THE BEHAVIOUR OF IODINE AND XENON
IN THE FIRST ASTEROIDS

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THE BEHAVIOUR OF IODINE AND XENON IN THE FIRST ASTEROIDS
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Results of I-Xe analyses have been obtained from meteorite samples that experienced different extents of thermal processing in the early Solar System in order to help characterise the movements of iodine and xenon in the early Solar System and constrain the timing of these movements using the I-Xe chronometer. Samples were irradiated to convert $^{127}$I to $^{128}$Xe* and allow simultaneous measurements of iodine and xenon isotopes. Xe isotopes were measuring using the RELAX mass spectrometer.

I-Xe ages of material of different metamorphic grade from R-chondrites NWA 6492, NWA 830 and NWA 3364 suggest a link between the time of closure to Xe-loss and extent of metamorphism on the R-chondrite parent body. However, further I-Xe analyses of R5 material from NWA 6492 and R4 and R6 material from other R-chondrites are needed to confirm this. The most primitive material analysed give I–Xe ages between 4559 – 4554 Myr, slightly later than reported Mn-Cr ages. This may support the ideal of radial heterogeneity of $^{53}$Mn in the early Solar System. However differences could also be due to variations in the samples analysed. Future analyses of I-Xe and Mn-Cr ages in mineral separates from the same R-chondrite are recommended in order to investigate this hypothesis. Closure to Xe-loss in chondrules on the R-chondrite parent body appears to have occurred ~5 – 10 Myr later than on the ordinary and enstatite parent bodies. This implies either later accumulation of material or slower cooling in a larger body.

Comparisons of I-Xe systematics in anomalous eucrites Bunburra Rockhole and Ibitira and “nomalous” eucrites Juvinas and Bérêba show lower $^{129}$I/$^{244}$Pu ratios in the “nomalous” eucrites. This is not due to formation on a less volatile-rich body but instead reflects extended loss of Xe on 4 Vesta. $^{129}$I/$^{244}$Pu ratios indicate igneous processing continued on 4 Vesta for ~50-100 Myr after geological activity had ceased on the anomalous eucrites parent bodies. The extended processing seen in Juvinas and Bérêba is attributed to formation on a larger body that retained heat for longer. If, as the data suggest, the anomalous eucrites formed on a separate parent body it must have been catastrophically disrupted as Vesta is thought to be the only remaining differentiated asteroid. The larger size of Vesta may explain why it has uniquely survived the impacts that destroyed its siblings.

Analyses of the unique achondrite GRA 06129 show that the I-Xe system in this meteorite has no chronological significance. The data instead suggest that iodine-bearing plagioclase formed early but thermal metamorphism resulted in loss of $^{129}$Xe* from iodine bearing sites. Uranium-bearing apatite appears to be a secondary mineral that incorporated parentless $^{129}$Xe* and $^{129}$Xe*that had been redistributed during earlier metamorphism. A trapped-Xe component released at high-temperatures may be a primitive component such as Q-Xe, though terrestrial–Xe acquired during weathering cannot be ruled out by this study. If Q-Xe is present, it is most likely hosted in a primary phase other than plagioclase. During its terrestrial residence time GRA 06129 acquired iodine via Antarctic weathering. I-Xe analyses on Antarctic meteorites should therefore be carried out with caution. Further Xe analyses of mineral separates from GRA 06129 would help constrain the host phase of the trapped Xe. That the I-Xe system of the plagioclase has been completely reset make it a good candidate mineral for I-Xe dating of primary processes whereas I-Xe dating of apatite appears more problematic.
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CHAPTER 1. INTRODUCTION.

This project was originally entitled “Investigating the Solar System using Noble Gases”. This broad title was designed to allow a great deal of freedom to explore the subject area and to contribute to an established, active research group. I decided to focus on the behaviour of iodine and xenon in the oldest asteroids.

In this chapter I briefly describe the various groups of meteorites and their significance; and the different noble gas components present in meteorites and use of noble gases in cosmochemistry. I then review the use of the I-Xe chronometer and give the specific aims and objectives of this project. Introductory remarks relevant to the samples studied are given at the beginning of chapters 3-5.

1.1. Introduction

The early Solar System environment can be better understood by analysis of meteorites. Meteorites originate on a range of asteroids and reflect the conditions of different regions of the original solar nebula and the processes that occurred during the evolution of early Solar System materials. All meteorites, including the most primitive, show some alteration or metamorphism which indicates that these processes were widespread throughout the early Solar System. By examining these elemental and isotopic signatures, produced in different environments over different lengths of time and retained in meteorites, these processes can be constrained in time and space.

It has been shown that materials from the early Solar System retain isotopic signatures caused by the decay of now-extinct radionuclides. These short-lived isotopes have half-lives of less than 100 million years (Myr) and must have been created just before, or during the formation of the Solar System. They must also have been present in large enough amounts for their daughter products to shown up as anomalies in isotopic ratios. By assuming that isotopes were well mixed in the early Solar System and that diffusive loss of the daughter isotope has not occurred, different ratios of daughter to parent isotopes in Solar System materials show that their host materials formed at different times. Short-lived radionuclides can therefore provide precise, relative ages of materials that formed in the first few million years of the Solar System. Consequently, short-lived isotope systems can be used to constrain the timings of processes that were occurring on asteroids in the early Solar System.
Noble gases are volatile elements and partition into the gas phase and so are not abundant in rocky materials, which are comprised mostly of refractory materials. Due to their scarcity and inert nature small changes in isotopic ratios of noble gases may be detected. This makes them ideal trace elements. Several radioactive isotopes decay to isotopes of noble gases making them excellent chronometers.

In recent years, astronomical observations, chemical analysis of meteorites, radiometric dating of Solar System objects, a better understanding of the nature of our own planet, and computer modelling has enabled tighter constraints to be put on the processes that occurred during Solar System formation. At Manchester the development of the RELAX (Refrigerator Enhanced Laser Analyser for Xenon) mass spectrometer has allowed high sensitivity measurements of xenon isotopes in very small samples of extraterrestrial materials.

1.2. Meteorites

In this work I report analyses of iodine and xenon isotopes in samples of Rumuruti (R) chondrites, eucritic meteorites and an anomalous achondrite. To put these into context I now describe our current understanding of the origin of the different meteorite groups.

Meteorites are broadly divided into two groups: those that originated on unmelted parent bodies and those that originated on parent bodies that have undergone some extent of melting and differentiation. These two groups are divided into several classes that are further categorised into groups based on their chemistry (Figure 1.1).

1.2.1. Chondrites

The unmelted meteorites are known as chondrites and are thought to be the most primitive material remaining in the Solar System. There are several lines of evidence indicating the chondrites have largely retained their original chemical composition:

1. Abundances of refractory elements in chondrites reflect that of the Sun as determined by spectral measurements of the photosphere. The Sun in thought to contain >99% of Solar System material and have experienced limited chemical evolution. Therefore the composition of the Sun is inferred to be representative of the solar nebula from which the Solar System condensed. Hence chondrites contain refractory material that condensed directly from this nebular and was not altered significantly.
2. Some chondrites contain calcium-aluminium-rich inclusions (CAIs). Calcium and aluminium are refractory elements which crystallise at a high temperature and are predicted to be the first solids to be present at equilibrium in cooling gas of solar composition. That they are dominant in CAIs implies that these materials were the first to condense from the nebular and have been preserved in chondrites.

3. Chondrites also contain material called chondrules (for which chondrites are named). These are round grains of silicate material (mostly olivine and pyroxene) the textures of which suggest they formed by rapid heating and cooling. The exact environment chondrules formed in is not well known, though they cannot have formed deep within an asteroid or planetary body. Chondrules are only present in chondrites (except for CI chondrites) and not in meteorites from differentiated asteroids, planetary bodies or in chondrites that have experienced high degrees of thermal metamorphism. This suggests they formed in the early Solar System and were preserved in unaltered chondrites. Use of the Al-Mg chronometer has shown that chondrule formation began shortly after CAI formation (Amelin et al., 2002) and was a more extended process than CAI formation, occurring over several million years.

4. The components found in chondrites, such as CAIs and chondrules are ancient. Isotopic chronometers such as the Pb-Pb system have shown that CAIs are the oldest Solar System materials, forming at 4568.2 Myr (Bouvier and Wadhwa, 2010).

5. The matrix material in chondrites contains small grains with isotopic ratios very different from the solar composition. These are thought to have condensed around other large stars such as supernovae or AGB stars before being injected into the ISM and incorporated into the solar nebula and are known as “presolar” grains. That these grains have survived unprocessed is further evidence for the primitive nature of chondrites.

That chondrites retain a primitive composition representative of the Solar System makes them invaluable for studying the processes that created the first planetesimals. Though chondrites show broadly solar compositions, on a finer scale differences in chemical composition can be seen allowing them to be divided into several groups (Figure 1.1). Different groups of chondrites show limited ranges of chemical composition, oxidation states and oxygen isotope ratios indicating that each group may have originated on a
separate parent body. The differences in chemistry seen between different groups of chondrites (different parent bodies) are thought to be the result of differences in the regions of space the chondrite parent bodies formed in. Studying different types of chondrites thereby constrains variations in the environment of the early Solar System.

**Figure 1.1.** *Classification of meteorites. This classification focuses on meteorites derived from asteroids and excludes lunar and Martian “planetary” meteorites (after The Natural History Museum, 2012).*

Chondrites are classified based on the following:

1. Chondrites are primarily divided based on bulk chemical compositions and modal abundances of components such as CAIs, chondrules, metals and surrounding matrix.

2. Oxidation state (Figure 1.2) may also be used to distinguish different classes of chondrite. Increased oxidation converts iron metal to iron oxide (FeO). Oxidising conditions cause pyroxene to be converted to olivine as there is more FeO available but the same amount of silica (Si) and olivine has a lower FeO/Si ratio than pyroxene. Rumuruti chondrites are predominantly olivine with little pyroxene whilst carbonaceous chondrites contain little-to-no iron metal. It
follows that both these classes formed under oxidising conditions. Enstatite meteorites are dominated by the pyroxene, enstatite. Enstatite chondrites are therefore thought to have formed under reducing conditions where pyroxene was not converted to olivine.

3. Oxygen isotope ratios are also used to classify meteorites (Clayton et al., 1976) and this method is thought to be the most robust. There are three stable isotopes of O: $^{16}$O, $^{17}$O and $^{18}$O. $^{16}$O is produced during stellar evolution of high mass stars (>10 solar masses). $^{17}$O and $^{18}$O are less abundant in the interstellar medium (ISM) than $^{16}$O because they are produced by secondary processes that require “seed” nuclei formed by earlier generations of stars. When variations in ratios of these isotopes are discussed there are often expressed as deviations ($\delta$) from the isotopic ratio of standard mean ocean water (SMOW) where:

$$
\delta^{18}O = \left( \frac{^{18}O/^{16}O}_{\text{sample}} / \left( \frac{^{18}O/^{16}O}_{\text{SMOW}} \right) - 1 \right) \times 1000
$$

$$
\delta^{17}O = \left( \frac{^{17}O/^{16}O}_{\text{sample}} / \left( \frac{^{17}O/^{16}O}_{\text{SMOW}} \right) - 1 \right) \times 1000
$$

Figure 1.3 shows $\delta^{18}$O and $\delta^{17}$O for different chondrite groups and the earth. Terrestrial samples fall on a line known as the terrestrial fraction line (TFL) whereby the variation in oxygen isotope ratios can be explained by mass fractionation. Chondrites lie on trend-lines with different gradients from the TFL suggesting mass fractionation is not responsible for the variation and that chondrites formed from different mixtures of different oxygen sources. Each meteorite group has its own unique composition allowing easy distinction.

Ordinary, enstatite and carbonaceous chondrites are further divided into several groups. Ordinary chondrites and enstatite chondrites are divided into H (high iron), L (low iron) and LL (low iron) groups based on contents of iron, iron metal and iron oxide (Fig. 1.2). Carbonaceous chondrites are divided into eight groups according to their chemical compositions. Of these, the CI group have chemical compositions closest to the Sun’s photosphere.
Figure 1.2. Urey-Craig (1953) diagram showing relative iron contents and oxidation state of chondrite groups. Reproduced from Brearley and Jones (1998).

Figure 1.3. Oxygen isotope compositions for chondrite groups (left) after Clayton (2003), including R-chondrites (samples of which are included in this study). Oxygen isotope compositions for achondrites groups (right) after Clayton and Mayeda (1996); HED and angrite fractionation lines from Greenwood et al. (2005). Also shown are data for achondritic samples studied in this work: GRA 06129 (Shearer et al., 2010); and anomalous eucrites Bunburra Rockhole (Bland et al., 2009) and Ibitira (Wiechert et al., 2004).
Spatial differences in the chemistry of the gas and dust cloud that material condensed out of during Solar System formation is thought to be linked to heliocentric distance. The temperature and density of this cloud would decrease with increasing distance from the Sun. Lower temperatures and densities produce more oxidising conditions so the more oxidised meteorites (such as Rumuruti (R) chondrites) may have formed at greater heliocentric distances than the more reduced meteorites (such as enstatite chondrites).

Though chondrites are primitive compared to other Solar System materials, many have still undergone some processing by aqueous alteration or thermal metamorphism. Along with their class and group, chondritic meteorites are assigned to a petrologic type based on how primitive they are. Petrologic types range from 1-6. One may think they type 1 are the least altered but in fact the type 3 are the most primitive with type 4-6 indicating increasing peak metamorphic temperatures and type 2-1 indicating increasing aqueous alteration. The criteria for classifying chondrites to a petrologic type is shown in Table 1.1 and is based on the classification system proposed by Van Schmus and Wood (1967). The content of primordial noble gas components also decreases with increasing alteration.

Thermoluminesence (TL) is also used to distinguish small degrees of alteration within the most primitive meteorites (Sears et al., 1980). The TL sensitivity is controlled by the degree of crystallisation of the mesostasis of the chondrule and as chondrules are thermally altered, feldspar crystallises from the glassy mesostasis. Measurement of the TL of chondrules thereby allows type 3 chondrites to be further divided into type 3.1-3.9.

Aqueous alteration is the result of interaction with fluids. The only chondrites that are categorised as petrologic types 1 and 2 are carbonaceous chondrites. These chondrites also show a high oxidation state indicating they formed at large heliocentric distances. This can be explained by higher ambient temperatures at closer heliocentric distances which prohibit condensation of more-volatile elements and ices and limit aqueous, or it could be due to spatial heterogeneity in the distribution of $^{26}$Al in the early Solar System.

That different chondrites have experienced different extents of metamorphism suggests that either different parent bodies were heated to different temperatures, or that different
parts of the same parent body were heated to different temperatures. The source of heat in the early Solar System is thought to be decay of short lived isotopes as $^{26}$Al and $^{60}$Fe. Rocks are poor conductors of heat so it is likely that the heat from an internal source such as this would not be distributed evenly throughout the planetesimal. The extent of heating and melting that occurred on chondrite parent bodies is limited (>1000 °C in the most metamorphose chondrites) which suggests that they were small (100s km) and lost heat.

The different conditions that could produce the range in thermal metamorphism can be explained by the onion-shell model, which proposes that an internal heat source (such as decay of $^{26}$Al) produced strongly metamorphosed rocks in the centre of the asteroid with the outer layers receiving little heat resulting in little alteration (Herndon and Herndon, 1977; Miyamoto et al., 1981). The material then cooled and recrystallised undisturbed. Type 6 material thereby originated deeper in an asteroid than type 4 and 5 material, and type 3 material represents the very outer layer.

This model can be tested by dating different petrologic types of chondrites as, if the onion model is true, the deeper, more metamorphosed rocks should have cooled more slowly and crystallised later. U-Pb dating by Gopel et al. (1994) and Ar-Ar dating by Trieloff et al. (2003) of phosphate and feldspar in H chondrites showed a correlation between cooling rate and extent of metamorphism, consistent with cooling in an undisturbed onion-like structure with an internal heat source for the H chondrite parent body. However, other studies do not show the expected correlation between metamorphic grade and age predicted by the onion-shell model (Williams et al., 2000). An alternative is the rubble-pile model where asteroids are fragmented by impacts and then reassemble due to their own gravity. The sudden exposure of interior material during an impact can result in rapid cooling of all material, irrespective of extent of metamorphism. Given the chaotic nature of the early Solar System, where collisions between asteroids are thought to be frequent, many favour the rubble-pile model. An example of early disruption of an asteroid that is thought to have experienced significant heating is the acapulcoite/lodranite parent body, where multiple phases with different closure temperatures produced the same early I-Xe age, indicating rapid cooling attributed to a collisional disruption (Crowther et al., 2009).
Table 1.1. Criteria for petrologic types of chondrites indicating extent of alteration (after Van Schmus and Wood, 1967; Brearley and Jones, 1998).

<table>
<thead>
<tr>
<th>Aqueous alteration</th>
<th>Petrologic Type</th>
<th>Thermal Metamorphism</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Chondrule texture</td>
<td>absent</td>
<td>sharply defined</td>
</tr>
<tr>
<td>Matrix texture</td>
<td>fine grain</td>
<td>mostly fine grain</td>
</tr>
<tr>
<td></td>
<td>undefined</td>
<td>defined</td>
</tr>
<tr>
<td>Feldspar</td>
<td>none present</td>
<td>grains &lt;2um</td>
</tr>
<tr>
<td></td>
<td></td>
<td>grains &gt;50um</td>
</tr>
<tr>
<td>Chondrule glass</td>
<td>-</td>
<td>mostly altered</td>
</tr>
<tr>
<td>Metal</td>
<td>absent</td>
<td>minor or absent</td>
</tr>
<tr>
<td>Low-Ca pyroxene</td>
<td>absent</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Uniformity of olivine &amp; Ca-poor pyroxene</td>
<td>-</td>
<td>&gt;5% deviation</td>
</tr>
<tr>
<td>Sulphide: Ni content</td>
<td>-</td>
<td>&gt;0.5 wt%</td>
</tr>
<tr>
<td>Carbon content</td>
<td>3-5 wt%</td>
<td>0.8-2.6 wt%</td>
</tr>
<tr>
<td>Water content</td>
<td>18-22 wt%</td>
<td>2-16 wt%</td>
</tr>
</tbody>
</table>

Meteorites from the Rumuruti (R) class of chondrites have experienced different degrees of metamorphism and fall into petrological types 3-6 (referred to as R5-R6 for Rumuruti chondrites). The majority of R-chondrites are R3 or R4, though all (except Rumuruti) are breccias that sample a range of material. Lingemann et al. (2000) has suggested that R-chondrite material was metamorphosed to R4, 5 and 6 during thermal metamorphism in an undisturbed onion-shell arrangement; where material buried deeper in the parent asteroid will reach a greater peak temperature and will cool over a longer period of time (as long as the system remains undisturbed) compared to material closer to the surface. R6 chondrites therefore originated deeper in asteroids than R3 chondrites and petrologic type is linked to cooling rate. No I-Xe dating has so far been carried out on R-chondrites though Nagao et al. (1999) showed the presence of excess $^{129}$Xe* in all.
five R-chondrites studied. The I-Xe system may therefore be useful in understanding the thermal history of the R-chondrite parent body.

Collisions such as those that occurred early in the Solar System and impacts that liberated meteorites from their parent body can result in “shock”. High velocity collisions can produce high pressures for a few seconds which, when released, produce heat. This shock metamorphism can produce new minerals and melt and fracture crystals. The extent of shock experienced by a meteorite has been classified into six stages (S1-S6) by Stöffler et al. (1991) (Table 2.2). Shock can reset isotopic systems meaning care has to be taken when dating heavily shocked materials. The effects of shock on the I-Xe system are discussed in section 1.3.

Table 1.2. Classification scheme for extent of shock in meteorites and associated pressure experienced (after Stöffler et al., 1991).

<table>
<thead>
<tr>
<th>Shock stage</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Unshocked</td>
<td>Very weakly shocked</td>
<td>Weakly shocked</td>
<td>Moderately shocked</td>
<td>Strongly shocked</td>
<td>Very strongly shocked</td>
</tr>
<tr>
<td>Shock Pressure (GPa)</td>
<td>&lt;4-5</td>
<td>5-10</td>
<td>15-20</td>
<td>30-35</td>
<td>45-55</td>
<td>75-90</td>
</tr>
</tbody>
</table>

1.2.2. Melted asteroids

Other, non-chondritic meteorites show chemical compositions very different from solar. This is the result of large scale melting and differentiation on their parent bodies. Meteorites from melted asteroids sample the various layers created by the differentiation process and therefore vary considerably in compositions. They are divided into three groups: stony (or achondrites), iron and stony-iron.

Achondrites are igneous rocks that formed from molten material. They do not contain chondrules, though they are assumed to have formed from precursor materials of chondritic composition. Complete melting of a rock requires very high temperatures and is rare. Most igneous rocks are produced by partial melting where often less than 25% of the source material is melted. As rocks are mixtures of materials, those with the lowest liquidus temperatures will be extracted into the melt first. This means the first
melts have very different compositions from the source. As partial melting continues, the composition of the melt approaches that of the source. The melt then segregates from the solid source material and rises to the surface due to buoyancy. Most melts solidify as plutons below the surface of the asteroid though some may erupt as lava and cool on the surface, or buried beneath later lava flows. In plutons fractional crystallisation may occur as different minerals crystallise in turn as during cooling of the magma. The minerals that form first may sink to the bottom of the pluton and form cumulate rocks. This changes the composition of the remaining magma and can make it more difficult to determine source compositions from melts.

Perhaps one of the most important groups of achondritic meteorites is the howardite–eucrite–diogenite (HED) group. These are igneous rocks related by their mineralogy and chemistry with oxygen isotope ratios that indicate they originated on the same parent body or related parent bodies (Clayton and Mayeda, 1996). There are two types of eucrites: basaltic (thought to have cooled on or near the surface) and cumulate (thought to have cooled more slowly at greater depths). Diogenites are composed mainly of orthopyroxene with small amounts of plagioclase or olivine. This indicates they are cumulates formed by fractional crystallisation. Howardites are regolith breccias that sample both eucrite and diogenites material. Previous Xe analyses of eucrites have concentrated on the Pu-Xe dating system (Shukolyukov and Begemann, 1996a; Miura et al., 1998; Park and Nagao, 2005). These analyses showed the presence of $^{129}\text{Xe}^*$ in eucrites and ancient Pb-Pb and Mn-Cr ages suggest eucrites could have contained $^{129}\text{I}$. I-Xe analyses has only previously been carried out on one eucrite (Asuka 881394) which did not yield a consistent $^{129}\text{I}/^{127}\text{I}$ ratio, though excess $^{129}\text{Xe}^*$ was observed (Busfield et al., 2008).

The HED meteorites are unique in that their parent body is thought to be known. The asteroid 4 Vesta (referred to as Vesta) and its family of Vestoids show reflectance spectra very similar to those of eucrites (McCord et al., 1970). Further studies by the Dawn mission have confirmed that Vesta’s surface is consistent with the inferences already made from HED material, with a eucritic crust and deeper diogenite material exposed by impacts (Sanctis et al., 2012). Vesta is the second largest asteroid in the Solar System and has been described as more like a proto-planet than an asteroid as it is the only known asteroid with a basaltic crust, ultramafic mantle and metallic core. This
makes Vesta (and the meteorites that originate there) a unique opportunity to study igneous processes in the early Solar System.

Several basaltic achondritic meteorites show major element chemistry and mineralogy similar to eucrites but deviate from the HED oxygen isotope mass fractionation line (Figure 1.3). These are known as anomalous eucrites. Their origin is not yet well understood but it is thought they either originated on a separate parent body (Scott et al., 2009) very similar to Vesta that has since been dismantled by collisions, or that Vesta and the Vestoids retain some heterogeneity (Wiechert et al., 2004). Investigating the thermal history of anomalous eucrites and “nomalous” eucrites via the I-Xe system may allow constraints to be placed on their respective origins.

The other types of achondrite are briefly described here:

Angrites are basaltic rocks enriched in refractory elements and depleted in volatiles. They have similar oxygen isotope ratios to HEDs but are thought to have formed on a separate body under more oxidising conditions. Aubrites are breccias, dominated by enstatite and may originate in a similar region of space to enstatite chondrites. Rare earth element patterns indicate that plagioclase was fractionated from the aubrites parent magma during fractional crystallisation but no related plagioclase-rich basaltic meteorites have been found which is puzzling.

The residues remaining from partial melting on achondrite parent bodies are thought to retain compositions close to chondritic. Primitive achondrites such as acapulcoites, lodranites brachinites and winnoaites are thought to be residues due to their chondritic abundances of Fe, Mn and Mg. Acapulcoites and lodranites are thought to originate on the same parent body due to similar oxygen isotope ratios (Clayton et al., 2004), chemistry (McCoy et al., 1996) and cosmic-ray exposure ages (Terribilini et al., 2000). These primitive achondrites may be better described as being heavily metamorphosed, rather than melted. It therefore follows that these primitive achondrites (residues) should share an origin with a co-genetic group of achondrites (melts) and iron meteorites.

Ureilites are coarse grained rocks that contain carbon-rich material. They are thought to have crystallised deep within their parent body though it is not yet understood whether they are residues of partial melting (primitive achondrites) or cumulates (achondrites)
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Some meteorites cannot be assigned to any existing meteorite classes and are known as “ungrouped”. These can allow investigation of previously unsampled early Solar System processes. It is likely that these ungrouped achondrites are rare due to sampling bias in the delivery of meteorites to Earth from the asteroid belt rather than limited occurrences of their type of parent body. Graves Nunataks (GRA) 06129 (and its pair GRA 06128) is an ungrouped achondrite that is thought to represent a unique example of felsic crust formation on a volatile-rich parent body. Previous Manchester work on unirradiated samples GRA 06129 included in Shearer et al. (2010) showed the presence of excess $^{129}$Xe from decay of $^{129}$I, either in situ or inherited, in all three samples studied. An ancient Al-Mg age of 4565.9 ± 0.3 Myr (Shearer et al. 2010) indicates that crystallisation of the GRA 06129 parent body occurred very early in the Solar System pointing towards formation whilst $^{129}$I was alive. I-Xe analyses of irradiated samples of GRA 06129 can determine whether $^{129}$Xe* was produced by in-situ decay of $^{129}$I.

Achondrites therefore record the evolution of igneous processes on asteroids, processes similar to those that occurred in our own planet’s early history. Studying the I-Xe system in these igneous rocks can help constrain the fundamental processes, such as the formation of planetary surfaces and the transport of volatiles, and establish the timings of these.

Stony-iron meteorites include the pallasites and mesosiderites. Pallasites consist of olivine crystals surrounded by metallic iron and nickel. The traditional theory of origin of pallasites is that they formed at the core-mantle boundary (Mittlefehldt et al., 1998) however others have suggested they are impact generated mixtures of core and mantle material (Scott et al., 2007). Recent work by Yang et al. (2010) on 8 main group pallasites showed that they had different cooling rates which supports formation from impact debris as material that formed at the core/mantle boundary should cool at the same rate. Mesosiderites are silicate-metal breccias, the silicate part being chemically similar to eucrites and diogenites. They do not contain any olivine so appear to represent the core and crust of an asteroid or asteroids. It had been suggested that the metal content came from the impact body (Rubin and Mittlefehldt, 1999) but Scott et al. (2001) questioned whether impact and target material would be mixed at low-speeds and proposed that mesosiderites formed by re-accretion of a shattered asteroid.
Iron meteorites consist predominately of Ni and Fe and are grouped by their chemistry and structure. Irons are thought to sample metallic cores that formed deep within differentiated asteroids. During core formation iron-loving elements are segregated into the centre of the asteroid. This results in depletion of metals in the achondrites that form by partial melting of the remaining mantle. That chondrites contain solar abundances of metals suggests they formed on bodies that did not differentiate. Some iron meteorites contain silicate inclusions. Silicates in the IIIAB group of irons, mesosiderites and HEDs show very similar oxygen isotope ratios (Clayton and Mayeda, 1996). This suggests a common origin for these three groups of meteorites. However, HEDs are thought to come from Vesta, which is still intact, so it is unlikely that they sample Vesta’s core or core boundary. This problem is still unresolved but may suggest (along with the anomalous eucrites) that asteroids with similar chemistry to Vesta were once more common in the Solar System. Further investigations of Vesta and the meteorites thought to originate on Vesta are needed to constrain the history of differentiated asteroids.

### 1.2.3. Timescale of meteorite formation and evolution

Establishing a timescale of the formation of early Solar System materials and the secondary processes that occurred on them is one of the fundamental areas of cosmochemistry. Various radiogenic isotopic systems are used to study the chronology of meteoritic components and can be broadly divided in to two types: relative chronometers and absolute chronometers.

Absolute chronometers use long-lived isotopes radionuclides with half-lives >10⁹ years that are still present in measurable abundances today. These include the K-Ar, Rb-Sr, Sm-Nd and U-Pb systems. Long-lived isotopes can give absolute ages but are often more imprecise than relative chronometers. Ages are calculated using equation 1.1 where $D$ is the number of daughter atoms; $D_0$ is the number of daughter atoms present before decay; $N$ is the number of parent atoms remaining; $\lambda$ is the decay constant of the parent nuclide; $t$ is the age of the sample.

$$D = D_0 + N(e^{\lambda t} - 1)$$

(Eq. 1.1)

The Pb-Pb system is a bit more complex as it uses two decay schemes ($^{235}$U-$^{207}$Pb and $^{238}$U-$^{206}$Pb) and measures the ratio of the two decay products, $^{207}$Pb*/$^{206}$Pb* . As the
half-life of $^{235}$U ($\sim$700 Myr) is much shorter than the half-life of $^{238}$U ($\sim$4.5 Gyr), the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio changed quickly in the early Solar System. This means the precision of the Pb-Pb increases with the age of the sample, meaning absolute ages of early Solar System materials can be determined with high precision using the Pb-Pb chronometer.

Relative chronometers use short-lived radionuclides, with half-lives $<10^8$ years. These isotopes were present in the early Solar System but have since decayed to undetectable amounts and so are called “extinct”. As the amount of parent nuclide remaining ($N$) cannot be measured a slightly different method is used to calculate the age of the sample (equation 1.2). Here the ratio of the excess daughter nuclide ($D^*$) to a stable isotope of the same element as $N$ is measured in the sample and in a sample of a standard material (usually with a known absolute age) and used to work out the time elapsed between them.

$$\frac{D^*}{N} = \frac{D^*}{N_{\text{STANDARD}}} e^{-\lambda t} \quad \text{(Eq. 1.2)}$$

Only relative ages can be obtained using short-lived isotope systems as the amount of parent nuclides remaining now is zero. However, if the same mineral phase is dated using both a relative and absolute chronometer, the relative chronometer can be tied or “anchored” to the absolute chronometer. This method is useful in obtaining precise absolute ages of early Solar System materials and processes. Relative chronometers include Al-Mg, Mn-Cr and I-Xe. The I-Xe system will be discussed in greater detail in section 2.3.

All isotope chronometers rely on the assumptions that: (1) the radioactive nuclide was homogenously spread throughout the Solar System; and (2) once closed, the system remained undisturbed with no loss or further additions of the daughter isotope. Therefore differences in the ratios of daughter to stable isotopes between samples are only due to differences in time. By using these isotope systems to date different samples and comparing the results of different chronometers these assumptions are tested.

Pb-Pb ages of CAIs indicate that they are the oldest surviving solids and that they formed at 4568.2 Myr (Bouvier and Wadhwa, 2010). As CAIs are the oldest Solar System material found so far and contain the first phases predicted to condense from the solar nebular, their age is often taken as the “formation of the Solar System”. Pb-Pb
analyses of CAIs have concentrated on the CV chondrites which have the largest CAIs (Amelin et al., 2002). Connelly et al. (2008) analysed chondrules from another CV chondrite (Allende) which gave a Pb-Pb age of 4565.45 ± 0.45 Myr, 1.66 Myr later than the CV CAIs. This resolvable difference in age has led to the hypothesis that chondrules formed ~1 Myr later than CAIs and that their formation period was longer, lasting 3-4 Myr (Amelin et al., 2002; Krot et al., 2005; Connelly et al., 2008).

CAIs also show the highest excesses of the short-lived isotope $^{26}$Al, supporting their origin as the first solids. A $^{26}$Al/$^{27}$Al ratio of $\sim5\times10^{-5}$ (references in Krot et al., 2009) has been found in many different CAIs from different groups of meteorites. This has become known as the “canonical” value. However, recent measurements using ICPMS techniques have produced $^{26}$Al/$^{27}$Al$_0$ ratios above the canonical value (e.g. Thrane et al., 2006). Most (though not all) of these supra-canonical values were obtained from whole-rock samples or samples with low Al/Mg ratios, which could have produced the anomalously high $^{26}$Al/$^{27}$Al$_0$ ratios. Chondrules show lower $^{26}$Al/$^{27}$Al$_0$ ratios from 0.5-2.0 $\times10^{-5}$ (Krot et al., 2009 and references therein) indicating formation ~2 Myr later than CAIs, consistent with the Pb-Pb ages.

Chondrite material that has been thermally metamorphosed or aqueously altered, records the timings of these secondary events. The heat that drove these processes is thought to be produced by decay of short-lived isotopes such as $^{26}$Al and $^{60}$Fe. It follows that these processes must have occurred early in Solar System history whilst these isotopes were still abundant and that chondrite parent bodies must have accreted quickly. I-Xe dating of Zag halite showed that aqueous processes were occurring within the first 2-3 Myr of the Solar System (Whitby et al., 2000). Mn-Cr dating of HED meteorites indicates that silicate differentiation of Vesta occurred soon after Solar System formation at ~4565 Myr (Trinquier et al., 2008). The timing of core formation of Vesta is not well constrained but is also thought to have been rapid, occurring $3 \pm 6$ Myr after CAIs (Kleine et al., 2009).

