Resonance Photo-ionisation Mass Spectrometry Techniques for the Analysis of Heavy Noble Gas Isotopes in Extra-terrestrial Samples.

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy (PhD) in the Faculty of Science and Engineering.

2016

Mark Christopher Nottingham
School of Earth and Environmental Sciences
# Table of Contents

Table of Contents ............................ 1  
Table of Figures ............................... 4  
Table of Equations ............................. 6  
Table of Tables ............................... 7  
Table of Appendices ........................... 8  
Abstract ...................................... 9  
Declaration .................................... 10  
Copyright Statement .......................... 10  
Acknowledgements ............................. 11  
1. Introduction ............................... 12  
   1.1 Aims of This Thesis ...................... 13  
2. Background Information ................... 15  
   2.1 Noble Gases ............................. 15  
      2.1.1 Krypton and Krypton Components  16  
      2.1.2 Controls on Krypton Components  20  
      2.1.3 Bonding Sites ....................... 23  
   2.2 Meteorites And Their Role in Our Understanding of The Solar System 23  
   2.3 The Early Solar System ................. 25  
      2.3.1 The First Surviving Solid Phases  25  
   2.4 Chronology of The First Surviving Solids 33  
   2.5 Radiation Environments and their Effect on Meteoritic Material 34  
      2.5.1 Cosmic Rays ......................... 34  
      2.5.2 Spallation Reactions ............... 38  
      2.5.3 The $^{81}$Kr-Kr Chronometer .... 38  
3. Instrumentation ............................ 46  
   3.1 Introduction ............................. 46  
   3.2 Features of the RIMSKI Instrument 47  
      3.2.1 Resonant Ionisation Scheme ....... 47  
      3.2.2 Cryogenic Sample Concentration and Spectrometer Volume 55  
      3.2.3 Ion Source Electronics and Mass Separation 59  
      3.2.4 Signal Detection .................... 61  
   3.3 Component Synthesis and Tuning ....... 63  
4. Instrument Development – Xe-Ar Four-wave Mixing Cell 68
4.1 Introduction

4.1.1 Principles of Four Wave Mixing

4.1.2 Control Over Formed Wavelength

4.1.3 Cell Design

4.1.4 Mixing Medium

4.1.5 Tuning Procedure Before Development

4.1.6 Reasons For Development

4.2 Development

4.2.1 Methods Discussion

4.2.2 Chosen Method

4.3 Characterising the New System

4.3.1 Results and Discussion

4.4 Conclusions

5. Development of Instrument Calibration Protocol

5.1 Introduction

5.2 Aims of Development

5.3 RELAX Data Treatment

5.3.1 Data Reduction

5.4 RIMSKI Data Treatment Differences

5.5 RIMSKI Data Treatment Method

5.5.1 Air Standards Validation

5.5.2 Eucrite Standards Validation

5.5.3 Eucrite Cosmic Ray Exposure Age Results and Method Discussion

5.5.4 An Alternative Cosmic Ray Exposure Calculation Method

5.6 Conclusions

6. Analysis of Calcium Aluminium-rich Inclusions from the Krypton Noble Gas Perspective

6.1 Previous Work

6.1.1 Chronology

6.1.2 Noble Gas Measurements

6.1.3 Application of the RIMSKI Instrument to Similar Samples

6.2 Premise of the Study

6.2.1 Factors to consider

6.3 Samples

6.3.1 CV Meteorites

6.3.2 Allende
TABLE OF FIGURES

Figure 2.1 – A spectrum for terrestrial air ................................................................. 18
Figure 2.2 – Krypton spallation spectra for primary target elements ............................ 21
Figure 2.3 – Amount of $^{83}$Kr produced from pure Kr spallation target elements .......... 22
Figure 2.4 – Meteorite classification diagram .............................................................. 24
Figure 2.5 – Examples of CAIs imaging using SEM Element Mapping ............................ 29
Figure 2.6 – P-T phase diagram showing the condensation of a hot solar gas ................. 31
Figure 2.7 – Illustration of Kr concentration in a single stage cosmic ray irradiation ......... 39
Figure 2.8 – Spallation spectrum for both lunar chondritic derived spallation component ... 44
Figure 3.1 – A labelled photo of the RIMSKI instrument .............................................. 47
Figure 3.2 – The krypton ionisation scheme employed on the RIMSKI instrument ........... 52
Figure 3.3 – A schematic diagram of the RIMSKI laser systems .................................. 53
Figure 3.4 – A diagram of the cold finger component .................................................... 56
Figure 3.5 – Vapour-pressure chart based on figure from Air liquide data sheet (1980) ...... 58
Figure 3.6 – An illustration of the ionisation volume and its effects on mass resolution ... 60
Figure 4.1 – An illustration of the principles behind the tuning of the Xe-Ar ratio ........... 70
Figure 4.2 – Schematic of the implemented Xe-Ar four-wave mixing cell filling system .... 76
Figure 4.3 – Summary data of the new MFC filling method ......................................... 81
Figure 4.4 – Graph of Xe-Ar ratio tuning data relative to DFMNIR output wavelength ... 83
Figure 4.5 – A real time observation of mixing cell pressure and its effects on signal intensity ... 86
Figure 4.6 – An examination of the periodicity of the signal intensity ............................ 87
Figure 4.7 – A plot of data from three days of wavelength against ratio analyses ................ 90
Figure 5.1 – An example of a summed mass spectrum for an air calibration measurement ... 97
Figure 5.2 – Illustration of the pump out curve for a given isotope ............................... 100
Figure 5.3 – The modelled decay constant of each isotope ........................................... 103
Figure 5.4 – The variation in air calibration amounts over time ..................................... 106
Figure 5.5 – A delta plot of 1/4, 1/2, and 1 aliquot air measurements ............................ 108
Figure 5.6 – Comparison of the predicted error and the standard deviation of measurements ... 113
Figure 5.7 – Histogram of the measurement to air delta values for $^{82}$Kr .......................... 114
Figure 5.8 – Histogram of the measurement to air delta values for $^{83}$Kr .......................... 114
Figure 5.9 – Comparison of day-to-day errors and whole dataset errors ......................... 116
Figure 5.10 – Comparison of $^{83}$Kr/$^{84}$Kr ratios across several days analysis, and individual days 116
Figure 5.11 – Analysis of the ionisation efficiency of $^{83}$Kr over a period of time ............. 117
Figure 5.12 – Three repeats of tuning curve measurements made at 1507.0320 nm .......... 119
Figure 5.13 – Comparison of $^{82}$Kr/$^{84}$Kr ratios across several days analysis, and individual days ... 120
Figure 5.14 – A summary plot of the Eucrite samples measured as standards .................. 123
Figure 5.15 – The three common ‘trapped’ components .............................................. 124
Figure 5.16 – Production rates of $^{81}$Kr relative to the production rate of $^{83}$Kr ................. 126
Figure 5.17 – An illustration of the developed CRE age calculation method .................... 128
Figures 5.18 (a & b) – Comparing detections and ratios as a means to evaluate data points ... 130
Figure 5.19 – $^{83}$Kr/$^{84}$Kr against $^{81}$Kr/$^{84}$Kr for a fragment of Stannern ...................... 131
Figure 5.20 – An illustration of the ratio distribution of measurements ............................ 132
Figure 6.1 – A $^{83}$Kr/$^{86}$Kr, $^{82}$Kr/$^{86}$Kr summary of the measurements of CAIs .................. 144
Figure 6.2 – A plot showing the $^{85}$Kr/$^{84}$Kr ratio measured against detections for $^{84}$Kr ... 145
Figure 6.3 – A delta plot of $^{86}\text{Kr}/^{84}\text{Kr}$ relative to the number of detections of $^{84}\text{Kr}$ .................. 146
Figure 6.4 – Gradients of each isotope’s best fit lines ................................................................. 147
Figure 6.5 – A delta plot for the average ratios of whole air aliquot measurements .................. 149
Figure 6.6 – Average delta values of air measurements relative to standard air values ............ 150
Figure 6.7 – Delta plots for $^{80}\text{Kr}$, $^{82}\text{Kr}$, and $^{86}\text{Kr}$ relative to $^{84}\text{Kr}$ ......................... 153
Figure 6.8 – Combined summary three isotope plot of all CAI data ......................................... 153
Figure 6.9 – Cumulative release diagrams for the CAI samples .................................................. 155
Figure 6.10 – $^{81}\text{Kr}/^{83}\text{Kr}$ and $^{82}\text{Kr}/^{83}\text{Kr}$ three isotope plots for CAI samples .................. 156
Figure 6.11 – The releases from a CAI extracted from slide 3a ..................................................... 159
Figure 6.12 – The releases from a CAI extracted from slide 3a ...................................................... 160
Figure 6.13 – Plots selectively using data that shows isotopically heavy compositions .......... 166
Figure 6.14 – Delta plots of heavy krypton releases ................................................................. 167
Figure 7.1 – An illustration of the difference in instrument sensitivity ........................................... 170
**TABLE OF EQUATIONS**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation 1</td>
<td>38</td>
</tr>
<tr>
<td>Equation 2</td>
<td>39</td>
</tr>
<tr>
<td>Equation 3</td>
<td>39</td>
</tr>
<tr>
<td>Equation 4</td>
<td>40</td>
</tr>
<tr>
<td>Equation 5</td>
<td>40</td>
</tr>
<tr>
<td>Equation 6</td>
<td>40</td>
</tr>
<tr>
<td>Equation 7</td>
<td>40</td>
</tr>
<tr>
<td>Equation 8</td>
<td>40</td>
</tr>
<tr>
<td>Equation 9</td>
<td>41</td>
</tr>
<tr>
<td>Equation 10</td>
<td>41</td>
</tr>
<tr>
<td>Equation 11</td>
<td>41</td>
</tr>
<tr>
<td>Equation 12</td>
<td>43</td>
</tr>
<tr>
<td>Equation 13</td>
<td>43</td>
</tr>
<tr>
<td>Equation 14</td>
<td>48</td>
</tr>
<tr>
<td>Equation 15</td>
<td>48</td>
</tr>
<tr>
<td>Equation 16</td>
<td>49</td>
</tr>
<tr>
<td>Equation 17</td>
<td>49</td>
</tr>
<tr>
<td>Equation 18</td>
<td>49</td>
</tr>
<tr>
<td>Equation 19</td>
<td>50</td>
</tr>
<tr>
<td>Equation 20</td>
<td>51</td>
</tr>
<tr>
<td>Equation 21</td>
<td>54</td>
</tr>
<tr>
<td>Equation 22</td>
<td>60</td>
</tr>
<tr>
<td>Equation 23</td>
<td>69</td>
</tr>
<tr>
<td>Equation 24</td>
<td>99</td>
</tr>
<tr>
<td>Equation 25</td>
<td>99</td>
</tr>
<tr>
<td>Equation 26</td>
<td>100</td>
</tr>
<tr>
<td>Equation 27</td>
<td>100</td>
</tr>
<tr>
<td>Equation 28</td>
<td>113</td>
</tr>
<tr>
<td>Equation 29</td>
<td>151</td>
</tr>
<tr>
<td>Equation 30</td>
<td>151</td>
</tr>
</tbody>
</table>
TABLE OF TABLES

Table 1.1 – Thesis aims and objectives.............................................................................................................. 14
Table 2.1 – Common krypton components........................................................................................................ 17
Table 2.2 – Spallation krypton values............................................................................................................... 17
Table 3.1 – Parameters that must be tuned well in order for good instrument performance..................... 67
Table 4.1 – Considered methods of filling the Xe-Ar mixing cell................................................................. 74
Table 4.2 – Transitions in Xe around 252nm................................................................................................... 77
Table 5.1 – Isotopic shift values for the two resonant steps used in the ionisation scheme..................... 112
Table 5.2 – Correction factors for the major even isotopes................................................................. 121
Table 5.3 – Correction factors calculated for the odd isotope $^{83}\text{Kr}$...................................................... 121
Table 5.4 – Calculated CRE ages for the Stannern and Bereba Eucrites................................................... 128
Table 6.1 – Samples provided by J. T. Wasson and A. E. Rubin, UCLA.................................................. 138
Table 6.2 – Mass discrimination correction values...................................................................................... 150
Table 7.1 – Reflection on original thesis aims.............................................................................................. 175
## Table of Appendices

Appendix 1 – Glossary of terms........................................................................................................ 182  
Appendix 2 – Tunable dye laser system details............................................................................. 185  
Appendix 2 – Photographs of Allende thick sections provided by J. Wasson and A. Rubin. Taken with a DSLR camera, prior to any work on the samples ........................................................................... 188  
Appendix 3 – Scans of the Allende thick sections provided by J. Wasson and A. Rubin. Scans at 600dpi using Canonscan scanner ............................................................................................... 190  
Appendix 4 – SEM EDS element maps from the two example CAIs shown in Chapter 2. (scale bars apply across all EDS maps for that sample) .............................................................................. 193  
Appendix 5 – A schematic diagram of the RIMSKI instrument ................................................................ 197  
Appendix 6 – Excerpts from the standard user protocol manual for RIMSKI - all protocols were developed over the duration of this thesis ............................................................................. 198  
Appendix 7 – Bereba Eucrite Reduced Data ................................................................................. 207  
Appendix 8 – Stannern Eucrite Reduced Data .............................................................................. 208  
Appendix 9 – Bereba Eucrite CRE Age Data ............................................................................... 209  
Appendix 10 – Stannern Eucrite CRE Age Data ............................................................................ 210  
Appendix 11 – Alternative Method CRE Age Calculation Data ...................................................... 211  
Appendix 12 – A table of measurements carried out for the CAI measurements ......................... 212  
Appendix 13 – A table of reduced CAI sample data. All ratios have been corrected for instrument mass discrimination, as well as instrument signal dependent mass discrimination ........................................................................ 216
ABSTRACT

Mark Christopher Nottingham
Doctor of Philosophy (PhD)
The University of Manchester

Resonance Photo-ionisation Mass Spectrometry Techniques for the Analysis of Heavy Noble Gas Isotopes in Extra-terrestrial Samples.

The field of noble gas mass spectrometry is a rapidly developing one. There is a sustained requirement for continuous development of instrumentation in order to allow researchers to answer critical questions facing their respective fields. Within planetary science, the question of whether our solar system is ‘typical’, has been a driving force behind many lines of research. This project sought to build upon the strong instrumental base of the Isotope Geochemistry and Cosmochemistry group of the University of Manchester, in order to develop the Resonance Ionisation Mass Spectrometer for Krypton Isotopes. From that basis, it then sought to develop techniques and protocols for the analysis of extra-terrestrial samples, particularly those of very low mass.

The thesis is broken down into three studies. The first involved the development of the mechanisms used to fill the Xe-Ar four-wave mixing cell. This section covers the development, implementation, and characterisation of the newly installed mass flow controllers. The additional control over the mixing ratio granted allowed an eightfold increase to the sensitivity of the instrument. The reproducibility of the gas ratio is consistently shown throughout, and has ultimately reduced the tuning time of the instrument from a number of weeks to a day.

The second section details the required procedures involved in data reduction, and the development of protocols and software for the RIMSKI instrument. A range of approaches are assessed, including a novel approach to cosmic ray exposure age calculations. The methods are discussed and implemented on extra-terrestrial samples, the Stannern eucrite and the Bereba eucrite.

Finally, the analytical limits of the RIMSKI instrument are expanded via the measurement of the krypton systems of individual calcium-aluminium-rich inclusions. It is observed that Allende CAIs show a trapped component, Br-derived Kr, as well as an anomalous ‘heavy Kr’ component (one that is enriched in $^{86}$Kr). It is additionally noted that there is a lack of cosmogenic krypton to be found in all but one of the measured inclusions. The implications of these findings are discussed.
DECLARATION

No portion of the work referred to in the thesis has been submitted in support of any application for another degree or qualification of this of any other university or other institute of learning.

COPYRIGHT STATEMENT

I. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

II. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

III. The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

IV. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property University IP Policy (see http://documents.manchester.ac.uk/display.aspx?DocID=24420), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.library.manchester.ac.uk/about/regulations/) and in The University’s policy on Presentation of Theses
ACKNOWLEDGEMENTS

Anyone who has carried out experimental work will know that things rarely go smoothly all the time (in fact, at times it can seem like things never go smoothly any of the time!). This thesis was no exception to this, and I have no doubt that I would not be at the point that I am now without the support I received throughout the last four years. To that end, this thesis is dedicated to everyone who has helped me get through these last four years. I would like to thank:

My supervisor, Prof. Jamie Gilmour, for guiding me through a very challenging thesis, for keeping me sane and thinking clearly, but most of all for teaching me the values of being a good researcher and how to go about achieving that. Dr John Cowpe, for all of his technical expertise and knowledge about the components that formed RIMSKI, for the never ending help in keeping RIMSKI running, and for reminding me that ‘it’ll all be fine’ - in the end it was! Dr Sarah Crowther, for her relentless help with the lab. Sarah taught me a lot of what I now know about the lab. We’ve had our fair share of lab challenges, but we came out on top. Thank you for putting up with me at my worst, as well as my best. Dr Jon Fellowes, for his help with SEM and microprobe characterisation of my samples and subsequently Dr. Rhian Jones who took the time to discuss the characterisation of the samples with me. It has been my privilege to have the opportunity to work with you all, and I am very grateful for everything you have shown me over the past four years.

To all my friends, I owe you so much gratitude for being there for me in each of your own ways. Whether you were the friendly faces that I had the privilege of sharing an office with, the friends that kept me sane whilst doing lab work and writing up (there really are too many of you to name - but you all know who you are - you all made me look forward to tea room lunches and really did make me feel a part of the department), Billy and Rhodri who helped me out by letting me live with them while I finished writing up, Nat and Katie who have always been pillars of support throughout the last four years, my friends outside of university who consistently reminded me that I had a life outside of research as well (Including the friends that shared in: nights of far too much good wine, weekends away hiking, the choirs I have sung in, or were team mates from my brief foray into rugby).

A special mention to two people, (soon to be Dr.) Jack Coffin and Dr. Dan Balfour, who both persuaded me to keep going when I was ready to give in and quit – you provided me with advice that I hope I will be able to pass on to others someday. Specifically, Jack, thank you for changing my view of a PhD - describing a PhD as ‘the equivalent to a driving test - you learn to pass the test then learn how to do research’, really changed my view on what I was doing. These thanks would not be complete without a special mention to my parents, Chris and Joanne Nottingham - and my brother, James Nottingham. Your support has made this achievement possible, and I cannot thank you enough for all of the love, advice, and support you have provided.

I thank you all for all of your help over the past few years. I am sure I owe you all a fair number of drinks, and I hope to be able to repay those over many years of friendships yet to come.

Last but by no means least; I would like to thank the Science and Technology Facilities Council (STFC) and the University of Manchester, for not only providing the funding without which this thesis would not have been possible, but also the invaluable training that I have received from their numerous workshops and training opportunities.
1. Introduction

The question ‘is our solar system typical, and if not what events led to its atypical nature?’ is central to planetary science. Investigating a question of this magnitude requires a wide range of phenomena, and samples, to be researched. To address this, a knowledge of how our solar system formed and whether it should be considered ‘typical’ when compared to other observed planetary systems is required. In essence, to further understand how planetary systems form and evolve, we must first understand our own.

Meteorites act as ‘snapshots’ of the solar system’s formational processes, with each sample providing a unique insight into processes that were ongoing throughout the evolution of the solar system. The isotopic systems that can be analysed for information about the early solar system are extensive, with each showing a subtly different process. One such system, the krypton system, is of interest to planetary sciences because of its ability to provide information about the radiation environment of the solar system. This system is the focus of the work carried out towards the completion of this thesis.

Meteorites are also rare and precious resources, with a finite supply available to the scientific community. It is therefore critical to ensure the maximum scientific gain from any one sample. With many techniques, the process is sample destructive, meaning the sample is damaged or destroyed in the process of analysis. One way we can maximise the scientific gain from a sample is to reduce the amount of material required for a given analysis. This was one of the significant motivations behind the development of the Resonance Ionisation Mass Spectrometer for Krypton Isotopes (RIMSKI).

Analytical instrumentation is a rapidly developing field. The RIMSKI instrument is an ultra-sensitive noble gas mass spectrometer, capable of measuring small quantities of krypton gas within milligram sized meteorite samples. So far, the instrument has been successfully used to measure eucrite meteorites (Strashnov et al., 2011), and the chondrule fraction of chondritic meteorites (Strashnov and Gilmour, 2013). Use of the instrument has been restricted to somewhat isolated analyses due to issues with the reproducibility of the tuning up procedure. Developing the tuning ability of the instrument, and increasing understanding of the calibration requirements of the instrument, were objectives of this project.
Within the krypton system, one commonly used technique is the cosmic ray exposure age dating scheme. The technique relies on accurate measurement of the isotope $^{81}$Kr, a radioisotope ($t_{1/2} = 2.29 \times 10^5$ years) of krypton that is absent (barring trace levels) within terrestrial material, and present in very low concentrations within material that has been exposed to cosmic ray radiation. The ability to measure $^{81}$Kr within extra-terrestrial samples is not new, the technique has been used consistently (with small revisions), since its inception (Marti, 1982; Marti, 1967). The ability to measure the concentration of $^{81}$Kr in individual meteorite inclusions is a more recent development, with many of the first measurements of meteorites and meteorite inclusions being carried out on the RIMSKI instrument (Strashnov et al., 2013; Strashnov and Gilmour, 2013).

1.1 AIMS OF THIS THESIS
This thesis is part instrument development based, and part sample analysis based. The core aims of the thesis are presented in Table 1.1.

<table>
<thead>
<tr>
<th></th>
<th>Aim</th>
<th>Justification</th>
<th>Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>To improve the reproducibility of measurements made using the RIMSKI instrument by enhancing the control over tuning procedures.</td>
<td>At the point of publication of the characterisation paper for the RIMSKI instrument (Strashnov et al., 2011), the instrument took several weeks to tune to a usable level. Additionally, methods were difficult to replicate without considerable experience and time using the instrument. The lack of reproducibility hampered the degree to which statistics could be constructed in order to better assess instrument function over a sustained period of time.</td>
<td>a) Identify areas for instrument development. b) Design and implement instrument modifications that will enhance reproducibility and control over the tuning procedure. c) Characterise the use of these modifications. d) Develop tuning protocols a new user could implement.</td>
</tr>
</tbody>
</table>
| 2) | To develop measurement and data reduction protocols. | As a relatively complicated analytical instrument, it is a benefit to have a defined measurement protocol and data handling procedure. Protocol ensures the data produced by the instrument are affected by the same biases and uncertainties, allowing comparisons between data sets more easily. | a) To comprehend the data reduction system being used on the RELAX spectrometer data.  
b) To assess differences in the data collection procedures between the RELAX and RIMSKI instruments.  
c) To develop a method for the measurement of data, allowing the maximum scientific gain from any given sample analysis.  
d) To produce a consistent and reproducible method of data handling, which accurately reduces the data and allows conclusions to be drawn with confidence. |
| 3) | To prove the function of both the modifications to the instrument, and the protocols developed. | This partially falls under characterisation of the instrument, but it is important that the revised instrument’s functioning is compared to measurements made previously using the instrument. This can be done by measuring meteorite samples that have previously been measured using the instrument. | a) Select a range of meteorite samples already measured using the RIMSKI instrument.  
b) Measure, and reduce the data collected using the new protocols.  
c) Compare data between previous analyses and the current instrument function.  
d) Revise protocols if necessary. |
| 4) | To push the limits of samples that can be measured using the RIMSKI instrument. | The opportunity for a collaborative analysis of krypton within CAIs serves as an ideal study to push the limits of the analytical abilities of the instrument. The measurement of inclusions such as CAIs is an ideal use of the RIMSKI instrument’s capabilities. | a) Identify a range of CAIs from Allende thick sections.  
b) Extract material for analysis.  
c) Measure the krypton gases within these inclusions.  
d) Constrain the krypton noble gas systems of Allende CAIs. |

*Table 1.1 – Thesis aims and objectives*
2. BACKGROUND INFORMATION

Preface
Terminology within an interdisciplinary field such as planetary sciences can be difficult to follow, with many terms being used to mean similar but different things by different fields of study. In many cases this is due to one field adopting a term already used in another field; the two terms generally refer to similar phenomena, but the nuanced differences in the details of the two phenomena leads to eventual misunderstanding across the fields. Terms are also sometimes simultaneously adopted by two different fields to denote very different phenomena. This is particularly prevalent in planetary sciences which have seen the marrying of many different disciplines required to fully understand our solar system. An example of this is the use of ‘trapped’ by lunar scientists to refer to purely solar wind composition gases, whilst the general noble gas community uses ‘trapped’ to refer to gases present in a sample at the time the sample formed. To alleviate this problem, terms of importance are defined in the glossary section (Appendix 1). These are the definitions intended throughout this thesis.

2.1 NOBLE GASES

Noble gases are commonly used as tracers for the processing of material within the solar system. In any given noble gas atom, in a neutral electronic configuration, all valence shell electron orbits are filled. This results in them being chemically inert, meaning that predominantly only physical fractionation will affect them. Also adding to their utility is how they form the end point for many nuclear decay chains, combining this with the inert nature of the gases this means nuclear processes and their effects on solar system materials can also be observed in measurements.

The absolute abundance of noble gases varies depending on the element, but all noble gases are considered rare within the volatile inventory of the earth, and other rocky extra-terrestrial bodies. This is an advantage when assessing measurements for processes that have adjusted the ratios between isotopes of a given noble gas. The relatively small inventory of noble gases within samples means that the addition of components from radioactive decay processes, and spallation type processes have a more distinguishable effect on isotopic ratios. In a system where the element is more abundant, those processes are harder to distinguish.

When discussing noble gas components within meteorites, it is worth distinguishing ‘trapped’ gases, and those that have been produced in situ. ‘Trapped’ components are gases that were
already present, or were incorporated into the meteorite by arriving materials, at the time of
the parent body formation. The gases produced in-situ are those which form within the rock,
after formation of the parent body, and are generally the result of nuclear reactions. Primordial
components are always considered ‘trapped’ components, whilst spallation products and those
components produced by nuclear decay processes are ‘in situ’ components.

The origin of these elements can be divided into two categories: primordial (material that was
incorporated into the Solar System when it formed), and radiogenic or cosmogenic (material
that has formed since the start of the solar system; this can be either by cosmogenic means or
by nuclear decay processes but is always produced in situ). These can be further divided into
reservoirs, each of which has a unique isotopic composition. These reservoirs are commonly
referred to as components because it is common for several reservoirs to be present in any one
meteorite. The exact origins of noble gas reservoirs in the solar system still proves controversial
to the planetary sciences community. Competing theories about the origins of these gases
include: Solar noble gases form the most primitive reservoir in the solar system and are then
subsequently added to via spallation mechanisms and radioactive decay processes to produce
several distinct solar system reservoirs. Contrasting against that is the view that these gases
were extrasolar in origin, possibly sampling a molecular cloud. There are reservoirs that each of
these ideas fail to explain, and additionally, the extrasolar theory would require the Sun’s
surface to be unrepresentative of the bulk solar system inventory. This seems implausible given
the Sun accounts for most of the mass in the solar system. For that reason it is generally
assumed that the bulk Q-phase gases are predominantly of solar composition and origin, with
additions to the systems derived from extrasolar sources, radiogenic processes, or spallation
reactions (Swindle, 1988).

2.1.1 KRYPTON AND KRYPTON COMPONENTS

Krypton is a heavy noble gas, with six naturally occurring stable isotopes; $^{78}$Kr, $^{80}$Kr, $^{82}$Kr,$^{83}$Kr,
$^{84}$Kr, and $^{86}$Kr. Compared to other noble gases, krypton shows remarkable consistency in its
isotopic composition between different solar system objects. Common krypton components are
summarised in Table 2.1. It is important to note that krypton measurements are standardised to
a terrestrial air composition, therefore there is no reported error associated with those values.
<table>
<thead>
<tr>
<th>Component</th>
<th>$^{78}$Kr</th>
<th>$^{80}$Kr</th>
<th>$^{82}$Kr</th>
<th>$^{83}$Kr</th>
<th>$^{86}$Kr</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial Air*</td>
<td>0.006087</td>
<td>0.03960</td>
<td>0.20217</td>
<td>0.20136</td>
<td>0.30524</td>
<td>[a]</td>
</tr>
<tr>
<td>Q-Kr</td>
<td>0.00603 (±0.00003)</td>
<td>0.03937 (±0.00007)</td>
<td>0.2018 (±0.0002)</td>
<td>0.2018 (±0.0002)</td>
<td>0.3095 (±0.0005)</td>
<td>[b]</td>
</tr>
<tr>
<td>Solar*</td>
<td>0.006365 (±0.000034)</td>
<td>0.04088 (±0.00014)</td>
<td>0.20482 (±0.00054)</td>
<td>0.20291 (±0.00026)</td>
<td>0.3024 (±0.0010)</td>
<td>[c]</td>
</tr>
<tr>
<td>HL</td>
<td>0.0042 (±0.0010)</td>
<td>0.04050 (±0.0010)</td>
<td>0.1590</td>
<td>0.1989 (±0.0010)</td>
<td>0.3623 (±0.0018)</td>
<td>[d]</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>0.0133 – 0.0183</td>
<td>0.4167</td>
<td>0.1192 (±0.0054)</td>
<td>0.454 – 1.176</td>
<td>[e]</td>
</tr>
<tr>
<td>AVCC</td>
<td>0.00597 (±0.00005)</td>
<td>0.039188 (±0.000295)</td>
<td>0.201487 (±0.000796)</td>
<td>0.201704 (±0.000796)</td>
<td>0.309789 (±0.000768)</td>
<td>[f]</td>
</tr>
</tbody>
</table>

Table 2.1 – Common krypton components. All ratios are relative to $^{84}$Kr=1. (Ref: [a] – Originally Basford et al. (1973) renormalized for $^{84}$Kr=1; [b] – Busemann et al. (2000); [c] – Originally Pepin et al. (1995) renormalized for $^{84}$Kr=1; [d] – Huss and Lewis (1994a) Renormalised by Ott (2002); [e] – Huss and Lewis (1994b); (*Values normalised to Terrestrial Air), (Wieler (2002b) present additional values for Solar wind, but these values include greater uncertainty and plot beyond the uncertainty of Pepin et al. (1995)); [f] Eugster et al. (1967 c), renormalized to $^{84}$Kr=1.

<table>
<thead>
<tr>
<th>Component</th>
<th>$^{78}$Kr</th>
<th>$^{80}$Kr</th>
<th>$^{82}$Kr</th>
<th>$^{84}$Kr</th>
<th>$^{86}$Kr</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lunar Spallation</td>
<td>0.20 (±0.02)</td>
<td>0.54 (±0.07)</td>
<td>0.72 (±0.05)</td>
<td>0.32 (±0.10)</td>
<td>0</td>
<td>[g]</td>
</tr>
<tr>
<td>Chondritic Spallation</td>
<td>0.18 (±0.04)</td>
<td>0.60 (±0.08)</td>
<td>0.76 (±0.08)</td>
<td>0.67 (±0.15)</td>
<td>0</td>
<td>[h]</td>
</tr>
</tbody>
</table>

Table 2.2 – Spallation krypton. All ratios are relative to $^{83}$Kr=1; (Ref: [g] – Pepin et al. (1995); [h] – Lavielle and Marti (1988), mean and standard deviation from 11 chondrites)

Each component can be thought of as sampling a distinct reservoir. Air is an average Earth atmospheric value; Q-Kr is thought to represent a primordial asteroid composition, it was found and documented in Busemann et al. (2000); Solar wind is calculated from the Genesis mission as well as lunar regolith analyses, it represents the composition of krypton being ejected from the Sun’s mass as solar winds, this is often taken as the bulk solar system composition, however it is possible due to the processes involved in forming the solar wind that these values have undergone mass dependent fractionation; Lunar and chondritic spallation are representative of the spallation gas compositions expected in lunar rocks and chondritic meteorites respectively.
and are based on experimental measurements, notably Pepin et al. (1995) for lunar measurements, and Lavielle and Marti (1988) for chondritic values. AVCC is the Average Chondritic Composition, the krypton measured to be preserved in an average chondritic meteorite. These archetypal component values are representative of the common dominant components in meteoritical noble gases. Imprinted over these dominant components are sometimes a series of rarer components. These additional components often do not make up significant proportions of the noble gas inventory of meteorites.

**Figure 2.1** – A spectrum for terrestrial air, as measured using the RIMSKI instrument. Note, the peak at 78 AMU is due to hydrocarbon interference at that mass.

Additional components are derived from the rare microscopic grains that sample the more exotic reservoirs of the solar system (and in some cases, extra solar sources), from radioisotopic decay, or from nucleosynthetic processes. These components are numerous, therefore this section discusses only the components discussed as a part of this thesis.

High-Low Kr (HL-Kr) has undergone several revisions since it was first discovered. In its current iteration HL-Kr refers to the relative enrichment of the heavy isotopes of Kr (whilst other elements are also enriched in light isotopes within the classification of HL gases, krypton does not show this trend, instead just showing enrichment in heavy isotopes, [Podosek ToG Noble gases]). The gas is found in nano meter sized diamond grains, which have been theorised to be the remnants of supernova ejections. This hypothesis is supported by the similarity of the HL component to that of two nucleosynthetic processes known to occur in supernova explosions. These processes, the r-process (leading to an enrichment in heavy Kr isotopes) and the p-process (leading to the enrichment of the light Kr isotopes) are necessarily distinct from each other due to the nucleosynthetic pathways involved in the formation of the respective isotope
masses. This dichotomy has led some (Meshik et al., 2001; Ott, 1996) to theorise that the nano diamond grains are two distinct types (some sampling r-process gases and other p-process gases) but, due to the impossibility of individual grain analysis, reflect a mix between the two components. This would imply a distinct H-Kr component and a distinct L-Kr component (although, as mentioned earlier, the presence of an L-Kr is unlikely).

G-Kr is thought to be representative of the composition of Kr produced by the s-process (Podosek, ). The G-Kr component is complex due to how the 85Kr s-process branches depending on the astrophysical parameters at the time of production. G-Kr is contained within silicon carbide grains (SiC) which are produced in a range of astrophysical settings, but predominantly within AGB stars, as is detailed in a range of sources: Hoppe & Ott (1997); Lewis et al., (1994); amongst others.

A rare component to observe in meteorites is fissogenic krypton. The low abundance of the two elements known to form krypton as a part of their radioactive decay chains, Pu and U, means that this component is often a very small fraction of the total krypton inventory of a meteorite. In turn this means radiogenic components are often unresolvable amongst the much more abundant trapped components. 244Pu is thought to produce pure 86Kr (Swindle, 1988). This is backed up by Lewis (1975), in which a near monoisotopic enrichment of 86Kr within mineral separates from the chondrite St. Severin was found. This enrichment was theorised to be the resulting product of 244Pu fission. Additionally, spontaneous fission of 238U produces 83Kr, 84Kr, and 86Kr at ratios of 0.03 ± 0.01, 0.13 ± 0.02, and 1 respectively (calculated based on nuclear characteristics). Finally, 235U can undergo neutron-induced fission to form 83Kr, 84Kr, and 86Kr at ratios of 0.27 ± 0.01, 0.50 ± 0.02, and 1 respectively. (Fission product data are from Ozima and Podosek, 2002).

