40Ar</td>
<td>58Fe40Ar</td>
</tr>
</tbody>
</table>

upper limit:

| Mo/Zr (#) | 0.01 | 0.005 |
| Ru/Zr (#) | 0.01 |
| Ti/Zr | 1* |
| V/Zr | 0.3* |
| Cr/Zr | 0.3 |
| Fe/Zr | 0.9 |

The upper limit indicates the maximum elemental contents that are permissible for the Zr solutions. Higher concentrations lead to erroneous Zr isotope data.

*The actual upper limit may be higher, but sample solutions are kept cleaner than this by the ion exchange chemistry.

(##) An interference correction is applied to account for the isobaric interferences from Mo and Ru. The Mo and Ru interferences can be adequately corrected, if the concentrations do not exceed the indicated limits.

runs of Zr standards at concentrations that are adjusted to match the samples to within 20%. Between the analyses, the sample introduction system is cleaned with 2% HNO3 – 0.01% HF. Washout of Zr usually requires < 5 min.

2.4.2 Data processing and interference correction

Instrumental mass fractionation is internally normalized to 94Zr/90Zr = 0.3381 (Minster and Ricard, 1981) with the exponential law. The interference of 94Mo on 94Zr (Table 2.2) is corrected with the following procedure. First, the mass fractionation of all relevant ratios is corrected by normalization to 91Zr/90Zr = 0.21798 (Minster and Ricard, 1981), because both 90Zr and 91Zr are free of isobaric interferences. Then the Mo interference on mass 94 is estimated based on the measured intensity at mass 95 using the Mo isotopic abundances of Lee and Halliday (1995). The obtained 94Mo/90Zr ratio is subtracted from the measured 94(Zr+Mo)/90Zr ratio. The resulting 94Zr/90Zr ratio is corrected for both Mo and mass fractionation. The mass fractionation correction is back-calculated to obtain the true measured 94Zr/90Zr ratio, which in turn
can be used to determine the mass fractionation based on $^{94}\text{Zr}/^{90}\text{Zr}$. This correction procedure is repeated and the newly obtained true measured $^{94}\text{Zr}/^{90}\text{Zr}$ ratio is used to correct for mass fractionation in the next iteration step until the calculated true measured $^{94}\text{Zr}/^{90}\text{Zr}$ ratios converge.

Molybdenum interferences on $^{92}\text{Zr}$ and $^{96}\text{Zr}$ also are corrected using $^{95}\text{Mo}$ as the interference monitor and $^{94}\text{Zr}/^{90}\text{Zr}$ for normalisation. The Ru interference on $^{96}\text{Zr}$ is estimated based on $^{99}\text{Ru}$ and the Ru isotopic abundances of De Bièvre et al. (1984).

2.5. Results and Discussion

2.5.1 Precision and accuracy of standard solutions

Four Zr standard solutions were analysed in this study. These are NIST SRM 3169, ICP standard solutions for Aldrich and Alfa-Aesar, and a solution made of the JMC (Johnson Matthey Company) Zr metal. All four solutions have the same Zr isotopic composition, within the analytical uncertainty (Fig. 2.1). These results do not agree with the TIMS data of Sahoo and Masuda (Sahoo and Masuda, 1997), who found isotopic differences between terrestrial standards. The most striking feature of their data is a difference in $^{96}\text{Zr}$ of $-8.6$ epsilon units between an Aldrich and a JMC Zr standard. Our data, however, do not display such variations (Fig. 2.1). This uniformity in Zr isotopic composition for terrestrial materials is supported by other workers, who analysed Zr isotopes in various terrestrial samples (Hirata and Yamaguchi, 1999; Münker et al., 2000; Hirata, 2001).

![Fig. 2.1: Zirconium isotopic compositions for Zr standard solutions (NIST SRM 3169, Aldrich and Alfa-Aesar ICP standards, solution of JMC Zr metal). Each point reflects the mean of at least 6 runs. Error are 2σ standard deviations. $\epsilon^x\text{Zr} = [(x^{90}\text{Zr})_{\text{meas}}/(x^{90}\text{Zr})_{\text{std}}] - 1] \times 10^4$, x = 1, 2, 6.](image-url)
In the present study, long-term averages of $^{91}\text{Zr}/^{90}\text{Zr} = 0.217926 \pm 0.0023$, $^{92}\text{Zr}/^{90}\text{Zr} = 0.333376 \pm 0.0025$, $^{96}\text{Zr}/^{90}\text{Zr} = 0.054371 \pm 0.0008$ (all 2σ standard deviations from the mean) were obtained for analyses conducted in 40 separate measurement sessions over a period of 2 years. These results lie in the range of previously published data acquired by both TIMS and MC-ICPMS (Rehkämper et al. (2001), see Münker et al. (2001) for compilation). The external precision for standard measurements conducted on a single day is always better than ±40 ppm for $^{91}\text{Zr}/^{90}\text{Zr}$, ±30 ppm for $^{92}\text{Zr}/^{90}\text{Zr}$, and ±120 ppm for $^{96}\text{Zr}/^{90}\text{Zr}$. These are maximum values, however, and the typical external precision is ±30 ppm, ±20 ppm, and ±80 ppm, for $^{91}\text{Zr}/^{90}\text{Zr}$, $^{92}\text{Zr}/^{90}\text{Zr}$, and $^{96}\text{Zr}/^{90}\text{Zr}$, respectively. The maximum values are used as a conservative estimate of the analytical uncertainty for the Zr standard measurements.

### 2.5.2 Spectral Interferences and Ion-Exchange Chemistry

For precise and accurate isotopic measurements by MC-ICPMS, it is crucial to pay attention to spectral interferences. Isobaric interferences from Mo and Ru (Table 2.2) are particularly problematic for Zr. Our ion-exchange procedure ensures a good separation of Zr from Mo, because Mo remains on the column in both the first and the second stage. For the terrestrial and extraterrestrial samples, the purified fractions have Mo/Zr ratios that are always less than $1 \times 10^{-3}$. Moreover, they possess Ru/Zr ratios that are generally less than $1 \times 10^{-3}$ even for Ru-rich samples, such as primitive chondrites. However, despite the good chemical separation, a correction for the isobaric interferences of Mo and Ru is necessary. Analyses of Zr standard

![Fig. 2.2: Zr isotopic compositions obtained for Alfa Zr standard solutions doped with (A) Mo and (B) Ru. A) An accurate correction for $^{92}\text{Zr}$ is possible up to Mo/Zr of $1 \times 10^{-2}$, whereas for $^{96}\text{Zr}$ the correction breaks down above $-0.5 \times 10^{-2}$. The gray bar shows the external reproducibility of the standard (2σ) for $^{86}\text{Zr}$, the dashed horizontal lines for $^{88}\text{Zr}$. Errors on data points are 2σ in-run precisions. B) The Ru interference on $^{96}\text{Zr}$ can be adequately corrected for Ru/Zr up to $-1 \times 10^{-2}$. The correction is usually negligible for terrestrial samples, while it is crucial for most of the primitive meteorites, because of their high Ru contents.](image-url)
solutions, which were doped with Mo and Ru, were used to investigate the reliability of the correction procedures for these elements. The Mo correction is accurate up to a Mo/Zr ratio of $1 \times 10^{-2}$ for $^{92}$Zr and $-0.5 \times 10^{-2}$ for $^{96}$Zr (Fig. 2.2a, Table 2.2). Larger amounts of Mo result in over- or undercorrected Zr isotopic ratios (Fig. 2.2a). Interferences from Ru can be adequately corrected for Ru/Zr up to $1 \times 10^{-2}$ (Fig. 2.2b). These results indicate that our chemical separation procedure yields Zr fractions with Mo and Ru concentrations that are low enough, such that the isobaric interferences of these elements can be adequately corrected during the analyses.

A particular difficulty of Zr isotopic measurements is that elements such as Ti, Cr and Fe are present at high concentration in many geological samples and they form argides that interfere with the masses of Zr (Table 2.2). This problem is circumvented by the ion-exchange procedure, because this efficiently separates Zr from these elements. The small residual amounts that are present in the Zr fraction, do not disturb the Zr isotopic measurements. No corrections are, therefore, needed for these interferences and this is ascertained by checking the concentrations of these elements on a small aliquot prior to the isotopic measurement. Titanium, V, Cr and Fe are efficiently separated from Zr and the Zr fractions generally display lower element/Zr ratios than required for accurate data acquisition (Table 2.2). Particular care is needed, if Cr or V is enriched in samples, which is the case for chromite. Passing V-rich samples through the second column twice optimise the V/Zr ratio. Following loading of the secondary columns with Cr-rich samples, the exposition of the resin to air for more than ~5 minutes should be avoided. Otherwise, some Cr is eluted in the Zr fraction. This results in a Cr/Zr ratio $> 0.25$, which may lead to erroneous Zr isotopic data. The elution of Cr is probably due to the oxidation of Cr$^{3+}$ to Cr$^{6+}$ on surface of the resin. The latter species is adsorbed onto the resin in 4 M HF, but partially released by 6 M HCl - 1 M HF. The maximum contents of Ti, V, Cr and Fe that can be tolerated in the sample solutions were determined by analysing Zr standards doped with these elements. The limits for Cr (Fig. 2.3) and the other elements (Table 2.2) are set conservatively to account for variations in the argide formation-rates. Such variations are observed between different measurement session. A Fe/Zr ratio of 0.9 in the sample solutions does not compromise the Zr isotopic measurement, while the Cr/Zr ratio needs to be less than ~0.3. Therefore, more Fe can be tolerated in the sample solution than Cr. This is surprising, because $^{52}$Cr and $^{56}$Fe have similar isotopic abundances and because $^{96}$Zr is much less abundant than $^{92}$Zr (2.8 % vs. 17.1 %). This indicates that Cr-argides have a higher formation rate than Fe-argides.
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2.0

1.5

1.0

<!N 0.5

ay

0.0

-0.5

-1.0

0.0 0.2 0.4 0.6 0.8 1.0

Cr/Zr

Fig. 2.3: Zr isotopic compositions obtained for the Alfa Zr standard solution doped with variable amounts of Cr. Chromium/Zr ratios of up to 0.3 are acceptable, but higher amounts of Cr may significantly influence $\varepsilon^{92}\text{Zr}$. The Cr/Zr ratios are therefore checked prior to the measurements. The gray bar denotes the external reproducibility of the standard (2σ).

Large amounts of Nb may generate peak-tailing effects on $^{92}\text{Zr}$ and $^{94}\text{Zr}$. However, only high Nb/Zr ratios of > 6 start to influence the Zr isotopic measurements. Our chemical separation produces Zr fractions that have much lower Nb contents.

Repeated analyses of Zr standards with different concentrations reveal an unidentified interference on $^{91}\text{Zr}$ (Fig. 2.4), which is common to all standard and sample solutions. The effect disappears at high signal size (total ion beam > 2.5 x 10^{-11} amps) and it can be compensated at lower ion beam intensities by measuring samples relative to standard solution that have similar (±20%) Zr concentrations.

Fig. 2.4: Ratios of $^{91}\text{Zr}/^{90}\text{Zr}$ for variably diluted solutions of NIST SRM 3169 Zr. The different total ion beam intensities correspond to Zr solutions with concentrations of 200 ppb, 100 ppb, 50 ppb and 20 ppb. Errors are 2σ in-run precisions. The results indicate the presence of an unknown interference on $^{91}\text{Zr}$. The $\varepsilon^{91}\text{Zr}$ data of samples are therefore determined relative to standards that are analysed using the same or similar (±20%) ion beam intensities.
2.5.3 Reproducibility and accuracy of sample measurement

The external reproducibility for sample measurements was estimated from 12 analyses of bulk Allende, a carbonaceous chondrite (Table 2.3). Most of the Allende data are for separate dissolution of a homogenous sample powder. The external reproducibility is ±39 ppm for $^{91}\text{Zr}/^{90}\text{Zr}$, ±25 ppm for $^{92}\text{Zr}/^{90}\text{Zr}$ and ±82 ppm for $^{96}\text{Zr}/^{90}\text{Zr}$ (Table 2.3). This is only slightly worse than the typical precision achieved for pure standard solutions. The external reproducibility estimated in this way, accounts for the total uncertainty introduced through sample digestion, ion exchange chemistry and mass spectrometry. Furthermore, the Allende data are in excellent agreement with results of previous isotopic studies (Table 2.3) and this demonstrates that our measurements are both precise and accurate.

The reliability of the method was further tested by analysing various terrestrial whole rocks and minerals, including ilmenite and chromite (Table 2.4). For all samples, the measured isotopic ratios are identical to the terrestrial standard given the analytical uncertainty. The Zr isotopic composition of the Earth is expected to be homogenous because extensive mixing should have destroyed any early reservoir with distinct Zr isotopic compositions and due to the lack of processes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon^{92}\text{Zr}$</th>
<th>±2σ</th>
<th>$\varepsilon^{91}\text{Zr}$</th>
<th>±2σ</th>
<th>$\varepsilon^{96}\text{Zr}$</th>
<th>±2σ</th>
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</thead>
<tbody>
<tr>
<td>Allende*</td>
<td>0.22</td>
<td>0.12</td>
<td>0.51</td>
<td>0.12</td>
<td>1.18</td>
<td>0.31</td>
</tr>
<tr>
<td>Allende*</td>
<td>-0.09</td>
<td>0.20</td>
<td>0.15</td>
<td>0.23</td>
<td>0.95</td>
<td>0.66</td>
</tr>
<tr>
<td>Allende*</td>
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<td>-0.04</td>
<td>0.17</td>
<td>1.08</td>
<td>0.37</td>
</tr>
<tr>
<td>Allende*</td>
<td>0.07</td>
<td>0.29</td>
<td>0.46</td>
<td>0.26</td>
<td>0.66</td>
<td>0.74</td>
</tr>
<tr>
<td>Allende*</td>
<td>-0.07</td>
<td>0.14</td>
<td>0.10</td>
<td>0.20</td>
<td>1.27</td>
<td>0.47</td>
</tr>
<tr>
<td>Allende 1</td>
<td>-0.08</td>
<td>0.15</td>
<td>-0.07</td>
<td>0.21</td>
<td>0.24</td>
<td>0.59</td>
</tr>
<tr>
<td>Allende 2</td>
<td>-0.09</td>
<td>0.13</td>
<td>0.19</td>
<td>0.19</td>
<td>0.40</td>
<td>0.52</td>
</tr>
<tr>
<td>Allende 3</td>
<td>0.14</td>
<td>0.15</td>
<td>0.16</td>
<td>0.16</td>
<td>0.68</td>
<td>0.48</td>
</tr>
<tr>
<td>Allende 4</td>
<td>0.01</td>
<td>0.15</td>
<td>0.01</td>
<td>0.18</td>
<td>1.29</td>
<td>0.45</td>
</tr>
<tr>
<td>Allende 5</td>
<td>0.08</td>
<td>0.14</td>
<td>-0.05</td>
<td>0.16</td>
<td>1.39</td>
<td>0.43</td>
</tr>
<tr>
<td>Allende 6</td>
<td>0.27</td>
<td>0.16</td>
<td>0.03</td>
<td>0.20</td>
<td>1.43</td>
<td>0.59</td>
</tr>
<tr>
<td>Allende 7</td>
<td>-0.10</td>
<td>0.17</td>
<td>-0.04</td>
<td>0.22</td>
<td>1.40</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Average 0.04 0.25 0.12 0.39 1.00 0.82

Other studies:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon^{92}\text{Zr}$</th>
<th>±2σ</th>
<th>$\varepsilon^{91}\text{Zr}$</th>
<th>±2σ</th>
<th>$\varepsilon^{96}\text{Zr}$</th>
<th>±2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende*</td>
<td>-0.30</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende*</td>
<td>-0.09</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The data were acquired over a period of 2 years. Allende 1-4 are repeat measurements of the same sample solution; all other data are for separate dissolutions. Errors are 2σ in-run precision, except for those of the average composition, which represent the 2σ standard deviation.

*Data from Schönbächler et al. (2003a), *Münker et al. (2000), ^Sanloup et al. (2000).
that can produce mass-independent Zr isotopic anomalies. The uniformity of our results (Table 2.4) demonstrates that the analytical method does not suffer from spectral interferences or matrix effects. The procedure is, therefore, suitable for the accurate and precise determination of Zr isotopic compositions in a wide range of geological samples with different compositions including meteorites and minerals such as ilmenite and chromite.

2.6. Conclusion

A new method is presented here for the determination of Zr isotopic composition in geological samples at high precision. Following the chemical separation of Zr by ion exchange chemistry, the isotopic measurements are conducted by MC-ICPMS. The technique is suitable for analyses of terrestrial and extraterrestrial rocks, including samples with high contents of Ti and Cr. This renders the procedure particularly useful for Zr isotopic measurements of various mineral separates. The method has been successfully applied to terrestrial samples and bulk meteorites ranging from carbonaceous chondrites to differentiated meteorites such as eucrites (Schönbächler et al., 2003a). Furthermore, the first internal isochrons for the $^{92}$Nb-$^{92}$Zr system (Schönbächler et al., 2002) were produced with this analytical procedure.
Acknowledgements

We thank G. L. MacPherson for access to the meteorite collection at the Smithsonian Institution of Washington (Allende USNM-6159).
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Chapter 3

Niobium-Zirconium Chronometry and Early Solar System Development

Abstract

\(^{92}\text{Nb}\) decays to \(^{92}\text{Zr}\) with a half-life of 36 million years and can be used to place constraints on the site of \(p\)-process nucleosynthesis and the timing of early solar system processes. Recent results have suggested that the initial \(^{92}\text{Nb}/^{93}\text{Nb}\) of the solar system was high (>10\(^{-3}\)). We report Nb-Zr internal isochrons for the ordinary chondrite Estacado (H6) and a clast of the mesosiderite Vaca Muerta, both of which define an initial \(^{92}\text{Nb}/^{93}\text{Nb}\) ratio of \(\sim 1 \times 10^{-5}\). Therefore, the solar system appears to have started with a ratio of <3 \(\times 10^{-5}\), which implies that Earth’s initial differentiation need not have been as protracted as recently suggested.

3.1 Introduction

Some extinct radionuclides were sufficiently abundant at the start of the solar system that they produced variations in the abundance of their daughter isotopes in early-formed objects (Podosek and Swindle, 1988). Such nuclides provide information about late stage presolar nucleosynthetic sites and the time-scales over which the early solar system formed and first differentiated (Podosek and Nichols, 1997; Swindle, 1993; Wasserburg, 1985). Of considerable interest in this regard is \(^{92}\text{Nb}\), which decays by electron capture with a half-life of 36 ±3 million years (m.y.) to \(^{92}\text{Zr}\) (Makino and Honda, 1982; Nethaway et al., 1978). \(^{92}\text{Nb}\) is a shielded nuclide that forms by the \(p\)-process only. Therefore, its initial abundance provides information on stellar nucleosynthesis prior to the start of the solar system.

Both Nb and Zr are refractory and lithophile, except under reducing conditions when Nb may become siderophile (Wade and Wood, 2001). Within the Earth the dominant Nb/Zr fractionation mechanisms are silicate partial melting (Jochum et al., 1986) and the crystallization of accessory minerals such as zircon, ilmenite and rutile. The Zr isotopic compositions of early reservoirs can therefore vary in response to early differentiation processes and help date planetary differentiation, if the initial abundance of \(^{92}\text{Nb}\) (or \(^{92}\text{Nb}/^{93}\text{Nb}\)) was sufficiently high.

Early results demonstrated that the initial \(^{92}\text{Nb}/^{93}\text{Nb}\) of the solar system was <0.007 (Minster and Allègre, 1982). Evidence of formerly live \(^{92}\text{Nb}\) was first identified in a Nb-rich rutile from the iron meteorite Toluca (Harper, 1996). An initial \(^{92}\text{Nb}/^{93}\text{Nb}\) of (1.6 ±0.3)
\[ x \times 10^{-5} \] was inferred. More recently, three studies using multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) proposed that the initial \(^{92}\text{Nb}/^{93}\text{Nb}\) ratio of the solar system was 2 orders of magnitude higher (\(~10^3\)) (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000). Such a high value limits the possible sites for \(p\)-process nucleosynthesis and places specific constraints on the time-scales for the development of differentiated reservoirs on the Earth and Moon. For example, it has been argued that large silicate reservoirs in the Earth and Moon formed 50 million years after the start of the solar system (Münker et al., 2000). However, such a result requires that the Tolucar rutile grew very late (>200 m.y.). In contrast, a combined \(Zr\) isotopic and U-Pb age study of an early zircon from a eucrite implied that the initial \(^{92}\text{Nb}/^{93}\text{Nb}\) ratio was <10\(^{-4}\) (Hirata, 2001).

Here we specifically determine the initial \(^{92}\text{Nb}/^{93}\text{Nb}\) ratio of the solar system using the internal isochron approach. Two meteorites in which ilmenite with high Nb/Zr is in textural equilibrium with other phases having intermediate Nb/Zr were studied. Because the half-life of \(^{92}\text{Nb}\) is long (36 m.y.) and the level of uncertainty concerning the initial solar system abundance is more than 2 orders of magnitude, the critical concern is not the exact age of the meteorite (provided it is reasonably early) but the acquisition of a reliable isochron from a co-genetic suite of phases that remained undisturbed after their formation. Therefore, we used the equilibrated but only weakly shocked (S1) H6 ordinary chondrite Estacado, which has a single generation of ilmenite, and a eucritic clast from the mesosiderite Vaca Muerta.

### 3.2 Analytical methods

Using a Nu Plasma MC-ICPMS we are able to measure \(\varepsilon\text{Zr}\) with an external precision of \(\pm 0.3 \varepsilon\) units (2\(\sigma\) standard deviation) for samples with only 50 ng of Zr (see chapter 2). The Nb/Zr ratios were determined by inductively coupled plasma dynamic reaction cell mass spectrometry (ICP-DRCMS) without chemical separation (Hattendorf et al., 2001).