Meteorites sample a wide range of materials thought to represent the different conditions and processes present in the early Solar System. A chronology of these events can help constrain the early Solar System environment. The use of different isotopic systems can help test the inherent assumptions made when carrying out radiometric dating.
1.3. Noble Gas Cosmochemistry

Noble gases in meteorites consist of several components that are referred to throughout this work. Here I summarise the different components that must be untangled in order to determine quantities and isotopic ratios of the various contributing parts.

*In situ* components are produced by nuclear reactions within the samples and include radiogenic and spallation noble gases. The *solar* component originates in the Sun and may have been implanted by solar wind and other energetic particles. The *exotic* component consists of presolar materials that have survived in Solar System materials. The *planetary* component consists of noble gas signatures that are not in situ, exotic or solar. Solar and planetary components are classified as *trapped*.

Different noble gas components are hosted in different sites within (or on the surface of) minerals. These different sites release noble gases at different temperatures depending on how retentive they are. If samples are heated up gradually as in step-heating, where the gas is collected and analysed at each step (also known as stepwise degassing), components are released from the different sites at different temperatures (they have different release patterns). By that rule components released from the same site will show the same release patterns. Step-heating can therefore shed light on the noble gas compositions of different host phases in the samples.

1.3.1. Solar

The Sun contains 99.9% of the mass of the Solar System and its composition is thought to be representative of the solar nebula. Terrestrial bodies in the Solar System formed from the solar nebula meaning the solar composition can be used as the starting point in planetary evolution models. Determining the elemental and isotopic compositions of the sun is therefore of great importance in cosmochemistry. Estimations of the solar composition are based on spectroscopy, solar wind and other energetic particles ejected from the sun and primitive chondritic meteorites. Anders and Grevesse (1989) list solar abundances based on spectroscopic measurements and solar wind data. Meteoritic and photospheric abundances are listed in K. Lodders (2003). Wieler (2002) reviews the knowledge of solar noble gas abundances.

Solar noble gas abundances are difficult to determine for several reasons: noble gases are not visible in photospheric spectra; meteoritic materials are likely to be heavily depleted in noble gases compared to the sun as the noble gases strongly partitioned into
the gas phase; the solar $^3\text{He}/^4\text{He}$ ratio has been altered due to deuterium burning producing $^3\text{He}$ and hydrogen fusion producing both $^3\text{He}$ and $^4\text{He}$ (Wieler, 2002). Solar abundances of He have been estimated using methods other than spectroscopy. The current luminosity of the sun is dependent on the initial He composition in the protosun so the initial He abundance can be calculated with an uncertainty of just a few percent by using the standard solar model (Christensen-Dalsgaard, 1998).

Ne abundances can be estimated from solar wind and other solar energetic particles implanted in meteorites and the lunar surface. “Photospheric” measurements of Ne have been made by observing extreme ultra violet spectra in active solar regions (Widing, 1997). Solar Ar abundances have been best measured using solar energetic particles (Reames, 1998) but coronal spectroscopy has also been used (Young et al., 1997). Solar wind measurements of Kr and Xe are compromised by the fact that these elements are enriched in the solar wind and not representative of the solar composition. This enhancement is thought to be due to fractionation controlled by the first ionisation potential of the element (Geiss et al., 1994). The enhancement of Xe and Kr in the solar wind has varied over time; recorded in lunar regolith samples (Wieler and Baur, 1995; Wieler et al., 1996). Xe and Kr abundances are therefore best estimated from concentrations of isotopes close to Kr and Xe in the periodic table in CI chondrites (Wieler, 2002). Solar abundances for Ne, Ar, Kr and Xe are therefore imprecise and carry uncertainties of up to 20% (Wieler 2002).

One of the top priorities of the Genesis mission is to measure noble gases in the solar-wind that was collected and returned to Earth by the spacecraft. RELAX measurements of Xe in Genesis sample collectors indicate that major Xe isotopes are identical to those determined from solar-wind implanted in lunar regolith samples with very minor mass fractionation (Crowther and Gilmour, 2012). This points towards a depletion in heavy Xe isotopes in the Earth’s atmosphere. Ar, Kr and Xe measurements of Genesis samples by Vogel et al. (2011) reported Ar/Kr ratios that agreed well with solar-wind implanted in lunar regolith but reported Kr/Xe ratios of Genesis and lunar regolith samples indicate that the Kr/Xe ratio has increased by a factor of 2 over the last 1-2 Gyr. The reason for this is not known but the lower ionisation potential of Xe relative to Kr was offered as a cause.
1.3.2. In situ
In situ noble gases are produced within meteorites by nuclear reactions. As noble gases are scarce in solid materials these additions show up as isotopic anomalies. A major in situ component is radiogenic nuclides produced by radioactive decay. Noble gases produced in this way include $^{4}\text{He}$ from alpha decay of uranium and thorium, $^{22}\text{Ne}$ from beta decay of $^{22}\text{Na}$, $^{40}\text{Ar}$ from beta decay of $^{40}\text{K}$, $^{129}\text{Xe}$ from beta decay of $^{129}\text{I}$, and Kr and heavy Xe isotopes from fission of $^{244}\text{Pu}$ and $^{238}\text{U}$. $^{36}\text{Ar}$ from $^{36}\text{Cl}$ may also have been present in the early Solar System but this has proved difficult to find (Wasserburg et al., 2006).

The other major in situ component is cosmogenic noble gases produced by spallation reactions or neutron capture. Galactic cosmic rays (GCR) which originate outside the Solar System are composed of protons plus other highly charged particles and induce nuclear reactions in meteoritic material. The products of these reactions include alpha particles, neutrons and secondary protons which can cause further reactions which can occur deeper in the rock. The production rate of spallation nuclides in a sample depends on shielding conditions (the size of the original meteoroid and how deep the meteorite was buried in the meteoroid). Solar cosmic rays can also induce nuclear reactions. Solar cosmic rays have a much smaller penetration depth but their higher flux means they make a large contribution to spallation noble gases in the very upper layer of a meteoroid (1-2 cm) and the lunar surface (Podosek, 2003). Spallation nuclides can provide information on the conditions experienced after ejection from the precursor asteroid and the length of time before landing on Earth (cosmic ray exposure age). Again, it is because of the scarcity of noble gases that the products of spallation are able to be measured. Spallation noble gases include $^{3}\text{He}$, $^{21}\text{Ne}$ and, to lesser extents, Kr and Xe isotopes.

1.3.3. “Planetary”
The planetary component, found in meteorites, was named for its similarity to the elemental abundance pattern of the Earth’s atmosphere: both are enriched in the heavier noble gases and depleted in the lighter noble gases relative to the solar composition. However there are differences in elemental and isotopic ratios between terrestrial atmospheric composition and the planetary component. The terrestrial atmosphere is depleted in Xe with respect to planetary Xe, the atmospheric $^{20}\text{Ne}/^{22}\text{Ne}$ ratio is lower than the planetary ratio and terrestrial Kr isotopes ratios differ from planetary Kr.
This makes the term “planetary” misleading but it is still widely used.

Previously the planetary component was thought to be a fundamental reservoir taken from the solar nebula, as Ar and Kr isotopic compositions can be explained by fractionation of solar material. However the isotopic compositions of planetary Ne and Xe are hard to explain by an origination in the same nebula and subsequent processing. Planetary noble gases are now thought to be a mix of “exotic”, presolar components and a “local” planetary component. Gilmour (2010) showed that Q-Xe (the most dominant planetary component for the heavy noble gases) is consistent with fractionated solar wind mixed with varying amounts of exotic material.

Q-Xe was originally identified by experimentation: after acid leaching by HCl or HF the trapped noble gases are left in a carbonaceous residue, the oxidisable part of which contains the majority of the noble gases. This was named Q (Lewis et al., 1975). It is now possible to measure the Q gases directly (Wieler et al., 1991). As it dominates the bulk “planetary” component, the Q component shows a similar elemental pattern: enriched in the heavier noble gas elements. However, it shows a larger depletion in the lighter noble gas elements which means that Q makes a greater contribution to Kr and Xe than it does to He and Ne. The existence of He-Q and Ne-Q had in the past been doubted but a precise measurement of He-Q has been obtained by Busemann et al. (2000).

Q gases are not thought to have been created by thermal processes on primitive terrestrial bodies and are therefore thought to be a major primordial component. They are found in different types of meteorite (primitive and differentiated) which suggests that the Q component was widely distributed throughout the early Solar System (Busemann et al., 2000). The fact that there is little variation in abundance patterns means that they must have been distributed homogenously. They may therefore have a common origin, though it is not yet fully understood.

It is not well known how the gases are trapped or what the host of the Q gases is. This makes it difficult to establish a relationship between Q gases and the solar component. Ozima et al. (1998) proposed that Q-gases could be produced by Rayleigh distillation but there is no known astrophysical scenario that could produce this effect. Huss and
Alexander (1987) suggested that Q is actually a pre-solar component which obtained its gases in the molecular cloud the sun formed from. Key factors which may control the relationships between Q and other components are mass fractionation or ionisation efficiency (Ott, 2002), as Q is defined by its elemental and isotopic patterns which are enriched in heavy species and depleted in light species. The enrichment in Kr and Xe may even be due to addition of another component enriched in the heavier elements (Ott, 2002).

If the planetary noble gases are made up of many different components that are hosted in different materials it is surprising that the “planetary” noble gases are present in different extra-terrestrial materials in the same abundances. It can be explained if the carrier material of the exotic and local components that make up planetary noble gases were well mixed in the early Solar System and sampled in similar proportions during planetesimal formation.

1.3.4. Exotic
Exotic components are also found in carbonaceous phases of primitive terrestrial materials. These components carry isotope signatures that vary significantly from solar values suggesting they formed outside the Solar System. Their different signatures are the result of nucleosynthetic contributions to the local environment they formed in, rather than reflecting the average composition of the interstellar medium. It was while searching for the carriers of these anomalous noble gas components that presolar grains were discovered. These grains formed before our Solar System, survived the formation process and were preserved during the Solar System’s history.

1.4. The I-Xe chronometer

1.4.1. Development and early use.
Excesses of $^{129}$Xe in meteorites were first demonstrated by Reynolds (1960a, b). These excesses were thought to be due to the decay of the short-lived isotope iodine-129 to xenon-129 with a half-life of 16 Myr. To test this hypothesis, the relationship between excess $^{129}$Xe ($^{129}$Xe*) and iodine in individual samples had to be examined to see whether $^{129}$Xe* was found in iodine-bearing minerals. Jeffrey and Reynolds (1961) designed a method of measuring both iodine and $^{129}$Xe in a single analysis by first irradiating samples with thermal neutrons in a reactor to generate $^{128}$Xe from $^{127}$I by the following reactions:
The sample was then outgassed in several steps of increasing temperature rather than in a single step. Using this method Jeffrey and Reynolds (1961) showed a good correlation between the $^{129}$Xe and $^{128}$Xe released from the meteorite Abee (enstatite) at temperatures higher than ~700 °C. At lower temperatures a higher proportion of $^{128}$Xe was released which can be explained by loss of $^{129}$Xe over the long lifetime of the sample or surface contamination by terrestrial iodine. This neutron-irradiation and heat-step technique was later applied to the K-Ar chronometer by Merrihue and Turner (1966) and forms the basis of the Ar-Ar method.

The measured $^{129}$Xe and $^{128}$Xe in meteorite samples is assumed to consist of an iodine-derived component and the original xenon already trapped in the meteorite. Therefore to work out the $^{129}$Xe/$^{128}$Xe ratio of the iodogenic component the two components must be separated. Fish and Goles (1962) treated the data as follows where total $^{129}$Xe is made up of a fraction $a$ of iodine ($^{128}$Xe*) and a fraction $b$ of trapped xenon ($^{132}$Xe):

$$^{129}\text{Xe} = a^{128}\text{Xe}^* + b^{132}\text{Xe} \quad (\text{Eq. 1.3})$$

Normalising to $^{132}$Xe gives:

$$^{129}\text{Xe}/^{132}\text{Xe} = a (^{128}\text{Xe}^*/^{132}\text{Xe}) + b \quad (\text{Eq. 1.4})$$

This method is particularly elegant as, if the assumption that $^{129}$Xe consists only of trapped and iodogenic components is correct, when $^{129}$Xe/$^{132}$Xe is plotted against $^{128}$Xe*/$^{132}$Xe the data should define a straight line (Figure 1.4). Also the $^{129}$Xe/$^{132}$Xe ratio of the trapped component will be defined by the intercept $b$ and the slope of the line will define $^{129}$Xe*/$^{128}$Xe. This is related to the age of the sample as discussed in section 1.2 by:

$$\frac{^{129}\text{Xe}^*}{^{127}\text{I}} = \frac{^{129}\text{Xe}^*}{^{127}\text{I}}_{\text{STANDARD}} e^{-\lambda t} \quad (\text{Eq. 1.5})$$

Where $t$ is the time that passed between closure to xenon in the two samples and:

$$\lambda = \frac{\ln(2)}{t^{1/2}} \quad (\text{Eq. 1.6})$$

$t^{1/2} = 16$ Myr (the half-life of $^{129}$I). By rearranging equation 1.5, $t$ can be solved for each sample.
Fish and Goles applied their approach to Jeffrey and Reynolds’ (1961) measurements of Abee and found a good linear correlation in the high-temperature steps, confirming their hypothesis. All data interpreted as forming an isochron in the work include heat-steps released in sequence only.

Figure 1.4. Schematic showing the presentation of I-Xe data devised by Fish and Goles (1962). Low temperature data shows uncorrelated iodine consistent with loss of $^{129}$Xe*. High temperature data shows a correlation between $^{129}$Xe* and $^{127}$I consistent with $^{129}$Xe* derived from iodine. The gradient of this correlation defines the initial $^{129}$Xe/$^{127}$I of the sample. Where the correlation intersects with the y-axis defines the composition of the trapped component.

The correlation is representative of an isochron if it is produced by more than one phase with the same $^{129}$I/$^{127}$I. The same correlation could also be produced by one dominant source of $^{129}$Xe* and $^{128}$Xe* mixing with another iodine-free component. This mixing line may also define “an event” but it is not an isochron and so caution must be taken when attributing chronological significance to correlation lines.

Later work by Gilmour et al. (2009) proposed an alternative way of presenting the data which is adopted throughout this work. This alternative method is mathematically identical to the conventional isochron plot. Here $^{128}$Xe* (from iodine) and $^{132}$XeTRAPPED are normalised to total $^{129}$Xe. This is shown in Figure 1.5. The x-intercept defines the $^{129}$Xe/$^{127}$I ratio and the y-intercept defines the composition of the trapped component. Data ideally define an isochron between these components. The advantage of this method is that pure-iodine sites (that do not contain a measurable amount of trapped Xe) plot on the x-axis where they can be included in the isochron fit, rather than at infinity where they cannot.
Following the development of the I-Xe dating technique by Jeffrey and Reynolds (1961), the method was applied to several chondrites by Hohenberg et al. (1967), results from which showed fairly uniform $^{129}\text{I}/^{127}\text{I}$ ratios only 1 or 2 million years apart, inferred to date chondrule formation. This uniformity gave weight to the assumption that iodine isotopes were homogenously mixed in the early Solar System. Due to the short half-life of $^{129}\text{I}$, the system also produced precise results with errors in the order of 1 Myr, proving it to potentially be a very useful chronometer. Studies of magnetite in the primitive chondrites Orgueil (CI) and Murchison (CM) by Herzog et al. (1973) and Lewis and Anders (1975) showed the highest $^{129}\text{I}/^{127}\text{I}$ ratios measured at that time with only 0.21 Myr between the two meteorites. It was therefore assumed that this ratio dated nebular condensation and could be used as “time zero” for Solar System formation.

However, the use of the I-Xe system as a chronometer was questioned. Drozd and Podosek (1976) analysed the metamorphosed ordinary chondrite Arapahoe (L5) and found it to be 3 million years older than the Orgueil and Murchison magnetite. This meant that the ages reported by Herzog et al. (1973) and Lewis and Anders (1975) could not date nebular condensation. Further experiments on ordinary chondrites investigated the relationship between initial iodine ratios and extent of metamorphism (Podosek, 1976). Figure 1.5. Schematic showing the Manchester presentation of I-Xe data (Gilmour et al., 2009). Low temperature data shows uncorrelated iodine consistent with loss of $^{129}\text{Xe}^*$. High temperature define a line between the trapped composition (Y-axis intercept) and the initial $^{127}\text{I}/^{129}\text{Xe}^*$ of the sample (X-axis intercept). A York (1969) regression can be used to determine the isotopic values of the trapped and iodine components.
1970; Jordan, 1980; Shukolyukov et al., 1985) to test the I-Xe chronometer; more metamorphosed meteorites are expected to close to Xe-loss later than more primitive meteorites. However, no relationship was found between metamorphic grade and relative I-Xe ages and Shukolyukov et al. (1985) found a negative correlation. However the enstatite chondrites did show some correlation between relative I-Xe ages and metamorphic grade (Podosek, 1970).

So if the high-temperature correlations seen between $^{129}$Xe* and iodine were not chronologically significant how were they produced? Various explanations were mooted including isotopic heterogeneity of iodine isotopes in the solar nebular with Crabb et al. (1982) suggesting mixing of two iodine components (one carried in gas, one in grains). Jordan et al. (1980) also argued for isotopic heterogeneity and spatio-temporal variations during the accretion process. Clayton (1975) proposed that $^{129}$I was never present in the Solar System but that $^{129}$Xe* could have been trapped in grains formed in/around supernovae so that the correlations seen represent mixing between two reservoirs of different isotopic compositions. Huneke (1976) suggested that isochrons could be artefacts generated by diffusion, whereby $^{129}$Xe and iodine (and other systems such as K/Ar, Pu/Xe and U/Xe) have been redistributed to give the appearance of a co-genetic link. Kuroda (1976) questioned the interpretation of the Arapahoe isochron by Drozd and Podosek (1976) proposing it could be produced by mixing of different mixtures of trapped and radiogenic xenon. Drozd and Podosek (1977) discussed all these hypotheses along with other methods that could produce the observed correlations including shock, recoil effects and pure coincidence. They concluded that the conventional interpretation of the I-Xe system as a chronometer was most likely though the other arguments could not yet be completely dismissed. However the lack of correlation between I-Xe age and petrologic type, along with I-Xe ages of magnetite in Orgueil and Murchison appearing to be older than CAIs, cast doubt on the systems used as a chronometer.

1.4.2. Verification of the I-Xe system as a chronometer

The chronological significance of the relationship between iodine and $^{129}$Xe* was not fully recognised for some time and was aided by more work on the host phases of iodine. To test the I-Xe system as a chronometer it can be compared to another, established chronometer and knowledge of the phase being dated must be known in order to fairly compare closure time. In enstatite meteorites iodine is incorporated into the enstatite (Crabb and Anders, 1982; Kehm et al., 1994) which explains the
correlation seen between metamorphic grade and I-Xe age in this meteorite group only. However, the major hosts of iodine in other meteorites are predominantly secondary minerals such as apatite and feldspar (Brazzle et al., 1999) so I-Xe therefore often may date later processes, which explains the lack of correlation seen between I-Xe ages and metamorphic grade in ordinary chondrites. Nonetheless, though I-Xe ages may not reflect the petrologic type of the rock, $^{129}$Xe*/I bulk ratios do show a relationship with extent of processing in ordinary chondrites. $^{129}$Xe*/I bulk ratios in H and L chondrites are higher in type 3 meteorites than in type 6 (Gilmour, 2000 and references therein) indicating that the type 3 samples retained more of their $^{129}$Xe* due to less extended processing. Therefore, even if I-Xe ages do not reflect differences in metamorphic grade amongst meteorites, the I-Xe system may still be useful in comparing the extent of processing on parent bodies.

Brazzle et al. (1999) sought to verify the I-Xe chronometer by comparing relative intervals of I-Xe and Pb-Pb ages in the same suite of meteorites. Göpel et al. (1994) had previously dated phosphate separates from a suite of chondrites using the Pb-Pb system. Comparing chronometers requires analyses of one phase that contains elements of both systems in order to ensure the same closure time is being dated. The phosphate Cl-apatite was chosen as it is uranium-rich and iodine rich, unlike the phosphate merrillite which is halogen depleted (Nichols et al., 1994). I-Xe ages of Cl-apatites separates from a suite of meteorites were compared with the Pb-Pb ages. Feldspar separates were also analysed, as they contain a larger fraction of iodine than the phosphates in H and L chondrites. The isochrons of the feldspars agreed well with the phosphate isochrons allowing I-Xe formation intervals of feldspars to be compared with the Pb-Pb ages as well as enabling further testing of the concordance of the chronometers when the phosphates failed to produce an isochron. Results showed strong agreement between the Pb-Pb and I-Xe systems supporting the chronological significance of the I-Xe system.

1.4.3. Closure to xenon loss

In this work the I-Xe system will be used to constrain the timings of events that occurred in different meteorites. The I-Xe system dates the last time the system closed to xenon-loss (as discussed above this is often a secondary event as Xe is a volatile element and easily mobilised). Closure to Xe-loss occurs when the meteorite is cooled through the temperature at which Xe can be lost (from that particular site) and then not re-heated past this closure temperature.
Dodson (1973) defined the closure temperature of a geochronological system as “its temperature at the time corresponding to its apparent age”. It therefore follows that the closure age of a system is the time when it cools through the closure temperature (Figure 1.6). The closure temperature is dependent on the host mineral, the concentrations of parent and daughter isotopes and the cooling rate. Dodson proposed the following equation for calculating closure temperature providing that the cooling time is slow compared to the diffusion time:

$$T_c = \frac{R}{E \ln(A \alpha^2/\tau)}$$  

(Eq. 1.7)

Where $R$ is the gas constant, $E$ is the activation energy, $\tau$ is the time constant with which the diffusion coefficient $D$ diminishes, $\alpha$ is a characteristic diffusion size and $A$ is a numerical constant depending on the geometry and the decay constant of the parent.

For a phase such as a mineral grain, at high temperatures rapid diffusion occurs and radiogenic isotopes can escape as fast as they are formed, producing a state of equilibrium between concentrations within the grain and in its surroundings. The equilibrium between these concentrations is initially maintained as cooling begins. As cooling continues the interior of the grain will gradually build up a greater concentration of daughter isotopes compared to the surface of the grain as the rate of diffusion slows so diffusion occurs in two stages; the first between the grain interior and the grain boundary surface and the second from the grain boundary surface out of the sample. With further cooling the interior of the grain will “close” to loss of the radiogenic isotope followed by closure nearer to the surface of the grain until the entire grain is isolated from its surroundings. Therefore a closure temperature (and hence time) profile is produced from the centre to the edge of a mineral grain. The very surface of the grain may maintain diffusion at the lowest temperatures reached and never reach closure.

A secondary thermal event, such as metamorphism, can remobilise atoms and result in re–equilibration of parent/daughter isotope and/or movement between different sites and phases. The least retentive sites will be most affected by thermal events, with increasingly retentive sites being affected as the extent and duration of the event continues. If the site or phase then re–cools through the closure temperature the atoms will be fixed and $^{129}$Xe* will continue to accumulate in proportion to the iodine present,
giving a secondary age. If the cooling is slow the $^{129}$I may have decayed away completely before the closure temperature is reached. If the thermal event is late (i.e. after the lifetime of $^{129}$I) any $^{129}$Xe* may escape with no further additions from $^{129}$I.

During step–heating, gas is released from increasingly retentive crystal sites and mineral phases so in effect the events that occurred are being revealed in reverse chronological order. Low temperature data is likely to contain no $^{129}$Xe* though $^{127}$I may be seen. This is usually due to either the late loss of $^{129}$Xe from low temperature sites or terrestrial contamination of late iodine. The $^{129}$Xe*/$^{128}$Xe ratio of the sample tends to increase with increasing temperature of heat step. If the $^{129}$Xe* has remained in situ with its parent a constant $^{129}$Xe*/$^{128}$Xe ratio will emerge which can be interpreted as the age of the last closure to Xe in the high temperature sites. If a constant correlation between $^{129}$Xe* and $^{128}$Xe* is not seen then the age of the highest temperature release can only be said to be a minimum age. This interpretation involves attributing excess $^{129}$Xe to in situ decay of iodine rather than an inherited trapped component.

The interpretation proposed by Fish and Goles (1962) is valid for the evolution of the $^{132}$Xe/$^{129}$Xe ratio towards an iodogenic component by the decay of $^{129}$I in a closed system. However, redistribution of iodine and xenon can give an erroneous value for the trapped component where the $^{132}$Xe/$^{129}$Xe ratio is greater than the limits imposed by the $^{132}$Xe/$^{129}$Xe ratios of the solar wind and planetary components. The $^{129}$Xe/$^{132}$Xe ratio is not expected to vary significantly as decay of $^{129}$I cannot have contributed more than 0.1 ‰ to the Solar System reservoir of $^{129}$Xe (Gilmour et al., 2001) and there is no known process for increasing this ratio, therefore high trapped $^{132}$Xe/$^{129}$Xe values must be attributed to a localised event. Shock processes can redistribute iodine and xenon that originate in less retentive sites into more retentive sites (Hohenberg et al., 2000) and a trapped component (assumed to be iodine free) can evolve to a mixture of Xe and I. During step–heating the releases will contain I and Xe that originated in high and low temperature sites which are indistinguishable resulting in a “pseudotrapped” component. The addition of iodine (and therefore $^{128}$Xe* following irradiation) to the trapped component produces an overestimation in the amount of $^{128}$Xe*, shifting data points to the right and resulting in an erroneously high $^{129}$Xe/$^{132}$Xe value of the trapped Xe.
Figure 1.6. Explanation of the closure temperature of a geochronological system from Dodson (1973). \( D = \) daughter isotope, \( P = \) parent isotope \( T_c = \) closure temperature. At high temperatures the daughter isotopes escape as fast as they are formed but at low temperatures the escape rate is negligible and the daughter products accumulate. The closure age corresponds to extrapolating the low temperature section of the rate of accumulation curve back to \( D/P = 0 \).

1.4.4. Irradiation standards

Once the I-Xe system was known to be chronologically significant, inconsistencies in previous published results had to be addressed. The lack of correlation between petrologic type and I-Xe age has been attributed to the I-Xe system predominantly dating minor phases that record later events, as discussed above. However, other results such as the anomalous old ages of magnetite in Orgueil and Murchison which predated the formation of CAIs could not be explained as easily.

The experimental method designed by Jeffrey and Reynolds (1961) required the inclusion of a monitor during sample irradiations in order to calculate the conversion rate of \(^{127}\text{I} \) to \(^{128}\text{Xe}^* \) from a known amount of iodine. During the early I-Xe analyses iodine salts (most often KI) were used which were later discovered to have produced inaccurate results. There are two major problems associated with the use of KI salts:
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1. During irradiation of iodine, over 50% of the neutron-capture reactions occur by resonance capture of epithermal neutrons. KI salts contain much larger (x10⁹) concentrations of iodine than meteorites which means the capture cross section of iodine to ¹²₈Xe* is more likely to be reduced by the effects of self-shielding as there is only a small probability of energy transfer by scattering between captures.

2. The capture probability of each irradiation must be known and this is calculated from the absolute amount of ¹²₈Xe* produced from iodine. In order to measure this isotopic dilution mass spectrometry is used whereby a spike of known amount of atmospheric ¹²₈Xe is used to calculate the amount of excess ¹²₈Xe*. However, the amount of ¹²₈Xe* produced from the iodine salts during irradiation are very large (10⁻⁵ cm³ STP ¹²₈Xe* from a 1 mg sample). This requires a very large reservoir of the atmospheric spike and can result in incomplete mixing due to the higher pressures produced.

The self-shielding problem described above can result in high initial ¹²⁹I/¹²⁷I ratios producing anomalously older I-Xe ages. This effect caused the ancient magnetite ages reported by Herzog et al. (1973) and Lewis and Anders (1975). Murchison magnetite was then used an irradiation monitor by other researchers, including Crabb et al. (1982), resulting in I-Xe ages that were “too old” and adding to the distrust of the I-Xe chronometer. However, the issues associated with the use of KI as a monitor should not prove problematic as long as the iodine ratios quoted are only used to normalise initial iodine ratios to the same standard material in order to achieve relative I-Xe ages within the same set of samples, and not used to compare initial iodine ratios of samples from different irradiations.

Instead of iodine salts, meteorite samples are now used as irradiation standards. These have two major advantages. 1. They contain lower concentrations of iodine, avoiding the problem of self-shielding. 2. The relative ages of the sample and the standard can be directly determined using the method devised by Fish and Goles (1962) without needing to determine the ¹²⁷I neutron capture probability. This also enables I-Xe ages of samples irradiated separately to be compared if the same standard meteorite is used. However this method relies on the assumption that the ¹²⁹I/¹²⁷I ratio of the standard meteorite is reproducible.
Whole-rock from Bjurböle (L4) and enstatite from Shallowater (aubrite) have been most commonly used as an I-Xe irradiation standard. Hohenberg and Kennedy (1981) tested the reproducibility of Bjurböle by examining results from several irradiations. The results agreed well suggesting isotopic homogeneity for the initial iodine ratio of the bulk ratio. Gilmour et al. (2006) compared the reproducibility of Bjurböle and Shallowater enstatite and reported more variation amongst Bjurböle results compared to Shallowater enstatite. For this reason Shallowater enstatite has become the adopted I-Xe irradiation standard. Hohenberg and Kennedy (1981) also reported an initial iodine ratio for Bjurböle of 1.095 ± 0.29 x 10^{-4} calculated from KI standards. Analyses of Shallowater and Bjurböle from the same irradiation allowed calculation of an initial iodine ratio for Shallowater of 1.072 x10^{-4} (Brazzle et al., 1999).

1.4.5. Absolute ages
The I-Xe system is a relative chronometer as $^{129}$I is now extinct in the Solar System so the ratio of $^{129}$I/$^{127}$I at the present time cannot be known. This means the I-Xe system can record formation intervals between ancient samples not an absolute age. The Pb-Pb system is an absolute chronometer as the isotopes of uranium that decay to produce lead isotopes have long half-lives (of the order of 10^9 years). By anchoring a the I-Xe system to an absolute dating system such as the Pb-Pb system, absolute ages of the events dated by the I-Xe system can be known.

Prior to the work by Brazzle et al. (1999), Nichols et al. (1994) used the reported ages from Göpel et al. (1994) to anchor the I-Xe system to the already established, absolute Pb-Pb chronometer. Phosphates were used as they were known to be uranium and halogen bearing. The Acapulco meteorite was chosen as it contains large phosphates making hand separation of apatite and merrillite easier. It was this work that established that iodine is hosted in Cl-apatite but not merrillite phosphates. I-Xe ages of the Acapulco phosphates showed they formed simultaneously (within a few million years). This I-Xe age was therefore anchored to the Pb-Pb age of 4.557 ± 0.002 Gyr. Nichols et al. (1994) used Bjurböle as an irradiation standard and so an absolute age could also be attached to Bjurböle and via that, to Shallowater. The most recent evaluation of the absolute age of Shallowater was carried out by Gilmour et al. (2009) who employed outlier rejection to produce a more precise result than that of Gilmour et al. (2006) where more scatter than expected was observed between I-Xe formation intervals and absolute Pb-Pb ages. The absolute age reported by Gilmour et al. (2009) of 4562.3 ± 0.4 Myr is used throughout this work when quoting absolute I-Xe ages.
Recent measurements by Brennecka et al. (2010) of $^{238}\text{U}/^{235}\text{U}$ ratios in Allende CAIs found that the ratios ranged from $137.409 \pm 0.039$ to $137.885 \pm 0.009$ rather than appearing uniform as previously assumed. This implies that Pb-Pb ages may have been overestimated by up to 5 Myr depending on the respective sample’s $^{238}\text{U}/^{235}\text{U}$ ratio. However the $^{238}\text{U}/^{235}\text{U}$ variation from the established value of 137.88 is largest in a group of CAIs that have experienced the largest Cm/U fractionation; for other CAIs the discrepancy in age is <1Ma. This means the effect may be limited to within error for those samples that have not experienced large Cm/U fractionation.

1.4.6. Recent use

Since its verification the I-Xe chronometer has been used to investigate the chronology of a range of Solar System materials. Recent work in the University of Manchester Isotope Geochemistry and Cosmochemistry is summarised here:

Busfield et al. (2008) measured I-Xe ages of four enstatites and a eucrite and compared their results with reported $^{53}\text{Mn}$ and Pb-Pb analyses. They found that the three chronometers behaved coherently in the asteroid belt region of the early Solar System and so the $^{53}\text{Mn}$ and $^{129}\text{I}$ systems can be compared directly. They also observed that with increasing metamorphic grade the iodine concentration decreases suggesting iodine hosts decrease with metamorphism.

Crowther et al. (2009) investigated the cooling history of two lodranites; GRA 95209 and LEW 88280. The mean age of two metal grains and a silicate grain from GRA 95209 is $4.19 \pm 0.53$ Myr after Shallowater. The small spread in age of the different minerals implies a rapid cooling event possibly caused by excavation during an impact. The mean age of LEW 88280 of $10.4 \pm 2.3$ Myr after Shallowater and the larger grain size implies slower cooling, possibly due to deeper burial in the parent body.