Neutron capture on 79Br and 81Br can occur when a neutron travelling at thermal or epithermal energies (100’s – 1000’s keV) impacts a Br atom. The s-process reaction (a slow neutron capture nucleosynthetic process) for 79Br and 81Br produces 80Kr and 82Kr respectively. Eugster et al. (1967 a) measured fourteen stone meteorites and concluded Br-neutron capture Kr is produced at a 80Kr/82Kr ratio of 2.25, which is in good agreement with the predicted rate based on resonance integrals of Br. This reaction pathway causes significant problems for the 80Kr-82Kr production rate method of calculating 81Kr production rates (see below). For most meteorites, particularly achondrites, the Br content is low enough to make this addition negligible. Whereas chondrites that have undergone alteration (particularly hydrothermal alteration, which tends to introduce larger quantities of halogen elements into the rock), these effects are more pronounced.
Additional nucleosynthesis of Kr is possible through the interaction of high energy cosmic rays, via spallation. The isotopic composition of Kr produced by spallation is typically dependent on the chemistry of the meteorite, in particular the concentrations of target elements. The most extreme differences commonly cited are that of the spallation gas spectrum of lunar rock samples, and that of the spallation gas spectrum of a typical chondrite. The literature values for both these end member components are shown in Table 2.2. Additional details about cosmogenic gas production are discussed in section 2.5.

2.1.2 Controls on Krypton Components

The homogeneity of krypton gases across rocky material on a macro scale does not apply to micro scale geological systems. The amount of a given component within a mineral grain will depend on the mineral’s ability to retain that gas, or in some cases the ability for it to be produced in the first place.

The occurrence of krypton spallation isotopes within minerals is strongly dependent on the concentration of target elements. Within rocky material, the dominant target elements are Sr, Y, Zr, and Rb. Each element has a subtly different spallation spectrum. These are shown in Figure 2.2. The main difference between the elements is the production rate of $^{84}$Kr, an isotope which is not commonly used for cosmic ray exposure age calculation. It should be noted that the assumption of $^{86}$Kr not being produced through spallation reactions is not strictly true, particularly for Rb. The production rate of $^{86}$Kr follows a similar trend to the production rate of $^{84}$Kr. The total amount of $^{86}$Kr produced is still a relatively small amount, and within the uncertainty associated with cosmic ray exposure age calculations, any $^{86}$Kr measured within a sample can reasonably be said to be from a trapped component or a radiogenic component.

From the spectra presented in Figure 2.2 it is apparent that the spallation spectra from a meteorite sample should be independent of chemistry effects. However, when looking at the absolute amount of produced spallation gases (Figure 2.3), there is a clear decrease with each additional step away from the atomic number of krypton. This can be attributed to the energy requirements for the spallation of an increasingly massive fragmented particle. It should be noted that the $^{86}$Kr discrepancy is most notable for Rb, which is also responsible for the highest spallation production rate for Kr.
Figure 2.2 – Krypton spallation spectra for primary target elements; data of measurements from Gilabert et al. (2002). Measurements were of pure target element samples at different shielding depths in a 50 cm diameter gabbro sphere (density 3.0 g/cm$^3$). The artificial meteoroid was irradiated with 1600 MeV radiation for the equivalent exposure of ~3 Ma. Depths are given as distance to meteoroid centre in g/cm$^3$: Rb 69.3, Y 68.1, Sr 69.0, Zr 66.6. Calculation of the depths are based on measured distance combined with an average gabbro density of 3.0 g/cm$^3$. Irradiation of an object this size can be considered 4π exposure at any depth.

Spallation gases are also affected by shielding. Any radiation passing through matter stands a chance of interacting with that matter. This results in the radiation energy being attenuated or deflected onto a different path. In the case of cosmic rays passing through a meteoroid, this attenuation has two noticeable effects: The amount of radiation making it to a given depth decreases as depth increases, thus decreasing the number of particles that could produce spallation krypton; and the distribution of energies carried by these particles is also changed as depth increases. These factors combine to decrease the amount of krypton produced, via spallation reactions, the deeper into a meteoroid body the radiation has to travel. In turn, the production of krypton from bromine increases at depth as the secondary neutron production peaks to its maximum. This is due to the slowing of significant populations of particles to
At these depths a spallation reaction is much less likely to occur due to energy attenuation, but the flux of secondary neutrons has increased (those released as a by-product of higher energy collisions) therefore increasing the production of krypton from neutron capture reactions. This reaction will also peak according to the production rate of secondary neutrons and their attenuation through the meteorite body. The ratios between each isotope, for each target element, do not significantly change with depth. Therefore the production of krypton can be said to be largely independent of shielding depth when looking at isotopic ratios. However, the total amount of krypton produced by spallation reactions is significantly affected by shielding depth.

Figure 2.3 – Amount of $^{83}$Kr produced from pure Kr spallation target elements, in the experiments described in Figure 2.2. (Gilbert et al., 2002). All measurements are the equivalent of 4π irradiation for a period of 3 Ma.

Very little research has been carried out to identify the minerals that host krypton gases, or whether certain minerals are more likely to host particular components. Based on work carried out using the RELAX spectrometer, it has been theorised that feldspars should present good minerals for hosting krypton spallation gases.

It could be theorised that minerals rich in the krypton spallation target elements (Rb, Sr, Y, Zr) would be likely to host greater quantities of spallation krypton gas. These are typically what are known as scattered elements, meaning they do not often reside in their own mineral phases, but are rather dispersed across many mineral types. Equally, these elements are often only found in minor or trace amounts within a meteorite. This dispersion is a result of the elements being incompatible with the geochemistry of many mineral types. Some minerals do more readily accept and concentrate incompatible elements. For example, Rb is known to
concentrate in potassium minerals as the mineral crystallises from a melt. The feldspar minerals are arguably most likely to contain the highest Rb concentration (Deer et al., 2001). It stands to reason that the feldspar minerals will also serve as hosts for the Sr, Y, Zr elements as well, due to the similarity in the chemistries of these elements.

2.1.3 Bonding Sites

Whilst noble gases are chemically inert, they are often found in particular adsorption sites. Due to the origin of some components, the locations they can be expected to be released from differs. On a micro-scale analysis of noble gas distribution one might expect implanted solar wind components to reside within a sub-micron thick layer on a grain surface that has been exposed to solar winds, and equally one might expect to find cosmogenic gases trapped within the crystal lattice of a mineral, rather than stuck to the grain surfaces.

The implications of this are entangled with the energy required to extract gases from these different sites. Each type of bonding site will require different energy input in order to liberate the gas from its adsorption. This means, with careful control of the energy supplied by step pyrolysis, it should be theoretically possible to extract the components of krypton in separate releases from the sample. Mineral-laser interactions are non-uniform, the energy imparted by the incident laser energy is dependent on how well the laser couples with the mineral, but such effects are unimportant as laser step heating small samples allows the sample temperature to come to equilibrium. The step heating method has been shown to work on the RELAX spectrometer (e.g. in Fernandes et al., 2013).

2.2 Meteorites and Their Role in Our Understanding of the Solar System

Meteorites are small fragments of larger parent bodies, often asteroids, which have fallen to Earth. When an asteroid is broken up, it alters the geological processes taking place within the rocks, in most cases preserving an indication of those processes in the liberated fragment. The asteroid belt has been preserving these indicators of geological processing since the start of the solar system. It is for that reason that we see the rocky HED type meteorites, the iron rich meteorites, and also why we still see chondritic meteorites which have not been formed into bodies large enough to cause differentiation of the lithophile and siderophile components. In essence, these meteorites preserve images of the stages a protoplanet, and its constituent pieces, went through during the formation of the solar system. In much the same way as if we were to examine a scene in a photograph, if we analyse the chemical systems of meteorites we
can decipher the histories of these rocks, in turn increasing our understanding about how our solar system formed into what we observe today. Many of these processes are now largely considered extinct within non-geologically active planetary bodies. Therefore, data collected from meteorite analyses form one of our only ways of directly studying the effects and results of processes that were crucial to the formation of the solar system.

Figure 2.4 – Meteorite classification diagram, showing only sections involved in measurements within this study. Italics indicates the type meteorite name.

Meteorites are largely derived from parent bodies within the asteroid belt, a region of the solar system theorised to be the residue from planet forming events. There are a wide variety of parent bodies found within the asteroid belt, ranging from those that have undergone differentiation to those that represent the most primitive, unaltered, material in the solar system. The class of meteorites considered most useful when investigating the early solar system are the chondrites. These are a collection of meteorites that have never been fully melted since their origin at the start of the solar system. These meteorites characteristically contain crystalline spherules called chondrules, whilst many also contain agglomerates of high
crystallisation temperature minerals in what are collectively called calcium-aluminium-rich inclusions (CAIs). The classification of chondrites is a very broad group, out of these the most primitive examples of meteorites within the solar system are the carbonaceous chondrites (Figure 2.4).

Studies of these samples can lead to information about the processes required to form the Solar System in the way that it has formed, and from that we can begin answering whether or not our Solar System can be considered ‘typical’.

2.3 THE EARLY SOLAR SYSTEM

The first 10 My after the start of the Solar System was a period of rapid chemical and physical change. It saw the cooling of the protoplanetary disk to below 1800 K, allowing the first native refractory Solar System solids to condense in what is thought to be a calm environment, forming the group of inclusions known as Calcium Aluminium-rich Inclusions (CAIs); it saw the formation of the chondrules, in a more violent environment, and also saw the onset of the planet forming processes. Understanding the first 10 million years of the solar system’s evolution is key to understanding why the solar system has evolved in the way it has, and whether events considered abnormal were key in shaping the solar system we know today.

2.3.1 THE FIRST SURVIVING SOLID PHASES

As the solar system formed, there was a significant increase in temperature across the accretion disk. This increase in temperature is poorly constrained, both in timing and in terms of the peak temperature reached. The lack of precision on those two parameters leads to uncertainty on the timings of the formation of the first solids within the solar system. It is broadly accepted when looking at geochemical models of mineral formation, that the very first solids to form are now almost entirely extinct within the solar system, now only being rarely found as remnant corundum grains in the oldest surviving solids from the early solar system. These solids, collectively termed ‘Calcium Aluminium-rich Inclusions (CAIs), have been shown via geochemical modelling (Ebel, 2006), and later on by chronometer systems such as U-Pb dating, to be the first materials to have formed within the solar system, predating the onset of chondrule formation by a few million years.
These inclusions are a collection of the most refractory elements arranged into high crystallization temperature minerals. Their existence implies that at least part of the solar system reached at least the temperature at which only these minerals will condense, as a lower limit to the maximum temperature the solar system reached during the formative millions of years.

Pre-solar grains provide an interesting potential dichotomy to the notion that the solar system collectively reached this temperature. Their presence in an unmelted state either implies a later arrival of these materials, or else the whole of the proto-planetary disk did not reach this temperature. A heat gradient across the proto-solar disk is further supported by the occurrence of iron meteorites (and other differentiated meteorites), alongside unmelted chondritic meteorites.

Chondrites
Chondrites are the fraction of planetesimals that formed late enough to prevent the short lived radionuclides within the rock from accumulating to a significant enough concentration to cause total melting and differentiation. So, although they are thought to have formed as parent bodies later than those parent bodies of differentiated meteorite types, chondrites can be accurately described as the remnants of the oldest materials that formed the solar system because of their relatively short period of ‘active’ geological processing, compared to the time period the differentiated asteroids were active for. They represent the product of accreting dust and types of small unique inclusions, found only in the chondrite meteorites. The chondrite parent bodies are chemically and morphologically diverse, as are the range of processes that have altered them through time.

The chondrites thought to most accurately represent the original materials found in the solar system adopt the prefix ‘carbonaceous’. The carbonaceous chondrites have been a focus for research aiming to understand the formation of the solar system, due to the now generally accepted idea that they represent the remnant components of terrestrial planet formation. Because these meteorites have not undergone differentiation and do not show signs of melting since their formation they may be considered ‘unaltered’. (The term ‘unaltered’ should be used loosely to mean they have not undergone large scale reprocessing, such as that which led to the formation of the HED parent body. These meteorites do show evidence of parent body alteration after their formation). Even though these meteorites are relatively unaltered, they are by no means homogenous in their compositions and textures, instead the carbonaceous
chondrites display a wide range of subtypes, many of which are named after the first meteorite of that type identified. These can be seen in Figure 2.4.

The majority of chondrites contain (amongst others) two types of inclusions: chondrules (the inclusion type from which the meteorite classification derives its name), and Calcium-Aluminium-rich Inclusions (CAIs). These inclusions, alongside average chondritic matrix material, show evidence of very different formation environments and processes.

**Calcium Aluminium-rich Inclusions**

Calcium Aluminium-rich Inclusions (CAIs) are a complex group of inclusions that are enriched in refractory elements (Ca, and Al being two of the more dominant elements). There are two conflicting explanations pertaining to the formation of CAIs. The first works on the basis that these inclusions condensed from a hot solar gas, entirely native to our solar system. The second treats the CAIs as remnants of partially vaporised pre-solar objects. Both of these theories are supported by the chemistry of refractory elements. These elements are the first condensates out of a hot solar gas, and the last things to vaporise (Grossman, 1980).

*Morphology and Characteristics* - MacPherson (2005) describes a ‘typical’ CAI morphology, although it should be noted that this is not all encompassing as a description, but it does help illustrate some of the important features of CAIs. The author describes fine grained hibonite and spinel enclosed by blocky melilitie, with fine grained alteration separating these melilitie blocks, in many cases appearing to replace the ‘primary’ melilitie. This is then surrounded by a series of thin but remarkably consistent thickness rims. These rims, originally described in Wark and Lovering (1977), have now become commonly referred to as Wark-Lovering rims. They are commonly monomineralic, and often replicate the minerals found as a part of the primary phases within the inclusion interior. It should be noted that, although the mineral assemblages are often identical, these rims are clearly a different generation of mineral formation, and represent separate events. These rims are considered to have formed before the incorporation of the inclusion into the chondrite parent bodies. Further surrounding these rims are layers of discontinuous accretion rims. These rims are completely different to the Wark-Lovering rims and have clearly formed from different formational events entirely.

It can be difficult to comprehend descriptions of CAIs, owing to the variation in terminology between sources, and equally due to the variations in meanings ascribed to terms. For example, the attempts to prescribe ‘primary’ and ‘secondary’ to minerals within a CAI assemblage has been proven somewhat futile, owing to the complexity behind the processes (and in many
cases, the timing) blurring the lines between what would traditionally be termed a primary mineral, and a secondary mineral. These inclusions formed within a continuously and rapidly changing environment. As with many geochemical systems, as conditions change, so do the mineral assemblages most stable at those given conditions. As such, in a situation of a mineral that first condensed out of a gas, we would expect to see several iterations of alteration to that first mineral as it became possible for more mineral species to exist in the progressively cooling gas. Adding to the complexity of this, these back reactions may not have completely replaced the original mineral due to slow reaction kinetics, or a change in the equilibrium before the reaction could complete. This principle can be seen in Figure 2.6, demonstrated via corundum; which out of any mineral can be plausibly termed ‘primary’. However, to only use primary to refer to corundum would be pointless due to its rarity within inclusions. The scarcity of corundum is a direct result of the back reactions as the protoplanetary disk environmental conditions changed. The model proposed and discussed in Ebel (2006) infers that corundum was a much more abundant mineral prior to the shift in equilibrium conditions within the early solar system, from which point the corundum was replaced by other minerals via a series of back reactions and substitution reactions.

MacPherson (2005) details the pervasive problems encountered when dealing with terminology within the study of CAIs, recounting similar conundrums as the corundum back reactions previously mentioned and the confusion over the use of the terms primary and secondary minerals. Therefore, for the means of understanding within this project the term ‘primary’ will be used to mean those minerals that would have originally formed the CAI, and ‘secondary’ will be used to refer to those minerals which show evidence of pre-accretion alteration or parent body alteration subsequent to the formation of the inclusion, in line with a general geochemistry use of the terms. This will facilitate an ability to distinguish between those inclusions where the krypton system is expected to show evidence of disruption.

Naturally, these descriptions do not encompass all events that may have affected any given CAI throughout the course of its existence. This is quite easy to see when comparing two examples of CAIs used throughout the course of this project, as are shown in Figure 2.5. Here we see two completely different textures, where one CAI shows evidence of compaction and re-melting (1), and the second acts as a good example of a loosely held together aggregation of fine grained primary phase minerals (2). This second texture has taken on the moniker ‘fluffy’, to describe its structure. It is clear that very different processes have to have affected these two types of inclusions, in order for such distinctly different textures to form.
There are many morphologies and chemistries found within the refractory inclusions. The range of variations observed gives rise to equally numerous theories pertaining to the mechanisms of formation for these inclusions. There are two theories that have now been broadly accepted as the mechanisms most likely as an explanation of these inclusions. In the interests of simplicity, only these two mechanisms are presented.

**Figure 2.5 – Examples of CAIs imaged using SEM Element Mapping;** (1) A melted CAI, showing strong Wark-Lovering rims around the inclusion, as well as alteration of accretionary rims. (2) A fluffy CAI, these are more difficult to map owing to their friable nature when polishing, and the fine grain size of the main constituents of the inclusion. Key: A – An example of a back reaction where one mineral is being converted to another due to equilibrium condition change in the formation environment; B – Blocky crystals of the original mineral (unaltered B); C – Wark-Lovering rims; D – Accretion rim, likely melted; E – void space caused by wearing of the friable exposed CAI minerals; F – Artefact, the copper pointer used to locate the sample; G – Fine grained, highly altered, CAI minerals; H – Representative texture of the fluffy CAI, preserved from wearing by being encased in resin. Element colour keys are derived from the images found in Appendix 5.

**Equilibrium Condensation**

Equilibrium condensation is a term used to explain the vapour to solid condensation sequence without progressing through an intermediate liquid phase. Figure 2.6 is a model commonly invoked to show the sequence of condensation from a hot solar composition gas. As with all of these theories there is a great deal of disagreement over the initial pressure, temperature and
gas composition. These parameters, as the figure implies, dictate the sequence through which minerals form. There are many routes that can plausibly explain the mineral assemblages observed in CAIs. It has been theorised in chemical evolution models, that if a gas of average solar composition were to be cooled slowly, the first minerals that formed would be refractory minerals such as those observed in CAIs. Due to this, it seems likely that condensation of a hot solar composition gas would be a likely mechanism of CAI formation.

This formation mechanism requires the CAIs to form entirely natively to the solar system. The issue caused by this is one of timing versus environmental conditions. It is suggested by analyses of the Al-Mg system, amongst others, that the CAI formation predates the onset of chondrule formation by several million years, although other studies debate the accuracy of this. Studies such as that of Connelly et al. (2012) found that U-corrected Pb-Pb chronometer ages suggest contemporaneous CAI and chondrule formation over a 3 Ma period. Therefore, there is a need to further understand the timing of these inclusions, something that requires greater understanding of their geochemical systems.

Given the delicate rim sequences observed as a part of many CAIs, it is widely accepted that their formation environment is necessarily calm. The chondrules on the other hand, have been shown to require rapid heating, followed by relatively rapid cooling. This implies a more violent environment than the CAIs are thought to have formed in. If this is the case, and CAIs do predate the formation of chondrules, how do we see the preservation of CAIs alongside chondrules entrained in the same meteorite parent bodies? Surely if CAIs had to reside in the violent environment of chondrule formation, there would be a more significant population of inclusions with damaged or entirely lost rim sequences. This is not the case. We therefore have to devise a mechanism by which these inclusions can be removed from the violent environment, preserved for the duration of chondrule formation, and then subsequently reintroduced to the environment before the completion of chondrite parent body formation.

Another feature that equilibrium condensation models struggle to explain, is the textural features observed in CAIs. This may be indicative of a flaw in these models of formation and their applicability to CAIs or it may indicate the degree to which secondary processing has obscured the formation textures of these original inclusions. An example of secondary processing is found in the now almost extinct corundum within CAIs. As can be seen in Figure 2.6, corundum is the first mineral formed by condensation over a wide range of pressures (plausibly, across all pressures that are viable within the early solar system nebula). The rarity of this mineral suggests that it was altered through a series of later reactions, changing it from corundum into a range of other minerals as the conditions of the nebula changed. As is seen in
examples of metamorphic rocks on Earth, this replacement via back reaction can often
drastically change the texture of the mineral assemblage. In general, it is now accepted that
episodes of mechanical and chemical alteration must have significantly affected these inclusions
in a series of back reactions, perhaps permanently removing our ability to decipher the exact
formation mechanisms of these inclusions forever.

**Figure 2.6 – P-T phase diagram showing the condensation sequence of a hot solar composition gas; Ebel (2006)**

**Extra-solar Origin**

The alternative theory goes against Ockham’s razor, in that it requires far more events to occur
in coincidental succession. This is not necessarily a problem, but it is worth bearing in mind
when considering these two theories.

Several people have theorised that a supernova event occurred near enough to our solar
system as it was forming, to seed our solar system with excess short lived radioisotopes. It is
postulated that the CAI populations could have been transported to our solar system along with
the radioisotopes. At the point of arrival these grains were then heated, and in turn fractionated
by the heat engine of the early solar system. This requires a very precise temperature, in order
to remove the less refractory minerals without completely vaporising the grains. This theory has
been strongly advocated for (e.g. in Cameron, 1995), but equally strongly contested by Nittler (2005).

CAIs are a common component of chondritic meteorites. They show a wide range of types, including variations in chemistry, and morphology. Regardless of the formation mechanism, it is accepted that CAIs are a diverse group, and are so because of secondary processing of the inclusions. These mechanisms of alteration are mostly chemical, allowing features like Wark-Lovering rims to remain intact throughout the process.

**Chondrules**

Chondrules form only a minor part to this thesis, so a broad introduction to these inclusions is provided here, mainly to aid in understanding the key differences between CAIs and chondrules.

Alongside the CAIs, chondrules were some of the first solids to form in the solar system that have survived until present day. They show a range of 6 different common types, with differences in their morphology and chemical composition. Similar to CAIs, there are a wide range of theories pertaining to chondrule formation. Grossman (1988) provides a good summary of the wide range of mechanisms proposed for chondrule formation. There is seemingly greater consensus over the particular mechanism behind the formation of chondrules than there is for CAI formation. General consensus leans towards a mechanism of nebula dust re-melting to form heterogeneous populations of chondrules.

The aspect which has proven more controversial relates to the location within the early solar system nebula that these inclusions formed. If the chondrule formation region was isolated, then that may explain how CAI populations remained intact throughout this period of solar system development. It does however raise problems with how the two were recombined prior to parent body accretion.

A few parameters that are roughly agreed upon are that the heating intensity was restricted, and that the duration of heating was short. It is also likely that the efficiency of the process forming chondrules was high. Textural features suggest that the cooling rates of chondrules vary from 100’s of K per hour, to 1000’s of K per hour (Grossman, 1988). Many of the different theories focus on how to produce this rapid cooling that is required to form the inclusions. Additionally, there is consensus that these formation events must have been violent, in order to produce heating on the time scales required. Events like collisions between proto-planets and the splash droplets produced from those impacts were proposed, but other features refute
those models. It is now thought that rapid heating from the proto-sun would be a viable mechanism for this sudden heating, followed by fairly rapid transition into cooling.

2.4 CHRONOLOGY OF THE FIRST SURVIVING SOLIDS

There are many important processes that are believed to have taken place within the first 10 million years of the solar system’s existence. Understanding our Solar System’s history, and the timing of events theorised to have happened, is key to understanding whether it is a typical or atypical solar system. Evidence for processes that took place can be difficult to source; the earliest minerals to form within the system have, in most cases, been replaced or significantly altered. This means the minerals can often be more representative of the resulting rock than the individual inclusions or parts that originally formed it. Extra-terrestrial samples of chondrites, particularly the carbonaceous chondrites, are some of the oldest surviving materials from the formation of the solar system. They therefore provide the most likely source of information on the processes and components that formed the Solar System. When trying to assess any process within the early Solar System, it is necessary to have an understanding of the materials present at the onset of the process, and from there the extrapolation of how these materials change during the process can take place. Chronology of processes known to have happened in the early Solar System is therefore fundamental to our understanding of how the Solar System has evolved from its initial genesis. There are many chronology systems that are in common use within planetary sciences, and each system facilitates an understanding of different processes that are preserved by its record.

CAIs represent some of the oldest mineral assemblages found within the solar system. The most precise age reported so far places two CV3 chondrite CAIs from the Efremovka meteorite at 4567.11 ± 0.16 Ma, as detailed by Amelin et al. (2002). This age is also recognized as a weighted mean CAI age of measurements using the Pb-Pb system, and corroborated by $^{235}\text{U}/^{238}\text{U}$ measurements detailed by MacPherson (2005).

Using systems such as Pb-Pb, or Al-Mg, it is possible to calculate that CAI formation predates chondrule formation by up to 3 million years (as shown in Amelin et al., 2002), although measurements of some CAIs suggest contemporaneous formation with chondrules (as shown in Connelly et al., 2012). It has therefore been suggested that the formation of CAIs either occurred in multiple cycles, or alternatively CAI formation was sustained until at least the onset of chondrule formation. Connelly et al. (2012) uses U-corrected data for the Pb-Pb chronometer, following the observation of $^{235}\text{U}$ variability in what was previously thought to be
a completely homogenous system. The variations were due to an additional decay chain of
$^{247}$Cm. The results of this recalibrated data show contemporaneous CAI and chondrule
formation, with CAIs forming in a short period at $4567.30 \pm 0.16$ My, and chondrules forming
over the range $4567.32 \pm 0.42 - 4564.71 \pm 0.30$ My. Connelly et al. (2012) provide compelling
evidence that brings the assertions of separated CAI and chondrule formation periods into
question. It also raises the question, if these two inclusion types formed contemporaneously,
then how do such different and diametrically opposed formation environments coexist within
the protoplanetary disk? Analysis of the radiation exposure of these inclusions may provide
insight into the formation processes and preservation mechanisms of these inclusions.

2.5 RADIATION ENVIRONMENTS AND THEIR EFFECT ON METEORITIC MATERIAL
Space is filled with different forms of radiation. This radiation affects matter that it collides with.
The effects are dependent on the energy of the radiation, and the likelihood of it interacting
with the matter it intersects. The mechanisms behind radiation effects on meteoritical material
are wide ranging, from processes such as spallation of elements by high energy cosmic rays, to
lower energy neutrons which provide the mechanism for the s-process nucleosynthesis (slow
neutron capture), and the r-process nucleosynthesis (rapid neutron capture). These processes
collectively form a group of mechanisms that can alter the noble gas ratios within meteoritical
material. As such, measurement of these gases grants a window to understanding of the
radiation environments of the early solar system and the history of individual meteorites or
meteorite inclusions.

2.5.1 COSMIC RAYS
Cosmic rays make up the bulk of space borne radiation. The exact particle composition of the
cosmic ray flux is a matter of some debate. That does not preclude understanding of the basic
premise of this radiation flux however, due to the energy of the particle being more significant
in the spallation processes discussed as a part of this study. Cosmic ray flux is primarily
composed of solitary protons (hydrogen nuclei, ~79%), alpha particles (He nuclei, ~14.7%), the
remaining fraction is nuclei of heavier elements and free electrons (Sanuki et al., 2000;
Engelmann et al., 1990). More important than the particle composition is the energy that each
of these particles has. These particles range in their kinetic energy, between 0.1 and $10^6$ GeV
per particle. It is this energy that allows the particles to interact with the matter of extra-
terrestrial materials, preserving that interaction in the form of spallation reactions, or other nuclear processes.

Cosmic ray radiation is commonly divided into sub-groups of solar cosmic rays (SCRs) – a flux originating from the sun, and galactic cosmic rays (GCRs) - those originating from outside the solar system. It is broadly accepted that solar cosmic rays do not significantly affect most meteorite samples, primarily due to the SCRs only interacting with the first millimetre of the meteoroid surface, which is almost always ablated during entry through the atmosphere.

However, it is necessary to readdress this supposition when looking at inclusions that formed in the early solar system; at a time when solar activity was considerably different from the more recent past. A question of whether the size of the condensing material could be affected by the solar cosmic ray flux as well as the galactic cosmic ray flux, must be asked. These interactions would be preserved on the surfaces of the inclusions inside the meteorite, so could in theory still be present within the noble gas systems. The origin of GCRs is a matter of debate, the result of which may have significant implications for methods such as the method used in this study, as discussed later in this thesis.

Solar cosmic ray flux has been established as being cyclical in its intensity. However, it is only generally GCRs that are considered when looking at meteoritical cosmic ray exposure, as SCRs are not expected to affect cosmogenic characteristics of meteorite materials (Nishiizumi et al., 1980), due largely to the lower energy range (The energy spectrum of SCRs ranges from tens of keV to a few GeV). This is also empirically backed up for the krypton system by the work of Gilabert et al. (1998), where the cross sections of the main target elements are greatly reduced at energies of lower than the order of $10^2$ MeV. However, as with any natural science system, it isn’t possible to simply say SCR flux variation is a negligible factor in cosmic ray exposure studies. The cyclical intensity of SCRs does affect the GCR flux via attenuation of the incoming GCR flux, but critically the periodicity of the SCR flux variation is an 11 year cycle. This means the increased and decreased periods of flux throughout the cycles average out for any measurements of cosmic ray exposure ages that are viable to measure.

There is an observed anti-correlation between solar activity and GCR radiation of 10 GeV and below. It has therefore been hypothesised that solar radiation acts to dampen the incoming galactic cosmic rays, decreasing their energy. Thus, as a result of the periods of increased solar activity, there will be a decrease in the GCR flux over the same time period- ultimately resulting in a lower cosmogenic isotope production rate over that time period. GCR flux is considered isotropic- approaching the solar system from all directions- whilst SCR flux originates from the Sun. Solar wind activity can be considered to dampen the effects of lower energy GCRs.
(anything below 10 GeV). The dampening comes from the deceleration effects of these charged particles moving through the expanding solar plasma. The intensity of this dampening will depend on the distance of the particles from the Sun, and the solar activity at the time. If this is an accurate modelling of the cosmic ray system, then there are implications for radiation environment studies of the early solar system. During a star’s formative years its activity (solar wind output) is much higher than during its main sequence phase. This may mean there is a noticeable difference in the dampening effect of SCRs on GCRs between the present and the early solar system. More research would be required to be able to understand the implications of this, but it is worth noting when analysing early solar system samples. Short term cycles such as those of solar activity are likely to become lost in the ‘noise’ of cosmic ray exposure, and thus should not noticeably affect measurements of cosmic ray exposure ages. The complexity of this situation is further added to if we consider that planet forming events may have been preceded by a nearby supernova event, and that GCRs are primarily produced by supernovae events, then it is plausible that the GCR flux during those initial stages of planet formation was higher than the current flux.

There are theories suggesting GCRs are the remnant radiation from supernovae, which may suggest a more variable GCR flux than many of the cosmic ray exposure age methods can mitigate against. The fact that the GCR flux is isotropic additionally suggests that a large number of supernovae are being integrated together. Whether the GCR flux has remained constant throughout the history of the Solar System is an important consideration. Cosmic ray exposure age calculations require the assumption of a constant stable flux of GCRs. If the GCR flux is inherently linked to the occurrence of supernovae, then it stands to reason that the flux will fluctuate on a large cyclical scale (as generations of stars come to the end of their lives). This presents a problem when calculating cosmic ray exposure ages, which rely on a constant and stable GCR flux. If we consider a system whereby we have continuous and stable production of meteoroids, and we cyclically vary the GCR flux, then we might expect to see cosmic ray exposure ages bunch together as younger meteorites were exposed to greater fluence giving them an apparent greater exposure duration than their older counterparts. This model does require removal of meteoroids from the exposure system. The true implications for cyclical variation of the GCR flux should be mostly mitigated by all objects being exposed at any given time being exposed to the same fluence, however the phenomenon does cast doubt on absolute cosmic ray exposure ages.

There is an additional potential source of periodicity in the GCR flux intensity. This variation is directly related to the solar system’s location within the galactic plane. The position of the solar system relative to the galactic plane changes over time, oscillating vertically through the galactic
plane and completing a full cycle every ~52 – ~74 My (Bahcall and Bahcall, 1985). It has long been known that the GCR intensity is greater in the galactic plane than at either extreme of the oscillation period. This periodicity will create an additional cycle that GCR flux will show throughout the meteorite record. While the periodicity of this oscillation may be predictable, the time scale over which the cycles occur is great enough that the averaging effect, which can be assumed for SCR oscillations, cannot be applied to this situation.

Voshage and Hintenberger (1963) found excesses in iron meteorites, suggesting no significant change in GCRs within last few My, but also found ~50% higher excesses than expected in ages between 100 My and 1 Gy. This can only partially be explained by a change in shielding conditions (via space weathering). There is no firm conclusion about the cause behind this excess, but it is thought to be indicative of a period of higher GCR flux. This is a longer period change than the modulation of GCRs by changes in the solar wind, which currently oscillates on an approximate 11 year cycle. The short period of these modulation cycles means they will largely average out against each other when looking at meteorites with exposure ages in the region of millions of years.

There are also questions surrounding the conditions within the early solar system, and the effects they may have had on the flux of energetic particles reaching materials. If we consider the accretionary disk during the time of CAI and chondrule formation, the closer the free moving inclusion is to the solar system orbital plane, the thicker the layer of dust and gas between it and the incoming GCR flux would be. This attenuation would not act the same as shielding mechanisms in meteorite bodies, due to the mobility of both the inclusions and the surrounding gas and dust. The densities per unit area would be in a state of continuous change, therefore making shielding conditions variable on a short time period. Little is known about how these conditions would affect the irradiation of material within the early solar system (Caffee et al., 1988). Kerridge and Matthews (1988) suggest there are also indications of a long-term change in the solar wind over the last 2-4 Gy, a change that will have affected the modulation of GCRs over a sustained period of time.

This uncertainty is in part why complex cosmic ray exposure ages cannot be relied on for an absolute exposure age, and must instead be treated with scepticism over how valid they are as measurements of exposure durations. In essence, the further back, and the more complicated the history of the object being examined, the more difficult it becomes to be certain that the effects being observed are a result of differences in exposure duration. This complexity is in addition to the effects burial depth can have on the signature of cosmic ray exposure of a meteorite.
2.5.2 SPALLATION REACTIONS

A spallation reaction occurs when a fast-moving particle with sufficient energy impacts a target element. The particle must be energetic enough to overcome the electrostatic forces of the atom. The resulting impact causes the target atom nucleus to fragment, a process called spallation.

For krypton spallation in a rocky body, the primary target elements are Sr, Y, Zr, and Rb. Other elements can undergo spallation to form krypton, but the efficiency of these reactions is so low as to be negligible. The controlling effects these elements have on the spallation of krypton are discussed in section 2.1.2 Controls on Krypton Components.

2.5.3 THE $^{81}$Kr-Kr CHRONOMETER

The principle of $^{81}$Kr-Kr cosmic ray exposure age calculation lies in calculating the ratio between a stable isotope, and the radioactive isotope $^{81}$Kr. The stable isotope normally used is $^{83}$Kr due to it being the most abundant cosmogenic isotope. The ratio between these isotopes informs us to the amount of time the stable isotope has been accumulating, whilst also self-correcting for variations in chemistry between different samples. This allows direct comparison between different meteorite types, whilst utilising the same method of calculation.

The spallation spectra for the main target elements (Rb, Sr, Y, Zr) follow the same general trend, meaning a variation in the ratios of these elements to each other will not significantly change the spallation spectrum. The relationship between the production rate and decay rate of $^{81}$Kr allows the equation to account for differences in absolute element concentrations between different samples. Therefore, these calculations are largely unaffected by differences in sample chemistry.