### 3.3 The Zirconium isotopic composition of the Earth

To check for terrestrial Zr isotope anomalies and test our ability to measure the isotopic composition of Zr extracted from different matrices, we analysed 12 early zircons (aliquots of those described by Amelin et al., 1999), 2 basalts and a rhyolite (from Iceland), a lherzolite
Table 3.1: Zr isotopic data for terrestrial samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{92}\text{Zr}$</th>
<th>$^{91}\text{Zr}$</th>
<th>$^{96}\text{Zr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>±2σ error</td>
<td>±2σ error</td>
<td>±2σ error</td>
</tr>
<tr>
<td>rhyolite (ATHO), Iceland</td>
<td>-0.29 ±0.15</td>
<td>0.10 ±0.21</td>
<td>0.79 ±0.46</td>
</tr>
<tr>
<td>basalt (BTHO), Iceland</td>
<td>-0.15 ±0.19</td>
<td>0.12 ±0.18</td>
<td>-0.31 ±0.39</td>
</tr>
<tr>
<td>basalt (BIR-1), Iceland</td>
<td>-0.04 ±0.13</td>
<td>-0.05 ±0.16</td>
<td>0.30 ±0.43</td>
</tr>
<tr>
<td>ilherzolite (C235A), Cameroon Line</td>
<td>0.20 ±0.15</td>
<td>-0.27 ±0.13</td>
<td>1.13 ±0.26</td>
</tr>
<tr>
<td>ilmenite ilmeni, Russia</td>
<td>0.01 ±0.12</td>
<td>-0.30 ±0.10</td>
<td>0.01 ±0.27</td>
</tr>
<tr>
<td>zircon Jack Hills (50), Aus, 4.01 Ga</td>
<td>0.13 ±0.13</td>
<td>0.25 ±0.13</td>
<td>-0.06 ±0.27</td>
</tr>
<tr>
<td>zircon Jack Hills (52), Aus, 3.5 Ga</td>
<td>0.29 ±0.29</td>
<td>0.27 ±0.16</td>
<td>-0.57 ±0.34</td>
</tr>
<tr>
<td>zircon Jack Hills (63), Aus, 4.1 Ga</td>
<td>0.01 ±0.24</td>
<td>0.20 ±0.09</td>
<td>0.55 ±0.19</td>
</tr>
<tr>
<td>zircon Jack Hills (65), Aus, 4.01 Ga</td>
<td>0.22 ±0.28</td>
<td>0.24 ±0.17</td>
<td>0.04 ±0.36</td>
</tr>
<tr>
<td>zircon Acasta Gneisses (AGOL z1), Canada, 3.6 Ga</td>
<td>-0.08 ±0.25</td>
<td>-0.13 ±0.13</td>
<td>0.61 ±0.27</td>
</tr>
<tr>
<td>zircon Acasta Gneisses (A(1)), Canada, 3.5 Ga</td>
<td>0.15 ±0.25</td>
<td>-0.14 ±0.12</td>
<td>0.03 ±0.27</td>
</tr>
<tr>
<td>zircon Jack Hills (45-1), Aus, 3.7 Ga</td>
<td>-0.12 ±0.26</td>
<td>0.04 ±0.10</td>
<td>-0.15 ±0.29</td>
</tr>
<tr>
<td>zircon Jack Hills (46-1), Aus, 4.0 Ga</td>
<td>-0.12 ±0.22</td>
<td>0.02 ±0.11</td>
<td>0.45 ±0.27</td>
</tr>
<tr>
<td>zircon Jack Hills (50), Aus, 3.4 Ga</td>
<td>0.02 ±0.22</td>
<td>0.07 ±0.09</td>
<td>0.27 ±0.25</td>
</tr>
<tr>
<td>zircon Jack Hills (57), Aus, 3.4 Ga</td>
<td>-0.13 ±0.27</td>
<td>0.07 ±0.14</td>
<td>-0.07 ±0.33</td>
</tr>
<tr>
<td>zircon Jack Hills (40), Aus, 4.0 Ga</td>
<td>0.00 ±0.17</td>
<td>0.13 ±0.11</td>
<td>0.18 ±0.23</td>
</tr>
<tr>
<td>zircon Jack Hills (41), Aus, 3.4 Ga</td>
<td>-0.01 ±0.24</td>
<td>-0.02 ±0.14</td>
<td>0.63 ±0.34</td>
</tr>
</tbody>
</table>

$\varepsilon^{\text{Zr}} = \left\{ \left( \frac{^{90}\text{Zr}}{^{90}\text{Zr}} \right)_{\text{mau}} - \left( \frac{^{90}\text{Zr}}{^{90}\text{Zr}} \right)_{J} \right\} \times 10^6$, with $\left( \frac{^{90}\text{Zr}}{^{90}\text{Zr}} \right)_{J} = 0.333383$ for $^{92}\text{Zr}/^{90}\text{Zr}$, 0.217930 for $^{91}\text{Zr}/^{90}\text{Zr}$, and 0.054372 for $^{96}\text{Zr}/^{90}\text{Zr}$. The quoted analytical uncertainties for the Zr isotopic compositions and $\varepsilon\text{Zr}$ values reflect the internal (2σ within-run precision) and external reproducibility for $^{92}\text{Zr}/^{90}\text{Zr}$, $^{91}\text{Zr}/^{90}\text{Zr}$, and $^{96}\text{Zr}/^{90}\text{Zr}$, respectively. (Aus = Australia)

(Cameroon Line) and ilmenite (from Russia) (Table 3.1). The analysed zircons have ages of up to 4.1 Ga (Amelin et al., 1999) and are among the oldest terrestrial minerals. Variations in the Zr isotopic composition of old rocks or minerals are only expected if the initial $^{92}\text{Nb}$ abundance is extremely high. For a solar system initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $\sim 10^{-5}$ there will be no detectable Zr isotopic effects even in the oldest terrestrial zircons. Earlier studies (Hirata, 2001; Münker et al., 2000; Sahoo and Masuda, 1997) reached differing conclusions regarding the homogeneity of terrestrial Zr. However, our $^{92}\text{Zr}/^{90}\text{Zr}$, $^{91}\text{Zr}/^{90}\text{Zr}$ and the $^{96}\text{Zr}/^{90}\text{Zr}$ ratios for terrestrial samples are identical with the value obtained for a standard solution of NIST SRM 3169 Zr and do not indicate any variation in the Zr composition of the Earth (Table 3.1). This implies a homogenous distribution of Zr isotopes for the bulk silicate Earth.
3.4 The initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the solar system

The mineral fractions and whole rock data for Estacado and the Vaca Muerta clast both define isochrons, but with limited variation in $^{92}\text{Zr}/^{90}\text{Zr}$ (Fig. 3.1). The Estacado whole rock sample and the mineral fractions of olivine/pyroxene and chromite all agree with the terrestrial Zr isotopic composition within analytical uncertainty. However, the ilmenite with a Nb/Zr ratio 20 times higher than chondritic ($-0.065$) yields an $\varepsilon^{92}\text{Zr}$ of $+1.0 \pm 0.4$. The results for Vaca Muerta are similar (Table 3.2). The slope of the regression line defines an initial $^{92}\text{Nb}/^{93}\text{Nb}$ at the time of closure of $(1.2 \pm 0.6) \times 10^{-5}$ for Estacado (Fig. 1A), and of $(0.6 \pm 0.3) \times 10^{-5}$ for Vaca Muerta (Fig. 1B). These values are effectively identical to the Toluca results (Harper, 1996) and are consistent with the zircon data for the Camel Donga eucrite (Hirata, 2001).

A high initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the order of $10^{-3}$ was obtained for specific calcium-aluminium-rich inclusions (CAI) from Allende (Münker et al., 2000; Sanloup et al., 2000). The CAIs are believed to be among the earliest objects that formed in the solar system (Göpel et al., 1994). The production rate of cosmogenic $^{92}\text{Zr}$ is too small to generate significant variations in the calculated initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratios (Leya et al., 2003). Both $^{92}\text{Zr}$ and $^{96}\text{Zr}$ isotope anomalies have been reported for CAIs (Sanloup et al., 2000). Therefore, the possibility remains that CAIs preserve a component with a presolar Zr isotope signature, analogous to those reported for presolar graphite grains (Nicolussi et al., 1998). A heterogeneous distribution of $^{92}\text{Nb}$ in the early solar system could also cause different estimates of the initial abundance of $^{92}\text{Nb}$. This would require a variability in the initial $^{92}\text{Nb}/^{93}\text{Nb}$ between $10^{-3}$ and $10^{-5}$ and should produce measurable $^{92}\text{Zr}$ anomalies in whole rock meteorites. However, the observed $^{92}\text{Zr}$ isotopic variations in bulk chondrites (Sanloup et al., 2000) have not been yet confirmed (Münker et al., 2000; Schönböchler et al., 2003a). This indicates that further work is needed to confirm and understand these reported $^{92}\text{Zr}$ anomalies (see chapter 5).

One way to reconcile the various results is resetting or slow cooling ($> 200$ m.y.) of the samples yielding low values: Toluca, Vaca Muerta, Camel Donga and Estacado. This is inconsistent with a considerable amount of independent age data. Estacado (H6) yields a $^{40}\text{Ar}/^{39}\text{Ar}$ age (4450 Ma) only 30 m.y. younger than Kernouvé (another H6 Chondrite) (Flohs, 1981), which is likely to have experienced the same events as all H6-Chondrites. The Pb-Pb age of phosphates extracted from Kernouvé (H6) and Guarena (H6) indicate that these meteorites underwent a metamorphic event or cooling around 45 m.y. and 61 m.y., respectively,
Fig. 3.1: Nb-Zr isochron diagrams for Estacado (H6) and a clast of the mesosiderite Vaca Muerta. Only the ilmenite and heavy mineral fraction show a $^{92}$Zr anomaly outside our analytical error of $\pm 0.3 \, ^{92}$Zr (A,B). Panel (C) shows the strong constraints that the Estacado and Vaca Muerta data provide on an initial $^{92}$Nb/$^{95}$Nb close to $10^{-5}$. The initial $^{92}$Zr/$^{95}$Zr ratios of the isochrons [0.333384 $\pm 6$ and 0.333382 $\pm 3$ for Estacado and Vaca Muerta, respectively] overlap with the terrestrial value. All data points for Estacado and Vaca Muerta with a Nb/Zr ratio greater than chondritic are plotted. Error bars reflect the $2\sigma$ internal run precision. (BSSI= bulk solar system initial).
Table 3.2: Zr isotopic and Nb, Zr concentration data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nb (ppm)</th>
<th>Zr (ppm)</th>
<th>$^{93}\text{Nb}/^{90}\text{Zr} \pm 2\sigma$ mean</th>
<th>$^{93}\text{Zr}/^{90}\text{Zr} \pm 2\sigma$ mean</th>
<th>$^{91}\text{Zr} \pm 2\sigma$ mean</th>
<th>$^{91}\text{Zr} \pm 2\sigma$ mean</th>
<th>$^{96}\text{Zr} \pm 2\sigma$ mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine+pyroxene</td>
<td>0.47</td>
<td>3.6</td>
<td>0.253 ±0.020</td>
<td>0.333387 ±12</td>
<td>0.13 ±0.35</td>
<td>-0.59 ±0.66</td>
<td></td>
</tr>
<tr>
<td>ilmenite</td>
<td>83</td>
<td>58</td>
<td>2.58 ±0.36</td>
<td>0.333417 ±13</td>
<td>1.01 ±0.38</td>
<td>0.11 ±0.38</td>
<td>1.73 ±1.12</td>
</tr>
<tr>
<td>whole rock</td>
<td>0.51</td>
<td>6.4</td>
<td>0.154 ±0.008</td>
<td>0.333387 ±7</td>
<td>0.11 ±0.22</td>
<td>0.12 ±0.26</td>
<td>0.27 ±0.90</td>
</tr>
<tr>
<td>chromite</td>
<td>0.29</td>
<td>1.2</td>
<td>0.466 ±0.004</td>
<td>0.333388 ±13</td>
<td>0.15 ±0.39</td>
<td>0.75 ±1.41</td>
<td></td>
</tr>
<tr>
<td>troilite (a)</td>
<td>0.057</td>
<td>0.83</td>
<td>0.132 ±0.018</td>
<td>0.333389 ±36</td>
<td>0.17 ±1.08</td>
<td>-1.37 ±1.00</td>
<td></td>
</tr>
</tbody>
</table>

**Estacado**

**Vaca Muerta**

The errors of $^{93}\text{Zr}/^{90}\text{Zr}$ refer to the least significant digits only. The $\varepsilon\text{Zr}$ values do not include uncertainties for the standard (see Table 3.1).

After the formation of the Allende CAIs (Göpel et al., 1994). The H6 chondrites are, therefore, early objects and their equilibrated textures cannot be of late origin. The Sm-Nd chronology of Vaca Muerta clasts (Stewart et al., 1994) and the U-Th-Pb systematics of Vaca Muerta zircons (Ireland and Wlotzka, 1992) yield similar ages of 4480 ±190 Ma and 4563 ±15 Ma respectively.

To provide more direct time constraints we have acquired Hf-W isotope data for some of the Estacado and Vaca Muerta mineral separates (Table 3.3). $^{182}\text{Hf}$ (half-life = 9 m.y.) decays to $^{183}\text{W}$ such that W isotopic variations can only be produced within the first 50 m.y. of the solar system. Small excesses of $^{182}\text{W}$ have previously been detected in Vaca Muerta zircons (Ireland, 1991). We find large W isotopic variations among the aliquots that we have analysed for Zr (Table 3.3). Sulfide equilibrates readily, yet the 2 troilite fractions of Estacado display negative $\varepsilon\text{W}$ values of −2.46 ±0.47 and −2.05 ±0.56, indicating that the latest time of sulfide/silicate equilibration was 3.8 ±1.2 and 4.9 ±1.5 m.y., respectively, after the origin of the solar system, assuming that the initial $^{182}\text{Hf}/^{184}\text{Hf}$ was $2.4 \times 10^{4}$. The W isotopic compositions and Hf/W ratios for the Vaca Muerta pyroxene and feldspar separates (Table 3.3) define a $^{182}\text{Hf}/^{184}\text{Hf}$ of $(7.8 ±0.8) \times 10^{-5}$. Therefore, these phases appear to have last equilibrated 14.5 ±1.5 m.y. after the start of the solar system. Even if this error is increased somewhat to
Table 3.3: Hf and W isotopic data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{180}\text{Hf}/^{184}\text{W}$</th>
<th>$^{182}\text{W}/^{184}\text{W}$</th>
<th>$\varepsilon^{182}\text{W}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>±2σ error</td>
<td>±2σ error</td>
<td>±2σ error</td>
</tr>
<tr>
<td>Estacado</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>olivine+pyroxene</td>
<td>0.865438 ±79</td>
<td>6.68 ±0.91</td>
<td></td>
</tr>
<tr>
<td>troilite (a)</td>
<td>0.864683 ±48</td>
<td>-2.05 ±0.56</td>
<td></td>
</tr>
<tr>
<td>troilite (b)</td>
<td>0.864647 ±41</td>
<td>-2.46 ±0.47</td>
<td></td>
</tr>
<tr>
<td>Vaca Muerta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>feldspar</td>
<td>8.025</td>
<td>0.866333 ±80</td>
<td>17.03 ±0.92</td>
</tr>
<tr>
<td>pyroxene</td>
<td>20.70</td>
<td>0.867306 ±88</td>
<td>28.3 ±0.8</td>
</tr>
</tbody>
</table>

The analytical procedure of the W and Hf measurements is the same as described in Lee and Halliday (2000), except that the NIST-3163 W standard yields a lower value of $^{182}\text{W}/^{184}\text{W} = 0.864860 ±13$ (2σ standard deviations) using the ETH Nu Plasma. The uncertainty in $^{180}\text{Hf}/^{184}\text{W}$ is ±0.5%. The errors (internal 2σ errors) of $^{182}\text{W}/^{184}\text{W}$ refer to the least significant digits.

Fig. 3.2: Variation in $\varepsilon^{92}\text{Zr}$ versus time, starting with the formation of the solar system and assuming an $^{92}\text{Nb}/^{93}\text{Nb}$ of $1.2 \times 10^{-5}$ for a $^{91}\text{Nb}/^{90}\text{Zr}$ ratio up to 100. The shaded area shows the external reproducibility for terrestrial standards. The numbers on the curves denote different $^{91}\text{Nb}/^{90}\text{Zr}$ ratios. (Chondritic $^{91}\text{Nb}/^{90}\text{Zr}$ ratio = -0.127).
allow for systematic Hf-W uncertainties, there is little doubt that Estacado and Vaca Muerta last underwent internal W isotope equilibration within the first 20 m.y. of solar system history. Therefore, the apparent discrepancy with other recently published Nb-Zr data cannot be explained easily by later equilibration. The Estacado initial $^{99}$Nb/$^{98}$Nb of $(1.2 \pm 0.6) \times 10^{-5}$ should be very close to the solar system initial abundance within a factor of 2 (Fig 3.2). The slightly lower initial $^{99}$Nb/$^{98}$Nb of Vaca Muerta is consistent with the Hf-W evidence for a later closure of the phases in the mesosiderite relative to Estacado. However, both initial $^{99}$Nb/$^{98}$Nb values are identical within the analytical errors, consistent with independent evidence for early planetesimal differentiation (Lee and Halliday, 1997; Lugmair and Shukolyukov, 1998). With a low initial $^{99}$Nb/$^{98}$Nb ratio of $\sim 10^{-5}$, the timing of terrestrial core formation, the growth-rate of Hadean continents, and the longevity of the lunar magma ocean (Münker et al., 2000; Jacobsen and Yin, 2001; Yin et al., 2001) can now be considered to be under-constrained from Nb-Zr systematics (Fig. 3.2).

### 3.5 Implications for stellar nucleosynthesis

The low initial abundance of $^{99}$Nb also reopens the range of possibilities that can be considered for $p$-process nucleosynthesis. As a $p$-only nuclide $^{99}$Nb is predominantly produced in supernovae by photodisintegration (Lambert, 1992). The modelling of other processes such as spallation synthesis (Clayton et al., 1977; Lambert, 1992; Harper, 1996) shows that these can be only a minor contributor in the synthesis of $p$-nuclei because they fail to explain the solar abundance pattern. The calculated production ratios for $^{99}$Nb/$^{87}$Nb, as predicted by several models for Type Ia and Type II supernovae (Woosley and Howard, 1978; Howard et al., 1991; Howard and Meyer, 1993; Rayet et al., 1995), are in the range of $(2.1-9.2) \times 10^{-3}$. Only one Type II model (Hoffman et al., 1996) yields a significantly higher production ratio of 0.35, and is able to explain the high abundance of stable $p$-process $^{92}$Mo in the solar system. However, it is inconsistent with the data presented here.

The range $(2.1-9.2) \times 10^{-3}$ in contrast, is in good agreement with our results. To deduce the abundance of $^{99}$Nb at the time of the formation of the solar system from this range, two factors are important: [1] the free decay time interval between the last nucleosynthesis and the formation of the solar system and [2] the amount of $^{99}$Nb at the start of this interval which is a function of the duration of nucleosynthesis. Due to the 36 m.y. half-life of $^{87}$Nb, an averaging model...
can be used (Cameron, 1993), which includes continuous nucleosynthesis at a constant rate (Wasserburg et al., 1960; Cameron, 1962). Assuming a 10 G.y. period of nucleosynthesis, such a model predicts that 0.5% of the total $^{92}$Nb produced, is present at the end of nucleosynthesis. This factor applied to the calculated production ratios (Woosley and Howard, 1978; Howard et al., 1991; Howard and Meyer, 1993; Rayet et al., 1995) yields an initial $^{93}$Nb/$^{92}$Nb for the solar system of $1 \times 10^{-5}$ to $4.6 \times 10^{-5}$, if the free decay interval is not considered. Our estimate based on Estacado falls into this range. Taking into account the free decay interval (up to 50 m.y.; Harper, 1996) may further lower the calculated value by a factor of 2 or more. Nonetheless, most production ratio yields of different supernova models [Type Ia and Type II] are extremely similar to our measured value of $(1.2 \pm 0.6) \times 10^{-5}$, but do not allow to identify an unequivocal source for $^{92}$Nb in supernovae.
Chapter 4*

Nb/Zr Fractionation on the Moon and the Search for Extinct $^{92}$Nb

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Abstract

A comprehensive Zr isotopic study was conducted on eleven lunar basalts and highland rocks to search for evidence of extinct $^{92}$Nb. Internal isochrons were furthermore determined for two early highland rocks, 77215 and 60025. No resolvable Zr isotopic variations were detected in this wide range of lunar samples and thus there is no evidence for the former existence of live $^{92}$Nb on the moon. This is most likely due to modest Nb/Zr fractionation. The Nb/Zr ratios of lunar ilmenites and bulk rock samples vary only by a factor of two to three relative to the chondritic Nb/Zr ratio and this indicates that lunar reservoirs with strongly fractionated Nb/Zr did not form. As a consequence, it is not possible to draw conclusions about the timing of early lunar differentiation and to constrain the role of ilmenite in the source region of high-Ti mare basalts. However, the fractionation is still sufficient to deduce an upper limit for the initial $^{92}$Nb/$^{93}$Nb of the solar system of $< 1 \times 10^{-4}$ or $< 5 \times 10^{-4}$ depending on the age assumed for the lunar anorthosite 60025.

4.1 Introduction

A giant impact is the most widely accepted model for the formation of the moon. This theory proposes that there was a collision between the Earth and a body of at least the size of Mars during the later stages of terrestrial accretion (Stevenson, 1987; Cameron and Benz, 1991). This collision generated hot debris from which the moon formed and it is responsible for the angular momentum of the Earth-moon system. According to various interpretations of published W isotope data, this event took place between 30 and 60 Myr after the formation of the solar system (Kleine et al., 2002; Lee et al., 2002), although the exact age is the subject of current dispute (Halliday et al., 2003; Kleine et al., 2003). Both $^{92}$Nb and $^{146}$Sm are among the few extinct radionuclides with have half-lives that are long enough (36 Myr (Nethaway et al., 1978) and 103 Myr (Firestone, 1996), respectively) to cause measurable isotopic anomalies on the daughter nuclides $^{92}$Zr and $^{142}$Nd as a result of decay within the moon itself. These isotopic anomalies could provide important information about the formation and early differentiation of the moon. Small isotopic effects from the decay of $^{146}$Sm have already been reported for lunar samples (Nyquist et al., 1995). However, the existence of isotopic effects from the decay of $^{92}$Nb in lunar rocks is still an open question. The potential of $^{92}$Nb to produce
Zr anomalies on the moon depend on (1) the initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the solar system, (2) the magnitude of early fractionations of Nb from Zr and (3) the time when the samples formed.