Filtness (2009) determined I-Xe ages in Barwell (L6), Krymka (LL3) and Bishunpur (LL3) and showed that I-Xe ages in LL3 chondrites reflect resetting events caused by collisions and that I-Xe ages of igneous clasts in Barwell and Krymka indicate that differentiated parent bodies predated chondritic parent bodies. Also, a very early age (4568.37 Ma) of matrix material from ALH 77307 was recorded which agrees with nanodiamond ages from this meteorite suggesting that ALH 77307 records very early Solar System processing and contains presolar components.
1.5. Thesis Aim and Objectives

The main aim of this thesis is to continue the on-going study within this research group to better understand the movements of iodine and xenon in the early Solar System and constrain the timing of these events using the I-Xe chronometer. Analysis of the xenon system in unirradiated and irradiated samples will also allow further study of the behaviour of plutonium, uranium, barium and tellurium on early Solar System bodies via radiogenic and cosmogenic xenon isotopes.

In order to achieve this, samples have been chosen that reflect different extents of magmatic and thermal processing and address some of the problems discussed in section 1.2:

1. Determine whether the $^{129}$Xe* found in GRA 06129 records in-situ decay of $^{129}$I, and if so constrain the I-Xe chronology of the sample.
2. Determine whether the $^{129}$Xe* found in eucrites records in-situ decay of $^{129}$I, and if so constrain the origins of the anomalous eucrite meteorites.
3. Determine whether $^{129}$Xe* in Rumuruti chondrites records in situ decay of $^{129}$I, and if so place chronological constraints on the history of the R-chondrite parent body.

The following objectives were set:

- Carry out I-Xe analyses of irradiated samples of the unique crustal achondrite Graves Nunataks (GRA) 06129 in order to determine whether $^{129}$Xe* present in this rock was produced from in situ decay of $^{129}$I. GRA 06129 is a unique achondrite with chemistry and petrology that do not fit in any established group of meteorites. GRA 06129 therefore represents a previously unsampled method of asteroidal magmatism which is thought to have occurred on a more volatile-rich parent than that of the HED meteorites. Previous work by this research group indicated the presence of $^{129}$Xe* in unirradiated samples of GRA 06129.

- Compare the I-Xe system in anomalous and “nomalous” eucrites in order to constrain their origins. Eucrites are thought to have originated on the asteroid Vesta. They were produced by basaltic magmatism and therefore represent the first basalts to form in the Solar System. Some meteorites show very similar
mineral compositions and textures to eucrites but have anomalous oxygen isotope ratios. This suggests that either Vesta has retained some heterogeneity or that the anomalous eucrites originated on another large, differentiated asteroid that has since been destroyed. Comparison of the products of radiogenic isotopes in different meteorites can shed light on any differences in their thermal histories.

- Constrain the thermal history of the R-chondrite parent body using the I-Xe system. R-chondrites have experienced different extents of thermal processing reflected in their varying petrologic types. The thermal histories of asteroids are not well constrained and two models have been proposed: the onion-shell model and the rubble-pile model. In the onion-shell model the extent of metamorphism is related to the cooling rate, and therefore the age of the sample. The chronology of R-chondrites has not been well studied but excesses of $^{129}\text{Xe}^*$ have been observed suggesting that $^{129}\text{I}$ may have been present. Here the I-Xe system will be used to date R-chondrites of different petrologic types.

Isotopic measurements of xenon and I-Xe analyses have been conducted on samples of: GRA 06129, anomalous eucritic meteorites Bunburra Rockhole and Ibitira, “nomalous” eucrites Juvinas and Béréba, R3 material from R-chondrite NWA 6492 and R5 material from R-chondrites NWA 830 and NWA 3364. The results are not presented in the chronological order in which the experiments were conducted, but rather in an order that reflects the increasing complexity of the I-Xe system on the parent bodies of the samples studied.

Chapter 2 describes the experimental techniques used and the ways in which the data were treated. Chapter 3 compares I-Xe ages of 4 samples of different petrologic type from the R-chondrite NWA 6492 along with samples of R-chondrites NWA 830 and NWA 3364, both of which have experienced metamorphism to petrologic type 5. Chapter 4 presents the relationship between Xe, $^{129}\text{I}$ and $^{244}\text{Pu}$ in anomalous eucrites Bunburra Rockhole and Ibitira and “nomalous” eucrites Juvinas and Béréba. Chapter 5 presents the results of I-Xe analyses of irradiated samples of the unique crustal meteorite GRA 06129 to follow up previous work on unirradiated samples of GRA 06129 by this research group. Chapter 6 summarises the findings of this work and provides some suggestions for future work needed.
2.1. The RELAX mass spectrometer

Samples were analysed using RELAX (Refrigerator Enhanced Laser Analyser for Xenon); an ultra-sensitive resonance ionisation time–of–flight mass spectrometer for the isotopic analysis of xenon. The principles of its operation and recent development are documented in Gilmour et al. (1991, 1994) and Crowther et al. (2008). A schematic of RELAX is shown in figure 2.1.

2.1.1. Resonance ionisation and detection of xenon

Resonance ionisation mass spectrometry (RIMS) is a chemically selective technique whereby only the target species is ionised efficiently. This is achieved by tuning the wavelength of a laser (or in some cases lasers) to the energy needed for the target species to reach an excited state from the ground state. Other atoms and molecules may be ionised but only inefficiently. This technique produces high sensitivity analyses and reduces isobaric interferences.

Gas is extracted from the sample by heating with a continuous wave Nd:YAG laser with a wavelength of 1064 nm. Samples analysed as part of this study were step-heated, so that the sample was heated for one minute at each increasing temperature-step, achieved by using a series of increasing laser powers. After each step the gas was admitted to the ionising region and the xenon isotopes measured. To excite xenon using one photon, a wavelength of ~130 or ~147 nm is needed. The RELAX system employs a two–photon excitation scheme followed by one–photon ionisation as described by Chen et al. (1980). Two 249.6 nm photons excite the xenon from a ground state via a virtual state. The atoms or molecules are then ionised by laser light of the same wavelength.

A commercial Nd:YAG infrared pump laser is used to produce laser light with a wavelength of 1064 nm. The laser beam is then frequency tripled to produce 654.7 nm light which excites the dye (Coumarin 307, also known as Coumarin 503) in the dye laser. The dye laser has been tuned to produce light with a wavelength of 499.2 nm; twice the wavelength needed to excite xenon. Coumarin 307 has been chosen as it has the best conversion for that wavelength. The light is then frequency doubled in a β–barium borate (BBO) crystal to produce 249.6 nm light.
Figure 2.1. Schematic of the RELAX mass spectrometer.
Q-switching pulses the laser beam at 10 Hz, with a pulse length of 10 ns. The laser energy is usually tuned to produce around 2 mJ per pulse, however, >7 mJ can be produced at 246.9 nm. Laser pulses are focused through a quartz window, into the ion source with a 23 cm (at 250 nm) focal length lens resulting in a nominal diameter of 0.01 cm for the focused beam. This yields a power density >$10^9$ W cm$^{-1}$, which is needed for efficient ionisation using a two-photon excitation scheme. The ionising beam exits the ion source through a port positioned opposite the entrance window.

The ion source consists of a Wiley–McLaren (1955) ion source with a curved back plate. This contains two accelerating regions; a shallow electric field followed by a stronger electric field. The ratio of the two fields can be optimised in order to focus ions of a given isotope to arrive at the detector at the same time; this allows the mass resolution (defined in section 2.1.3) of the instrument to be optimised. This is achieved by adjusting the voltage of the middle plate, with the back plate remaining at a fixed voltage of 3 kV and the front plate at ground voltage.

An einzel lens collimates the beam of ions down a time–of–flight tube towards the detector. The time–of–flight mass spectrometer (TOFMS) allows ions of different masses to be detected separately as the velocity of an ion is proportional to its mass. The effects of acceleration of an ion species of mass ($m$) and charge ($q$) in a field of potential ($V$) can be described as:

$$E = qV = \frac{1}{2}mv^2$$  \hspace{1cm} (Eq. 2.1)

where $E$ is the energy of an ion and $v$ is its velocity.

As the ions leave the field they will therefore have a velocity of:

$$v = \sqrt{\frac{2qV}{m}}$$  \hspace{1cm} (Eq. 2.2)

The ions can then be separated according to their mass–to–charge ratio ($m/q$):

$$\frac{m}{q} = \left[ \frac{2V}{d^2} \right]^2$$  \hspace{1cm} (Eq. 2.3)
where \( t \) is the time taken by an ion to travel the length of the flight path \( (d) \). Lighter ions therefore have higher velocities and will arrive at the detector ahead of heavier ones. Xe isotopes can then be measured individually over a time period of \( \sim 1\mu s \).

The TOFMS also allows ions of all isotopes produced in each laser pulse to be detected in one measurement. This is important as the laser pulse energies, and hence ionisation efficiency can vary from pulse to pulse. The length of the TOF tube has been determined by a compromise between high mass resolution and high sensitivity. Mass resolution of the instrument can be increased by use of a long time–of–flight tube; however, prior to the introduction of the sample concentrator (section 2.1.2) the sensitivity was controlled by the ratio of the laser beam volume to the total volume of the spectrometer. A tube–length of 65 cm gave the mass resolution needed to resolve xenon isotopes and limited the volume of the spectrometer during the initial development of RELAX.

Ions are detected at the end of the flight–tube using a microchannel plate detector. Microchannel plates are used because the surfaces of the plates are flat. This means the time of arrival of the ion can be recorded precisely and improves mass resolution. Each microchannel acts as an electron multiplier: an ion entering the detector hits the wall of the channel and generates a secondary electron which starts a cascade of electrons that propagate through the channel and amplifies the original signal. The microchannels in the plates are angled at \( 13^\circ \) to the normal which has been shown to produce the optimum detection efficiency (Fraser, 2002).

After the light from the ionising laser passes through the ion source it is detected by a photodiode that triggers the data acquisition system. Flight times between 8.8 and 9.8 \( \mu s \) (the xenon spectrum) are monitored.

2.1.2. Sample concentrator

To increase the sensitivity of RELAX, a cryogenic sample concentrator (based on the atom buncher reported by Hurst et al. (1984) and Thonnard et al. (1984)) has been included within the ion source region of the spectrometer. Installation of the sample concentrator improved the sensitivity of the instrument by a factor greater than 100. Previously the detection limit of RELAX was \( 3 \times 10^4 \) atoms \(^{132}\text{Xe}\) (Gilmour et al., 1991), now it is around \( \sim 1 \times 10^3 \) atoms \(^{132}\text{Xe}\) and only limited by fluctuations in the instrumental blank.
A localised “cold spot” in the ion source is created by way of a “cold finger” (a long copper rod with an indium tip) that remains in contact with a thin steel plate located on the back plate within the spectrometer. The cold finger is cooled to a constant temperature using a commercial cryogenerator. The sample is admitted to the spectrometer and condenses on the cold spot from where it is re–released using an infrared (IR) laser and ionised. The resulting plume of atoms released from the cold–spot has an elevated gas concentration. The ionising laser then passes through the plume of gas.

The sample is released from the cold spot every 0.1s which corresponds to a duty cycle of 10 Hz. Between each laser pulse (i.e. over 0.1 s) around 1% of the sample builds up on the cold spot. After the first condensed fraction is released by the IR laser and removed by ionisation, 1% of the remaining sample is then condensed and re–released. This process repeats continuously throughout the analysis.

The region where the sample condenses must not exceed the area that is reached by the IR laser or the sample will not be released. In order to achieve this, the cold spot must be surrounded by a steep thermal gradient (~100 K/mm) which requires a heat–current to flow from the cold spot to a heat sink.

2.1.3. Mass resolution
Mass resolution ($R$) is a measure of how well the instrument can distinguish between different masses and is defined by the International Union of Pure and Applied Chemistry (IUPAC) as:

$$R = \frac{M}{\Delta M}$$  \hspace{1cm} (Eq. 2.4)

where $M$ is the mass of the ion of interest and $\Delta M$ is the width of the peak at a specified fraction of the maximum peak height. $\Delta M$ is also known as the resolving power. The better separated the peaks, the higher the $R$ value. The width at 50% of the peak height, also known as “full width at half maximum” (FWHM), is most often used for $\Delta M$. The FWHM of RELAX is ~5 ns (Crowther et al., 2008) which gives an $R$ value of ~900 as the flight time for xenon is ~9 µs.
2.1.4. Air calibrations
Measurements of known amounts of terrestrial air allow the instrument discrimination due to mass fractionation effects to be corrected for and also allow the sensitivity of the instrument to be monitored and used to calculate absolute amount of xenon. These air calibration measurements are typically carried out after every 3 or 4 sample analyses.

Air calibrations are carried out by expanding an aliquot from the calibration bottle (primary reservoir) and releasing fractions of known volume for analysis. Two primary reservoirs are available (PR1 and PR2), aliquots of which (SR1 and SR2) give different concentrations of atmospheric xenon. Usually, the reservoir which will produce xenon amounts (signal heights) most similar to the sample size is used. Analyses by Crowther et al. (2008) indicates that the PR1 aliquot consists of $1.48 \times 10^7$ atoms of atmospheric $^{132}$Xe and the PR2 consists of $6.1 \times 10^8$ atoms of atmospheric $^{132}$Xe. A schematic of the air calibration system is shown in Figure 2.2.

Air calibrations show deviations corresponding to mass discrimination (Figure 2.3) which is dependent on the operating conditions. It has been shown that these effects
remain constant as long as operating conditions remain fixed: the reproducibility of RELAX data has been demonstrated by repeated measurements of air calibrations over several days with standard deviations of repeated measurements agreeing with predicted errors (Crowther et al., 2008). Therefore an average of all air calibrations carried out during a set of sample analyses can be reliably used to correct for mass discrimination in sample measurements as long as operating conditions have not been changed.

\[ \text{Mean of 83 analyses} \]

**Figure 2.3.** Mean delta values for 83 separate analyses air calibrations compared to terrestrial air. A blank correction has been made. \(^{124}\text{Xe}\) and \(^{126}\text{Xe}\) are more affected by variations in the baseline as they are less abundant. Low \(^{128}\text{Xe}\) ratios are due to the correction made for the large interference at mass 128 (See Figure 2.7). Low \(^{130}\text{Xe}\) ratios may be due to disturbance of the baseline by \(^{129}\text{Xe}\).

A correction for mass discrimination (Eq. 2.5) is calculated for each isotope \((Z)\) by dividing the measured isotopic ratio by the isotopic ratio of the terrestrial atmosphere, values of which are taken from Wieler (2002) and given in Table 1. The measured sample isotope ratios are multiplied by this value to correct for mass discrimination.
The errors (\(\Delta\)) associated with the correction (\(C\)) for each isotope ratio (\(Z/\text{REF}\)) are calculated using equation 2.6:

\[
\Delta C = C \sqrt{\left(\frac{\Delta (Z/\text{REF})}{Z/\text{REF}}\right)_{\text{Actual}}^2 + \left(\frac{\Delta (Z/\text{REF})}{Z/\text{REF}}\right)_{\text{Measured}}^2} 
\]

(Eq. 2.6)

**Table 2.1.** Isotopic composition of xenon in the terrestrial atmosphere (Wieler, 2002). Isotopes are referenced to \(^{130}\text{Xe}\).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{124}\text{Xe})</td>
<td>2.337</td>
</tr>
<tr>
<td>(^{126}\text{Xe})</td>
<td>2.18</td>
</tr>
<tr>
<td>(^{128}\text{Xe})</td>
<td>47.15</td>
</tr>
<tr>
<td>(^{129}\text{Xe})</td>
<td>649.6</td>
</tr>
<tr>
<td>(^{130}\text{Xe})</td>
<td>100</td>
</tr>
<tr>
<td>(^{131}\text{Xe})</td>
<td>521.3</td>
</tr>
<tr>
<td>(^{132}\text{Xe})</td>
<td>660.7</td>
</tr>
<tr>
<td>(^{134}\text{Xe})</td>
<td>256.3</td>
</tr>
<tr>
<td>(^{136}\text{Xe})</td>
<td>217.6</td>
</tr>
</tbody>
</table>

Knowledge of the number of atoms admitted to the instrument in an air calibration allows the sensitivity of the instrument to be monitored. The sensitivity (\(S\)) is calculated from the ratio of atoms admitted (\(A\)) to the absolute peak height of the signal (\(P\)) (equation 2.7). An average sensitivity for a set of measurements can then be applied to sample measurements to calculate absolute amounts of atoms of each isotope.

\[
S = \frac{A}{P} 
\]

(Eq. 2.7)

The variation in the sensitivity of the instrument is the major source of error on the absolute amount of xenon released (and therefore on any concentrations of xenon calculated). Absolute amounts of gas are calculated by multiplying the peak height of each isotope by the average sensitivity of a set of air calibrations and this sensitivity varies due to fluctuations in ionisation efficiency. During this work the standard deviation on the sensitivity of the instrument for each set of analyses was \(~15\%). Concentrations of atoms for each heat-step therefore have an error of \(~15\%\).

2.1.5. Data acquisition and reduction

Data from the detector is sampled by an Acqiris digitizer card every 1 ns. During routine sample analyses 100 mass spectra from 100 laser pulses are stored by the
digitizer and then transferred to the PC as a block of data every 10 s. Each set of 100 spectra is summed to give a single mass spectrum of the integrated signal at each isotope over 10 s. Data acquisition is carried out for 300 s which results in 30 spectra.

The data are reduced using a Microsoft Excel program written by J. D. Gilmour. The software sums the area under each peak and subtracts a mean value for the baseline. Isotope ratios are then calculated by reference to the chosen isotope and extrapolated back to $t_0$, the time the sample was admitted to the spectrometer. Ratios are extrapolated rather than peak heights to avoid the effect of variations in pulse–to–pulse sensitivities. Before this process, the user may check the peak positions for all isotopes in all thirty spectra and make any adjustments to the baseline (which is calculated from regions either side of the peak) if needed. If the baseline of a peak is affected by the signal from the preceding peak a correction can be made based on the signal height of the preceding peak.

The error on the peak area ($E$) for a peak summed over ($m$) points is calculated using the following equation (Crowther et al., 2008):

$$ E^2 = m\Delta b^2 + c^2 S $$  \hspace{1cm} (Eq. 2.8)

Where $\Delta b$ is the standard deviation of the signal height in the region where the baseline is determined, $S$ is the total signal and $c$ is a constant reflecting the performance of the channel plates. The error of the ratio is then determined from the errors on the two peak areas. The isotope ratio at $t_0$ is determined using a linear least square fit from the 30 measured ratios. The constant ($c$) is adjusted until the $\chi^2$ value of the fit is equal to the number of degrees of freedom. The error on the intercept is then calculated.

The data can then be corrected by reference to the air calibrations and procedural blanks as discussed earlier. The number of atoms of the reference isotope is calculated from the sensitivity (equation 2.7), the average blank is subtracted for each isotope and the correction for mass discrimination (equation 2.5) is applied. This raw data for each of the samples analysed is given in appendices I-IV on the additional CD.

Some irradiated samples measured as part of this study produced very large abundances of $^{128}$Xe (Chapter 5) and $^{131}$Xe (Chapter 4). In some cases these peaks were $> 100$ times
bigger than the reference isotope (\(^{129}\text{Xe}\)). These large abundances were not seen in
unirradiated samples and so have been attributed to neutron–capture on iodine and
barium respectively. Large releases of one isotope can compromise the precision of
other isotopes ratios. After the sample is admitted to the spectrometer and immediately
before data collection starts the scale used by digitizer data collector is chosen based on
the signal peak height. The lowest 1–2 bits are subject to noise. Therefore if a larger
scale if chosen due to a high signal from only one isotope, the measurements of the
other, less abundant isotopes are more affected by noise.

2.1.6. Instrument sensitivity
The sensitivity of RELAX is controlled by the following:

(1) The temperature of the cold–spot. If the temperature is too low the thermal gradient
surrounding the cold spot decreases, allowing the sample to be trapped on areas not
illuminated by the IR laser. This “trapping” then becomes the dominant cause of signal
decrease, rather than removal of Xe by ionisation. If the temperature is too high then the
rate at which xenon condenses on the cold spot is reduced which reduces the proportion
of the sample that is ionised and decreases the sensitivity of the instrument. An
optimum is needed whereby the cold–spot is cold enough for xenon to condense but not
so cold that the sample remains trapped.

If the cold spot is not at the optimum temperature, this can be seen in the pump–out
curves of the sample. A pump–out curve shows the initial signal height and the rate at
which the sample is removed from the system. Figure 2.4 considers signal intensity for
the same number of atoms at different temperatures and shows how the shape of the
pump–out curve varies with temperature of the cold finger. The temperature of the cold
finger is monitored using a thermocouple mounted on the cold finger. In Figure 2.4 the
optimum temperature is 105 K as can be seen by the high signal intensity and the
efficient removal of the sample over time by ionisation. At 90 K the cold spot is too
cold as can be seen in the low signal intensity and the inefficient removal of the sample.
This is due to the sample “trapping” on the region outside the area heated by the IR
laser and not being released. At 190 K the cold spot is not cold enough. Here the
ionisation process is removing the xenon but a smaller fraction of the sample is being
concentrated into the ionisation region resulting in low initial signal intensity.
Figure 2.4. The temperature of the cold–finger controls the sensitivity of the instrument as can be seen in the pump–out curves shown here (data collected by S. A. Crowther). The same numbers of atoms of Xe were used in each case considered. The optimum temperature (white diamonds) shows the largest signal intensity and most efficient removal of the sample from the spectrometer by ionisation. If the temperature is not cold enough (black squares) a smaller fraction of xenon condenses on the cold finger resulting in a lower signal height and lower rate of signal decrease. If the temperature is too low (grey triangles) xenon condenses on regions not illuminated by the IR laser and this becomes the dominant cause of signal decrease.

(2) The length of delay between firing the IR laser and firing the ionising laser. If the ionising laser is fired too soon or too late then the optimum concentration of atoms will either have not reached the ionising region or will have already passed through it. This decrease in ionisation efficiency will result in decreased signal intensity. Figure 2.5 again considers signal intensity for the same number of atoms at various delay lengths and shows that the initial signal intensity is dependent on the length of the delay, with a peak initial signal height reached at a delay of 0.5 µs. In turn the initial signal intensity shows a linear relationship with the speed at which the sample is removed from the spectrometer (pump–out speed). This shows that ionisation is the dominant process in removing xenon from the spectrometer.
Figure 2.5. (reproduced from Crowther et al., 2008). (a) The initial signal height is dependent on the length of delay between firing the IR laser (which releases the sample from the cold-spot) and the ionising laser. The peak initial signal intensity is reached when the delay is 0.5 µs. (b) The signal decay (the rate at which xenon is removed from the spectrometer) shows a linear relationship with initial signal intensity demonstrating that ionisation is the dominant process of removing xenon from the spectrometer. The same numbers of atoms of xenon were used in each case considered.

(3) **Laser repetition rate?** In theory a higher laser repetition rate produces a better duty cycle (the fraction of the time between detections that the system is active). However, since the installation of the sample concentrator, the duty cycle is effectively controlled by the rate at which the sample can condense onto the cold spot which has been found to be linear with time for short periods compared to the return time to the cold spot (Gilmour et al., 1994). This means that if the duty cycle was increased, though the dead–time would decrease (with more laser pulses fired over the same amount of time) the length of time available for xenon to build up on the cold spot would also decrease, resulting in ionisation of a smaller fraction of the sample with each pulse. This would therefore produce no increase in sensitivity.

(4) **Instrumental blank.** The variation in the blank determines the detection limit of RELAX. Though RIMS is a selective technique, the high power density of the laser light required can produce ions with the same mass as xenon isotopes and hydrocarbons are seen at masses 12, 24, 36 and 48. The hydrocarbon peaks that fall outside the xenon
spectrum are monitored daily. The background of the xenon spectrum is measured periodically throughout analyses (typically 3 or 4 times a day) by running a procedural blank, whereby the procedure for measuring a sample is followed but a sample is not admitted to the system. Figure 2.6 shows the spectrum of a typical blank acquired during this work. During the parts of this work covered in Chapter 3 and Chapter 5, the blank at the region covered by the $^{128}\text{Xe}$ peak has been much more of a problem than at the regions of the other Xe peaks and is higher than previously seen, equivalent to ~2000 atoms $^{128}\text{Xe}$ with a standard deviation of 1000 atoms. The exact reason for this large interference is not known, although gas coming off one of the ion pumps has been suggested as a source. In this work a correction has been made to the measured $^{128}\text{Xe}$ peak by subtracting the area under the interfering peak that falls within the $^{128}\text{Xe}$ peak boundary (Figure 2.7).

(5) **Sample size.** The sensitivity of the microchannel plates can be reduced by large sample sizes. Large numbers of isotopes (such as $^{128}\text{Xe}$ or $^{129}\text{Xe}$) can discharge a large fraction of the microchannels. The time taken for the channel to recharge is 0.1 ms (the “dead–time”) – much longer than the flight–time of xenon of ~9 µs – therefore the sensitivity of the detector would be reduced for later arrivals of heavier xenon isotopes (e.g. $^{134}\text{Xe}$, $^{136}\text{Xe}$) introducing a mass discrimination effect in favour of the lighter ions.

The mass resolution of the instrument can also be compromised by large samples sizes due to space charge effects. Increasing the number of ions in the spectrometer increases the probability of interactions. This can result in ions departing from the direct path down the flight–tube towards the detector. This results in greater spread in the arrival time of ions of one isotope of xenon. This increases the width of the peak, decreasing the mass resolution.
Figure 2.6. A spectrum for a typical instrumental blank measured during this work. The interference at the $^{128}$Xe is much larger than for other xenon isotopes, ~2000 atoms in this case.

Figure 2.7. Demonstration of method used to correct the $^{128}$Xe* peak for the interference shown in Figure 2.6. The region of the interference that falls within the boundaries of the $^{128}$Xe peak is subtracted from the integrated area under the $^{128}$Xe peak.
2.1.7. Operating Procedure

RELAX must be turned on ~1 hour before sample analysis to allow the cold finger to cool to the required temperature. During this time the dye laser is also turned on to allow the doubling crystal to stabilise and the IR laser is turned on to prevent build–up on the cold spot. Once the lasers have warmed up and the cold finger has reached equilibrium at the required temperature the instrument is tuned to optimise the xenon signal. This is achieved by:

1) Optimising the power output of the dye laser to ~2 mJ.

2) Adjusting the lens the ionising laser passes through before it enters the spectrometer to optimise the saturation region and ensure the beam is not hitting the ion source.

3) Optimising the delay between firing the IR laser and the ionising laser.

The operational procedure of RELAX varies depending on the nature of the sample. For samples reported in this work the following procedure was used. Samples are loaded into a holder positioned underneath a second continuous–wave infra–red (IR) laser beam which is used to heat the sample. The beam is aligned over the hole that contains the sample and focused to be approximately the same size as the hole in the sample holder and larger than the sample to ensure the whole sample is heated. The sample line is then isolated from the mass spectrometer and the IR laser is switched on for one minute to heat the sample. During this time the sample gases released are exposed to a getter to remove active gases before being admitted into the mass spectrometer. The sample is exposed to the getter for a further minute after the IR laser is switched off. The actual temperature the sample is heated at is not available as it is dependent on the size of the beam diameter and the way the sample couples with the laser light.

During step heating the power of the laser is increased incrementally between repeated heating and analysis of the sample. The size of the increments is gauged to produce similar amounts of gas at each heating-step. Heat–steps that release large amounts of gas are often repeated to ensure all gas has been released at that temperature. If gas is still released from the sample when the maximum heating power has been reached the beam is focussed tighter to increase the power density (though the beam diameter must be large enough to cover the sample) and heating begins again, starting at a lower power which is gradually increased.
After exposure to the getter, the sample gas is admitted to the spectrometer where ~1% of the gas condenses onto the cold spot over 0.1s (the frequency of the laser pulses). The condensed sample is then released, ionised and detected and another 1% condenses, is released, ionised and detected. This continues for 5 minutes. After this time, any remaining gas is pumped away by ion pumps.

Air calibrations are run throughout the day after blocks of 3 or 4 sample analyses as previously discussed. Procedural blanks are carried out by isolating the sample line from the pumps for an amount of time equal to heating and exposure to the getter of the sample. The valve to the mass spectrometer is then opened and the normal data acquisition procedure is used. Procedural blanks are run less frequently than air calibrations (typically 3 or 4 times a day) though if samples release especially large quantities of gas the blanks are run more often to make sure that the background levels have not increased significantly.

2.1.8. Xenon components
The Xe contained in the sample is made up of several components and these differ in unirradiated and irradiated samples due to neutron–capture reactions. The contributing components to each isotope of xenon for the samples used in this work are shown in Table 2.2.

Xenon released from samples is usually a mix of spallation–Xe, fission–Xe and a “trapped” component. This trapped component is most likely to be composed of the primitive planetary component (Q–Xe), terrestrial atmospheric–Xe that has been adsorbed onto the sample, solar–wind, or a combination of some or all of these. The isotopic compositions of these components are given in Table 2.3.

Spontaneous fission of $^{238}\text{U}$ and $^{244}\text{Pu}$ and neutron–induced fission of $^{235}\text{U}$ (predominantly seen in irradiated samples) produce the heavy isotopes of xenon ($^{131–136}\text{Xe}$). Corrections for the fission component must be made before the trapped and iodine–derived xenon components can be determined. It is especially important to remove fission produced $^{132}\text{Xe}$ as this isotope is most often used as the normalising isotope. $^{130}\text{Xe}$ is not produced by fission so can also be used as a reference isotope. However, it is not usually as abundant as $^{132}\text{Xe}$ and so can produce less precise isotope ratios and Figure 2.7 showed that the baseline around the $^{130}\text{Xe}$ peak may be disturbed by $^{129}\text{Xe}$. For these reasons $^{132}\text{Xe}$ is used as a reference isotope where possible in
unirradiated samples. In irradiated samples $^{129}\text{Xe}$ is used as the reference isotope to reduce errors when plotting $^{128}\text{Xe}/^{129}\text{Xe}$ and $^{132}\text{Xe}/^{129}\text{Xe}$ ratios to construct isochrons.

Table 2.2. Contributing components to each isotope of xenon in samples studied as part of this work († indicates predominant in irradiated samples; ‡ indicates the reaction may also contribute to the spallation component via secondary neutron reactions in unirradiated samples). Neutron capture on $^{135}\text{Xe}$ producing $^{136}\text{Xe}$ occurs during neutron-induced fission of $^{235}\text{U}$.

<table>
<thead>
<tr>
<th>Component</th>
<th>$^{124}\text{Xe}$</th>
<th>$^{126}\text{Xe}$</th>
<th>$^{128}\text{Xe}$</th>
<th>$^{129}\text{Xe}$</th>
<th>$^{130}\text{Xe}$</th>
<th>$^{131}\text{Xe}$</th>
<th>$^{132}\text{Xe}$</th>
<th>$^{134}\text{Xe}$</th>
<th>$^{136}\text{Xe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trapped (Q–Xe/terrestrial atmosphere/solar wind)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Spallation reactions on barium and rare earth elements</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Spontaneous fission of $^{244}\text{Pu}$ or $^{238}\text{U}$</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Neutron induced fission of $^{235}\text{U}$†‡</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Neutron capture on $^{135}\text{Xe}$†</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron capture on barium†‡</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron capture on $^{127}\text{I}$†‡</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Excess $^{129}\text{Xe}$*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3. Isotopic compositions of Xe in terrestrial atmosphere, solar–wind (Wieler, 2002 and references therein) and Q–Xe (Busemann et al., 2000). The error on the last digit(s) is given in parentheses.

<table>
<thead>
<tr>
<th>Xe</th>
<th>$^{124}\text{Xe}$</th>
<th>$^{126}\text{Xe}$</th>
<th>$^{128}\text{Xe}$</th>
<th>$^{129}\text{Xe}$</th>
<th>$^{130}\text{Xe}$</th>
<th>$^{131}\text{Xe}$</th>
<th>$^{132}\text{Xe}$</th>
<th>$^{134}\text{Xe}$</th>
<th>$^{136}\text{Xe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial atm.</td>
<td>0.00354</td>
<td>0.0033</td>
<td>0.0714</td>
<td>0.983</td>
<td>0.151</td>
<td>0.789</td>
<td>0.388</td>
<td>0.329</td>
<td></td>
</tr>
<tr>
<td>Solar–wind</td>
<td>0.00488</td>
<td>(116)</td>
<td>0.00423</td>
<td>(14)</td>
<td>0.0848</td>
<td>(1)</td>
<td>1.04</td>
<td>(1)</td>
<td>0.166</td>
</tr>
<tr>
<td>Q</td>
<td>0.455</td>
<td>(2)</td>
<td>0.4057</td>
<td>(18)</td>
<td>8.22</td>
<td>(2)</td>
<td>1.042</td>
<td>(2)</td>
<td>0.1619</td>
</tr>
</tbody>
</table>
Table 2.4. Composition of xenon isotopes from spontaneous (sp) fission of $^{238}$U, $^{244}$Pu and neutron–induced fission (nf) of $^{235}$U from Ozima and Podosek (1983). Neutron–induced fission of $^{235}$U can also produce $^{136}$Xe via neutron–capture on $^{135}$Xe.