A stable isotope that is produced in a single stage reaction, at rate $P_s$, over time $t$ may be described using the equation:

$$N_s(t) = P_s t$$

Equation 1

Where $P$ represents the production rate, $s$ is a stable isotope, $t$ the exposure time, and $N_s(t)$ the number of atoms of the produced stable isotope.
Similarly, the production of a radioisotope may be represented by:

\[ N_r = \frac{P_r \left(1 - e^{-\lambda t}\right)}{\lambda} \]

*Equation 2*

Where additionally \( \lambda \) represents the decay constant and \( r \) indicates a radioisotope. These two equations (Equation 4 and Equation 5) are illustrated in Figure 2.7. The point at which the radioisotope concentration plateaus is where time within Equation 6 can be considered to effectively be infinite. At which point, Equation 2 becomes:

\[ \lim_{t \to \infty} \left( N_r = \frac{P_r}{\lambda} \right) \]

*Equation 3*

*Figure 2.7- Illustration of the change in concentration of Kr within a meteorite sample, for a single stage exposure to cosmic ray radiation. Both the concentration for a radioisotope (R, \(^{81}\)Kr, in black) and the concentration for a stable isotope (S, in blue) are shown. Based on Equation 3, the plateau in concentration for the radioisotope \(^{81}\)Kr can be shown to be \( P_{81}/\lambda \) (red dashed line), where \( P_{81} \) is the \(^{81}\)Kr production rate and \( \lambda \) is the \(^{81}\)Kr decay constant.*

The decay rate of \(^{81}\)Kr is a constant, therefore \( P_{81}/\lambda_{81} \) forms a ratio of the production rate relative to this fixed decay rate. The decay rate is inherently connected to a duration of time, shown best in its application as a mean lifetime (\( \tau \)), the reciprocal of \( \lambda_{81} \). Within the context of Figure 2.7 this is the plateau in the concentration of the radio isotope (R). The amount of time taken for the system to reach this plateau is a few half-lives (\( t_{1/2} = 2.29 \times 10^5 \) years), and is commonly quoted in literature as \(~1\) million years.
From these equations it can therefore be said, a ratio of a stable isotope to a radioisotope may be represented by:

\[
\left( \frac{N(s)}{N(r)} \right)_c = \frac{P_s t}{P_r (1 - e^{-\lambda t})}
\]

*Equation 4*

To ascertain the value of t, we can rearrange that equation:

\[
\left( \frac{N(s)}{N(r)} \right)_c = \frac{\lambda P_s}{P_r} \frac{t}{(1 - e^{-\lambda t})}
\]

*Equation 5*

If we accept that the value of t is such that the following is satisfied:

\[
\lim_{t \to \infty} 1 - e^{-\lambda t} \approx 1
\]

*Equation 6*

Then the equation further simplifies to:

\[
\left( \frac{N(s)}{N(r)} \right)_c = \frac{\lambda P_s}{P_r} t
\]

*Equation 7*

In order to solve the equation for t, it helps to rearrange it:

\[
\frac{1}{t} = \lambda \frac{P_s}{P_r} \left( \frac{N(s)}{N(r)} \right)_c^{-1}
\]

*Equation 8*
The resulting equation is the reciprocal of the CRE equation. Which, when arranged for $t$ becomes:

$$ t = \frac{1}{\lambda} \frac{P_r}{P_s} \left( \frac{N(s)}{N(r)} \right)_c $$

*Equation 9*

It is possible to simplify further by noting the relationship between the reciprocal of the decay rate, and the mean lifetime of the isotope:

$$ \tau = \frac{1}{\lambda} $$

*Equation 10*

Thus, we end up with the cosmic ray exposure age equation devised by Marti (1967):

$$ T_{81}(My) = \tau_{81} \left( \frac{P_{81}}{P_{83}} \right) \left( \frac{83Kr}{81Kr} \right)_c $$

*Equation 11*

The parameter $\tau_{81}$ was defined in literature by Baglin (1994), and was calculated as $0.330 \pm 0.011$. This was the value adopted for use in this work. The ratio of cosmogenic krypton is a measured value, thus all that remains is to estimate the value of $P_{81}/P_{83}$.

**Assumptions**

The calculation of cosmic ray exposure ages requires a series of assumptions about the sample being analysed. These caveats, summarised from Eugster *et al.* (2006), are:

- The cosmic ray flux must remain constant in time.
  - The production of all nuclides is predominantly dependent on the flux of radiation through the sample, a change in the cosmic ray flux will permanently affect the stable nuclides, whilst only temporarily adjusting the equilibrium of the radionuclides.
- The cosmic ray flux must remain constant in space.
  - Similar to remaining constant in time, it is easy to forget that meteors are mobile, and as such will pass through different parts of space before impacting Earth. If the flux of cosmic rays is different in these areas of space, then the same effect will be observed as is observed with changes in flux over time.

- The sample size and shape must have remained relatively constant.
  - The shape of the sample is important in terms of the type of exposure a meteorite receives. A significant change in shape will affect the flux of radiation reaching a particular location within the meteorite, thereby affecting the equilibrium of the radioisotopes, and enabling more rapid production of stable nuclides. This in turn will make the original exposure duration seem shorter than it was.

- The chemistry of a sample cannot have significantly changed during the exposure.
  - Sample chemistry is another factor that governs the production rate of cosmogenic gases. Most samples’ target element concentrations can be considered infinitely in excess of the amount lost via spallation. Therefore the chemistry can effectively be said to be the same. If the concentration of target elements changes significantly over the course of exposure, then the production rate will also be changing, making the cosmic ray exposure calculation invalid.

- The pre-exposure of a sample must be known.
  - Pre-exposure, or complex exposure history in a sample, makes the interpretation of calculated ages difficult. This features heavily in chapter 6 and will be discussed further there.

- The non-cosmogenic gas fractions must be known.
  - In order to apply the cosmic ray exposure equations, the gas must be purely cosmogenic. Therefore, a way of splitting the cosmogenic and non-cosmogenic gases must be possible.

- The only loss of cosmogenic gases must be radioactive decay.
  - Disruption of a system is impossible to account for. Any system that appears to have been disturbed, or reset, provides a wide array of problems for the calculation of cosmic ray exposure ages and it is therefore better to avoid samples where this has occurred.
Many of these assumptions pertain to the same basic principle—$^{81}$Kr is used to define the production rate, so it is assumed that the $^{81}$Kr production rate over the last ~million years is representative of the production rate experienced over the duration of the total exposure.

Production Rates
The calculation of a cosmic ray exposure age involves accurately calculating the production rate of $^{81}$Kr, relative to the production rate of the stable isotope used for calculating the exposure age. The calculation of production rates can be carried out in a number of ways, each holding distinct advantages and disadvantages over the other methods. This section will present the common methods used, and investigate which of those methods produces the most accurate and defensible cosmic ray exposure ages.

The calculation of the $^{81}$Kr production rate can be carried out by one of two distinct methods. The first was devised by Marti and Lugmair (1971). This equation was devised specifically for the Apollo 12a rocks. It was found that the subgroup 12b lunar rocks also fit this equation, whilst groups like those of the Apollo 11 rocks do not. This is due to differences in the Zr/Sr ratio. It is therefore possible to conclude that this method is sensitive to target chemistry, at least within lunar rocks.

\[
\frac{P_{^81\text{Kr}}}{P_{^{83}\text{Kr}}} = 1.262 \times \left(\frac{^{78}\text{Kr}}{^{83}\text{Kr}}\right)_c + 0.381
\]

\textit{Equation 12}

The second takes the average of the $^{80}$Kr/$^{83}$Kr, and $^{82}$Kr/$^{83}$Kr ratios, accounting for isobaric fraction yield (Equation 13). This was the first method devised, and was presented by Marti (1967). The equation is derived from nuclear principles, and should therefore be applicable across a wider range of meteorite types.

\[
\frac{P_{^81\text{Kr}}}{P_{^{83}\text{Kr}}} = \frac{[0.95, 0.92]}{2} \left[ \left(\frac{^{80}\text{Kr}}{^{83}\text{Kr}}\right)_c + \left(\frac{^{82}\text{Kr}}{^{83}\text{Kr}}\right)_c \right]
\]

\textit{Equation 13}

For both equations: $P_x$ indicates the production rate of isotope $x$, $c$ indicates the cosmogenic gas fraction, $[0.95, 0.92]$ is the isobaric fraction yield (explained below).
The isobaric fraction yield is a modifier to the averaging calculation, which accounts for the slight difference between the theoretical expected and actual yield from the nuclear spallation reactions. The original 0.95 value was presented by Marti (1967). This was determined via nuclear reaction systematics and measurements of Silver. Leya et al. (2015) presents a recalculated value for chondritic material, of 0.92, based on the proton cross-section measurements on the main target elements for Krypton spallation. Overall these different isobaric fraction yields are not expected to greatly alter the calculated cosmic ray exposure ages, due to the relatively small difference in the yield corrections compared to the precision with which $^{81}$Kr can be measured. Due to the method through which it was derived, it seems prudent to use the isobaric fraction yield presented by Leya et al. (2015).

![Figure 2.8](image_url)

*Figure 2.8- Spallation spectrum for both lunar derived spallation component, and chondritic derived spallation component. This figure shows two endmember spectra for spallation, numbers and errors from Wieler (2002a).*

The principle presented by Marti (1967) works on the clear correlation between the spallation spectrum of the lighter massed krypton isotopes, shown in Figure 2.8. In theory the principle could be applied across any collection of these isotopes. Given the range of applicability, it would be sensible to select the isotopes with the lowest predicted error (based on the measurement of air calibration aliquots) because the predicted error is a good metric for how precisely the data reduction algorithm has calculated the ratios. This becomes difficult, the uncertainty on $^{80}$Kr/$^{83}$Kr and $^{82}$Kr/$^{83}$Kr are greatest within the spallation spectrum, however, the measurement uncertainty on these isotopes is lower than those for the other isotopes measured on the RIMSKI instrument.
The $^{78}\text{Kr}$ method’s use of a sample to calibrate this method impacts how applicable it is to samples of differing chemistries. In theory, it is most accurate to only use this method when looking at lunar rocks, or rocks with comparable chemistry. However, the method is robust against bromine contamination. Neutron capture reactions on Br lead to a further addition of krypton to the system. These reactions affect the relative production rates of $^{80}\text{Kr}$, and $^{82}\text{Kr}$.

The production rates of all isotopes of Kr are connected, and equally influenced by both changes in target chemistry and changes in flux. As was shown in section 2.1.2, Figure 2.2, the chemistry of the sample can have subtle effects on the resulting cosmogenic gas spectrum of a sample. This is why the spallation end member values are quoted as chondritic or lunar spallation. Although the spectra are similar, and there are limited reasons to believe the geochemistry of the incompatible elements that make up the Kr spallation target elements would behave differently in other samples, there is potential for the more exotic types of inclusions found in some meteorites to carry different cosmogenic gas compositions.

Shielding will also affect the rate of production. Shielding is a measure of how much of the ambient cosmic ray flux reached the sample. Sample material held within the centre of the meteorite body, will receive a lower amount of radiation than sample material located on the outer surface of the meteorite body. The exact process is more complicated, in part due to the different types of exposure a sample can be exposed to, for example whether the exposure is considered $2\pi$ (hemispherical surface area for approaching radiation vectors, such as that found on the surfaces of large asteroids or planets) or $4\pi$ exposure (spherical surface area for approaching radiation vectors, such as 1 m diameter meteorites or similar).

It therefore stands to reason that there cannot be a ‘catch all’ method of calculating the production rate within a meteorite without introducing the potential for incorrect assumptions affecting the validity of the results. Each of the mentioned factors will affect the production of Kr isotopes, but it will affect all to the same extent. That is to say, the gradient across the spallation spectrum (the amounts of each isotope produced via spallation) will differ according to the factors mentioned, but will remain a linear correlation. It is this property that allows Equation 12 to calculate the production rate of $^{81}\text{Kr}$. The production rate calculation inherently includes these factors because it is calculating the production rate of $^{81}\text{Kr}$ based on the gradient between three other cosmogenic isotopes.
3. **INSTRUMENTATION**

The Resonance Ionisation Mass Spectrometer for Krypton Isotopes (RIMSKI) is an ultrasensitive mass spectrometer, designed to measure krypton ratios in extra-terrestrial samples. The instrument forms the basis of all work carried out towards this thesis. This chapter explains the key features of the instrument and how they are combined to allow the measurement of krypton gases from milligram sized samples.

3.1 **INTRODUCTION**

The RIMSKI instrument incorporates work from many sources to form an ultrasensitive time of flight mass spectrometer capable of measuring krypton isotopic ratios within small mass samples. The instrument was designed and built at the University of Manchester. The system incorporates a photo-resonance ionisation scheme (Thonnard *et al.*, 1987), a low volume refrigeration enhanced spectrometer (Gilmour *et al.*, 1992), an advanced ion source based on the designs discussed in Wiley and McLaren (1955), and a signal amplifying pair of chevron mounted micro channel plates, amongst other components. The design is predominantly based on the designs of the RELAX spectrometer, characterised most recently in Crowther *et al.* (2008).

The RIMSKI instrument has shown its utility in measuring cosmogenic krypton gases from both eucrite samples (Strashnov *et al.*, 2013), and from chondrule fractions of chondritic meteorites in Strashnov and Gilmour (2013). The majority of the uses for the instrument thus far have involved the measurement of $^{81}$Kr, an isotope of very low natural abundance in any sample. The measurement of this isotope forms an important step within the $^{81}$Kr-Kr chronometer, which is used to date cosmic ray exposure ages of extra-terrestrial samples. Measurement of an isotope of such low natural abundance requires design features that are not commonly found on conventional mass spectrometers.

Figure 3.1 introduces the instrument and its key components. These components are discussed and described throughout this chapter and the remainder of the thesis. Additionally, a schematic diagram of the instrument, including laser line components can be found in Appendix 6.
3.2 FEATURES OF THE RIMSKI INSTRUMENT

3.2.1 RESONANT IONISATION SCHEME

The instrument ionises krypton atoms via a photo-resonant ionisation scheme. This exploits the unique energy levels found within the electron configurations of elements, to form a species-selective method of ionising the krypton gas contained within a sample. The technique involves sequentially adding energy, in the form of precisely tuned photon wavelengths, into the target atom until ionisation is achieved. In principle even specific isotopes of elements may be individually ionised, although commercially available lasers have bandwidths too great for this process to be possible. Hurst et al. (1985) discusses how the advent of new slab geometry lasers should enable these next steps in resonance ionisation mass spectrometry to be taken.

The heating of a sample releases gaseous elements other than the intended target element of krypton. The use of a species-selective method enables the targeting of just the krypton gas within the total gas released from a sample. This greatly reduces the need to separate the krypton gas from the other gases, a process that is required for analyses using many of the more conventional noble gas mass spectrometers.
The process involves the elevation of a target species (in this case Kr) from a ground energy state, to an energetic state via a series of specific photon absorptions. The probability of a photon being adsorbed is a function of how close the photon’s energy is to the energy difference of a given allowed transition in the target atom’s electronic structure. The closer the incident photon wavelength is to a permissible energy level, relative to the current energy level, the more likely a photon is to be absorbed. Absorption and the time taken to re-emit the photon (or constituent parts thereof) depends on the photon’s tuning to distinct energy level transitions present within the atom’s (valence shell) electrons. The time an electron remains in an energetic state, following a photon absorption, greatly increases as the wavelength of the photon approaches the wavelength which corresponds to the energy change between the two levels. Theoretically the wavelength required to excite an electron to a ‘stable’ excited state is infinitely narrow.

Each energy level represents a total amount of energy within an atom, and thus a transition represents the amount of energy gain/loss required to move between two energy levels. Each energy level represents a particular configuration of the electrons of a given element. These energy levels are unique to each element, and can be seen represented in phenomena such as emission spectra, where each distinct wavelength of emitted light represents a possible transition from one energy level to another. Herein we find a way to artificially excite a target element from its ground state to a higher energy level by, effectively, reversing the emission process.

The relationship between energy \( (E) \) and frequency \( (\nu) \), via Planck’s constant \( (h) \), is shown in Equation 14:

\[
E = h\nu
\]

\textit{Equation 14}

From this equation, it is possible to substitute frequency using Equation 15:

\[
\nu = \frac{c}{\lambda}
\]

\textit{Equation 15}

Where \( c \) indicates the speed of light in a vacuum, and \( \lambda \) signifies wavelength (in meters).
This leads to the following equation:

$$E = \frac{hc}{\lambda}$$

*Equation 16*

Therefore, Equation 16 shows the relationship between light and the energy level transitions, and creates a means of carrying out resonance ionisation via laser light excitation. The energy transitions used in a resonance scheme must individually and collectively meet the Bohr condition, shown in Equation 17:

$$\Delta E = E_2 - E_1 = h\nu$$

*Equation 17*

Where $E_x$ identifies the energy of a specific energy level $x$. Therefore, there is an established link between the energy transitions within an atom’s electronic structure, and the frequency of laser light, most effectively summarised as:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

*Equation 18*

There are further postulations that must be met in order for individual transitions to be allowed; the transition must be allowed under a series of selection rules. Transitions from one electron orbital to a like electron orbital are not allowed ($\Delta J=\pm1$), following the Laporte selection rule. Photons have a spin of ±1, so a single photon excitation has to be ±1 difference in the angular momentum, whereas a two photon excitation can result in a spin change of +2/0/-2. In a two photon excitation, the transition can pass through an intermediate state, sometimes referred to as a virtual transition. The stability of these transitions is low, but provided the further excitation is achieved in a short space of time, the transition is achieved. The total spin quantum number must be the same in both the electronic configurations.

The uniqueness of elements’ transitions from each other is vital to the success of resonance ionisation. The selective absorption of certain wavelengths by distinct chemical species, even under low photon flux, allows the construction of ionisation schemes that limit the ionisation of non-target elements. This feature proves invaluable when analysing samples with small total quantities of gas, such as the heavy noble gases within certain meteoritical components. The ionisation of krypton, and the detection of isotopically rare components like $^{81}$Kr are made possible predominantly by this method—more conventional electron impact ion sources are not
chemically selective, and as such elements like bromine can contribute a signal that would render the measurement of $\text{Kr}$ impossible.

The greater the energy gap between transitions, the shorter the wavelength required to span that transition. Shorter wavelengths deliver more energy per incident photon (Equation 16), and thus have greater chance of ionising non-target elements. Thus, if one were to use a single photon ionisation step, the purpose of using photo-resonant ionisation would be null. At the energies involved with a single step ionisation process, the range of elements that would also be ionised non-resonantly would be significant, and would present problems for precise analyses.

It therefore becomes a balancing act between using enough low energy transitions as possible (to avoid direct ionisation of non-target species) and using as fewer transitions as possible, so as to increase the likelihood of all required wavelengths interacting with one target atom in the amount of time available before the raised energy state decays. Addition of energy to a population of atoms, which corresponds to that of an allowed transition of the species creates the potential of a population inversion. A population inversion is defined as when more atoms exist in the higher energy state than in the lower, more stable, energy state, thereby meaning the flux of energy is equal to, or greater than, the energy loss due to decays (photo-emission) back down to a lower energy level. In order for this population inversion to take effect both the intensity of laser light must saturate the transition, and the wavelength of the laser light must be close enough to the ‘critical wavelength’ for that transition so as to remain stable for long enough to permit a second transition step. In an optical sense, laser light of frequencies that correspond to allowed transitions within the target element are absorbed, whilst the element appears transparent to light of different frequencies. The uniqueness of these transitions necessarily makes the process species selective. Theoretically the transition value is an infinitely precise value, however the probability of a photon being absorbed is not immediately zero either side of that precise value. The length of time the energy is retained for is also dependent on the difference between of the incident frequency to the frequency of the transition.

For a given transition (spanning $E_1$ to $E_2$), in a given element with a population of $N$ atoms, then we may postulate that:

$$N = N_{E_1} + N_{E_2}$$

Equation 19
This population of these atoms can be statistically represented using a Boltzmann distribution, and the ratio between the atoms in each energy state, the Boltzmann factor. In this case, we are interested in the ratio between the two populations:

\[
\frac{N_2}{N_1} = e^{-\frac{(E_2-E_1)}{kT}}
\]

Equation 20

Where \( N \) indicates the number of atoms in a given state, \( E \) the energy of a given state, \( k \) the Boltzmann constant, \( T \) the thermodynamic temperature. Using Equation 20, as the temperature of the system increases, so too does the number of atoms in the higher energy population. In practice however, the ratio between the populations never exceeds 0.5, at thermal equilibrium. To increase the number of atoms in state 2, where \( N_2 > N_1 \), the system must be pushed out of equilibrium. This is caused by the addition of energy from the incident laser light. As the resonance scheme is built up, the likelihood of an atom making it to that level of excitation decreases. This is because the population inversion is never 100\%, meaning a fraction of each energy level does not progress on to the next energy level. As a result of this, with each subsequent additional transition that is used, the number of atoms that make it to the point of ionisation decreases. Because of this decreased efficiency, a balance must be sought to use as few transitions as possible, without encumbering unacceptable non-resonant ionisation effects.

The excitation process can only be an effective means of ionisation if it is possible to create a ‘stable’ population of atoms in the energetic state for long enough to either initiate a further resonant transition step, or cause ionisation. In this case, the term ‘stable’ is used as a relative term to distinguish the length of time an atom at a permitted energy level for its electronic structure will remain at that level, as opposed to an atom where its energy is not that of a permitted energy level. Both lengths of time are short, however the ‘stable’ atoms remain in that state for substantially longer times than those considered ‘unstable’.

The initial transition employed on the RIMSKI system is within the vacuum ultraviolet spectrum, a region that is not accessible with common commercially available laser systems. The first transition used corresponds to a 116.4866 nm (85846.7624 cm\(^{-1}\); Saloman, 2007) photon absorption. This raises the krypton atom from the ground state \( 4s^24p^6^1s \) to the \( 4s^24p^5(^2P_{3/2})5s^2[1/2]^0 \) level. From this state, a photon of wavelength 558.1935 nm (17914.9335 cm\(^{-1}\)) is absorbed. This raises the total wavenumber to 103761.6959 cm\(^{-1}\) (Saloman, 2007), or an electron configuration of \( 4s^24p^5(^2P_{3/2})6p^2[1/2] \). From here, the minimum energy required to reach the continuum is equivalent to a 1255.7167 nm (7963.5798 cm\(^{-1}\)) photon, hence, a
photon of 1064 nm (9398.4924 cm⁻¹) is suitable to cross beyond the continuum threshold and ensure an efficient ionisation step of the energised krypton atoms.

Figure 3.2 - The krypton ionisation scheme employed on the RIMSKI instrument, including the four-wave mixing process carried out in the Xe-Ar mixing cell.

The scheme is identical to the scheme discussed in Chen et al. (1984) and Thonnard et al. (1987), however the laser systems used on RIMSKI to achieve each transition wavelength are different.

The spectrometer employs a range of tuned wavelength laser systems in order to resonantly ionise krypton gas. Five beamlines originate from a Continuum Powerlite DLS 9010 Nd:YAG, and are then divided and admitted into Sirah tuneable dye laser systems. The details of which are found in the following section. The resulting beams are 252 nm, 558 nm, 1064 nm and 1507 nm, which are passed through the spectrometer.

Ionisation Laser Systems

Laser systems are utilised widely across the RIMSKI instrument, from sample heating, gas desorption and the ionisation process. An injection seeded Continuum Powerlite 9010 Nd:YAG produces a 1064 nm fundamental beam, which undergoes a series of second harmonic generation, and third harmonic generation, with a fraction of the beam removed at each stage.
to produce 5 beams. These beams are 355 nm, 532 nm (×2), and 1064 nm (×2). These beams then undergo different processes to produce the required wavelengths for the krypton ionisation scheme. Figure 3.3 shows a schematic view of the laser systems involved in the resonance ionisation scheme.

![Figure 3.3 - A schematic diagram of the laser systems involved in the resonance ionisation scheme. Abbreviations are noted in each laser section.](image)

The 355 nm beam is passed into a Sirah Cobra Stretch tunable dye laser. This converts the 355 nm pump beam to a 504.971 nm wavelength. The laser dye used in the oscillator and amplifier of the cobra stretch is coumarin 503 (also referred to as coumarin 307), with a peak output at 505 nm. This is then passed through a frequency doubling beta barium borate (BBO) crystal to produce a 252.4855 nm beam. This beam is fitted with a compensator crystal, in order to mitigate beam path changes as a result of tuning the BBO crystal angle. This tuning is a necessary part of the daily tuning of the spectrometer to maintain an ‘at spectrometer’ laser energy of 3–3.5 mJ per pulse (‘at spectrometer’ being defined as the energy of the laser as it enters the mixing cell cavity). Further details on the coumarin Cobra Stretch tunable dye laser can be found in Appendix 2.

One of the 532 nm beams is directed into a second Sirah Cobra Stretch tunable dye laser. This laser runs on DCM laser dye, and is used to convert the 532 nm beam into a 623 nm beam. This beam is then passed into a DFMNIR unit.

The DFMNIR unit primarily consists of a LiNbO₃ crystal, within which the process of difference frequency mixing (DFM) takes place between the 623 nm beam from the DCM tunable dye laser, and an additional 1064 nm pump beam from the Continuum Powerlite Nd:YAG. The crystal allows the combination of the 623 nm beam, and the 1064 nm beam into a single 1507.3 nm beam. This beam is polarised using a rotational polariser before entering the Xe-Ar mixing cell. The energy of this beam is fairly static, as the dye is very stable; at spectrometer energies of ~2.4 mJ per pulse. (Additional details on the DCM Cobra Stretch tunable dye laser, and the associated DFMNIR unit can be found in Appendix 2).
The 252 nm beam, and the resulting 1507 nm beam then undergo four-wave mixing within a cell containing a mixture of xenon and argon. Four-wave mixing (FWM) is a non-linear optical process which involves a series of three laser light frequencies being combined into a fourth outputted frequency. The process takes place in a non-linear optical medium, in this case an inert atmosphere of xenon and argon. A target atom will adsorb photons that correspond to a transition, or near a transition. Within the RIMSKI system, we see the xenon acting as a lasant. Within xenon, it is possible to combine several frequencies ($\omega$) of laser light, into a one frequency photon emission, described as:

$$\omega_4 = \omega_1 + \omega_2 + \omega_3$$

*Equation 21*

In order for this process to be allowed, the change in wave vector must be approximately zero. It is because of this, that argon is used as a buffer gas alongside the active lasant gas, xenon. The argon component of the mix acts as a positively dispersive medium, whilst the xenon acts as a negative dispersive medium, thus by combining the two, the net vector change can be reduced to near zero. Similar systems have been implemented successfully in other instrument applications, such as the system described in Hurst et al. (1985). Within this system, the same resonance scheme was used although the processes used in beam formation are different. (The topic of four-wave mixing is extensively covered in section 4.1).

The remaining 532 nm beam acts as a pump beam for a Sirah Cobra tunable dye laser. The laser uses pyrromethene 580 as its laser dye, with a peak energy output at 557 nm. This is used to produce a 558 nm beam, which spans the energy difference across the second transition of the krypton resonance scheme used on the RIMSKI instrument. (Additional information on the pyrromethene Cobra tunable dye laser can be found in Appendix 2). This beam is polarised using a rotational polariser before entering the mass spectrometer. The polarisation of this beam, relative to the polarisation of the 1507.3 nm beam affects the availability of hyperfine splitting excitation pathways, and therefore the ionisation efficiency difference between the odd and even isotopes. This is discussed further in section 5.4.

The laser systems employed on the RIMSKI instrument are pulsed, and have a duty cycle of 10 Hz. The timings of the laser pulses are controlled by a signal generation box. This control box is set to pulse the flash lamps of both the desorption and the ionisation lasers 10 times per second.
3.2.2 Cryogenic Sample Concentration and Spectrometer Volume

The RIMSKI spectrometer is approximately 1 litre in internal volume (working on the basis that the design for the RELAX spectrometer is very similar, and that spectrometer was calculated to be 1 litre in volume by Crowther et al., 2008). This is a volume that is far smaller than conventional magnetic sector noble gas mass spectrometers. This reduced volume acts to decrease the rate at which the background blank builds up (the measurement expected when no sample is heated or released into the spectrometer). The blank of an instrument is strongly dependent on the desorption of gases adsorbed to the internal surfaces of the instrument. This can be limited by baking out the spectrometer, which causes the gases adsorbed to the walls of the spectrometer to desorb, and then be pumped out of the spectrometer volume. A low blank is important when measuring samples for $^{81}$Kr, due to the low abundance of $^{81}$Kr. A blank signal over the 81 mass arrival time would make the resolving of the $^{81}$Kr peak more difficult, and also increase the uncertainty associated with that measurement.

The cryogenic sample concentrator mechanism utilised on the RIMSKI instrument also has the secondary benefit of reducing the background hydrocarbons of the spectrometer. The RIMSKI instrument uses a method of cryogenic sample concentration that was first devised by Hurst et al. (1984). The mechanism has been used on the RELAX spectrometer to great effect in increasing the ionisation efficiency of that instrument (Gilmour et al., 1992). Similarly, it is that same reason that led to the mechanism being included in the RIMSKI instrument designs.

Cryogenerator Design

The back plate of the ion source is 0.4mm thick stainless steel. This plate is connected to the refrigeration head via a copper rod, with an intermediate layer of indium foil to ensure good thermal contact. The contact spot is ~1.5 mm in diameter. The copper rod is connected to the refrigeration head via an intermediate stage, allowing electrical isolation of the back plate (held at -3 kV) from the spectrometer casing. This intermediate layer involves a 1 mm thick sapphire plate, pressed between two foil layers of indium (~0.5mm thick). The sapphire acts as a good electrical insulator whilst maintaining good thermal conductance, whilst the indium acts to ensure good contact between each stage of the cryogenerator head. The copper rod is given flexibility via a woven copper braid, located along the rod structure. A plastic spacer keeps the rod centred in the feedthrough. The entire cold head is pumped to a rough pump vacuum in order to decrease the heat transfer to the copper rod from any source barring the back plate.
Figure 3.4 – The cold finger component, allowing the atom bunching to be concentrated on the back plate of the spectrometer. (1) – The Cryogenerator head, this expands helium to draw the heat away from the cold finger mechanism; (2) – Resistor heater; (3) – Thermocouple; (4) Indium-Sapphire-Indium electrical isolation plates; (5) – Copper braid to allow cold finger flexibility; (6) – Spacer and indium cap in contact with the spectrometer back plate.

The cooling and temperature stabilisation is maintained using a Eurotherm temperature controller (Schneider Electric). This is monitors the temperature of the cold finger via a pair of thermocouples located at the base of the copper rod. The control unit can also vary the current through two resistors, mounted at the same location as the thermocouples (equidistant from both thermocouple attachment points), in order to stabilise the temperature profile of the system.

Desorption of Gas from the Cold Spot

A Continuum Minilite Nd:YAG laser is used to release a plume of condensed gas from the back plate. The beam is pulsed at 10 Hz, out of phase with the Powerlite 9010 Nd:YAG pulses by ~0.5-1.5 µs. The laser systems are setup in a way to allow the easy variation of this delay. It is necessary to tune this parameter with every re-alignment of the ionisation or desorption beams. The delay between the two lasers relates to the difference in arrival times of the ionising laser pulses, and the desorption laser pulses. The optimum delay will correspond to the ionisation pulse arriving at the ionisation region, at the same time as the optimum quantity of released krypton arrives in the same volume, thereby maximising the efficiency of potential krypton ionisation.
**Principles of the Cryogenerator**

The idea behind sample concentration is to increase the number of target atoms within the ionisation region, thereby increasing the ionisation efficiency. On the RIMSKI this is achieved through cryogenic means.

The temperature of a surface has a direct influence on the retention time of that surface, for gases that impact it. Below a critical temperature and the retention time for a surface approaches infinity. This means that when an atom impacts the surface, it will remain there indefinitely. This is exploited on the RIMSKI system, where a localised spot within the ion source is chilled to the critical temperature for krypton.

The quantity of krypton gas admitted into the spectrometer volume during a standard analysis is small, and the total volume of the spectrometer accessible to the gas is orders of magnitude larger than the ionisation region (the space within which the ionisation beams converge in space and time).

Efficiency of ionisation against the number of atoms of krypton available within the system is governed by the average number of krypton atoms present in the ionisation region at the time that the laser pulses arrive. The number of incident photons of each wavelength is far greater than the potential maximum number of krypton atoms within the ionisation region. Another way of thinking about this is that the system becomes more efficient at ionising the total krypton contents of the sample when the effective volume the gas is permitted into is the same size as the ionisation region. It is therefore beneficial to the sensitivity of the instrument to maximise the concentration of krypton atoms within the ionisation volume. Practicality dictates that this maximisation is not possible via conventional machining of spectrometer parts, because of which, a form of cryogenic sample concentration is employed on the RIMSKI instrument.

In order to achieve a high number of target atoms in the ionisation region at the time the ionising laser pulse passes through the volume, requires a method of sample concentration. The instrument incorporates a cryogenic refrigeration system, in order to produce a mechanism by which atom bunching can take place. The feature was derived from aspects of the RELAX spectrometer (described in Gilmour *et al.*, 1994) and Hurst *et al.* (1984).

Theoretically, the condensation of krypton will occur at 120 K at room temperature, however the ultrahigh vacuum (UHV) pressure within the spectrometer means that a lower temperature is necessary in order to condense the gas.
Operational pressures within the spectrometer are $\sim 10^{-12}$ Atm, thus it is implied that a cold spot temperature of 35K is required for krypton condensation. The localised pressure around the cold spot is likely higher, due to the cyclic process of atom bunching and desorption, and thus it may be extrapolated that the temperature required for krypton adsorption onto the cold spot is actually higher than that stipulated in Figure 3.5.

Extrapolation from work carried out by Gilmour et al. (1994) shows that the thermal profile, and equilibrium temperature of the cold spot is partly dependent on the surface area of the contact interface between the back plate and the cold finger assembly, as well as a range of factors that are already built into the RIMSKI spectrometer design and are thus impractical to change.

Calibration of this system must be carried out in order to maximise the region over which krypton will condense, whilst not exceeding the area that is illuminated by the desorption laser. In practice, the calibration of the system requires occasional retuning, primarily due to mechanical drift of the components within the cryogenerator. Temperatures are measured using two thermocouples. One functions as a control- allowing a Eurotherm temperature control unit to precisely mediate the temperature the cold spot is held at. The other thermocouple acts as an over temperature safety system. Continuous expansion and contraction caused by the repeated cooling cycles can cause periodic movement of the thermocouples, which affects the thermal contact between the thermocouples and the copper rod. The result of this is a temperature readout that is different to the temperature before the thermocouple moved. This in turn changes the nominal temperature the system must be set to, in order to provide the optimum actual temperature at the cold spot.
The measurement is taken some distance away from the cold spot, and as such is a (proxy) for the temperature that the cold spot is actually held at. However, the controller allows the system to maintain a continuous thermal profile when running optimally.

In practice, the set point temperature is 70-80 K, a value which is experimentally identified after any maintenance is carried out on the cryogenic stage. We have found that the ambient heat flux is such that the lowest temperature the system will achieve measures as ~80 K. This is not necessarily representative of the temperature at the cold spot, but it has shown that the cryogenerator can run flat out and the temperature not appear to get ‘too cold’.

3.2.3 Ion Source Electronics and Mass Separation

In order to form a mass spectrum, the newly formed ions must be separated according to mass. The easiest way to do this is a time of flight system. If the ions are subjected to an electric field then they will be given the same energy as each other. The inertia of the different mass isotopes causes a difference in their speeds, with lighter isotopes being accelerated to higher speeds than heavier isotopes. Additionally, these ions are not formed in an infinitely small space; the ionisation region has a volume. The ions are also not completely static when they are ionised, they have a pre-acceleration velocity. The time spread (or peak width) for a given mass is a function of the spatial distribution of the atoms at the point of ionisation; in essence, the volume of the ionisation region, as well as the spectrum of velocities the atoms had before they were ionised. Atoms that had high velocity in an opposite direction to the electric field acceleration will take longer to reverse direction than ions that had a velocity matching the direction of the accelerating electric field. Thus, mass resolution control is largely dominated by the mitigation or limitation of this spread in space and energy variations. The mass resolution can also be affected by the distribution of ion formation in time.

In order to mitigate the time spread of each mass, the ion source design follows that of the Wiley and McLaren (1955) design. As proposed, the ion source allows a small acceleration from
the ionisation region, to the acceleration region, by the imposition of an intermediate plate, held at a potential difference closer to that of the back plate than the final accelerating plate.

Figure 3.6 – An illustration of the ionisation volume and its effects on mass resolution.