### 4.1.1 The initial abundance of $^{92}\text{Nb}$ in the solar system

The initial abundance of $^{92}\text{Nb}$ in the solar system has been a matter of recent debate. In the earliest study of the Nb-Zr system (Minster and Allègre, 1982), no evidence for the former existence of $^{92}\text{Nb}$ was found. The first hint of formerly live $^{92}\text{Nb}$ was discovered in rutile from the iron meteorite Toluca (Harper, 1996) and an initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $(1.6 \pm 0.3) \times 10^{-5}$ was inferred. Three subsequent studies proposed an initial $^{92}\text{Nb}/^{93}\text{Nb}$ for the solar system that is more than two orders of magnitude higher ($\approx 10^{-4}$), mainly based on results for calcium-aluminium-rich inclusions (CAI) from Allende (Münker et al., 2000; Sanloup et al., 2000) and a zircon from the Chaunskij mesosiderite (Yin et al., 2000). However, other recent studies of zircons from the Camel Donga eucrite (Hirata, 2001) and Allende CAIs (Schönbächler et al., 2003a), deduced upper limits for the initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $10^{-4}$ and $2 \times 10^{-4}$, respectively. These results are in agreement with the first internal isochrons for the Nb-Zr system presented for the mesosiderite Vaca Muerta and the ordinary chondrite Estacado (Schönbächler et al., 2002). In both cases the isochrons yielded an initial solar system $^{93}\text{Nb}/^{93}\text{Nb}$ of close to $3 \times 10^{-5}$. With such a low initial $^{93}\text{Nb}/^{93}\text{Nb}$, $^{92}\text{Zr}$ anomalies due to the decay of $^{92}\text{Nb}$ are only to be expected if Nb was strongly fractionated from Zr. As Nb and Zr are both refractory and incompatible lithophile elements, they are observed to display only limited fractionation in most terrestrial rocks and meteorites. However, fractionation of Nb from Zr occurs during the crystallisation of minerals such as ilmenite, rutile, baddeleyte and zircon. In lunar ilmenites, Nb/Zr ratios of up to ~8 have been reported (Blank et al., 1984), which is about 100 times the chondritic value of ~0.076. Such a large fractionation would generate measurable $^{92}\text{Zr}$ anomalies for samples that formed during the first 200 Myr of the solar system, even if the initial $^{92}\text{Nb}$ abundance was as low as $3 \times 10^{-5}$. The oldest lunar samples are highland rocks and they display ages that fall in this time interval. The most reliable age has been determined for the ferroan anorthosite 60025, which appears to have formed only 50 to 130 Myr (Hanan and Tilton, 1987; Carlson and Lugmair, 1988) after the start of the solar system at 4.568 Ga, which is defined by the age of CAI (Amelin et al. 2002). Another early lunar rock is the norite 77215 with a Sm-Nd age of 4.37 ±0.02 Ga (Nakamura et al., 1976). Both the ferroan anorthosite 60025 and the norite
77215 are therefore old enough to have incorporated live $^{92}\text{Nb}$. As they have probably been components of the early lunar crust, Nb-Zr chronometry applied to these rocks could potentially provide important information about lunar differentiation and constrain a minimum formation age for the moon. For these reasons, internal Nb-Zr isochrons for large samples of the lunar rocks 60025 and 77215 were determined.

4.1.2 Early lunar evolution and Nb/Zr fractionation

It is a widely held view that a lunar magma ocean existed at \(~ 4.55\) Ga (Shearer and Papike (1999) for review). Models of lunar magma ocean crystallisation suggest that the earliest cumulates consisted mainly of olivine and variable amounts of low-calcium pyroxene (Duncan et al., 1974; Longhi, 1977; Unruh et al., 1984; Snyder et al., 1992). Later, plagioclase started to form, which floated upwards due to its low density compared to the residual liquid magma ocean. This produced the anorthositic crust. Ilmenite crystallised (together with clinopyroxene ± plagioclase) from the late-stage liquid when 90-95% of the magma ocean had solidified (Snyder et al., 1992; Shearer and Papike, 1999 for review) and formed ilmenite-bearing cumulate layers (IBCL). Crystallisation of ilmenite, clinopyroxene ± plagioclase continued until KREEP, the final liquid differentiate, solidified beneath the anorthositic crust. The KREEP model age of 4.42 Ga (Nyquist and Shih, 1992) is thought to mark the completion of magma ocean crystallisation. This implies that the IBCL formed within the first 200 Myr of the solar system.

The IBCL are expected to have fractionated Nb/Zr ratios, because of distinct distribution coefficients for Nb and Zr between ilmenite and basaltic melt. Considering the age and the fractionation of these early rocks, distinct $^{92}\text{Zr}$ anomalies could have formed, which may constrain the age of the IBCL more precisely. Unfortunately, no samples of these cumulate layers are available. However, there is a general consensus that they were involved in the generation process of lunar high-Ti basalts (Longhi et al., 1974; Duncan et al., 1974; Nyquist et al., 1975; Unruh et al., 1984; Snyder et al., 1992). The high-Ti basalts may therefore have inherited $^{92}\text{Zr}$ anomalies from the early cumulate layers. We conducted a comprehensive Zr isotopic study of 3 low-Ti and 6 high-Ti mare basalts to investigate, whether these samples display such inherited $^{92}\text{Zr}$ anomalies.
4.2 Analytical procedure

All samples were crushed in a boron carbide mortar under a laminar flow of filtered air. The feldspar and pyroxene of the highland rocks 60025 and 77215 were separated with a Frantz magnetic separator. Heavy liquid separation was carried out with Clerici solution to obtain a heavy mineral fraction. Ilmenite was separated from this fraction by selective dissolution with an HCl/HF mixture (Schönbächler et al., 2003c). Other minerals such as chromite remain unaltered and form the so-called heavy mineral residue. The mineral separates for the high-Ti basalts (70035, 75075 and 77516) and the Apollo 15 olivine-basalt (15555) were produced with a Frantz magnetic separator following the procedure of Lee et al. (2002).

The chemical purification of Zr is described in Schönbächler et al. (2003c), as well as the protocols for the isotopic measurements, which were performed by MC-ICPMS. Epsilon Zr values for samples were calculated relative to the mean value obtained for a NIST SRM 3169 Zr standard solution on the same day using $\varepsilon^{90}Zr = \left\{\frac{(^{90}Zr/^{90}Zr)_{\text{meas}} - (^{90}Zr/^{90}Zr)_{\text{std}}}{(^{90}Zr/^{90}Zr)_{\text{std}}}\right\} \times 10^4$.

The $^{93}Nb/^{90}Zr$ ratios of the samples were measured with a quadrupole ICPMS instrument using sample solution aliquots that did not undergo chemical separation to avoid any potential chemical fractionation of Nb from Zr (Hattendorf et al., 2001). In these measurements, spectral interferences were accounted for by using dynamic reaction cell technology with hydrogen as reactive gas. Single ilmenite grains that were handpicked for 60025, 70035, 75075, 77516 and 15555 were dissolved in HCl-HF and analysed for Nb/Zr ratios only.

4.3 Results and Discussion

4.3.1 Highland rocks

The internal isochrons determined for the anorthosite 60025 and the norite 77215 show identical Zr isotopic compositions for all mineral separates and whole rocks, within the analytical uncertainty (Fig. 4.1, Table 4.1). This observation can be explained by (1) late formation of 60025 and 77215 or late resetting of the Nb-Zr system in these rocks; (2) limited fractionation of Nb from Zr; (3) a low initial $^{93}Nb/^{93}Nb$ of the solar system; or (4) combinations of these factors. Late formation of 60025 and 77215 can be excluded because the evidence from
Fig. 4.1: Internal isochrons for the anorthosite 60025 and the norite 77215. The analytical uncertainties reflect the internal (2σ, int) within-run precision except for bulk silicate Earth, where the external reproducibility (2σ) is plotted. The grey bars show the external reproducibility (2σ) for terrestrial standards.

Sm-Nd (Nakamura et al., 1976; Carlson and Lugmair, 1988) and 207Pb/206Pb (Hanan and Tilton, 1987) indicates that they formed within the first 200 Myr of the solar system. Moreover, it is unlikely that the Nb-Zr system was reset while Sm-Nd and 207Pb/206Pb remained largely undisturbed, because Nb and Zr both are refractory and immobile elements.

The Nb/Zr ratios of the mineral separates vary from 0.4 to 3 times the chondritic value (Nb/Zr = 0.076). The Nb/Zr ratios of the 60025 ilmenite in the hand picked fraction and the fraction treated by selective dissolution are identical within the analytical uncertainties (Table
<table>
<thead>
<tr>
<th>Sample</th>
<th>Nb (ppm)</th>
<th>Zr (ppm)</th>
<th>Nb/Zr ±2σ</th>
<th>$^{92}$Zr/$^{90}$Zr ±2σ</th>
<th>ε$^{92}$Zr ±2σ</th>
<th>ε$^{91}$Zr ±2σ</th>
<th>EM$^{92}$Zr ±2σ</th>
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<td>0.049</td>
<td>0.004</td>
<td>0.333386 ± 3</td>
<td>0.09</td>
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<td>0.002</td>
<td>0.333379 ± 6</td>
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<td>0.333383 ± 3</td>
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<tr>
<td>77215 - norite</td>
<td>whole rock</td>
<td>0.021</td>
<td>0.43</td>
<td>0.049</td>
<td>0.004</td>
<td>0.333386 ± 3</td>
<td>0.09</td>
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<td>0.333383 ± 3</td>
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<td>498</td>
<td>0.051</td>
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<tr>
<td>15382 KREEP</td>
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<td>0.049</td>
<td>0.004</td>
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<td>0.09</td>
</tr>
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<td>0.24</td>
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<td>0.19</td>
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<td>0.34</td>
<td>0.13</td>
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<tr>
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<td>0.06</td>
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<td>whole rock</td>
<td>0.333380 ± 2</td>
<td>-0.09</td>
<td>0.17</td>
<td>-0.23</td>
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<td>0.333384 ± 4</td>
<td>0.03</td>
<td>0.20</td>
<td>0.00</td>
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<td>0.333384 ± 4</td>
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<td>0.19</td>
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<td>0.333380 ± 3</td>
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<td>-0.08</td>
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<td>0.34</td>
</tr>
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<td>0.20</td>
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<td>77516 - high-Ti-mare basalt</td>
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<td>0.16</td>
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</table>

The analytical uncertainties for the $^{92}$Zr/$^{90}$Zr ratios reflect the internal (2σ) within-run precision. For the ε$^{92}$Zr values, the external reproducibility (2σ) of the sample is given, which is estimated by the standard deviation of all analysed lunar samples. The uncertainties of ε$^{91}$Zr refer to the least significant digits only.

4.1). This shows that the selective dissolution procedure works adequately. The ilmenites of 60025 and 77215 display Nb/Zr ratios that are rather low (2 to 3 times the chondritic value) compared to terrestrial ilmenites, for which ratios as high as 200 times chondritic have been reported (Table 4.1, Table 4.2). This modest Nb-Zr fractionation of the lunar minerals can therefore explain the lack of $^{92}\text{Zr}$ anomalies. Despite of the modest fractionation, the lack of Zr isotopic anomalies places important constraints on the initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the solar system. The formation age of 60025 has been estimated at 4.51 ±0.01 Ga by $^{207}\text{Pb}/^{206}\text{Pb}$ systematics (Hanan and Tilton, 1987) and 4.44 ±0.02 Ga by Sm-Nd (Carlson and Lugmair, 1988). Depending on which age is used, the lack of a resolvable $^{92}\text{Zr}$ anomaly in this rock requires an initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the solar system of < 1 x 10^{-4} and < 5 x 10^{-4} respectively. This is consistent with our earlier results (Schönbächler et al., 2002).

### 4.3.2 Mare basalts

The analysed samples include 6 high-Ti, an olivine-normative and a quartz-normative mare basalts, and a KREEP basalt (Table 4.1, Fig. 4.2). Mineral separates (pyroxene, feldspar and ilmenite) were analysed for 3 high-Ti mare basalts (70035, 75075 and 77516) and the olivine mare basalt (15555). Despite of this wide range of investigated samples, they all display Zr isotopic compositions that are identical to the terrestrial standard, within the 2σ analytical uncertainty (Table 4.1). This implies that the moon and bulk silicate Earth possess the same Zr isotopic composition. The isotopic uniformity furthermore demonstrates that the lunar samples do not contain measurable cosmogenic contributions of Zr. This is in agreement with the work of (Leya et al., 2003), who showed that, in contrast to W, the cosmogenic production of Zr on the moon is negligible. Without a relevant cosmogenic production of Zr, a homogeneous Zr isotopic composition is expected for olivine-normative
Table 4.2: Nb/Zr ratios in lunar and terrestrial samples.

<table>
<thead>
<tr>
<th>Lunar ilmenites</th>
<th>Nb/Zr</th>
<th>2 σ ad</th>
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*average value

and quartz-normative mare basalts, and the KREEP basalts, because they are unlikely to have formed from an early reservoir with strongly fractionated Nb/Zr ratios (McCallum and Charette, 1978; Shearer et al., 1996b). However, the high-Ti mare basalts are different in this respect. The source region of these rocks should have significantly fractionated Nb/Zr ratios because it contains considerable amounts of ilmenite (0.5 to 10%; e.g. Nyquist et al., 1975; Unruh et al., 1984; Snyder et al., 1992). Nevertheless, the high-Ti samples do not display measurable \(^{87}\)Zr anomalies (Fig. 4.2). Possible reasons for this include (1) late formation of the IBCL, (2) a low Nb/Zr ratio in source
region of high-Ti mare basalts or (3) dilution of the $^{92}\text{Zr}$ anomalies during the formation of the high-Ti mare basalts. These possible explanations are discussed in the following.

### 4.3.2.1 Formation interval for the source region of high-Ti mare basalts

It is possible that the IBCL formed late, when most or all $^{92}\text{Nb}$ had decayed, such that the remaining $^{92}\text{Nb}$ was insufficient to generate measurable $^{92}\text{Zr}$ anomalies. This explanation can be evaluated using age constraints for the IBCL. The IBCL can not be younger than the high-Ti mare basalts themselves, which display ages of between 4.0 and 3.6 Ga (Nyquist and Shih, 1992). Ilmenite appears on the liquidus after crystallisation of about 90-95% of the lunar magma ocean (Shearer and Papike, 1999). This implies that the IBCL are among the latest cumulates. The completion of crystallisation is thought to be marked by the formation of KREEP, which has a Rb-Sr model age of 4.42 ±0.07 Ga (Nyquist and Shih, 1992). Hence, the IBCL should display ages that are slightly older than those of KREEP.

The isotopic systematics of mare basalts and ferroan anorthosites provide further age constraints on the duration of the lunar magma ocean. Samarium-Nd model ages for mare basalts indicate that their source region (magma ocean cumulates) was isotopically closed at approximately 4.32 Ga. The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ferroan anorthosites approach those of primitive meteorites and they imply an early segregation of these rocks (Nyquist and Shih, 1992). This is in agreement with the ages reported for ferroan anorthosite 60025 and norite 77215 (Nakamura et al., 1976; Hanan and Tilton, 1987; Carlson and Lugmair, 1988). The Sm-Nd model age for ferroan anorthosite 62236 indicates an extremely rapid crystallisation of the lunar magma ocean, within 20 - 60 Myr after the moon was formed (Borg et al., 1999). Hafnium-W model ages for lunar mare basalts suggest a time interval of 20 - 40 Myr (Lee et al., 1997; Shearer and Newsom, 2000). However, with the limited radiogenic $^{182}\text{W}$ excess in lunar samples, this is a weak constraint. In addition, thermal modelling has been used to estimate a time interval of between 100 and 200 Myr for the duration of the lunar magma ocean (Solomon and Longhi, 1977; Longhi, 1980).

Considering these results, there is substantial evidence that the IBCL may have formed within the first 200 Myr of the solar system. Since this is approximately the time interval, for which live $^{92}\text{Nb}$ is expected, the lack of $^{92}\text{Zr}$ anomalies in high-Ti mare basalts can not easily be explained by late formation of the IBCL.
4.3.2.2 Nb-Zr fractionation in the source region of high-Ti basalts

Various models have been suggested for the crystallisation of the lunar magma ocean (e.g. Longhi et al., 1974; Duncan et al., 1974; Unruh et al., 1984; Snyder et al., 1992) and these can be used to estimate the Nb-Zr fractionation generated by this process. In this study, the most recent model of Snyder et al. (1992) was used to calculate the Nb/Zr ratios for the cumulate sequence that crystallised from the magma ocean (Fig. 4.3). The same assumptions applied by Snyder et al. (1992) were adopted for the sequence and mechanisms of crystallisation (equilibrium crystallisation up to 78%, followed by fractional crystallisation) and the bulk magma ocean composition. In this model, ilmenite crystallises at 95 to 99.5% solidification as part of the IBCL. The model assumes that the mafic minerals sink after 78% crystallisation and accumulate at the base of the magma ocean, while plagioclase floats upwards. It also accounts for trapped interstitial liquid and small proportions of plagioclase that are entrained into the denser mafic cumulate mush. Snyder et al. (1992) proposed

![Diagram](image)

**Fig. 4.3:** (a) Modelled Nb/Zr ratios for the lunar magma ocean considering 2% of entrained plagioclase. Curves are shown for Nb/Zr evolution during lunar magma ocean crystallisation for (1) liquid and (2) cumulates including 3% of trapped instantaneous residual liquid (TIRL); (3) cumulate with 1% TIRL. (b) Crystallisation sequence for the lunar magma ocean from Snyder et al. (1992).
a trapped instantaneous residual liquid (TIRL) of 1 to 3% and entrainment of a small proportion of plagioclase (2-5%) in the late stage cumulate pile, in order to account for both the observed Al concentrations and the trace element characteristics of high-Ti mare basalts. For the calculation presented here (Fig. 4.3), 2% of entrained plagioclase and 1 to 3% of TIRL were used. The percentage of the minerals is decreased proportionally as the amount of trapped liquid increases. The mass fraction of entrained plagioclase does not significantly influence the Nb/Zr ratio. Larger amounts of TIRL produces higher, more chondrite-like Nb/Zr for the early cumulates, but do not significantly alter the Nb/Zr ratios of the IBCL (at >95% fractional crystallisation) (Fig. 4.3). The modelled Nb/Zr of the lunar magma ocean liquid increases slightly during the crystallisation. The cumulate pile displays Nb/Zr lower than chondritic during the first 95% of magma ocean evolution and this changes slightly due to the varying proportions of olivine, orthopyroxene, pigeonite and clinopyroxene in the crystallising assemblage (Fig. 4.3). The Nb/Zr ratios of the cumulates significantly increase above chondritic to a value of ~0.1 for the IBCL with the crystallisation of ilmenite together with clinopyroxene and plagioclase at 95% solidification. This model result is very close to the Nb/Zr ratios observed for high-Ti basalt (~0.09; Duncan et al., 1974; Wänke et al., 1975). If the model is correct, then the formation of the high-Ti basalts does not involve a significant fractionation of Zr from Nb, such that the high-Ti basalts reflect the low Nb/Zr ratio of their source.

The composition of the ilmenite in the IBCL can be calculated with the following equation:

\[ C_i = D_i \times C_l \]  

(1)

Here, \( C_i \) is the concentration of an element in the cumulate, \( C_l \) the concentration in the liquid and \( D_i \) the partition coefficient of the element. Using distribution coefficients of \( D_{(Nb)} = 0.8 \) (McCallum and Charette, 1978) and \( D_{(Zr)} = 0.33 \) (McKay et al., 1986; Nakamura et al., 1986) for the partitioning of Nb and Zr between ilmenite and basaltic melt, the IBCL ilmenites display Nb/Zr ratios of ~0.2. This is much lower than the value of 55 proposed by Shearer et al. (1996a). The latter value is erroneous in any case, due to a typographical error (Shearer, pers. comm.) that has hitherto not been corrected. With a Nb/Zr ratio of 55 for ilmenites, \( \varepsilon^{92}Zr \) anomalies would have been expected in high-Ti mare basalt even if the cumulate layers formed as late as 200 Myr after the solar system (Fig. 4.4). However, the ilmenite of the high-Ti basalts displays Nb/Zr ratios as low as 0.1-0.15 (Table 4.2), while the bulk rock has an average Nb/Zr of ~0.09 (Duncan et al., 1974; Wänke et al., 1975). This is comparable to our modelled Nb/Zr ratio of ~0.2 and ~0.1 for IBCL ilmenite and the bulk cumulate layer, respectively. Ilmenites from the low-Ti mare basalt 15555 have a
Fig. 4.4: Variations in $\varepsilon^{92}$Zr versus time, starting with the formation of the solar system and assuming an initial $^{92}$Nb/$^{93}$Nb ratio of $3 \times 10^{-3}$, $1 \times 10^{-4}$ and $5 \times 10^{-4}$, respectively. The numbers on the curves denote the Nb/Zr ratios (chondritic = 0.076). The grey bar shows the external reproducibility for terrestrial standards.
Nb/Zr ratio that is similar to the result for ilmenites of high-Ti basalts. These observations are in agreement with the experimentally deduced partition coefficient (McCallum and Charette, 1978; McKay et al., 1986; Nakamura et al., 1986; Jones, 1995) and provide evidence for a modest Nb/Zr fractionation in the source region of mare basalts in general. Therefore, we conclude that the result of our model calculations (Nb/Zr ~ 0.2) for IBCL ilmenites is likely to be adequate.