<table>
<thead>
<tr>
<th>Fission source</th>
<th>$^{131}$Xe</th>
<th>$^{132}$Xe</th>
<th>$^{134}$Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U (sp)</td>
<td>0.076 ± 0.003</td>
<td>0.595 ± 0.017</td>
<td>0.832 ± 0.012</td>
</tr>
<tr>
<td>$^{244}$Pu (sp)</td>
<td>0.246 ± 0.020</td>
<td>0.885 ± 0.030</td>
<td>0.939 ± 0.008</td>
</tr>
<tr>
<td>$^{235}$U (nf)</td>
<td>0.453 ± 0.013</td>
<td>0.677 ± 0.020</td>
<td>1.246 ± 0.036</td>
</tr>
</tbody>
</table>

3–isotope plots are used to determine which of the fission end–members to correct for: $^{244}$Pu, $^{238}$U, or $^{235}$U. Xe isotopic ratios for these end–members are given by Ozima and Podosek (1983) and listed in Table 2.4. To correct the total measured $^{132}$Xe for a fission contribution the fraction of the measured $^{132}$Xe that is derived from the “planetary” component must be determined. In a two component system (planetary + fission) this is achieved by reference to $^{134}$Xe using equation 2.9 (a version of the “lever rule”), where $p$ represents ‘planetary’, $f$ represents ‘fission’ and $m$ represents ‘measured’. $^{134}$Xe is used rather than $^{136}$Xe as neutron irradiation can result in the overproduction of $^{136}$Xe by neutron capture on the $^{135}$Xe produced during fission of $^{235}$U. In this work fission corrections are applied to data that shows $^{134}$Xe/$^{132}$Xe ratios two standard deviations higher than the trapped component. The methods used are discussed in each chapter.

$$\frac{^{132}Xe_p}{^{132}Xe_p + ^{132}Xe_f} = \left[\frac{^{134}Xe}{^{132}Xe}_m \left(\frac{^{134}Xe}{^{132}Xe}ight)_f\right]$$

(Eq. 2.9)

The calculated $^{132}Xe_p$ value is used to calculate excesses in Xe isotopes over an assumed trapped component. Excess $^{128}$Xe* can then be converted to $^{127}$I using the conversion factor calculated from the Shallowater irradiation monitor (see section 2.2). By using the irradiation fluence (calculated from the $^{129}$Xe*/$^{127}$I ratio of the irradiation monitor) and known thermal neutron cross sections, uranium and/or plutonium concentrations and Ba concentrations can be calculated from $^{134}$Xe and $^{131}$Xe abundances.
Exposure of meteorites to cosmic rays can produce all isotopes of xenon (except \(^{136}\text{Xe}\)) via spallation and secondary neutron reactions. Secondary neutron reactions are dependent on the depth of the sample within the meteorite during transit to Earth; its “shielding”. Compositions of spallation–Xe used in this work are from Hohenberg et al. (1981) and shown in table 2.5. If spallation xenon is present along with fission xenon this complicates the determination of the trapped content of the normalising element as all xenon isotopes (except \(^{136}\text{Xe}\)) contain more than two components (trapped, fission, spallation, and neutron–capture on iodine/barium in some isotopes). In this case matrix algebra has been used to solve three–component mixing, choosing isotopes composed only of trapped, fission and spallation. This method is more difficult in irradiated samples where many isotopes contain more components due to neutron–induced reactions (Table 2.2). The matrix algebra used is described in detail in Chapter 5.

**Table 2.5.** Spallation compositions for pure–Ba, pure REE and a chondritic ratio of Ba/REE (the composition of \(^{129}\text{Xe}\) is an adopted value) from Hohenberg et al. (1981). The error on the last two digits is shown in parentheses.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(^{124}\text{Xe})</th>
<th>(^{128}\text{Xe})</th>
<th>(^{129}\text{Xe})</th>
<th>(^{130}\text{Xe})</th>
<th>(^{131}\text{Xe})</th>
<th>(^{132}\text{Xe})</th>
<th>(^{134}\text{Xe})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.5441</td>
<td>1.621</td>
<td>1.6</td>
<td>1.248</td>
<td>4.36</td>
<td>1.053</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>(51)</td>
<td>(19)</td>
<td>(4)</td>
<td>(31)</td>
<td>(11)</td>
<td>(33)</td>
<td>(14)</td>
</tr>
<tr>
<td>REE</td>
<td>0.770</td>
<td>1.22</td>
<td>1.6</td>
<td>0.04</td>
<td>1.64</td>
<td>0.06</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>(15)</td>
<td>(03)</td>
<td>(4)</td>
<td>(09)</td>
<td>(24)</td>
<td>(07)</td>
<td>–</td>
</tr>
<tr>
<td>Chondritic</td>
<td>0.595</td>
<td>1.52</td>
<td>1.6</td>
<td>0.98</td>
<td>3.77</td>
<td>0.83</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>(10)</td>
<td>(10)</td>
<td>(4)</td>
<td>(06)</td>
<td>(16)</td>
<td>(06)</td>
<td>(15)</td>
</tr>
</tbody>
</table>

Excesses of xenon isotopes produced from sources such as uranium, plutonium, barium and iodine via fission and neutron–capture reactions have been used in this work to calculate concentrations of those elements in the samples.

For calculating concentrations of barium or tellurium the following method is used:

The conversion factor for neutron–capture on \(^{130}\text{Ba}/^{130}\text{Te} \rightarrow ^{131}\text{Xe}\) is calculated by multiplying the cross–section of thermal neutron capture (in cm\(^{-2}\)) by the thermal fluence of the irradiation. The cross–sections used were obtained from the Korea Atomic Energy Research Institute (2000). The cross section is then multiplied by the number of atoms of excess \(^{131}\text{Xe}*\) in the sample to give the number atoms of \(^{130}\text{Ba} or
$^{130}\text{Te}$. This is then combined with the natural atomic abundance of $^{130}\text{Ba}$ or $^{130}\text{Te}$ (Korea Atomic Energy Research Institute, 2000) to give the total number of atoms of barium or tellurium in the sample. The mass of this total is then calculated and ratioed to the mass of the sample to give the concentration.

To calculate concentrations of plutonium when the sample formed the following method is used:

The percentage yield of $^{136}\text{Xe}$ from spontaneous fission of $^{244}\text{Pu}$ is 5.6 (Ozima and Podosek, 1983). This is multiplied by the number of excess atoms of $^{136}\text{Xe}^*$ in the sample to give the number of “fissions” of $^{244}\text{Pu}$ needed to give that amount of excess $^{136}\text{Xe}$. The number of “fissions” are then divided by the branching ratio for spontaneous fission of $^{244}\text{Pu}$ which is given as $1.25 \times 10^{-3}$ (Ozima and Podosek, 1983) to give the number of atoms of $^{244}\text{Pu}$ at formation. The mass of this total is then calculated and ratioed to the mass of the sample to give the concentration of plutonium.

In Chapter 5, concentrations of uranium are calculated. This is done by combining the two methods described above. The % yield for $^{134}\text{Xe}$ from neutron–induced fission of $^{235}\text{U}$ is calculated by multiplying the % yield for $^{136}\text{Xe}$ by the $^{134}\text{Xe}/^{136}\text{Xe}$ ratio (both reported by Ozima and Podosek, 1983). The number of atoms of excess $^{134}\text{Xe}^*$ (from uranium) is then divided by the yield to give the number of “fissions” of uranium needed. Atoms of $^{235}\text{U}$ in the sample are then calculated by dividing the number of “fissions” by the conversion factor (the cross–section of thermal neutron capture of $^{235}\text{U}$ (Ozima and Podosek, 1983) multiplied by the fluence). Total atoms of uranium are then determined from the natural atomic abundance of $^{235}\text{U}$ (Korea Atomic Energy Research Institute, 2000) The mass of this total is then calculated and ratioed to the mass of the sample to give the concentration of uranium.

Iodine ($^{127}\text{I}$) concentrations are calculated from the number of atoms of $^{128}\text{Xe}^*$ released from each sample, using the $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratio of Shallowater from the relevant irradiation and the accepted initial $^{129}\text{I}/^{127}\text{I}$ ratio of $1.072 \times 10^{-4}$ (Brazzle et al., 1999).

Specific details related to the separate analyses are revisited in the corresponding chapters.
2.2. Irradiation

Before I–Xe analyses, samples are irradiated to convert $^{127}$I to $^{128}$Xe via neutron capture: $^{127}$I (n$\gamma$) $\rightarrow$ $^{128}$I ($\beta$) $\rightarrow$ $^{128}$Xe. This enables simultaneous analysis of $^{129}$Xe from decay of $^{129}$I and a stable iodine isotope ($^{127}$Xe via $^{128}$Xe) for I–Xe dating. Samples are weighed and wrapped in Al–foil, re–weighed and loaded into quartz tubes which are then sealed and evacuated. Each tube contains 2–4 samples of the irradiation monitor Shallowater spaced at regular intervals and one sample of the neutron flux monitor HB3gr hornblende (Roddick, 1983). More than one sample is used in order to monitor for any horizontal variations in neutron flux. The effect of variations in neutron flux on the radial axis is minimised by rotating the sample capsule about its vertical axis during irradiation. The samples are then sent away for irradiation. On return the samples are unwrapped, weighed to identify the samples and loaded into the RELAX sample port.

Samples included in this work were part of two separate irradiations: MN10–a and MN11–c. Irradiation MN10–a was sent to the Petten nuclear reactor, Netherlands and irradiated on 25th September 2009. However it was cadmium–shielded in error, reducing the thermal neutron fluence needed to convert $^{127}$I to $^{128}$Xe. When the mistake was realised the samples were sent back to be irradiated correctly, however the Petten nuclear reactor was out of operation. The samples were then sent to the SAFARI 1 reactor in Pelindaba, South Africa where they were irradiated correctly on 15th July 2010. The problems encountered whilst attempting to irradiate these samples delayed work for this study by ~9 months. MN11–c was irradiated at Petten nuclear reactor on 20th/21st November 2011 without any problems.

Integrated neutron fluences close to $10^{19}$ n cm$^{-2}$ were chosen to yield $^{127}$I conversion efficiencies close to initial Solar System $^{127}$I/$^{129}$I ratio of $\sim10^4$. This then should produce similar sized $^{129}$Xe* and $^{128}$Xe* signals during analysis (Gilmour et al., 2006). Details of each irradiation, including the neutron fluences received, are shown in Table 2.6.

Samples of enstatite from the aubrite Shallowater provided by the Natural History Museum, London, were included in each irradiation. Samples were prepared by gently crushing bulk samples of Shallowater and magnetic material removed with a hand magnet. Enstatite is used as it is the host phase of iodine in Shallowater. Following irradiation Shallowater samples were analysed and data collected and corrected using
procedures described in section 2.1. Xenon isotopic data for Shallowater samples analysed here are included in Appendix I.

Amounts of trapped $^{132}$Xe were calculated by applying a fission correction where necessary (as described by equation 2.9) to the total $^{132}$Xe. Excesses of $^{128}$Xe* were then calculated over trapped $^{132}$Xe using the composition of Q–Xe (Busemann et al., 2000) and $^{128}$Xe*/$^{129}$Xe ratios plotted against $^{132}$XeQ/$^{129}$Xe (Figure 2.8). Only the high temperature releases where $^{129}$Xe* correlated with $^{128}$Xe* are shown in Figure 2.8. Consecutive heat–steps evolve from a trapped composition towards a single $^{128}$Xe*/$^{129}$Xe ratio where $^{132}$XeQ/$^{129}$Xe =0, defining an isochron. The $^{128}$Xe*/$^{129}$Xe ratio of the isochron is then used to calculate the conversion factor for each irradiation by reference to the Shallowater $^{129}$Xe*/$^{127}$I ratio of $1.072 \pm 0.003 \times 10^{-4}$ (Brazzle et al., 1999). $^{128}$Xe*/$^{129}$Xe of Shallowater samples and the associated $^{127}$I $\rightarrow$ $^{128}$Xe conversion factors are given in Table 2.6.

Table 2.6. Details of irradiations used in this study, thermal neutron fluence ($n \text{ cm}^{-2}$) experienced during each irradiation, $^{127}$I $\rightarrow$ $^{128}$Xe conversion factor calculated from analyses of Shallowater enstatite.

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>Reactor</th>
<th>Date irradiated</th>
<th>Samples included</th>
<th>Thermal fluence ($n \text{ cm}^{-2}$)</th>
<th>$^{132}$XeQ/$^{129}$Xe</th>
<th>$^{129}$I $\rightarrow$ $^{128}$Xe conversion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MN10–a</td>
<td>Petten, NL.</td>
<td>25/09/09</td>
<td>GRA 06129</td>
<td>$2.20 \times 10^{17}$</td>
<td>0.806 ± 0.016</td>
<td>$8.64 \times 10^{-5}$</td>
</tr>
<tr>
<td>MN10–a</td>
<td>Pelindaba, SA.</td>
<td>15/07/10</td>
<td>GRA 06129</td>
<td>$9.5 \times 10^{18}$</td>
<td>0.512 ± 0.011</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>MN11–c</td>
<td>Petten, NL.</td>
<td>20/11/11</td>
<td>R–chondrites, Eucrites</td>
<td>$6.82 \times 10^{18}$</td>
<td>0.512 ± 0.011</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Figure 2.8. (top) Isochron plot for two Shallowater enstatite samples (SW0.77 & SW1.45) from irradiation MN10–a. (bottom) Isochron plot for three Shallowater enstatite samples (SW1, SW6 and SW8) from irradiation MN11–c. Analysis of sample SW6 was carried out by S. A. Crowther. Only high-temperature, correlated data are shown. The dashed line has been fitted using a York (1969) fit which assumes that any scatter from the line is only due to assigned errors.
CHAPTER 3. CONSTRAINING THE THERMAL HISTORY OF THE R-CHONDRITE PARENT BODY

3.1. Introduction
This work forms part of a new group project investigating xenon in Rumuruti (R) chondrites. Here I present results from the first I-Xe analyses of R-chondrites and the preliminary conclusions drawn from these results.

Though excesses of \(^{129}\text{Xe}\) have been reported in R-chondrites (Nagao et al., 1999; Schultz et al., 2005), the I-Xe system has not previously been studied in them. Here I-Xe dating has been carried out on samples of different lithologies from a thin section of NWA 6492 and on two strongly metamorphosed (R5) R-chondrites NWA 830 and NWA 3364, to determine whether there is a relationship between the extent of thermal processing and the time of closure to xenon-loss. The original aim was to analyse six samples of NWA 6492 which included two R5-6 clasts. Unfortunately, problems thought to be associated with the sample preparation methods (discussed in more detail in section 3.2) did not allow Xe analyses to be carried out of the R5-6 clasts. In order to enable comparison between highly metamorphosed rocks and those of a lower petrologic type, two samples of R5 R-chondrite material from NWA 830 and NWA 3364 have been included in this study. Analyses of irradiated NWA 830 were carried out by S. A. Crowther and P. Lee as part of P. Lee’s MEarthSci project.

R-chondrites have experienced different degrees of metamorphism and are divided into petrological types R3-R6 where R3 have experienced the least thermal metamorphism and R6 the most. Lingemann et al. (2000) studied primitive components in Rumuruti and suggested that R-chondrite material experienced thermal metamorphism in an undisturbed onion-shell arrangement; where material buried deeper in the parent asteroid reached a greater peak temperature and cooled over a longer period of time compared to material closer to the surface, with the system remaining undisturbed. The extent of metamorphism is then linked to closure age and can be tested by radiometric dating of samples of different metamorphic grade. This thermal model has also been suggested for the ordinary chondrites (Trieloff et al., 2003).

An alternative heating model for ordinary (and therefore R-chondrites) is the “rubble-pile”. Rubble pile asteroids consist of reassembled pieces of a shattered asteroid or
asteroids. If an asteroid is disrupted early in its thermal history then pieces that originated in the interior (R6) may be reassembled into the crust and cool quickly. A correlation between cooling rate (age) and extent of metamorphism is therefore not expected. This is seen by some as a more likely scenario than the onion-shell as early Solar Systems models suggest a high chance of collision amongst bodies in the asteroid belt (Chambers, 2004).

Comparison of I-Xe ages of R-chondrites of different petrologic type may therefore constrain the thermal history of the R-chondrite parent body. Prior to I-Xe analyses xenon isotopes in unirradiated samples R-chondrites were measured in order to study the different xenon components present.

3.2. Sample descriptions and preparation
R-chondrites are characterised by their distinct O isotope ratios (Figure 1.3), their highly oxidised state (Figure 1.2) and their high ratio of matrix/chondrules. Olivine is the dominant mineral with a modal abundance >50%, pyroxene (in low abundances) and plagioclase are also present along with high abundances of sulphides (~11 wt%) plus chromite, phosphates and small amounts of magnetite (Kallemeyn et al., 1996). Many R-chondrites are brecciated including all the samples studied here. Many contain material of varying petrologic type, such as NWA 6492 and NWA 3364. Samples of primitive (R3) and metamorphosed (R5) material from NWA 3364 have been analysed here. To avoid confusion the metamorphosed R5 material from NWA 3364 will be referred to as 3364M. All samples studied here have experienced some shock and were found in deserts and so have been affected by terrestrial weathering.

Whole-rock samples of NWA 3364, NWA 755, NWA 830 and NWA 3364M were provided by A. Bischoff, University of Münster. Six clasts of varying metamorphic grade from a well characterised sample of NWA 6492 were provided by A. Ruzicka of Cascadia Meteorite Laboratory, Portland State University. NWA 6492 contains material of petrological type 3-6 (Jamsja and Ruzicka, 2011) and the clasts were chosen to sample material of varying petrological types. A section of matrix material from NWA 6492 was also included. Details of the samples studied are given in Table 3.1. Unirradiated samples of NWA 3364, NWA 755 and NWA 830 were analysed to investigate the contributing Xe components. Irradiated samples of NWA 6492, NWA 3364M and NWA 830 were analysed to investigate the I-Xe system.
Table 3.1. Table showing details of samples, analyses of which are reported here. Attempts were made to analyse irradiated samples of two R5 clasts from NWA 6492; however these samples released extremely large amounts of hydrocarbons meaning the analyses had to be abandoned. Weathering scale given by Wlotzka (1993) from W0 (pristine) to W6 (heavy alteration). Shock classification scheme is given in Table 1.2.

<table>
<thead>
<tr>
<th>Petrologic Type</th>
<th>Meteorite</th>
<th>Sample Name</th>
<th>Weathering</th>
<th>Shock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>3</td>
<td>NWA 3364</td>
<td>3364</td>
<td>W3</td>
</tr>
<tr>
<td></td>
<td>3.7</td>
<td>NWA 755</td>
<td>755</td>
<td>W4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>NWA 830</td>
<td>830</td>
<td>W3</td>
</tr>
<tr>
<td>Irradiated</td>
<td>3 (Low subtype)</td>
<td>NWA 6492</td>
<td>L3</td>
<td>W1-W2</td>
</tr>
<tr>
<td></td>
<td>3(Mid subtype)</td>
<td>NWA 6492</td>
<td>M3</td>
<td>W1-W2</td>
</tr>
<tr>
<td></td>
<td>3 (High subtype)</td>
<td>NWA 6492</td>
<td>H3</td>
<td>W1-W2</td>
</tr>
<tr>
<td></td>
<td>Mixture (matrix)</td>
<td>NWA 6492</td>
<td>MX</td>
<td>W1-W2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>NWA 830</td>
<td>830</td>
<td>W3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>NWA 3364M</td>
<td>3364M</td>
<td>W3</td>
</tr>
</tbody>
</table>

Samples of R5-6 material from NWA 6492 produced very large amounts of hydrocarbons during low-temperature heating which rendered the mass spectrometer unusable for several days. These large releases have been attributed to remnants of the epoxy the samples had been mounted in during their preparation before arrival in Manchester. The R5-6 clasts are more porous than those of a lower petrologic type and any epoxy that entered these pores may not have been removed by the grinding process that was used to remove the majority of the epoxy from all samples. This problem was not seen in the samples of matrix material I analysed suggesting the matrix does not contain a large amount of R5-6 material. An attempt was made to remove more of the epoxy from samples of these clasts by washing the samples in acetone in an ultrasonic bath for ~3 hours before RELAX analyses; however, this did not work. Xe isotopic data for R-chondrite samples reported here are included in Appendix II.

3.3. Xe components

3.3.1. Unirradiated samples
Unirradiated samples of 3364 (R3), 755 (R3.7) and 830 (R5) were laser step-heated and the isotopic signatures of the xenon released examined, in order to determine the nature of any trapped component, and any contributions from spallation-Xe or fission-Xe. The results are discussed here.
Two releases of gas from 3364 released very large amounts of gas (>10^6 atoms ^{132}\text{Xe}); twice as much as the average release for this set of samples. RELAX is designed to analyse small amounts of gas, not large releases and it is thought that this resulted in undercounting of ^{136}\text{Xe} due to disruption to the baseline for the data obtained from these two releases. In addition, several low-temperature releases from all samples were collected whilst large amounts of peaks consistent with sulphur and SO were released. This is thought to have compromised these results. The data from these releases of gas are therefore not considered further.

Spallation-Xe is produced by spallation reactions between cosmic-rays and the major target elements: Ba and rare earth elements (REE). Spallation contributions are most noticeable in the lighter xenon isotopes (which are also not produced by fission) so ^{124}\text{Xe} and ^{126}\text{Xe} and ^{130}\text{Xe} have been examined here (Figure 3.1.). ^{130}\text{Xe} is chosen as the normalising isotope as it is released in the largest abundances.

![Figure 3.1. 3-isotope plot of the light-isotopes: ^{126}\text{Xe}, ^{124}\text{Xe} and ^{130}\text{Xe} for unirradiated samples of NWA 3364 (R3), NWA 755 (R3.7) and NWA 830 (R5). If any spallation component is present it would be most easily observed in the lighter isotopes of Xe. Data from all samples cluster around a trapped component consistent with terrestrial atmosphere (Wieler, 2002), Q-Xe (Busemann et al., 2000) or solar-wind (Wieler, 2002) (or a mixture of these) and far from the spallation composition defined by Hohenberg et al. (1981).]
Data from all samples plot close to a trapped composition consistent with terrestrial atmospheric xenon, primitive Q-Xe or solar-wind. They plot far away from spallation-Xe compositions for pure-Ba spallation, pure-REE spallation and the chondritic mix of Ba/REE given by Hohenberg et al. (1981). A calculation was made to determine the proportion ($x$) of any contributions from spallation to $^{130}$Xe using the following:

$$x = \frac{\frac{^{124}Xe}{^{130}Xe_{SAMPLE}} - \frac{^{124}Xe}{^{130}Xe_{SPALLATION}}}{\frac{^{124}Xe}{^{130}Xe_{TRAPPED}} - \frac{^{124}Xe}{^{130}Xe_{SPALLATION}}}$$  

(Eq. 3.1)

This calculation was made using all combinations of trapped and spallation endmembers (atmospheric-Xe, Q-Xe, solar-wind; pure-Ba, pure-REE, chondritic Ba/REE). The result was the same within error for all releases using all combinations of trapped and spallation endmembers: the contribution from spallation ($x$) is within error of zero. It therefore appears that the spallation component in these samples is negligible. This could be due to a young cosmic-ray exposure age or lack of target elements such as barium and the light rare earth elements (La, Ce, Pr, Nd, Pm, Sm, Eu and Gd). $^{21}$Ne cosmic-ray exposure ages for 3364, 755 and 830 are 19.3, 27.3 and 10.7 Myr respectively (Vogel et al., 2011). Spallation Xe has been seen in eucrites with similar cosmic-ray exposure ages (Chapter 4) which points to low abundances of Ba and REE in R-chondrites. REE elemental abundances in R chondrites (Bischoff et al., 2011 and references therein) are similar to those of ordinary chondrites (Wasson and Kallemeyn, 1988) and a factor of 10 smaller than in eucrites (Kitts and Lodders, 1998). Abundances of Ba have not been measured in R-chondrites. Spallation-Xe is not observed in clasts from ordinary chondrites (Gilmour et al., 2000) but is in eucrites (Chapter 4). This suggests that low concentrations of REE are the reason for the absence of spallation-Xe in these samples.

$^{129}$Xe/$^{132}$Xe ratios higher than any of the trapped components considered are seen in all samples, with 830 (R5) showing the highest $^{129}$Xe/$^{132}$Xe ratios (Figure 3.2). This indicates the presence of excess $^{129}$Xe* which could have been produced by in-situ radioactive decay of $^{129}$I or it could be due to an inherited evolved xenon component. This can only be determined by examining the relationship between $^{129}$Xe* and iodine in irradiated R-chondrite samples.
Heavier Xe isotopes ($^{131}$Xe-$^{136}$Xe) in unirradiated samples are expected be dominated by trapped-Xe, spontaneous fission of $^{244}$Pu and/or $^{235}$U and any excess $^{129}$Xe* (Table 2.2). The majority of the $^{136}$Xe/$^{132}$Xe ratios (Figure 3.2) fall between Q-Xe and atmospheric-xenon compositions, with no evidence for solar-wind Xe. This trend can be explained by either mixing between Q-Xe and atmospheric-Xe or addition of fission-Xe to Q-Xe. $^{134}$Xe is examined along with $^{136}$Xe and $^{132}$Xe in Figure 3.3. Here contributing components are expected to be trapped-Xe and fissiogenic-Xe only. Again there is no evidence for solar wind Xe, with all of the data consistent with mixing between Q-Xe and atmospheric Xe (within error). Busemann et al. (2011) measured Xe isotopes in six R-chondrites. They argued that the results could be explained by mixing atmospheric-Xe, solar-wind plus a small contribution from fission, without the need for Q-Xe. The data presented here does not appear to require this hypothesis.
Figure 3.3. 3-isotope plot of $^{136}\text{Xe}$, $^{134}\text{Xe}$ and $^{132}\text{Xe}$ for unirradiated samples of NWA 3364 (R3), NWA 755 (R3.7) and NWA 830 (R5). Mixing lines between Q-Xe and endmembers of spontaneous fission of $^{238}\text{U}$ (dotted-line) and $^{244}\text{Pu}$ (dashed-line) (Ozima and Podosek, 1983) are shown. The data form a mixing line that can be explained by mixing of either Q-Xe and fission-Xe or Q-Xe and atmospheric-Xe. If a fission component is present, the data do not allow direct determination of its endmember.

After examining all the data, it cannot be said with great confidence that there is a fission component present, as the higher $^{134}\text{Xe}/^{132}\text{Xe}$ and $^{136}\text{Xe}/^{132}\text{Xe}$ ratios can be explained by contributions from atmospheric-Xe. However, if fission-Xe is present the source can either be spontaneous fission of $^{238}\text{U}$ or $^{244}\text{Pu}$. Figure 3.3 considers mixing between Q-Xe and spontaneous fission of $^{238}\text{U}$ or $^{244}\text{Pu}$. The errors associated with the data do not allow distinction between the two fission endmembers. However, decay of $^{244}\text{Pu}$ is expected to dominate fission-Xe before 4.4 Gyr (Turner et al., 2004) and here, in the unirradiated samples, excesses in heavy xenon isotopes are attributed to fission of $^{244}\text{Pu}$ only, though a small contribution from $^{238}\text{U}$ may also be present. That the R-chondrites appear to show a small contribution from Pu-fission is consistent with an absence of spallation-Xe due to low abundances of target elements, as Pu and REE are geochemically similar (Lugmair and Marti, 1977).
As there is no evidence to suggest a significant contribution to Xe from solar-wind, the data can instead be explained by any of the following:

1. Mixing of Q-Xe and atmospheric-Xe.
2. Q-Xe with addition of fissionogenic-Xe (assumed to be from radioactive decay of $^{244}\text{Pu}$).
3. Contributions from Q-Xe and atmospheric-Xe with addition of fissionogenic–Xe.

The fractions of Q-Xe ($1-x$) that contribute to each release for hypotheses (1) and (2) have been calculated by the following where $Y$ is either the $^{244}\text{Pu}$ endmember or atmospheric Xe and $x$ is the proportion of $^{132}\text{Xe}$ contributed by $Y$.

$$x = \frac{\left(\frac{^{136}\text{Xe}}{^{132}\text{Xe}_{\text{SAMPLE}}} - \frac{^{136}\text{Xe}}{^{132}\text{Xe}_Y}\right)}{\left(\frac{^{136}\text{Xe}}{^{132}\text{Xe}_Y} - \frac{^{136}\text{Xe}}{^{132}\text{Xe}_Q}\right)}$$

(Equation 3.2)

If mixing between Q-Xe and $^{244}\text{Pu}$ is assumed here, then Q-Xe contributes $>96\%$ to each release. If mixing between Q-Xe and atmospheric-Xe is assumed (with no fission component) then Q-Xe contributions vary widely and no trend is seen between contributions from atmospheric-Xe and the temperature of the heat-step, which would be expected if terrestrial xenon had been adsorbed onto the sample. The most appropriate way to treat the data therefore appears to be as a mixture of Q-Xe and fission of $^{244}\text{Pu}$ with no contribution from spallation. This agrees with findings by Nagao et al. (1999) who studied Xe isotopes in five R-chondrites and concluded that the heavy isotopes were best described by Q-Xe with addition of fission of either $^{238}\text{U}$ or $^{244}\text{Pu}$. Reported total $^{136}\text{Xe}/^{132}\text{Xe}$ and $^{134}\text{Xe}/^{132}\text{Xe}$ ratios in Nagao et al. (1999) showed definite excesses of fission-Xe above atmospheric-Xe. The data reported here will be treated in the same way; as a mixture of Q-Xe and fission-Xe attributed to $^{244}\text{Pu}$.

To test what effect the decision to treat the data as mixing between Q-Xe and fission of $^{244}\text{Pu}$ would have, number of atoms of $^{132}\text{Xe}_{\text{TRAPPED}}$ were calculated assuming, firstly mixing between Q-Xe and $^{244}\text{Pu}$ and, secondly mixing between atmospheric-Xe and $^{244}\text{Pu}$. Mixing between atmospheric-Xe and $^{244}\text{Pu}$ results in a very slight increase in the number of atoms of trapped $^{132}\text{Xe}$ but falls within the errors placed on concentrations of
atoms released by the sensitivity of the instrument as described in Chapter 2. Concentrations of $^{132}\text{Xe}_{\text{TOTAL}}$, $^{132}\text{Xe}_Q$ $^{136}\text{Xe}$ (Pu) and $^{129}\text{Xe}^*$ ($^{129}\text{I}$?) based on this conclusion are given in Table 3.2.

**Table 3.2.** Concentrations (cc STP×$10^{-10}$ g$^{-1}$) of $^{132}\text{Xe}_{\text{TOTAL}}$, $^{132}\text{Xe}_Q$, $^{129}\text{Xe}^*$ (which may have been produced by in-situ decay of $^{129}\text{I}$) and $^{136}\text{Xe}^*$ (attributed to spontaneous fission of $^{244}\text{Pu}$) in unirradiated samples. It can be seen that the contribution from Pu fission is very small as $^{132}\text{Xe}_{\text{TOTAL}}$ and $^{132}\text{Xe}_Q$ (corrected for a fission contribution are the same within error). Errors are $\sim 5\%$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{132}\text{Xe}_{\text{TOTAL}}$</th>
<th>$^{132}\text{Xe}_Q$</th>
<th>$^{129}\text{Xe}^*$ (I?)</th>
<th>$^{136}\text{Xe}^*$ (Pu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWA 3364</td>
<td>6.9</td>
<td>6.9</td>
<td>2.3</td>
<td>0.003</td>
</tr>
<tr>
<td>NWA 755</td>
<td>3.6</td>
<td>3.7</td>
<td>2.1</td>
<td>0.003</td>
</tr>
<tr>
<td>NWA 830</td>
<td>3.7</td>
<td>3.7</td>
<td>2.5</td>
<td>0.003</td>
</tr>
<tr>
<td>NWA 830</td>
<td>4.1</td>
<td>4.1</td>
<td>4.3</td>
<td>0.001</td>
</tr>
</tbody>
</table>

3.3.2. **Irradiated samples**

In order to determine I-Xe ages of R-chondrite samples, I-Xe analyses were carried out on irradiated samples of well characterised clasts from NWA 6492 and whole-rock samples of NWA 830 and NWA 3364M. All were included in irradiation MN11-c (Chapter 2). Before examination of the I-Xe system, the different Xe components present in these irradiated samples are discussed in order to test the arguments made in the previous section.

Light Xe-isotope ratios (Figure 3.4) are very similar to those of the unirradiated samples: data plot close to a trapped component consistent with atmospheric-Xe or Q-Xe with a very small contribution from spallation-Xe. Again, to test whether there is any significant contribution from a spallation component, the fraction contributed by the spallation component was calculated using equation 3.1. Again this contribution was found to be within error of zero for all releases from all samples.

Heavy Xe-isotopes in irradiated samples show $^{134}\text{Xe}^{/132}\text{Xe}$ and $^{136}\text{Xe}^{/132}\text{Xe}$ ratios (Figure 3.5) higher than those seen in unirradiated samples. These excesses above atmospheric-Xe indicate a fissionogenic component. That the fission component makes a much more significant contribution to irradiated samples than to unirradiated samples points towards neutron induced fission of $^{235}\text{U}$ during the irradiation process. Data fall
on a mixing line between Q-Xe and a fission endmember with a higher $^{136}\text{Xe}/^{132}\text{Xe}$ than the $^{235}\text{U}$ endmember. This is most likely due to production of $^{136}\text{Xe}$ from neutron-capture on $^{135}\text{Xe}$, which is produced during fission of $^{235}\text{U}$. A fission-correction has been made to data that falls more than $2\sigma$ away from Q-Xe based on mixing between a trapped component consistent with Q-Xe and a fission endmember with a $^{134}\text{Xe}/^{132}\text{Xe}$ ratio consistent with neutron-induced fission of $^{235}\text{U}$. Sample 3364M produced much higher $^{134}\text{Xe}/^{132}\text{Xe}$ and $^{136}\text{Xe}/^{132}\text{Xe}$ ratios than the other sample. This could be due to higher concentrations of U in this sample, or smaller amounts of trapped $^{132}\text{Xe}$.