The relatively small acceleration condenses the effective ion packet before the significant acceleration stage. The ionisation region may, in a 3D sense, be best represented as a cylinder passing through the ion source volume. In Figure 3.6 the ionisation region is shown as a spherical cut through. The figure demonstrates the differing potential difference experienced by two ions at different locations within the ionisation volume. Between the two plates, the potential difference and therefore the potential kinetic energy decreases the closer the particle is to the mid-plate. Therefore, the ions closer to the back plate are accelerated more than those towards the mid-plate. The result is a compression of the spherical ion packet, into an elliptical packet.

\[
U = U_0 + q s E_s + q d E_d
\]

Equation 22

Initial energy \(U_0\), final energy \(U\), \(s\) distance to midplate from back plate, \(d\) distance from midplate to final plate, \(q\) is charge, \(E\) the electric field in volts/cm. This design feature aims to
improve the mass resolution of the spectrometer, allowing the range of arrival times for a given isotope to be compressed into a smaller range of time. The benefit of high mass resolution is the ability to isolate individual isotopes from each other and from hydrocarbon mass peaks-which are observed under certain running conditions, with slightly later arrival times than each respective krypton isotope. The ion packet is divided according to mass, using a time of flight system. Within this system, the ions are all imparted with the same kinetic energy, meaning the lighter ions travel at a higher speed than those with heavier masses. The flight tube is a 16 mm internal diameter stainless steel CF tube, of ~650 mm length (Strashnov et al., 2011). The design, combined with the electronic configurations, leads to a krypton arrival time of ~7-8 µs. Each mass arrives and is detected as a peak of ~8 ns full width, half max (FWHM).

A range of factors can affect the mass resolution:

Charge space effects – Any two similarly charged ions will electrostatically repel each other. The effect of this repulsion on an ion packet is observed if the local pressure within the ion packet exceeds charge space permittivity. This occurs when too many ions of one mass are accelerated towards the detectors. The result is a loss of mass resolution and is observed as a broadening of the FWHM of a given isotope peak.

Duration of the laser pulse- a fundamental principle of ToF mass spectrometry is the generation of a pulsed source of ions. The shorter the ion generation time, the higher the mass resolution. The fundamental control on the duration of ion generation is the pulse length of the lasers fundamental to the ionisation process. It stands to reason that the 1064 nm laser light pulse that forms the final ionisation step of the resonance scheme, would be the limiting factor on pulse duration of the ion packet, providing the other wavelength pulse durations are in excess of the final 1064 nm pulse (thus the duration of the 1064 nm pulse necessarily becomes the ion generation duration).

Efficiency relative to pulse shape- the energy distribution across the duration of a laser pulse follows a gaussian profile, modified slightly by the use of a seeder. Even so, the rise time for energy entering the ion source will contribute to the spread in arrival times of the ionised gas. In practice, there is no practical method of mitigating this contribution to the spread, without in turn inducing another factor that will contribute to ion arrival time spread.

3.2.4 Signal Detection
The number of ions impacting the detectors of the RIMSKI instrument at any given time is small. An individual ion impacting a detector would normally impart $\pm 1.6 \times 10^{-19}$ coulombs of charge.
This is a very small quantity to measure. In order to allow an easily measured charge flow the ion signal must be amplified. Within RIMSKI this is carried out by a pair of chevron mounted microchannel plates (MCPs).

A microchannel plate is an array of microscopic glass tubes (or channels) arranged in a honeycomb type structure. A thin slice of these channels is made and coated to allow electron flow across the structure. In normal operation, the MCP is given a charge and depletion of the charge is monitored by an electrode. When an ion impacts the MCP it causes a release of electrons from the surface. If this release is within one of the channels (an active site) then the release of electrons will cause a cascade of releases down the channel. The approximate ‘active’ surface area is 50% of the MCP (Wiza, 1979). This means that an incident ion has a 50% chance to cause a cascade release down a channel.

Two of these plates are arranged so that their channels form a chevron shape, maximising the likelihood of an ion impacting the surface whilst travelling down a channel, and also allowing a secondary cascade to be formed by the electrons emitted by the first plate.

At present, the MCP voltage of RIMSKI is held at 1.64 kV, although the potential difference can be adjusted to maintain the measured signal intensity for a given sample size. The channel plates are held above an impedance matched (50Ω) anode, which allows a change in potential difference to be measured as an analogue signal over time.

An 8 bit digitiser card converts the analogue output from the instrument’s detector plates, into a digitally structured signal, at a sample rate of 1 GS/s (Strashnov et al., 2011). Each triggering of the photodiode causes a recorded sample space of 1 µs, or 1000 1 ns spaced data points. Therefore, for any one spectrum (synonymous to each ionising laser pulse), there are 1000 data points. A data file is composed of 3,000,000 bits of data. The data file is read into data reduction software (Originally discussed in Crowther et al., 2008), and reduced to 30 spectra, each spectrum of which is a summed spectrum of 100 individual laser pulse spectra, each of which in turn is composed of 1000 samples of the data stream.

These features provide the RIMSKI instrument with its unrivalled sensitivity for krypton measurements, whilst also resulting in an instrument that is less user friendly than conventional commercially available spectrometers.
3.3 COMPONENT SYNTHESIS AND TUNING

As has been mentioned before, the RIMSKI instrument is a complex instrument. The number of components and parameters that have to be synthesised together to in order for the instrument to perform well means that tuning is a time intensive task. Table 3.1 details the range of parameters that must be individually tuned well, and must also be integrated and tuned to other components well in order for the instrument to function properly. The difficulty of tuning the instrument lies in the interdependency between components and how well each is tuned. Tuning any one parameter is significantly less difficult than tuning all parameters in conjunction with each other. Acquisition of a signal from the instrument, particularly following the developments detailed in Chapter 4, is significantly less difficult than tuning that signal to the optimum performance for the instrument.

Many of the parameters discussed vary as the ionisation region positioning is changed. Given the issue of hysteresis associated with some of the laser systems, the ionisation region positioning is prone to movement. Even small variations in the ionisation region position results in additional tuning requirements. To that end, many of the control mechanisms seek to restrict this movement, or provide easy reproducibility of the ionisation region location.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Explanation</th>
<th>Control Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Wavelength</td>
<td>There are 3 laser wavelengths that must be tuned to specific resonance transitions.</td>
<td>The 252 nm wavelength is fixed by tuning to a detector cell filled with Xe. The maximum signal from the detector is indicative of the optimum location of the wavelength for four-wave mixing within the Xe-Ar mixing cell. Similarly, the tuning of the other beams is built up using a detector cell filled with NOx to test VUV generation (controlled by the 1507 nm beam tuning), and finally a cell filled with Kr in order to tune the 558 nm beam.</td>
</tr>
<tr>
<td>Parameter</td>
<td>Explanation</td>
<td>Control Mechanisms</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Laser Power Density</td>
<td>Each beam has a minimum energy per unit area required to saturate the respective transition. The power density must be such that this requirement is met across the entire ionisation volume but is not high enough to cause damage to the MgF$_2$ viewports. The power density profiles of the beams vary when secondary optics of the dye lasers are retuned (Both the BBO doubling crystal, and the LiNbO$_3$ difference frequency mixing crystal). This retuning is required to maintain the energy output of the beams, and is also required when the wavelength is changed. This is because the optimum crystal orientation is a function of the wavelength of the incoming beam.</td>
<td>Each beam energy is measured before analyses start on any given day. Additionally, the Sirah dye lasers are fitted with a tracking software, allowing them to automatically adjust the angle of the secondary optics to maintain beam energy as the wavelength is changed.</td>
</tr>
<tr>
<td>Laser Alignment (Spatial and Temporal)</td>
<td>Beams passing through the ion source must overlap across the ionisation region, both in terms of their path, and also in terms of when each pulse from the respective lasers arrives at that space. Due to different optical components and conversions that each beam goes through, if a direct path to the ion source was followed then the laser pulses would arrive at different times.</td>
<td>The beam path was defined using two irises, once a strong ionisation signal was achieved. These irises are positioned at either end of the instrument, allowing alignment of the beam through the spectrometer. This allows rapid re-alignment of the beams following large wavelength changes, as well as laser maintenance.</td>
</tr>
<tr>
<td>Parameter</td>
<td>Explanation</td>
<td>Control Mechanisms</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Delay Settings</td>
<td>The desorption laser releases a plume of gas from the cold spot. This gas will only occupy the ionisation volume for a fixed amount of time. The arrival of the ionisation laser pulses must coincide with the time that the krypton gas is passing through that ionisation volume. This is controlled by a delay in the signal generation which triggers the desorption laser, and the Continuum Powerlite 9010 Nd:YAG which pumps the ionisation lasers. This delay timing is strongly affected by the position of the ionisation region within the ion source.</td>
<td>The delay settings remain fixed, and are only optimised when the beam path through the ion source is changed. Following the initial tuning procedure, the retuning of this component should be rare.</td>
</tr>
<tr>
<td>Cryogenerator</td>
<td>The cold spot must be at a temperature low enough to condense Kr, but not so low as to condense Kr outside the area illuminated by the desorption laser.</td>
<td>Periodic measurements of the lifetime against detection within the instrument are carried out. A rapid pump out and high plateauing of the signal is indicative of the cold spot being too cold, and condensing Kr outside of the desorption laser’s spot size. A poor pump out curve is indicative of the temperature being too high for effective condensation of Kr.</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe-Ar Mixing Cell Ratio</td>
<td>The efficiency of VUV production at the required wavelength for the resonance ionisation scheme is a direct function of the ratio between Xe and Ar within the mixing cell.</td>
<td>This was originally controlled using rough adjustment valves, and subsequently there was very little control over this component. The new control mechanisms are discussed in the following chapter.</td>
</tr>
<tr>
<td>Parameter</td>
<td>Explanation</td>
<td>Control Mechanisms</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Acceleration Voltages</td>
<td>Mass resolution is in part a function of the balance between the primary and secondary acceleration voltages. These voltages are affected by the positioning of the ionisation region within the ion source.</td>
<td>These are maintained at fixed values, requiring retuning intermittently when the beam path is significantly altered, or the instrument undergoes significant maintenance.</td>
</tr>
<tr>
<td>Ion Optic Voltages</td>
<td>Ion pulses are dispersed to cover the maximum surface area of the MCPs. This requires an Einzel ion lens. The effect of this lens on the ions is dependent on the location of the ionisation region within the source, and also the electronic configuration of the acceleration voltages.</td>
<td>The Einzel lens setting is similar to the acceleration voltages, but is subject to change more commonly. This is tuned by adjusting the voltage until a well-defined signal (in terms of mass resolution) of a known intensity is measured.</td>
</tr>
<tr>
<td>Desorption Laser Energy and Alignment</td>
<td>The energy imparted to release the gas trapped on the cold spot must be great enough to release the optimum amount of gas, whilst not being so high as to release hydrocarbons and other gases that interfere with the ionisation and detection of krypton gas.</td>
<td>This is now controlled using a series of neutral density filters. Between measurements the desorption laser energy is increased, in order to clean the cold spot whilst the system is pumping. The energy used during an analysis was defined following experiments that assessed mass resolution and hydrocarbon release (and build up time) into the system.</td>
</tr>
<tr>
<td>Parameter</td>
<td>Explanation</td>
<td>Control Mechanisms</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Rotational Polarisers</td>
<td>The effective angle between the polarisation of the 558 nm beam, and the polarisation of the 1507 nm beam leads to differences between the ionisation efficiency of the even isotopes relative to the odd isotopes. This phenomenon is also affected by 558 nm beam power density, and wavelength tuning.</td>
<td>This is entirely user controlled, there are no other control mechanisms, but is not changed during a day of analyses.</td>
</tr>
</tbody>
</table>

Table 3.1 – Parameters that must be tuned well in order for good instrument performance. A flaw in any one of these parameters can reduce the performance of the instrument. Poor performance is normally a result of slight imperfections in the tuning of several of these parameters. In order to reduce tuning time as much as possible, several control mechanisms have been installed to ensure tuning of those components is easily monitored and as a result can be effectively removed from consideration when tuning the instrument.
4. INSTRUMENT DEVELOPMENT – XE-AR FOUR-WAVE MIXING CELL

Premise
As is shown in section 3.3, the RIMSKI instrument is complex and relies on the fine tuning of numerous components in order to produce reliable results. Improving the reproducibility of optimum tuning parameters was deemed an important step in progressing the instrument from its initial stages, to a more widely used and user friendly instrument.

One system that is more sensitive to tuning is the ionisation laser system. The ionisation laser system includes the Continuum Powerlite 9010 Nd:YAG, and the subsequent Sirah tunable dye lasers. The system tuning is dominated by three factors: Beam alignment, wavelength tuning, and beam power density.

Further to this, the beams undergo the process of four-wave mixing within a cell containing Xe and Ar at a precise ratio. The original method of filling this cell was imprecise, with the mechanisms being capable of only rough adjustment of the ratio within the cell. There was clear potential to improve the reproducibility of this Xe-Ar ratio within the mixing cell by modifying the system, and subsequently the method, for filling the mixing cell.

4.1 INTRODUCTION

In order to resonantly ionise krypton, an initial transition must be spanned, all of which almost exclusively reside within the vacuum ultra-violet (VUV) spectrum (116.4867 nm, 85846.7051 cm⁻¹). Resonance ionisation of krypton using VUV laser light has been in use within planetary sciences since 1984, where it is first introduced by Thonnard et al. (1984), and then subsequently Lehmann et al. (1985) and others. The process of four-wave mixing to produce VUV radiation with xenon as the lasing medium is a much older concept, and there are a great number of papers discussing the matter. There is a common theme across all presentations of these investigations, the use of commercial systems is impractical – that they are either unavailable, or do not tune to sufficient wavelengths to allow the resonant ionisation of krypton. A further problem for many system designs was the inability to produce a high enough power VUV beam, to initiate the resonant ionisation of krypton. Hilbig and Wallenstein (1981) present a method of forming VUV beams of 20W power, from an atmosphere of xenon gas, the importance of which is highlighted in Hurst et al. (1985). For this reason, a custom system was
constructed, based on a system described in Lehmann et al. (1985) (among others); the initial design implemented on the RIMSKI instrument, is documented in Strashnov et al. (2009).

4.1.1 Principles of Four Wave Mixing

Four-Wave Mixing is a non-linear optical process involving a series of three laser light frequencies being combined into a fourth outputted frequency. The process takes place in a non-linear optical medium, in this case an inert atmosphere of xenon and argon.

A target atom will absorb photons that correspond to a transition, or near a transition. The absorption of photons by media is a function of probability, with the highest probabilities of absorption at wavelengths corresponding to permissible transitions from the current state.

Within the RIMSKI system, we see the xenon acting as a lasant. Within xenon, it is possible to combine several frequencies ($\omega$) of laser light, into a one frequency photon emission, described as:

$$\omega_4 = \omega_1 + \omega_2 + \omega_3$$

Equation 23

In order for this process to be allowed, the change in wave vector must be approximately zero. It is because of this, that argon is used as a buffer gas alongside the active lasant gas, xenon.

The argon component of the mix acts as a positively dispersive medium, whilst the xenon acts as a negative dispersive medium, thus by combining the two, the net vector change can be reduced to near zero.

Similar systems have been implemented successfully in other instrument applications, such as the system described in Hurst et al. (1985). Within this system, the same resonance scheme was used although the processes used in beam formation are different.

4.1.2 Control Over Formed Wavelength

Krypton atoms will only efficiently absorb photons of a precise bandwidth into the ground state to first level transition. Equally, a cell of xenon and argon will output a small, but appreciable bandwidth of wavelengths.

Within Figure 4.1, this bandwidth is illustrated by the vertical black lines; produced photons of a wavelength throughout this region are very likely to be absorbed into the krypton atom. Within
this illustration we can also hypothesise two theoretical cell fills, with different peak production wavelengths, the red and blue curves. It is clear that the red curve will ultimately more efficiently generate photons resonant with Kr, due to the higher number of photons present over the bandwidth that will efficiently couple to krypton. From this illustration, it is a simple step to understanding the reason for precise control, and an understanding of that control, over the ratio of the two gases within the mixing cell.

![Graph showing likelihood of formation against wavelength](image)

**Figure 4.1 – An illustration of the principles behind the tuning of the Xe-Ar ratio within the mixing cell.**

The output wavelength is fixed by the tuning of the input wavelengths. For any given combination of input wavelengths, the efficiency of the VUV production is dependent on the Xe-Ar ratio, and how close that ratio is to the optimum ratio.

Based on the hypothetical evidence, it becomes apparent that a reproducible way of filling the mixing cell to a known and precise ratio of xenon and argon would be a significant development step in the use of this analytical instrument. Allowing certainty in the reproducibility of sensitivity and certainty of the instrument’s functioning.

### 4.1.3 Cell Design

A standard stainless steel, ultra-high vacuum grade, cylindrical cell is sealed using two magnesium fluoride (MgF₂) viewports mounted onto zero-length reducer flanges. Input to the cell is regulated using a micrometre screw gauge valve in series with a standard coarse adjustment valve allowing isolation of the cell from the input line. Evacuation of the cell is carried out on the opposite side to the input, allowing for a through-flow of gas, in order to
flush any contained gases through the system. The entire system is rough pumped using a rotary pump to maintain a pumping cell pressure in the order of $10^{-3}$ mbar.

Associated with this system is a series of similarly designed detector cells. These detector cells have the same structure as the Xe-Ar mixing cell, with the exception of an additional ceramic feedthrough, which allows a pair of stainless steel electrodes to be connected to a pair of charge sensitive amplifiers. These cells, described in Strashnov et al. (2009) are filled with an amount of either nitric oxide (to detect the production of any VUV wavelength), or krypton (to check for VUV generation that is resonant with krypton).

VUV wavelengths easily ionize NOx gas, and as such it is easy to use a simple set up, characterised by Strashnov et al. (2009), to sequentially scan through gas mixtures of different ratios of Xe/Ar in order to identify the ideal gas ratio for VUV generation.

4.1.4 Mixing Medium

Out of the two gases that are used to fill the mixing cell, xenon acts as the medium within which the incident photons are combined. The argon atmosphere provides phase matching between the two incident wavelengths. This is necessary to counteract the negative dispersion effect of the xenon gas (Strashnov et al., 2009).

Strashnov et al. (2009) outlines an ideal pressure to fill the mixing cell to, which optimises VUV generation, whilst also minimising reabsorption and subsequent scattering of the laser light. It is set out in Kramer et al. (1984) that total pressure does not affect the generation of the VUV laser light until very low partial pressures of each gas. However, absolute cell pressure effects can be demonstrated within our experimental setup. These effects are hypothesised to be caused by a shift between effective fluid dynamic conditions— in particular a shift from molecular flow to Knudsen flow, and possibly towards viscous flow as the cell pressure approaches atmospheric pressure.

4.1.5 Tuning Procedure Before Development

Before these developments the instrument had a lengthy tuning procedure, often requiring several days of filling and re-filling the mixing cell to achieve a stable Kr ionisation signal. This was due to the use of coarse adjustment valves which only permitted an imprecise amount of either gas into the cell and filling line volume. User control relied on response to the measurements made by a baratron capacitance manometer, measuring the pressure within the
filling line and mixing cell. The method involved adding a small amount of xenon to the cell using one valve, and then a second valve to allow argon to flow into the cell. This was controlled by the user and allowed to flow until a signal was observed on the RIMSKI spectrometer, the appearance and disappearance of which was a short period of time (<10 seconds). The uncertainty on the timing of closing the inlet valve was compounded by the time taken for equilibration of the gas mix. The result of this method was a poorly mixed gas mixture, which would normally be left to equilibrate over a prolonged time period (generally, overnight). After this equilibration, there would generally be a lower signal or no signal present at all within the spectrometer. Thus, the necessity to repeat the procedure multiple times and the subsequent long tuning up times.

The laser system setup for this old method involved theoretically derived optimum wavelengths for krypton ionisation. From this, the wavelengths were set, and remained un-changed throughout any filling procedure. The xenon and argon were then added to the cell, until a signal was observed, thus proving that the ratio was correct. At this point the wavelengths were adjusted (±<0.01nm) to optimise the signal. The signal produced would decay over time, typically a fill would be usable for 3 weeks before it required refilling. This decay in signal was assumed to be due to the desorption of gases stuck to the mixing cell walls, which when desorbed would alter the ratio between the gases within the cell.

This method, although it evidently worked, gave very little understanding or control over the system. Should the laser output and the GUI reported wavelength become uncalibrated (as is observed to happen over time with any tunable dye laser), then the setup would have been reduced to having no known settings, as was proven early on in this study. Furthermore, an understanding of how the instrument behaved relative to the tuning of each wavelength was considered desirable.

4.1.6 REASONS FOR DEVELOPMENT

Instrumentation is only truly useful if the mechanisms and behaviours of the instrument are understood and predictable. The range of components used in the RIMSKI instrument which are strongly affected by user defined parameters provides a vast number of parameters that can affect the outputted data. This reduces the viability of comparing data from different analytical periods.
In order for RIMSKI data sets to be more viably compared, the number of parameters that are directly affected by the user must be reduced. A significant source of tuning variation is found in the laser systems, specifically the lasers involved in the Xe-Ar four-wave mixing cell.

Therefore, the first aim of these developments is to improve the reproducibility of the instrument setup, and within that reduce the amount of time taken to tune the instrument to a desired operating sensitivity. Additionally, the development of a system which allows precise control over the ratio of gases used to fill the Xe-Ar cell allows as of yet untenable access to investigate the effects of wavelength tuning across a range of ratios. So far, the wavelengths of the tunable dye lasers have remained relatively fixed in order to ensure the ionisation of krypton is possible (if the wavelengths were significantly adjusted then the signal may be lost entirely, re-tuning from this point would be very time consuming). The ability to freely adjust wavelengths would increase the understanding of the tuning curves each of these wavelengths has and how they interact with each other across a range of gas mix ratios. Therefore, a secondary objective of these developments is to make progress towards a more complete understanding of the behaviour of the laser systems used on the RIMSKI instrument as the gas ratio is changed.

4.2 Development

4.2.1 Methods Discussion
Methods to increase the reproducibility of the filling procedure were critiqued; both a method involving controlled continuous filling, and a method involving pre-mixing of gases in a secondary reservoir were assessed.

Maintenance of a constant ratio of Xe-Ar can be achieved either by passing a continuous flow of gas at a precisely known ratio through the cell, or by filling the cell to a set pressure at a ratio that is precisely known. Additionally, whether the equilibration of the gases takes place within the Xe-Ar mixing cell, or in a secondary reservoir changes the speed at which the cell signal becomes stable. Each of these approaches has benefits and drawbacks; these are discussed in Table 4.1.
<table>
<thead>
<tr>
<th>Method</th>
<th>Discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1)</strong> A continuous flow of Xe-Ar is passed through a restricted volume, such as a differentially pumped viewport. This gas is bled out continuously, maintaining a constant pressure of flowing gas through the cell.</td>
<td><strong>Advantages:</strong> The cell contents do not degrade over time. The gas ratio could also be fine-tuned in real time by observing a signal in the mass spectrometer and adjusting the gas inlet ratios to optimise the signal. <strong>Disadvantages:</strong> Slight fluctuations in the amount of each gas passing through the cell would be much more noticeable. The relatively small amount of gas passing through the cell would change more dramatically if there was a momentary decrease in the flow of either of the two gases. This in turn would result in greater potential pulse by pulse variation in the measured signal.</td>
</tr>
<tr>
<td><strong>2)</strong> A litre volume is filled using a precise ratio of Xe-Ar. This volume acts as a secondary reservoir, allowing the gases to mix to equilibrium within the reservoir, to then be used to fill the mixing cell as required.</td>
<td><strong>Advantages:</strong> The gas mix would be allowed to pre-mix, so theoretically the gas would be at equilibrium when they were added to the mixing cell. This would mean the signal at the inlet of gas into the cell would be immediately stable, rather than requiring time to equilibrate. <strong>Disadvantages:</strong> There is no reason that a litre volume of gas would not drift in composition due to desorption of gas from the container walls. The effect could be mitigated by increasing the reservoir pressure, but an additional problem with the lack of robustness to change the ratio used to fill the cell is unavoidable with this method.</td>
</tr>
<tr>
<td><strong>3)</strong> A precise ratio of Xe-Ar is slowly added to the mixing cell, which is an isolated volume. Once a set pressure has been reached, the gas flow is stopped and the cell isolated.</td>
<td><strong>Advantages:</strong> The method could robustly vary the ratio being used to fill the cell. It would allow a variable total pressure, reducing the effects of minor gas flow variations on the ratio within the cell. <strong>Disadvantages:</strong> When isolated the cell has been shown to drift, therefore it would require periodic refilling to maintain the ratio. Mass flow controllers are not really designed to fill a static volume, they rely on a constant flow into a vessel with essentially static pressure (the addition of gas does not noticeably change the pressure within the vessel being filled), therefore problems with this method may arise.</td>
</tr>
</tbody>
</table>

*Table 4.1 – Considered methods of filling the Xe-Ar mixing cell.*
4.2.2 CHosen Method

It was decided that the third method discussed was the simplest and most versatile system to implement. The wavelength required is a specific 116 nm wavelength. The set up requires that the 252 nm beam be tuned to the xenon resonance, to allow the optimum excitation (and therein population inversion) of the xenon atoms within the cell used to generate the VUV wavelength. The 1507 nm beam is less restricted and can be tuned as a final adjustment to the intensity of produced VUV laser light. Due to these constraints, it is the gas cell ratio that acts as the primary means of coarse adjustment of the wavelength produced. Once a strong VUV signal is attained using this set up, an identical cell is filled with Kr gas and the 1507 nm wavelength is then adjusted to provide the optimum generation of the VUV wavelength required for Kr ionization.

Implementation and Design

Figure 4.2 shows a schematic of the system that was implemented for the Xe-Ar four-wave mixing cell filling method selected. The initial system configuration is mirrored for each gas, in any description below ‘Xe’ may be substituted for ‘Ar’ to describe the complete system. A Xe gas bottle, fitted with a two stage regulator, is attached via stainless steel VCR vacuum grade components to one of the mass flow controllers. This backing line is maintained at ~2 Bar pressure of the pure Xe gas. This fulfils the requirement of the MFC, which requires a stable constant backing pressure in order to calculate the gas flow through the unit. Moving along the system towards the mixing cell, a quarter turn valve acts to isolate the slow leak through the MFC from the rest of the filling line. At this point in the system, the two gas flows intersect. They connect to the filling line in opposition to each other. This means there is a potential for an interface between the gases, and that their laminar flow vectors are in opposition to each other. The potential implications of this are discussed in section 4.3.1, under the heading ‘Gas Flow and the Physical Design of the System’. The combined gas flows pass through a micrometre screw gauge valve, a feature that is rarely used on this system but serves as a secondary failsafe valve between the Xe-Ar mixing cell and the gas bottles. An MKS Baratron capacitance manometer is located above this valve, and is the pressure gauge from which the filling of the mixing cell is monitored and the total cell pressure is recorded. The cell is then isolated from the entire filling line by a right-hand turn T-valve. The cell design itself has not been modified from the design described in section 4.1.3, Cell Design.
Mass Flow Controllers are installed in-line with the gas flow system, and are designed to allow a precise flow of gas through the unit, over a specified length of time. The unit controls this flow by restricting, or opening a calibrated diaphragm valve, which is opened or closed based on feedback from a flow meter found further down-line to the valve. The use of flow meters allows continuous re-calculation of the required valve settings, in order to maintain the user defined flow rate. The calculation necessarily takes into account the fore line pressure and the aft line pressure. However, it would stand to reason that the greater the changes that the unit must make in order to maintain the correct flow rate, the greater the errors in the overall flow become. This is due to overshooting (opening or closing the valve more than is necessary) as the re-calculation are made, a factor that becomes more prominent the more the fore and aft line pressures vary. To moderate one of these factors, gas bottle regulators are fitted between the MFC units and the gas bottles. These provide a continuous steady pressure of each gas as a backing pressure before the MFC units. In theory, because these regulators are pressure driven physical mechanisms, they provide a constant pressure of gas which is defined by the user. This regulator pressure should not vary regardless of the rate of flow through the MFC unit.

There are additional features that were developed in order to facilitate the rigorous characterisation of this new tuning method. These are detailed in the following sections:
Xenon Detector Cell

The foundation of the four-wave mixing process is two photons of wavelengths ~252 nm. These photons correspond to a two photon transition within xenon. The tuning of the UV Cobra Stretch dye laser very strongly affects the resultant ionisation efficiency of the spectrometer. However, the tuning of the 1507.3 nm beam can also cause a similar effect to be observed. It was therefore beneficial to devise a method by which the tuning of the 252 nm beam could be independently checked.

<table>
<thead>
<tr>
<th>Electronic Transition Configuration</th>
<th>J</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Single photon wavelength (nm)</th>
<th>Distance to Theoretical ideal wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p[2p²][3/2]6p[2p²][3/2]</td>
<td>2</td>
<td>79212.464</td>
<td>252.4855</td>
<td>N/A</td>
</tr>
<tr>
<td>5p[2p²][3/2]5d[2½][1/2]</td>
<td>0</td>
<td>79771.268</td>
<td>250.7168</td>
<td>1.7687</td>
</tr>
<tr>
<td>5p[2p²][3/2]5d[2½][1/2]</td>
<td>1</td>
<td>79986.619</td>
<td>250.0418</td>
<td>2.4437</td>
</tr>
</tbody>
</table>

Table 4.2 – Transitions surrounding the theoretical ideal wavelength setting for the UV cobra stretch laser system. Data are from Saloman (2004).

A reservoir of pure Xe was installed on the detector cell filling line. This allowed the addition of a quantity of Xe to a detector cell, where the same two photon resonance transition would furtherly be ionised by a third photon, allowing the tuning of this transition to be assessed. Confirmation that the wavelength is tuned to the correct transition was based on the relative changes to the wavelength that are required to reach a different transition. Table 11.1 shows the transitions that were scanned through in order to confirm the correct transition for Xe four-wave mixing was selected.

Lasers are rated, and described as producing an infinitely defined wavelength of laser light. In reality the wavelength displayed is the centre of a distribution of produced wavelengths. This phenomenon is often called laser bandwidth. This is seen to affect all the beams used on the RIMSKI instrument, and as such it is often necessary to tune beyond the perceived optimum wavelength, and then step the wavelength back to the optimum in order to ensure the peak wavelength generation of the laser is tuned to optimise Xe excitation.

Beam Alignment

Ionisation occurs across a volume within the ion source. It is beneficial to think of this region as the volume across which each wavelength provides enough energy to saturate the transition that beam corresponds to. This is not the same as the volume over which the entire beam may
be spread as the fringes of a beam are often much lower in energy than the centre. The RIMSKI laser systems display different beam profiles depending on the system they originate from.

The 252 nm, and 558 nm beams are formed in quartz cuvettes, and therefore show comparable beam profiles, whilst the 1507.3 nm beam is formed from a quartz capillary beam which is mixed with a 1064 nm beam which has a Gaussian profile. The profile of the 1507.3 nm beam is non-uniform.

The size of the ionisation region is governed by the alignment of the beams as they pass through the ion source, in particular the region filled by the krypton plume released from the back plate. It stands to reason that a collinear alignment of the beams will be advantageous to the running of the instrument, it also allows easy assessment of the location of the ionisation region across the length of the ion source.

A series of iris optical components have been installed in order to allow co-linear alignment of each ionisation beam. Two irises are equipped with micrometre adjustment gauges, the purpose of which is to allow adjustment of the beam path whilst keeping the angle of the beams through the source the same in each iteration. One of these irises is located before the input side of the spectrometer and the other on the output side.

For the ionisation process to be at its most efficient, the peak energy from each laser pulse, has to pass through the same volume of the ionisation region. The same is true of the temporal overlap for each pulse of each wavelength. In order to create as little spread on same mass ions as possible, the lasers are pulsed at 10 Hz, however each individual pulse of energy is significantly shorter. Each pulse has a duration of ~8 ns and follows a roughly Gaussian distribution.

At these pulse durations it becomes necessary to ensure the beams overlap in time as well as in space. A simple calculation shows that a pulse of light travelling across the laser table will take $3.33 \times 10^{-9}$ seconds to traverse a meter in distance. Therefore, for every meter difference in the beam paths, there is a 0.42 s arrival time difference in the pulses. The difference in arrival time can lead to significant differences in the peak energy of a given wavelength at the time it is required. Interaction with laser components can also delay the pulse’s arrival time.

The density and distribution of energy across the ionisation region is likely a dominant factor to the overall efficiency of the ionisation process, and by extension the signal strength measured. It is therefore necessary to understand the energy distribution of each beam within the resonance scheme used on the RIMSKI instrument, in order to fully understand the workings of the instrument. The energy across a TEM$_{00}$ standard Nd:YAG beam is Gaussian in distribution,
this is displayed in the beam profile of the 1064 nm attenuated YAG beam, used in the final ionisation step of the krypton resonance scheme. The tunable dye lasers produce non-gaussian beam profiles. The overall profile is strongly dependent on the tuning of the beam path through the optical components within the final stages of the dye laser unit.

4.3 CHARACTERISING THE NEW SYSTEM

The cell is evacuated to a low $10^{-3}$ mbar rough vacuum. With the pump open, the cell is flushed through with a high flow of both xenon and argon, this is in order to purge the gas lines and the cell of residual gases, as well as any desorbed air composition gases. The flow is stopped and the cell allowed time to pump down to its baseline again. The ratio is then set, keeping the xenon set point above 5 SCCM (standard cubic centimetres per minute). The flow is allowed to equilibrate and stabilise (measured on the control unit, which feeds back the values of the flow meters associated with each input line). The cell is isolated from the pump out line, and the cell allowed to fill up to a given total pressure.

The MFC units require laminar flow to work - this is due to how the MFC calculates the flow rate. A small amount of the gas flow is tapped off the main line and fed across a filament with known power flowing through it (and thus, a known heat emission). The flow of gas is heated, and the temperature change measured down flow. The meter can then calculate whether a change in the solenoid valve aperture is required to reach the flow rate defined (J. Cowpe, personal communication, Nov 2015).

4.3.1 RESULTS AND DISCUSSION

Throughout the characterisation results, it is apparent that the mechanisms and protocols developed throughout this study have granted vastly improved control over the ratio of gas within the mixing cell compared to previous methods and mechanisms. It has also become apparent that there are a number of behaviours observed whilst using the system that must be acknowledged. These behaviours do not infringe on the control over the produced ratio significantly, but it is worth bearing in mind the effect these affects may have over the continued use of this instrument.

A procedure for filling the four wave mixing cell was devised; the cell is first purged using a continuous flow of even parts xenon and argon gas. The flow of gas is allowed through the system for at least 5 minutes prior to any further step. This is to remove any built up air within
the gas cell as well as the fore-line section of each MFC. The gas flow is stopped and the system is allowed to pump down to mid-range $10^{-3}$ mbar pressures. Full equilibration normally occurs within two minutes of pumping, after which a flow of the gases at a calculated ratio is allowed through the cell. This is continued until a stable equilibrium is met (variation on the reported flow rates, displayed on the MFC control box, is reduced to $<0.01$ SCCM per 10 seconds of filling time). This level of precision is difficult to enhance any further with the system implemented on the RIMSKI instrument. The cell is then isolated from the pumping line, and allowed to fill to a predetermined total pressure (typically 400-500 Torr, but the value varied depending on the experiment being carried out at the time), as measured using an MKS baratron manometer gauge. Once the pressure is achieved, the MFC units are turned off, reducing their flow rates to a minimal level, and they are immediately isolated from the gas cell, to prevent slow deviation from the defined gas ratio.