Ilmenite is thought to be the major phase that is responsible for Nb-Zr fractionation on the moon. If this is correct and the Nb/Zr fractionation in lunar ilmenites is modest (Nb/Zr ratios of 2 to 3 times chondritic), then lunar rocks in general should display only a limited variation in Nb/Zr. The Nb/Zr data of bulk lunar samples support this idea (Table 4.2), because they show low Nb/Zr ratios that vary between 0.05 for KREEP, 0.09 for high-Ti mare basalts and 0.12 for single lunar highland rocks.

The model calculations for the lunar cumulates (Nb/Zr = 0.03 - 0.1, Fig. 4.3) are in agreement with this limited variation in Nb/Zr. However, the mare basalts are not direct products of the lunar magma ocean crystallisation. Their ratios are probably slightly enhanced compared to the cumulate source rock by partial melting (e.g. Snyder et al., 1992; Shearer et al., 1996a) The fact that they do not display particularly high Nb/Zr ratios argues that only limited Nb/Zr fractionation took place in the source region of high-Ti mare basalts.

The conclusion that fractionation of Nb from Zr is limited on the moon is also supported by data for terrestrial samples. Many terrestrial rocks display Nb/Zr ratios that are similar to those observed for lunar samples. The Nb/Zr ratios range from 0.03 to 0.17 for MORB (mid-ocean ridge basalts), primitive mantle, continental crust and ocean island basalts (Table 4.2). Terrestrial ilmenites display a wider range of Nb/Zr ratios from 0.1 to 16, depending on the geological setting (Table 4.2). Ilmenites from the Skaergaard layered intrusion have low Nb/Zr ratios similar to those of lunar mare basalts, whereas ilmenites from kimberlites and rhyolites can display significantly stronger Nb/Zr fractionations. Therefore, distinct positive Nb/Zr fractionation because of ilmenite formation occurs in terrestrial rocks but must be of minor importance, because the major terrestrial silicate reservoirs appear to display a limited range of Nb/Zr ratios (Nb/Zr = 0.03 - 0.07). The slightly elevated Nb/Zr ratios of ilmenites from more differentiated rocks are also a feature of lunar samples. Highland rocks have ilmenites that display the highest Nb/Zr ratios measured so far for lunar samples (Table 4.2).
4.3.2.3 The formation process of high-Ti mare basalts

It is possible that a $^{92}\text{Zr}$ anomaly was originally present in the IBCL ilmenites. This signature may have been lost, if dilution occurred during the formation of the high-Ti basalts. Any estimate for the extent of the dilution is therefore dependent on the formation process of the high-Ti basalts. Two types of models have been favoured in recent years: source hybridisation and assimilation. These models are briefly discussed in the following and the mass fraction of Zr in high-Ti mare basalts that originates from the IBCL is estimated.

Ringwood and Kesson (1976) suggested that the high density of the IBCL caused them to sink. This overturned the cumulate pile into density-stratified layers and hybrid regions consisting of early and late stage cumulates. Such hybrid regions formed at depths of 400-500 km (Green et al., 1975; Delano, 1980) and they were remelted to form high-Ti magmas. Such models suggest an ilmenite content of 0.5% to over 10% in the source of the high-Ti basalts (Nyquist et al., 1975; Unruh et al., 1984; Snyder et al., 1992). However, these models have been questioned based on problems related to the separation of the high-Ti magmas from the source rocks and their migration to the lunar surface (Shearer and Papike, 1999). An alternative model was first proposed by Hubbard and Minear (1975). This model type suggests that low-Ti basalt magmas rose from the lunar interior and assimilated IBCL at shallower depth. Assimilation of 20 – 30% of IBCL is required to match the Ti-content and the high trace element abundances of high-Ti mare basalts (Shearer and Papike, 1992; Beard et al., 1998). Shearer and co-workers (Shearer et al., 1996a; Shearer, 1999) stated that assimilation of IBCL is not consistent with the high Nb/Zr ratio for IBCL ilmenites. In contrast, the low Nb/Zr value of ~0.2 for IBCL ilmenites deduced in this study does not exclude the assimilation of ilmenite by a low-Ti magma, but it is also consistent with source hybridisation models. Therefore, the Nb/Zr ratios of IBCL ilmenites do not provide constraints on the formation process of high-Ti mare basalts. However, a recent experimental study (Van Orman and Grove, 2000) showed that assimilation of late stage cumulates does not appear to be a viable mechanism for the production of high-Ti mare basalts, because this process is not able to produce liquids with appropriate abundances of Ti and Ca.

Both assimilation and source hybridisation models generally suggest an ilmenite content in the range of 0.5% - 10% for the source of high-Ti mare basalts. The percentage of Zr from the IBCL in high-Ti mare basalts can be deduced by assuming (1) that the ilmenite originates from the IBCL and (2) Zr concentrations of 200 ppm and 2 ppm for ilmenite and early cumulates...
respectively, based on the model of Snyder et al. (1992). If 0.5 - 10% of ilmenite are present in the source of high-Ti basalts, 36 - 92% of the Zr originates from the ilmenite. This estimate is tentative, nevertheless, it suggests that a considerable fraction of the Zr originate from the ilmenites. In the worst case, if only 36% of the total Zr is derived from IBCL ilmenites, they must only display anomalies of $\varepsilon^{92}\text{Zr} = +1$ to generate measurable isotopic effects for the high-Ti mare basalts.

4.3.2.4 Implications

In the preceding, it was concluded that: (1) the source region of high-Ti basalts have Nb/Zr ratios that are at maximum 2 to 3 times the chondritic value and (2) $\varepsilon^{92}\text{Zr}$ values of $>1$ for IBCL ilmenites are likely to cause measurable anomalies in high-Ti mare basalts. What are the implications of these conclusions, regarding the generation of $^{92}\text{Zr}$ anomalies? The modest Nb/Zr fractionation of lunar rocks strongly limits the generation of $^{92}\text{Zr}$ anomalies. Fig. 4.4 shows that the fractionation expected for IBCL ilmenites (Nb/Zr $\sim$0.14-0.21) can only generate resolvable $^{92}\text{Zr}$ anomalies if the IBCL formed within the first $\sim$130 Myr or $\sim$60 Myr of the solar system, assuming an initial $^{92}\text{Nb} / ^{93}\text{Nb}$ ratio of $5 \times 10^{-4}$ or $1 \times 10^{-4}$, respectively. The latter values are the maximum initial values deduced from the isochrons of lunar highland samples. A previous isochron study, however, indicates that the initial $^{92}\text{Nb} / ^{93}\text{Nb}$ of the solar system is $<3 \times 10^{-5}$ (Schönbächler et al., 2002). Such a low initial $^{92}\text{Nb} / ^{93}\text{Nb}$ combined with the observed fractionation (Nb/Zr $\sim$0.14-0.21) is not able to produce detectable $^{92}\text{Zr}$ anomalies in the IBCL at any time. Given the evidence for a low initial $^{92}\text{Nb} / ^{93}\text{Nb}$ of the solar system, this is our preferred explanation for the observed lack of $^{92}\text{Zr}$ anomalies in high-Ti samples.

Münker et al. (2000) used the absence of $^{92}\text{Zr}$ anomalies for two highland breccias to conclude that ilmenite reservoirs on the moon formed more than 50 million years after the start of the solar system. With the limited Nb/Zr fractionation observed for lunar samples (Nb/Zr $\sim$0.14 - 0.21) and the low initial $^{92}\text{Nb} / ^{93}\text{Nb}$ of the solar system ($<3 \times 10^{-5}$), the conclusions are not valid, however, because measurable $^{92}\text{Zr}$ anomalies can not be formed at any time (Fig. 4.4).

4.4 Conclusion

No evidence for extinct $^{93}\text{Nb}$ on the moon was found in this study, despite of a broad range of investigated samples including the early anorthosite 60025, a norite, KREEP and various mare
basalts. The most likely reason for the identical Zr isotopic compositions in lunar samples is a modest Nb/Zr fractionation (Nb/Zr = 2 to 3 times the chondritic values), which prevents the formation of \(^{92}\text{Zr}\) anomalies. The Nb/Zr ratios of lunar ilmenites and bulk rock samples as well as calculations based on the model of Snyder et al. (1992) provide evidence for such a limited Nb/Zr fractionation. Our data, therefore, indicate that lunar reservoirs with strongly fractionated Nb/Zr did not exist. This implies that the role of ilmenite in the source region of high-Ti mare basalts is underconstrained from Nb/Zr. Moreover, it is not possible to draw conclusions about the timing of early differentiation on the moon.

The observed lack of \(^{92}\text{Zr}\) anomalies in the anorthosite 60025 constrains the initial \(^{92}\text{Nb}/^{95}\text{Nb}\) of the solar system to \(< 1 \times 10^{-4}\) and \(< 5 \times 10^{-4}\), respectively, depending on the age assumed for this rock.

**Acknowledgements**

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**Chapter 5**

**Zirconium Isotope Evidence for Incomplete Admixing of \( r \)-process Components in the Solar Nebula**

Abstract

Isotopic anomalies in Mo and Zr have recently been reported for bulk chondrites and iron meteorites and have been interpreted in terms of a primordial nucleosynthetic heterogeneity in the solar nebula. Here, we report precise Zr isotopic measurements of carbonaceous, ordinary and enstatite chondrites, eucrites, mesosiderites and lunar rocks. All bulk rock samples yield isotopic compositions, that are identical to the terrestrial standard within the analytical uncertainty. There exists a trace of isotopic heterogeneity in the form of a small excess of r-process $^{96}$Zr in some refractory calcium-aluminium-rich inclusions (CAIs) and some metal-rich phases of Renazzo. A more striking enrichment in $^{96}$Zr is found in acetic acid leachates of the Allende CV carbonaceous chondrite. These data indicate that the r- and s-process Zr components found in presolar grains were well mixed on a large scale prior to planetary accretion. However, some CAIs formed before mixing was complete, such that they were able to sample a population of r-process enriched material. The maximum amount of additional r-process component that was added to the otherwise well-mixed Zr in the molecular cloud or disk corresponds to ~0.01%.

5.1. Introduction

The isotopic homogeneity of the early solar nebula is a central issue of cosmochemistry. Until the early seventies, the isotopic compositions of a range of elements in meteorites had been found to be identical, within uncertainties, to those in the Earth. For example, no significant variation could be found in the isotope abundances of K, Rb and Sr in chondrites, eucrites and the Earth, once the effects of mass-dependant fractionation, cosmic-ray induced spallation and radioactive decay were removed (Reynolds, 1969). This large-scale homogeneity led to the view that the protoplanetary disk was made of material that condensed from a hot well-mixed nebular gas.

This paradigm gradually changed, however, with the detection of small-scale isotopic anomalies in chondrites. Previously unknown isotopic effects in oxygen were discovered in refractory calcium-aluminium-rich inclusions (CAIs) (Clayton et al., 1973). Subsequently, further isotopic heterogeneities in CAIs were found for a variety of elements such as titanium (Niemeyer and Lugmair, 1981), samarium (Lugmair et al., 1978), neodymium and barium (McCulloch and Wasserburg, 1978). The discovery of presolar grains (Lewis et al., 1987) and dispersed $^{54}$Cr
isotopic anomalies in Orgueil (Rotaru et al., 1992) provided strong evidence that the disk also contained presolar material that had not condensed from a hot nebular gas.

With small-scale heterogeneity in chondrites now well established, one has to re-examine the question of what large-scale homogeneity signifies if it is not produced in a well-mixed gas. Two extreme models can be considered:

1. The various pre-solar components were already well mixed in the molecular cloud before the collapse of the solar nebula.

2. There were processes in the disk that averaged out heterogeneity. The early dynamics of disks are thought to be dominated by settling of dust onto the mid-plane, the swirling motion of the nebula, the rapid accretion of planetesimals and the overall migration of material in toward the sun (Weidenschilling, 1977). Some have proposed that material also may have been transported outwards from the sun across the disk (Shu et al., 1997). It is conceivable that disks develop into conveyor belts prior to the creation of major gaps that are formed by incorporating gas and dust into large planetary objects. This swirling “conveyor belt” might be the most likely environment for mixing.

Although the evidence for large-scale homogeneity in the disk is overwhelming, there also exist indications of large-scale heterogeneity. The first clear evidence followed the realisation that basaltic achondrites such as angrites, eucrites and martian meteorites possess distinctive oxygen isotopic compositions that are characteristic of their parent bodies and different from those of the Earth and Moon (Clayton, 1993). It has become well established that the solar system possesses a large-scale heterogeneity in oxygen isotopes. The heterogeneity in $\Delta^{17}$O is not a function of heliocentric distance and may be caused by varying degrees of exchange between a gas and a solid reservoir (Thiemens and Heidenreich, 1983). Why gases and solids should have had different oxygen isotope compositions is unclear.

Evidence for large-scale isotopic heterogeneity that cannot be explained by gas–solid mixing is far more equivocal, however. From the discovery of small $^{53}$Cr abundance variations, that are a function of heliocentric distance, a former radial zonation in $^{53}$Mn in the inner solar system has been proposed (Shukolyukov and Lugmair, 2000). Alternatively, this observation can also be explained by volatility-induced Mn/Cr fractionation, with the exception of the $^{53}$Cr abundances in enstatite chondrites (EH) (Halliday et al., 1996; Cassen and Woolum, 1997; Birck et al., 1999). Recently, it has been proposed that there are small molybdenum isotopic variations
in bulk rock chondrites and iron meteorites (Dauphas et al., 2002a; Yin et al., 2002). However, other studies based on more extensive replication and/or higher precision indicate that these effects are not yet well-defined (Lee and Halliday, 2002; Becker and Walker, 2003).

The best way to approach this issue is with high-precision measurements of the relative abundances of isotopes produced via different nucleosynthetic pathways. A constant proportion of isotopes produced in different stellar environments would indicate very efficient mixing of components at some early or presolar stage. Small variations in the relative abundances have implications for how components must have been introduced and admixed into the solar nebula.

Zirconium is a promising element to address the question of isotopic homogeneity in the inner solar system. It is refractory and, therefore, insensitive to early solar system processes controlled by volatility that may influence elements like Mn, and hence Mn-Cr systematics. All Zr isotopes have mixed nucleosynthetic sources, but are dominated by one process. The $^{96}$Zr is primarily produced by the r-process, whereas all the other Zr isotopes ($^{90}$Zr, $^{91}$Zr, $^{92}$Zr, $^{94}$Zr) predominately originate from the s-process. Excess $^{96}$Zr relative to the other Zr isotopes and the terrestrial standard was reported for presolar grains (Nicolussi et al., 1998b; Davis et al., 1999), and explained as due to r-process material produced in supernovae (Wallerstein et al., 1997). It may also be that some of the $^{96}$Zr was made by the s-process if the neutron density were unusually high (Nicolussi et al., 1998b). However, this is speculative at this stage. A complementary pattern with a deficit of $^{96}$Zr was found in presolar grains (Nicolussi et al., 1997). Such grains display an overabundance of s-process nuclides, which may have formed in AGB-stars (Wallerstein et al., 1997). Furthermore, two independent studies have claimed that there are well-resolved bulk rock isotopic variations of zirconium in chondrites (Sanloup et al., 2000; Yin et al., 2001), and these were interpreted to reflect incomplete mixing of different nucleosynthetic components. In particular, Yin et al. (2001) reported a very large $^{96}$Zr anomaly for the carbonaceous chondrite Murchison.

The isotope $^{92}$Zr is also produced by the radioactive decay of the short-lived radionuclide $^{92}$Nb ($\lambda = 36 \pm 3$ Myr) (Nethaway et al., 1978). For the application of this short-lived isotopic system, it is crucial to know if Nb and Zr isotopes are distributed homogeneously in the solar system. The initial abundance of $^{92}$Nb has been a matter of recent debate. Current estimates range from an initial $^{92}$Nb/$^{93}$Nb ratio of $10^{-5}$ up to a value as high as $10^{-3}$ (Harper, 1996; Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000; Hirata, 2001; Schönbachler et al., 2002).

The aim of this study was to investigate if Zr isotopes are indeed distributed heterogeneously in the inner solar system. For this purpose, a comprehensive Zr isotopic study was
conducted on a wide range of samples, including CAIs, chondrites, differentiated meteorites, lunar and terrestrial samples. The results provide new constraints on the maximum amount of incompletely admixed Zr from hypothetical triggering stars and on the initial abundance of $^{92}$Nb in the solar system.

### 5.2. Analytical procedure

The samples were crushed in a boron carbide or an aluminium oxide mortar under a laminar flow of filtered air to avoid contamination. Subsequently, a Parr acid digestion bomb was used to ensure the complete dissolution of the samples, including any zircons. The mineral separates and leachates of Allende and Renazzo were obtained as outlined in Table 5.1. We started with 2 g of Allende, which was treated sequentially with a series of progressively stronger reagents. After each treatment, the sample was centrifuged and the supernatant was removed by pipette. Renazzo was first separated mechanically with a hand magnet (Table 5.1) to obtain a magnetic and a non-magnetic (n.m.) fraction. A second magnetic separation was performed for the magnetic fraction only. The non-magnetic residue of the second step was then combined with the bulk rock sample to form the metal-rich whole rock sample (m.r. w.r.). The magnetic fraction was subsequently leached for five minutes with 6 M HCl - 0.01 M HF to produce a magnetic leachate (m.l.). The residue was too small for further treatment.

Zirconium was chemically separated from the whole rock matrix using a two-stage ion-

<table>
<thead>
<tr>
<th>Allende</th>
<th>Step</th>
<th>Reagent</th>
<th>Procedure</th>
<th>Percent* Total Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>50% HAc</td>
<td>2 days, RT</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4 M HNO$_3$</td>
<td>5 days, RT</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>6 M HCl</td>
<td>1 day, 80°C</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>13.5 M HCl + 3 M HCl</td>
<td>4 days, 100°C</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Aqua Regia</td>
<td>3 hours, 220°C, high pressure asher</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Renazzo</th>
<th>Fraction</th>
<th>Mechanical separation</th>
<th>Chemical separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>n.m.</td>
<td>non magnetic fraction</td>
<td>metal removed with a hand magnet</td>
<td>6 M HCl + 0.01 M HF, 5 min, 40°C</td>
</tr>
<tr>
<td>m.l.</td>
<td>magnetic leachate fraction</td>
<td>metal cleaned up twice with an handmagnet</td>
<td>6 M HCl + 0.01 M HF, 5 min, 40°C</td>
</tr>
<tr>
<td>m.r. w.r.</td>
<td>metal-rich whole rock</td>
<td>whole rock + metal rich residue of second clean up of the magnetic fraction</td>
<td>6 M HCl + 0.01 M HF, 5 min, 40°C</td>
</tr>
</tbody>
</table>

*RT = room temperature
HAc = CH$_3$COOH
*Percentage of total recovered Zr dissolved in this fraction
exchange procedure. The first and the second stage are adapted from Salters and Hart (1991) and Barovich et al. (1995), respectively. The details are discussed elsewhere (Schönbächler et al., 2003c). The ion-exchange procedure for the Allende leachates did not use hydrofluoric acid for the elution of Zr and an additional elution step for matrix elements with 15M HF was included, such that we could also obtain a clean Te fraction. The Te data will be presented in a separate paper (Fehr et al., 2003). The modifications reduced the Zr yield to only about 30%. Such a low yield could potentially induce mass-dependent fractionation of isotopes during chemistry. However, no such mass-dependent fractionation has been observed. The total chemistry blank for the Allende leachates was less than 3 ng Zr. This is negligible, considering that each sample fraction contained more than 300 ng Zr. The total chemistry blank for all other samples was always less than 1 ng Zr.

The Zr isotopic measurements were performed with a Nu Plasma multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS) at the ETH Zürich. All Zr isotopes were measured, as well as \(^{98}\text{Mo}\), \(^{91}\text{Nb}\) and \(^{99}\text{Ru}\) in order to monitor potential isobaric interferences and peak-tailing effects. Instrumental mass fractionation was internally normalised to \(^{94}\text{Zr}/^{90}\text{Zr} = 0.3381\) (De Bièvre et al., 1984) using the exponential law. Epsilon Zr values were calculated relative to the mean values of the NIST SRM 3169 Zr standard solution measured the same day using \(\varepsilon\text{Zr} = \left(\frac{\text{Zr}_{\text{std}}}{\text{Zr}_{\text{std}}}\right)_\text{measured} - \left(\frac{\text{Zr}_{\text{std}}}{\text{Zr}_{\text{std}}}\right)_\text{mean} \right) \times 10^4\). The 2σ reproducibility obtained for 100 ppb solutions of the NIST SRM 3169 Zr standard is better than ±0.3, ±0.6 and ±1.2 ε-units for \(^{92}\text{Zr}\), \(^{91}\text{Zr}\) and \(^{99}\text{Zr}\), respectively, within one day. We use these values as a conservative estimate of the analytical uncertainty for our standard solution. The long term reproducibility is only slightly larger than the within-day precision (Rehkämper et al., 2001).

The \(^{91}\text{Zr}\) analysis is hampered by a minor unidentified isobaric interference, which is common to all samples and standards analysed at low ion beams (total ion beam < 2.5 \times 10^{-11} \text{ A})}. The effect disappears at low ion beam. It was compensated by measuring standards and samples with the same beam intensities (Schönbächler et al., 2003c). However, most samples achieved total ion beams > 5 \times 10^{-11} \text{ A}. The Mo interference on mass 92 can be adequately corrected, if Mo/Zr in the sample solution is < 0.01, as inferred from repeated measurements of synthetic Mo-Zr mixtures. For an adequate correction of the \(^{96}\text{Mo}\) interference an even smaller Mo/Zr ratio of < 0.005 is required, and a Ru/Zr ratio of < 0.01 is necessary to adequately correct for the \(^{96}\text{Ru}\) interference. These limits correspond to a relative magnitude of the Mo and Ru corrections in the order of 1 - 3%. The Mo/Zr and Ru/Zr ratios of the analysed sample solutions were always far below these limits. The Ru correction is essential for undifferentiated meteorites because they generally possess high Ru
contents compared to the differentiated meteorites, lunar and terrestrial samples. For all differentiated samples, the Ru contribution to mass 96 was negligible and did not require correction. All samples were also carefully checked for interferences from Ti-, V-, Cr- and Fe-argides, which overlap with the masses of zirconium.