**Figure 3.4.** 3-isotope plot of $^{126}\text{Xe}$, $^{124}\text{Xe}$ and $^{130}\text{Xe}$ released from irradiated samples of NWA 6492: M3 (mid R3), L3 (low R3), H3 (high R3) and MX (matrix) and irradiated samples of NWA 830 (R5) and NWA 3364 (R5). Data from all samples cluster around a trapped component consistent with terrestrial atmosphere, Q-Xe or solar-wind and far from the spallation composition defined by Hohenberg et al. (1981), consistent with the unirradiated samples. Error bars have been removed for clarity; the maximum error observed is shown in the top-left corner.
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**Figure 3.5.** 3-isotope plot of $^{136}$Xe, $^{134}$Xe and $^{132}$Xe for irradiated samples of NWA 6492 M3 (mid R3), L3 (low R3), H3 (high R3) and MX (matrix) and NWA 830 (R5) (top) and NWA 3364 (R5) (bottom). The line defined by the 3365M data is shown on the top plot. Mixing lines between Q-Xe (Busemann et al., 2000) and endmembers of neutron-induced fission of $^{235}$U and neutron-capture on $^{135}$Xe (Ozima and Podosek, 1983) are shown. The data form a mixing line that can be explained by mixing of Q-Xe and fission-Xe though some contribution from terrestrial atmosphere may also be present. Sample 3364M shows much higher $^{134}$Xe/$^{132}$Xe and $^{136}$Xe/$^{132}$Xe ratios suggesting either higher abundances of U, or lower contributions from trapped $^{132}$Xe. Note the difference in scale between the axes of the top and bottom plots.
Figure 3.6. 3-isotope plot of $^{131}\text{Xe}$ (produced from neutron-capture on tellurium and/or barium during irradiation), $^{134}\text{Xe}$ (produced by neutron-induced fission of uranium during irradiation) and $^{132}\text{Xe}$. Irradiated NWA 830 shows higher $^{131}\text{Xe}/^{132}\text{Xe}$ and $^{134}\text{Xe}/^{132}\text{Xe}$ ratios than unirradiated NWA 830, showing the presence of Te/Ba and U in the sample. Due to the lack of spallation xenon seen in these samples and the high sulphide contents of R-chondrites, Te is thought to dominate production of $^{131}\text{Xe}^*$ here.

The irradiation process can also produce excesses of $^{131}\text{Xe}^*$ via neutron-capture on Ba or Te. Figure 3.6 compares $^{131}\text{Xe}$, $^{134}\text{Xe}$ and $^{132}\text{Xe}$ in unirradiated and irradiated samples of NWA 830. Irradiated samples show higher $^{131}\text{Xe}/^{132}\text{Xe}$ ratios indicating Xe has been produced from neutron-capture on barium or tellurium. Barium is a target element for spallation-Xe and no evidence has been seen for the presence of spallation-Xe in these samples (Figures 3.1 and 3.4). The lack of Ba means that neutron capture on Te may be a more likely source for excess $^{131}\text{Xe}$ in these samples. R-chondrites are known to contain abundant (up to ~11 wt%) sulphides (Kallemeyn et al., 1996) and Te is known to have affinities to sulphur. Te is therefore thought to be the more likely source of excess $^{131}\text{Xe}$. As concentrations of Ba have not been measured in R-chondrites this cannot be confirmed here.
Figure 3.7. 3-isotope plot of $^{129}$Xe (which can be produced from decay of $^{129}$I), $^{131}$Xe* (produced by neutron-capture on barium and corrected for a fission contribution) and $^{132}$XeQ for irradiated samples of NWA 6492 M3 (mid R3), L3 (low R3), H3 (high R3) and MX (matrix) and NWA 830 (R5) (top) and NWA 3364 (R5) (bottom). Samples of NWA 6492 and NWA 830 show tellurium and iodine released separately. NWA 3364 shows tellurium released with iodine.
When releases of $^{131}$Xe (corrected for a fission contribution) are compared to releases of $^{129}$Xe in irradiated samples (Figure 3.7), all samples except for 3364M show the same distinctive release pattern:

- Large excesses of $^{131}$Xe* above a trapped composition are seen at lower heating temperatures with no excess $^{129}$Xe*.
- As heating temperature increases excesses of $^{129}$Xe*, above a trapped composition are seen and the $^{131}$Xe/$^{132}$Xe_Q ratio tends back towards the trapped composition.
- At the highest heating temperatures excess $^{129}$Xe* is released but not excess $^{131}$Xe*.

Sample 3364M shows the same initial pattern at low-temperatures with increasing amounts of $^{131}$Xe* released without $^{129}$Xe. However at higher temperature a second release of $^{131}$Xe* is seen, with $^{129}$Xe*.

Concentrations of $^{132}$Xe_Q and $^{127}$I, and $^{129}$Xe* appear to correlate with petrologic type in NWA 6492 samples (Table 3.3), with L3 releasing the highest concentrations and H3/MX the least. This is consistent with increasing loss of volatiles during thermal processing. Sample 830 (R5) produced higher concentrations of $^{132}$Xe_Q and iodine than H3 which is inconsistent with increasing loss of volatiles during thermal processing. NWA 830 is known to be more weathered (W3) than NWA 6492 (Table 3.1) so this result could be produced by greater adsorption of atmospheric xenon during terrestrial weathering. 3364M is also weathered to W3 but does not show large $^{132}$Xe_Q concentrations, however it does show larger concentrations of $^{127}$I than all other samples except L3 which may have been incorporated during its terrestrial residence time.

In figure 3.5 and 3.7 sample 3364M showed higher $^{131,134,136}$Xe/$^{132}$Xe ratios. It was suggested this could be due to higher U and Te contents or to smaller contributions from trapped $^{132}$Xe to 3364M. Table 3.3 shows that 3364M has $^{132}$Xe_Q concentrations comparable to samples MX and H3. The high $^{131,134,136}$Xe Xe/$^{132}$Xe ratios therefore appear to be due to higher U and Te concentrations It also appears that the higher $^{132}$Xe_Q concentration of 830 has suppressed the fission signature and tellurium signature of this sample as concentrations of $^{131}$Xe* and $^{134}$Xe* are comparable to those of 3364M.
That 830 and 3364M contain larger concentrations of $^{131}\text{Xe}^*$ and $^{134}\text{Xe}^*$ suggest that U and Te contents are linked to metamorphism. However, samples from NWA 6492 did not show a correlation between $^{131}\text{Xe}^*$ and $^{134}\text{Xe}^*$ concentrations and increasing metamorphism. It is hard to understand how metamorphism could concentrate particular elements rather than just redistribute them. Therefore these differences may again be due to differences in the chemical compositions of the different meteorites. To place better constrains on volatile loss during metamorphism and the behaviour of U and Te in R-chondrites, samples of R5 and R6 material from NWA 6492 should be analysed.

**Table 3.3.** Concentrations of $^{132}\text{Xe}_{Q}$, $^{129}\text{Xe}^*$, iodine (from concentrations of $^{128}\text{Xe}^*$), tellurium (from concentrations of $^{131}\text{Xe}^*$) and uranium ($^{134}\text{Xe}^*$ assumed to dominated by neutron-induced fission U) in irradiated samples. Errors are ~5%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{132}\text{Xe}_Q$ (cc STP g$^{-1}$)</th>
<th>$^{129}\text{Xe}^*$ (cc STP g$^{-1}$)</th>
<th>Iodine (ppb)</th>
<th>Tellurium (ppb)</th>
<th>Uranium (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3</td>
<td>$1.7 \times 10^{-10}$</td>
<td>$7.4 \times 10^{-10}$</td>
<td>119</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>M3</td>
<td>$6.0 \times 10^{-10}$</td>
<td>$3.2 \times 10^{-10}$</td>
<td>73</td>
<td>29</td>
<td>40</td>
</tr>
<tr>
<td>H3</td>
<td>$2.5 \times 10^{-10}$</td>
<td>$2.2 \times 10^{-10}$</td>
<td>54</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>MX</td>
<td>$2.2 \times 10^{-10}$</td>
<td>$2.4 \times 10^{-10}$</td>
<td>39</td>
<td>27</td>
<td>37</td>
</tr>
<tr>
<td>830</td>
<td>$5 \times 10^{-10}$</td>
<td>$5.2 \times 10^{-10}$</td>
<td>66</td>
<td>89</td>
<td>121</td>
</tr>
<tr>
<td>3364M</td>
<td>$2.5 \times 10^{-10}$</td>
<td>$1.7 \times 10^{-10}$</td>
<td>83</td>
<td>71</td>
<td>98</td>
</tr>
</tbody>
</table>

### 3.4. 1-Xe results

**3.4.1. Correlation between $^{129}\text{Xe}^*$ and iodine in irradiated samples**

Atoms of excess $^{128}\text{Xe}^*$ (from iodine) above the $^{128}\text{Xe}^{132}\text{Xe}_Q$ ratio (corrected for addition of fission-Xe to $^{132}\text{Xe}$) were calculated and the relationship between $^{129}\text{Xe}$ and $^{128}\text{Xe}^*$ examined to look for any correlation that would indicate the presence of iodogenic $^{129}\text{Xe}^*$. The data for each of the R-chondrite samples were normalised to $^{129}\text{Xe}$, the most abundant isotope, and 3-isotope diagrams of $^{128}\text{Xe}^*/^{129}\text{Xe}$ and $^{132}\text{Xe}_Q/^{129}\text{Xe}$ were then plotted (Figure 3.8). All samples show large amounts of uncorrelated iodine at low heating-temperatures. This can be explained by loss of $^{129}\text{Xe}^*$ from iodine sites over time, late-stage incorporation of iodine on the parent body, or terrestrial contamination. At high-temperatures, consecutive heat-steps (labelled “included” in Figure 3.8) produced isochrons. Sample L3 data are consistent with two isochrons. These are referred to as “low-T” and “high-T”, for the relative temperatures the data were released at.
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NWA 6492 (L3)

NWA 6492 (M3)
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NWA 6492 (H3)

NWA 6492 (MX)
Figure 3.8. Isochron plots for irradiated samples. All samples showed a correlation between $^{129}$Xe and $^{128}$Xe* (from $^{127}$I) from a series of consecutive steps at high-temperatures indicating $^{129}$Xe* was produced by in-situ decay of $^{129}$I. Isochrons (long dashed-lines) have been fitted to data (black squares) using a York (1969) regression. Sample NWA 6492 (L3) produced two isochrons at different temperatures (an enlarged area of the relevant part plot is shown as an in insert).
3.4.2. I-Xe ages derived from isochrons
As all samples show a relationship between $^{128}$Xe* (from iodine) and $^{129}$Xe consistent
with an isochron, I-Xe ages can be calculated. The x-intercept (corresponding to the
$^{128}$Xe*/$^{129}$Xe ratio of the pure-iodine endmember with no contribution from trapped
xenon) and the y-intercept (corresponding to the trapped component with no
contribution from iodine) were calculated for each isochron using the a York (1969) fit,
which assumes that the only reason for the data to deviate from the fitted line is due to
the assigned errors. These intercept values are given in Table 3.4.

The $^{128}$Xe*/$^{129}$Xe ratio of the pure-iodine endmember (which is representative of the
$^{127}$I/$^{129}$I ratio at closure to xenon) was then used to calculate the age of each sample by
comparison to the $^{128}$Xe*/$^{129}$Xe ratio of the Shallowater irradiation standard given in
Table 2.6, using equations 1.5 and 1.6. The I-Xe ages relative to Shallowater and
absolute ages calculated from the age of Shallowater of 4562.3 ± 0.3 (Gilmour et al.,
2009) for the R-chondrites studied here are given in Table 3.5 and Figure 3.9.

Table 3.4. Initial iodine ratios ($^{128}$Xe*/$^{129}$Xe) and trapped compositions ($^{132}$XeQ/$^{129}$Xe)
of each sample obtained from isochrons shown in Figure 3.8. All trapped compositions
are within error of Q-Xe. Also given are the mean square weighted deviation (MSWD)
associated with each isochron.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Sample name</th>
<th>$^{128}$Xe*/$^{129}$Xe</th>
<th>$^{132}$XeQ/$^{129}$Xe</th>
<th>MSWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWA 6492</td>
<td>L3 (high-T)</td>
<td>0.687 ± 0.027</td>
<td>0.947 ± 0.017</td>
<td>1.5</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>L3 (low-T)</td>
<td>0.753 ± 0.048</td>
<td>0.978 ± 0.030</td>
<td>0.62</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>M3</td>
<td>0.658 ± 0.078</td>
<td>0.967 ± 0.087</td>
<td>1.4</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>H3</td>
<td>0.836 ± 0.160</td>
<td>0.898 ± 0.140</td>
<td>1.14</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>MX</td>
<td>0.862 ± 0.072</td>
<td>0.889 ± 0.100</td>
<td>0.73</td>
</tr>
<tr>
<td>NWA 830</td>
<td>830</td>
<td>0.634 ± 0.130</td>
<td>1.080 ± 0.230</td>
<td>0.59</td>
</tr>
<tr>
<td>NWA 3364M</td>
<td>3364M</td>
<td>0.947 ± 0.071</td>
<td>0.950 ± 0.160</td>
<td>4.7</td>
</tr>
</tbody>
</table>
**Table 3.5.** I-Xe ages relative to Shallowater enstatite and absolute ages calculated using the Shallowater age 4563.2 Myr (Gilmour et al., 2009) obtained from isochrons shown in Figure 3.8.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Sample name</th>
<th>Age relative to SW (Myr)</th>
<th>Absolute Age (Myr)</th>
<th>Error (Myr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWA 6492</td>
<td>L3 (high-T)</td>
<td>-6.8</td>
<td>4555.5</td>
<td>1.0</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>L3 (low-T)</td>
<td>-8.8</td>
<td>4553.4</td>
<td>1.6</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>M3</td>
<td>-5.6</td>
<td>4556.7</td>
<td>2.8</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>H3</td>
<td>-10.9</td>
<td>4551.4</td>
<td>4.5</td>
</tr>
<tr>
<td>NWA 6492</td>
<td>MX</td>
<td>-11.9</td>
<td>4550.4</td>
<td>2.0</td>
</tr>
<tr>
<td>NWA 830</td>
<td>830</td>
<td>-4.4</td>
<td>4557.9</td>
<td>4.8</td>
</tr>
<tr>
<td>NWA 3364M</td>
<td>3364M</td>
<td>-14.1</td>
<td>4548.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Figure 3.9.** Absolute I-Xe ages of NWA 6492 M3 (mid R3), L3 (low R3), H3 (high R3) and MX (matrix) and NWA 830 (R5) and NWA 3364 (R5).
3.5. Discussion

3.5.1. Link between I-Xe age and metamorphism?
If the different petrologic types found in R-chondrites are produced by cooling in an undisturbed onion-shell model and the I-Xe ages are dating metamorphism, then a correlation may be expected between the age of the sample and the extent of metamorphism. So is that seen in these results?

The least metamorphosed sample, L3, shows I-Xe ages ~7 Myr older than 3364M, one of the most metamorphosed samples. These ages are not within error of each other. This therefore indicates that more metamorphosed samples closed to xenon-loss later than unaltered samples. 3364M also appears to have closed after samples MX (which may contain material of a mixture of metamorphic grade) and H3 (experienced limited metamorphism) though errors produce some overlap in these ages. This trend of later closure to xenon-loss with increasing petrologic type is highlighted in Figure 3.10. This trend points towards slower cooling of more metamorphosed samples, consistent with the onion model. Further I-Xe analyses of R5-6 material from NWA 6492 and studies of other R4 and R6 R-chondrites would test this theory and help constrain the thermal history of the R-chondrite parent body.

Sample M3 (mid R3) shows a slightly earlier closure age than sample L3 (low R3) though the large errors on M3 do mean it may still fall within the correlation shown in Figure 3.10. However that M3 shows a similar age to L3 suggests it contains similar material.

Sample L3 produced two I-Xe ages at different temperature ranges during step-heating. The major components of R-chondrites are chondrules (35-50 vol%) and matrix (50-65 vol %) (Bischoff et al., 2001 and references therein). It could therefore be possible that the high-temperature I-Xe age dates Xe closure in chondrules and the low-temperature I-Xe age dates low degrees of metamorphism of the matrix material in L3. The average size of chondrules in R-chondrites ~0.4 mm though larger ones (up to 3mm) have been found (Bischoff et al., 2011). The clasts analysed here are ~1mm diameter aliquots of the 3mm clasts separated by A. Ruzicka have been analysed here so it may be that the aliquot of M3 used was dominated by relatively unprocessed chondrules/chondrules, similar to those found in L3.
If the I-Xe age of high temperature L3 and M3 samples are dating closure to Xe loss in chondrules, it seems unlikely they are dating chondrule formation as the ages reported here of ~4555 Myr fall after the accepted period of chondrule formation of a few millions years from ~1-2 Myr after formation of the Solar System.

Figure 3.10. The I-Xe ages of samples L3, H3, MX and 3364M appear to show a correlation between extent of metamorphism and closure to Xe-loss. This supports the hypothesis that the different petrologic types were produced by cooling in an undisturbed parent body consistent with the onion-shell model. More data are needed to confirm this hypothesis.

3.5.2. “Old” age of NWA 830
Sample 830 is classed as R5; however, the I-Xe age reported for 830 here is earlier than all the other sample studies and earlier than the other R5 sample (3364M) by almost 10 Myr. Three lines of thought are discussed here to explain this “old” age:

1. Misclassification
Sample 830 not only produced an older age than 3364M, but appeared to show contributions from fission (Figure 3.5) and tellurium (Figure 3.7) more comparable to the R3 samples from NWA 6492 than the other R5 sample (3364M). This could point towards a misclassification of NWA 830 as R5 when in fact it not has experienced such
high degrees of thermal metamorphism. However, when concentrations of contributions to total Xe are examined (Table 3.3) it appears that the lower Te/\(^{132}\)Xe and U/\(^{132}\)Xe ratios seen in 830 are due to a larger contribution from \(^{132}\)Xe\(_Q\) in NWA 830 compared to NWA 3364M. Concentrations of \(^{131}\)Xe\(^*\) (from Te) and \(^{134}\)Xe\(^*\) (from U) are in fact comparable in 830 and 3364M. It therefore appears that 830 shows trace element chemistry more alike to 3364M than the R3 samples and has not been misclassified.

2. Relict type 3 clasts/chondrules
All the R-chondrites studied here are breccias which indicate they sample a variety of material. NWA 6492 is classed as a R3-6 but metamorphic grade of the clasts analysed here have been well characterised studying the petrology of the samples (carried out by A. Ruzicka) before analysis. NWA 830 is classed as R5 but it is conceivable that less metamorphosed material may be present in small quantities. The size of samples used in this study was about ~1mm diameter. Chondrules can occur as relict objects in R5 material (Bischoff et al., 2011) and chondrules as large as ~3 mm have been found (Bischoff et al., 2011). If primitive material was present in NWA 830 in the form of relict chondrules, this may explain the higher concentrations of a primitive trapped component. However, even if a chondrule was present, the iodine signature of the R5 surrounding material should still be visible. Figure 3.11 shows the isochron plot of 830 from Figure 3.8, but with the isochron from sample 3364M added. Four data from 830 appear to fall on the 3364M isochron, so this may be the iodine signature of the R5 material, though only four data forming an isochron is not convincing. Fitting an isochron to the four data points gives an I-Xe age of 4548 ± 9. This agrees with the age of 3364M but the large errors do not allow distinction from the I-Xe ages of the other samples.

3. Higher stage of shock of NWA 830
NWA 830 has experienced more shock than the other samples and shock veins were observed by Bischoff et al. (2011). Shock compression of minerals can alter I-Xe isochrons by implanting low-temperature \(^{128}\)Xe\(^*\) (from iodine) from less retentive sites into more retentive sites independent of thermal properties. This can produce pseudotrapped components with \(^{132}\)Xe/\(^{129}\)Xe ratio above the planetary components (Caffee et al., 1982). Sample 830 shows an elevated \(^{132}\)Xe\(_Q\)/\(^{129}\)Xe ratio indicating that shock has disturbed the I-Xe system in this sample. The larger errors on the I-Xe age of
NWA 830 also indicate disturbance to the I-Xe system as the data do not form a well-defined isochron.

Of the above hypotheses the most simple and most likely explanation is that the I-Xe system in NWA 830 has been affected by shock resulting in an erroneously old I-Xe age.

**Figure 3.11.** The isochron plot of NWA 830 reproduced from Figure 3.8 but with the isochron of NWA 3364M added. Four 830 data (circled) appear to fall on the 3364M isochron.

### 3.5.3. I-Xe ages compared to reported ages of R-chondrites

The chronology of the R-chondrite parent body is not well known. Few studies have been carried out on R-chondrites using geological chronometers and the majority have focussed on K-Ar and Ar-Ar dating; systems which are often reset by impact events. Nagao et al. (1999) reported K-Ar ages ranging from 3.9 – 4.2 Gyr for four Antarctic R-chondrites. Dixon et al. (2003) then applied the more accurate Ar-Ar method to four R-chondrites, three of which are regolith breccias. Ar-Ar ages ranged from 4.3-4.47 Ga. Dixon et al. (2003) concluded that this large range of ages was more likely to be explained by resetting of the K-Ar system by an impact after brecciation of the R-chondrite parent body, rather than slow cooling at depth over time for the later samples.
These relatively young ages (<4.5 Gyr) imply that the K-Ar system can tell us little about the formation history of the R-chondrite body. The I-Xe ages reported here are older than the Ar-Ar ages suggesting that a late impact event reset the K-Ar system on the R-chondrite parent body, but temperatures reached were not sufficiently high to reset the I-Xe clock.

The Mn-Cr system has also been used to date R-chondrites. Sugiura and Miyazaki (2006) measured Mn/Cr ratios in two R-Chondrites: NWA 753 (R3.9) and Sahara 99531 (R3-5). If petrologic types of the samples analysed by Sugiura and Miyazaki (2006) are compared to those here, NWA 753 should have experienced a similar extent of metamorphism to sample H3 from NWA 6492 whilst Sahara 99531 may contain material that covers the whole range of sample studied here. Mn-Cr ages were quoted with respect to LEW 86010, which has an absolute Pb-Pb age of 4557.8 ± 0.5 Myr (Lugmair and Galer, 1992). Reported ages were 4559.87 Myr for olivine in NWA 753 and 4562.02 and 4552.79 (lower limit) Myr for two chondrules in Sahara. The different ages in the two chondrules from Sahara has been attributed to prolonged metamorphism. The Mn-Cr age of ~4562 Myr may therefore be inferred to date R3 material while the later ~4553 Myr age dates the more metamorphosed material.

If the early ages of L3 (High-T) and M3 do date chondrules then the I-Xe ages reported here of chondrules that have experienced limited metamorphism range from 4559 to 4554 Myr. This time interval is slightly later (~3 Myr) than Mn-Cr ages of unmetamorphosed olivine and chondrules in NWA 753 (R3.9) and Sahara 99531 (R3). The Mn-Cr age attributed to metamorphism in Sahara 99531 falls within the I-Xe ages of metamorphism (4555 – 4546 Myr), though at the earlier end.

It therefore appears absolute ages obtained using the I-Xe system give younger ages than those obtained using the Mn-Cr system in R-chondrites. As both systems date silicate minerals this is not expected. Busfield et al. (2008) compared the I-Xe and Mn-Cr chronometers in enstatite chondrites and found that enstatite chondrites consistently gave Mn-Cr ages ~2 Myr younger than I-Xe ages when both systems were calibrated by Pb-Pb ages of LEW 86010 and Shallowater. Shukolyukov and Lugmair (2004) proposed that the $^{53}$Mn/$^{55}$Mn ratio in the early Solar System exhibited radial heterogeneity and that a correction factor should be applied to allow comparison of Mn-Cr ages of chondrites that formed at different distances from the Sun. When Busfield et
al. (2008) applied this correction factor to initial Mn ratios of enstatite chondrites, the correlation between I-Xe and Mn-Cr ages dramatically increased, supporting the hypothesis.

Birck et al. (1999) argued that manganese was initially homogenous and that the data can be explained by differences in the volatilities of Mn and Cr. Trinquier et al. (2008) revisited the Mn-Cr system in meteorites and reported very little variation in $^{53}\text{Cr}/^{52}\text{Cr}$ ratios in all inner Solar System material ($\varepsilon^{53}\text{Cr} \approx 0.2$, where $\varepsilon$ is 1 part in $10^4$) with ordinary chondrites and angrites showing lower $\varepsilon^{53}\text{Cr}$ values than reported by Shukolyukov and Lugmair (2004) and consistent with enstatite chondrites. They argued there was therefore no need for a heliocentric gradient for $^{52}\text{Cr}$ in the early Solar System.

Enstatite chondrites (the most reduced group of chondrites) are thought to have formed closer to the Sun than ordinary chondrites and angrites. The highly oxidised nature of the R-chondrites suggests that they formed at greater distances. If the differences between Mn-Cr and I-Xe ages observed in enstatite chondrites by Busfield et al. (2008) are due to the heterogeneity of $^{53}\text{Mn}$, it follows that samples that formed further away from the Sun than LEW 86010 would have incorporated more $^{53}\text{Mn}$ than angrites and show old Mn-Cr ages compared to I-Xe ages. This may explain the older Mn-Cr ages of R-chondrites seen here and add further support to the idea of radial heterogeneity of $^{53}\text{Mn}$ in the early Solar System. However, it must be remembered that the Mn-Cr and I-Xe ages compared here do not date the same meteorites so differences in age may be due to variations in samples. To test this hypothesis and further examine the coherency between the Mn-Cr and I-Xe chronometers, I-Xe and Mn-Cr analyses should be carried out on mineral separates from the same R-chondrite material.

3.5.4. I-Xe ages of R-chondrites compared with other chondrites

The I-Xe ages of metamorphism on the R-chondrite parent body and earlier ages inferred to date unprocessed material (possibly dominated by chondrules) reported in his work are compared with I-Xe ages reported for components from ordinary and enstatite chondrites in Figure 3.12.

Closure to Xe loss in chondrules on the R-chondrite parent body appears to have begun later (<4560 Myr) than on the ordinary chondrite or enstatite chondrite parent bodies. The ages of metamorphosed clasts in R-chondrites also postdate clasts and mineral
separates from ordinary and enstatite chondrites except in the case of phosphates from Kernouve (H6), Modoc (L6) and Walters (L6) and chondrules from Krymka (LL3.2), Bishunpur (LL3.15) and Chainpur (LL3), though the later Chainpur ages have been attributed to shock (Swindle et al. 1991) and the large spread in Krymka ages (~20 Myr) has been attributed to resetting events prior to accretion (Filtness, 2009). The results therefore appear to suggest that the R-chondrite parent body closed to xenon-loss later than ordinary and enstatite chondrite parent bodies.

Later closure to xenon-loss could be produced by later accretion of the R-chondrite parent body. As discussed earlier, the oxidised nature of the R-chondrites suggests they formed at greater heliocentric distances than enstatite or ordinary chondrites. The density of the cloud of dust and gas that material condensed from in the early Solar System is thought to decrease with distance from the Sun. Therefore there may have been less material available where the R-chondrite parent body formed leading to slower accretion time.

Carbonaceous chondrites show similar oxidation states to R-chondrites, suggesting they formed in the same region of the Solar System. If the above hypothesis is true, one may therefore expect to see slower accretion of the carbonaceous parent body as well. However, I-Xe ages of magnetite show that aqueous alteration was occurring in carbonaceous chondrites from ~4565 Myr (Pravdivtseva et al., 2003).

If the R-chondrite parent body did accrete at the same rate as those of other chondrites, later closure to Xe-loss could have been produced by slower cooling. This implies a larger parent body of the R-chondrites than those of ordinary and enstatite chondrites.
Chapter 3 – Constraining the Thermal History of the R-chondrite Parent Body

Figure 3.12. I-Xe ages of chondrules and metamorphism in R-chondrites (this work) compared with I-Xe ages of other chondrite components available in the literature. Absolute ages have been calculated from the age of Shallowater of 4562.3 ± 0.3 Myr (Gilmour et al., 2009). Parnallee (Gilmour et al., 2000); Barwell (Hutchison et al., 1988; Gilmour et al., 2000; Filtness, 1999); Indarch and Khairpur (Busfield et al., 2008); Ste. Marguerite phosphate, Modoc phosphate, Walters phosphate, H4 feldspar, Richardton feldspar (Brazzle et al., 1999); Monahans halite and Kernouve phosphate (Busfield et al., 2004), Richardton pyroxene (Pravdivtseva et al., 1998); Richardton and Parnallee chondrules (Gilmour et al., 2000), Semarkona chondrules (Swindle et al., 1991), Chainpur chondrules (Swindle et al., 1991; Holland et al., 2005); Bishunpur, Krymka and Barwell chondrules (Filtness, 2009); Qingzhen and Kota Kota chondrules (Whitby et al., 2002).
3.6. Summary

- Xe components in R-chondrites are consistent with Q-Xe with a small contribution from spontaneous fission of $^{244}$Pu to the heavy isotopes. No significant contribution from spallation-Xe was observed. A contribution from terrestrial atmosphere is expected to also be present but absolute amounts could not be determined.

- Higher concentrations of $^{131}$Xe* (attributed to Te) and $^{134}$Xe* (attributed to neutron capture on $^{235}$U) were measured in the more metamorphosed (R5) samples. This is not well understood and may result from difficulties in comparing samples from different meteorites that have been prepared separately.

- $^{129}$Xe* correlated with iodine was seen in all samples. The R-chondrite parent body therefore incorporated $^{129}$I during formation which decayed to $^{129}$Xe*.

- The anomalous “old” I-Xe age obtained for NWA 830 (R5) has been attributed to the effects of shock.

- I-Xe ages appear to vary with extent of metamorphism. The most primitive sample closed to xenon-loss ~8 Myr before the most metamorphosed samples. This supports the theory that different metamorphic grades of R-chondrite material are produced by thermal metamorphism in an onion-shell model that remained undisturbed throughout thermal processing. However, I-Xe analyses of more samples including R5-6 material from NWA 6492 are needed to confirm this.

- Closure to Xe loss in chondrules on the R-chondrite parent body is thought to have occurred between 4559 – 4554 Myr. This is unlikely to date chondrule formation.

- Differences between Mn-Cr ages and I-Xe ages of chondrule formation in R-chondrites could support the ideal of radial heterogeneity of $^{53}$Mn in the early Solar System. However differences could also be due to variation in the samples analysed. Further analyses of I-Xe and Mn-Cr ages in mineral separates from the same R-chondrite are needed to support this hypothesis.

- Closure to xenon-loss on the R-chondrite parent body appears to have occurred later than on the ordinary and enstatite parent bodies. This implies either later accumulation or slower cooling in a larger body.
CHAPTER 4. IODINE AND XENON IN THE FIRST BASALTS

4.1. Introduction

Eucrites are basaltic meteorites thought to originate on the proto-planet Vesta (discussed in Chapter 1). Several basaltic achondritic meteorites that show major element chemistry and mineralogy similar to eucrites deviate from the HED oxygen isotope mass fractionation line (Figure 1.3). This suggests they either originated on a separate parent body (Scott et al., 2009) or that Vesta (and its family of Vestoids) retain some heterogeneity (Wiechert et al., 2004).

Xe studies of eucrites have previously concentrated on Pu–Xe dating, with spallation and fission xenon components of eucrites examined by Park and Nagao (2005), Miura et al. (1998) and Shukolyukov and Begemann (1996a). Pu–Xe ages showed good agreement with Sm–Nd and Pb–Pb and the oldest Pu–Xe ages of ~4.56 Gyr are thought to date crystallisation. Eucrites are therefore thought to have formed early in Solar System history. Shukolyukov and Begemann (1996a) reported excesses of $^{129}$Xe* in several eucrites. The I–Xe system is investigated here in two eucrites (Juvinas and Béréba) and two anomalous eucritic meteorites (Bunburra Rockhole and Ibitira) that may or may not have originated on Vesta, to test whether this $^{129}$Xe excess is derived from $^{129}$I and to compare volatile contents.

Ibitira and Bunburra Rockhole have both been classed as anomalous eucrites due to their anomalous oxygen isotope ratios (Figure 1.3) (Wiechert et al., 2004; Bland et al., 2009). They are quite different from each other; mineral compositions in Ibitira are very uniform (Wilkening and Anders, 1975) suggesting that the elements have been redistributed homogenously throughout the rock, probably during a heating event, whereas Bland et al. (2009) reported variation in oxygen isotope composition between lithologies in Bunburra Rockhole indicating it is unequilibrated. Ibitira is also unusual in that it contains vesicles, indicating rapid cooling close to the surface.