The ratio within the cell can be described by two means, a nominal ratio (based on values input into the MFC control unit), or as implied ratios (theoretical ratios that should be present within the cell to enable mixing at a given wavelength). Errors on the nominal ratio within the cell are derived from a number of sources, but are thought to be dominated by systematic error from the design of the system. This means that whilst the filling procedure is highly reproducible, the ratio that the cell is filled can only be accepted as a nominal ratio, and is not necessarily an accurate reflection of the exact mix within the cell. With the experimental setup currently employed, there is no reliable scientific way of ascertaining exactly what is leading to the discrepancy in nominal versus implied gas ratios, but it is clear that there is a consistent offset of mixing wavelength from both the previous mixing system on the RIMSKI instrument as detailed by Strashnov et al. (2009), as well as theoretical model data for ratios and the wavelengths they should mix.

Bandwidth of VUV production is also difficult to reliably assess with the implemented system on the RIMSKI instrument. The system employs a pair of detector cells, and with them charge sensitive amplifiers. However, the amplifiers are sensitive enough to pick up electrical noise and jitter from other instruments and devices used around the lab. The noise manifests itself as a combination of variable standard deviation on the baseline noise level, rogue packets of signal that move erratically along the signal trace on the oscilloscope, and rising and falling of the baseline in periodic motions. The result of this is a difficulty in assessing signal height, which becomes more prominent when looking for the point where a measured signal is one standard deviation above the baseline. These errors make a measurement of signal intensity to any degree further than a basic measurement a fruitless venture. There is also no viable way of mitigating the jitter and variation derived from other laboratory equipment. Thus, it is
impractical to use signal intensity as a reliable means of assessing VUV generation from the four-wave mixing procedure.

**Formed Wavelength as a Function of Mass Flow Controller Set-Point**

The cell is filled, with the set points for both Ar and Xe being noted, then the wavelength of the DCM Cobra Stretch laser is tuned until a signal is detected within the NO$_x$ detector cell. The set point of Ar is varied, whilst the Xe flow rate is kept fixed. In order to minimise any fluid dynamic flow effects on the ratio of Xe and Ar in the mixing cell, it is necessary to maintain a fixed xenon set point, and vary the argon set point. This results in an overall minimal change to the conditions each gas is flowing under (i.e. changes to the argon input rate are a lower percentage of the total gas flow than any change to the xenon input rate). This also allows more precise control over the nominal ratio flowing into the cell. This was decided in an attempt to minimise possible flow issues that would be encountered if changing the flow of a low-flow gas which is mixing with a high-flow gas.

An overarching view of the data collected over the duration of this project, shown in Figure 4.3, illustrates the high degree of reproducibility using the MFC unit filling method.

![Formed Wavenumber vs Ratio (Ar/Xe)](#)

*Figure 4.3 – Summary data measured across the duration of 3 years of running the newly adopted MFC filling method. The line shown in red indicates the theoretical ideal wavenumber corresponding to the first transition within the RIMSKI ionisation scheme.*
The generated VUV wavelength is a function of the DFM-NIR wavelength. The sum of the two UV photons’ wavenumber combined with the wavenumber corresponding to the wavelength of the DFM-NIR beam, gives the wavenumber of the outputted VUV beam. This number is easily converted into a VUV wavelength, to be plotted against the ratio of Ar to Xe.

The plot between these two variables shows the degree of control afforded to the mixing cell ratio by the installation of the MFC units, and thusly the precision with which the VUV wavelength can be tuned to the $4s^24p^63^1S$ to $4s^24p^5(2P^0_{3/2})5s\,^2P^0_{1/2}0$ krypton transition.

The Sirah dye lasers emit a narrow, but not wholly isolated, band of wavelength values. This creates one of a number of tuning curve variables within the system. In practice, efficient absorption occurs in a small band, surrounding the theoretically infinitely defined energy level. The reason for the broadening of the absorption range lies in the constraints imposed by the laser systems employed. Selection of a specific wavelength of light is an imperfect process. The produced beam is not a precise mono-wavelength spectrum, instead, it is a distribution of wavelengths around the specified calibrated wavelength. The laser output is comprised of a range of wavelengths, centred about the software defined wavelength. This results in an apparent range, across which a target will be excited by a seemingly off-resonance wavelength. In reality, the process taking place is related to the energy distribution across this range of wavelengths, and thus, the positioning of the specific resonance wavelength from that of the centre of the set wavelength. It stands to reason that a wavelength closer to the resonance wavelength will result in a stronger signal. However, the practical application of this theory is more complicated, as is demonstrated within the responses observed whilst utilising the RIMSKI system.

From Figure 4.4 it is clear that there is an offset between the data collected for this study, and the data from previous calibration work of the old Xe-Ar mixing cell filling method. It has been shown that there is a high degree of control over the reproducibility with this new filling method, it must therefore be considered how such a deviation could arise.

The possibility of the data being vertically displaced due to a change in the calibration of the dye laser GUI, between the previous data and the data collected for this study, was ruled out by measurement of the wavelengths using a wave meter. These wave meter measurements showed no significant difference between the reported wavelength and the actual output wavelength.
Figure 4.4 – Graph of Xe-Ar ratio tuning data relative to DFMNIR output wavelength, comparing data from this study to previous calibration curve reported in Strashnov et al. (2009), also included are data from an independent measurement of the mixing ratio required to form VUV wavelengths, Kramer et al. (1984).

VUV Generation Bandwidth

There are a collection of factors within the system that cause a range over which the excitation of the transition can be observed. This is shown as a tuning range, over which an ionisation signal will be detected in the NOx cell, for any one given ratio of Xe-Ar. The implication of this inherent bandwidth differs depending on the source of the transition broadening. Therefore, the conditions and reasons behind this phenomenon should be constrained to facilitate understanding of the tuning process and thusly enable easier tuning of the Xe-Ar mixing cell.

Analysing data from the tuning of the mixing cell, rapidly reveals that the transition lines do not behave in a straight-forward way. The variation in the mixing DFM-NIR bandwidth, and the centring of the peak output relative to the full range of detected signal changes. It is possible to explain this variation, according to different phenomena that are known to affect the instrument tuning.
Motor Hysteresis – The LiNbO$_3$ crystal is mounted to a motor, in turn controlled through a GUI. The motor movement is not completely reproducible, and due to this, displays differing characteristics depending on the direction of movement. This is observed in tuning curves and appears to be a factor of the direction of travel. When the motor is moving to compensate a shift to longer wavelength, the peak shifts to a slightly longer wavelength and a higher total signal. Movement in the opposite direction shows a slightly shorter wavelength, with a lower total signal height.

Human Error – It is an inescapable factor of measurements made by humans, that any measurement has an inherent uncertainty. In this situation, the presence of a signal is defined as a certain number of mV above an average baseline reading. However, the charge sensitive amplifiers display jitter and baseline noise that varies over time, and as a function of electrical interference from sources beyond the control of this experiment. This baseline noise provides one source of uncertainty when looking for a definitive signal passing above a defined baseline. The occasional pulses of electronic interference, characterised by rapid ‘bounces’ of the otherwise static baseline, also add uncertainty to the measurement. This is particularly apparent when the interference is observed at rapid intervals.

Stability of the Detector Cells – The response from the cells, to any given signal is dependent on a range of factors, all of which conspire to create an inconsistent average baseline and peak signal height. These factors can include, the length of time the cell has been filled for, the alignment of the beams through the cell, and the energy of those beams.

Tunable Dye Laser Wavelength Bandwidth – As with all laser systems, the DFM-NIR beam consists of a range of wavelengths, with a peak centred on the wavelength set point. The beams used on the RIMSKI system have an inherent wavelength bandwidth, over which the energy of the beam is distributed. This leads to an apparent bandwidth over which the production of VUV laser light is possible. The average range over which a measurable signal was detected was found to be ~0.7 nm centred on the reported wavelength of the 1507.3 nm beam.

Total Cell Pressure Effects
Previous attempts at four wave mixing similar to that carried out on the RIMSKI system had indicated that total system pressure does not affect the generation or tuning of the emitted laser light. However, in practice (both with the old filling method, and the new system), the RIMSKI system appears to display a degree of sensitivity to the total cell pressure. The total cell pressure has previously been described as only affecting the wavelength that is formed at
extremes of pressure, ranges through which this experiment is never run (Strashnov et al., 2009). It was stated in Strashnov et al. (2009), that the optimum partial pressure of xenon within the cell is 20 Torr, at the optimum stated ratio this would give an Ar pressure of ~184 Torr.

An interesting new avenue of investigation that this filling method opened was to monitor the spectrometer signal as the cell was being filled. This allowed a comparison of signal intensity against the total pressure within the cell, as the pressure increased in real time. It allowed the investigation of the validity that total cell pressure had no effect on the efficiency of VUV production.

The experimental setup was as follows: A single aliquot of air ($1 \times 10^6$ atoms total Kr of terrestrial average atmospheric composition) was admitted to the spectrometer volume whilst the Xe-Ar cell was empty and pumping. The flow of gas through the cell was allowed to stabilise, and then the pump valve was shut. The acquisition of data began at this time, using the standard RIMSKI data acquisition software. The total pressure within the cell was also measured using a MKS baratron manometer, as a function of the time since the cell was isolated from the pump. Laser wavelengths were maintained at constant values throughout. The ratio between the Xe and Ar gases was maintained at a constant value throughout.

Each summed spectrum was collated, and the signal height at the arrival time corresponding to the centre of the $^{84}$Kr peak was plotted as a function of spectrum number.

The increase in pressure is linear over time, indicating the mass flow controllers are not encountering any significant difficulty in maintaining a continuously stable gas flow. The deviation on recorded pressures at set times is likely due to slight variation in baratron display response times as well as human error. If the deviation was caused by random variation in the gas flow then you would expect the deviation across the complete dataset to increase with each sequential minute, due to each subsequent step adding an additional margin of uncertainty on the amount of gas admitted to the cell. If however, the uncertainty is based on discrete measurements, such as the precise time a measurement is taken versus the actual amount of time the gas has been flowing for, then you might expect a more random variance in the deviation of each measurement, with some time values seeming more precise, and other less so, but in a non-sequential way. It is therefore safe to assume the deviation observed in the measurements is derived from measurement error rather than any actual deviation in the gas flow.
Signal intensity oscillates with increasing amplitude. It is clear that signal intensity increases rapidly between 450 Torr and 500 Torr, total pressure. The decrease in overall signal height is between each measurement repeat, is thought to be caused by a noticeable decrease in the UV laser power over the time these repeat measurements were carried out. It should be noted in addition to the measurements shown in Figure 4.6, the signal intensity in each measurement dropped off rapidly after ~600 Torr total pressure was reached, with a peak in intensity between 450 Torr and 550 Torr. These changes were not measured due to limitations imposed by the data collection software system requiring a fixed total scale prior to the onset of measurements being taken. In order to use a full-scale voltage that allowed the observation of the fine detail cyclicity in signal intensity, the scale was such that the final peaks measured would saturate the measurement scale.
Figure 4.6- An examination of the periodicity of the signal intensity spikes, highlighting the low $^{84}$Kr count peaks early in the measurements. The deviation on the peak centring is expected, as the number of counts decreases, the addition of noise and the jitter on the maximum signal data point will increase. The smaller the population of arriving krypton ions, the less well the point of maximum signal intensity is defined. This is clearly observed in how the peak centres ‘lock in’ with each other as the peak heights increase.

There is only one series of measurements that shows a clear offset from the other measurements. These peaks appear to be consistently occurring at an earlier time than the other four data series’ peaks. This suggests the timing of starting this filling and the subsequent data recording from the spectrometer were mismatched, with data collection on the computer starting at a later time, after the start of the gas flow, than in the other four measurements. Given the degree of alignment observed for all other peaks, the disparity is likely caused by inaccurate alignment of the cell pressure data set and the measurements acquired using the RIMSKI instrument for that data file. This is further supported by the degree of consistency in the offset observed for that data file.

The oscillating signal intensity and its periodicity seemingly being strongly connected to the pressure within the cell is an interesting discovery. This is in direct contradiction to the conclusions of Strashnov et al. (2009) and Kramer et al. (1984). Given the theoretical and experimental assertions of these previous works, it suggests that there is a feature or parameter of the RIMSKI instrument that is leading to this phenomenon occurring.
**Optimum Cell Pressure**

Within section 4.3.1, under heading ‘Total Cell Pressure Effects’ it was discussed that the pressure within the mixing cell appears to affect the signal intensity within the spectrometer. This oscillation in signal intensity was unexpected, especially given the previous work of Strashnov *et al.* (2009) and Kramer *et al.* (1984).

It is plausible that the effects observed in the process of filling the mixing cell are a result of a change in the total pressure of the cell. Consider, two gases being inputted at two different rates; above a critical pressure, you might expect the gases to behave as they would in a laminar flow situation. This transition would necessarily alter how the influx of the two gases mix. Due to the path from the mass flow controllers, it is possible that beyond the threshold pressure, the efficiency of mixing is decreased - resulting in a lower input rate of xenon than expected for the controller settings.

The pressure of the mixing cell should not cause a delay in any one beam (involved in the ionisation process) more than any of the others. The increase in pressure will retard the beams collectively, as would be expected of light travelling through a medium that is denser than air. Exceptions are made for the 252 nm beam, which will be slowed more than the non-resonant beams. However, this beam is only used in the mixing process, and thus is unimportant after this cell- as such, its phase matching with the other beams in the ion source is unimportant.

Importantly, the pressure related effects seem to be reproducible and predictable. This is demonstrated in Figure 4.6. Based on those measurements it seems logical to use a total cell pressure of 450-500 Torr. This accounts for the sharp signal intensity drop above 550 Torr.

**Gas Flow Speed and Limitations**

Mass Flow Control units are devices that allow a precise flow of gas through an aperture in a given amount of time. The mechanism that allows the unit to calculate the gas flow it is allowing through it is as follows: A laminar flow of gas is permitted through the unit, and a small fraction of the gas flow (a known volume) is tapped off the line and passed over a filament heater. This heater is designed to give out a known amount of heat. Each control unit is calibrated using a pure gas, and the unit is capable of calculating the flow rate of the gas based on the amount of heat absorbed by the flowing gas (via a detector further down the gas flow line). The control unit requires a laminar flow of gas through it, where the fore-line pressure is greater than that of the aft-line pressure. The MFCs are also designed to operate a flow of gas into a volume held at a steady state.
Long Term Calibration Drift

Mass flow controller calibration drifts over time. This would be observed as a progressive change in the set points required to achieve the optimum ratio for VUV formation at the required wavelength.

It was observed that the MFC control unit was exhibiting faster drift on the calibration than expected. Over the course of a day the reported flow rate through the MFC would drift away from zero. The MFC have a natural leak rate due to their design. The gas flow is controlled by a diaphragm valve which cannot completely shut off gas flow through the MFC. However, the drift away from the calibrated zero value cannot be attributed to that mechanism because the leak rate would necessarily be included in the zeroing mechanism incorporated into the MFC control unit.

The control unit has a function to ‘auto zero’ itself. This function corrects the point at which the controller considers there to be no gas flow. Figure 4.7 illustrates the influence using the ‘auto zero’ function has on the offset of the dataset. The clustering of data for a given day is high, showing a reproducibly precise filling method. However, the use of the ‘auto zero’ function appears to cause an unpredictable offset of the trend. Within the Day 1 dataset, the right-most outlier was observed to show two distinct peaks in the NO\textsubscript{x} cell signal.

This sort of drift is perhaps indicative of changing conditions within the lab. The MFC units rely on several physical parameters remaining constant. For the MFCs to function optimally, the fore-line pressure must be constant, the gas must be at a known temperature (the controller moderates this itself), and the aft-line pressure must be maintained at a constant pressure. The last parameter is incompatible with the implemented method, but calibration data would suggest this is well accounted for by the controllers and effects of this changing aft-line pressure are well controlled. It is plausible that the fore-line gas parameters are variable over the duration of the day. Temperature is particularly liable to vary; the heat output by the cryogenerator compressor is significantly greater during the morning, when the cold head is drawing a greater amount of heat away from the instrument, and subsequently releasing it via the compressor unit. This heat release may be slightly raising the fore-line temperature, increasing the backing pressure on the MFC, which would theoretically increase the leak rate through the ‘closed’ valve.
Ultimately the cause of this drift is unidentifiable with the equipment available. However, it has been proven that the effect can be controlled and does not significantly affect the tuning reproducibility of the cell filling method.

![Figure 4.7](image)

**Figure 4.7** — A plot of data from three days of wavelength against ratio analyses, showing the precision of ratio control for a given calibration, and also the zeroing error observed as an effect of using the ‘auto zero’ function on the MFC control unit. The controllers were ‘auto zeroed’ before starting analyses on each day.

**Mass Flow Controller Precision and Uncertainty**

An amount of jitter within the mass flow controller system is apparent, in the real-time variations of flow rates reported on the controller interface. This variation averages ±0.01 SCCM deviation from the set point. The frequency of the jitter varies, and the cause for the variance is difficult to define—however, an experiment was devised to assess the expected variance per minute of filling time. The cell was flushed and then pumped out, followed by the setting of the controllers to the relevant set points, and allowing them to stabilise a continuous gas flow into a dynamically pumped volume. The cell is then isolated from the pumping line and allowed to fill to a total pressure of 400 Torr. During the filling time, a series of minute long observations are made, detailing the number of fluctuations and the degree of variation of each fluctuation from the set point. From these measurements, an estimated variance on the actual ratio of gases contained within the cell can be calculated, and compared with the ratio indicated by the DFM-NIR wavelength required to generate a VUV signal.
Mass flow controllers are precisely calibrated to a specific gas, in the case of the controllers used on the RIMSKI system, they were calibrated to measure the flow of the gas they fill the cell with. As with any component there are inherent uncertainties and errors, within the MFC system the dominant source of this is likely to be the calculation speed of the computer that monitors the gas flow and adjusts the diaphragm valve to maintain a steady flow of gas. It is though that the jitter observed on the control unit is a result of the calculation time lag.

**Gas Flow and the Physical Design of the System**

It was hypothesised that the structure of the filling line affects the flow of gases into the mixing cell. The flow of gases into the cell is a complex process, throughout which the conditions that the gases are flowing into are undergoing constant change. This is particularly prominent as the cell transitions from normal vacuum to coarse vacuum, and the associated mean free path changes associated with that.

As mentioned in section 4.2.2 under heading ‘Implementation and Design’, the two MFC gas flows intersect facing each other. At the set point flow rates experimentally devised, the flow rate difference between the gases is nominally approximately five times greater for Ar than it is for Xe. The large difference between these flow rates, in conjunction with the observed difference in theoretical optimum ratios and experimentally derived optimum ratios, has led to questions about whether the interface between these two gases is inadvertently affecting the flow rate of one of the gases. If so, the effect would have to be highly reproducible to account for the reproducibility of the method.

The lower than theoretically predicted ratio (based on Strashnov *et al.*, 2009) of Ar-Xe supports the idea that the flow of Xe into the mixed gas flow is being restricted. It is possible that the flow rate of Ar is causing this flow restriction. However, the reproducibility of this effect would be a surprising outcome of such an unpredictable system as fluid dynamics. If Ar gas flow was restricting the Xe gas flow I would expect to see a greater range of ratios being produced over the full suite of reproducibility experiment measurements.

Another mechanism that may be responsible for this phenomenon is introduced in section 4.3.1, under heading ‘Gas Flow Speed and Limitations’. The jitter observed on the MFC control unit may be indicative of small fluctuations in the gas flow through the MFC. In this case, over the times the cell is filled for, it is plausible that these jitters would average out. If the MFC jitter is causing an average lower than expected flow of each gas then it is expected that this would lead to a difference in the nominal gas ratio against the actual gas ratio. This difference is a
result of the jitter being a fixed deviation from the set point, and the respective gas flows being significantly different from each other. The flow of Xe is lower than the flow of Ar, meaning a fixed deviation jitter on the Xe flow would be equivalent to a higher percentage of the total gas flow (and therefore total gas amount); a 0.01 SCCM jitter on a 5 SCCM flow is a far greater uncertainty on the flow rate than the equivalent 0.01 SCCM jitter on a ~26 SCCM flow. With that said, the observed jitter on the MFC control unit cannot solely account for the near 50% deviation from the theoretical optimum ratio (~9.2 Ar/Xe), to the experimentally derived optimum ratio (~5.2 Ar/Xe).

It seems unlikely that, with the setup of the instrument the way it is, this effect will be completely understood. What is more important is the lack of an effect it appears to have on the control and reproducibility demonstrated over the mixing cell gas ratio.

4.4 CONCLUSIONS

The newly implemented system allows an as of yet unparalleled ability to fill the cell with both a known ratio of Xe-Ar, and also to a relatively precise total pressure, this is demonstrated by the reproducibility of the 1507.3 nm wavelength required to generate VUV after the mixing cell has been filled. The absolute ratio within the cell is difficult to constrain, as shown by the disparity between the reproducible measurements using the MFC filling method, and the data presented by Strashnov et al. (2009), as well as Kramer et al. (1984). The exact reason for this offset has eluded this study, however speculation leads to a problem in being able to accurately mix these two gases within the given apparatus. This is possibly due to a change in fluid flow as the two gases meet each other within the filling line. An investigation of differing the input direction of the Xe and the Ar relative to each other should be considered to further understand the cause of this disparity.

Method for filling the Xe-Ar Cell

A protocol for reproducibly filling the Xe-Ar mixing cell has been established. This method is shown below:

1. Open all valves and ensure the cell is pumping.
2. Tune the 252 nm beam to the required transition using the Xe detector cell.
3. Open the regulators to the gas bottles (Xe and Ar), so that a stable backing pressure of ~2 Bar is let through to the MFCs.
4. Set the flow rate on the control unit to 20 SCCM of each gas and proceed to flush the cell through for 5 minutes. Repeat this 3 times to ensure all gas from the previous fill is purged.

5. Stop the gas flow and allow the line to pump down to its baseline pressure, leave for 10 minutes.

6. Set the Ar set point to ~26.20 SCCM and the Xe set point to 5 SCCM. These are experimentally defined values so may need revision periodically. If the cell is left unused for extended periods of time it is worth creating a new tuning curve, starting with measurements around the ratio of 5.2 Ar/Xe.

7. Set the gas flowing and allow the MFC readouts to stabilise.

8. Once stabilised, isolate the mixing cell from the pump.

9. Allow gas to flow into the cell until the total pressure measured by the MKS Baratron manometer is 450-500 Torr. The exact optimum pressure varied over time during this study.

10. Once the pressure is reached, stop the gas flow and isolate the cell from the filling line (the valves of the filling line can now be closed).

11. If the wavelengths are expected to be far away from resonance: Tune the wavelength of the 1507.3 nm beam using the NO\textsubscript{x} detector cell; if not, then tune the 1507.3 nm beam using a whole aliquot of air in the mass spectrometer.

12. Repeat the process with the 558 nm beam, using a whole aliquot of air in the mass spectrometer to examine the signal intensity.

13. When the signal appears optimised, block the 1064 nm beam and repeat the tuning process for the 1507.3 nm beam using the mass spectrometer signal (the signal should decrease to 10’s of mV on the oscilloscope, and similarly for the 558 nm beam. This ensures optimal ionisation efficiency.
5. **DEVELOPMENT OF INSTRUMENT CALIBRATION PROTOCOL**

**Premise**
In order to measure gases of unknown composition with the RIMSKI instrument, a series of calibration protocols must be followed. This ensures the reported data are as representative of the actual gas ratios within the sample, as possible. The following chapter details the sequence of calibrations and corrections made to the data that I have developed to this end.

5.1 **INTRODUCTION**

**Data Acquisition Terminology**
There are several terms used regularly when discussing data acquisition on the RIMSKI or RELAX instruments. Each term refers to a particular length of time, and the data collection encompassed within that timeframe. The smallest unit is a sampling point, representing the electronic output of the detectors as a numerical value (relative to the full-scale setting), at a particular point in time. Each sampling point indicates a 1 ns glimpse at the detector output. This unit is discrete, its smallest value is an integer value and a function of the total voltage scale value. The ‘full-scale voltage’ setting is a requirement for the digitisation of the analogue signal produced by the instrument - the digitiser card takes a maximum voltage and divides the range (from 0 V to the set maximum) into 256 discrete units, each sampling point is then assigned a value based on the its value within this discrete value scale. This means, a smaller full scale value results in more precise data collection, whilst a larger full scale value would necessarily have a more coarse value range for each sampling point. The output is a transient current from the micro-channel plates (MCPs), and from that the electrode measures a voltage drop across a 50 Ω resistor. The initial signal from the instrument is analogue, and as such needs to be converted into a digital signal. To do this an 8 bit digitiser card converts the analogue output from the instrument’s detector plates, into a digitally structured signal at a sample rate of 1 GS/s. It is because of this conversion into a digital signal that the value for each data sampling point is discrete and is a function of the full scale value.

The second unit is a ‘data collection window’; this corresponds to the time data is collected for between each laser pulse. Each data collection window represents one full recording of a spectrum of ions, formed and triggered by a singular laser pulse. The duration of each data collection window is 1 μs, or 1000 individual 1 ns sampling points. Each laser pulse triggers the
formation of ions, which arrive at the detectors over a short duration of time. The data
collection window is therefore tuned to overlap with the arrival times of the krypton isotopes.

Finally, data is collected for a 5 minute period, representing 3000 individual laser pulses (or data
collection windows). This will be referred to as a ‘data collection period’. The RIMSKI
instrument is designed to output a single data file per 5 minutes of analysis. Each data file is
composed of 3,000,000 bytes of data. This represents a continuous string of 3000 individual
spectra, each representing a single laser pulse’s collection window.

Data Acquisition

The instrument design of RELAX is comparable to that of RIMSKI (described in Chapter 3). As the
ions impact the MCPs, a current is formed. This current fluctuates according to the number of
ions impacting the MCPs at any given time. The effects of this fluctuating current are measured
as a voltage across a 50 Ω resistor. In order to be processed and recorded on a computer, the
signal is digitised into an 8 bit signal sampled at 1 ns intervals by an Acquiris 8 bit high speed
digitiser PCI card.

An analogue signal is continuous, where as a digital signal is discrete; A digital signal is measured
in discrete units. This means that to digitise the signal measured, a scale must be enforced. The
digitiser is capable of dividing any full scale into 256 divisions. In order for the measured signal
to be accurately preserved, the voltage of the maximum sampling of a given spectrum must be
less than the value of 256 ‘units’ of the divided full scale voltage. Additionally, the minimum
resolvable digitised signal is $1/256$ of the full scale voltage. This means that the range the
signal is ‘allowed’ to reside between is finite, and dictated by the full scale voltage. The digitiser
has an intrinsic baseline noise which will be covered in detail in section 5.3.1, for understanding
here it is assumed that the baseline noise obscures peaks which are 2/256 bits high or smaller.

The above details the method by which the RELAX instrument acquires data. The RIMSKI
instrument has an additional feature built in, due to the significant difference in the expected
signal intensity for $^{81}$Kr compared to $^{84}$Kr ($^{84}$Kr is used here as an example peak). The full scale
setting that would be required to ensure the full $^{84}$Kr peak fits within the scale means that an
expected $^{81}$Kr signal would be completely or at least partially obscured in the intrinsic baseline
noise. In order to measure both $^{84}$Kr and $^{81}$Kr the system must use a ‘dynamic range’. This
means that the digitiser switches scales between a defined full scale voltage, and a 0.05 V full
scale voltage. This dynamic range means that only 15 spectra are recorded for $^{81}$Kr, and likewise
for the defined full scale voltage. The system alternates between the two scales every 100 laser pulses. The implications of this are covered in section 5.4.

5.2 AIMS OF DEVELOPMENT

The data treatment protocols and the data reduction software developed throughout this project are based on the RELAX instrument’s protocols and software. I sought to modify that software, and the protocols associated with it, to be used more effectively for the RIMSKI instrument. This was in order to fulfil the second aim discussed in Table 1.1. A main objective of this was to develop a means of accounting for the variable pump out rates between isotopes, as well as accounting for the dynamic range. Finally, I sought to validate the approach I had developed by testing it against a series of previously measured standards.

5.3 RELAX DATA TREATMENT

In order to accurately analyse a sample, the measured gas composition at t=0 needs to be established. This can be achieved one of two ways. The first involves modelling the pump out rate for an individual isotope, and extrapolating that back to t=0, and the second involves plotting the changes in isotopic ratios relative to a reference ratio, against time, and extrapolating back to t=0.

The RELAX data reduction procedure is explained in Crowther et al. (2008). The procedure progresses through several stages in order to convert the digitised signal into a comprehensible and utilisable data set. The following is a summary of the explanation of the RELAX data reduction procedure provided by Crowther et al. (2008).

5.3.1 DATA REDUCTION

**Summing of Individual Laser Pulses**

The first step of the data reduction process is to condense the 3000 spectra from the measurement into a more valid number of spectra. A data file consists of a continuous binary string of 3000 spectra traces, each with 1000 8 bit sampling points. This continuous string of numbers is read by a data reduction algorithm and distributes the data into a matrix. This matrix serves to sum 100 data collection windows (or 100 individual laser pulses) into one spectrum. It carries this out 30 times, to reduce the data into a series of 30, 10 second long summed spectra.

The purpose of this process is to limit the effect of Poisson counting statistics on the data set. Each sampling point has a probability function to its value. That is, a given point on a spectrum
is affected by minor perturbations otherwise known as noise. The principle is, for a small number of detections, the slight variations in how many detections are made for a given point is a more significant percentage of the signal than for a larger number of detections. Given noise is random, if several spectra are summed together then you would expect the noise to average out to give a more valid representation of the measurement. The sources and explanations of noise are covered in greater detail below.

Figure 5.1 – An example of a summed mass spectrum for an air calibration measurement. The features such as the reference peak selection and the peak tracking points illustrate how the software (described below) achieves data reduction.

**Calculation of a Peak Area and Ratios**

The next stage involves calculating a peak area for each isotope. In order to achieve this, a baseline must be established, as well as a duration over which the signal is considered to be caused by the arrival of the isotope in question.
The user selects appropriate regions over which the peaks for each respective krypton isotope can be found. This is generally the point at which the baseline and the peak meet, but is occasionally a few points into the baseline to ensure the peak arrival region is applicable for all measurements during that day. The user also inputs an appropriate baseline series of data points, from which the software can calculate a baseline correction. These designated durations remain fixed for an entire day of measurements (providing the ion manipulation electronics are also static throughout the day). Because the ion manipulation components are reset with each day of data collection, the exact arrival times of isotopes vary by small amounts, making the redefining of the durations for each isotope peak necessary for each day of data collection.

The software then calculates the sum of the area between the baseline (an average of the points from the spectrum selected as the baseline) and the signal trace. This is carried out for each of the 30 spectra present within the data file. The certainty of the peak area is also calculated based on a series of noise parameters. The software incorporates the various forms of noise and uncertainty in order to calculate an error for each isotope peak area calculation. If this is working as intended, then the error predicted by the software is approximately equal to the standard distribution of a range of measurements of that isotope.

Uncertainty is a factor that should be considered a part of any real measurement. The performance on even the most highly tuned analytical instrument is subject to variations and deviations in the measured values from the real values. Within the confines of the RELAX or RIMSKI instruments, uncertainty may be categorised into one of two groups. These are either baseline noise, or counting statistics noise. There is an additional noise attribution as a result of the signal digitisation.

The baseline of the instrument is not a completely flat line, it shows series of small peaks and troughs throughout the spectrum. The deviations displayed in this baseline are not due to any incident atoms, ions, or particles causing a signal, but rather due to small electronic fluctuations in the received analogue trace. This type of noise is expected to have a normal distribution, as the probability of a deviation decreases proportionally to the magnitude of the deviation, meaning large variations from the average baseline are less likely than smaller deviations. To account for this baseline noise, the standard deviation across the series of baseline sampling points is calculated. This is then used in conjunction with the average of the series of baseline sampling points in order to provide an average baseline and uncertainty on that baseline average. Extrapolation of this baseline uncertainty can be applied to how they affect the measurement of the peak area (baseline noise is not just limited to the baseline, it represents the electronic jitter across the entire spectrum trace).
Counting statistics noise, otherwise known as Poisson counting statistics, is a measure of how closely each of the 100 sampling points (from the 100 summed spectra) match each other. It is expected that these points would follow a Poisson distribution. The ionisation process, as with many steps in the resonance ionisation scheme used on the RIMSKI instrument, is based in statistical probability. As such, there is an inherent scatter to the number of detections made for any one data collection window. Variation in the number of detections relies on not only the likelihood of a photon interacting with an atom in an excited state, but also that the resulting vector of that newly formed ion will impact an ‘active’ site on the first MCP. An ‘active’ site on a MCP is considered to be any surface that will result in a release of electrons in the direction of propagation required to form a detection signal at the detector. There are added complications with how well the charge release from the first MCP is multiplied by the second of those plates. Across the entire system there is a compound statistical probability that an atom will be ionised and detected. An important distinction must be raised here; the MCP function discussed within this section is different to the charge replenishment related signal suppression. When discussing the pulse by pulse variation, it can be assumed that the plates are successfully returning to optimum charge capacitance between each incident ion. The variation observed in this pulse by pulse variation situation is whether or not the incident ion is ‘accepted’ into a channel, or whether it impacts the front of the detector on a site which will not end in charge transmission to the back of the plate. The pulse-by-pulse variation in signal is represented by:

\[ \Delta P = k \sqrt{P} \]

\textit{Equation 24}

Where \( P \) represents the peak area, and \( k \) an unknown constant. In order to determine the value of \( k \) the following process is used. The rate of change of a given isotope \( (N_1) \) is shown as:

\[ N_1 = N_{1(0)} e^{-\lambda_1 t} \]

\textit{Equation 25}

Where \( N_1 \) is the isotope peak area, \( 0 \) is the value of \( N \) at time 0, \( \lambda_1 \) is the decay constant of the isotope, and \( t \) is the time elapsed. This is the pump out curve of the isotope, illustrated in Figure 5.2.
Figure 5.2 – Illustration of the pump out curve for a given isotope, where $N$ is the number of detections for a given spectrum number. Each spectrum represents 10s of pulsed data collection. If ionisation efficiency is taken as a constant across the duration of an analysis then each pulse of the laser will ionise a set fraction of the gas within the plume. This gas is therefore removed from the system, in a process called ionisation pumping. The result is a decrease in the number of atoms of gas in the plume released from the back plate during the next laser pulse. This stepwise fractional removal of gas from the system roughly follows the form $\ln(2)/12$, although the exact decay constant can differ due to random perturbations of the system, and natural drift of the ionisation efficiency over the course of a day.

To compare the rate of change between two isotopes, $N_1$ and $N_2$:

$$\frac{N_1}{N_2} = \frac{N_{1(0)}}{N_{2(0)}} \left( \frac{e^{-\lambda_1 t}}{e^{-\lambda_2 t}} \right)$$

Equation 26

Which simplifies to:

$$\frac{N_1}{N_2} = \frac{N_{1(0)}}{N_{2(0)}} \left( e^{-t(\lambda_1-\lambda_2)} \right)$$

Equation 27

If $\lambda_1$ and $\lambda_2$ are similar values then this equation approximates a straight line (the form will actually be exponential but over a much longer range than dealt with in these situations). The implication of this is that $N_1/N_2$ plotted against time should also approximate a straight line.

If we select a value for $k$, we can calculate the error on each isotope for that value of $k$. The fit of this line to the data can be calculated using a chi squared evaluation ($\chi^2$). The software then varies $k$ until the value of $\chi^2$ is approximately equal to the number of degrees of freedom. At
this point, we have a model with which we can calculate the ratio between two isotopes at the
time the gas was let into the spectrometer alongside a calculation of the uncertainty with which
the model fits the data. This establishes the output ratios, and their associated errors within the
data reduction software.

**Validation of the RELAX Protocols**

The approach has been shown to be valid by the comparison between the predicted errors from
the RELAX data reduction software, to the standard deviation of a statistically significant
number of standard air aliquot measurements. This is carried out on the basis that the amount
of gas and ratios between the isotopes are standardised and those values are well defined
within literature. The measured values can therefore be compared to the known values, and
calibrated to them. The coefficient between the measured and known values allows a
correction for the measurement bias inherent within the instrument’s running, (Crowther et al.,
2008) concludes that the software accounts for all sources of error within the measurement
system and the method accurately predicts the error for a given measurement.