The $^{93}\text{Nb}/^{90}\text{Zr}$ ratios of the samples were measured with a quadrupole ICP-MS on sample solution aliquots that did not undergo chemical separation, to avoid any chemical fractionation of Nb from Zr. Spectral interferences in these measurements were accounted for by using dynamic reaction cell technology with hydrogen as reactive gas (Hattendorf et al., 2001).

### 5.3. Results

The Zr isotopic compositions ($\varepsilon^{91}\text{Zr}$, $\varepsilon^{92}\text{Zr}$, $\varepsilon^{96}\text{Zr}$) for bulk samples of 4 carbonaceous, 8 ordinary and 3 enstatite chondrites are shown in Fig. 5.1a together with data for eucrites, a mesosiderite silicate clast and three lunar samples. Fig. 5.1a displays clearly that all bulk rock data are identical to the terrestrial standard within the 2σ analytical uncertainty. Thus, there is a striking homogeneity of Zr isotopic compositions.

Once the current analytical precision is improved, it is possible that carbonaceous chondrites such as Murchison and Allende may reveal a slight shift to positive $\varepsilon^{96}\text{Zr}$ values. At present, this is not clearly resolvable. The repeated analyses of different Murchison and Allende aliquots (Table 5.2), however, show a small and systematic shift in $\varepsilon^{96}\text{Zr}$. Furthermore, the application of a statistical t-test to compare the Murchison and Allende datasets with the terrestrial standard yields an explicit difference at the 99% confidence level. If this effect is not an analytical artefact, it indicates that Murchison and Allende have a slightly different Zr isotopic composition than the Earth or that small-scale heterogeneities may exist within each sample. The $\varepsilon^{91}\text{Zr}$ values of the carbonaceous chondrites (Table 5.2) show a similar but even smaller offset. However, this may be related to the minor isobaric interference on $^{91}\text{Zr}$ referred to above. In summary, the primary conclusion is that bulk meteorite samples display identical Zr isotopic composition within the analytical uncertainty. Some results for carbonaceous chondrites hint at very small differences in $\varepsilon^{96}\text{Zr}$, but the differences cannot be resolved unambiguously at present.

In contrast to the bulk rock data, two Allende leachates (acetic and hydrochloric acid steps) and three Renazzo fractions reveal evidence of significant excess $^{96}\text{Zr}$ (Fig. 5.2). Interestingly,
Fig. 5.1: (a) Zirconium isotopic compositions for various bulk meteorite samples. (b) Zirconium isotopic compositions for CAIs (calcium-aluminium-rich inclusions) of Allende and Efremovka. Errors (2σ) given for the samples include the external reproducibility of the sample and the standard combined as follow: 
\[ \sigma = \sigma_{\text{sam}} + \sigma_{\text{std}} \]
where \( \sigma \) is the external reproducibility of the standard (std) or the sample (sam). If several analyses of a single sample exist (Table 5.2), the mean value is plotted. No \( \varepsilon^{91}\text{Zr} \) and \( \varepsilon^{92}\text{Zr} \) values are shown for some samples because of known interference problems and/or low signal intensities for the minor \( ^{90}\text{Zr} \).

(Eu = eucrite)

The results for Allende show that the Zr leached by the acetic acid displays the largest excess in \( ^{96}\text{Zr} \) (\( \varepsilon^{96}\text{Zr} = 10.0 \pm 1.5 \)). Around 6% of the total Zr recovered (Table 5.1) was released in this leaching step. The Zr was probably hosted in alteration phases and/or metal (Rotaru et al., 1992; Podosek et al., 1997). In the nitric acid fraction (second step), the small Zr content of 6 ng did not permit precise isotopic analysis. Subsequent leaching with hot HCl yielded 20% of the total Zr. This fraction displays a small excess of \( ^{96}\text{Zr} \). The two last leaching steps using HCl/HF and aqua regia represent chemically resistant phases and account for most of the Zr in the whole rock. Their Zr isotopic
signature is identical to the terrestrial standard. A mass balance calculation of all Allende leach fractions results in $\epsilon^{96}\text{Zr} = +1.4$ for bulk Allende. This is identical to the mean value measured for bulk Allende ($\epsilon^{96}\text{Zr} = +1.0 \pm 1.2$), within uncertainty.

The Renazzo sample was separated into different fractions in order to identify carrier phases anomalous in $^{96}\text{Zr}$ (Table 5.1). The results (Fig. 5.2) show that all Renazzo fractions have an identical Zr isotopic pattern and display a small but significant excess of $^{96}\text{Zr}$. Therefore, the carrier phase of the excess $^{96}\text{Zr}$ must be homogeneously distributed in the magnetic and non-magnetic phases. The same observation was made for the carrier phase of anomalous $^{54}\text{Cr}$ in Orgueil (Podosek et al., 1997).

![Fig. 5.2: Zirconium isotopic compositions for separates of Allende and Renazzo.](image)

$1 = \text{acetic acid leachate}, 3 = \text{HCl leachate}, 4 = \text{HF/HCl leachate}, 5 = \text{aqua regia leachate}, \text{m.r. w.r.} = \text{metal-rich whole rock}, \text{n.m.} = \text{non-magnetic fraction}, \text{m.l.} = \text{magnetic leachate fraction. For details see Table 5.1.}
Table 5.2: Zr isotopic data and Nb/Zr ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\epsilon^{\text{eZr}}$</th>
<th>$\epsilon^{\text{eZr}}$</th>
<th>$\epsilon^{\text{NbZr}}$</th>
<th>Nb/Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orgueil (CI1)</td>
<td>0.2 ± 0.6</td>
<td>0.0 ± 0.4</td>
<td>-0.1 ± 1.5</td>
<td>0.085 ± 0.004</td>
</tr>
<tr>
<td>Murchison (CM2)</td>
<td>0.2 ± 0.7</td>
<td></td>
<td></td>
<td>0.063 ± 0.003</td>
</tr>
<tr>
<td>Murchison (CM2)</td>
<td>0.1 ± 0.6</td>
<td>0.0 ± 0.4</td>
<td>1.2 ± 1.6</td>
<td>0.076 ± 0.004</td>
</tr>
<tr>
<td>Murchison (CM2)</td>
<td>0.1 ± 0.6</td>
<td>-0.1 ± 0.4</td>
<td>1.2 ± 1.6</td>
<td>0.072 ± 0.004</td>
</tr>
<tr>
<td>Murchison (CM2)</td>
<td>0.3 ± 0.6</td>
<td>0.3 ± 0.4</td>
<td>0.4 ± 1.5</td>
<td>0.063 ± 0.003</td>
</tr>
<tr>
<td>Allende (CV3)</td>
<td>0.5 ± 0.6</td>
<td>0.2 ± 0.4</td>
<td>1.2 ± 1.4</td>
<td>0.074 ± 0.005</td>
</tr>
<tr>
<td>Allende (CV3)</td>
<td>0.2 ± 0.6</td>
<td>-0.1 ± 0.4</td>
<td>0.9 ± 1.5</td>
<td>0.077 ± 0.004</td>
</tr>
<tr>
<td>Allende (CV3)</td>
<td>0.0 ± 0.6</td>
<td>0.0 ± 0.4</td>
<td>1.1 ± 1.4</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>Allende (CV3)</td>
<td>0.5 ± 0.6</td>
<td>0.1 ± 0.5</td>
<td>0.7 ± 1.6</td>
<td>0.076 ± 0.005</td>
</tr>
<tr>
<td>Allende (CV3)</td>
<td>0.1 ± 0.6</td>
<td>-0.1 ± 0.4</td>
<td>1.3 ± 1.5</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>Allende (CV3)</td>
<td>0.3 ± 0.6</td>
<td>-0.1 ± 0.4</td>
<td>0.4 ± 1.5</td>
<td>0.071 ± 0.006</td>
</tr>
<tr>
<td>Indarch (EH4)</td>
<td>0.4 ± 0.6</td>
<td>0.1 ± 0.4</td>
<td>-0.1 ± 1.4</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>Allende leach 1 (HAc)</td>
<td>0.1 ± 0.6</td>
<td>0.1 ± 0.4</td>
<td>0.3 ± 1.4</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 4698</td>
<td>0.0 ± 0.6</td>
<td>0.0 ± 0.4</td>
<td>2.1 ± 1.5</td>
<td>0.015 ± 0.001</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-21</td>
<td>0.6 ± 0.6</td>
<td>0.5 ± 0.4</td>
<td>0.3 ± 1.4</td>
<td>0.45 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-21</td>
<td>0.4 ± 0.6</td>
<td>0.2 ± 0.4</td>
<td>1.2 ± 1.4</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-21</td>
<td>0.6 ± 0.6</td>
<td>0.4 ± 0.4</td>
<td>0.4 ± 1.7</td>
<td>0.050 ± 0.002*</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-41</td>
<td>0.3 ± 0.6</td>
<td>0.1 ± 0.4</td>
<td>2.5 ± 1.4</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-41</td>
<td>0.6 ± 0.6</td>
<td>0.1 ± 0.4</td>
<td>1.1 ± 1.5</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-41</td>
<td>0.2 ± 0.6</td>
<td>0.1 ± 0.4</td>
<td>2.1 ± 1.5</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-41</td>
<td>0.1 ± 0.6</td>
<td>0.0 ± 0.4</td>
<td>1.8 ± 1.5</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-44</td>
<td>0.3 ± 0.6</td>
<td>0.1 ± 0.4</td>
<td>2.0 ± 1.4</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-44</td>
<td>0.5 ± 0.6</td>
<td>0.3 ± 0.4</td>
<td>2.3 ± 1.5</td>
<td>0.074 ± 0.003</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-47</td>
<td>-0.2 ± 0.6</td>
<td>-0.3 ± 0.4</td>
<td>1.3 ± 1.5</td>
<td>0.116 ± 0.006</td>
</tr>
<tr>
<td>CAI Efremovka E49</td>
<td>-0.1 ± 0.6</td>
<td>0.2 ± 0.4</td>
<td>1.3 ± 1.5</td>
<td>0.081 ± 0.004</td>
</tr>
</tbody>
</table>

The quoted analytical uncertainties for the $\epsilon^{Zr}$ values reflect the external ($2\sigma_{\text{mean}}$) reproducibilities including the uncertainties for the standard.*Nb/Zr ratio from Mason and Taylor (1982).
In addition, six CAIs separated from Allende and Efremovka were analysed (Fig. 5.1b). Three of the Allende CAIs reveal a small excess of $^{96}\text{Zr}$. The observed excess $^{96}\text{Zr}$ is not large enough to produce a well-resolved difference in the bulk Allende data presented here. However, the CAIs could be responsible for some of the excess $^{96}\text{Zr}$ in the Allende leachates. CAIs contain a significant amount of melilite, which can be attacked by hydrochloric acid.

5.4. Discussion

5.4.1 The bulk rock analysis

All the bulk rock data (Fig. 5.1a) show a remarkable homogeneity in Zr isotopic compositions. This observation contrasts with the results of previous studies on bulk rock meteorites (Sanloup et al., 2000; Yin et al., 2001) that identified Zr isotopic anomalies well outside the stated analytical uncertainties. It is notable, that some meteorites were analysed both in this and previous studies such as Murchison (CM2), Allende (CV3), Abee (EH4), Orgueil (CI) and Forest Vale (H4). For the first three meteorites, $\varepsilon^{96}\text{Zr}$ values up to +50 were reported (Yin et al., 2001). The isotope $^{96}\text{Zr}$ has a low abundance (2.8%) and two sources of isobaric interferences, $^{96}\text{Mo}$ and $^{96}\text{Ru}$. The three meteorites for which Zr anomalies are cited (Allende, Murchison, Abee) are primitive meteorites, which require a Ru correction on mass 96. Unfortunately, the authors (Yin et al., 2001) provide no information about the Ru correction and they demonstrate only that the Mo interference on $^{92}\text{Zr}$ can be adequately corrected for solutions with Mo/Zr <0.01. It is unclear, if this also applies to the correction on mass 96. Until these issues are resolved, it remains possible that the reported $^{96}\text{Zr}$ anomalies are analytical artefacts that reflect insufficiently corrected interferences.

The uniformity of our bulk rock data (Fig. 5.1a) provides compelling evidence that the inner solar system is generally well mixed in terms of the Zr isotopic composition and this implies that the protosolar nebula was also well mixed on a planetary scale before planetesimal accretion occurred. The isotope data for other elements such as iron are in accord with this conclusion, because the observed Fe isotope variations are solely due to mass dependent fractionation (Zhu et al., 2001). However, disk-scale isotopic heterogeneity has been proposed for e.g., $^{26}\text{Al}$, $^{41}\text{Ca}$ (Lee et al., 1998), $^{53}\text{Mn}$ (Shukolyukov and Lugmair, 2000), O isotopes (Clayton et al., 1973; Clayton, 1993) and, most recently, for Mo isotopes (Dauphas et al., 2002a;
Although some of these isotopic variations might relate to processes associated with the early evolution of the sun and inner disk, the Mo isotopic variations have been interpreted in terms of a very early isotopic heterogeneity in the region of the disk that supplied the materials forming iron meteorite and chondrite parent bodies. The existence of these Mo isotopic variations, particularly in iron meteorites, is a matter of debate (Lee and Halliday, 2002; Becker and Walker, 2003). However, the fact that there exist effects that vary with normalization scheme provides strong evidence of real, albeit poorly resolved heterogeneity.

Evidence of large Mo and Zr isotopic heterogeneity at a very small scale is provided by presolar grains. Figure 5.3 illustrates two signatures of Zr isotopes discovered in presolar grains, and similar observations exist for Mo isotopes (Nicolussi et al., 1998a; Nicolussi et al., 1998b). If such presolar grains with different isotopic patterns were not distributed evenly within the disk, this could result in large-scale heterogeneities. Considering the concentration of Mo and Zr in Allende (Jarosewich et al., 1987), the average abundance and isotopic composition of these elements in SiC grains (Nicolussi et al., 1997; Nicolussi et al., 1998a; Nicolussi et al., 1998b; Kashiv et al., 2001), Allende should display isotopic anomalies in the same order of magnitude for both Mo and Zr. It is puzzling, therefore, why such heterogeneities are found in Mo but not in Zr isotopic compositions.

Fig. 5.3: a) Zirconium isotopic patterns as a function of mass for presolar SiC-grains (Davis et al., 1999) and graphite grains (Nicolussi et al., 1998) with an r-process signature from the Murchison meteorite. (b) Isotopic pattern for SiC grains with an s-process signature (Nicolussi et al., 1997). For further details see references. On the bottom, the nucleosynthetic processes by which each Zr isotope can be formed are shown. Highlighted in bold is the primary nucleosynthetic process.
It is conceivable that such effects may exist for Zr, but they are just below the detection limit, as the effects claimed for Mo are only a few epsilon units (Dauphas et al., 2002a, Yin et al., 2002, Becker and Walker, 2003).

5.4.2 Separates of Allende and Renazzo

For the first time, Zr isotopic data of selectively dissolved fractions of carbonaceous chondrites are presented (Fig. 5.2). In contrast to the homogeneity of the bulk rock data, two of the Allende leachates and all separates of Renazzo display significant excess $^{96}\text{Zr}$. Isotopic heterogeneities measured in leach fractions of carbonaceous chondrites, therefore, not only exist for $^{54}\text{Cr}$ (Rotaru et al., 1992; Podosek et al., 1997), $^{40}\text{K}$ (Podosek et al., 1999) and Mo isotopes (Dauphas et al., 2002b), but also for $^{96}\text{Zr}$. This provides evidence for isotopic heterogeneities at a small scale in the solar system. Small-scale heterogeneities were also discovered in presolar grains (Lewis et al., 1987) and argue for a solar nebula with colder regions that contain gas and distinct solid particles.

The production of $^{96}\text{Zr}$ by cosmic-ray induced spallation or special irradiation scenarios of the early sun needs to be verified by model calculations. Nevertheless, it is unlikely, that these processes are able to produce significant levels of $^{96}\text{Zr}$ within the solar system (I. Leya, pers. comm.). Therefore, the excess $^{96}\text{Zr}$ in the Allende and Renazzo fractions probably have the same nucleosynthetic origin as those in presolar grains (Fig. 5.3). This leads to the question, of whether presolar grains are the host phase of excess $^{96}\text{Zr}$ in Allende and Renazzo. The largest excess of $^{96}\text{Zr}$ was found for the acetic acid leachate. Although acetic acid leaching should predominantly attack phases in the matrix, where the bulk of presolar grains is situated, it is unlikely that this treatment will dissolve the known varieties of presolar grains, since these are very acid resistant. The matrix materials of primitive meteorites experienced much less thermal alteration than CAIs and chondrules. Therefore, it is possible that some previously unidentified and chemically less resistant presolar grains were preserved and contributed to the excess $^{96}\text{Zr}$ in the acetic acid leachate.

Alternatively, the excess $^{96}\text{Zr}$ may be hosted in phases that formed within the solar system. Presolar grains that were incorporated to solar system material could have been affected by aqueous alteration, thereby transferring their exotic isotopic signatures to easily leachable minerals. Furthermore, presolar grains could already have reacted with other phases or been melted or vaporised within the solar nebula transferring there their isotopic signature to solids formed in the solar system. The
observation that three Allende CAIs preserve a significant amount of excess $^{96}$Zr indicates that part of the excess $^{96}$Zr is hosted in such a phase. CAIs are generally regarded as high temperature condensates that formed very early in the solar system. Although extremely chemical resistant, presolar grains are unlikely to have survived at such high temperatures. The observed $^{96}$Zr anomalies in CAIs, therefore, must be inherited and preserved in material that formed in the early solar system.

Comparing the present results with leaching data for other elements may help to identify the nature of the carrier phase(s). In Allende, variations of $^{54}$Cr (Rotaru et al., 1992) and $^{96}$Zr were observed in different leaching steps. In the present experiment, excess $^{96}$Zr was released by acetic and hydrochloric acid, but not by HCl/HF (Table 5.1, Fig. 5.2). In contrast, excess $^{54}$Cr only occurs to a limited extent in the acetic acid leachate, and is more pronounced in the HCl/HF leachate. It is important to note, that the leaching procedures for Cr and Zr differ slightly. The hydrochloric acid step was only performed for Zr. Therefore, the excess $^{54}$Cr of the Allende HCl/HF leachate could be hosted in the same HCl soluble carrier phase, that contains excess $^{96}$Zr. This conclusion is supported by the results of Podosek et al. (1997), who found the largest excess of $^{54}$Cr for Orgueil in the hydrochloric acid leachate. This indicates that excess $^{54}$Cr and part of excess $^{96}$Zr may be hosted in similar or identical carrier phases, which have different Zr/Cr ratios. In view of nucleosynthetic models, this is viable, because most models indicate that both $^{54}$Cr (Rotaru et al., 1992) and $^{96}$Zr are predominantly produced in a supernova environment.

### 5.4.3 Modelling

The uniformity of the bulk rock data (Fig. 5.1) and the magnitude of the isotopic anomalies in presolar grains (Nicolussi et al., 1998b) can be used to estimate the magnitude of possible Zr isotope heterogeneities in the solar system. This is of more than academic interest. It is a widely held view that short-lived radionuclides like $^{53}$Mn could represent freshly synthesised stellar products, that were injected into the protosolar nebula. The accompanying shock wave may have triggered the collapse of the protosolar nebula (Cameron and Truran, 1977; Nichols et al., 1999). Because of the short time-scale between injection of the material and collapse of the protosolar nebula, the freshly injected material may not have had sufficient time to be completely admixed into the protosolar nebula material and this could have generated isotopic heterogeneities. The large-scale heterogeneity in $^{53}$Mn may be due to such a late injection of freshly produced nucleosynthetic material (e.g. Nichols et al., 1999).
Chapter 5  
Zirconium Isotopes and the r-process

Assuming that a supernova triggered the collapse of the protosolar nebula and injected new material (Cameron and Truran, 1977), it is possible to calculate the atom fraction of r-process Zr that can be heterogeneously distributed in the inner solar system without causing any measurable isotopic effect. This restriction is imposed by the homogeneity of Zr isotopic compositions observed for the Earth, moon, eucrites and chondrites. The calculation was performed using the following equation:

\[
\frac{N_i}{N_e} = \frac{f \times a_{i,\text{solar}} + (1-f) \times a_{i,\text{inj}}}{f \times a_{i,\text{solar}} + (1-f) \times a_{i,\text{inj}}}
\]

(1)

In this equation, 'N represent the abundance of a specific Zr isotope with mass i in the mixture, 'ab the abundance of a specific isotope in the solar system (solar) or in the injected material (inj) and f is the atom fraction of solar system isotopes in the mixture. The isotopic composition of the interstellar graphite grain C.14 (Fig. 5.3) was used as a lower limit of the r-process composition of the injected material. The calculation shows that the proportion of Zr derived from r-process presolar grains can only vary by less than 130 ppm for the various solar system bodies (Fig. 5.4). Assuming that the graphite grain 5.01 with a very high excess $^{96}$Zr displays the average r-process composition, the variation is restricted to less than 15 ppm.

It is also possible, that an AGB star triggered the collapse of the solar system (Wasserburg et al., 1994). In this case, Zr isotopes provide constraints for the differences in the proportion of Zr originating from s-process grains. Using the Zr isotopic composition of the SiC grain 126 (Fig. 5.3), the difference has to be < 300 ppm, which is somewhat higher than in the supernova scenario.