Ibitira and Juvinas were chosen as Xe isotopes reported by Shukolyukov and Begemann (1996a) indicated large excesses of $^{129}$Xe* ($^{129}$Xe/$^{132}$Xe$^{\text{AIR}} > 1.5$). Béréba was included as its reported $^{129}$Xe/$^{132}$Xe ratio is much lower (~1) which will enable investigation of $^{129}$Xe loss/late closure to xenon on Vesta. Bunburra Rockhole is of interest as its descent was observed and recorded by the Desert Fireball Network and numerical modelling...
suggests it originated in the inner main belt and most likely came from a V–type asteroid (Bland et al., 2009). V–type asteroids show emission spectra similar to Vesta; this, along with shared orbital characteristics, suggests that V–type asteroids may have been blasted off the surface on Vesta during an impact. Triangulation methods were used to determine the landing site of Bunburra Rockhole (Bland et al., 2009) enabling a quick recovery. This means Bunburra Rockhole has experienced very little terrestrial weathering. No measurements of Xe in Bunburra Rockhole have previously been made.

Samples of Ibitira, Juvinas and Béréba were provided by the Natural History Museum, London. Bunburra Rockhole was provided by the sample curator of the Desert Fireball Network. Masses of samples analysed are given in Tables 4.1 and 4.2. The Xe isotopic data for the samples studied here are given in appendix III.

4.2. Results

4.2.1. Xenon components in eucritic meteorites

The first 2–3 temperature steps in each sample produced large amounts of hydrocarbons which affected xenon measurements. These data are therefore excluded from further discussion. Large amounts of $^{131}$Xe released from irradiated samples, produced by neutron–capture on barium during neutron irradiation, meant smaller increases in heating–temperature had to be made between each heat–step (compared to unirradiated samples) in order keep signal heights at an appropriate level. This affected the precision of the irradiated data, as discussed in Chapter 2.

Initially, the data appear to show a mix of spallation xenon, fission xenon, a trapped component consistent with planetary–xenon or atmospheric–xenon (Figures 4.1 and 4.2) Excesses of $^{129}$Xe (discussed later) are usually measured over a trapped component such as terrestrial atmosphere or Q–Xe. So to establish whether the excesses here are real the contributions from other components (spallation and fission) must be determined. The approach to data employed here to untangle these components is discussed below. Table 2.2 in Chapter 2 shows which components contribute to each isotope in unirradiated and irradiated samples.
Figure 4.1. 3–isotope plot of $^{126}$Xe, $^{124}$Xe and $^{130}$Xe in unirradiated samples. Compositions of spallation produced by pure Ba, a chondritic mix of Ba/REE and pure REE (Hohenberg et al., 1981) are shown along with compositions of Q–Xe (Busemann et al., 2000) terrestrial atmosphere and solar wind (from Wieler, 2002). Data show mixing between a trapped component and a spallation endmember consistent with the chondritic mix of Ba and REE. The trapped component only contributes at low heating–temperatures except in Ibitira.

Figure 4.2. 3–isotope plot of $^{136}$Xe, $^{134}$Xe and $^{132}$Xe in unirradiated samples. The composition of terrestrial atmosphere (Wieler, 2002), spallation from a chondritic mix of Ba and REE (Hohenberg et al., 1981) are shown along with spontaneous fission of $^{244}$Pu and $^{238}$U endmembers (Ozima and Podosek, 1983). Data appear to show mixing between atmospheric xenon and fission of $^{244}$Pu with little contribution from spallation.
Spallation xenon is produced by reactions on barium and rare earth elements by cosmic rays. Exposure of meteorites to cosmic rays can produce all isotopes of xenon (except $^{136}$Xe) but the excesses are most noticeable in the lighter, less abundant, xenon isotopes. Also these isotopes are not produced by fission. Therefore the lighter xenon isotopes ($^{124,126,130}$Xe) are expected to be composed of a mixture of a trapped component and a spallation component. Hohenberg et al., (1981) determined spallation xenon isotopic compositions for pure Ba, pure REE and a “chondritic” mixture of Ba/REE using data from Angra dos Reis (angrite). These compositions are used here as reference endmembers for spallation xenon.

Here, the light isotopes show mixing between a spallation component and a trapped component (the data do not allow distinction between terrestrial atmosphere, Q–Xe or solar wind) (Figure 4.1). Bunburra Rockhole, Juvinas and Béréba data cluster around the pure–Ba end−member whilst Ibitira data show a more defined mixing line between the trapped component and the spallation end−members. This suggests that Ibitira contains a higher concentration of trapped xenon. High temperature data for all samples plot close to the spallation endmembers. Low temperature data from Ibitira and Juvinas plot within error of a trapped composition whilst Bunburra Rockhole and Béréba do not. The exact temperatures associated with the laser powers used here are not known, however a step−heating experiment on the eucrite Pomozdino (Shukolyukov and Begemann, 1996b) showed <2% of spallation $^{124}$Xe was released at temperatures lower than 900°C with the majority (>50%) released above 1100°C.

Differences between samples in the lighter xenon isotope ratios could be due to different lengths of exposure to cosmic rays (cosmic ray exposure age). Strashnov et al. (submitted) measured Kr−Kr cosmic ray exposure ages in several eucrites including the meteorites studied here. The results are as follows: Bunburra Rockhole 27.6 ± 1.4 Myr, Ibitira 13.3 ± 0.7 Myr, Juvinas 11.9 ± 0.5 Myr, Béréba 25.0 ± 2.1 Myr. The latter three ages are consistent with previous Kr−Kr ages. Bunburra Rockhole and Béréba have comparable CRE ages, >10 Myr longer than those of Juvinas and Ibitira. Their longer exposure ages may explain why Bunburra Rockhole and Béréba data falls further away from a trapped component.

Ibitira and Juvinas have comparable CRE ages but whilst Juvinas data show two distinct groups (close to the spallation end−member at high−temperature and at the trapped
Chapter 4 – Iodine and Xenon in the First Basalts

composition at low–temperature) Ibitira data define a mixing line between spallation and trapped–Xe. As both samples have CRE ages within error of each other, this release pattern may be better explained by a larger contribution from a trapped component to Ibitira that is released at all temperatures.

Bunburra Rockhole, Juvinas and Béréba only show a trapped component at low–temperatures. This is consistent with the release of adsorbed terrestrial atmosphere. It therefore appears reasonable to assume that low–temperature releases of a trapped component are due to adsorption of atmospheric–Xe in these samples, though Ibitira may also retain a separate trapped component.

The heavy xenon isotopes ($^{132,134,136}\text{Xe}$) are expected to be dominated by fission xenon and a trapped component. The data in Figure 4.2 appear to be consistent with mixing between terrestrial atmosphere and a spontaneous fission end–member with no obvious modification by spallation–xenon. The errors on the data do not enable distinction between $^{238}\text{U}$ and $^{244}\text{Pu}$ as the source of spontaneous fission. Typically $^{130}\text{Xe}$ or $^{131}\text{Xe}$ would be used to help distinguish whether the fission–Xe is derived from Pu or U, but contributions from spallation make this difficult here. However, eucrites are ancient meteorites and $^{244}\text{Pu}$ decay is expected to dominate before 4.4 Gyr (Turner et al., 2004) so the fission–Xe in these data has been attributed to $^{244}\text{Pu}$. Previous work has also identified Pu as the major source of fission Xe based on the expected ancient formation ages of meteorites from Vesta (Park and Nagao, 2005; Miura et al., 1998; Shukolyukov and Begemann, 1996a). Again, only low temperature releases are dominated by the trapped component.

Figure 4.1 showed that spallation is the dominating component at high–temperatures however the data in Figure 4.2 can be explained by mixing between terrestrial atmosphere and spontaneous fission of $^{244}\text{Pu}$ with no need for a contribution from spallation. Therefore the presence of a spallation component may be “hidden” in Figure 4.2 due to the presentation of the data (the mixing lines between spallation and fission and atmosphere and fission lie almost on top of each other). The relationship between the three components (terrestrial atmosphere, Pu fission and spallation) is best explained in Figure 4.3 which shows a three–isotope diagram for $^{130}\text{Xe}$ (dominated by spallation), and $^{134}\text{Xe}$ and $^{136}\text{Xe}$ (dominated by fission).
Figure 4.3. Three isotope plot of $^{134}\text{Xe}$, $^{130}\text{Xe}$ and $^{136}\text{Xe}$ in unirradiated samples of Bunburra Rockhole (left) and Ibitira, Juvinas and Béréba (right). Bunburra Rockhole data has been plotted separately for clarity. The compositions of terrestrial atmosphere (Wieler, 2002) and spallation from a chondritic mix of Ba and REE (Hohenberg et al., 1981) are shown. The thin dashed-line is the mixing line between Pu fission and a spallation endmember based on the $^{134}\text{Xe}/^{130}\text{Xe}$ ratio of the chondritic mix of Ba/REE (Hohenberg et al., 1981). Spallation does not contribute to $^{136}\text{Xe}$ (Hohenberg et al., 1981) so $^{134}\text{Xe}/^{136}\text{Xe}$ and $^{130}\text{Xe}/^{136}\text{Xe} = \infty$. Low-temperature releases are dominated by trapped–fission mixing whilst high-temperature releases consist of spallation–fission mixing.
Figure 4.3 shows low–temperature xenon is consistent with terrestrial atmosphere and then evolves towards the fission–spallation mixing line. The spallation/fission ratio of the xenon increases with increasing temperature. Bunburra Rockhole data show a more constrained fission/spallation ratio compared to the other samples. Terrestrial atmosphere, spallation–Xe and fission–Xe therefore contribute at all temperatures. However, the data are dominated by mixing between atmospheric–Xe and fission–Xe at lower–temperatures and mixing between fission–Xe and spallation–Xe at higher–temperatures.

In order to resolve whether excess $^{129}\text{Xe}$ is present in these samples the quantity of atmospheric $^{129}\text{Xe}$ released from each temperature step must be determined. As discussed above, the samples contain fission–xenon from $^{244}\text{Pu}$, a spallation component and a trapped component that has been attributed to contamination by terrestrial atmosphere. Usually un-mixing of xenon components is carried out by applying the lever rule to a two–component system. The only isotopes of xenon composed of just two components are the lighter isotopes ($^{124,126,130}\text{Xe}$), which contain spallation and atmospheric–Xe, and $^{136}\text{Xe}$, which contains Pu–fission and atmospheric–Xe. As $^{124}\text{Xe}$ and $^{126}\text{Xe}$ are released in small quantities compared to the other isotopes (total amounts of $^{132}\text{Xe}$ are around a factor of 10 larger than total amounts of $^{126}\text{Xe}$) they are not ideal reference isotopes. $^{136}\text{Xe}$ is released in relatively large quantities but there is not another isotope composed only of fission and atmospheric–Xe, as spallation contributes to the other heavy isotopes as has been shown in Figure 4.3.

Therefore three–component mixing of atmospheric–Xe, spallation and fission seems a more appropriate way to treat the data. This requires use of matrices to untangle the components. Three isotopes were chosen based on the size of their releases of xenon and their components: $^{130}\text{Xe}$ (spallation and atmosphere), $^{132}\text{Xe}$ (spallation, fission and atmosphere) and $^{134}\text{Xe}$ (spallation, fission and atmosphere) and referenced to $^{132}\text{Xe}$, as it produced the largest releases. The chondritic mix of Ba and REE (Hohenberg et al., 1981) was chosen for the spallation endmember as it best reflected the data (Figure 4.1).
The total amounts of $^{130}$Xe, $^{132}$Xe and $^{134}$Xe released from each heat-step consist of:

$^{130}$Xe$_{\text{TOTAL}} = (x \times ^{130}\text{Xe}_{\text{AIR}}) + (y \times ^{130}\text{Xe}_{\text{SPALL}}) + (z \times ^{130}\text{Xe}_{\text{Pu}})$

$^{132}$Xe$_{\text{TOTAL}} = (x \times ^{132}\text{Xe}_{\text{AIR}}) + (y \times ^{132}\text{Xe}_{\text{SPALL}}) + (z \times ^{132}\text{Xe}_{\text{Pu}})$

$^{134}$Xe$_{\text{TOTAL}} = (x \times ^{134}\text{Xe}_{\text{AIR}}) + (y \times ^{134}\text{Xe}_{\text{SPALL}}) + (z \times ^{134}\text{Xe}_{\text{Pu}})$

Where $x + y + z = 1$.

The following compositions of atmospheric–Xe, spallation–Xe (a chondritic ratio of Ba/REE) and fission–Xe ($^{244}$Pu) were used and normalised to $^{132}$Xe to build a matrix (M) shown below:

<table>
<thead>
<tr>
<th></th>
<th>$^{130}$Xe/$^{132}$Xe</th>
<th>$^{132}$Xe/$^{132}$Xe</th>
<th>$^{134}$Xe/$^{132}$Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric–Xe</td>
<td>0.151</td>
<td>1</td>
<td>0.388</td>
</tr>
<tr>
<td>Spallation–Xe</td>
<td>1.181</td>
<td>1</td>
<td>0.053</td>
</tr>
<tr>
<td>$^{244}$Pu fission</td>
<td>0</td>
<td>1</td>
<td>1.041</td>
</tr>
</tbody>
</table>

The inverse ($M^{-1}$) of this matrix (M) was then taken, where:

$$
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
= M \times M^{-1}
$$

The measured isotope ratios for each heat-step are then multiplied by $M^{-1}$.

$$
\begin{align*}
^{130}\text{Xe}_{\text{M}}/^{132}\text{Xe}_{\text{M}} &= 1 \times M^{-1} \times x \\
^{132}\text{Xe}_{\text{M}}/^{132}\text{Xe}_{\text{M}} &= 0 \times M^{-1} \times y \\
^{134}\text{Xe}_{\text{M}}/^{132}\text{Xe}_{\text{M}} &= 0 \times M^{-1} \times z
\end{align*}
$$

Thereby $x$, $y$ and $z$ can be solved for each release.

Using Q–Xe rather than the composition of atmospheric–Xe produces no significant difference, with calculated numbers of atoms of $^{132}$Xe$_{\text{TRAPPED}}$ within error of each other.

Now that contributions from the various components have been disentangled, the presence of any excess $^{129}$Xe* can be examined. Figure 4.4 shows $^{129}$Xe and $^{132}$Xe (both corrected for a spallation component consistent with a chondritic ratio of Ba/REE) normalised to $^{136}$Xe. The data should therefore be consistent with mixtures of trapped–Xe, Pu–fission and any excess $^{129}$Xe*. All data show evidence for some $^{129}$Xe* though
Bunburra Rockhole and Ibitira show the larger excesses of $^{129}\text{Xe}^*$ than Béréba and Juvinas across the majority of gas releases, with very large $^{129}\text{Xe}/^{136}\text{Xe}$ ratios observed in some Ibitira releases. Juvinas show excesses of $^{129}\text{Xe}^*$ released with a pure fission component, suggesting iodine (if that is the source of the $^{129}\text{Xe}^*$) may be hosted along with Pu.

![Figure 4.4. 3–isotope plot for $^{132}\text{Xe}$, $^{129}\text{Xe}$ (both corrected for a contribution from spallation) normalised to $^{136}\text{Xe}$. The data are therefore a mixture of trapped–Xe, fission of $^{244}\text{Pu}$ and any excess $^{129}\text{Xe}^*$ present. All samples show some $^{129}\text{Xe}^*$. Juvinas shows excess $^{129}\text{Xe}^*$ released with a pure–Pu component. Bunburra and Ibitira show larger contributions from $^{129}\text{Xe}^*$ across all releases than Juvinas and Béréba, with Ibitira also producing large $^{129}\text{Xe}/^{136}\text{Xe}$ ratios at low–temperatures with $^{132}\text{Xe}/^{136}\text{Xe}$ consistent with a trapped component.](image)

The anomalous eucrites Bunburra Rockhole and Ibitira therefore appear to show larger excesses of $^{129}\text{Xe}^*$ compared to Juvinas and Béréba. If this is due to differences in age (i.e. $^{129}\text{Xe}^*$ is from in situ decay of $^{129}\text{I}$) one may expect to see a relationship between $^{129}\text{Xe}^*$ and $^{136}\text{Xe}_{\text{Pu}}$ as both are produced over time and share similar chemistry, both being incompatible elements and expected to partition into the melt phase (though it must be noted than iodine is a volatile element and Pu is not so they may exhibit different chemical behaviour). This has been hinted at in the Juvinas data in Figure 4.4 where $^{129}\text{Xe}^*$ is released at the pure-Pu $^{132}\text{Xe}/^{136}\text{Xe}$ composition. Figure 4.5 shows
\(^{129}\text{Xe}^*\) (from iodine, corrected for air and spallation) and \(^{136}\text{Xe}^*\) (from Pu, corrected for air) normalised to \(^{132}\text{Xe}_{\text{AIR}}\). Samples all show a correlation between \(^{136}\text{Xe}_{\text{Pu}}\) and \(^{129}\text{Xe}^*\) though it is not well defined. The \(^{129}\text{I}/^{244}\text{Pu}\) ratios associated with these correlations are higher in the anomalous eucrites than in Juvinas and Béréba. This may suggest the anomalous eucrites are older, as \(^{129}\text{I}\) has a shorter half–life than \(^{244}\text{Pu}\). However, iodine is much more volatile than plutonium. Therefore higher iodine/plutonium ratios may be a result of formation on a more volatile rich body, rather than earlier closure to xenon–loss.

Concentrations of total \(^{124}\text{Xe}_{\text{Spallation}},^{129}\text{Xe}^*,^{132}\text{Xe}_{\text{AIR}}\text{ and }^{136}\text{Xe}_{\text{Pu}}\) are given in Table 4.1, calculated using the matrix method described above. Also shown are concentrations for Ibitira, Juvinas and Béréba from Xe isotope ratios reported by Shukolyukov and Begemann (1996a) (in italics) calculated using the same matrix method as part of this work. Concentrations of \(^{124}\text{Xe}_{\text{Spallation}}\) and \(^{129}\text{Xe}^*\) measured as part of this study agree well with the reported data. Concentrations of \(^{136}\text{Xe}_{\text{Pu}}\) are quite consistent with Shukolyukov and Begemann (1996a) for Juvinas and Béréba however Ibitira concentrations are much smaller. The large variation (~50\%) seen in the two samples of Ibitira measured here suggests that Pu may not be evenly distributed in Ibitira. Pu is geochemically similar to rare earth elements (Lugmair and Marti, 1977), the main carriers of which are phosphates. Phosphates in eucrites are known to be heterogeneously distributed (Hsu and Crozaz, 1996). This heterogeneity may explain the differences between concentrations of \(^{136}\text{Xe}_{\text{Pu}}\) measured here and by Shukolyukov and Begemann (1996a).

The concentration of \(^{132}\text{Xe}_{\text{AIR}}\) released from Ibitira agrees quite well with the concentration measured by Shukolyukov and Begemann (1996a). However, concentrations of \(^{132}\text{Xe}_{\text{AIR}}\) in Juvinas and Béréba reported here are a factor of 10 smaller than those measured by Shukolyukov and Begemann (1996a). The release pattern of trapped Xe from Ibitira has been shown to differ from the other samples (Figure 4.1). As proposed earlier, this difference could be produced by incorporation of terrestrial atmospheric–Xe into Bunburra Rockhole, Juvinas and Béréba with no/little other trapped component whilst Ibitira contains a trapped–Xe component not present in the other samples. If Ibitira does contain a reproducible trapped–Xe component this may explain why similar concentrations of \(^{132}\text{Xe}_{\text{TRAPPED}}\) are seen here and in the results reported by Shukolyukov and Begemann (1996a). Variations between concentrations of
Figure 4.5. 3–isotope plots of $^{129}$Xe* (corrected for spallation and air), $^{136}$Xe* (corrected for air) and $^{132}$Xe$_{AIR}$ (corrected for spallation and fission contributions) for unirradiated samples of Bunburra Rockhole, Ibitira and Béréba (left) and Juvinas (right). Samples show $^{136}$Xe (from Pu fission) and $^{129}$Xe* (possibly from $^{129}$I). $^{129}$Xe correlates with $^{136}$Xe suggesting a chronological significance as both $^{244}$Pu and $^{129}$I are produced over time. However higher $^{129}$Xe/$^{136}$Xe ratios could also be due to formation on a more volatile rich parent body. Dotted lines are guidelines to the Pu/I trends defined by the data, not fits. High ratios in Juvinas data are thought to be due to small amounts of $^{132}$Xe$_{AIR}$. 
In other samples, the concentration of atmospheric–Xe adsorbed into samples during their terrestrial residence time. An alternative explanation is that the varying concentrations are an artefact of the experimental processes used. These analyses used laser extraction to release xenon from small (<5 mg) samples whereas Shukolyukov and Begemann (1996a) applied a furnace extraction technique to larger (100–500 mg) samples.

Table 4.1. Concentrations of $^{124}$Xe$_{Spallation}$, $^{129}$Xe*, $^{132}$Xe$_{Air}$ and $^{136}$Xe$_{Fission}$ in unirradiated samples. Values in italics were calculated from reported Xe isotope ratios from Shukolyukov and Begemann (1996a). Errors on RELAX measurements are ~5%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>$^{124}$Xe$_{Spallation}$</th>
<th>$^{129}$Xe*</th>
<th>$^{132}$Xe$_{Trapped}$</th>
<th>$^{136}$Xe$_{Pu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bunburra Rockhole 1</td>
<td>1.0</td>
<td>0.6</td>
<td>5.1</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Bunburra Rockhole 2</td>
<td>1.8</td>
<td>1.1</td>
<td>7.5</td>
<td>6.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Bunburra Rockhole 3</td>
<td>3.1</td>
<td>1.1</td>
<td>6.3</td>
<td>4.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Bunburra Rockhole 4</td>
<td>3.4</td>
<td>1.2</td>
<td>6.6</td>
<td>5.2</td>
<td>4.9</td>
</tr>
<tr>
<td>Ibitira 1</td>
<td>1.6</td>
<td>0.6</td>
<td>8.7</td>
<td>5.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Ibitira 1</td>
<td>4.6</td>
<td>0.5</td>
<td>6.6</td>
<td>5.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Juvinas</td>
<td>4.3</td>
<td>0.4</td>
<td>2.7</td>
<td>0.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Béréba</td>
<td>3.4</td>
<td>0.8</td>
<td>2.4</td>
<td>2.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Summary: unirradiated samples

- Excesses seen in the lighter xenon isotopes in all samples are consistent of spallation of a chondritic Ba/REE ratio.
- Bunburra Rockhole and Béréba show larger contributions from spallation. This is most likely to be due to their longer cosmic ray exposure ages (>25 Myr) compared to Ibitira and Juvinas (<15 Myr).
- Heavy xenon isotopes in all unirradiated samples show evidence of fission-Xe. This may be produced by spontaneous fission of $^{244}$Pu or $^{238}$U. However, $^{244}$Pu is thought to dominate in ancient samples such as these. This is consistent with previous reports.
- Bunburra Rockhole, Béréba and Juvinas show a small contribution from a trapped component that is only present in low-temperature releases. This is consistent with adsorption of terrestrial air. Ibitira shows a larger contribution from a trapped component over a larger temperature range.
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- Lower temperature releases are dominated by mixing between trapped–Xe and fission Xe. Higher temperature releases are dominated by mixing between fission–Xe and spallation–Xe.
- All samples show excesses of $^{129}\text{Xe}^*$ which may have been produced from in situ decay of $^{129}\text{I}$.
- Bunburra Rockhole and Ibitira show higher $^{129}\text{Xe}^* /^{136}\text{Xe}^*$ ratios than Juvinas and Béréba.

The next section will address the following questions by investigating the relationship between $^{129}\text{Xe}^*$ and iodine in these samples.

- Was the excess $^{129}\text{Xe}^*$ seen in Bunburra Rockhole, Ibitira and Juvinas produced by in situ decay of $^{129}\text{I}$?
- Are the higher $^{129}\text{Xe}^* /^{136}\text{Xe}^*$ ratios of anomalous eucrites Bunburra Rockhole and Ibitira a result of earlier closure to xenon? Or are they due to formation on a more volatile–rich parent body?

4.2.2. $^{129}\text{Xe}^*$ and iodine in eucritic meteorites.

Samples of Bunburra Rockhole, Ibitira, Juvinas and Béréba were included in irradiation MN11–c (see Chapter 2 for details) to convert $^{127}\text{I}$ to $^{128}\text{Xe}^*$. Samples were then analysed using RELAX and the relationship between $^{129}\text{Xe}$ and $^{128}\text{Xe}^*$ examined. To initially determine whether iodine is present in the samples or not, $^{128}\text{Xe}$ and $^{129}\text{Xe}$ were referenced to $^{130}\text{Xe}$ to see whether $^{129}\text{Xe}$ showed a correlation with $^{128}\text{Xe}$ consistent with an isochron (Figure 4.6). $^{130}\text{Xe}$ was chosen as it does not have a fission component and can only be composed of spallation and air. Usually, when plotting isochrons the non–iodine bearing isotope is corrected for any contributions from spallation or fission etc. Here the $^{130}\text{Xe}$ has not been corrected for spallation contributions as earlier examinations of the data showed that a contribution from atmospheric–Xe is only seen at low temperatures in the lighter isotopes (Figure 4.1), though Ibitira showed a larger contribution across a larger temperature range.

Low–temperature releases for all samples show high $^{128}\text{Xe}/^{129}\text{Xe}$ ratios uncorrelated with $^{130}\text{Xe}/^{129}\text{Xe}$. This could be produced by loss of $^{129}\text{Xe}^*$ at less retentive sites over time or contamination by terrestrial iodine. Higher–temperature releases from all samples fall to the right of the spallation–atmospheric mixing line indicating the presence of $^{127}\text{I}$ in the samples. Béréba $^{130}\text{Xe}/^{129}\text{Xe}$ ratios do not fall below the trapped
composition suggesting an absence of $^{129}$Xe*. However the presence of $^{129}$Xe* in all samples including Béréba has already been demonstrated in Figure 4.4. This points towards contributions from iodine and spallation with little/no trapped Xe, consistent with the results discussed in section 4.2. Figure 4.6 therefore appears to show that the data are forming isochrons that originate at a spallation composition rather than a trapped composition. There is especially strong evidence for this in Bunburra Rockhole and Ibitira data which show well defined trends. Juvinas and Béréba isochrons (if present) are not as coherent.

As the data in Figure 4.6 have not been corrected for a spallation component, the isochron plots do not conclusively show that $^{129}$Xe* is released along with $^{128}$Xe*. Neither do they allow determination of how much excess $^{128}$Xe* and $^{129}$Xe* are present. Figure 4.6 potentially shows three components (atmospheric–Xe, spallation–Xe and iodine) and in order to determine an initial $^{129}$I/$^{127}$I ratio of the sample (via $^{129}$Xe*/$^{128}$Xe) the data must be corrected so that only two components (iodine and usually a trapped component) remain.

For the unirradiated samples a matrix method was used to deconvolute the $^{132}$Xe, which was composed of contributions from air, spallation and spontaneous fission of Pu. In the irradiated samples this process is not so simple. The irradiation process can produce heavy isotopes of xenon ($^{131,132,134,136}$Xe) via neutron capture on $^{235}$U; $^{136}$Xe can also be produced via neutron–capture on $^{135}$Xe during fission of $^{235}$U (Table 2.2.).

Figure 4.7 shows the irradiated data plotted on the same 3–isotope plot as shown in Figure 4.2. The higher $^{134}$Xe/$^{132}$Xe and $^{136}$Xe/$^{132}$Xe ratios show that there is a bigger contribution from fission xenon in the irradiated samples. This demonstrates that fissiogenic–Xe has been added from neutron–induced fission of uranium. Again, the data tend from a trapped–Xe composition towards a fission end–member and then back towards a spallation component with increasing temperature.
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Figure 4.6. Isochron plots for irradiated samples of (a) Bunburra Rockhole, (b) Ibitira, (c) Juvinas and (d) Béréba. $^{128}\text{Xe}$ and $^{130}\text{Xe}$ are normalised to $^{129}\text{Xe}$. Xe compositions for air and spallation produced by a chondritic mix of Ba and REE are also shown. Bunburra Rockhole, Ibitira and Juvinas show $^{130}\text{Xe}/^{129}\text{Xe}$ ratios lower than air indicating a definite excess of $^{129}\text{Xe}$. An excess of $^{129}\text{Xe}$ in Béréba is dependent on whether a trapped component is present or whether the data show iodine-spallation mixing. Previous results (Figure 4.4) point towards the latter. Bunburra Rockhole and Ibitira data show strong evidence for isochrons produced from iodine and spallation with no trapped component. Juvinas and Béréba show less well defined trends. Dashed lines show isochrons discussed fitted using Method 1 discussed in section 4.2.3.
Figure 4.7. 3–isotope plot of $^{136}$Xe, $^{134}$Xe and $^{132}$Xe in irradiated samples. The compositions of terrestrial atmosphere (Wieler, 2002) and spallation from a chondritic mix of Ba and REE (Hohenberg et al., 1981) are shown along with Xe–endmembers for spontaneous fission of $^{244}$Pu and $^{238}$U, neutron–induced fission of $^{235}$U and complete conversion of $^{135}$Xe to $^{136}$Xe by neutron–capture (Ozima and Podosek, 1983). Data show higher $^{136}$Xe/$^{132}$Xe and $^{134}$Xe/$^{132}$Xe ratios than unirradiated samples indicating the addition of xenon from neutron–induced fission of uranium. Irradiated data show a trend from trapped–Xe, to fission–Xe to spallation–Xe with increasing temperature.

So, whilst in the unirradiated samples $^{132}$Xe was composed of three components (air, spallation and fission of Pu) in the irradiated samples there are now four components with the addition of uranium fission. Previously $^{136}$Xe, $^{132}$Xe and $^{134}$Xe were used to untangle the different components. With the addition of uranium fission, four isotopes are now needed. However neutron–capture on $^{135}$Xe contributes to $^{136}$Xe, neutron–capture on barium and /or tellurium contributes to $^{131}$Xe and iodine may contribute to $^{128}$Xe and $^{129}$Xe. This leaves just the light isotopes $^{124}$&$^{126}$Xe that are only present in small amounts and do not contain a fission component. It has hard to distinguish between $^{244}$Pu fission and neutron–fission of $^{235}$U using just $^{132}$Xe/$^{134}$Xe ratios therefore matrix algebra cannot be used to untangle the contributions to xenon in irradiated samples here.
The lighter isotopes contain only two components (spallation and atmospheric–Xe), but have been disregarded from the correction process up until now as they are released in smaller amounts compared to the other isotopes. However other ways of calculating amounts of excess $^{128}\text{Xe}^*$ and $^{129}\text{Xe}^*$ using more abundant isotopes have been exhausted. Amounts of $^{130}\text{Xe}_{\text{AIR}}$ were therefore calculated assuming the $^{124}\text{Xe}/^{130}\text{Xe}$ ratio was produced by mixing between atmospheric–Xe and spallation of a chondritic Ba/REE ratio which has been shown to be true for these samples (Figure 4.1). This produced amounts of atmospheric xenon within error of zero across the majority of releases; again consistent with results discussed earlier that implied a very small contribution from trapped–Xe. These results suggest that $^{130}\text{Xe}$ in these samples is almost completely composed of spallation. Therefore figure 4.6 appears to show mixing between spallation and iodine only (if this is the case then Béréba does show an excess of $^{129}\text{Xe}^*$, in line with the results of the unirradiated sample). If this is true then an age can be defined for each sample from the intercept with the X-axis of a line fitted to the data.

This interpretation of an I–Xe isochron plot is unconventional so in order to clarify the relationship between iodine ($^{128}\text{Xe}^*$), $^{129}\text{Xe}^*$ and spallation ($^{130}\text{Xe}$) the graphs shown in Figure 4.6 are now discussed in terms of concentrations of atoms released at each heat–step, rather than isotopic ratios.

Figure 4.8a shows concentrations (atoms/g) of $^{130}\text{Xe}$ and $^{128}\text{Xe}$ released from each heat–step during analyses of unirradiated samples of Bunburra Rockhole. The data show a single well–defined ratio consistent with a spallation $^{128}\text{Xe}/^{130}\text{Xe}$ ratio with no/very little contribution from air. Concentrations of $^{130}\text{Xe}$ and $^{129}\text{Xe}$ in unirradiated and irradiated Bunburra Rockhole also show a single defined ratio (Figure 4.8b); however it lies above the spallation composition. This could be produced by a contribution from air, however $^{129}\text{Xe}^*/^{132}\text{Xe}_{\text{AIR}}$ and $^{129}\text{Xe}/^{136}\text{Xe}$ ratios of unirradiated samples reported earlier suggest it is due to excess $^{129}\text{Xe}^*$.

To find out whether this $^{129}\text{Xe}^*$ is associated with iodine, concentrations of $^{130}\text{Xe}$ and $^{128}\text{Xe}$ in irradiated samples of Bunburra Rockhole were also examined (Figure 4.8c). The well–defined $^{128}\text{Xe}/^{130}\text{Xe}$ ratio is still there (apart from in some low–temperature releases that show large $^{128}\text{Xe}^*$ excesses) but it has shifted higher up the graph. This shows that $^{128}\text{Xe}^*$ has been produced from iodine during the irradiation. The releases
that produced iodine ($^{128}$Xe*) also produced $^{129}$Xe*. This is compelling evidence for the in–situ production of $^{129}$Xe* from the decay of $^{129}$I in these samples.

The major contributing components to $^{128}$Xe, $^{129}$Xe and $^{130}$Xe in these releases therefore appear to be spallation and iodine with very little or no contribution from a trapped component. This is consistent with the earlier examination of the spallation component that showed a significant contribution from atmospheric-Xe only in low–temperature steps.