5.4 **RIMSKI DATA TREATMENT DIFFERENCES**

The RIMSKI instrument is more complicated in its setup, and as a result there are a few
necessary changes to the data treatment protocols. There are two principle differences
between the RIMSKI instrument’s function, and the RELAX instrument’s proven function:

The first is the use of a dynamic range; the RIMSKI instrument switches scales periodically
throughout a sample analysis in order to be able to measure $^{81}\text{Kr}$ as well as the more abundant
isotopes. For air calibration aliquots, the instrument runs on a continuous applicable scale. The
same is true for procedural blank analyses. Samples must be collected using an alternating scale
system. One large scale is applied for the abundant isotopes, and a smaller scale is used to
detect the $^{81}\text{Kr}$ peak, this scale is standardly set at 0.05 V full scale. This scale alternates once
every 100 laser pulses. Therefore, when handling sample data, the number of applicable data
points is effectively halved. This scale change is necessary to ensure both $^{81}\text{Kr}$ and the larger
abundance isotopes are measured accurately. On a large scale, the $^{81}\text{Kr}$ would become lost in
the background noise of the instrument, and on a small scale the higher abundance isotopes
would appear saturated and therefore prohibit an accurate isotopic ratio from being calculated.
The scale switching means that half of the data accurately measures $^{81}\text{Kr}$, whilst the remaining
half can be used to measure the abundant isotopes. Because of signal truncation effects, it is
not possible to measure the abundant isotopes on the $^{81}\text{Kr}$ scale. Equally, the amount of $^{81}\text{Kr}$
present in even the youngest samples (meaning the highest $^{81}$Kr-Kr ratios possible) would be difficult to accurately measure on the larger scale setting due to background noise.

The second difference is related to a potential difference between the ionisation efficiencies of the odd mass isotopes relative to the even mass isotopes (illustrated in Figure 5.3). This phenomenon occurs due to the potential for differences in the total angular spin momentum of the odd isotopes, whilst even isotopes are necessarily more restricted in their summed spin momentum. Even isotopes do not have a net nucleus spin, and therefore the addition of spin from photon interactions gives an average net spin of zero. For odd isotopes, it is possible for the nucleus to have a non-zero spin. Adding spin from photon interactions to this atom will have differing results depending on the direction of the spin the incident photon imparts. These different net spin values all represent different energy levels for the atom. Therefore, the overall result of this quantum level interaction is the creation of several more available levels for the electron energy to be raised to. This phenomenon is termed ‘hyperfine splitting’.

The consequence of this hyperfine splitting phenomenon in context of the RIMSKI instrument is dominated by the $4s^24p^5(2p^0_{3/2})6p^2[1/2]$ transition, spanned by the 558 nm beam. The increased number of total pathways an atom can progress through towards ionisation should theoretically increase the ionisation rate. However, the RIMSKI instrument is designed to limit the number of pathways possible for the odd isotopes to facilitate, by way of limiting the polarity of the light reaching the ion source. A rotational polariser along the 558 nm beam path allows direct mechanical control of this variable, and use of this mechanism has been shown to affect the ratio between of the odd and even massed isotopes’ ionisation efficiencies. Therefore, there is an additional factor that could contribute to uncertainty of a measurement that the data reduction software cannot account for.

Each laser pulse removes gas from the system, leading to a smaller and smaller ‘gas reservoir’ to sample from with subsequent laser pulses. Combined with the potential for different ionisation rates between different isotopes this means the gas composition found within the plume will be continuously changing over the duration of a data collection period. If each isotope were ionised at the same rate, and therefore pumped away at the same rate, the issue would resolve itself. However, due to hyperfine splitting, ionisation of odd mass krypton isotopes is possible through different (and more) pathways than the ionisation of even mass isotopes of krypton. As a direct consequence of this there is a distinct difference in the pumping speed of the odd isotopes relative to the even isotopes of krypton. Adding to the complexity, instrument bias also affects the ionisation of isotopes of different masses. The rate of change between ratios of different isotopes is linear in most cases. The implication of this changing gas composition is
that, for each of the 100 summed data collection windows, the composition of the gas is subtly different. On a pulse by pulse basis this may not be apparent, but the difference between the isotopic composition of the first and last of those 100 spectra will be much more apparent, particularly when the RIMSKI instrument is at peak sensitivity, and therefore ionising very efficiently.

![Graph showing modelled decay constant of each isotope]

*Figure 5.3 – The modelled decay constant of each isotope, relative to the decay constant calculated for Kr\(^{84}\). This shows the difference in pump out rate for the odd massed isotope Kr\(^{83}\), compared to other even massed isotopes. Errors are the standard deviation of 83 measurements made over 13 days of analyses, days were not consecutive. Data points are representative of an average k value for that isotope, for the 83 analyses.*

It is also important, given the modifications to the instrument, that the validity of the data reduction methods still applies. A new baseline for calibration must be established. Calibration requires characterisation of two distinct aspects of an instrument’s performance. The measured values of a well-defined sample must be compared to the known values for that sample. The reproducibility, or constancy of measurements made for identical samples must also be characterised.
5.5 RIMSKI Data Treatment Method

Importance of Accurate Calibration of the Odd Mass Isotopes

One of the most significant uses of krypton isotopic compositions is in the calculation of cosmic ray exposure ages. These calculations rely on accurate measurement of the isotope $^{83}$Kr, and even more so, on the isotope $^{81}$Kr. Therefore, the accurate characterisation of the behaviour of these isotopes is crucial in producing a valid data set.

Increased uncertainty over the $^{81}$Kr isotope leads to improper accounting for the chemistry of the sample. As is discussed in section 2.5.3, $^{81}$Kr is measured in order to exploit the equilibrium reached between the radioactive decay and the production rate, as a calibration for the sample chemistry. Combined with the low abundance of the isotope, small variations in the calculated amount of $^{81}$Kr within a sample can lead to significantly different calculated cosmic ray exposure ages.

Further complication arises when $^{83}$Kr is improperly calibrated. The cosmic ray exposure (Equation 11) relies on the reference isotope $^{83}$Kr, for the cosmogenic gas ratios used within the formula. Although the isotope is more abundant than the $^{81}$Kr isotope, uncertainty in the calculation of the $^{83}$Kr composition iterates through the subsequent calculations, leading to higher errors on the calculated age, or a miscalculation of the age. The certainty of the correction factor calculated for the $^{83}$Kr isotope also has a direct effect on the accuracy of the $^{81}$Kr isotope. $^{81}$Kr is in such low abundance within the terrestrial air reservoir, it may effectively be considered a negligible component due to its abundance being well below the detection limits of the RIMSKI spectrometer. Therefore, an alternative method of calculating a correction factor for this isotope must be used. Conventionally, data analysis from the RIMSKI instrument has utilised the correction factor calculated for $^{83}$Kr as a best guess approximation for the calibration of $^{81}$Kr. This is viable due to similar hyperfine electronic structure of the two isotopes.

Collectively, the odd isotopes of the $^{83}$Kr-Kr system are arguably most important to have accurate measurements of. Therefore, the ability to increase the certainty of the measurements made would be a significant advantage to the use of the measured data. Whilst the even isotopes can be well calibrated as a bulk data correction factor, the odd isotopes may benefit from further characterisation, on a day to day basis for example.
5.5.1 Air Standards Validation

Producing a Reproducible Standard

The RIMSKI instrument is used to measure krypton isotopic compositions of gases released from predominantly solid extra-terrestrial samples. To that extent, the use of a solid sample standard would be ideal, as that would be measured using the exact same protocol as the unknown samples. However, the use of a solid sample is impractical for the purpose of calibration of gas quantity because of the variability in the amount of gas contained within a solid sample. Regardless of how homogenous the sample may be, the amount of gas released is not assured to be the same for any two equal massed samples. The amount of gas contained within a large rock sample may be homogenous, but small variations in porosity can result in large differences in contained gas, over a small volume of rock.

However, principles of gas laws can be exploited to create artificial ‘releases’ of the same quantity of gas. A small aliquot of a large gas reservoir can be extracted many times before there is a significant change in the amount of gas each aliquot extraction will contain. It is this principle that was exploited when the air calibration standard for the RIMSKI instrument was devised.

Production of a standardised reservoir turns out to be a simple procedure. A large, continuously available, reservoir that has been shown to be reproducibly constant around the world is air. The krypton content and isotopic composition of air has been well defined and shown to be homogenous in composition around the world by many groups using a wide range of analytical instrumentation. It therefore provides an opportune reservoir to sample from.

In order to provide a standardised calibration sample for the RIMSKI instrument, a 1 litre primary reservoir was filled with 1 mbar of atmospheric air. Under standard temperature and pressure (STP), 1 cm$^3$ will contained $2.6868 \times 10^{19}$ atoms of gas (Porcelli et al., 2002). A container 1 litre in volume, filled from an atmospheric reservoir, will therefore contain $2.6868 \times 10^{22}$ atoms of gas (of an average air mix). 4% of this mix is water. An average atmospheric air reservoir has a krypton volume mixing ratio of $1.14\pm0.01 \times 10^{-6}$. Therefore the total number of krypton atoms within this volume is $3.06295 \times 10^{13}$ atoms, accounting for the container being filled to 1 mbar, and $2.94 \times 10^{13}$ atoms given a 4% contribution from water. From that primary reservoir, a secondary reservoir is filled, via an aliquot measuring mechanism, which samples 0.2 cm$^3$ of the primary reservoir. This secondary reservoir is also 1 litre in volume. A further aliquot sampling mechanism is used to extract 0.2 cm$^3$ of the secondary reservoir, resulting in
an air calibration aliquot containing an average $1.176 \times 10^6$ total number of atoms of krypton (simplified to $1 \times 10^6$ atoms in Strashnov et al., 2011).

The use of a fixed volume aliquot ensures that the amount of gas admitted to the spectrometer is approximately the same with each subsequent air calibration shot. This allows a calibration of the gas quantity released from a sample heating step. Because the volume, and therefore the number of atoms of gas, within an aliquot remains approximately constant, it is possible to attribute a signal size to that known quantity of gas. The signal size is approximately linearly correlated to the amount of gas analysed. Therefore, this measured signal for the known quantity of gas can be extrapolated out for measurements of samples, where gas quantity is an unknown.

The small variation in the quantity of gas admitted with each aliquot arises because of minor fluctuations in the ambient laboratory room temperature, as well as the very small decrease in secondary air reservoir pressure with each removal of an air aliquot. Although these variations are well below the variations that arise from instrument function variability and the pulse by pulse variation observed.

**Figure 5.4: Subsequent Air Aliquot amounts of gas and their difference from the original aliquot contents, showing the 1% change in the amount of gas within an aliquot over the extraction of 50 aliquots from the secondary air reservoir.**

With respect to the variation observed due to the removal of an aliquot of gas: The amount of gas admitted to the spectrometer with each subsequent aliquot extraction may be modelled. If it is assumed that the gas equilibrates so that the concentration across the whole volume is homogenous at the time the aliquot valve is closed (and the gas is constantly at standard
temperature and pressure), each aliquot extracts 0.02% of the remaining gas within the secondary reservoir. The point where there is a 1% difference in the theoretical amount of gas per aliquot is after 50 aliquots have been extracted from the secondary reservoir. This is summarised in Figure 5.4. Over the number of aliquots conceivably used before re-filling the secondary reservoir, the quantity of gas analysed per aliquot can be said to remain constant compared to the instrument sensitivity variation between sequential air calibration analyses.

**Air Calibration Aliquots**

Measurements of the isotopic composition of air samples allow statistics to be built on the constancy of these measured ratios. The greater the constancy, the more accurately a correction may be calculated and applied to measurements of a range of samples throughout a duration of time. Measuring air aliquots, of a constant volume, admits the same amount of gas into the spectrometer for each measurement. This in turn provides the same sample conditions for each measurement made, therefore making gas quantity effects negligible across a sample set of air aliquots. Overall, the process allows the calibration of how the instrument is functioning, and how that may be changing, over the duration of a series of measurements.

In recent practice it has become necessary to further divide the aliquot of air, into a quarter aliquot. During early stages of the data analysis, whilst data collection was ongoing, it was noticed that the residuals behaved in an unexpected, yet reproducible, way throughout the duration of a measurement. At this time, the entire air calibration aliquot was being used as a calibration standard.

When a whole aliquot of gas is admitted to the spectrometer a fractionation effect is observed across the spectrum. This is best shown via a delta plot, as depicted by Figure 5.5. A delta calculation (Equation 28) is a representation of the deviation of a measured value from a defined fixed value (in ‰).
Figure 5.5 – A delta plot of air measurements, showing an average plot for measurements of ¼ aliquot amounts and whole aliquot measurement amounts. Delta calculations are relative to a standard terrestrial air composition. The deviation of $^{83}$Kr is predominantly governed by the tuning of the 558 nm wavelength, its position through the ionisation volume, and its energy per pulse. Therefore, it does not make a useful reference point for the measurement of air quantities carried out on different days, as these data were collected on different days, with different tuning conditions.

A delta plot represents the deviation of the measured ratios from the defined air ratios. Figure 5.5 shows the effects of increased gas amounts on instrument discrimination. $^{82}$Kr, $^{84}$Kr and $^{86}$Kr serve as a good marker for assessing the discrimination effects caused by saturation of the detectors. Even mass isotopes should all ionise with approximately the same efficiency, unlike the odd massed isotopes, which have been shown to display differing ionisation efficiency, discussed in later in this section (under heading: The difference between odd and even massed isotope calibration). The similarity in ionisation efficiency effectively eliminates that from affecting delta distributions of even isotopes, therefore, the remaining factor that can affect the distribution is the detector sensitivity changing. Other than the MCP components breaking, rapid changes in detector sensitivity are a result of depletion of charge from the MCP surface area. The MCPs have a finite rate at which charge is replenished, the impacting of a further particle before full replenishment has occurred will result in fewer electrons being released in the resultant cascade, and thus a lower measured signal, for the same number of particles.

Effects are most noticeable in the apparent depletion of $^{86}$Kr as the gas amount increases. This is due to $^{86}$Kr arriving close to, but after, the arrival of the most abundant isotope $^{84}$Kr (the reference isotope within Figure 5.5). The measured enrichment in $^{82}$Kr and $^{80}$Kr also indicates suppression of peaks that arrive beyond this isotope. Given the composition of the gas cannot
change, the enrichment of $^{82}$Kr must necessarily indicate that rather than a greater amount of $^{82}$Kr being detected, the detection of subsequent isotopes is reduced. As previously mentioned, it can be surmised that this is due to incomplete replenishment of the MCP charge. The delta variations of quarter aliquots (excluding the deviation of the odd isotopes) do not significantly deviate from 0, and thus show near equal ionisation efficiency as each other. The depletion of measured $^{80}$Kr is likely due to the large $^{76}$Kr peak, that was present in the blank whilst those measurements were taken, causing suppression of the $^{80}$Kr signal.

Therefore, a quarter aliquot of standard atmospheric air provides a good calibration standard for the RIMSKI instrument. This is free of saturation effects which would otherwise distort the calibration effectiveness, as well as increasing the uncertainty on measurements of unknown samples.

**Instrument Stability**

The stability of an instrument is represented by how consistent the measured values of a well-defined sample are. Assessing this requires multiple measurements of a standardised sample.

This standardised sample must be reliably reproducible in order to allow direct comparison between the calibration measurements. As mentioned before, the data collected using the RIMSKI instrument aims to provide information on both the isotopic composition and the quantity of gas released from a sample. Therefore, the selected standard must satisfy two key criteria: The isotopic composition of the standard must be well defined by a range of sources, allowing analysis of differences in instrument bias between different isotopes. The second criteria is the amount of gas admitted to the instrument must be constant between measurements and a well constrained quantity. This allows the amount of gas released from an unknown sample to be quantised.

**Forming a Data Set**

A data set from select days was analysed. These days were selected based on a series of requirements; the instrument was only tuned up at the start of the day (after which instrument configuration remained the same), the data files were collected in one continuous set of analyses, and the wavelength (along with other dye laser parameters) are known for that day of analyses. These parameters were put in place to reduce the number of variables that could cause variation in the instrument’s performance.
The changes to the air calibration aliquot use restricted the number of data files that fit these parameters. In the interest of certainty, only the measurements made after the re-filling of the air calibration reservoir, and the subsequent use of a quarter aliquot of air were considered in this stage of the analysis process. This was to ensure the efficacy of the calibration statistics and the behaviour they displayed. The data collected prior to this protocol change will be more difficult to calibrate, and will be discussed in greater detail within chapter 6, section 6.4.1.

The resulting data set was comprised of a select 11 days of analysis, over which 81 measurements were individually made. Days spanned approximately two months of continuous running, with a single significant re-tuning of the instrument during that time.

**Measurement Reproducibility and Error Prediction**

Measurements are influenced by a range of small perturbations of the instrument’s function. Applying this to the repeated measurement of gas of a precisely known isotopic composition, it becomes clear that a range of measured compositions will be possible, owing to this natural random variation. Within the construction of this statistical representation of the measurements, we establish two key parameters: The mean value, or the average measured composition of the gas, and the standard deviation, or the range of values for the measured compositions. These two statistics are inherently linked to the instrument’s performance. There is an expected source of deviation from the statistical method with which the data is analysed. Variation in excess of this is expected to be caused by how well the instrument is performing.

As the statistics are built up, the certainty with which the mean can be defined increases. In the confines of the RIMSKI instrument, the statistics for a given isotope can be added to, providing the range of the values (or standard deviation of the measured values) does not start exceeding the software predicted errors. If the deviation from this range exceeds the predictions, it indicates a deviation causing factor that is not accounted for within the data reduction software is affecting the measurement of that isotope. The data reduction software is designed to predict errors for each isotope of krypton, based on a range of already established statistical uncertainty factors. The predicted errors should therefore take into account all expected sources of deviation. The range of values centred about the mean value may be represented by the standard deviation of the measurements. To check this, the standard deviation of a data set can be compared to the average error. This enables an easy check of the validity of the data, and the precision on the error estimations.
As the precision with which the mean can be defined increases, the validity of applying a standard error to the resulting ratios increases. This greatly reduces the errors associated with the measurements, but should only be applied if the statistics justify it. In order to maintain data integrity, the aim should be to accurately represent the measurement uncertainty, not to wantonly use the lowest calculated error without justification.

**The difference between odd and even massed isotope calibration**

A statistical approach to data calibration requires reproducibility, this reproducibility can then be exploited to condense a series of calibration measurements into a lower error calibration step. A way of showing the efficacy of this process is to compare the data reduction software’s error prediction against the standard deviation of the measured ratios. Figure 5.6 shows the predicted error, calculated by the data reduction software, and the standard deviation between a series of 81 analyses of a standardised air reservoir. From the graph, it is clear that the even isotopes are accurately modelled, and the errors accurately predicted, by the software. The exception to that being $^{78}\text{Kr}$. The RIMSKI instrument intermittently displays a hydrocarbon peak centred on mass 78. It is believed that the hydrocarbon is benzene, or some fragment thereof. This hydrocarbon peak overlaps the $^{78}\text{Kr}$ peak.

The second isotope that noticeably is not accurately predicted is the $^{83}\text{Kr}$ isotope. The RIMSKI instrument displays a variable bias between the measurement of even and odd massed isotopes. This manifests itself as a difference in the ionisation efficiencies between the odd and even massed isotopes. This variation can be observed as both an immediately apparent difference in the measured peak heights of $^{82}\text{Kr}$ and $^{83}\text{Kr}$.

The method of detection of the ions within the RIMSKI instrument is not capable of discriminating between odd and even isotopic masses, therefore this disparity must be derived from the ionisation process. Because of this, the decay constants for the two isotopes can be directly compared as a measure of the ionisation efficiency difference between the two.

If the decay constants (k) are plotted as a ratio to a reference isotope, $^{84}\text{Kr}$ for example, then it becomes apparent that the odd massed isotope $^{83}\text{Kr}$ is removed from the system at a slower rate than the even isotopes are. This is summarised in Figure 5.5, where the even isotopes pump out at the same rate as one another – displayed as ratios that are (within error) equal to one - whilst the ratio of $^{83}\text{Kr}/^{84}\text{Kr}$ is below one. This depiction is showing the average k value (the pump out rate, or decay constant) of 83 analyses run over 13 days. As a further complication to the characterisation of the $^{83}\text{Kr}$ decay rate, the error (calculated as the standard deviation of the k values for that isotope, across the 83 data files) on $^{83}\text{Kr}$ is higher than for the even isotopes. $^{80}\text{Kr}$ is an exception to this, but the error on this isotope is readily explained by the low
abundance of $^{80}$Kr within air. The larger error on $^{81}$Kr indicates a wider range of values associated with that decay constant. This wider range of values may be possible to further characterise, and therefore correct for. The variation may occur on a day by day basis, where the k value would change each day but remain constant for that entire day. It may also be random, changing between each measurement, making it more difficult to constrain.

So far, all stated transitions have been specific to the isotope $^{86}$Kr. While the electron configurations remain the same, there is an appreciable difference in energy level frequency between this reference isotope and the frequencies of other isotopes. This means the precise wavelength required to resonantly excite a specific isotope is subtly different to the wavelength required for other isotopes.

For the even isotopes of krypton, the isotopic shift is small enough to be fully encompassed by the bandwidth of the laser systems used on the instrument. The lasers have a bandwidth of approximately 0.2 cm$^{-1}$ (Strashnov et al., 2010). The odd isotopes however have much more extensive ranges of hyperfine levels, all of which are greater than the bandwidth of the lasers. These are summarised in Table 5.3

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Isotopic Shift - Transition 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta v^{78,86}$</td>
<td>-0.00689 cm$^{-1}$</td>
</tr>
<tr>
<td>$\delta v^{80,86}$</td>
<td>-0.00526 cm$^{-1}$</td>
</tr>
<tr>
<td>$\delta v^{81,86}$</td>
<td>-0.00348 cm$^{-1}$</td>
</tr>
<tr>
<td>$\delta v^{82,86}$</td>
<td>-0.00434 cm$^{-1}$</td>
</tr>
<tr>
<td>$\delta v^{83,86}$</td>
<td>-0.00148 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Table 5.1- Isotopic shift values for the two resonant steps used in the RIMSKI ionisation scheme. Data are from Strashnov et al. (2010), originally Trickl et al. (1989)

Predicted Errors and Standard Deviation

The even isotopes have been shown to display almost identical behaviour to each other (as demonstrated in Figure 5.5). Therefore, to facilitate easy comparison, the isotopes $^{83}$Kr and $^{82}$Kr will be identically analysed for their predicted errors, and the standard deviation of the measurements.
Figure 5.6 - Comparison of the predicted error and the standard deviation of 81 data files measured over 11 days. The days were not always consecutive, and the instrument was not always tuned to the same settings. $^{78}$Kr is high due to interference from a hydrocarbon peak which partially overlaps the $^{78}$Kr peak at the mass resolution of the instrument. $^{83}$Kr is showing greater variation in its ratios across a series of data than the software is predicting.

A cursory glance at the data presented in Figure 5.6 shows how comparable the even isotopes are, in how closely the standard deviation of the data set is predicted by the error propagation modelling of the data reduction software. The clear outlier (excluding $^{79}$Kr), is $^{83}$Kr.

To further demonstrate the statistical difference between the $^{82}$Kr isotope, and the $^{83}$Kr isotope, histogram analyses of the 81 data files were carried out. To create the histograms, the measured ratios were converted into delta values, as a per mil deviation from the standard air value, using Equation 28.

$$
\Delta = (\frac{xK_{\text{Measured}}}{xK_{\text{Actual}}} - 1) \times 1000
$$

*Equation 28*
Figure 5.7 - Histogram of the measurement to air delta values for $^{83}\text{Kr}$, set to be directly comparable to Figure 5.8

Figure 5.8 – Histogram of the measurement to air delta values for $^{83}\text{Kr}$, set to be directly comparable to Figure 5.7
In Figure 5.7 the clearly defined mean value can be identified, and the range of values is narrow. Figure 5.8 alternatively, shows a much less well defined mean value, with two bins forming equally significant peaks. The range is also far larger than for the even isotope histogram. It can therefore be surmised that there are additional factors influencing the odd isotope behaviour, whilst the even isotope behaviour is not noticeably influenced by the daily tuning procedure, laser dye changes, and minor wavelength retuning, all of which took place at several times throughout the period of data collection for this data set.

There is a clear deviation on the $^{83}$Kr isotope, however it remains unclear as to whether this deviation arises as a day to day effect, or whether the effect is observed between individual analyses (or even between individual data sampling windows). This can be assessed by looking at the day to day variation, and comparing it to the variation across several days’ analyses.

**Day to day variation or Random variation**

To do this, the decay constants for each isotope are taken from the 83 data files used in Figure 5.6, excluding $^{81}$Kr because of its very low abundance in air, and also excluding $^{78}$Kr due to the hydrocarbon interference over that isotope. These are then normalised to $^{84}$Kr and its decay constant. The standard deviation on these decay constant ratios are then calculated for each day. In order to assess whether day to day variation is causing the discrepancy, or whether the variation occurs on a file by file basis, the average standard deviation for a series of days is compared to the standard deviation of the same ratios across all days of analysis. If the variance is caused by day to day variations in the ratio, but throughout that day the ratio were to remain approximately constant, it would be expected that the standard deviation across all data files would be higher than that of the standard deviation across individual days (then averaged to produce a fair comparison between data sets).

The alignment of the average standard deviation between days across multiple isotopes, including $^{83}$Kr (shown in Figure 5.9) indicates the standard deviation of measured values is what is predicted by the software, when looking at the measurements from a solitary day. This implies, rather than a difference in the expected range of measurements, it is a shift in the mean value that causes this increased error when the full data set is analysed.
Figure 5.9- Comparison between the day to day deviation of the ratios between the decay constant of an isotope (x) and the decay constant for $^{84}$Kr, and the deviation of those same ratios across the full set of data. A greater deviation in the combined data set, over the data split into days, indicates a day to day variation rather than file to file variation. The larger deviation observed for $^{80}$Kr across both methods is caused the relatively small quantity of $^{80}$Kr within air. The disparity between the two methods with regards to $^{83}$Kr shows that the ratio between the decay constants for $^{83}$Kr and $^{84}$Kr changes on a day to day basis, but for any one day the variation observed is equal to that of the major even massed isotopes. Errors represent the standard deviation of the day to day deviation calculations.

Figure 5.10 – Comparison of the average combined $^{83}$Kr/$^{84}$Kr ratio across several days analysis, and the average values for each individual day. It is clear that certain days show far larger variability, a cause for further investigation. The error bars represent the standard deviation of measurements made across the duration of that individual day. The upper and lower bounds (red) of the combined average line (black) represent the standard deviation across the combined data set.
Because of the variation on the average ratio (Figure 5.10) and also the significant differences in the range of values measured on particular days, it was deemed best to calculate the $^{83}$Kr correction factor for each day individually. The range of variation, both in the mean values and the standard deviation each day means that the most accurate way of representing the behaviour of this data is to look at the odd isotopes and their correction on a day to day basis, in order to ensure the integrity of the data and what it shows.

![Figure 5.11 – Analysis of the ionisation efficiency of $^{83}$Kr over a period of time shows a point of marked change in ionisation efficiency. This marked change appears to reflect the extensive retuning of the instrument. This included new laser dyes, a re-alignment of the beams, and the retuning of the dye laser wavelengths. It is therefore impossible to conclude if any one retuning process caused the difference, or whether it was a combination of all retuning procedures. Each datum represents the average $k_{83}/k_{84}$ value for a day of analyses, with error bars representing the standard deviation of those same $k$ value ratios. The vertical lines represent days of laser dye change.](image)

In principle, a difference such as that seen for $^{83}$Kr can be caused by two aspects of the instrument. Both a difference in the detection of isotopes (including both whether the ions are split out of the approaching ion packet, and the selective detection of certain isotopes over others), and a difference in ionisation efficiency can cause the behaviour observed.

With respect to the detection of the formed ions, both the method of time of flight, and the type of detectors are not capable of discriminating between odd/even isotope masses. The detectors work on ion impacts releasing cascades of electrons from their surface. The release of electrons is most closely dependent on the energy the impacting particle has. Given the acceleration of the ions is uniform, the energy each ion carries is approximately equal. Therefore, the odd/even mass of the particle impacting the surface could not lead to the
preferential detection of the even massed isotopes over the odd massed isotopes. Similarly, the
only way the $^{83}$Kr could be separated from the ion packet during the flight time towards the
detectors, is by being ionised beyond the +1 state. This is not plausible when using a resonance
ionisation scheme such as the one employed on the RIMSKI instrument.

It can therefore be assumed that the bias occurs due to an aspect of the ionisation process.
Previous work using the RIMSKI instrument identified the cause for differing ionisation
pathways, hyper-fine splitting. This work, presented by Strashnov et al. (2009), showed that the
energy levels of isotopes of krypton with odd masses allow certain additional spectroscopic
pathways to ionisation. Strashnov et al. (2010) explains that, the range of hyperfine levels
available for the odd isotopes are greater than the bandwidths of the laser pulses which form
the first two resonant transitions within the RIMSKI system. It was shown that the first transition
did not show hyperfine splitting effects whilst the second transition showed clearly
distinguishable hyperfine structure effects. In essence, the ionisation efficiency of the odd
isotopes could be modified by changes in the laser wavelength.

**Power Broadening**

An additional complication is added to this phenomenon when the variable of beam power
intensity is considered. As the power per unit area of a beam increases, the spectroscopic line
width is seen to increase. The phenomenon is referred to as power broadening; the principle
states that as the energy increases, the output wavelength becomes less well defined. This
translates through the system as an increase in the bandwidth of the laser. It is possible that the
decreased efficiency in $^{83}$Kr ionisation is attributable to the decreasing power of the 558 nm
beam, responsible for spanning the transition associated with the most prominent hyperfine
splitting. The power of this beam decreases as the dye decays, this can be caused by laser
induced breakdown of the dye, or by spontaneous breakdown of the dye during the time it is
occupying the dye circulator.

It is possible that the beam power is more significant than the beam alignment. The profile of
the 558 nm beam shows a gradient in power density across the beam. This beam profile is fairly
homogenous along a vertical axis, adding validity to the hypothesis by the fact that the vertical
alignment of the beam is shown to affect the overall signal height, but not the ratio between
$^{83}$Kr and $^{82}$Kr. The horizontal alignment affects the ratio between the two isotopes, as well as the
overall signal height. Therefore, it seems more likely that the variation in ionisation efficiency is
a function of power, rather than directly a function of alignment.
Power broadening seems the likely explanation of why the power so directly affects the ratio between the $^{82}\text{Kr}$ and $^{83}\text{Kr}$ isotopes.

**Wavelength Tuning Effects**

An experiment into how the even and odd isotope ionisation efficiency changes across a range of wavelengths was carried out. One aliquot of standard air was admitted to the spectrometer, whilst just the 116 nm and 558 nm beams were passing through the ion source (excluding the 1064 nm beam which forms the final ionisation step). This produced a smaller signal, and importantly maintained the amount of gas within the spectrometer, over the course of a 5 minute analysis, at effectively a constant value. A slow scan of the 558 nm beam was then started, moving between 558.6700 nm to 558.6845 nm at a rate of 0.0005 nm per 10 s. The data acquisition software was used to collect a 5 minute window in this scan. The 255 nm wavelength was maintained at a constant value throughout, whilst the 1507 nm wavelength was adjusted between each measurement, to collect a range of 1507 nm values, ranging from 1506.8740 nm, to 1507.2320 nm.

![Figure 5.12](image.jpg)

*Figure 5.12* - Three repeats of measurements made at 1507.0320 nm, showing the reproducibility of the experiment and the trends observed within.
It is apparent that the peak ionisation efficiency for the even massed isotopes of krypton does not overlap with the peak ionisation efficiency of the odd massed isotopes. It is also apparent that the 558 nm wavelength required for peak ionisation efficiency varies as a function of the vuv wavelength (controlled by the wavelength of the 1507.3 nm beam).

With a combination of power broadening, wavelength tuning, and the isotope shift bandwidth, it is clear why the calibration of this even-odd mass isotope ionisation efficiency effect is difficult to calibrate.

**Even Isotope Characterisation**

The even isotopes $^{80}$Kr, $^{82}$Kr, $^{84}$Kr and $^{86}$Kr do not show significant day to day variation in their ionisation efficiencies. It is therefore possible to characterise these isotopes with a greater degree of accuracy across several days of analysis. The benefit of amalgamating the series of measurements is the decrease in uncertainty. The number of measurements made over a series of days is great enough, whilst also being consistent enough, to apply a standard error to those isotopes.

---

**Figure 5.13** - Comparison of the average combined $^{82}$Kr/$^{84}$Kr ratio across several days analysis, and the average values for each individual day. The error bars represent the standard deviation of measurements made across the duration of that individual day. The upper and lower bounds (red) of the combined average line (black) represent the standard deviation across the combined data set. The scale is such that it can be directly compared with Figure 5.10.
Resulting Air Calibration Methods

The aim of this section was to produce a standardised method of calibrating the major isotopes measures by the RIMSKI instrument.

For even isotopes (excluding $^{78}$Kr), the correction factor can most accurately be calculated by averaging the measurements made over the entire duration of analysis, and thereby allowing the calculation of a standard error for these isotopes. The accuracy of the odd isotope measurements benefits from restricting the data set to a single day’s worth of analyses. This correction factor must be calculated for each day individually. The justification for this lies in the deviation of measurements during a day, compared to the deviation of measurements over a longer period. The odd isotopes maintain the same amount of deviation from an average value as the even isotopes, when examined on a day to day basis.

Correction factors are calculated as the defined literature value for the isotope, divided by the measured ratio. This gives a numerical constant, with which the measurements can be calibrated.

<table>
<thead>
<tr>
<th>Date</th>
<th>$^{80}$Kr/84Kr Average Ratio</th>
<th>Average Error</th>
<th>Standard Deviation</th>
<th>Ratio and Error Used</th>
<th>Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>22/02/2016</td>
<td>0.1563</td>
<td>0.002775</td>
<td>0.005066</td>
<td>0.1563 (±0.0051)</td>
<td>1.2886 (±0.0418)</td>
</tr>
<tr>
<td>14/03/2016</td>
<td>0.1307</td>
<td>0.002709</td>
<td>0.006708</td>
<td>0.1307 (±0.0067)</td>
<td>1.5408 (±0.0791)</td>
</tr>
<tr>
<td>16/03/2016</td>
<td>0.1229</td>
<td>0.00278</td>
<td>0.008017</td>
<td>0.1229 (±0.008)</td>
<td>1.6390 (±0.1070)</td>
</tr>
<tr>
<td>17/03/2016</td>
<td>0.1300</td>
<td>0.002138</td>
<td>0.013749</td>
<td>0.1300 (±0.0137)</td>
<td>1.5487 (±0.1638)</td>
</tr>
<tr>
<td>18/03/2016</td>
<td>0.1291</td>
<td>0.002492</td>
<td>0.010942</td>
<td>0.1291 (±0.0109)</td>
<td>1.5601 (±0.1323)</td>
</tr>
<tr>
<td>22/03/2016</td>
<td>0.1477</td>
<td>0.002957</td>
<td>0.011016</td>
<td>0.1477 (±0.011)</td>
<td>1.3631 (±0.1016)</td>
</tr>
<tr>
<td>30/03/2016</td>
<td>0.1652</td>
<td>0.001596</td>
<td>0.007922</td>
<td>0.1652 (±0.0079)</td>
<td>1.2187 (±0.0584)</td>
</tr>
<tr>
<td>06/04/2016</td>
<td>0.1448</td>
<td>0.00151</td>
<td>0.004624</td>
<td>0.1448 (±0.0046)</td>
<td>1.3907 (±0.0444)</td>
</tr>
<tr>
<td>07/04/2016</td>
<td>0.1376</td>
<td>0.00187</td>
<td>0.022095</td>
<td>0.1376 (±0.0221)</td>
<td>1.4632 (±0.2349)</td>
</tr>
<tr>
<td>15/04/2016</td>
<td>0.1501</td>
<td>0.001816</td>
<td>0.003151</td>
<td>0.1501 (±0.0032)</td>
<td>1.3417 (±0.0282)</td>
</tr>
<tr>
<td>19/04/2016</td>
<td>0.1458</td>
<td>0.001726</td>
<td>0.008221</td>
<td>0.1458 (±0.0082)</td>
<td>1.3811 (±0.0779)</td>
</tr>
<tr>
<td>All</td>
<td>0.1411</td>
<td>0.002322</td>
<td>0.015826</td>
<td>0.1411 (±0.0158)</td>
<td>1.4269 (±0.1600)</td>
</tr>
</tbody>
</table>

Table 5.2 – Correction factors for the major even isotopes. Reference isotope is $^{84}$Kr. Errors are the standard deviation on the 81 measurements combined for these calibration corrections.