![Fig. 5.4: The curve indicates the maximum atom fraction (f) of Zr with distinct $\varepsilon^{96}$Zr (inj = injected) that can be injected into a system with $\varepsilon^{96}$Zr = 0 without producing a significant change ( $\varepsilon^{96}$Zr >1.2 ) in the Zr isotopic composition. The gray bars show the $\varepsilon^{96}$Zr for the presolar graphite grains C.14 and 5.01 (data from Nicolussi et al., 1998). The maximum atom fraction increases from 100 ppm to 130 ppm, if the exact isotopic composition of the grain C.14 is used ( $\varepsilon^{96}$Zr , $\varepsilon^{92}$Zr and $\varepsilon^{90}$Zr ≠ 0).
5.4.4 The calcium-aluminium-rich inclusions

Only three of the six analysed CAIs display a small, resolvable excess of $^{96}$Zr (Fig. 5.1b). This is consistent with Zr isotopic measurements for coarse-grained Allende CAIs (Harper et al., 1991; Yin et al., 2001) and the evidence for $r$-process signatures preserved in FUN-inclusions for samarium and neodymium (Lugmair et al., 1978; McCulloch and Wasserburg, 1978). However, there seems to be a difference between the $^{96}$Zr and $^{50}$Ti anomalies observed in normal CAIs. The $^{96}$Zr excess are smaller and rarer compared to the ubiquitous excesses of $^{50}$Ti. The occurrence of $^{96}$Zr anomalies does not correlate with the petrographic type of the CAIs or with the rare earth element patterns (Table 5.3) (Amelin et al., 2002; Mason and Martin, 1977; Mason and Taylor, 1982). The observation that isotopic effects are not pervasive in CAIs has also been made for the abundances of the short-lived radionuclides $^{26}$Al and $^{41}$Ca (Sahijpal and Goswami, 1998). Diverse models have been proposed to explain this feature. Among these are the suggestions for a heterogeneous distribution of $^{26}$Al in the solar nebula (e.g. MacPherson et al., 1995; Wood, 1998) and special irradiation scenarios including the X-wind model during the evolution of the young sun (Shu et al., 1997). The production of $^{96}$Zr within the solar system by irradiation is unlikely, but this does not provide constraints against the X-wind model. A heterogeneous distribution of $^{96}$Zr, however, cannot be excluded.

The existence of $^{96}$Zr anomalies supports the idea that CAIs originated from material that was isotopically distinct from average solar system. The CAIs may simply have formed from too little material to sample the exact average solar system composition. The isotopic data obtained from stepwise dissolution of carbonaceous chondrites (Rotaru et al., 1992; Podosek et al., 1997; Podosek et al., 1999; Dauphas et al., 2002b; this work) and the occurrence of presolar grains (e.g. Anders and Zinner, 1993; Huss and Lewis, 1995) indicates that the average solar system material is built up of distinct nucleosynthetic components which can, in part, be separated.

Table 5.3: Description of the CAIs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size</th>
<th>Groups*</th>
<th>Excess $^{96}$Zr</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAI Allende USNM 4698</td>
<td>fine grained</td>
<td>Group III</td>
<td>yes</td>
<td>Mason and Martin (1977)</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-21</td>
<td>coarse grained</td>
<td>Group V</td>
<td>no</td>
<td>Mason and Taylor (1982)</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-41</td>
<td>coarse grained</td>
<td>Group III</td>
<td>yes</td>
<td>Mason and Taylor (1982)</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-44</td>
<td>medium grained</td>
<td>Group VI</td>
<td>yes</td>
<td>Mason and Taylor (1982)</td>
</tr>
<tr>
<td>CAI Allende USNM 3529-47</td>
<td>fine grained</td>
<td>Group VI</td>
<td>no</td>
<td>Mason and Taylor (1982)</td>
</tr>
<tr>
<td>CAI Efremovka E49</td>
<td>coarse grained</td>
<td>-</td>
<td>no</td>
<td>Amelin et al. (2002)</td>
</tr>
</tbody>
</table>

* on the basis of rare earth pattern
Heterogeneities at a very small scale, therefore, exist in solar system materials and could have been sampled by CAIs. Another explanation is that CAIs formed before homogenisation of the material in the protoplanetary disk was completed. As a consequence, CAIs sampled either a heterogeneity that was already present for a longer time-scale in the protosolar nebula or the heterogeneity developed through a late injection of freshly synthesised material. Assuming a late injection, the introduced material may have been dominated by either r-process or s-process products depending on its stellar source. In the first case, the CAIs would preserve the diluted r-process signature of the injected material, in the latter the signature of the former average solar system composition. The latter case entails that the composition of the whole solar system was changed through the injection of predominately s-process material from an AGB- or Wolf-Rayet-star. Clearly, this scenario requires the injection of huge amounts of material, whereas the alternative model only requires that small local isotopic heterogeneities of injected r-process material are preserved.

However, although possible, it is not clear that the observed excess of $^{96}\text{Zr}$ is related to a late injection of material. In any case, some CAIs formed before mixing of solar system material was complete, such that they were able to sample a population of r-process enriched material.

### 5.4.5 $^{92}\text{Nb}$-$^{92}\text{Zr}$

Evidence for formerly live $^{92}\text{Nb}$ was first identified in a Nb-rich rutile from the iron meteorite Toluca (Harper, 1996). An initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $(1.6 \pm 0.3) \times 10^{-5}$ was inferred. Three subsequent studies proposed that the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of the solar system was in fact more than 2 orders of magnitude higher at $\sim 10^{-3}$ (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000). A combined Zr isotopic and U-Pb age study of an early zircon from a eucrite yielded an initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $<10^{-4}$ (Hirata, 2001). This result agrees with the most recent work, which produced the first isochrons for the Nb-Zr system and inferred a low initial of $<3 \times 10^{-5}$ (Schönbächler et al., 2002).

The Nb/Zr elemental ratio and the age of a sample determines, whether the decay of the extinct radionuclide $^{92}\text{Nb}$ would produce a measurable $^{92}\text{Zr}$ anomaly, given that the solar system started with a sufficiently high initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio. Hence, a high Nb/Zr ratio in an old sample results in a large $^{92}\text{Zr}$ excess. Although the Nb/Zr ratios of the different bulk meteorite samples and CAIs (Table 5.2) vary by a factor of 10, no $^{92}\text{Zr}$ anomaly is found. Since these samples are generally
regarded as the oldest of the solar system, this requires a low initial $^{92}\text{Nb}/^{91}\text{Nb}$ ratio for the solar system.

Münker et al. (2000) analysed a bulk rock sample (60 mg) of the ordinary chondrite Adrar 003 (LL3) and found a Nb/Zr ratio of 0.166 and an $\varepsilon^{92}\text{Zr}$ excess of $+2.7 \pm 1.0$. In comparison, the bulk rock samples of the eucrites Sioux County and Bereba analysed in this work have similar Nb/Zr ratios of 0.111 and 0.191, respectively, and they display no effects in $^{92}\text{Zr}$. Furthermore, Münker et al. (2000) presented data for a CAI, which is characterised by a Nb/Zr ratio of $-0.015$ and a $^{92}\text{Zr}$ deficit of about $-2$ epsilon units. In contrast, the Allende CAI USNM4698 analysed in this study also has a Nb/Zr = 0.015, but it does not display a $^{92}\text{Zr}$ anomaly (Table 5.2).

These results cannot easily be explained by age differences. Sioux County and Bereba are dated by Pb isotope systematics to ~ 40 Myr after the start of the solar system (Tatsumoto et al., 1973; Carlson et al., 1988; Tera et al., 1997) and can only be reconciled with Adrar003 data by allowing large analytical uncertainties. However, age differences cannot account for the discrepancies between the CAI data, because this would require that these CAIs formed over a period of more than 80 Myr, which is highly implausible (Amelin et al., 2002).

The initial abundance of $^{26}\text{Al}$ shows significant variations in CAIs (MacPherson et al., 1995). This may be due to age differences or special irradiation scenarios like the X-wind model (Shu et al., 1997). According to this model, the variations in $^{26}\text{Al}$ originate from different irradiation times of the proto-CAIs during the evolution of the early sun. Recent model calculations show that $^{92}\text{Nb}$ could also be produced by the X-wind model (I. Leya, pers. comm. 2003). As a consequence, CAIs with variable initial abundances of $^{92}\text{Nb}$ in CAIs may be produced, if they differ in their exposure to the early solar irradiation. However, unlike $^{26}\text{Al}$, the high initial abundances of $^{92}\text{Nb}$, that have been proposed, are based on $^{92}\text{Zr}$ deficits relative to average solar system (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000). This implies that the initial $^{92}\text{Zr}^{90}\text{Zr}$ ratio of the entire solar system was more than 2 epsilon units lower than the present-day value. Significant amounts of $^{92}\text{Nb}$ have to be produced by the X-wind scenario to enable such an evolution. It is feasible to consider a model in which the material that formed the Earth, moon, chondrites and eucrites was enriched in $^{92}\text{Nb}$ by being processed through the inner part of the accretion disk, while some CAIs escaped irradiation. Recently, a similar scenario was proposed by Clayton (2002) for oxygen. In this case, the CAIs are depleted in $^{17}\text{O}$ and $^{18}\text{O}$ compared to the rest of the solar system. Irradiation by the early sun increases the $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios of the remaining meteoritic and planetary
material by up to several percent. However, some isotopic heterogeneity in oxygen still survives in bulk rock samples, whereas the homogeneity of the $^{92}$Zr values (Fig. 5.1) requires that both $^{92}$Nb and $^{92}$Zr were homogeneously distributed in the solar system. This entails that a very efficient mixing process must have erased any heterogeneities after the solar system material was exposed to the irradiation of the early sun. In summary, it is possible to explain the different $^{92}$Nb data of CAIs with the X-wind model, but this requires very special circumstances, that are rather unlikely.

The new CAI data can be used to infer an upper limit for the initial $^{92}$Nb/$^{93}$Nb of the solar system. A chondritic Nb/Zr ratio of 0.076 was deduced from the chondrite data of Table 5.2 and this value was applied in the following age calculation. Note that this value is slightly higher than the previously applied value of ~0.065 (Jochum et al., 2000), but in excellent agreement with a recent estimate of Weyer et al. (2002). The strongest constraint on the initial $^{92}$Nb/$^{93}$Nb is provided by CAI USNM3529-21. Even if this CAI formed as late as 10 Myr after the start of the solar system, the initial $^{92}$Nb/$^{93}$Nb ratio has to be less than $2.5 \times 10^{-5}$. This is in agreement with our previous result (Schönbächler et al., 2002). Mason and Taylor (1982), however, determined a much higher Nb/Zr ratio of 0.076 for the same CAI. This difference may reflect sample heterogeneity. If the Nb/Zr ratio is 0.076 (i.e. chondritic), the data does not constrain the initial $^{92}$Nb abundance in a useful way. Nevertheless, further support for a low initial $^{92}$Nb abundance is provided by the results for CAI USNM3529-47 and CAI USNM4698, which both require an initial $^{92}$Nb/$^{93}$Nb for the solar system of less than $2 \times 10^{-4}$.

5.5. Conclusions

The new Zr isotopic data show that chondrites, eucrites as well as the moon and the Earth have identical Zr isotopic compositions despite compositions that must represent a mixture of r- and s-process components. Homogeneity in Zr isotopes thus extends over a broad range of heliocentric distance. The data, therefore, provide powerful evidence that the solar nebula was well mixed at a large scale and that presolar grains were present in nearly identical proportions through the investigated region of the disk. The presence of r-process components can be partly resolved by stepwise dissolution of carbonaceous chondrites as shown for Allende. The carrier phase is not yet identified. Some CAIs in Allende also display a small but distinct r-process signature.

The Nb/Zr ratio and the Zr isotopic data acquired for some CAIs require an initial $^{92}$Nb/$^{93}$Nb ratio of $< 2 \times 10^{-4}$. All of the presented data are consistent with a low initial $^{92}$Nb/$^{93}$Nb
ratio of $< 3 \times 10^{-5}$ (Harper, 1996; Schönbächler et al., 2002).

Acknowledgement

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Chapter 6

Zirconium Isotopes in Carbonaceous Chondrites

Abstract

In contrast to the Zr isotopic compositions of bulk carbonaceous chondrites, stepwise dissolution of the carbonaceous chondrites Orgueil, Murchison and Allende reveal nucleosynthetic anomalies for Zr isotopes. Two complementary nucleosynthetic components are observed: an r- and a s-process component. The r-process component, characterised by excess $^{96}$Zr, is most distinctive in the acetic acid leachate (up to $\varepsilon^{96}$Zr ~ 50) and provides evidence of an unidentified presolar phase as a carrier phase that is easily leachable. Excess $^{96}$Zr decreases with increasing acid strength and the final leaching steps of the experiment are enriched in s-process nuclides (depletion in $^{96}$Zr). Known varieties of presolar grain (graphite and SiC) could account for anomalous Zr released during these later stages, although other presolar or solar phases can not be excluded. The data provide evidence that average solar system material consists of a homogenised mixture of different nucleosynthetic components, which can be partly resolved by leaching experiments of carbonaceous chondrites.

6.1 Introduction

A variety of isotopically anomalous components has been reported for carbonaceous chondrites. This includes refractory inclusions (e.g. Clayton et al., 1973), presolar dust grains (Anders and Zinner, 1993) and acid leachates, that display nucleosynthetic anomalies for $^{54}$Cr, $^{40}$K and Mo isotopes (Rotaru et al., 1992; Podosek et al., 1997; Podosek et al., 1999; Dauphas et al., 2002b).

Presolar grains are primitive dust particles, which are characterised by isotopic compositions that are very different from average solar system values (Huss and Lewis, 1995). It is generally believed that these grains condensed in stellar outflows and survived the formation of the solar system, such that they preserved the original elemental and isotopic compositions. In contrast, refractory inclusions probably formed very early within the solar system from material that was originally formed by many different nucleosynthetic processes. The isotopic anomalies of refractory inclusions are more modest than those of presolar grains and their origin is generally not well understood. Some anomalies may have developed within the solar system (e.g. Shu et al., 1997), while others may reflect different proportions of distinct nucleosynthetic components (e.g. Lugmair et al., 1978). Therefore, the isotopic anomalies of carbonaceous chondrites reveal nucleosynthetic sources of solar system material and they can
be used to study stellar nucleosynthesis and conditions during circumstellar grain formation. Furthermore, they provide information about the solar nebula and the formation process of the solar system.

Zirconium is a promising element to address these issues. Its isotopes are synthesised by three distinct nucleosynthetic mechanisms, the s-, r- and p-process, which are characteristic of different stellar environments (Burbidge et al., 1957; Wallerstein et al., 1997). The s-process of elements such as Zr is believed to occur in asymptotic giant branch (AGB) stars, while the r- and p-process are thought to take place in supernova environments (Wallerstein et al., 1997). All Zr isotopes have mixed nucleosynthetic sources, but each one is predominately formed by one process. The s-process accounts for most of the $^{90}$Zr, $^{91}$Zr, $^{92}$Zr and $^{94}$Zr. The r-process is the dominant production mechanism for $^{96}$Zr, although it can also be produced by the s-process if the neutron density at the production site was unusually high (Nicolussi et al., 1998).

Large excesses of $^{96}$Zr relative to the other Zr isotopes and a terrestrial standard were reported for single presolar grains (Nicolussi et al., 1998; Davis et al., 1999), whereas others displayed complementary patterns with a deficit of $^{96}$Zr due to an overabundance of s-process nuclides (Nicolussi et al., 1997). Presolar grains thus have distinct abundance patterns that match the Zr isotopic compositions produced by the s- and r- process (Nicolussi et al., 1997; Nicolussi et al., 1998; Davis et al., 1999). In addition to the $^{96}$Zr anomalies of presolar grains, excess $^{96}$Zr was also observed in calcium-aluminium rich inclusions (CAI) (Harper et al., 1991; Yin et al., 2001; Schönbächler et al., 2003a). In a previous investigation, we have identified excess $^{96}$Zr in leachates of Allende (Schönbächler et al., 2003a). In the present study, we have conducted additional leaching experiments on the carbonaceous chondrites Allende (CV3.2), Murchison (CM2) and Orgueil (CI1) and determined the Zr isotopic compositions of the leachates. The results are used to discuss and constrain the origin and carrier phases of the isotopic anomalies.

6.2 Analytical procedure

The powdered samples were sequentially digested with reagents of increasing acid strength. The leaching procedure is identical to that previously applied for Allende (Allende-a) (Schönbächler et al., 2003a), except for the final dissolution steps. The digestion with aqua regia in a high pressure asher was skipped (Table 6.1), because (1) this leachate did not reveal isotopic anomalies and (2) it renders the leaching experiments more comparable to
Table 6.1: Experimental procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Reagent</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50% HAc</td>
<td>2 days, RT</td>
</tr>
<tr>
<td>2</td>
<td>4 M HNO₃</td>
<td>5 days, RT</td>
</tr>
<tr>
<td>3</td>
<td>6 M HCl</td>
<td>1 day, 80°C</td>
</tr>
<tr>
<td>4</td>
<td>13.5 M HF + 3 M HCl</td>
<td>4 days, 100°C</td>
</tr>
<tr>
<td>5</td>
<td>Aqua Regia</td>
<td>3 hours, 220°C, high pressure asher</td>
</tr>
<tr>
<td>6</td>
<td>Conc. HF + conc. HNO₃</td>
<td>41/2 days, Teflon bomb, 170°C</td>
</tr>
</tbody>
</table>

RT = room temperature
HAc = CH₃COOH

Step 5 was only performed for Allende-a, while all other steps were applied to all samples

those previously conducted by others for additional elements (Rotaru et al., 1992; Podosek et al., 1997; Podosek et al., 1999; Dauphas et al., 2002b). For the latter reason, Murchison and Orgueil were also leached with 2.5% acetic acid for 2 hours prior to the first leach step shown in Table 6.1. However, no measurable quantity of Zr was detected. This leachate will therefore not be considered in the following.

The ion-exchange procedure for the chemical separation of zirconium is described in (Schönbächler et al., 2003c), together with the protocols for the isotopic measurements, which were performed using a Nu Plasma MC-ICPMS instrument. Epsilon Zr values were calculated relative to the mean values of the NIST SRM 3169 Zr standard solution measured the same day as the samples using $\varepsilon^{\text{Zr}} = \frac{\left(\frac{^{90}\text{Zr}}{^{91}\text{Zr}}\right)_{\text{meas}} - \left(\frac{^{90}\text{Zr}}{^{91}\text{Zr}}\right)_{\text{std}}}{\left(\frac{^{90}\text{Zr}}{^{91}\text{Zr}}\right)_{\text{std}}} \times 10^4$. The Zr concentration of each leach fraction was measured semi-quantitatively by comparing of the size of the sample signals with that obtained for Zr standards of known concentration. These measurements have uncertainties of about 20 – 30 %. As the concentrations are measured after the sample passed through the ion exchange chemistry, they are further influenced by the yield of the column separation, which varies between 70 and 100 %. For this reason, the Zr concentrations are expressed relative to the total Zr recovered after the ion-exchange chemistry (Table 6.2).
6.3 Results

The results for the three investigated carbonaceous chondrites show a consistent pattern (Fig. 6.1, Table 6.2). With the exception of Orgueil, the acetic acid leachate displays the largest $^{96}\text{Zr}$ excess, reaching $\varepsilon^{96}\text{Zr} = 48.6 \pm 1.4$ in the case of Murchison. For Orgueil, the low Zr content of 4 ng prevented a precise isotopic measurement for this fraction. In subsequent dissolution steps, the abundance of $^{96}\text{Zr}$ decreases to the terrestrial value and even below this for Murchison ($\varepsilon^{96}\text{Zr} = -12.5 \pm 1.4$) and Allende-b ($\varepsilon^{96}\text{Zr} = -3 \pm 1.4$). Orgueil and Murchison display isotopic effects of similar magnitude, whereas they are significantly smaller for
Allende. Variations in $\varepsilon^{91}\text{Zr}$ and $\varepsilon^{92}\text{Zr}$ are not observed for the Allende leachates. Murchison and Orgueil, in contrast, yield small variations (Table 6.2, Fig. 6.2). Because the isotope data are corrected for instrumental mass discrimination relative to $^{94}\text{Zr}/^{90}\text{Zr}$, it is possible that they are affected by anomalous abundances of $^{90}\text{Zr}$ and/or $^{94}\text{Zr}$. Recalculating the raw data with internal normalization schemes that apply Zr isotopes other than $^{90}\text{Zr}/^{95}\text{Zr}$ show that more than two of these isotopes have to be anomalous. Regardless of how the mass fractionation is corrected in detail, the anomalies for