Table 4.2. Concentrations (cc STP g$^{-1}$) of $^{124}$Xe$_{spall}$, $^{127}$I, $^{129}$Xe* and $^{132}$Xe$_{trapped}$ in irradiated samples. Errors are ~2%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>$^{124}$Xe$^{spall}$ (cc STP g$^{-1}$)</th>
<th>Iodine (ppb)</th>
<th>$^{129}$Xe* (cc STP g$^{-1}$)</th>
<th>$^{132}$Xe$^{trapped}$ (cc STP g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bunburra Rockhole</td>
<td>3.71</td>
<td>$1.4\times10^{-12}$</td>
<td>0.53</td>
<td>$4.7\times10^{-12}$</td>
<td>$3.4\times10^{-12}$</td>
</tr>
<tr>
<td>Ibitira</td>
<td>3.88</td>
<td>$0.5\times10^{-12}$</td>
<td>1.1</td>
<td>$16.0\times10^{-12}$</td>
<td>$3.4\times10^{-12}$</td>
</tr>
<tr>
<td>Juvinas</td>
<td>4.15</td>
<td>$0.4\times10^{-12}$</td>
<td>0.80</td>
<td>$2.6\times10^{-12}$</td>
<td>$2.7\times10^{-12}$</td>
</tr>
<tr>
<td>Béréba</td>
<td>2.64</td>
<td>$1.3\times10^{-12}$</td>
<td>0.70</td>
<td>$4.5\times10^{-12}$</td>
<td>$5.5\times10^{-12}$</td>
</tr>
</tbody>
</table>

Ibitira, Juvinas and Béréba (Figure 4.9–4.11) showed similar release patterns to Bunburra Rockhole with $^{129}$Xe* released along with iodine–derived $^{128}$Xe* and $^{128}$Xe/$^{130}$Xe ratios consistent with spallation with little contribution from terrestrial air.

The major features of the release patterns of the samples are as follows:

- Ibitira data show high $^{129}$Xe/$^{130}$Xe ratios at low–temperatures. Excesses of $^{129}$Xe* were seen at similar temperatures in unirradiated samples indicating this could be a low–temperature phase containing excess $^{129}$Xe rather than air contamination. $^{128}$Xe/$^{130}$Xe ratios for the same releases are very high (suggesting some terrestrial iodine contamination) and do not correlate with $^{129}$Xe. The $^{128}$Xe*/$^{130}$Xe ratio is well defined.

- Juvinas shows two $^{128}$Xe/$^{130}$Xe and $^{129}$Xe/$^{130}$Xe ratios, both at higher–temperatures indicating a varying (Ba & REE)/I ratio in the host phase(s). Pun and Papike (1996) have reported evidence of REE redistribution in Juvinas pyroxenes. The $^{128}$Xe*/$^{130}$Xe ratios are not as well defined as those of the anomalous eucrites.

- Béréba shows a consistent $^{129}$Xe/$^{130}$Xe ratio but the $^{128}$Xe/$^{130}$Xe is not consistent.
Figure 4.8. Concentrations (atoms/g) of $^{130}$Xe released along with $^{128}$Xe (a and c) and $^{129}$Xe (b) in unirradiated and irradiated samples of Bunburra Rockhole. The number of atoms/g of xenon released for each heat-step are lower in the irradiated sample due to the larger number of heat–steps used. The spallation composition range between pure–Ba and a chondritic mix of Ba and REE is highlighted along with the composition of air. The $^{128}$Xe/$^{130}$Xe ratio of the unirradiated samples is consistent with spallation whilst the $^{129}$Xe/$^{130}$Xe ratio lies above spallation. $^{129}$Xe/$^{132}$Xe$_{Air}$ ratios of unirradiated samples of Bunburra Rockhole point towards this being due to excess $^{129}$Xe* and not atmospheric-Xe (supported by $^{129}$Xe/$^{132}$Xe$_{Air}$ ratios above air in unirradiated samples). The higher $^{128}$Xe/$^{130}$Xe ratio of the irradiated sample shows that iodine is present. This figure demonstrates that excess $^{129}$Xe* is associated with iodine in Bunburra Rockhole.
Figure 4.9. Concentrations (atoms/g) of \(^{130}\)Xe released along with \(^{128}\)Xe and \(^{129}\)Xe in unirradiated and irradiated samples of Ibitira. The number of atoms/g of xenon released for each heat-step are lower in the irradiated sample due to the larger number of heat–steps used. The data define a \(^{128}\)Xe/\(^{130}\)Xe ratio consistent with spallation with minor modification by atmospheric-Xe (a) and show a \(^{129}\)Xe/\(^{130}\)Xe ratio above spallation (b) indicating the presence excess \(^{129}\)Xe* (supported by \(^{129}\)Xe/\(^{132}\)Xe\text{Air} ratios above air in unirradiated samples). High \(^{129}\)Xe/\(^{130}\)Xe ratios are seen at low–temperatures which were not seen in Bunburra Rockhole. The irradiated sample shows large amounts of uncorrelated iodine released at low–temperature (c). Higher temperature steps (d) maintain the correlation seen in (a) but lie above the spallation \(^{128}\)Xe/\(^{130}\)Xe ratio, showing the presence of iodine. \(^{129}\)Xe* is associated with iodine in Ibitira.
Figure 4.10. Concentrations (atoms/g) of $^{130}$Xe released along with $^{128}$Xe and $^{129}$Xe in unirradiated and irradiated samples of Juvinas. The number of atoms/g of xenon released for each heat-step are lower in the irradiated sample due to the larger number of heat–steps used. The data define a $^{128}$Xe/$^{130}$Xe ratio consistent with spallation (a) and show two $^{129}$Xe/$^{130}$Xe ratios, both above spallation (b) indicating the presence excess $^{129}$Xe* (supported by $^{129}$Xe/$^{132}$Xe$_{\text{Air}}$ ratios above air in the unirradiated sample). The irradiated sample shows large concentrations of $^{128}$Xe, uncorrelated with $^{130}$Xe at low–temperatures (c). At higher temperatures data lie above the spallation $^{128}$Xe/$^{130}$Xe ratio showing the presence of iodine. Two $^{128}$Xe/$^{130}$Xe ratios are seen though they are not well defined. $^{129}$Xe* is released with iodine in Juvinas but the $^{128}$Xe*/$^{130}$Xe ratio is not as well constrained as in the anomalous eucrites.
Figure 4.11. Concentrations (atoms/g) of $^{130}$Xe released along with $^{128}$Xe and $^{129}$Xe in unirradiated and irradiated samples of Béréba. The number of atoms/g of xenon released for each heat-step are lower in the irradiated sample due to the larger number of heat-steps used. The data define a $^{128}$Xe/$^{130}$Xe ratio consistent with spallation (a) and show a $^{129}$Xe/$^{130}$Xe ratio above spallation (b) indicating the presence excess $^{129}$Xe* (supported by $^{129}$Xe/$^{32}$Xe$_{Air}$ ratios above air in the unirradiated sample). The irradiated sample shows $^{128}$Xe/$^{130}$Xe ratios above spallation showing iodine is present but there is a lot of scatter and the data do not produce one well defined $^{128}$Xe/$^{130}$Xe ratio (c). $^{129}$Xe* and iodine are released together but a consistent $^{128}$Xe*/$^{130}$Xe ratio is not produced.
4.2.3. Chronological meaning?
A conventional isochron (iodogenic and trapped xenon) has not been seen in these samples with results instead indicating mixing between a pure–spallation and a pure–iodine endmember with an insignificant contribution from a trapped component (Figure 4.6). High resolution step–heating has revealed a correlation between $^{128}\text{Xe}^*$ and $^{129}\text{Xe}^*$ and $^{130}\text{Xe}$, across multiple releases (Figures 4.7–4.11), again consistent with mixing between iodogenic xenon and spallation xenon with very little contribution from a trapped component. Initial $^{129}\text{I}/^{127}\text{I}$ ratios can therefore be determined and I–Xe ages calculated using the data shown (Table 4.3). Two methods have been used to do this:

1. Lines were fitted to the “isochron” plots shown in Figure 4.6, using a York (1969) method to give the $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratio at the intercept with the x–axis. The low–temperature Juvinas and Béreba data produced poor fits. Isochrons produced by Bunburra Rockhole, Ibitira and high-temperature Juvinas data are shown in Figure 4.6.

2. The $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratio of each sample has been calculated using Figures 4.8–4.11. In order to determine the $^{129}\text{Xe}^*/^{128}\text{Xe}^*$ ratio of the pure–iodine endmember the spallation component must be subtracted from the total $^{129}\text{Xe}/^{128}\text{Xe}$ ratio. The initial iodine ratio can then be referenced to the Shallowater standard to calculate a relative age. Though this could be referred to as a “model age” it is more robust as it is derived from not just one measurement, but multiple releases that reproduce the same result.

To do this lines were fitted (York, 1969) to the $^{128}\text{Xe}/^{130}\text{Xe}$ and $^{129}\text{Xe}/^{130}\text{Xe}$ ratios defined by the data for each sample. The lowest temperature data that contained a major contribution from air were excluded from these fits. The $^{128}\text{Xe}/^{130}\text{Xe}$ ratio of the unirradiated data (the spallation component) was then subtracted from the $^{128}\text{Xe}/^{130}\text{Xe}$ ratio of the irradiated data (spallation + iodine) to give $^{128}\text{Xe}^*/^{130}\text{Xe}$ (iodine). The $^{129}\text{Xe}/^{130}\text{Xe}$ ratio of the spallation component could not be directly determined as the presence of $^{129}\text{Xe}^*$ elevates it above the spallation composition. However, the data have been shown to be consistent with a chondritic Ba/REE ratio (Figure 4.1) so this was used. As briefly discussed above, Juvinas appears to show two $^{128}\text{Xe}/^{130}\text{Xe}$ ratios at different temperatures. This same method was used for each $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratios of samples were then referenced to the $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratio of the Shallowater standard included in the same irradiation to obtain relative ages. Béreba showed too much scatter in $^{128}\text{Xe}/^{130}\text{Xe}$ ratios to produce meaningful $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratios.
The data have shown throughout that air may contribute to Ibitira at all temperatures rather than just at low-temperatures as in the other samples. This could affect the age as the amount of $^{129}\text{Xe}^\ast$ may be overestimated if the “baseline” is actually a mix of spallation and air and not just spallation. To test how much the age could be affected I calculated the proportion of air contributing to the $^{128}\text{Xe}/^{130}\text{Xe}$ ratio in unirradiated Ibitira assuming mixing between air and chondritic spallation (Figure 4.1). From this a $^{129}\text{Xe}/^{130}\text{Xe}$ ratio based on mixing of the same proportions of air and spallation was calculated. Using this $^{129}\text{Xe}/^{130}\text{Xe}$ ratio gave the same age within error of the age reported here.

I-Xe ages could not be determined using both methods for both high and low temperature phases of Juvinas due to the larger amount of scatter in the data. This suggests that the relationship between $^{129}\text{Xe}^\ast$ and $^{128}\text{Xe}^\ast$ in Juvinas is not well defined. Figure 4.12 considers the Bunburra Rockhole, Ibitira and Juvinas isochrons shown earlier in Figure 4.6 again, this time with just the high temperature data for Juvinas and excluding the low-temperature releases that produced large amounts of uncorrelated iodine from Bunburra Rockhole and Ibitira. The anomalous eucrites show much better constrained $^{128}\text{Xe}/^{129}\text{Xe}$ ratios than Juvinas. This, coupled with the fact that Method 2 did not produce a meaningful age for Juvinas suggests that while confidence can be placed on the Bunburra Rockhole and Ibitira I-Xe ages calculated using Method 1, the I-Xe age of Juvinas calculated using Method 1 may not be reliable.

Table 4.3. $^{128}\text{Xe}^\ast/^{129}\text{Xe}^\ast$ ratios produced by fitting lines to data shown in Figures 4.8–4.11 using Methods 1 and 2 as described in the text. I–Xe ages are relative to Shallowater (absolute age of 4562.3 Myr (Gilmour et al., 2009)). A dash indicates the $^{128}\text{Xe}^\ast/^{129}\text{Xe}^\ast$ ratio was not precise enough to allow an age to be calculated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{128}\text{Xe}^\ast/^{129}\text{Xe}^\ast$</td>
<td>$^{128}\text{Xe}^\ast/^{129}\text{Xe}^\ast$</td>
</tr>
<tr>
<td></td>
<td>MSWD</td>
<td>Age relative to Shallowater (Myr)</td>
</tr>
<tr>
<td>Bunburra Rockhole</td>
<td>0.645 ± 0.24</td>
<td>1.8</td>
</tr>
<tr>
<td>Ibitira</td>
<td>0.688 ± 0.038</td>
<td>0.85</td>
</tr>
<tr>
<td>Juvinas (high–T)</td>
<td>0.75 ± 0.32</td>
<td>0.34</td>
</tr>
<tr>
<td>Juvinas (low–T)</td>
<td>1.82 ± 0.71</td>
<td>–</td>
</tr>
<tr>
<td>Béréba</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
4.3. Discussion

The behaviour of iodine in early igneous materials is poorly constrained. These data allow an opportunity to study the behaviour of iodine during the formation of some of the first basalts and put this behaviour into a chronological context using the I–Xe dating system.

4.3.1. Comparison of absolute ages of Ibitira

The I-Xe age of ~7 Myr after Shallowater for Bunburra Rockhole (Table 4.3) agrees with that of Ibitira and corresponds to an absolute age of ~4555 using the most recent Shallowater age of 4562.3 (Gilmour et al., 2009). That both samples produce I-Xe ages that agree within error is consistent with an origin on the same parent body, though...
The I-Xe age of Ibitira reported here is in very good agreement with the Pb-Pb (Chen and Wasserburg, 1985) and Mn-Cr (Lugmair and Shukolyukov, 1998) ages (Table 4.4) and agrees with the Pu-Xe age of one of the samples studied by Shukolyukov and Begemann (1996a). The other reported Pu-Xe is not considered to be real. This agreement between chronometers shows that the I-Xe system can be used to constrain the chronology of eucrites and that the $^{129}$Xe* seen here is chronologically significant.

Ibitira shows evidence of metamorphism in its chemical equilibration. That all chronometers given in Table 4.4 produce the same age could suggest that they date this metamorphic event. However, Bunburra Rockhole is unequilibrated (Bland et al., 2009) and gives the same I-Xe age suggesting the age may predate metamorphism. The later Ar-Ar age of 4486 ± 38 Myr (Bogard and Garrison, 2003) is likely to be more representative of metamorphism on the parent body of Ibitira.

**Table 4.4. Comparison of absolute ages of Ibitira.**

<table>
<thead>
<tr>
<th>Chronometer</th>
<th>I–Xe</th>
<th>Pu–Xe*</th>
<th>Pb–Pb</th>
<th>Mn–Cr</th>
<th>Ar–Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age (Myr) of Ibitira</td>
<td>4555 ± 1*</td>
<td>4595 ± 22</td>
<td>4556 ± 6</td>
<td>4556 ± 6</td>
<td>4557 ±2</td>
</tr>
</tbody>
</table>

*Shukolyukov and Begemann (1996a); bChen and Wasserburg, (1985); cLugmair and Shukolyukov (1998); dBogard and Garrison (2003). *Method 1, ** Method 2 (see Section 4.2).*

4.3.2. Xe in the anomalous eucrite Ibitira vs. “nomalous” eucrites

Ibitira has been shown here to produce a Xe isotopic signature that is different from the “nomalous” eucrites Juvinas and Béréba, and from the anomalous eucrite Bunburra Rockhole. This has been interpreted as a more significant contribution from trapped-Xe to Ibitira. The composition of this trapped component could not be distinguished here due to the complex xenon systematics described in section 4.2; however, the fact that it is released at high-temperatures from more retentive sites than the trapped Xe released from Bunburra Rockhole, Béréba and Juvinas makes an increased addition from terrestrial air unlikely. The presence of a different Xe component, along with the older I-Xe age adds to the differences between Ibitira and other eucrites and supports the hypothesis that Ibitira did not form on Vesta (Mittlefehldt, 2005).
The major feature of Ibitira that marks it out from other eucritic meteorites, is that it contains vesicles (Wilkening and Anders, 1975). Only three vesicular eucrites have been found: Ibitira, Pecora Escarpment 91007 and Yamato 981651. The vesicles and fine grain size of Ibitira suggest that it formed in a lava flow with vesicles produced by CO and CO\(_2\) (McCoy et al., 2006). Vapour deposited minerals later formed within the vesicles (Wilkening and Anders, 1975; Wadhwa and Davis, 1998). These lava flows are thought to have formed at depth, as gas escape on the surface would be efficient (Wilson and Keil, 1997). As Ibitira is different from the other samples in that it appears to contain a trapped component other than adsorbed terrestrial atmosphere, and it is different in that it contains vesicles, it follows that this component may be trapped in these vesicles. The presence of vesicles in Ibitira has been attributed to formation at depth (~5 km (McCoy et al., 2006)). It may be that at such depths primordial-Xe was present, but Xe closer to the surface was lost.

This trapped component was released at low end of the temperature range. Excesses of \(^{129}\text{Xe}\) were also released at low-temperatures from Ibitira (Figure 4.9) that did not fall on the same \(^{129}\text{Xe}/^{136}\text{Xe}\) correlation line defined by the higher temperature data. This suggests that \(^{129}\text{Xe}^*\) is associated with the trapped phase. A \(^{128}\text{Xe}/^{129}\text{Xe}\) correlation could not be defined for this low-temperature data. This could be due to addition of terrestrial iodine or the \(^{129}\text{Xe}^*\) seen could represent an evolved trapped component, not hosted in iodine sites. An evolved trapped composition may be more likely as the \(^{129}\text{Xe}^*\) released along with the trapped-Xe here, is released at lower temperatures than the confirmed, iodine-derived \(^{129}\text{Xe}^*\) suggesting it is retained in a site other than iodine.

More noble gas analysis of Ibitira is needed in order to further examine the nature of the trapped component in Ibitira and investigate the excess \(^{129}\text{Xe}\) associated with it. This could be best achieved by vacuum crushing experiments, allowing vesicle gases to be measured separately from the whole-rock. I-Xe analyses could then allow determination of whether the vesicles formed before or after the I-Xe clock was set.

4.3.3. \textit{Xe in the anomalous eucrite Bunburra Rockhole vs. “nomalous” eucrites}

Examining the spallation, fission and trapped components in anomalous and “nomalous” eucrites allows the xenon systematics to be compared and contrasted. In the case of Bunburra Rockhole no obvious differences were seen, with contributions from spallation (Figure 4.1) and fission (Figures 4.2 and 4.7) being very similar to those seen...
in Béréba and Juvinas. This suggests that if Bunburra Rockhole did originate on a separate parent body, as its oxygen isotope ratio suggests, it contained very similar trace element chemistry. However, Bunburra Rockhole showed a defined $^{128}\text{Xe}^*/^{129}\text{Xe}^*$ ratio more consistent with that seen in Ibitira than in Juvinas and Béréba. This suggests an origin on an asteroid other than Vesta.

If Bunburra Rockhole did originate on the same parent body as the other HEDs it may have been ejected during the same impact event. Welten et al. (2012) measured cosmogenic nuclides and light noble gases in Bunburra Rockhole. They determined cosmic ray exposure age from measurements of $^{38}\text{Ar}$ of ~22 ± 3 Myr. Cosmic–ray exposure ages of HED meteorites show clusters at 23 and 40 Myr. This makes Bunburra Rockhole the first eucrite with an anomalous oxygen isotope ratio to have a cosmic–ray exposure age consistent with a major HED cluster age and could indicate that Bunburra Rockhole was released during the same event and that is may possibly have originated on Vesta. However the Kr–Kr cosmic–ray exposure age of Bunburra Rockhole measured by Strashnov et al. (submitted) of 27.6 ± 1.4 Myr does not agree with the Kr-Kr HED cluster age (Strashnov et al., submitted). The advantages of the Kr–Kr system are that it is independent of the shielding conditions of the sample and the chemical composition of the sample and an isotopic ratio is measured, rather than absolute amounts of cosmogenic atoms. The Kr–Kr cosmic ray exposure age is therefore seen as the more reliable one here and adds support to the hypothesis that Bunburra Rockhole formed on a differentiated asteroid other than Vesta.

4.3.4. Extended Xe-loss on Vesta?

It was shown in section 4.1 that the anomalous eucrites produced higher $^{129}\text{Xe}^*/^{244}\text{Pu}$ ratios than the “nomalous” eucrites. This could have been produced by earlier closure to Xe-loss in the anomalous eucrites or by formation on a more volatile-rich body.

Section 4.2 showed that $^{129}\text{Xe}^*$ seen in these samples is derived from $^{129}\text{I}$ and that the concentrations of iodine do not vary significantly between samples (Table 4.2). Béréba, which shows the lowest $^{129}\text{Xe}/\text{Pu}$ ratio, contains 0.7 ppb of iodine, slightly more than Bunburra Rockhole (0.53 ppb) that showed one of the higher $^{129}\text{Xe}/\text{Pu}$ ratios. Pu contents of the four meteorites are also very similar (Table 4.1). This demonstrates that there is no large variation in iodine or plutonium contents of the anomalous and “nomalous” eucrites and that any small variations do not correlate with $^{129}\text{I}/^{244}\text{Pu}$ ratio. The $^{129}\text{I}/^{244}\text{Pu}$ ratios therefore do not represent the volatile content of the parent bodies
and instead reflect the different chronologies of the anomalous and “nomalous” eucrites. Comparison of the I-Xe age of Ibitira compared with other chronometers (Table 4.4) shows that confidence can be placed on chronological information gained from the I-Xe system in these meteorites.

The I-Xe ages of Bunburra Rockhole and Ibitira of $4555 \pm 9$ and $4555 \pm 1$ Myr are similar to reported ages of Juvinas: $4554 \pm 15$ (Pu-Xe) (Shukolyukov and Begemann, 1996a) and $4562.5 \pm 1$ (Mn-Cr) (Lugmair and Shukolyukov, 1998). This suggests that crystallisation on the anomalous eucrite parent bodies and on Vesta began at the same time. However the lower $^{129}\text{I}/^{244}\text{Pu}$ ratios of Juvinas and Béréba and the scatter seen in their isochrons (Figure 4.6) suggests that less $^{129}\text{Xe}^*$ was retained by the “nomalous” eucrites. This spread in time of closure to xenon loss points towards extended processing on Vesta compared to the anomalous eucrite parent bodies.

Bulk $^{129}\text{I}/^{244}\text{Pu}$ ratios of 2, 1, 0.25 and 0.1 for Ibitira, Bunburra Rockhole, Juvinas and Béréba respectively have been estimated from the guidelines drawn on Figure 4.5. These have then been fitted to a curve of how $^{129}\text{I}/^{244}\text{Pu}$ changes with time to establish at what time Xe-loss stopped (Figure 4.13). The I-Xe age of Ibitira is taken as $t_0$. Figure 4.13 shows that total Xe-loss (not just closure to xenon loss from iodine sites) in Bunburra Rockhole is likely to have ceased within ~20 Myr (or around one half-life of $^{129}\text{I}$). The $^{129}\text{I}/^{244}\text{Pu}$ ratios of Juvinas and Béréba indicate that Xe-loss continued for ~50-100 years after the I-Xe age of Ibitira. This corresponds to processing on Vesta until ~4450 Myr, if the 4555 Myr age (I-Xe) of Ibitira is used. Reported Pb-Pb and Sm-Nd ages of eucrites also span 4.4 – 4.5 Gyr (Wadhwa and Lugmair, 1995; Tera et al., 1997, Nyquist et al., 1999).

The $^{129}\text{I}/^{244}\text{Pu}$ ratios reported here suggests that the parent body of the anomalous eucrites ceased being geologically active earlier in Solar System history than Vesta and retained more $^{129}\text{I}$. Vesta is the second largest large asteroid in the Solar System and a larger body will retain heat for longer than a smaller one. The results seen here can be explained by formation of Bunburra Rockhole and Ibitira on smaller parent bodies than Vesta, where igneous activity had stopped by ~4535 Myr. Vesta however, continued to be geologically active and lose Xe for another 30-80 Myr. The smaller parent bodies of the anomalous eucrites have since been catastrophically disrupted by collision, whereas
Vesta has survived. The large size of Vesta may therefore have protected it from catastrophic collisions and be the reason why it has uniquely survived.

![Diagram showing the ratio of $^{129}$I/$^{244}$Pu over time using half-lives of 16 Myr ($^{129}$I) and 80 Myr ($^{244}$Pu).]

**Figure 4.13.** $^{129}$I/$^{244}$Pu ratios of samples (estimated from Figure 4.5) fitted to the curve of how $^{129}$I/$^{244}$Pu changes with time using half-lives of 16 Myr ($^{129}$I) and 80 Myr ($^{244}$Pu). The lower x-axis indicates time Xe-loss stopped after the I-Xe age of Ibitira. The upper x-axis gives the absolute time scale using the I-Xe age of Ibitira (4555 Myr). Xe-loss on Bunburra Rockhole’s parent body stopped within ~20 Myr, whilst Xe-loss on Vesta appears to have continued for ~50-100 Myr.

### 4.5. Summary

- Excesses seen in the lighter xenon isotopes in all samples are consistent with spallation on material with a chondritic Ba/REE ratio.

- Bunburra Rockhole and Béréba show larger contributions from spallation. This is most likely to be due to their longer cosmic ray exposure ages (>25 Myr) compared to Ibitira and Juvinas (<15 Myr).

- Heavy xenon isotopes in all unirradiated samples show evidence of fission xenon. This may be produced by spontaneous fission of $^{244}$Pu or $^{238}$U. However, in ancient samples such as these $^{244}$Pu is thought to dominate. This is consistent with previous reports.
• Bunburra Rockhole, Béréba and Juvina s show a small contribution from a trapped component that is only present in low–temperature releases. This is consistent with adsorption of terrestrial air.

• Ibitira shows a larger contribution from a trapped component over a larger temperature range, thought to be released with low-temperature excess $^{129}$Xe. This component may be associated with the vesicles in Ibitira. Further noble gas analyses of Ibitira are needed to confirm this.

• Lower temperature releases are dominated by mixing between trapped–Xe and fission Xe. Higher temperature releases are dominated by mixing between fission–Xe and spallation–Xe.

• All samples show $^{129}$Xe* associated with $^{128}$Xe*. This indicates the former presence of $^{129}$I. Ibitira and Bunburra Rockhole closed to Xe loss at ~4555 Myr. This I-Xe age agrees with reported Pb-Pb and Mn-Cr ages for Ibitira.

• Variations in $^{129}$I/$^{244}$Pu ratios seen in these samples have chronological significance and are not due to differences in volatile contents.

• It is proposed that lower $^{129}$I/$^{244}$Pu ratios seen in Juvinas and Béréba compared to Ibitira and Bunburra Rockhole are the result of Vesta retaining less $^{129}$Xe* due to extended Xe loss.

• Bulk $^{129}$I/$^{244}$Pu ratios indicate that Xe-loss on the anomalous eucrite parent body had ceased by ~4535 Myr whilst Xe-loss on Vesta continued for another ~80 Myr. It is suggested that geologically activity continued on Vesta after it had stopped on the smaller anomalous eucrite parent bodies due to Vesta’s larger size.

• By protecting it from the collisions that catastrophically disrupted its siblings, the larger size of Vesta may be the reason it uniquely survived intact.
5.1. Introduction

Understanding the role of volatiles in crustal processes on asteroids in the early Solar System is essential to developing a coherent picture of planet formation and evolution. The paired meteorites GRA 06128 and GRA 06129 are unique examples of ancient asteroid crust, with affinities to the primitive achondrite group, brachinites (Zeigler et al., 2008). GRA 06128/06129 are thought to be the products of low–degrees of melting on a volatile rich parent body, followed by the accumulation of Na–rich plagioclase (Arai et al., 2008; Shearer et al., 2008, 2010). The combination of mineral assemblage, texture and composition observed in GRA 06128 and GRA 06129 has not been seen before in crustal meteorites; however clasts of similar material have been seen in ureilites, winonaites and iron meteorites suggesting that this type of crustal formation is not confined to the GRA 06128 and GRA 06129 parent body (Shearer et al., 2010).

Previous analysis of unirradiated GRA 06129 whole-rock samples using RELAX was reported in Shearer et al. (2010) and showed the presence of excess $^{129}\text{Xe}$ either from in situ decay of $^{129}\text{I}$ or inherited in all three samples studied. To follow up on this work, whole–rock samples of GRA 06129 were irradiated in order to determine whether the $^{129}\text{Xe}^\ast$ has remained in situ in iodine sites and to investigate the I–Xe system further in this unusual meteorite. Between planning and completion of this aim, Bajo et al. (2010) reported the presence an evolved trapped component with a $^{129}\text{Xe}/^{132}\text{Xe}$ ratio of 1.5 ± 0.02 and an I–Xe age of 75 Myr after Shallowater. This work allows the validity of the interpretation of xenon isotopes in GRA 06129 by Bajo et al. (2010) to be assessed.

5.2. Sample description

A whole-rock sample of GRA 06129 was provided by C. K. Shearer at the Institute of Meteoritics, University of New Mexico, Albuquerque. GRA 06129 is an ungrouped achondrite: its combined chemistry and petrology do not fit into any established group of achondritic meteorites (Satterwhite et al., 2007). GRA 06129 is dominated by Na–plagioclase (>75% modal abundance (Shearer et al., 2010; Day et al., 2009)). The large amount of Na–plagioclase classes GRA 06129 as a felsic rock; all other ancient achondrites found have been basaltic (mafic and containing Ca–plagioclase). Normative mineralogy (weight %) is given as follows by Shearer et al. (2010): plagioclase (48.86),
diopside (19.24), nepheline (11.69), olivine (7.48), pyrite (4.88), magnetite (1.78), orthoclase (1.48), apatite (0.44), ilmenite (0.13) and chromite (0.01). The rock shows a granoblastic texture, consisting of equant, anhedral grains. This texture is consistent with slow cooling and partial re–equilibration. Some plagioclase crystals show undulose extinction indicating the meteorite has experienced some shock.

It is thought that GRA 06128 and GRA 06129 were produced by small degrees of melting on a chondritic parent body, as these conditions have been shown to be important in generating Na–feldspar rich material in ureilites (Ikeda and Prinz, 2001). Shearer et al. (2010) modelled equilibrium and fractional melting of an L chondrite. An L chondrite was chosen as Feldstein et al. (2001) had observed melting of an L6 could produce melt with high amounts of Na and plagioclase. Shearer et al. (2010) compared elemental abundances of K, Ba and Sr in GRA 06129 with those produced by their modelling experiments along with results from Kita et al. (2004) who showed that Na-rich melts can be produced from CI CM chondrite compositions Shearer et al. (2010) concluded that of these potential precursors, 10 % fractional melting of an L chondrite is most likely to produce GRA 06128 and GRA 06129.

GRA 06128 and GRA 06129 have oxygen isotope ratios (Figure 1.3) that overlap with those of the brachinite group of meteorites (Zeigler et al., 2008) suggesting they may have originated on the same parent body. Day et al. (2009) reported that compositions of GRA 06128/06129, brachinites and brachinites–like achondrites could all could be produced by partial melting of a volatile–rich, oxidised chondritic source, pointing towards a genetic link.

An Al–Mg model age of 4565.9 ± 0.3 Myr (Shearer et al., 2010) indicates that crystallisation of the GRA 06129 parent body occurred very early in the Solar System, ~2 Myr after the formation of CAIs (Bouvier and Wadhwa, 2010). Following crystallisation, GRA 06128 and GRA 06129 have been thermally metamorphosed and partially brecciated (Day et al., 2009) and experienced several post–magmatic crystallisation processes including multiple stages of low–temperature alteration. The following sequence of early asteroidal events has been proposed for GRA 06129 by Shearer et al. (2010):
Chapter 5 – Volatile Movements in the Unique Crustal Achondrite GRA 06129

- Accumulation of a plagioclase crust.
- Re-equilibration of magmatic phases and/or formation of a granoblastic texture, thought to have been produced by impact metamorphism. This event has been associated with the resetting of the Ar–Ar system at ~4420 Myr (Shearer et al., 2010).
- Replacement of primary phases (pyroxene and merrillite) by Cl–apatite during interactions with a resudium melt/fluid phase.
- At least three stages of later alteration are seen along grain boundaries and fractures.

As stated above, previous Manchester work on GRA 06129 included in Shearer et al. (2010) showed excess $^{129}\text{Xe}$ either from in situ decay of $^{129}\text{I}$ or inherited, in all three samples studied. Concentrations of iodogenic xenon varied between the samples ($10^8 – 10^{10}$ atoms g$^{-1}$) with 70% of iodogenic xenon in one sample released in a single step. Shearer et al. (2010) suggested this release pattern could be produced by iodine hosted in a minor phase. Evidence for $^{244}\text{Pu}$ (which decays by spontaneous fission to $^{134}\text{Xe}$ and $^{136}\text{Xe}$) was seen in one of the three samples. Merrillite is known to be a host phase of fission Xe from Pu decay in Acapulco (Nichols et al., 1994) and is suggested to be the host in GRA 06129 (Shearer et al. 2010). The composition of the trapped component was consistent with Q–Xe (Busemann et al., 2000) which is typical of primitive chondritic meteorites and indicates that volatiles had been retained on a primitive parent body. No spallation component was seen. This may be due to the short cosmic-ray exposure age of ~3 Myr (Matsuda et al., 2008).