Table 5.3 – Correction factors calculated for the odd isotope $^{83}$Kr
5.5.2 *Eucrite Standards Validation*

To further characterise the current function of the instrument, and to complete the validation of the modifications I implemented to the handling of data from the instrument, an assessment of the protocols used to calibrate the data for a cosmic ray exposure age calculation was required. The RIMSKI instrument has so far been predominantly used in the calculation of cosmic ray exposure ages of eucrites. The protocol and methods associated with carrying out these calculations have been discussed at length in early examples of the implementation of the instrument. The methods discussed in Strashnov *et al.* (2013) has been critiqued by peers of the planetary science community, and therefore serve as a good starting point for the analyses carried out during the course of this project.

One of the first meteorites to be measured using the RIMSKI instrument was the Stannern eucrite meteorite. This fall occurred in 1808, and the samples measured throughout this project were sourced from the Natural History Museum, London. The previous measurements made of this meteorite, and the high ratio of cosmogenic gases to trapped gases, made it an obvious choice to use as a standard for measurements. Additionally, samples of the Bereba eucrite were also analysed (These were also provided by the Natural History Museum, London).

We attempted step heating on a series of samples. The purpose was simple, with multiple krypton components bound to different adsorption sites we hoped to extract each component separately, or at least reduce the amount of trapped gas, or bromine derived gas, that was released at the same time as the cosmogenic gas fraction. If successful, it would allow cosmic ray exposure age calculations to be made more accurate, given the likelihood of contamination from other components would be reduced.

We took a series of samples of the eucrite meteorites Bereba and Stannern, and step heated them. The resulting ratios of these samples are shown in Figure 5.14. The results for both eucrites show a progressive release of the cosmogenic gases within the sample, observed as a string of releases that plot along the spallation tie-lines.
Cosmic ray Exposure Age Calculations

The equations for calculating the cosmic ray exposure age of a sample were detailed in section 2.5.3, the cosmic ray exposure age equation, Equation 11 and the production rate equation, Equation 12.

The assumptions for any krypton cosmic ray exposure age require the cosmogenic gas fraction to be distinguished from the non-cosmogenic fraction. A gas release from a sample is typically made up of a fraction of cosmogenic gases, mixed with one or more trapped components (or potentially components from radioactive decay processes). In order to calculate accurate cosmic ray exposure ages, the gas ratios used in the calculation must purely represent the cosmogenic fraction of the sample gas release.

A simple way of doing this is to assume a single trapped component mixed with the cosmogenic component. If this trapped component is assumed to be ‘Air’ then the extrication process is easy. Commonly cited literature sources often suggest $^{86}$Kr is not produced at all during spallation reactions within rocky bodies. Given the presence of $^{86}$Kr in air, it is therefore straight
forward to remove the $^{86}$Kr. If the sample gas release reference ratio is $^{86}$Kr then a subtraction of the standard air spectrum from those ratios should leave just the cosmogenic gas ratios as the result.

Figure 5.15- The three common ‘trapped’ components, with errors reflective of the measurements in literature, and the average error of measurements made using RIMSKI added to them. The shaded boxes show the total range and overlap between different reservoirs for the errors encountered whilst using measurements from the RIMSKI instrument. It is clear that the identification of a specific reservoir is implausible based on just the data.

The use of ‘Air’ as the standard trapped component is not perfect, but as can be seen in Figure 5.15 the most common trapped components do not plot far enough away from each other for measurements on the RIMSKI instrument to be attributed to another reservoir. Seeing as ‘Air’ lies between the primordial ‘Q-Kr’, and Solar Wind (SW) krypton, it was an obvious choice to mitigate the uncertainty on the resulting cosmic ray exposure calculation. Essentially, ‘Air’ is a precisely known composition, and is a rough average of Solar Wind and ‘Q-Kr’, meaning it holds the lowest average imprecision from the true composition of the trapped component.

There is an argument that ‘Q-Kr’ may be more likely to be the trapped component for certain meteorite samples, particularly those with old ages and those from chondritic parent bodies. But for the sake of ease when accounting for the blank correction within the removal of the trapped component, the values for air are used.
5.5.3 Eucrite Cosmic Ray Exposure Age Results and Method Discussion

Calculated using the conventional data reduction and cosmic ray exposure age calculation methods, the measurements show a range of ages. Some of which fit literature values more than others. The exact numbers are tabulated within Appendix 10 and Appendix 11. There are a range of possible explanations for these disparities, although it should be highlighted that the close fit of several releases to the literature values is a positive sign towards the validity of the data handling protocols. The most likely reason for the inaccurate calculated ages is the lack of $^{81}$Kr released during that step. This may be indicative of a requirement for more strenuous data vetting before CRE age calculations are carried out.

The Trapped Component

The assumption of $^{86}$Kr production via spallation reactions in rocky bodies is arguably incorrect. Findings presented by Gilabert et al. (2002) show a small quantity of $^{86}$Kr being produced in target element samples encased in a gabbro sphere, as described in section 2.1.2. If a small amount of $^{86}$Kr is due to cosmogenic spallation, then the method used to remove the trapped component will also remove a (small) fraction of the other stable cosmogenic isotopes. It will however not affect $^{81}$Kr, which is not corrected for any trapped component addition. This error would lead to a lower calculated CRE age than expected, because the $^{83}$Kr/$^{81}$Kr ratio would decrease.

Production Rate Variability

The standard cosmic ray exposure calculation requires a production rate calculation for each measurement taken. There is reason to believe that the production rate does not vary significantly enough to warrant this, and the continuous calculation of this value unnecessarily increases the uncertainty on the resulting calculation.

In order to properly assess the variability in production rates, a range of krypton ratios were extracted from literature sources, and applied to the production rate equation (Equation 12). The resulting data are presented in Figure 5.16.
Figure 5.16 - Production rates of $^{81}$Kr relative to the production rate of $^{83}$Kr, based on a collection of literature data, the $^{80}$Kr/$^{83}$Kr and $^{82}$Kr/$^{83}$Kr compositions, of a range of meteorite types. Samples with extreme errors associated with the production rate are excluded from the plot. The theoretical production rates based on lunar and chondritic spallation (at either extreme) are plotted as solid lines across the data set. There are questions regarding the lack of several chondritic meteorites not plotting along the chondritic spallation line. The number of sources for chondrite data are few, and generally older sources than other meteorite types. This limits the validity of these points, due to the lower accuracy (as is observable in the errors associate with those points). (Eugster et al., 1969; Leya et al., 2004; Strashnov et al., 2013; Eugster et al., 2002).

5.5.4 AN ALTERNATIVE COSMIC RAY EXPOSURE CALCULATION METHOD

I experimented with an alternative method to calculate a cosmic ray exposure age. The application of principles discussed throughout section 5.3, it is possible to plot each individual spectrum of a sample measurement as a calculated CRE age. If these are plotted out, then an extrapolation of the data, taking into account the weighting of the associated error with each spectrum, will provide the calculated cosmic ray exposure age of the gas composition at inlet.

By calculating a cosmic ray exposure age value for each individual spectrum for a measurement, and then plotting these as against the time each spectrum samples, it allows a series of 15 cosmic ray exposure ages to be calculated per sample measurement. These are not true cosmic ray exposure ages, but their calculation allows a line to be fitted through the resulting data points. This line is a more complicated form of the method used to plot the air measurement.
ratios and extrapolate to the starting gas composition. The reason the calculated CRE ages are not true ages lies entangled with the way the ratio between even and odd isotopes changes over time.

Taking the cosmic ray exposure equation (Equation 11), there are essentially two separate components. The calculated production rate of $^{81}\text{Kr}$ relative to the production rate of $^{83}\text{Kr}$, via the averaging of the $^{80}\text{Kr}/^{83}\text{Kr}$ and $^{82}\text{Kr}/^{83}\text{Kr}$ ratios; this is expected to change over the duration of the measurement. The change is caused by the difference in the rate of extraction from the system, between the even massed and odd massed isotopes.

The principle behind this plot is simple, if there is a rate of change across any of the variables within the data entered into the equation, it will present as a gradient between the calculated ages. This enables the extrapolation to the inlet time.

$$T_{81}(My) = \tau_{81} \left( \frac{P_{81}}{P_{83}} \right)^{83\text{Kr}}_{81\text{Kr}}$$

Equation 11 (Repeated)

Once each of the 15 points is calculated, a line of best fit can be calculated, weighted according to the error associated with each data point. In theory, this allows extrapolation back to the effective CRE age at t=0.

An Example of the Method

Using the Stannern data for the 3.19 mg fragment, for which four pyrolysis steps were carried out, I calculated CRE ages for each individual spectrum. The resulting values were plotted against the laser pulse number (the value for which the software keeps track of its progression through a complete analysis). I then applied the least squares fitting software to the values for each measurement individually. This process is illustrated in Figure 5.17.

It was assumed that the change in ratio for the major isotopes over the period of two spectra being collected would be minor, and within the tolerance allowed to CRE age calculations (~10% uncertainty). The two spectra period accounts for one on the 0.05 V full scale, required for $^{81}\text{Kr}$ data collection, and one on the larger full scale voltage. Therefore, it was unnecessary to extrapolate the data between these points. The validity of this is discussed further in the discussion section of this experiment.
Figure 5.17 – An illustration of the process by which the calculation of a CRE age at \( t=0 \) is carried out using the method of calculating a CRE age for each individual spectrum and regressing the fit between those points back to \( t=0 \). This example uses data from analysis 1119, and results in a CRE age at \( t=0 \) of 38.89 ± 12.42 My.

The cosmic ray exposure age calculated for Stannern prior to any of the modifications within this thesis was 38.9 ± 2.8 My, placing it in the middle of literature ages also reported in Strashnov et al. (2012), 36.4 ± 2.1 My (originally from Freundel et al., 1986) and 41.0 ± 1.3 My (originally from Hudson, 1981). Similarly, Bereba was calculated as having a CRE age of 25.0 ± 2.1 My by Strashnov et al. (2012), alongside a literature range of 24.9 ± 2.3 (originally from Hudson, 1981) and 27.2 ± 2.3 My (originally from Shukolyukov and Begemann, 1996).

<table>
<thead>
<tr>
<th>Laser Power (W)</th>
<th>Stannern 3.19 mg</th>
<th>Bereba 8.28 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>29.64</td>
<td>14.83</td>
</tr>
<tr>
<td>2.5</td>
<td>35.26</td>
<td>46.62</td>
</tr>
<tr>
<td>5</td>
<td>38.90</td>
<td>23.69</td>
</tr>
<tr>
<td>9</td>
<td>43.23</td>
<td>26.32</td>
</tr>
<tr>
<td>Age at ( t=0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error on Age</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.07</td>
<td>3.64</td>
<td>2.20</td>
</tr>
<tr>
<td>12.42</td>
<td>10.09</td>
<td>7.18</td>
</tr>
<tr>
<td>14.83</td>
<td>2.20</td>
<td>4.26</td>
</tr>
<tr>
<td>46.62</td>
<td>7.18</td>
<td>4.94</td>
</tr>
<tr>
<td>23.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4 – Calculated CRE ages for the Stannern and Bereba Eucrites. Showing the degree of precision with which the newly developed method of calculating the CRE ages of individual spectra can be applied.

Comparison between the data presented in Strashnov et al. (2012) and the data within Table 5.4 shows good agreement between Stannern measurements, whereas Bereba measurements are more varied, with two measurements lying outside of the error limits of the literature data. The poor fit of these measurements are likely due to the small amount of cosmogenic gas released for these steps (1.5 W and 2.5 W). The disparity between the two eucrites and when they release their cosmogenic gases is likely an artefact of having a larger sample mass, and therefore a more diffuse energy per unit mass of the meteorite from the CW heating laser.
Discussion
Examination of the full set of data calculated for this experiment, found in Appendix 6, shows clear evidence for this method holding validity in the calculation of cosmic ray exposure ages. The ages calculated by this method appear to more accurately match the ages of these meteorites within literature. A significant advantage of this method lies within its ability to account for unexpected fluctuations in the $^{81}$Kr measurements.

The data reduction software works on the basis of a predictable change in the measured ratio with each subsequent spectrum. Therefore, the method is reliant on $^{81}$Kr following a predictable trend. Due to the low abundance of $^{81}$Kr, the peak area values tend to fluctuate much more than with the more abundant isotopes. This is manifestation of pulse-by-pulse variation, where a small number of atoms being detected means that a jitter on that number is more noticeable than for a more abundant isotope. This method, allows the validity of each spectrum to be individually assessed and its calculated CRE age to be weighted accordingly. The differences in perceived errors from the software, and the uncertainty that each spectrum would introduce into the CRE age calculation are illustrated in Figures 5.18 (a & b).

Figures 5.18 (a & b) show the different ways to assess the error of each spectrum data point. The software treats each point within (a) as relatively equal in importance, however (b) suggests that many of the later spectra should be represented with higher uncertainty. (b) is more representative of what I opted to believe was representative of the system, due to the expectation that the subsequently smaller amount of gas remaining in the system after each sequential spectrum should show increasing jitter on the pulse-by-pulse number of detections from each of the 100 summed spectra making up each summed spectrum shown in the figure.

This is not to say that the method is without need of further development. There are a number of reasons the method should be investigated further, in order to confirm the validity of its use.
Figures 5.18 (a & b) – Graphs comparing the measured counts of $^{81}$Kr against spectrum number (a), and the $^{81}$Kr/$^{83}$Kr ratio against spectrum number (b). Demonstrating the difference in perceived error of one method against the other.

The validity of each calculated cosmic ray exposure age is dependent on the input data being accurately representative of the values at one specific point in time. While the time offset between the measurement of $^{81}$Kr and the major isotopes is small, it should be possible to improve the validity of the calculations by modelling one set of data through time, and interpolating the isotopic composition during the measurement of the other data set (The two data sets being the different scaled collections for a given measurement).

The relatively small quantity of $^{81}$Kr would make modelling that particular isotope difficult, and introduce large errors into the calculations. It is easier to take the more abundant isotopes and interpolate those to the same time as the $^{81}$Kr is measured at. Therefore, it would be worth developing a method with which the value of the peak areas for the major isotopes could be
accurately modelled and interpolated, to then be used in conjunction with the measured values for the $^{81}$Kr peak in order to calculate a CRE age for a given spectrum.

$^{81}$Kr and $^{83}$Kr Ionisation Efficiencies
An unforeseen addition to the use of this method is its inherent ability to assess the ionisation efficiency of $^{81}$Kr relative to $^{83}$Kr. By disentangling the calculation of the $^{81}$Kr/$^{83}$Kr ratio from the data reduction software there is the ability to plot the rate of change between these two isotopes. This allows for the validation of the assumption behind the application of the $^{83}$Kr correction factor to the $^{81}$Kr values.

![Graph](image1)

Figure 5.19 – $^{81}$Kr/$^{84}$Kr against $^{83}$Kr/$^{84}$Kr for two pyrolysis steps (1118, and 1119) of a fragment of Stannern. Showing the uncertainty of whether $^{81}$Kr and $^{83}$Kr have a common ionisation efficiency.
**Error Propagation Methods**

It was suggested that the propagation of the errors involved in this method was not as accurate as is possible. The changes would correct for the errors that lead to a potential negative age range, such as those of the last three spectra in Figures 5.18. The calculation of these errors is complex, and unfortunately I did not have the time required to fully validate the error propagation required for this method. The principle behind them is discussed below.

The errors up until this point have followed a Gaussian distribution, where the mean and standard deviation conform to a normal distribution. This means that the standard deviation acts as a good measure for the overall uncertainty on a measurement. The process of taking the reciprocal of $^{81}\text{Kr}/^{83}\text{Kr}$ causes the distribution of error to change, away from a Gaussian distribution. This renders the standard deviation inaccurate as a measure of uncertainty.

If the $^{81}\text{Kr}/^{83}\text{Kr}$ ratio is plotted $x_1, x_2, x_3 \ldots x_{10}$, then the probability distribution takes the form:

![Probability distribution graph](image)

**Figure 5.20 – An illustration of the ratio distribution of measurements. The form is a normal distribution.**

The cosmic ray exposure equation requires a ratio of $^{83}\text{Kr}$ to $^{81}\text{Kr}$. That is, a large value with small errors, over a much smaller value with comparatively large uncertainty. The best method of data reduction produces a value of $^{81}\text{Kr}/^{83}\text{Kr}$, in order to maintain lower uncertainty. This leads to the requirement of taking the reciprocal of the ratio in order to apply it to the cosmic ray exposure equation. By taking the reciprocal of the ratio, the uncertainty also undergoes change. This change means the average value becomes offset from the centre of the standard deviation of the points, creating a skewed distribution.

It was suggested that the method I have developed would avoid the problems created by this error skew if the data was plotted without the reciprocal of the $^{81}\text{Kr}/^{83}\text{Kr}$ value being taken with each calculation, and instead applying that as a final step to calculate the CRE age from the
resulting intercept. Therefore, maintaining the error propagation validity, and constraining the regression model with greater validity.

5.6 CONCLUSIONS
It can be concluded that the data handling developments produce reliable and valid results. Although there are also indications of further validation being required for cosmic ray exposure age calculation, particularly relating to the viability of lower temperature pyrolysis steps being used in the calculations. It may be worth assessing a ‘combined measurement’, where the data from all pyrolysis steps is combined to effectively produce one data set. Investigation into this method would aid in eliminating the cause of age discrepancies being related to the step pyrolysis procedure.
6. **ANALYSIS OF CALCIUM ALUMINIUM-RICH INCLUSIONS FROM THE KRYPTON NOBLE GAS PERSPECTIVE**

Calcium Aluminium-rich Inclusions (CAIs) are a fantastically diverse range of inclusions, and their cosmochemical systems can provide us with a wealth of information about the early solar system.

The size of these inclusions makes it difficult to measure noble gas systems from just one inclusion. However, the RIMSKI instrument is more than capable of measuring samples of just one CAI, at optimum performance, measurement of individual mineral separates from an individual CAI would be possible. Given the improvements to instrument sensitivity, and the revised protocols, it seems an opportune time to investigate these samples, providing evidence towards whether or not this technique is possible to apply to CAIs, and hopefully gaining some of the first measurements of krypton systems within individual CAIs.

6.1 **PREVIOUS WORK**

CAIs have been widely studied. Perhaps unsurprisingly, their cosmochemical systems have been shown to vary as much as their morphological textures. This has led to a wide range of theories to explain each phenomenon. To cover all the facets of work carried out looking at CAIs would be a monumental task on its own, instead, this section summarises the most important findings that relate to the work carried out measuring the krypton systems of CAIs in this study.

6.1.1 **CHRONOLOGY**

There is growing evidence towards the CAI formation period being offset from the chondrule formation period. This being progressively corroborated by different isotopic systems, notable so far are the Pb-Pb system (e.g. Amelin et al., 2002), and the Al-Mg system (e.g. Kita et al., 2013). That is not to say the field is devoid of contention against this, observations of canonical Al-Mg ratios within CAIs have led some to suggest supra-canonical values are the result of post formation alteration, and mobilisation of Mg isotopes preferentially into particular minerals (Jacobsen et al., 2008).
6.1.2 **Noble Gas Measurements**

There is a relatively small, but growing, and significant body of evidence that indicate a fraction of the surviving earliest solar system solids, such as CAIs, underwent irradiation prior to their incorporation into the general Chondritic parent body material (Vogel et al., 2004).

It stands to reason, that if early solar system solids have been found to contain cosmogenic neon 21, and argon 36, in excess of the amount accounted for by bulk meteorite exposure after accretion to the parent body, that a cosmogenic krypton spectrum will also be observed in these samples. Krypton, as a system, is far less susceptible to disturbance (such as thermal diffusion) than either argon or neon- suggesting the presence of a krypton excess is likely, if the excess in both the neon and argon systems are due to spallation reactions from a pre-exposure period of the CAIs.

6.1.3 **Application of the RIMSKI Instrument to Similar Samples**

The RIMSKI instrument is, in theory, capable of measuring the cosmic ray exposure (CRE) age of individual Calcium, Aluminium-rich Inclusions (CAIs). Measurement of similarly sized inclusions has been carried out before by Strashnov and Gilmour (2013), wherein the instrument is used to measure chondrule samples.

6.2 **Premise of the Study**

This predates the formation of the chondrule populations by up to 2 Ma. These two types of inclusions require very different formation environments. The rim sequences observed around CAIs indicate they formed in a calm environment, and crucially have not been exposed to violent collisions before being incorporated into the chondrite parent body. Chondrules on the other hand, are widely thought to form in a more violent environment. Given the CAIs do not show evidence of exposure to this violent environment, and are also accepted to predate the onset of chondrule formation by up to 2 Ma, a dichotomy is apparent. How do two types of inclusions, with opposing formation environments, end up being incorporated into the same parent body?

Several theories have been proposed as an explanation for this dichotomy. The CAIs may have been temporarily ejected from the turbulent proto-planetary disk via bi-polar outflows from the proto-sun. These outflows would remove the CAIs from the turbulent flow of gas into the inner disk, and protected them from impacts and shockwaves during the chondrule formation period.
The slow return to the outer edge (and subsequent fall back towards the inner solar system) would have to remove the CAI population from the region of chondrule formation and then replaced them shortly before the onset of chondrite parent body formation. Another suggested explanation is that of extra-solar delivery. It is accepted that a nearby supernova is required to explain the enrichment of short-lived radionuclides within the Solar System. It is plausible that these CAIs were a part of the material transmitted to the Solar System during this seeding event. Allowing the chondrules to form within our Solar System, followed by the delivery of the radionuclides, and CAIs, prior to the formation of the chondrite parent bodies.

The uncertainty surrounding the history of these important inclusions is a clear indication of the necessity for further studies into the processes that have led to their formation and incorporation into the chondrite parent bodies.

An investigation into the radiation history of these inclusions may help our understanding of CAIs. The two proposed theories of their origins would leave very different impressions on the radiation histories of the inclusions. It stands to reason that contemporaneous formation would leave near identical cosmogenic gas amounts within the two types of inclusions, whilst formation at different times would likely show a disparity between the CRE ages of the inclusions. Additionally, proximity and formation closer to a supernova event would likely lead to the CAIs receiving a short burst of much higher cosmic ray flux- which would be observed as a much older CRE age. As previously discussed, the calculated CRE age is a function of the radiation fluence over the time the inclusion is exposed for. This is extrapolated to an exposure age via the assumption of a constant radiation flux. If the flux were to change (specifically, if there was a period of higher radiation flux) then the cosmogenic nuclide production rate would increase; assuming the flux then dropped to present day levels, the radionuclide concentration would stabilise at a lower level (this plateau level is then used to calculate the CRE age for the sample).

Measurement of the radiation history of individual CAI inclusions is a complex task. These are small samples, with low concentrations of krypton spallation target elements. Combining this with the expected amounts of trapped krypton, the measurement of these samples will require greater levels of consideration than standard analyses using the RIMSKI instrument.

This study is the first attempt made to measure the cosmic ray exposure ages of individual CAIs, using the \(^{81}\)Kr-Kr chronometer. It is in part a proof of concept stage study, although the overall aim will be to maximise the scientific output of the research.
Two mechanisms dominate the theories behind CAI formation. One relies on native solar system development, whilst the other requires a source of extra-solar objects to be delivered to our solar system, where they were then fractionated by the early solar system heat sources to result in an inclusion enriched in high vaporisation temperature minerals. Both theories cannot fully explain the evidence observed in the CAI populations.

6.2.1 Factors to Consider
A number of considerations must be taken into account if a comparison between CAIs and Chondrules is to be made. These two components are of a suspected different age to each other, and are also mixed within a matrix component. Each of these components can in turn display a complex exposure history.

Spallation Target Element Systematics
Based on data from Martin and Mason (1974), Mason and Martin (1974) CAIs and similar components display a range of abundances in terms of the krypton spallation target elements. They outline two groups solely defined as Ca-Al-rich aggregates, one with fractionation within the REEs, and another without the fractionation trend; these are termed group II and group III within the text. In order to better assess necessary sample mass, a comparison was carried out between the chemistry data from the aforementioned papers, and the bulk chemistry for eucrite standards- based upon data reported in Kitts and Lodders (1998).

From this data, it is possible to surmise, the unfractionated group of CAIs is more likely to yield sufficient spallation krypton to form a cosmic ray exposure age. The difference in summed target element chemistry is a cause for concern however; the difference in target element abundances between the CAIs termed group II and those termed group III is significant and possibly great enough to present a problem in sample mass selection. If too the amount of released krypton is too great, the ionised gas will saturate the detectors and render the analysis useless. Equally, if the release of cosmogenic krypton is too small, then the number of $^{81}$Kr counts is likely to be lost within the baseline noise, and errors in the CRE age calculation would rise- ultimately reducing the accuracy of the final age reported.

It is not practical to measure the REE abundances of the sample set in the remit of this project, therefore an alternative was devised. Wherever possible, the sampled CAI will be divided into two fragments, one of larger mass than the other.
6.3 Samples
A sample set, selected by J. T. Wasson and A. E. Rubin (UCLA), was obtained for this collaborative work. The samples provided were produced from a pebble sized fragment of the Allende meteorite, with a fraction of the fusion crust present along one face of the fragment. This was subsequently embedded into epoxy resin and sliced into 2-4 mm slices. Not all slices were presented as the sample set.

Allende is classified as a CV3 chondrite. It is an example of the oxidised subgroup of these meteorites. This introduces the distinct possibility for alteration processes to have affected these samples. However, the mass of the meteorite available, and the average size of CAIs within the CV3 group, makes the Allende sample a suitable candidate for proving the experimental concept of this study.

<table>
<thead>
<tr>
<th>Origin Slide</th>
<th>Details</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a + 2b</td>
<td>Dense-looking white fine grained inclusion.</td>
<td>2x3mm</td>
</tr>
<tr>
<td>3a + 3b</td>
<td>Visible on both sides of slab, irregular fine-grained inclusion.</td>
<td>5x2.5mm</td>
</tr>
<tr>
<td>6a + 6b</td>
<td>Visible on back, fine grained inclusion near fusion crust.</td>
<td>3.3x1.5mm</td>
</tr>
<tr>
<td>6a + 6b</td>
<td>Visible on both sides of slab, irregular fine-grained inclusion.</td>
<td>2x1.3mm</td>
</tr>
<tr>
<td>7a +7b</td>
<td>Visible on both sides of slab, rounded fine grained inclusion with projections at surface.</td>
<td>1.6x2mm</td>
</tr>
<tr>
<td>8a + 8b</td>
<td>Fine grained inclusion- white centre with dark margin.</td>
<td>3x1.5mm</td>
</tr>
<tr>
<td>9a +9b</td>
<td>Bi-mineralic (light+dark) fine grained inclusion, front face.</td>
<td>2.8x1.1mm</td>
</tr>
<tr>
<td>9a +9b</td>
<td>Visible on back, elongate fine grained inclusion.</td>
<td>5x1.5mm</td>
</tr>
<tr>
<td>10a +10b</td>
<td>Fine grained polymineralic inclusion, just about visible on both sides of the slide.</td>
<td>6x2mm</td>
</tr>
<tr>
<td>12a + 12b</td>
<td>Amoeboid Olivine Inclusion</td>
<td>2x0.75mm</td>
</tr>
</tbody>
</table>

Table 6.1 - Samples provided by J. T. Wasson and A. E. Rubin, UCLA

The samples were analysed using a combination of optical microscopy, SEM techniques, and Ion Microprobe techniques. Outcomes of this characterisation procedure were often limited by the necessity to preserve sample mass (limiting the ability to polish the samples).
6.3.1 **CV Meteorites**

It is common to find compositions of 45%(vol.) chondrules, 40%(vol.) matrix, and 10%(vol.) refractory inclusions abundances within the CV meteorites (Brearley and Jones, 1998). Guimon et al. (1995) identified a series of CV3.0 chondrites, representing the least equilibrated members of the CV group, and due to their lack of equilibration and alteration may represent the ideal samples with which to expand this study.

6.3.2 **Allende**

The Allende meteorite is an oxidised CV chondrite, and is described in Brearley and Jones (1998) as having a lower matrix/chondrule ratio (0.7 as opposed to 1.2) and a higher abundance of chondrules containing opaque minerals. The meteorite is classified as CV3.2, in accordance with the level of metamorphism it has experienced (Krot et al., 1995).

6.3.3 **Sample Selection**

Some of the provided samples were not viable for measurement in the RIMSKI spectrometer. Therefore, a subsection of the provided samples were selected for analysis. Initial analyses focussed on the larger examples of CAIs, in order to provide as much mass as possible for analysis, with minimal interference from the residual matrix veins.

A tiered characterisation system was devised - with several levels of classification applied to samples. The simplest level utilised optical microscopy, alongside notes provided with the samples, to identify the target inclusions within each slide. Second tier characterisation involved the application of either SEM EDS element mapping, or Microprobe element mapping, in order to identify sites of high calcium and aluminium, as well as identifying magnesium and iron contents within the samples as well. This allowed cross correlation between objects that optically looked like potential CAIs, and locations that revealed high elemental concentrations of the two primary elements enriched in CAIs, calcium and aluminium. A final level of classification was carried out on a smaller subset of samples, to try ascertain the exact petrologic type of CAI being analysed. This was not applied to all samples for practical reasons - the time required and potential for disruption of the krypton system. Risks involved the release of gases from the interaction volume of the beam impact site, a process that is known to affect some noble gas groups. The higher energy intensity beam causes higher heating to take place within the interaction volume. Further disruptions to the classification attempts include the inability to finely polish the samples - due primarily to the friability of the sample, and the desire to retain as much mass as possible of the sample. The retention of mass was seen as a paramount concern.
and resulted in only a low level polish of the sample slide surface. The samples observed under reflected light microscopy occasionally displayed high levels of topography, a feature that was hypothesised as being caused by the original polishing efforts, but may have also been a result of pore spaces within the CAI structures.

Characterising the CAIs proved a difficulty in itself. Comprehensive analysis of the morphology and features that would normally allow the classification of the CAIs into their most comprehensive types would require significant polishing of the samples. This proved problematic for two reasons; the process of polishing the samples necessarily requires material loss during the process, and whilst this could be mitigated as much as possible, a small amount of loss is always going to happen. Equally, the loss of materials is against the interests of the focus of this project, the accurate analysis of the krypton system within these individual CAIs. The second reason for foregoing polishing the specimens involved the pitted nature of many of the CAIs provided. Very few samples showed a relatively flat surface when examined with a reflected light microscope. Therefore, the polishing of the samples until the entire surface of the CAI was flat would have been near impossible without significant material loss. It was hypothesised that the pitting of the CAIs may have been caused by the polishing procedure used to form the thick sections, indicating that any attempt at polishing the sections may have been fruitless and ultimately a detriment to the focus of the project.

Due to these factors, samples were analysed using reflected light microscopy, as well as backscatter electron images on an ESEM, which when combined with element maps from the ESEM, allowed for identification of CAI phases relative to the matrix. These element maps also proved useful for interpretation of the morphologies of the CAIs, thus allowing a rudimentary conclusion about the likely morphological type of each CAI.

6.3.4 Sample Extraction

Samples were cut out of the thick sections using sharpened dental tools. Tools were sharpened using a diamond file. All tools were cleaned thoroughly before use using a 3% aqueous solution of Decon 90, deionised water, and acetone.

Samples were identified and a 1 mm perimeter around each grain was etched into the slide using the dental tools. The residual matrix surrounding the sample was scraped off using the dental tools, and dust was occasionally removed by washing the surface with isopropanol. This process was repeated until a fragment of the sample broke free of the slide, or the sample was
completely removed. Individual fragments of samples were preferred, but the friability of the CAIs meant this was difficult to achieve.

The method was imperfect at removing the matrix contamination, but seemed the best method for concentrating the amount of CAI within a sample aliquot, relative to the amount of matrix within that aliquot. An assumption was made, that minor matrix veins, and the remnant amounts of matrix that could not easily be removed would not significantly affect the measurements.

In order to measure the krypton contents of individual CAIs using the RIMSKI instrument, it is necessary to first extract the target sample from the bulk meteorite. In this situation, the provided samples were in the form of thick sections, embedded in epoxy resin disks, collectively mounted onto glass slides. CAIs were either visible on one side of the section, or pervasive throughout the section.

Sample extraction was approached from the perspective of retaining as much CAI material as possible, whilst minimising potential for disruption to the krypton system. Disruption can occur if samples are heated, or if particular phases are lost from the sample during processing. The elimination of matrix material from the sample was the ideal goal, however complete removal was unnecessary- the minimisation of the matrix component to the sample should in theory allow a difference in cosmic ray exposure age to be ascertained. It is the case with many CAI samples presented, that matrix material had infilled veins and other pore-space type voids within the CAIs, making total elimination of the matrix material from the sample impossibly difficult with the tools available.

A variety of methods were considered, based on a comprehensive interrogation of sample preparation literature, as well as suggestions from academic members of the School of Earth, Atmospheric, and Environmental Sciences.

Methods considered, within the scope of this project, included: Laser cutting, freeze-thaw separation, drill extraction, and manual cutting. Each method proved to have benefits and drawbacks.

**Laser Cutting**

The principle of this technique would be to use a CAD program to trace the outline of the CAI and then use a laser cutter to cut the sample loose of the section. This would be best practically applicable to the samples that were pervasive throughout the slide.
There are significant drawbacks to the laser cutting method. Samples are very rarely uniform in shape through the section, whilst the laser software is imperfect at adjusting for this, and thus less capable at providing a degree of control to eliminate matrix from a changing volume around a target sample. The thermal aureole created around the laser cutting site can cause unintentional loss of gases via sample heating. To further complicate the loss mechanism, the temperature gradient of the thermal aureole could cause mineral phases to preferentially degas, or even lead to loss of particular fractions of the krypton gas. The lack of literature surrounding this aspect and an inability to accurately predict how the sample would react made this method a less suitable option.

**Freeze-Thaw Extraction**

This is a method well documented by Tizard *et al.* (2005). The method involves the repeated freezing and thawing of a fragment of the bulk meteorite. Progressively the sample is broken down. This has proven successful towards the extraction of chondrule inclusions. Although CAI extraction is mentioned in some literature sources, the details about how intact the CAIs were after separation is scarce (Matsuda *et al.*, 1999). Investigation of the samples provided showed many of them to be fine grained and highly friable material, and as such, freeze-thaw extraction was deemed likely to result in disintegration of the samples. Although this would not directly affect the krypton system, it opens up the potential for loss of mineral phases, as well as giving a larger overall surface area for terrestrial air to adsorb onto. The resulting larger surface area and gas adsorbed onto it can make the cosmogenic fraction of gas difficult to disentangle from other component fractions.

A freeze thaw method was considered following the successful use of such a method in analyses discussed in Matsuda *et al.* (1999). The literature is not clear on whether the CAI fragments were retained intact or whether they disintegrated throughout the process (Matsuda *et al.*, 1999). It seems likely that, due to the friability of the CAI material, the grain would not be retained as one fragment. As a result of this uncertainty, mechanical extraction was favoured over freeze-thaw methods.