Table 6.2: Zr isotopic data for Allende, Murchison and Orgueil

<table>
<thead>
<tr>
<th>Sample</th>
<th>Step number</th>
<th>Fraction (%)</th>
<th>$\varepsilon^{92}\text{Zr} \pm 2\sigma$</th>
<th>$\varepsilon^{91}\text{Zr} \pm 2\sigma$</th>
<th>$\varepsilon^{98}\text{Zr} \pm 2\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende (CV3.2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende whole rock#</td>
<td></td>
<td>0.0 ±0.3</td>
<td>0.1 ±0.4</td>
<td>1.0 ±1.2</td>
<td></td>
</tr>
<tr>
<td>Allende-a</td>
<td>50% HAc*</td>
<td>1</td>
<td>0.06 ±0.4</td>
<td>0.0 ±0.6</td>
<td>10.0 ±1.5</td>
</tr>
<tr>
<td></td>
<td>6 M HCl*</td>
<td>3</td>
<td>0.21 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>2.6 ±1.5</td>
</tr>
<tr>
<td></td>
<td>13.5 M HF + 3 M HCl*</td>
<td>4</td>
<td>0.65 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>0.5 ±1.5</td>
</tr>
<tr>
<td></td>
<td>aqua regia*</td>
<td>5</td>
<td>0.07 ±0.4</td>
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<td>-0.1 ±1.5</td>
</tr>
<tr>
<td></td>
<td>Teflon bomb</td>
<td>6</td>
<td>0.01 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>-0.2 ±1.4</td>
</tr>
<tr>
<td>Allende-b</td>
<td>50% HAc</td>
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<td>0.06 ±0.4</td>
<td>0.2 ±0.4</td>
<td>7.0 ±1.4</td>
</tr>
<tr>
<td></td>
<td>4 M HNO$_3$</td>
<td>2</td>
<td>0.18 ±0.4</td>
<td>0.0 ±0.4</td>
<td>4.8 ±1.4</td>
</tr>
<tr>
<td></td>
<td>6 M HCl</td>
<td>3</td>
<td>0.28 ±0.4</td>
<td>0.0 ±0.4</td>
<td>0.0 ±1.4</td>
</tr>
<tr>
<td></td>
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<td>4</td>
<td>0.43 ±0.4</td>
<td>0.1 ±0.4</td>
<td>-0.1 ±1.3</td>
</tr>
<tr>
<td></td>
<td>Teflon bomb</td>
<td>6</td>
<td>0.05 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>-3.0 ±1.4</td>
</tr>
<tr>
<td>Murchison (CM2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>whole rock</td>
<td></td>
<td></td>
<td>0.1 ±0.3</td>
<td>0.0 ±0.4</td>
<td>0.9 ±1.5</td>
</tr>
<tr>
<td>50% HAc</td>
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<td>1.0 ±0.4</td>
<td>2.6 ±0.6</td>
<td>48.6 ±1.4</td>
</tr>
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<td>4 M HNO$_3$</td>
<td>2</td>
<td>0.10 ±0.4</td>
<td>0.5 ±0.4</td>
<td>1.9 ±0.5</td>
<td>28.4 ±1.4</td>
</tr>
<tr>
<td>6 M HCl</td>
<td>3</td>
<td>0.13 ±0.4</td>
<td>0.6 ±0.4</td>
<td>1.3 ±0.5</td>
<td>19.0 ±1.4</td>
</tr>
<tr>
<td>13.5 M HF + 3 M HCl</td>
<td></td>
<td>4</td>
<td>0.24 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>-4.3 ±1.3</td>
</tr>
<tr>
<td>Teflon bomb</td>
<td>6</td>
<td>0.47 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>-1.0 ±0.5</td>
<td>-12.5 ±1.4</td>
</tr>
<tr>
<td>Orgueil (CI1)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>whole rock*</td>
<td></td>
<td></td>
<td>0.0 ±0.4</td>
<td>0.2 ±0.6</td>
<td>-0.1 ±1.5</td>
</tr>
<tr>
<td>50% HAc</td>
<td>1</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 M HNO$_3$</td>
<td>2</td>
<td>0.21 ±0.4</td>
<td>0.6 ±0.4</td>
<td>1.3 ±0.5</td>
<td>20.8 ±1.4</td>
</tr>
<tr>
<td>6 M HCl</td>
<td>3</td>
<td>0.24 ±0.4</td>
<td>0.5 ±0.4</td>
<td>1.1 ±0.6</td>
<td>19.6 ±1.4</td>
</tr>
<tr>
<td>13.5 M HF + 3 M HCl</td>
<td></td>
<td>4</td>
<td>0.55 ±0.4</td>
<td>-0.1 ±0.4</td>
<td>-1.8 ±1.3</td>
</tr>
</tbody>
</table>

The quoted analytical uncertainties for the $\varepsilon$Zr values reflect the external (2$\sigma_{\text{mean}}$) reproducibilities including the uncertainties for the standard. The step number refers to the experimental procedure described in Table 6.1. The fraction (%) represents the total amount of Zr recovered after ion-exchange chemistry. Note that the last leaching step (6) of Orgueil is missing, which may contain up to 40% of Orgueils total Zr content according to the Zr bulk rock content. # Data from Schönbächler et al. (2003a), * Data from Schönbächler et al. (2003c).
$^{90}\text{Zr}$, $^{91}\text{Zr}$, $^{92}\text{Zr}$ or $^{94}\text{Zr}$ are small compared to those for $^{96}\text{Zr}$. The $^{96}\text{Zr}$ anomalies furthermore have very similar magnitudes, independent of which ratio is used for the mass fractionation correction.

Mass balance calculations based on $\varepsilon^{96}\text{Zr}$ (and also $\varepsilon^{91}\text{Zr}$, $\varepsilon^{92}\text{Zr}$) were performed for the different leachate fraction of Allende and Murchison. For Orgueil, such calculations are not meaningful, because the dissolution sequence is incomplete (Table 6.2). The mass balance calculations for Allende and Murchison yield mean isotopic compositions that are identical, within uncertainties, to the values measured for the bulk meteorite and the terrestrial standard (Fig. 6.2).

![Fig. 6.2: Zirconium isotopic compositions as a function of mass for Murchison leachates. On the bottom, the nucleosynthetic processes by which each Zr isotope can be formed are shown. Highlighted in bold is the primary nucleosynthetic process. The numbers refer to the leaching steps. The star represents the calculated $^{96}\text{Zr}$ value for bulk rock composition by mass balance. w.r. refers to the filled squares that show the measured Zr composition of bulk Murchison.](image)

Allende-a and Allende-b are leach experiments performed on the same batch of Allende powder and the Zr isotope data for these two aliquots are very similar (Fig. 6.1, Table 6.2). This provides a strong indication of the reproducibility of the leaching experiments. In detail, however, there are small but significant differences. The Zr concentration of the Allende-a HNO$_3$ fraction was too low for a precise isotopic measurement, while it was sufficient for Allende-b. The measurement yielded a resolvable excess of $\varepsilon^{96}\text{Zr}$ of $4.8 \pm 1.4$, and this is identical to the excess $^{96}\text{Zr}$ of the
Allende-a HCl fraction within the analytical uncertainty (Fig. 6.1, Table 6.2). In contrast, the Allende-b HCl fraction displays no excess $^{96}\text{Zr}$. Hence, for some unknown reason, the carrier phase of excess $^{96}\text{Zr}$ was not attacked by HNO$_3$ in the Allende-a leaching experiment and Zr was only liberated in the following step, where hot HCl was utilized for leaching. Because the same batch of powdered Allende was used in the leaching experiments, these differences most likely indicate that slightly different mixtures of distinct Zr components were released in identical leaching steps.

6.4 Discussion

In the following our data and those previously published by others are used to constrain the nature and number of phases with anomalous Zr isotopic composition that are present in carbonaceous chondrites. The simplest case is to assume that only a single carrier phase with a large excess of $^{96}\text{Zr}$ is progressively dissolved during leaching. This model can explain the decrease in $\varepsilon^{96}\text{Zr}$ with increasing acid strength, if the excess $^{96}\text{Zr}$ is increasingly diluted by Zr from a matrix, that is characterised by $\varepsilon^{96}\text{Zr} < 0$. There are, however, hints for additional carrier phase(s) with anomalous Zr. The existence of only a single carrier phase with excess $^{96}\text{Zr}$ would imply that it was admixed to a matrix that is deficient in $^{96}\text{Zr}$ relative to the present day composition of the solar system. Furthermore, it has to be easily leachable, because the largest excess is displayed by the acetic acid leachate. In this case, final leaching steps should reveal the isotopic composition of the matrix, which would carry the average isotope composition of the solar system without the addition of excess $^{96}\text{Zr}$. The final leachates of each experiment, however, have isotopic composition with $\varepsilon^{96}\text{Zr}$ values that vary between -12.5 and 0 (Fig. 6.1, Table 6.2). These differences are most reasonably explained by variable mixing of two or more components or carrier phases with distinct Zr isotopic compositions. The isotopic variation is caused either by the heterogeneous distribution of the carrier phases ("nugget effect") or small differences in the efficiency of the leaching process.

The conclusion, that several host phases of anomalous Zr probably exist, is strongly supported by the observation that single presolar SiC and graphite grains exhibit either a depletion or an excess of $^{96}\text{Zr}$ (Fig. 6.3). The Zr isotopic patterns of these grains are furthermore similar to those observed for the different leachate fractions of Allende, Murchison (Fig. 6.2) and Orgueil. The only difference is the magnitude of the $^{96}\text{Zr}$ anomalies, which is up to 2000 times larger in presolar grains (Fig. 6.2, Fig. 6.3). Both presolar grains and the leachates of Orgueil and Allende show only limited variation in the relative abundances of $^{90}\text{Zr}$, $^{91}\text{Zr}$,
The similarity in the $\text{Zr}$ isotopic patterns of leachates and presolar grains suggests that such grains may be the host for isotopically anomalous Zr resolved by the leach experiments. However, the largest $^{96}\text{Zr}$ excesses were found for the acetic acid leachates (Fig. 6.1). This observation stands in contrast to results obtained for other elements that also display isotopic anomalies in leaches of carbonaceous chondrites. The isotopes of Mo, $^{54}\text{Cr}$, and $^{40}\text{K}$ display the largest excess or depletion in the HCl or else in the HCl/HF leachate (Rotaru et al., 1992; Podosek et al., 1997; Podosek et al., 1999; Dauphas et al., 2002b). It is unlikely that the difference is observed because Zr is more mobile during leaching than Cr, Mo, or in particular K. The excess $^{96}\text{Zr}$ of the acetic acid leachate is, therefore, tied to a distinct and easily leachable carrier phase. This phase is probably not a known variety of presolar grain, because these can withstand even very harsh leaching procedures (e.g. treatment with HCl/HF for several days; Amari et al., 1994). It is therefore unlikely, but not impossible, that Zr is leached from such grains by acetic acid alone. The possibility, that acetic acid attacks the refractory minerals of CAI, which are known to display excess $^{96}\text{Zr}$, is also rather improbable. It is more likely that another unknown phase is responsible for the $^{96}\text{Zr}$ excesses of the acetic acid leachate. Acetic acid is known to dissolve alteration phases and metal (Podosek et al., 1997; Rotaru et al., 1992). Both Murchison and Orgueil experienced stronger aqueous alteration than Allende (Busek and Hua, 1993) and they display larger $^{96}\text{Zr}$ anomalies (Fig. 6.1). This implicates two possibilities. Either the alteration phases incorporated the excess $^{96}\text{Zr}$ of their precursors or the alteration did not significantly affect the original carrier
phase of excess $^{96}$Zr. In both cases, the excess $^{96}$Zr was not completely mobilised and redistributed during alteration. It is possible that the host of excess $^{96}$Zr detected in the acetic acid leachate is related to organic material, as shown for the carrier of anomalous $^{51}$Cr (Alexander, 2002). Further investigations are required to address this issue, because the present leaching procedures were not designed to separate and investigate organic material.

Although the known varieties of presolar grains and CAI are not considered to be the carrier of the excess $^{96}$Zr released by the acetic acid, they are likely to be the host phase for the $^{96}$Zr anomalies of the mineral acid leachates. The presolar graphite grains of the Murchison chondrite have been reported to display large $^{96}$Zr isotopic anomalies (Nicolussi et al., 1998) (Fig. 6.3). Some grains carry s-process signatures (depletion in $^{96}$Zr), but the largest anomalies are observed for excess $^{96}$Zr. Leaching of such material could liberate excess $^{96}$Zr and this may be responsible for the positive anomalies observed in the HNO$_3$ or HCl leachates of Murchison and Orgueil. Alternatively, it is possible that the excess $^{96}$Zr is provided by CAIs or the phases that are responsible for the anomalies of the acetic acid leachates.

Leaching of SiC grains has been considered as a viable mechanism to explain the Mo isotope s-process signature for the HCl/HF leachate of Orgueil (Dauphas et al., 2002b). Most SiC grains display considerable Mo and Zr concentrations (Kashiv et al., 2001) and a strong depletion in $^{96}$Zr (Nicolussi et al., 1997). Moreover, they are chemically resistant phases, which survive treatments with hot HCl/HF mixture (Amari et al., 1994). Based on these observations, leaching of SiC grains could account for negative $\varepsilon^{96}$Zr values observed for leachates of more resistant phases in the present study (HCl/HF leachate of Murchison and Orgueil; final dissolution steps of Murchison and Allende; Table 6.2). Leaching of Zr from presolar grains with a hot HCl/HF mixture can not be excluded. The final leaching step of our experiment (performed in a Teflon bomb, Table 6.1) is more aggressive than the HCl/HF step and thus even more likely to leach or maybe dissolve SiC grains. This could explain why anomalies observed for the HCl/HF leachate are smaller than those for the final leaching step (Table 6.2). Furthermore, the lower magnitude of the negative $^{96}$Zr anomaly observed in Allende-b compared to those in Murchison is in agreement with the lower abundance of SiC grains in Allende (Huss and Lewis, 1995). For these reasons, presolar SiC grains are the most probable host phase of anomalous Zr that causes the negative $\varepsilon^{96}$Zr values of the later dissolution steps of Orgueil, Murchison and Allende.
Chapter 6 Carbonaceous Chondrites

6.5 Summary and Conclusion

Leachates of the carbonaceous chondrites Orgueil, Murchison and Allende reveal the existence of a phase carrying an excess of $^{96}\text{Zr}$ that is easily leachable. This provides evidence of a presolar phase present in these meteorites, that has not been previously identified, although it can not be excluded that $^{96}\text{Zr}$ excess originated from a carrier phase formed in part from r-process enriched presolar material within the solar nebula. The exact nature of the carrier phase is unknown.

The overall Zr isotopic pattern observed in the leaching experiments, shows a distinctive $^{96}\text{Zr}$ excess in the acetic acid leachate, which decreases to $^{96}\text{Zr}$ values below average solar system with increasing strength of the acid. The experiment reveals two components: an r-process (excess $^{96}\text{Zr}$) and a s-process (depletion in $^{96}\text{Zr}$). Recently reported Zr data show, that the bulk rock Zr isotopic compositions of various solar system materials (e.g. chondrites, eucrites, moon and Earth) do not vary outside of the analytical uncertainty (Schönbächler et al., 2003a). This led to the conclusion that Zr isotopes were distributed evenly in the solar system at bulk rock and larger scale. While this homogeneity demonstrates that the solar nebula was well mixed on a large scale, the new results on leachates provide evidence for a heterogeneous distribution of r- and s-process components on a smaller scale. Distinct components preserved in carbonaceous chondrites survived the formation of the solar system, which suggests that the solar nebula must have, at least partly, contained cold regions. The data further imply that the solar system consists of a mixture of material with various nucleosynthetic sources, which average out to solar system composition and can be resolved by leaching of carbonaceous chondrites.
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Chapter 7

The Abundance of $^{92}$Nb
in the Early Solar System

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Chapter 7 Abundance of $^{92}$Nb

Abstract

The initial abundance of a short-lived radionuclide at the start of the solar system is critical for tracing nucleosynthetic, nebular or planetary processes. The initial abundance of $^{92}$Nb (with a half-life of 36 Myr) has been a matter of debate and current estimates of the initial $^{92}$Nb/$^{93}$Nb range from $\sim 10^{-5}$ to values as high as $10^3$. Here, we report a new internal Nb-Zr isochron for the eucrite Juvinas, an early igneous rock, which defines an initial $^{92}$Nb/$^{93}$Nb of $\sim 10^{-5}$, consistent with some of the previously published data including isochrons for the ordinary chondrite Estacado (H6) and the mesosiderite Vaca Muerta. This further substantiates the evidence that the solar system started with a low initial $^{92}$Nb/$^{93}$Nb of $< 3 \times 10^{-5}$ and greatly limits the usefulness of $^{92}$Nb as a chronometer of early solar system processes and as a diagnostic fingerprint of specific $p$-process nucleosynthetic sites.

7.1 Introduction

Evidence for the former existence of an extinct radionuclide in the solar system was first provided by Reynolds (1960) who found excess $^{129}$Xe in the Richardton chondrite. This was subsequently shown to be correlated with I/Xe implicating the former presence of live $^{129}$I ($T_{1/2}=17$ Myr). Advances in analytical techniques and more extensive sampling of meteoritic material led to the discovery of more than 10 additional short-lived radionuclides that were once alive in the early solar system. These decay systems have offered new insights into nucleosynthetic, nebular and planetary processes.

Whether a short-lived radionuclide can be used as a chronometer depends on the degree to which early solar system processes fractionate the parent / daughter ratio over time-scales corresponding to the first few half-lives. However, unless the initial abundance of the parent nuclide also is sufficiently high, the isotopic effects on the daughter element will not be resolvable. The initial abundance also places strong constraints on the likely sites of stellar nucleosynthesis.

The focus of this paper is on the initial abundance of the short-lived radionuclide $^{92}$Nb, which decays to $^{92}$Zr with a half-life of $36 \pm 3$ Myr (Nethaway et al., 1978). In the case of $^{92}$Nb the various nucleosynthetic models predict abundances that differ by more than two orders of magnitude (Woosley and Howard, 1978; Howard et al., 1991; Howard and Meyer, 1993; Rayet
et al., 1995; Hoffman et al., 1996). Therefore, ascertaining the correct initial abundance is essential. Unfortunately, the initial abundance of $^{92}$Nb determined from meteorite studies has been clouded in disagreement. The estimates fall into two distinct groups. On the one hand there are data from an iron meteorite, eucritic zircons, Allende CAIs and internal isochrons for a mesosiderite and an ordinary chondrite indicating an initial $^{92}$Nb/$^{93}$Nb of $<10^{-4}$ or $\sim 10^{-5}$ (Harper, 1996; Hirata, 2001; Schönbächler et al., 2002; Schönbächler et al., 2003a). On the other hand a value of $\sim 10^{-3}$ has been proposed by Yin et al. (2000), Münker et al. (2000) and Sanloup et al. (2000) on the basis of data for an mesosiderite zircon, Allende CAIs, a IAB iron meteorite and an ordinary chondrite. This discrepancy of almost two orders of magnitude severely limits the usefulness and interpretation of $^{92}$Nb-$^{92}$Zr data.

Internal isochrons for early, equilibrated meteorites provide the most reliable evidence for extinct radionuclides and are particularly useful for constraining the initial abundance. The Nb-Zr isochrons combined with Hf-W data for the ordinary chondrite Estacado and the mesosiderite Vaca Muerta (Schönbächler et al., 2002) indicate an initial $^{92}$Nb/$^{93}$Nb ratio that is significantly lower than that proposed by others (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000). This discrepancy can be reconciled by assuming that the Nb-Zr isochrons were reset, such that they date an event that occurred more than 100 Myr after the start of the solar system, Hf-W remaining undisturbed. Although this is possible, it is unlikely, because both Zr and W are refractory, immobile elements. To provide a convincing test of this we have studied an early relatively undisturbed igneous rock in an attempt to obtain an unequivocal isochron upon which to base an estimate of the initial $^{92}$Nb abundance. The non-cumulate eucrite Juvinas is a promising sample for these purposes. It is brecciated, but it displays an equilibrated igneous texture. Furthermore, a variety of chronometers (see Carlson and Lugmair, (2000) for compilation) attests that Juvinas formed early, between a few and about 36 Myr (one half-life of $^{92}$Nb) after the start of the solar system. No thermal or metamorphic events are indicated after this time interval. Therefore, the initial $^{92}$Nb abundance for Juvinas and the solar system should be identical within a factor of 2. For these reasons, we obtained mineral separates for Juvinas and used these to determine a precise internal Nb-Zr isochron.
7.2 Analytical procedures

About 8 g of Juvinas were crushed in a boron carbide mortar under a laminar flow of filtered air to avoid contamination. The mineral separation of pyroxene, feldspar, heavy minerals and ilmenite, and the chemical separation of Zr is identical to that given in previous papers (Schönbächler et al., 2002; Schönbächler et al., 2003c). The Zr isotopic measurements were performed with a Nu Plasma MC-ICPMS (multiple collector inductively coupled plasma mass spectrometer). Aliquots for the determination of Nb/Zr ratios were taken from sample solutions that did not undergo chemical separation. The $^{93}\text{Nb}/^{90}\text{Zr}$ ratios of the samples were measured with a quadrupole ICPMS. Spectral interferences in these measurements were accounted for by using dynamic reaction cell technology with hydrogen as reactive gas (Hattendorf et al., 2001).

7.3 Results

The Zr isotopic compositions of bulk Juvinas and the mineral separates are all identical within analytical uncertainty (Fig. 7.1, Table 7.1) and no $^{92}\text{Zr}$ anomalies from the decay of formerly live $^{92}\text{Nb}$ can be resolved. The slope of the regression line in the isochron diagram (Fig. 7.1) defines an initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $(0.8 \pm 0.9) \times 10^{-5}$ at the time of closure for Juvinas. The precision of the isochron slope is slightly poorer for Juvinas than that previously reported for Estacado and Vaca Muerta because the Juvinas mineral separates display a relatively small variation in Nb/Zr ratio.

The internal isochron data for Juvinas can be combined with data for bulk samples of other eucrites (Schönbächler et al., 2003a) to yield a best fit eucrite Nb-Zr isochron of $(0.9 \pm 0.7) \times 10^{-5}$ (Fig. 7.2A). This can be compared with the initial $^{52}\text{Nb}/^{53}\text{Nb}$ of $(0.6 \pm 0.3) \times 10^{-5}$ as defined by the internal isochron for Vaca Muerta (Fig. 7.2B) and $(1.2 \pm 0.6) \times 10^{-5}$ as defined by the internal isochron for Estacado (Fig. 7.2C). Our previously reported data for the carbonaceous chondrites Allende and CAIs (calcium-aluminium rich inclusions) (Schönbächler et al., 2003a) are shown in Fig. 7.2D. These data define a best fit line of $(1.2 \pm 4.2) \times 10^{-5}$ (Fig. 7.2D). All of these isochron data sets agree within analytical uncertainties and, given the immobility of Zr, provide compelling evidence that the initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the solar system was $< 3 \times 10^{-5}$. This is also consistent with Nb-Zr isochrons of lunar samples (Schönbächler et al., 2003b). The value is furthermore in agreement with the Nb-Zr
data for rutiles in the Toluca iron meteorite (Harper, 1996) and zircons from the eucrite Camel Donga (Hirata, 2001).