5.3. Results of I–Xe analysis

Three samples of GRA 06129 were included in irradiation MN10a and Xe isotopes measured using RELAX. The xenon isotopic data for the three samples are given in Appendix IV. The samples are referred to here as Sample 1, Sample 2 and Sample 3 and have masses of 3.56 mg, 0.5 mg and 0.4 mg respectively; these masses correspond to samples sizes ~1-2 mm in diameter. The grain size of GRA 06129 is variable but ranges between <0.1 to >0.5 mm (Day et al., 2009). Therefore the larger sample (Sample 1) may be more representative of the bulk rock composition than the smaller samples. Air calibrations were used to make a correction for instrumental bias and to calculate absolute amounts of atoms released from the sample. The background blank of the instrument was also monitored throughout analysis. Typical blanks were $\sim10^{-16}$ cc
STP $^{132}$Xe. These analyses were carried out before the large interference at $^{128}$Xe appeared (Chapter 2).

5.3.1. Fissiogenic xenon
All samples showed mixing between a fission endmember and a trapped component consistent with Q–Xe (Busemann et al., 2000) (Figure 5.1). This agrees with previous Xe analyses of unirradiated samples of GRA 06129 (Shearer et al., 2010). The irradiated samples analysed here show higher $^{136}$Xe/$^{132}$Xe ratios than the unirradiated samples reported by Shearer et al. (2010). This indicates that neutron–induced fission of $^{235}$U contributes to fissiogenic–Xe in these irradiated samples, as well as spontaneous fission of $^{244}$Pu. A fission correction has therefore been made to the data based on mixing between Q–Xe and a fissiogenic endmember with contributions from plutonium and uranium. To achieve this, the Pu/U ratio of the sample material at closure to Xe–loss (Bajo et al. (2010) reported this to be ~80 Myr after Solar System formation) was estimated resulting in $^{134}$Xe/$^{132}$Xe$_{\text{Mix}} = 1.65$. This ratio is representative of plutonium producing only 15% of the $^{134}$Xe*. A fission correction was then made using this value.

To test the effect of the assumption that the sample closed to Xe–loss 80 Myr after Solar System formation, the calculation was made assuming the sample closed to Xe–loss at 10 Myr after Solar System formation. This gives $^{134}$Xe/$^{132}$Xe$_{\text{Mix}} = 1.5$. Using this correction the difference in the number of atoms of $^{132}$Xe$_{Q}$ and $^{134}$Xe* calculated was less than the error, for each release.
Figure 5.1. 3–isotope plot of $^{136}$Xe, $^{134}$Xe and $^{132}$Xe for irradiated samples analysed here and unirradiated samples of GRA 06129 reported in Shearer et al. (2010) (data supplied by S. Crowther). Compositions of fission endmembers (Ozima and Podosek, 1983) and Q–Xe (Busemann et al., 2000) are given. Unirradiated samples are dominated by Q–Xe with a small contribution from fission. Irradiated data show a larger contribution from fission–Xe, though whether it is produced from plutonium or uranium cannot be directly determined from the data. The larger contribution from fission seen in the irradiated samples suggests that neutron–induced fission of $^{235}$U contributes to the fission component.
Figure 5.2. Large excesses of $^{128}\text{Xe}^*$ were released from samples of GRA 06129 at lower temperatures during step-heating. This has been attributed to iodine contamination during residence in the Antarctic. (Dreibus et al., 1985; Heumann et al., 1987, 1990).
Figure 5.3. Concentrations (atoms/g) of iodine, barium (left-hand y-axis) $^{129}\text{Xe}$, Q-Xe and uranium (right-hand y-axis) released during step-heating. Varying mixtures of these components were released at distinct temperature ranges, over several heat steps, separated by steps that produced little or no Xe. These distinct releases have been grouped according to these mixtures into three groups (G1, G2 and G3).
Table 5.1. Concentrations (ppb) of I, Ba and U released from samples of GRA 06129 calculated from excesses of $^{128}\text{Xe}^*$, $^{131}\text{Xe}^*$ and $^{134}\text{Xe}^*$. $^{131}\text{Xe}^*$ is attributed to neutron capture on B rather than Te due to the high feldspar content of the samples. Spontaneous fission of $^{244}\text{Pu}$ is estimated to have contributed 15% of the excess $^{134}\text{Xe}^*$ so concentrations of U are based on calculations using 85% of the atoms of $^{134}\text{Xe}^*$ released from each sample. Also shown are concentrations of $^{132}\text{Xe}_0$ and $^{129}\text{Xe}^*$ (cc STP g$^{-1}$). Errors are ~2%.

<table>
<thead>
<tr>
<th>GRA 06129</th>
<th>Concentration (ppb)</th>
<th>Concentration (cc STP g$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>I</td>
<td>Ba</td>
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<tr>
<td>Sample 1</td>
<td>215</td>
<td>8000</td>
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<tr>
<td>Sample 2</td>
<td>185</td>
<td>8500</td>
</tr>
<tr>
<td>Sample 3</td>
<td>400</td>
<td>24000</td>
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</tbody>
</table>

5.3.2. Large amounts of excess $^{128}\text{Xe}^*$

The corrected data showed very large excesses of $^{128}\text{Xe}^*$ at low heating–temperatures (Figure 5.2). These large excesses were not seen in unirradiated samples (Shearer et al., 2010) which indicate they were produced from iodine during the irradiation. That they are not seen at higher heating–temperatures points towards terrestrial contamination. GRA 06129 is an Antarctic meteorite and over abundances of iodine in the surface layers of Antarctic meteorites previously been reported (Dreibus et al., 1985; Heumann et al., 1987, 1990) and were attributed to a contribution by methyl iodide in the Antarctic atmosphere. This is believed to be the cause of the large $^{128}\text{Xe}^*$ seen here. The large signal heights of the $^{128}\text{Xe}$ peaks produced during analyses distorted the baseline for all xenon isotopes heavier than $^{128}\text{Xe}$. Therefore only the higher–temperature steps, not compromised by Antarctic contamination, are discussed here. These are steps 85–117 in Sample 1, steps 40–64 in Sample 2 and steps 36–60 in Sample 3.

5.3.3. Distinct releases

All three samples showed excesses in the following Xe isotopes: $^{128}\text{Xe}^*$ (from I), $^{129}\text{Xe}^*$ (from extinct $^{129}\text{I}$) $^{131}\text{Xe}^*$ (from Ba or Te) and $^{134}\text{Xe}^*$ (dominated by neutron–induced U fission with some U/Pu spontaneous fission). $^{131}\text{Xe}^*$ in these samples is attributed to neutron-capture on Ba rather than Te, due to the high content of the Ba-bearing mineral plagioclase (>75 modal %) compared to sulphides. Concentrations of I, $^{129}\text{Xe}^*$, Ba, $^{132}\text{Xe}_0$ and U are given in Table 5.1. The method of calculation used to obtain these concentrations is discussed in Chapter 2 (only 85% of the atoms of excess $^{134}\text{Xe}^*$ were
used as 15% are expected to be produced by Pu). Varying mixtures of these excesses (along with Q–Xe) were released at distinct temperature ranges, over several heat steps, separated by steps that produced little or no Xe (Figure 5.3).

All releases produced by the three samples have been divided into “Groups”: G1, G2 and G3. These consists of sets of consecutive heat–steps over which the Xe was released with distinct relative abundances of $^{128}\text{Xe}^*$ (from iodine), $^{129}\text{Xe}^*$, $^{131}\text{Xe}^*$(from barium), trapped Xe and $^{134}\text{Xe}^*$ (dominated by uranium). These groups are separated by several heat–steps that released small amounts of Xe. The chemical behaviour of each group will be discussed in more detail in the next section. The temperature these groups of components were released at increases through G1 $\rightarrow$ G2 $\rightarrow$ G3. Not all samples produced releases in all groups: Sample 1 produced releases in G1, G2, G3, Sample 2 produced G1 and G3 releases, and Sample 3 produced G1 and G2 releases.

5.3.4. I–Xe “Age”/Initial iodine ratio

Figure 5.4 shows an isochron diagram for significant releases, G1, G2 and G3 (left–hand figure) and all releases (right–hand figure). G1 shows large excesses of uncorrelated iodine. This is most likely produced by loss of $^{129}\text{Xe}^*$ over time or contamination from terrestrial iodine. G2 releases plot close to the isochron reported by Bajo et al. (2010). G3 data show $^{129}\text{Xe}^{/132}\text{Xe}_Q$ ratios consistent with Q–Xe but a non–zero $^{128}\text{Xe}^*/^{129}\text{Xe}$ pointing towards to presence of iodine.

When all the data are considered (Fig. 5.4, right) any suggestion that the data may form an isochron consistent with that reported by Bajo et al. (2010) disappears. Rather the data appear to form two mixing lines. The first (at lower temperatures) shows mixing between a fairly consistent $^{132}\text{Xe}^{/129}\text{Xe}$ ratio with a lower limit of $\sim$0.4 and varying amounts of $^{128}\text{Xe}^*$ (from iodine). The $^{129}\text{Xe}^{/132}\text{Xe}$ limit defined by these data is lower than that of the trapped component reported by Bajo et al. (2010) of 0.66. The second mixing line shows that at higher-temperatures the $^{129}\text{Xe}^{/132}\text{Xe}$ ratios of the data evolve towards a composition consistent with Q–Xe, with a non–zero $^{128}\text{Xe}^*/^{129}\text{Xe}$ ratio.

5.3.5. Trace–element chemistry

The data show distinct releases containing varying mixtures of iodine, barium, uranium, Q–Xe and excess $^{129}\text{Xe}^*$. This suggests more than one phase releasing xenon at different temperatures. Figure 5.3 shows that the majority of iodine and uranium are
produced during the lower-temperature G1 and G2 releases (though iodine also contributes at higher temperatures) with G3 releases dominated by barium. The chemistry of the releases can therefore be used to constrain what these host phases may be.

Previous RELAX analysis of unirradiated GRA 06129 samples where fissiogenic–Xe was produced by Pu fission, suggested merrillite as a likely carrier of fission Xe (Shearer et al., 2010). Here, where fissiogenic-Xe is dominated by uranium, apatite is a more likely host phase for several reasons:

1. Nichols et al. (1994) analysed phosphate grains separated from the Acapulco achondrite and found that while merrillite was enriched in Pu, apatite was the major carrier of U.
2. The uranium concentrations of the whole-rock samples measured here of 10–50 ppb (Table 5.1) are consistent with the concentrations of uranium in GRA 06129 Cl–apatite (~500 ppb) measured by Ash et al. (2008) when the abundance of Cl–apatite in GRA 06129 of 5 % (Zeigler et al., 2008) is taken into account.
3. Iodine is also released with uranium and iodine is likely to be hosted in halogen–bearing apatite rather than merrillite as iodine can be incorporated as an interstitial element in Cl–bearing minerals. In support of this, studies of Acapulco phosphates by Nichols et al. (1994) showed iodine present in apatite but not in merrillite.

The trace-element chemistry is therefore consistent with apatite releasing Xe during the lower-temperature G1 and G2 releases with varying amounts of iodine.

Inferred Ba concentrations calculated from excess $^{131}\text{Xe}^*$ of 8–24 ppm are consistent with concentrations determined for bulk GRA 06129 of 24.81 ppm (Shearer et al., 2010). This supports the assumption that $^{131}\text{Xe}^*$ is dominated by production from Ba rather than Te. The major mineral phase in GRA 06129 is plagioclase (80 modal %). Plagioclase is also a major Ba carrier. It is therefore likely that production of the high temperature G3 releases (which are dominated by barium but do not contain uranium) is dominated by plagioclase. This is consistent with previous analyses of the plagioclase– and nepheline–rich achondritic clast, Feline, (Gilmour et al., 2000) which showed the presence of iodine and barium in plagioclase but no uranium.
Figure 5.4. 3-isotope plot showing $^{128}\text{Xe}^*$, trapped $^{132}\text{Xe}Q$ (corrected for a mix of U & Pu fission) and total $^{129}\text{Xe}$. The composition of Q-Xe (Busemann et al., 2000) and the Shallowater isochron for MN10a (Chapter 2) are also shown. (left) Only significant releases of Xe (G1, G2, G3) from all three samples are shown. G1 show large excesses of uncorrelated $^{128}\text{Xe}^*$, G2 fall close to the Bajo et al. (2010) isochron, G3 are consistent with Q-Xe but show a non-zero $^{128}\text{Xe}^*/^{129}\text{Xe}$ ratio. (right) All releases are shown, not just those that produced a significant amount of gas. Any suggestion of an isochron given by the G2 data in the right-hand plot disappears when looking at all the releases. Data instead appear to show mixing between uncorrelated iodine ($^{128}\text{Xe}^*$) and a consistent evolved $^{132}\text{Xe}/^{129}\text{Xe}$ ratio which increases towards Q-Xe with increasing temperature.
Figure 5.5. 3-isotope plot showing $^{128}\text{Xe}^*$ (from iodine), $^{134}\text{Xe}^*$ (dominated by fission of uranium), and $^{131}\text{Xe}^*$ (from barium). The data evolve with increasing temperature to a fixed I/Ba ratio with no uranium suggesting an I/U rich phase (apatite) has overprinted an original phase that is the major Ba carrier and has a reproducible non-zero I concentration (plagioclase).

Figure 5.6. 3-isotope plot showing trapped $^{132}\text{Xe}_Q$ (corrected for a mix of U & Pu fission), $^{129}\text{Xe}^*$ and $^{131}\text{Xe}^*$ from Ba. 1 datum from the G1 release was excluded due to large error bars. $^{129}\text{Xe}^*$ does not correlate well with Q-Xe. The $^{132}\text{Xe}_Q$/$^{131}\text{Xe}^*$ ratio varies across the same range in plagioclase (high-T) and apatite (low-T). This suggests the trapped component may not be hosted by either of the iodine carriers and is instead a separate phase that overprints the apatite and plagioclase releases.
5.4. Discussion

The relationships between iodine, $^{129}\text{Xe}^*$, Q–Xe, uranium and barium in GRA 06129 have been examined using three–isotope diagrams (Figure 5.5–5.6). The data show that the high–temperature phase has a consistent, non–zero iodine/barium ratio (Figure 5.5). This has been attributed to plagioclase. Uranium is thought to be hosted in apatite, which also contains some iodine. The uranium/barium increases as the temperature of gas–release decreases (along with the retentiveness of the host phase) indicating xenon is released from U–bearing apatite at lower–temperatures than from Ba–bearing plagioclase. This is consistent with previous work by Crowther et al. (2009), which reported $^{136}\text{Xe}^*$ released at lower temperatures than $^{131}\text{Xe}^*$ in irradiated samples of the primitive achondrites GRA 95209 and LEW 88280.

The $^{129}\text{Xe}^*$ varies independently from either of the iodine bearing phases (Figure 5.6), indicating it has not decayed in situ. $^{129}\text{Xe}^*$ does not correlate with Q–Xe either. $^{129}\text{Xe}^*$ is released with an I/Ba ratio consistent with plagioclase but is not present in the high–T releases so may have originally been present in plagioclase but lost at some point in time (Figure 5.6).

The metamorphic texture of the plagioclase in GRA 06129 suggested it has equilibrated. Therefore if Q–Xe was hosted in plagioclase, an equilibrated Q–Xe/Ba ratio would be expected. All except two of the $^{132}\text{Xe}_Q$/Ba ratios vary over the same large range (0.02 – 0.2) at all temperatures. This suggests that Q–Xe is not hosted in plagioclase. It is released at high-temperatures however suggesting it is hosted in another primary phase.

5.4.1. Origin of the excess $^{129}\text{Xe}^*$

The data suggest that a uranium–rich phase (apatite) has overprinted a barium–rich phase (plagioclase). Both are iodine–bearing. Two trapped xenon components are present; one consistent with primitive Q–Xe, one showing parentless excess $^{129}\text{Xe}$.

An Al–Mg model age of 4565.9 ± 0.3 Myr (Shearer et al., 2010) demonstrates that $^{129}\text{I}$ was alive during crystallisation of primary phases on the GRA 06129 parent body. Plagioclase is thought to be the primary phase in GRA 06129 and the data has shown that it is iodine–bearing. The lack of $^{129}\text{Xe}$ found in the plagioclase therefore points towards loss of xenon from plagioclase, but retention of at least some of the iodine. Shearer et al. (2010) link the formation of the granoblastic texture in plagioclase with an
impact event recorded by the Ar–Ar system at 4420 Ma. Impact heating such as this could have resulted in the xenon loss.

Parentless $^{129}$Xe* has been observed in apatite but not plagioclase, as shown by the evolved $^{129}$Xe/$^{132}$Xe ratio. The nature of the formation of apatite in GRA 06129 has been debated. Treiman et al. (2008) identified it as a primary phase; Shearer et al. (2010, 2011) argue that Cl–apatite in GRA 06129 formed as a replacement mineral at the expense of merrillite and pyroxene. If the apatite did form as a late–stage mineral by fluid interaction as suggested by Shearer et al. (2010, 2011) this evolved $^{129}$Xe/$^{132}$Xe ratio may be representative of the halogen–rich fluid that produced the Cl–apatite. The introduction of $^{129}$Xe* by a fluid that produced secondary apatite explains how the apatite came to have an excess $^{129}$Xe signature but not the plagioclase. If apatite is a primary phase this is less easy to reconcile.

The apatite has been shown to host iodine but the $^{129}$Xe* has not decayed in situ. For the above explanation to hold up, the halogen–rich fluid must have been introduced late; after the lifetime of $^{129}$I, which is estimated to be within the first 100 Myr of the Solar System (>4465 Ma). Shearer et al. (2011) propose that GRA 06129 phosphates can have formed anytime between crystallisation at 4564.25 ± 0.21 Myr (Shearer et al., 2011) and resetting of the Sm–Nd system at 3.4 ± 0.4 Gyr (Park et al., 2010). This later Sm-Nd age has been attributed to interactions between the primary magmatic phase and a fluid phase (Park et al., 2010). The Pb–Pb age for Cl–apatite of 4.517 ± 0.06 Gyr given by Day et al. (2009) limits the youngest age of Cl–apatite to ~4460 Myr. The younger ends of these age brackets are consistent with apatite forming after the lifetime of $^{129}$I.

The Cl–rich fluid may therefore post–date the formation of the primary GRA 06129 assemblage significantly and could have been produced via separate processes on the parent body. Jones et al. (2011) proposed that a halogen–rich (and S bearing) fluid was produced on the Zag/Monahans parent body by partial melting driven by high temperatures in the interior of the body as a result of metamorphism. A similar process may have occurred on the GRA 06129 parent body.

As stated above, the $^{129}$Xe/$^{132}$Xe ratio may be representative of the halogen–rich fluid that produced the Cl–apatite. The apatite releases appear to define a mixing line with varying amounts of $^{128}$Xe* and a fairly consistent $^{129}$Xe/$^{132}$Xe ratio with a lower limit of
~2.5. The source rock of this fluid would therefore be expected to have a bulk $^{129}\text{Xe}/^{132}\text{Xe}$ ratio higher than ~2.5. Gilmour (2000) reviewed the Xe isotopic ratios for various chondritic types and all showed $^{129}\text{Xe}/^{132}\text{Xe}$ ratios lower than 2.5 (database supplied by S. A. Crowther) with the exception of Karoonda (CK). Of the L chondrites, the L4 group show the highest average $^{129}\text{Xe}/^{132}\text{Xe}$ ratio of $1.65 \pm 0.4$. The L5 and L6 give average $^{129}\text{Xe}/^{132}\text{Xe}$ ratios of $1.30 \pm 0.18$ and $1.06 \pm 0.12$ respectively. An L4 source may therefore be more suitable precursor than an L6. However, it is unlikely that the Cl–rich fluid formed directly from melting of the chondritic precursor material. If some of the $^{129}\text{Xe}^*$ was endogenic and had been released from the plagioclase the required $^{129}\text{Xe}/^{132}\text{Xe}$ of the external source region could be lowered from 2.5.

Measured Xe isotope ratios of brachinites (Swindle et al., 1998 and references therein) show $^{129}\text{Xe}/^{132}\text{Xe}$ ratios greater than ~2.5 for Brachina ($^{129}\text{Xe}/^{132}\text{Xe} = 6.9 \pm 0.1$), ALH 84025 ($^{129}\text{Xe}/^{132}\text{Xe} = 6.4 \pm 0.1$) and Eagles Nest ($^{129}\text{Xe}/^{132}\text{Xe} = 3.0 \pm 0.5$). The Cl–rich fluid may therefore have originated in the olivine rich–cumulate that the brachinites sample. Ar–Ar ages of brachinites Brachina and EET 99402 show that a degassing event occurred at $4.13 \pm 0.06$ Gyr, likely to have been caused by an impact (Mittlefehldt et al., 2003) which could have produced a Cl–rich fluid by partial melting. However this age is at least 330 Myr after Pb–Pb age of the Cl–apatites (Day et al., 2009).

5.4.2. Origin of the Q–Xe
The high–temperature (G3) releases show a trapped Xe component consistent with Q–Xe along with a $^{129}\text{Xe}^*$–free iodine component. This suggests that an original trapped component consistent with Q–Xe has been retained in GRA 06129. As it is released at high–temperatures the first thought is that this primitive component is hosted by the plagioclase. However, this is inconsistent with lack of $^{129}\text{Xe}^*$ which points towards xenon loss from the plagioclase. The $^{132}\text{Xe}_Q$/Ba ratios also vary widely suggesting the $^{132}\text{Xe}_Q$ is not released from the plagioclase as one would expect a re–equilibrated phase to produce a consistent ratio.

These observations point towards the Q–Xe hosted in a phase other than plagioclase. The other major primary phases in GRA 06129 are nepheline, olivine, and pyroxene. Merrillite is not thought to host Q-Xe as previous analyses showed that $^{136}\text{Xe}$ from Pu was not released in proportion with Q-Xe (Shearer et al. 2010), and Pu is thought to be
hosted by merrillite. Gilmour et al. (2000) examined the I-Xe system in the plagioclase-nepheline rich clast Feline from Parnallee (LL3.6). They concluded that the iodine was hosted in the plagioclase and not the nepheline. Feline was also reported to be fission-free. This suggests nepheline may be a good candidate for the Q-Xe host which contains no other Xe parent nuclides. Further analyses on mineral separates from GRA 06129 are needed to constrain the host phase of Q-Xe.

5.4.3. Terrestrial atmosphere rather than Q–Xe?
Shearer et al. (2010) noted that GRA 06129 had experienced at least three types of significant low–temperature alteration: Fe–rich; Fe–rich with S– and Cl– bearing phases; alteration of olivine to iddingsite. If some of this alteration occurred on Earth (it is not certain to what extent the observed alteration is terrestrial in origin) it is possible that the trapped $^{132}$Xe component seen in the high–temperature releases is terrestrial Xe that was adsorbed onto GRA 06129 minerals during its terrestrial residence time. Noble gas measurements of several brachinites have shown evidence of terrestrial contamination at high–temperatures (Swindle et al., 1998). As plagioclase makes up the majority of the rock it would be more affected by weathering than the phosphates accounting for the higher $^{132}$Xe/$^{129}$Xe ratios seen in the high–T releases. Sample 3, which did not show a high–temperature release, produced lower amounts of $^{132}$Xe (0.7 $\times$10$^{-10}$ cc STP/g) than Sample 1 and Sample 2 (1.2 $\times$10$^{-10}$ cc STP/g and 1.1 $\times$10$^{-10}$ cc STP/g) and contained higher abundances of U, I and B than the other two samples. Sample 3 was one of the smaller (~1 mm diameter) samples and so may not contain mineralogy representative of bulk GRA 06129.

The spread of $^{132}$Xe/$^{129}$Xe ratios seen in the low– and intermediate–T releases could also be caused by variation in overprinting of terrestrial $^{132}$Xe during weathering processes. Due to the complicated Xe components, which included fission Xe as well as I and Ba derived xenon, I am unable to distinguish between Q–Xe and terrestrial Xe in the high–T releases. However previous analyses of unirradiated GRA 06129 by S. Crowther, reported in Shearer et al. (2010) showed a trapped component consistent with Q–Xe rather than terrestrial atmosphere.

5.4.4. Implications for I–Xe dating
GRA 06129 has experienced thermal disturbance and shock over its history. It is proposed by this work that a metamorphic event resulted in complete loss of $^{129}$Xe* in plagioclase and reset the I–Xe clock. This behaviour suggest that plagioclase makes a
good candidate for I-Xe dating primary processes as the $^{129}\text{Xe}/^{132}\text{Xe}$ ratio in plagioclase in GRA 06129 has been reset by complete loss of $^{129}\text{Xe}^*$ during secondary events. If it had retained some $^{129}\text{Xe}^*$ as an evolved trapped component that could be misinterpreted as an in situ iodine derived component.

The suitability of feldspar can be seen in results reported by Brazzle et al. (1999) who carried out I–Xe dating on apatite and feldspar separates from a suite of ordinary chondrites. The feldspar separates produced very well defined isochrons for all six meteorites analysed. Apatites on the other hand did not form well-defined isochrons and three meteorites that did produce isochrons from feldspar failed to define an isochron from apatite.

5.5. Conclusions and implications of this work

5.5.1. Summary of results

- The data suggest that an I/U rich phase (apatite) has overprinted an original Ba/I–carrying phase (plagioclase). As temperature decreases the releases are increasingly dominated by apatite. This suggests that apatite is a replacement mineral.
- The ancient formation age of GRA 06129 indicates $^{129}\text{I}$ would have been present during crystallisation. However any $^{129}\text{Xe}^*$ that accumulated in situ has been lost or redistributed from its original sites. This could have occurred during the metamorphism that re–equilibrated the Na–plagioclase.
- Parentless $^{129}\text{Xe}^*$ was introduced later via metasomatism and mixed with $^{129}\text{Xe}^*$ released from Na–plagioclase. $^{129}\text{Xe}^*$ was incorporated into apatite during its formation.
- No confidence can be placed on a chronological interpretation of the I–Xe system in these samples.
- The high $^{129}\text{Xe}/^{132}\text{Xe}$ ratio of this fluid indicates the source could have been derived from the suite of rocks that the brachinite meteorites sample.
- The trapped Xe released at high–temperature is most likely hosted in a phase other than plagioclase, possibly nepheline. Further Xe analyses of mineral separates from GRA 06129 would help constrain the host phase of the trapped Xe component.
• The composition of the trapped Xe is consistent with Q-Xe however it cannot be ruled out by this study that the trapped component is terrestrial–Xe acquired during weathering.

• The I-Xe in plagioclase has been completely reset, making it a good candidate for I-Xe dating of primary processes. Apatite on the other hand has shown it will incorporate parentless $^{129}$Xe* which may compromise I-Xe analyses.

5.5.2. Order of events on GRA 06129 and its parent body

The following series of events are proposed for GRA 06129 during its time on the parent body and on Earth:

1. Na–rich plagioclase crystallises early (~4565 Ma) containing iodine and barium. $^{129}$I decays and $^{129}$Xe* builds up within the Na–plagioclase. A primitive trapped Xe component, consistent with Q–Xe is incorporated into one of the primary phases. Some $^{244}$Pu decays.

2. Metamorphism on the GRA 06129 parent body re–equilibrates the Na–plagioclase and results in loss of $^{129}$Xe (and any other Xe present) from plagioclase. Some iodine is retained in Na–plagioclase. Q–Xe is retained.

3. Apatite replaces merrillite. Parentless $^{129}$Xe* is introduced via metasomatism and mixes with existing $^{129}$Xe* from plagioclase and is incorporated into apatite during formation. Fission–Xe from $^{244}$Pu fission may also have been incorporated into the apatite at this point.

4. During the meteorites’ terrestrial residence time, it acquires iodine via Antarctic weathering. Atmospheric–Xe could also be acquired during this time.
CHAPTER 6. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

Results of I-Xe analyses have been obtained from meteorite samples that experienced different extents of thermal processing in the early Solar System in order to help characterise the movements of volatile elements and constrain the timing of these movements using the I-Xe chronometer. Samples were irradiated to convert $^{127}$I to $^{128}$Xe and allow simultaneous measurements of iodine and xenon isotopes. Xe isotopes were measuring using the RELAX mass spectrometer. The results of this work are summarised here and recommendations for future work given.

Objective 1: Carry out I-Xe analyses of irradiated samples of the unique crustal achondrite Graves Nunataks (GRA) 06129 in order to determine whether $^{129}$Xe present in this rock was produced from in situ decay of $^{129}$I.

Between planning and completion of this aim, Bajo et al. (2010) reported the presence of an evolved trapped component with a $^{129}$Xe/$^{132}$Xe ratio of $1.5 \pm 0.02$ and an I–Xe age of 75 Myr after Shallowater. My work allowed the validity of this interpretation to be assessed.

My analyses of the unique achondrite GRA 06129 have shown that the I-Xe system in this meteorite has no chronological significance. The data instead suggest that iodine-bearing plagioclase formed early but thermal metamorphism resulted in complete loss of $^{129}$Xe from iodine bearing sites. The $^{129}$Xe host phase appears to be the uranium-bearing apatite. This is thought to have formed as a replacement mineral during fluid interactions and incorporated parentless $^{129}$Xe from a halogen-rich fluid along with redistributed $^{129}$Xe from plagioclase.

A trapped-Xe component released at high-temperature may be a primitive component such as Q-Xe though terrestrial–Xe acquired during weathering cannot be ruled out by this study. If Q-Xe is present it is most likely hosted in a phase other than plagioclase, possibly nepheline. Further Xe analyses of mineral separates from GRA 06129 would help constrain the host phase of the trapped Xe, however during the terrestrial residence time of GRA 06129 it acquired iodine via Antarctic weathering so further I-Xe analyses on GRA 06129 (and other Antarctic meteorites) should therefore be carried out with caution.
That the I-Xe system of the plagioclase has been completely reset makes it a good candidate mineral for I-Xe dating of primary processes. Apatite on the other hand has been shown to incorporate parentless $^{129}$Xe* which may compromise I-Xe analyses. This may explain work by Brazzle et al. (1999) that showed well-defined I-Xe isochrons in analyses of feldspar separates, but disturbed I-Xe systems in analyses of apatite from the same meteorites.

**Objective 2: Compare the I-Xe system in anomalous and “nomalous” eucrites in order to constrain their origins.**

I investigated the I-Xe system in anomalous eucrites Bunburra Rockhole and Ibitira and “nomalous” eucrites Juvinas and Béréba. The I-Xe age of Ibitira of ~4555 Myr agrees with reported Pu-Xe, Pb-Pb and Mn-Cr ages, supporting the validity of the I-Xe chronometer. The I-Xe age of Bunburra Rockhole agrees within error with Ibitira. That both samples produce I-Xe ages that agree within error is consistent with an origin on the same parent body, though origins on separate bodies at the same time cannot be ruled out.

No differences in Xe isotope signatures were seen between Bunburra Rockhole and the “nomalous” eucrites. This suggests Bunburra Rockhole formed on a parent body chemically very similar to Vesta. The anomalous eucrite Ibitira appears to contain a trapped-Xe component (that may be associated with excess $^{129}$Xe*) not present in the other samples analysed. This component may be associated with the vesicles present in Ibitira. Future noble gas analyses on crushed samples of Ibitira can help constrain the nature of this trapped component.

Comparisons of I-Xe systematics in the anomalous eucrites Bunburra Rockhole and Ibitira and “nomalous” eucrites Juvinas and Béréba show lower $^{129}$I/$^{244}$Pu ratios in the “nomalous” eucrites. I-Xe analyses of irradiated samples demonstrated that this is not because they are poorer in volatiles but instead reflects extended loss of Xe on Vesta. $^{129}$I/$^{244}$Pu ratios therefore indicate that igneous processing continued on Vesta for ~50-100 Myr after geological activity had ceased on the anomalous eucrites parent bodies.
The extended processing seen in Juvinas and Béréba is attributed to formation on a larger body that retained heat for longer. If, as the data suggest, the anomalous eucrites formed on a separate parent body it must have been catastrophically disrupted as Vesta is thought to be the only remaining differentiated asteroid. The larger size of Vesta may explain why it has uniquely survived the impacts that destroyed its siblings.

**Objective 3: Constrain the thermal history of the R-chondrite parent body using the I-Xe system.**

This work forms part of a new group project on Xe isotopes in R-chondrites and a preliminary interpretation has been presented in this thesis. I carried out I-Xe analyses on well characterised samples of different metamorphic grade from the R-chondrite NWA 6492 and on whole-rock R5 material from R-chondrites NWA 830 and NWA 3364. The I-Xe ages of these samples suggest a link between the time of closure to Xe-loss and extent of metamorphism on the R-chondrite parent body supporting the onion shell model. However, further I-Xe analyses of R5 material from NWA 6492 and samples of R4 and R6 R-chondrites are needed to confirm this.

The most primitive materials analysed (assumed to be chondrules) give I–Xe ages between 4559 – 4554 Myr, slightly later than reported Mn-Cr ages. This may support the ideal of radial heterogeneity of $^{53}$Mn in the early Solar System. However differences could also be due to variation in the samples analysed. Future analyses of I-Xe and Mn-Cr ages in mineral separates from the same R-chondrite are recommended to investigate this hypothesis.

Closure to Xe-loss in chondrules on the R-chondrite parent body appears to have occurred ~5 – 10 Myr later than on the ordinary and enstatite parent bodies. This implies either later accumulation of material or slower cooling in a larger body.
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