This low initial $^{92}\text{Nb}^{93}\text{Nb}$ is difficult to reconcile with some of the Zr isotope data reported by others (Münker et al., 2000; Yin et al., 2000). The data from these studies are plotted in Fig. 7.3. The data with chondritic Nb/Zr ratios ($^{93}\text{Nb}/^{90}\text{Zr} = -0.148$) yield precise Zr isotopic compositions that are fully consistent with the low initial $^{92}\text{Nb}$ abundance reported here. However, the remainder would appear inconsistent with the data presented here unless there are additional sources of isotopic heterogeneity or there has been isotopic resetting of the samples studied at ETH. The latter appears unlikely. The best-fit line calculated using the data shown in Fig. 7.3 defines a slope that would correspond to an initial $^{92}\text{Nb}^{93}\text{Nb}$ of $(6.0 \pm 2.2) \times 10^{-4}$ (Fig. 7.3). The difference in time implied between this slope and those shown in Fig. 7.2 is $>100$ Myr, far longer than is expected for cooling of the wide range of objects shown in Fig. 7.2.
### Table 7.1: Zr isotopic compositions and Nb and Zr concentration data for Juvinas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nb (ppm)</th>
<th>Zr (ppm)</th>
<th>(^{93}\text{Nb}/^{93}\text{Zr} \pm 2 \sigma_{\text{mean}} )</th>
<th>(^{93}\text{Zr}/^{98}\text{Zr} \pm 2 \sigma_{\text{mean}} )</th>
<th>(e^{\text{Zr}} \pm 2 \sigma_{\text{mean}} )</th>
<th>(e^{\text{Zr}} \pm 2 \sigma_{\text{mean}} )</th>
<th>(e^{\text{Zr}} \pm 2 \sigma_{\text{mean}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juvinas whole rock</td>
<td>3.2</td>
<td>46</td>
<td>0.136 ±0.007</td>
<td>0.333389 ±5</td>
<td>0.17 ±0.15</td>
<td>-0.04 ±0.18</td>
<td>-0.29 ±0.51</td>
</tr>
<tr>
<td>Juvinas whole rock</td>
<td>3.6</td>
<td>49</td>
<td>0.142 ±0.007</td>
<td>0.333385 ±4</td>
<td>0.06 ±0.11</td>
<td>-0.26 ±0.22</td>
<td>0.03 ±0.48</td>
</tr>
<tr>
<td>Feldspar</td>
<td>3.6</td>
<td>69</td>
<td>0.103 ±0.004</td>
<td>0.333387 ±6</td>
<td>0.12 ±0.17</td>
<td>0.05 ±0.17</td>
<td>0.26 ±0.45</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>2.8</td>
<td>31</td>
<td>0.178 ±0.009</td>
<td>0.333378 ±4</td>
<td>-0.15 ±0.13</td>
<td>-0.18 ±0.15</td>
<td>-0.26 ±0.50</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>165</td>
<td>351</td>
<td>0.916 ±0.045</td>
<td>0.333391 ±4</td>
<td>0.23 ±0.14</td>
<td>0.08 ±0.13</td>
<td>0.25 ±0.40</td>
</tr>
<tr>
<td>Ilmenite h.p.</td>
<td>142</td>
<td>272</td>
<td>1.013 ±0.050</td>
<td>0.333391 ±4</td>
<td>0.23 ±0.12</td>
<td>0.04 ±0.18</td>
<td>0.53 ±0.39</td>
</tr>
<tr>
<td>Heavy mineral residue</td>
<td>1.1</td>
<td>1052</td>
<td>0.0020 ±0.0002</td>
<td>0.333383 ±4</td>
<td>-0.01 ±0.12</td>
<td>-0.17 ±0.14</td>
<td>0.96 ±0.38</td>
</tr>
<tr>
<td>Heavy mineral residue h.p.</td>
<td>1.5</td>
<td>165</td>
<td>0.017 ±0.004</td>
<td>0.333375 ±9</td>
<td>-0.25 ±0.27</td>
<td>0.21 ±0.30</td>
<td>0.39 ±1.05</td>
</tr>
</tbody>
</table>

\(e^{\text{Zr}} = [(^{93}\text{Zr}/^{98}\text{Zr})_{\text{sample}} - (^{93}\text{Zr}/^{98}\text{Zr})_{\text{ref}}] / (^{93}\text{Zr}/^{98}\text{Zr})_{\text{ref}} \times 10^4\), with \((^{93}\text{Zr}/^{98}\text{Zr})_{\text{ref}} = 0.333383\) for \(^{92}\text{Zr}/^{98}\text{Zr}\), 0.217930 for \(^{91}\text{Zr}/^{98}\text{Zr}\), and 0.054372 for \(^{90}\text{Zr}/^{98}\text{Zr}\). The quoted analytical uncertainties for the Zr isotopic compositions and \(e^{\text{Zr}}\) values reflect the internal (2\(\sigma_{\text{mean}}\)) within-run precision. The errors of \(^{93}\text{Zr}/^{98}\text{Zr}\) refer to the least significant digits only. The \(e^{\text{Zr}}\) values do not include uncertainties for the standard, which is ±40 ppm for \(e^{\text{Zr}}\), ±30 ppm for \(e^{\text{Zr}}\) and ±120 ppm for \(e^{\text{Zr}}\) determined by multiple standard measurements (Schönböchler et al. 2003c). Within these uncertainties, the data display an identical Zr isotopic composition. Ilmenite h.p. denotes a handpicked ilmenite fraction, from which ilmenite was selectively dissolved. The occurrence of a residue (heavy mineral residue) indicates that the fraction also included other opaque phases.

### 7.4 Evidence against isotopic resetting

If only the Zr data set of Schönböchler and co-workers (Schönböchler et al., 2002; Schönböchler et al., 2003a; Schönböchler et al., 2003b) are considered, there are no discrepancies. The results are self-consistent and imply a low initial \(^{93}\text{Nb}/^{93}\text{Nb}\) ratio for the solar system.

A higher initial of \((6.0 ±2.2) \times 10^{-4}\) would require that the Nb-Zr isochrons of Estacado, Vaca Muerta and Juvinas date an event that took place more than 100 Myr after the start of the solar system. If this is true, this event should also be recorded by other isotopic systems. However, it has to be considered that different decay systems do not necessarily date the same event. The age constraints of different chronometers for Estacado, Vaca Muerta and Juvinas are shown in Table 7.2. No direct Pb-Pb phosphate ages are available for Estacado. However, the \(^{244}\text{Pu}\) cooling time intervals for Estacado and other H6 chondrites such as Kernouve and Guarena indicate that Estacado experienced the same events as all H6 chondrites (Trielloff et al., 2003). The Pb-Pb phosphate ages of H6 chondrites are rather old at no more than 60 Myr post-dating the Allende CAIs (Goepel et al., 1994; Allègre et al., 1995). Phosphate in ordinary chondrites is a secondary mineral phases, that was produced during post-formational thermal processing (Goepel et al., 1994). As ilmenite is generally also of metamorphic origin, both
minerals should record similar ages. A broad comparison of the diffusion rates of Pb in phosphate (Cherniak et al., 1991) and Zr in ilmenite (Taylor et al., 1975) indicates that both are relatively rapid (Fig. 7.4). Therefore, the U-Pb phosphate data imply that closure of phosphates and ilmenites in H6 chondrites took place within the first 60 Myr of the solar system. Evidence for an old age of Estacado is furthermore provided by Hf-W ages of 9 ±3 Myr and 11 ±4 Myr after CAIs, which were reported for troilite (Schönbächler et al., 2002). Troilite is easily disturbed by metamorphism and these data appear inconsistent with a resetting at or after 100 Myr.

The Hf-W data for coexisting feldspar and pyroxene of Vaca Muerta define an age of < 15 Myr (after CAI). Nevertheless, these early phases do not have Zr isotope anomalies
Chapter 7 Abundance of $^{92}$Nb

Fig. 7.3: Zirconium isochron diagram for data from (a) Münker et al. (2000) and (b) Yin et al. (2000).

(Schönbächler et al., 2002). There are only few diffusion data available but it is clear that quadravalent cationic species diffuse extremely slowly in most silicates. Diffusion in silicates can be modelled to first order in terms of valency and site elasticity (Van Orman et al., 2001). Based on the behaviour of U and Th it can be concluded that diffusion of Hf, W, Zr and Nb in feldspar and pyroxene is likely to be similar and very slow (Fig. 7.4). The Nb-Zr and Hf-W data presented for feldspar and pyroxene from Vaca Muerta was determined on exactly the same sample aliquots (Schönbächler et al., 2002). If an initial $^{92}$Nb/$^{93}$Nb of $(0.6 \pm 0.2) \times 10^{-4}$ as suggested above is combined with the Hf-W age of 14.8 Myr, $\varepsilon^{92}$Zr $> +1.2$ would be expected for feldspar. This effect would be resolvable with our mass spectrometric techniques. However, no Zr isotope anomalies were observed for these minerals that exceed the 0.3 $\varepsilon$-unit analytical uncertainty (Schönbächler et al., 2002).

The $^{40}$Ar-$^{39}$Ar age (Flohs, 1981; Trieloff et al., 2003) of Estacado and the Sm-Nd age of Vaca Muerta (Stewart et al., 1994) indicate metamorphic or thermal events that reset these chronometers at about a 100 - 170 Myr after the start of the solar system (Table 7.2). Resetting of the Nb-Zr system at 100 Myr could explain the low initial $^{92}$Nb/$^{93}$Nb reported for those meteorites. However, such an event is not indicated for Juvinas based on Sm-Nd systematics (Lugmair, 1974), even though its initial $^{92}$Nb/$^{93}$Nb is identical to that of Vaca Muerta and Estacado. This similarity suggests that all three meteorites were closed to Zr diffusion.

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reasonably early, whereas the Ar and Sm-Nd data reflect later perturbations at lower temperature.

Juvinas is a brecciated eucrite, but all reported ages indicate that this meteorite is a very old rock. Sm-Nd systematics yield an age, albeit imprecise, of 6 ±80 Myr after the start of the solar system (Table 7.2). An old age of 27 ±7 Myr is deduced from the Pb-Pb data and has been attributed to the brecciation event (Tatsumoto and Unruh, 1975; Manhés et al., 1984). Evidence for a formation of Juvinas within the first few Myr of the solar system is provided by the existence of excess $^{53}$Cr (Lugmair and Shukolyukov, 1998; Trinquier et al., 2003) and excess $^{60}$Ni (Shukolyukov and Lugmair, 1993a; Shukolyukov and Lugmair, 1993b) hinting at the decay of formerly live $^{53}$Mn (half-life =3.7 Ma) and $^{60}$Fe (half-life = 1.5 Ma), respectively. It is unlikely that Nb-Zr systematics was reset more than 100 Myr after the start of the solar system if no disturbance is recorded by the other isotopic systems.

There also exists independent isotopic age constraints for other samples that indicate an low initial $^{92}$Nb/$^{93}$Nb, namely the bulk eucrites Sioux County and Béréba (Schönbächler et al., 2003a), the zircons from the Camel Donga eucrite (Hirata, 2001), and bulk CAIs (Schönbächler et al., 2003a). These all indicate short cooling intervals.

Sioux County and Béréba have the youngest ages of about ~ 40 Myr after the start of the solar system, as indicated by Pb-Pb data (Tatsumoto et al., 1973; Carlson et al., 1988; Tera et al., 1997). CAIs are thought to be the first condensates of the solar nebula and they are commonly used to define the start of the solar system. They display age differences of less than 3 Myr as deduced from Pb-Pb and Al-Mg studies (MacPherson et al., 1995; Amelin et al.,

![Fig. 7.4: Compilation of selected diffusion coefficients for Zr, W, Hf and Pb at a temperature of 1200°C. The Pb values are taken from Cherniak et al. (1991), Zr in ilmenite from Taylor et al. (1975). The W, Hf and Zr data for pyroxene are calculated as described by Van Orman et al. (2001), based on an elastic diffusion model.](image)
Table 7.2: Radiometric ages for Juvinas, Vaca Muerta and some H6 chondrites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minerals*</th>
<th>U-Pb</th>
<th>Sm-Nd</th>
<th>Rb-Sr</th>
<th>Pb-Pb</th>
<th>$^{244}$Pu-Xe</th>
<th>$^{238}$Pu fission track cooling time interval</th>
<th>$^{39}$Ar-$^{39}$Ar</th>
<th>Hf-W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estacado (H6)</td>
<td>pyroxene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64 ± 8 (i)</td>
<td>4450 ± 15 (j)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>feldspar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4420 ± 20 (j)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>troilite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4435 ± 5 (l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kernouvé (H6)</td>
<td></td>
<td>4522 ± 1 (d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61 ± 8 (i)</td>
<td>4469 ± 6 (i)</td>
<td></td>
</tr>
<tr>
<td>Guarena (H6)</td>
<td></td>
<td>4504 ± 1 (d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56 ± 9 (i)</td>
<td>4454 ± 6 (i)</td>
<td></td>
</tr>
<tr>
<td>Vaca Muerta</td>
<td>zircon</td>
<td>4563 ± 15 (a)</td>
<td>4480 ± 190 (b)</td>
<td>4480 ± 90 (b)</td>
<td>4420 ± 20 (b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>feldspar + pyroxene</td>
<td>4560 ± 80 (c)</td>
<td>4500 ± 70 (l)</td>
<td>4556 ± 12 (e)</td>
<td>4551 ± 15 (g)</td>
<td>4539 ± 4 (f)</td>
<td>4548 ± 23 (h)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*indicates if single mineral phases are dated

*calculated relative to CAI (4.568 Myr; Amelin et al., 2002) by assuming an initial $^{182}$Hf/$^{180}$Hf of $2.4 \times 10^{-4}$, new lower estimates of the initial ratio (Kleine et al. 2002) yield ages that are closer to the start of the solar system.

*absolute age calculated relative to Angra dos Reis

(a) Ireland and Wlotzka (1992); (b) Stewart et al. (1994); (c) Lugmair (1974); (d) Göpel et al. (1994); (e) Tatsumoto and Unruh (1975); (f) Manhès et al. (1984); (g) Shukolyukov and Begemann (1996); (h) Miura et al. (1998); (i) Trieloff et al. (2003); (j) Flohs (1981); (k) Schönbächler et al. (2002); (l) Allègre et al. (1975).
Therefore, the different slopes in Fig. 7.2 and 7.3 can not be explained by differences in age or cooling history.

In fact if one considers just the isotopic data for CAIs relative to the chondritic reservoir this yields the same conclusion. An initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of $\sim 2 \times 10^{-4}$ is the upper limit deduced from analyses of single CAIs, that have non-chondritic Nb/Zr ratio combined with $\varepsilon^{93}\text{Zr} = 0$ (Schönbächler et al., 2003a). The same calculations performed for the CAIs that display $^{92}\text{Zr}$ anomalies (Fig. 3), yield lower limits of $8 \times 10^{-4}$ to $6 \times 10^{-4}$ for the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio. These estimates do not overlap. Hence, there exists an unequivocal discrepancy between the two data sets that cannot be reconciled by age differences.

### 7.5 Evidence against nucleosynthetic, cosmogenic or spallogenic isotopic heterogeneity?

The production rate of cosmogenic $^{92}\text{Zr}$ is too small to generate significant variations (Leya et al., 2003) to explain the discrepancy in the Zr isotopic results. A heterogeneous distribution of $^{92}\text{Zr}$ in the solar system at bulk rock or planetary scale can not be completely excluded, but is unlikely given that chondrites, eucrites, lunar and terrestrial samples all display identical Zr isotopic compositions (Schönbächler et al., 2003a). The high initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio is mainly constrained by the results for Allende CAIs (Münker et al., 2000; Sanloup et al., 2000). The production of $^{92}\text{Nb}$ in these CAIs within the solar system by irradiation of the early active sun has been considered previously (Schönbächler et al., 2003a) and was not considered as an appropriate explanation. It was previously reported that CAIs carry various nucleosynthetic isotope anomalies (e.g. Lee, 1988). Furthermore, the CAI data of Fig. 7.2D show some scatter, which could indicate that the plotted error bars (based on within-run statistics) may underestimate the actual analytical reproducibility. However, it is also possible that the scatter is due to small variations in the abundance of $^{92}\text{Zr}$. Therefore, a heterogeneous distribution of $^{92}\text{Zr}$ in CAIs can not be excluded.

These considerations indicate that there is, at present, no definitive explanation for the discrepancy between the Zr isotopic data shown in Fig. 2 and 3. Further investigations that address this problem are therefore highly desirable.
7.6 Conclusions

A new internal isochron for the eucrite Juvinas indicates an initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratios of $(0.8 \pm 0.9) \times 10^{-5}$. Based on age constraints from various decay systems, we conclude that the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of Juvinas as well as those previously determined for Vaca Muerta and Estacado closely reflect the initial abundance $^{92}\text{Nb}$ of the solar system. The assumption that these meteorites formed within the first 36 Myr of the solar system (one half-life of $^{92}\text{Nb}$) yields an initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of $< 3 \times 10^{-5}$ for the solar system. Further work is required to resolve the discrepancies between these results and the Zr isotopic data of other workers. Such investigations should strive to determine high precision isochrons for additional meteorites with further cross calibration by using data from other isotopic systems.

Acknowledgements

We would like to thank Tim Grove and Carsten Münker for helpful discussions and the Museum of Natural History in Paris for provision of the Juvinas sample.
8.1 Summary and conclusions

The aim of this thesis was to investigate whether the $^{92}\text{Nb}-^{92}\text{Zr}$ decay system could be used to date and trace early solar system processes. The following criteria must be fulfilled, if the application of the decay scheme is to be successful.

1) **the availability of samples with an appropriate old age:**

Meteorites provide a large reservoir of suitable samples, which formed very early in the solar system, probably within one half-live of $^{92}\text{Nb}$ (Carlson and Lugmair, 2000).

2) **the magnitude of fractionation of Nb from Zr:**

Niobium and Zr are both refractory and incompatible, lithophile elements. Therefore, only limited fractionation is observed. The investigated bulk samples of eucrites and mesosiderites all display Nb/Zr ratios close to those of chondrites. The Nb/Zr ratios of lunar ilmenites and bulk samples only vary by a factor of two to three relative to the chondritic value and this indicates that reservoirs with strongly fractionated Nb/Zr ratios did not form on the moon. However, larger fractionations of Nb from Zr occur during the crystallisation of ilmenite in the parent bodies of meteorites. Niobium/Zr ratios of up to $20 \times$ chondritic were measured for ilmenites of the ordinary chondrite Estacado.

3) **the initial abundance of $^{92}\text{Nb}$ in the solar system:**

This work provides important constraints on the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of the solar system:

(a) The internal isochron of the lunar highland rock 60025 implies an initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $< 5 \times 10^{-4}$.

(b) Bulk CAIs of Allende constrain the initial $^{92}\text{Nb}/^{93}\text{Nb}$ to $< 2 \times 10^{-4}$.

(c) Internal isochrons for the ordinary chondrite Estacado, the eucrite Juvinas and a clast of the mesosiderite Vaca Muerta define initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratios of between $0.6 \times 10^{-5}$ and $3 \times 10^{-5}$.

Therefore, these data imply that the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of the solar system is in the range of $0.6 \times 10^{-5}$ to $3 \times 10^{-5}$. This result is at odds with the data of previous studies (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2000), which deduced an initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio close to $10^{-3}$ from the analyses of single minerals and bulk CAIs. Further work is required to resolve the discrepancies.
between these results. However, the entire data (including internal isochrons) of the present study are internally consistent and imply that the solar system started with a low initial $^{92}\text{Nb}/^{93}\text{Nb}$ value of $< 3 \times 10^{-5}$.

4) the homogeneous distribution of Nb and Zr in the solar system

The Zr isotopic composition was determined for carbonaceous, ordinary and enstatite chondrites, eucrites, mesosiderites, lunar and terrestrial rocks to investigate the distribution of Zr isotopes in the solar system. All bulk rock samples display identical Zr isotopic compositions and, in particular, no anomalies were detected for either $^{92}\text{Zr}$ or $^{96}\text{Zr}$. These results imply that the solar nebula was well mixed at the scale of bulk rock and beyond. In contrast, some refractory calcium-aluminium-rich inclusions (CAI) of Allende show a small excess of $r$-process $^{96}\text{Zr}$. This suggests that CAIs may have formed before mixing of the solar nebula was complete, such that they were able to sample a population of $r$-process enriched material.

The stepwise dissolution of carbonaceous chondrites revealed distinct $r$-process and $s$-process components. The acetic acid leachates display the most pronounced $^{96}\text{Zr}$ excesses, which provides evidence for the presence of a previously unidentified presolar phase present in these meteorites. However, it is also possible that $^{96}\text{Zr}$ excess stems from a carrier phase, that formed, at least in part, within the solar system from $r$-process enriched presolar material. Depletion of $^{96}\text{Zr}$, which represents a $s$-process component, was observed for the later dissolution steps of the leaching experiments. This $s$-process component could have been released from known varieties of presolar grain (graphite and SiC).

The Zr isotopic data for meteorite, terrestrial and lunar bulk rock samples, as well as CAI and carbonaceous chondrites leachates provide evidence that average solar system material consists of a homogenised mixture of different nucleosynthetic components. The homogeneity of the Zr isotopic compositions for bulk rock samples demonstrates that the solar nebula was well mixed on a large scale. The results obtained for the stepwise dissolution of carbonaceous chondrites, however, provide evidence for a heterogeneous distribution of $r$- and $s$-process components on a smaller scale. Distinct components preserved in carbonaceous chondrites survived the formation of the solar system and this suggests that the solar nebula must have, at least partly, contained cold regions.
The homogeneity of $^{92}$Zr is important for the application of the short-lived $^{92}$Nb-$^{92}$Zr chronometer. Only some leachates of carbonaceous chondrites display evidence for small abundance variation of $^{92}$Zr that are of nucleosynthetic origin and there is a possible hint that some CAI could show minor $^{92}$Zr anomalies. However, such variation are absent in all other meteoritic, lunar and terrestrial sample. This absence is a necessary prerequisite for the reliable application of the $^{92}$Nb-$^{92}$Zr decay system.

In summary, it can be concluded that the low initial $^{92}$Nb/$^{91}$Nb ratio of the solar system, combined with the modest Nb/Zr fractionation drastically limits the utility of the Nb-Zr system in tackling problems of planetary accretion and differentiation. The timing of the early differentiation of Earth and moon is under-constrained from the Nb-Zr decay system. However, Zr isotopes provide a useful tracer of different nucleosynthetic components in the solar system.
References


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Lugmair G. W. and Shukolyukov A. (1998) Early solar system timescales according to \(^{53}\text{Mn}-


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