**Mechanical Separation (Drilling)**

The idea of this method would be to drill around the sample using a mechanised dental drill. This method has been attempted several times before, on different samples. The issue found with many of these attempts was the shear stress applied by the rotational torque of the drill caused friable samples to disintegrate—often with significant material loss due to the drill throwing liberated fragments clear of the drill site. It would be plausible to use this method for powdered samples, but the degree of control over the release of material was considered
inappropriate for the extraction of CAI samples. The issue with powdered samples has been covered in a previous method.

**Manual Separation**

The most simple of the methods, and ultimately the method that was deemed most suitable for successful extraction of fragments of CAIs from a solid thick section. The method maximises control over the manipulation of the material, thus allowing a maximum amount of matrix material to be removed, without disrupting the CAI structure.

The method involved the use of sharpened dental tools, cutting around the greatest extent of the CAI surface, allowing an average of a 1 mm margin around the grain throughout the initial extraction. The incision was made using dental tools, rendered free of hydrocarbon contamination via a series of three standard Decon-90, de-ionised water, and acetone cleaning cycles. The initial incision was made perpendicular to the surface of the slide all the way through the slide; freeing a section, containing the CAI, from the main slide. This fragment also retained significant portions of matrix material, due to the 1 mm border around the CAI. This boundary was then scraped away using the same dental implements to leave a predominantly CAI grain.

### 6.4 RESULTS AND ADDITIONAL DATA TREATMENT

The CAIs were found to be very gas rich, releasing large amounts of trapped gas, as well as Br-Kr, and a heavy Kr component. The summary data in Figure 6.1 show indications of cosmogenic gas releases as well. However, those points, and the points representing the heavy krypton measurements, plot close to the mass fractionation line. The potential for instrumental signal dependent mass fractionation to affect the data validity is high, given the large quantities of gas released from the CAI samples. The data were therefore investigated for signs of signal dependent mass fractionation.
6.4.1 **Signal Dependent Instrumental Mass Discrimination**

The ratio data for the air calibration measurements were plotted against the calculated initial peak height ($N_0$), with a distinction being made between those measurements representing a quarter aliquot of gas, and those representing a whole aliquot. An illustration of the resulting plot for $^{86}\text{Kr}/^{84}\text{Kr}$ is provided by Figure 6.2, with a literature terrestrial air value marked as a dashed line. For illustration purposes the data for the CAIs are also plotted.

*Figure 6.1 – A $^{83}\text{Kr}/^{86}\text{Kr}$ summary of the measurements of CAIs. Showing data corrected for instrument bias, but not corrected for signal dependent mass discrimination.*
Looking at Figure 6.2 it becomes apparent that there is likely a mass discrimination effect. This is where the instrument detects fractionally smaller amounts of an isotope the greater the signal is. It is primarily a result of the recovery time of the MCP channels. The greater the number of ions impacting the MCPs, the more likely any given ion will be to impact a channel that has already released an electron cascade. Over sufficiently long times, this is not a problem because the MCP recovers the charge. However, the recharging of the MCPs is not instantaneous, therefore, if sufficient numbers of ions are impacting the channels the chance of an ion impacting an ‘inactive’ channel increases. A charged MCP may essentially be modelled as a grid of ‘active’ sites. As ions from a given spectrum impact those sites, they become ‘inactive’ for the remainder of that spectrum (this is a simplification, the site may still be ‘active’ after one ion impact but gives off a reduced amount of charge, but the true effect is similar). For most measurements, the number of channels that become ‘inactive’ is small compared to the number of remaining ‘active’ channels. However, as the number of ions impacting the MCP increases, there will eventually be a noticeable number of ions impacting ‘inactive’ sites. This manifests itself as a perceived decrease in the detection rate of heavier isotopes.

It is also clear in Figure 6.2 that the effect is fairly predictable. Therefore, it should be possible to correct for these mass fractionation effects. Selecting solely at the air calibration measurements, allows the production of a sample set for which the precise ratios of the
Krypton within the measured gas are known. Comparing the delta values of measurements, there is a clear difference in the quarter air aliquot measurements relative to the whole air aliquot measurements. This is shown in Figure 6.3. It is clear that there is mass discrimination within the whole aliquot measurements, whilst the quarter aliquot measurements plot acceptably close to zero as to be correctable without considering mass discrimination.

Figure 6.3 – A delta plot of $^{86}$Kr/$^{84}$Kr relative to the number of detections of $^{84}$Kr for that measurement.

Looking just at the whole aliquot measurements, if a line is fit through the data, we can calculate the gradient for that isotope, alongside the number of detections at which mass discrimination effects begin to occur. Combining these allows the calculation of a per-mill per-AMU mass discrimination factor. Using this, it will then be possible to correct for mass discrimination across those sample measurements with $^{84}$Kr detection numbers that are above the intercepts for Figure 6.3.
The best fit through the gradients gives a mass discrimination factor of -0.000274 ‰/AMU (±7.44 × 10⁻⁶). Using the $^{86}$Kr data, an intercept of ~170,000 counts (±15,000 counts) is calculated. Therefore, it can be concluded that there is a discrimination effect of -0.000274 ‰/AMU (±7.44 × 10⁻⁶), at $^{84}$Kr $N_0$ values of >170,000 counts (±15,000 counts).

**Signal Dependent Mass Discrimination**

Instrumental mass discrimination is observed as a function of the number of ions being detected. Figure 6.5 shows the delta values of the measurements relative to air for both whole aliquot measurements (~1×10⁶ atoms) and ¼ aliquot measurements (2.5×10⁵ atoms); deltas calculated from an averaged 86 measurements for ¼ aliquots and 51 measurements for whole aliquots. We see an apparent enrichment of the lighter isotopes, and a depletion of the heavier isotopes. In Figure 6.7 the delta deviations from air values are compared to the initial signal height. The signal height is a good proxy for the ionisation efficiency of the instrument, something that changes on a daily basis due to minor variations in the instrument tuning. The linear trend observed in the whole aliquot measurements indicates that the discrimination is a direct result of the increasing number of ions.

There are many features of this instrument that, if improperly tuned, could result in a mass discrimination effect being observed across measurements. We can rule out most of these discrimination effects due to the statistics of the quarter air aliquot measurements. Because the deviation is only observed at the higher gas amounts, it seems likely that the mass
discrimination is related in part to the amount of gas within the spectrometer or the number of ions formed.

The phenomenon can be explained by looking at the detection method. Ions that are detected have their relative charge amplified by a pair of microchannel plates (MCPs), glass honeycomb structures with cylindrical channels running through the short dimension of the plate. When an ion impacts the plates, a cascade of electrons are released down the channels. This enables numbers of ions that would be too small for a Faraday cup detector to be measured. The MCP surfaces are charged up, a process that takes a short but not infinitely short space of time. This means that if the number of ions impacting one particular channel is greater than the MCP charge replenishment rate, each subsequent impact will release fewer electrons in the cascade. The result of this is a decrease in the apparent signal produced by sequentially higher masses.

If the ion numbers are causing the mass discrimination then we are presented with a dichotomy; given the relative apparent enrichment of the lighter isotopes, we can form two possible explanations for the mass discrimination:

1) A sustained decrease in charge present on the plates throughout the duration of the arrival of krypton ions. Under this premise, the charge maintained on the MCP active surface is continuously being depleted.

2) Arrival of the most abundant isotope ($^{84}$Kr) leads to a sudden marked depletion of charge, observed as a marked deficit in the apparent $^{86}$Kr signal. Combining this with a slight amount of saturation on $^{84}$Kr, it is possible to explain the relative apparent enrichment of lighter isotopes.

Both of these hypotheses are viable to explain the evidence. First, it is worth noting that $^{83}$Kr should be discounted when looking at the figure; the ionisation efficiency of $^{83}$Kr is significantly affected by hyperfine splitting effects, and therefore is not directly comparable to the even isotopes which are not affected by hyperfine splitting. Taking just the average delta values for whole aliquot measurements presented in Figure 6.7, there is an apparent near linear trend between masses $^{82}$Kr and $^{86}$Kr. It remains unclear as to whether $^{83}$Kr should follow this linear trend, or whether the degree to which mass discrimination affected it would be similar to $^{82}$Kr. The similarity between the $^{80}$Kr apparent enrichment and the $^{83}$Kr apparent enrichment would suggest that the isotopes lighter than $^{84}$Kr are all apparently enriched by the same factor.
Figure 6.5- A delta plot for the average ratios of whole air aliquot measurements. 51 measurements were used in the averages and are relative to standard terrestrial air as presented by Basford et al. (1973). $^{79}$Kr is unresolvable from benzene contamination within the spectrometer, and so is removed from this plot. The lesser apparent enrichment of $^{80}$Kr is not a result of suppression by the peak at mass 78 as it is not observed within the $^{80}$Kr measurements of ¼ aliquot samples. $^{83}$Kr is heavily reliant on instrument tuning factors, and as such is less reliable on this plot.

Calculating a Correction Factor

Across the full krypton mass spectrum, the mass discrimination effect does not seem to follow a linear trend. For that reason, the correction was calculated for each isotope individually, with the average of adjacent masses used to correct those isotopes for which a direct calculation could not be made.

Whole aliquot air measurement data were plotted against $^{84}$Kr signal height ($N_0$, synonymous with number of detections). A line of best fit was then plotted through the data using a least squares linear regression macro within the data reduction software. The macro calculates a gradient, intercept, and covariance value, as well as the errors associated with each of the gradient and intercept. This is shown alongside a chi squared appraisal of the linear fit through the data.
Table 6.2 – Mass discrimination correction values. The results of the least squares linear regression through 51 whole aliquot air measurements, plotting measured ratio against $^{84}$Kr detections. The isotopes $^{80}$Kr, $^{82}$Kr, and $^{86}$Kr are calculated using the least squares linear fit algorithm; the isotopes $^{81}$Kr, $^{83}$Kr, and $^{84}$Kr were calculated as averages of the nearest isotopes with calculated correction factors.

**Application ofCorrection Factor**

The effect of applying the correction factors on average delta values for the same data set is shown in Figure 6.6. If we compare Figure 6.5 and Figure 6.6, we can see that the mass discrimination correction has clearly mitigated the deviation brought about by instrument mass discrimination.

![Averaged](image)

*Figure 6.6 – Average delta values of whole aliquot air measurements relative to standard terrestrial air values after mass discrimination correction, assuming $^{83}$Kr fits the near linear trend between $^{86}$Kr and $^{82}$Kr. Deltas are relative to air values presented by Basford et al. (1973).*
If we look at Figure 6.7, a comparison of data for each isotope both before and after application of the correction factor, we can see that application of the correction factor to the ¼ aliquot measurements both increases the uncertainty on the measurement and also causes greater deviation from the otherwise well constrained values. This is indicative of a threshold requirement for the application of this correction. The x axis intercept of the regression line gives us that threshold value, above which the correction should be applied. Calculating this across the three isotopes ⁸⁰Kr, ⁸²Kr, and ⁸⁶Kr, which are only affected by mass discrimination effects, the average resulting intercept is ⁸⁴Kr \( N_0 = 156,773 \pm 15940 \) counts. We therefore set the threshold of correction implementation at 150,000, the precision of this threshold is relatively unimportant because the correction over that \( N_0 \) region is small and does not greatly influence the resulting ratios.

As a result, an algorithm was written to selectively apply the mass discrimination factor as a correction based on the ⁸⁴Kr \( N_0 \) value. The threshold for application of the correction factor was 150,000 detections, above which the correction was applied according to the formula:

\[
R^x_c = R^x_0 / ((1 + (gN_0^{84} + i))/1000)
\]

*Equation 29*

Where \( R \) is a given ratio, \( c \) is a mass discrimination corrected value, \( 0 \) is the value of that parameter before correction, \( g \) is the gradient of linear regression for isotope \( x \) relative to ⁸⁴Kr, and \( i \) is the intercept for the linear regression for isotope \( x \).

Ratio uncertainties were also adjusted to account for the uncertainty on the mass discrimination correction. This was carried out according to the equation:

\[
\sigma = R^x_c \sqrt{\left\{ \left( \frac{\sigma^2}{Cov} + \frac{\sigma^2}{N_0} + \frac{(gN_0^{84} + i)^2}{1000^2} \right) / \left( 1 + \frac{gN_0^{84} + i}{1000} \right) \right\}^2 + \left( \frac{\sigma_0}{R^x_0} \right)^2}
\]

*Equation 30*
Figure 6.7 - Delta plots for $^{80}$Kr, $^{82}$Kr, and $^{86}$Kr relative to $^{84}$Kr. $^{83}$Kr is excluded due to measured ratios being governed by instrument tuning, rather than number of detections. These plots clearly show the mass discrimination encountered when measuring larger amounts of gas. ¼ aliquot measurements average within error of no discrimination, where as there is a clear increasing mass discrimination with increasing numbers of detections (synonymous with increasing gas amounts). (1 Aliquot measurements in red, ¼ aliquot measurements in blue). Plot x and y axes are reversed compared to the calculations presented in Table 1. Graphs on the left are uncorrected, graphs on the right have had the instrument signal dependent mass discrimination correction applied.

6.5 **CALCIUM ALUMINIUM INCLUSIONS**

CAIs are a complex range of inclusions, so it should be no surprise that their krypton systematics are equally as varied. Figure 6.8 shows all gas releases from the measured CAIs and the tie lines for krypton components thought to be present within the samples.

The tie lines represent the direction of change the measured ratio would move in if a pure amount of either spallation gas, or neutron capture bromine gas was added. If there are no additional gas components, and the data are accurately corrected then the data points should plot between the bounds of the two tie lines.

![Graph showing isotope plots of krypton ratios for CAIs](image)

*Figure 6.8 – Combined summary three isotope plot of all CAI data, showing $^{83}$Kr/$^{86}$Kr, and $^{82}$Kr/$^{86}$Kr. These data have been corrected for instrument bias as well as signal dependent mass discrimination. In comparison to Figure 6.1, the number of points suggesting a cosmogenic gas composition have decreased.*
Another informative way to summarise the data is to plot the release patterns for the major isotopes (see Figure 6.9, Plot key found in caption text).
Figure 6.9- Cumulative release diagrams for the CAI samples measured by stepwise heating. Cumulative release key: Red indicates $^{80}\text{Kr}$; Black, $^{82}\text{Kr}$; Blue, $^{83}\text{Kr}$; All ratios are relative to $^{86}\text{Kr}$; Isotope ratio plot key: Green = Br-Kr; Red= Chondritic spallation. Upper and lower limits for each isotope are representative of the calculated uncertainty for that measurement, wider separation indicates greater uncertainty.
With the exception of 3a CAI 3 (4), each measurement releases a burst of bromine neutron capture krypton first, shown by an elevation in the $^{80}\text{Kr}/^{86}\text{Kr}$ and $^{82}\text{Kr}/^{86}\text{Kr}$ ratios whilst the $^{83}\text{Kr}/^{86}\text{Kr}$ ratio remains unchanged. The relative amount of bromine derived krypton varies from sample to sample, with 10a Fluffy CAI showing the largest.

We see a relatively small amount of bromine derived krypton within the 3a CAI 3 (4). This is either a result of the prior heating of the larger fragment before being further fragmented, or alternatively the release is being skewed by the larger amount of gas released by this sample in comparison to the amount of gases released by other samples.

A noticeable feature of the bromine releases is the then seemingly exponential decay in the contribution from this component. This leads to the question, is this the result of incomplete gas release equilibrium, thereby releasing smaller and smaller fractions of the gas within the sample until it was entirely depleted? This may also indicate that bromine derived krypton is more easily extracted than trapped gas, and we are observing a progressive change in the adsorption sites being released from.

6.5.1 $^{81}\text{Kr}$ CONTENT

An isotope of particular interest is $^{81}\text{Kr}$, due to its importance in the calculation of cosmic ray exposure ages. The gas releases from the CAIs do not appear to have significant amounts of $^{81}\text{Kr}$, or any spallation gases within them. If we look at Figure 6.10 then we can clearly see that most of the measurements plot at, or within error, of 0.

---

Figure 6.10 – $^{81}\text{Kr}/^{83}\text{Kr}$ and $^{82}\text{Kr}/^{83}\text{Kr}$ three isotope plot with the expected trajectories of target element spallation products. Spallation products are based on data from Gilabert et al. (2002)
It is clear that the releases do not contain enough $^{81}\text{Kr}$ to make a cosmic ray exposure age calculation viable. There are clearly very few measurements with a significant cosmogenic gas component. The low abundance of $^{81}\text{Kr}$ within each gas extraction means that any CRE calculation carried out on these samples is likely to result in a figure with considerable uncertainty.

### 6.5.2 Bromine Component

A prominent component within the CAI samples was krypton derived from the neutron capture reaction bromine undergoes when exposed to thermal and epithermal energy neutrons. This component was found in varying concentrations across all samples of CAIs that were measured, with the exception of 3a CAI 3.

Bromine derived krypton (formed via neutron capture reactions) increases the $^{80}\text{Kr}$ and $^{82}\text{Kr}$ contents of a sample. Evidence of this component was observed in several of the CAIs measured, where the $^{82}\text{Kr}/^{86}\text{Kr}$ ratio is elevated.

If we look at Figure 6.9, we can see the release patterns of the gases from both a representative CAI measurement, and a measurement of matrix material. It is immediately apparent that there are differences in the gases contained within each type of sample. The bromine produced krypton dominates the early releases for the CAI samples, whilst it does not seem to feature within the matrix material, or at least it does not dominate any of the releases. It would appear that the matrix does not show a release pattern of Br-Kr that matches the release pattern from the CAI Br-Kr. The CAI bromine is released very early on in the heating steps, whereas the matrix based Br-Kr is released late on in the heating steps. There are a variety of ways this can be explained:

The CAIs are enriched in bromine relative to the matrix material — SEM EDS analysis of the CAIs indicated rim phases that are highly likely to be enriched in halogen components. If this is the case then then the alteration of CAI minerals may be the source of the Br-Kr component. Additionally, it may be inferred from this that either the formation of the Br-Kr component occurred before parent body incorporation, or that concentration of Br within these rim structures is much higher than in the matrix. The latter explanation seems unlikely, given the alteration of rim phases such as those observed are thought to occur after parent body accretion, as a result of parent body alteration. Therefore, it would be highly likely that the matrix would be equally altered, and lacking in a mechanism by which the bromine can be concentrated into the CAI rim phases.
The CAIs experienced a higher flux of secondary neutrons than the matrix material – it is plausible that the CAIs existed in a dense dust cloud within the proto-planetary disk. A sufficiently dense layer of dust would act much in the same way as a low density covering of rock, in the way that it would attenuate the transmission of cosmic ray energy particles, and promote the formation of secondary neutrons. These secondary neutrons could then go on to form the Br-Kr component within the CAIs prior to incorporation into the parent body. This however necessitates the formation of the matrix material after the formation of the CAIs.

Finally, it is possible that the heterogeneity of Allende resulted in a random sampling difference between the CAIs and the matrix, showing a difference in alteration and hydrothermal processing on a small scale within the meteorite.

6.5.3 Sample 3a CAI 3

The sample from slide 3a, CAI 3, has consistently shown different noble gas systematics than the other samples measured from Allende. At a cursory glance it is not only the only set of measurements that showed a cosmogenic spallation component that was clearly distinguishable from the trapped component, but also displayed a heavy krypton component which plotted at a higher $^{86}\text{Kr}$ content than the expected trapped component.

The differences in components measured within this CAI leads to an intriguing question, what is unique about this CAI and how best is the difference in composition explained. Figure 6.11 shows the combined data from all fragments of CAI 3. Within the figure is the release from the initial heating of the 24 mg fragment of the CAI, this release showed a strong cosmogenic composition, Questions remain as to why the data point lies at a higher $^{82}\text{Kr}/^{86}\text{Kr}$ ratio than a pure mix between the trapped component and one of the spallation gas endmembers, particularly given some of the fragment measurements also plot along this same trajectory. The simplest of explanations is that the raised $^{82}\text{Kr}/^{86}\text{Kr}$ ratio is due to the addition of a small amount of Br-Kr. However, there is also potential for the plotted cosmogenic spallation gas endmembers to be unrepresentative of pure cosmogenic gases from CAIs. Each of the cosmogenic endmembers is based on measurements of specific types of samples. The reason for the difference between the two plotted endmembers is the slight effect that chemistry has on the resultant cosmogenic gas ratios. In order to disentangle Br contributions from the spallogenic gases, Figure 6.12 can be used. This shows the $^{84}\text{Kr}/^{86}\text{Kr}$ instead of the $^{82}\text{Kr}/^{86}\text{Kr}$ ratio, the latter of which is produced by bromine neutron capture reactions as well as spallation
reactions. From this figure it is clear that the obvious spallation releases are plotting along a predominantly chondritic spallation composition. There are however a few well constrained points which plot above the expected trapped composition, as well as the chondritic spallation tie-line. These two points lead to the question, could vastly different mineral chemistry be producing an as of yet unobserved spallation spectrum, that has higher \(^{84}\text{Kr}\) concentrations than either average lunar or chondritic spallation spectra. These two points (additional points lie along the same trajectory but are also within error of the chondritic spallation tie-line) are also interesting on the basis of how closely they seem to fit the heavy krypton trend line.

Figure 6.11 – The releases from a CAI extracted from slide 3a. Showing \(^{83}\text{Kr}/^{86}\text{Kr}\) against \(^{82}\text{Kr}/^{86}\text{Kr}\). Data have been corrected for instrument discrimination, and mass discrimination. The 2013 data represents the first step of heating for the CAI, that 24 mg fragment was then further divided into analyses 1, 2, and 4, shown on the graph. Fragments 3 and 5 were not measured.

Considering Figure 6.11 and Figure 6.12, it appears that chondritic spallation best fits the cosmogenic gas component within sample 3a CAI 3. It can be concluded that the deviation
above the chondritic spallation tie-line within Figure 6.11 is due to a small amount of Br-Kr in addition to the cosmogenic fraction.

There is an additional observation to be made about the dataset; the occurrence of this phenomenon is most easily seen in Figure 6.12. The apparent trend through the majority of data points does not intersect with the assumed trapped component. The most obvious explanation for this is that $^{83}\text{Kr}/^{86}\text{Kr}$ is underrepresented after the corrections have been applied. If the data are transposed to a slightly higher $^{83}\text{Kr}/^{86}\text{Kr}$ ratio, then the fit to chondritic spallation within Figure 6.11 is also improved. However, such an offset is difficult to calculate and justify based on the data available. It also would not largely affect the conclusions drawn from these data.

![Figure 6.12 - The releases from a CAI extracted from slide 3a. Showing $^{83}\text{Kr}/^{86}\text{Kr}$ against $^{84}\text{Kr}/^{86}\text{Kr}$. Data have been corrected for instrument discrimination, and mass discrimination. The 2013 data represent the first step of heating for the CAI, that 24 mg fragment was then further divided into analyses 1, 2, and 4, shown on the graph. Fragments 3 and 5 were not measured.](image-url)
**Heavy Kr Component**

Perhaps the most interesting feature of the analyses carried out is the presence of a ‘heavy’ krypton component, shown in Figure 6.8 as the plotting of data from the trapped component compositions towards the origin. At first glance the component seems to be represented by an excess of $^{86}\text{Kr}$, however, it is difficult to constrain whether other isotopes have also been added to by this component. Similar effects have previously been observed within the Allende meteorite, although these studies have not specifically been addressing the krypton systematics of the CAI phases of Allende. Studies such as Frick (1977), observed a negative light isotope anomaly and a positive heavy isotope anomaly within the krypton systems of Allende. The author also finds that the majority of Kr gas within the sample is of normal planetary (assumed trapped) composition, with only small amounts of the gas showing these isotopic anomalies. It is plausible that, given the dominance of the anomalous gas within the sample measured for this study, the anomalous gas is derived from CAI mineral phases. However, further investigation would be required to properly explore this possibility.

The indication of a heavy krypton component introduces a significant obstacle in calculating the spallation gas amounts within a gas release. A central assumption in how we extricate the trapped krypton from the spallation krypton is that the $^{86}\text{Kr}$ is entirely trapped in origin, this allows the trapped component to be subtracted from the remaining ratio to result in the spallation ratios for the gas. If we accept that there is a heavy krypton component then we can no longer hold that assumption to be true. In essence, it makes the subtraction of the trapped component impossible, without a method to also account for the additional heavy krypton component.

The occurrence of isotopically heavy krypton has only been observed in samples originating from slide 3a, CAI 3, the data for which can be seen as summarised in Figure 6.11. At least one measurement from each of two out of the four fragments of this CAI were observed to be isotopically heavier than the expected trapped component.

The sample (a large, well consolidated, fluffy type CAI) was originally broken into several fragments, one of which was 24 mg. This fragment was heated during the proof of concept stage of the study, and was observed to release gas with a prominent cosmogenic gas fraction. The sample however was not melted; it was too large of a fragment. The sample was subsequently further fragmented to form several smaller samples. These were measured using step heating protocols.
One significant issue with mass fractionation is the degree to which the gas is fractionated. This is compounded by the fact that it is not only large gas amounts that show the trend along a mass fractionation trajectory.

An explanation that can be invoked to explain the trends across all graphs in Figure 6.13 is an addition of HL-Kr as well as an addition of Br-Kr, possibly with a small G-Kr contribution however that G-Kr addition is only required to explain the trend towards lower 83Kr/86Kr ratios on the 82Kr/86Kr against 83Kr/86Kr (Graph a).

Looking collectively at Figure 6.13 it is possible to see that the data plot as though the 86Kr content is higher than in a standard trapped component. Prudence would suggest that the new signal dependent mass discrimination is likely to have affected the data in an unexpected way. The fact that the mass discrimination corrected data plots in the same restricted region as the data that has not had the correction applied is strong evidence that the correction is working as intended, and without exception. This is also supported by how the corrected data are evenly intermixed with the uncorrected data. Therefore, it is fair to conclude that the signal dependent mass discrimination correction has not led to this observed effect, and works well in correcting the ratios of the data it has been applied to.

The sample was also previously heated before being re-fragmented and re-analysed until melting occurred. Uneven heating, or incomplete equilibrium during heating can lead to mass fractionation. For this reason, it is worth analysing the trend in the data for a mass dependent fractionation effect. To do this, we plot a per mil per AMU line, indicated as a red tie-line (Figure 6.13). Mass fractionation is generally a very small effect when it is present, in the case of these samples, the degree to which the data would need to have undergone fractionation is extreme. With the most extreme cases reflecting a ~70-75 per mil per amu deviation. On these grounds, this seems implausible as an explanation. Adding to that, the occurrence of Br-Kr within the samples at the same time as this heavy component suggests that mass fractionation is not the cause of the deviation towards an isotopically heavy composition.

This leaves the possibility of an additional rare component added to the already discussed composition. There are two obvious candidates for this component: HL-Kr, a component found in presolar diamonds; and G-Kr, a component found in SiC grains. Although these types of grains are low in abundance in samples of this mass, there is evidence in Gilmour et al. (2005) that would suggest large quantities of Kr would be present in these types of grains providing a similar behaviour to the xenon system (there is no reason these systems should not be comparable). Nevertheless, the amount of gas extracted with this heavy composition is surprising, especially if the explanation behind this gas is a rare component found within...
nanometre sized rare inclusions. If for the sake of this explanation it is accepted that the quantity of gas released could be expected from these grains, then the next step is to identify the component best represented by the isotopic ratios.

Throughout the graphs of Figure 6.13 the tie-lines between the expected trapped component, HL-Kr, and G-Kr are plotted. G-Kr plots as a range due to how variable $^{86}$Kr contents are within that component. Lewis et al. (1994) devised the numbers used for this component, the process behind which involved an assumption of the $^{84}$Kr/$^{82}$Kr ratio being 2.40. Additionally, the $^{86}$Kr/$^{84}$Kr, and $^{80}$Kr/$^{84}$Kr ratios act as a sensitive measure of the physical conditions during the formation of this component. In many ways the mechanism behind G-Kr is comparable to the mechanism that forms Br-Kr. Both are a result of s-process reactions, slow secondary neutrons formed as a result of other nuclear reactions, such as cosmic ray spallation reactions or similar. There are other components that are possibly entrained within the overall composition, but the similarity between those components (P6, P6 exotic for example) and those components already included in the plots, is so great that it would be impossible to definitively show the gas was of one particular composition. Instead it can be assumed that if one of the dominant components plotted is theorised to be contained within the sample, it could be fairly accurately said that the other lesser components associated with that source grain are likely to be included in the gas mix as well.

It is apparent that the component best suited for explaining the measured isotopic ratios is HL-Kr. To further reinforce the validity behind this observed effect being a real isotopic effect, rather than a mass fractionation effect, the measurements lie well constrained between the HL-Kr endmember and the assumed trapped component. Specifically, Figure 6.13.b, which shows very strong agreement across almost the entire dataset. That said, Figure 6.13.f shows several points which more clearly show a G-Kr composition (assuming that mass fractionation is not the mechanism causing this isotopically heavy component phenomenon). This is also reflected in Figure 6.13.a and d.

Within the graphs of isotopes affected by Br-Kr additions, it is clear that there is a bromine derived krypton source being released alongside these isotopically heavy krypton releases. This is exemplified by Figure 6.13.c, which plots both $^{80}$Kr/$^{86}$Kr and $^{82}$Kr/$^{86}$Kr, the isotopes produced by bromine neutron capture. Also interesting are the slightly low $^{82}$Kr/$^{86}$Kr ratios for the most Br-Kr rich measurements. If this is indicative of an under-correction of this isotope, then it may affect which rare component is most likely to be added to the trapped component composition. If the $^{82}$Kr/$^{86}$Kr ratios were to be raised slightly, it would draw them towards a G-Kr composition on the graphs where HL-Kr is currently the most favoured additional component.
The assignment of a specific component to this data is perhaps premature, as not all isotopes reflect the same degree of agreement on the HL-Kr tie-line. It is perhaps interesting to note that the graphs where lighter isotopes ($^{80}$Kr, $^{82}$Kr) are plotted tend to indicate a HL-Kr composition, whereas those graphs where heavier isotopes ($^{83}$Kr, $^{84}$Kr) are plotted lean towards a G-Kr composition. More specifically, if we assume the HL-Kr component is accurate to what is contained within the sample, it would appear that the $^{84}$Kr concentrations are underrepresented within the ratios. Unfortunately, there is no way to test for this using the data available. Nevertheless, there is clearly an interesting difference in this sample, and it is worth further investigation in order to pin down the exact composition of this component, and further to that the repercussions of this on the mechanisms and processes that affected the CAIs during their history.
Figure 6.13 – Plots selectively using data that shows isotopically heavy compositions. The plots are looking at the potential of additions to the measured gas ratios by rare components.
Figure 6.14 – Delta plots of heavy krypton releases, relative to standard terrestrial air. Lines plotted represent the rare components discussed in the text.

Implications of this heavy krypton component – The occurrence of this apparent raised $^{86}\text{Kr}$ content creates a problem for the $^{81}\text{Kr}$-$^{86}\text{Kr}$ chronometer method applied so far. It stands that, if $^{86}\text{Kr}$ is not entirely of the trapped component, then the extrication of the cosmogenic gases from the other gas components is more difficult.

It is apparent from the plots presented in Figure 6.14, that the measurements for 3a CAI 3 do not fit any one given component line across all isotopes. Therefore, it would be unwise to draw conclusions regarding the exact component that is also included within these releases, however it does suggest the need for further investigation into this component and its source. Such further investigation may be achieved via investigating the Kr systems of individual mineral separates from these CAIs.
6.6 **CONCLUSIONS AND FUTURE WORK**

There are several routes this research should take, in order to fulfil the potential of this study.

1) A broader sample selection, with CAIs from different classifications of meteorites.
2) Mineral separate studies- gentle purely physical separation of CAIs to extract pristine mineral examples from them. Measurement using the RIMSKI instrument would allow krypton schematics to be established for each part of the CAIs.
3) Needle coring of CAIs to avoid contamination with matrix.
4) Complete characterisation prior to analysis. Possibly including micro-CT to aid in sample extraction.

It has been suggested that anomalous Kr measurements, such as those presented here, can be better interpreted when compared to Xe data for the same samples. The recent developments of the RIMSKI instrument towards measurement of Kr and Xe in tandem should enable additional avenues with which to explore the phenomena discussed throughout this study.

It is near impossible to draw any firm conclusions from this relatively small study. There are many areas which could benefit from revision in terms of the methods used. The study suffered due to the number of relatively new methods and techniques that were being implemented in quick succession. Arguably, many of these methods would have constituted an entire project of work in their own right.

The sample extraction method should be further developed to reduce the amount of matrix contamination within the CAI samples. An assumption at the start of this study was that a CAI enriched sample would be sufficient to see the difference in cosmic ray exposure age. This relied on the matrix and CAI having comparable gas quantities which is worth questioning given the results of this study. It would in hindsight have been better to extract the samples without any matrix contamination. However, it is noted that this is difficult due to the pervasive veins of matrix through some fluffy CAIs. Several methods were investigated for this study, only towards the end of analyses did a more suitable needle-coring method arise. In future analyses it would be worthwhile to extract samples this way.

The heating duration used for the majority of analyses within this thesis was maintained at one minute’s heating. In order to rule out heating based fractionation effects a study should be carried out to investigate whether heating duration affects the ratios measured by the instrument. This will enable a user to ensure uniform and complete equilibrium of the gas released at each step. This suggestion is based on evidence of different release rates between different CAIs, for the same component. This may indicate that the sample had not reached
equilibrium at the point the heating was stopped. Different samples, with different characteristics would therefore reach equilibrium at different rates to each other. Perhaps the prolonged release of components, such as Br derived Kr, shows disequilibrium in the gas release steps.

The study focussed on the Allende meteorite, a sample known to be highly altered. This alteration, has been observed to affects the krypton system of a meteorite. It was noted in Vogel et al. (2004) that cosmogenic light noble gases were observed in reduced CV meteorites, whereas the absence of these gases was noted in the oxidised subgroup. It would therefore seem worthwhile to extend the study to a wider range of meteorite types, and the CAIs within them.
7. **CONCLUSIONS AND STATE OF KNOWLEDGE**

7.1 **Thesis Conclusions**

This thesis represents the product of four years’ work towards improving the tuning reproducibility, characterisation, and ionisation efficiency of the RIMSKI instrument. Throughout this thesis, steps have been successfully made towards improving the usability of the RIMSKI instrument. This was achieved through both development of the physical instrumentation, as well as the implementation of new, and modified, protocols.

A mass flow controller system was installed and the resulting control over the ratio within the Xe-Ar gas cell reduced the tuning time from an order of weeks, to a matter of hours. The precision on the tuning curve demonstrates the control over the resulting wavelength, using this new filling method.

![Figure 7.1](image)

*Figure 7.1 – An illustration of the difference in instrument sensitivity achieved via the control over the Xe-Ar mixing ratio afforded by the revised method for filling the Xe-Ar Cell, alongside the range of other tuning features implemented throughout this thesis. Data represent ~2.5 × 10⁵ atoms total Kr (current system setup) and 1 × 10⁶ atoms total Kr (Previous system setup), this represents an eightfold increase in sensitivity.*
The range of samples proven to be measurable using the RIMSKI instrument has also been expanded, and now includes calcium-aluminium rich inclusion phases of chondritic meteorites as well as mineral separate phases of chondritic meteorites.

Table 7.1 breaks down the aims and objectives outlined in Table 1.1 and assesses the successes and failures of achieving them.
1) To improve the reproducibility of measurements made using the RIMSKI instrument by enhancing the control over tuning procedures.

| a) Identify areas for instrument development. | These areas were identified as the method for filling the Xe-Ar four-wave mixing cell. (Successful) | Section 4.1.6 (Page 72) |
| b) Design and implement instrument modifications that will enhance reproducibility and control over the tuning procedure. | A series of Mass Flow Controllers were integrated with a new filling line. (Successful) | Section 4.2.2 (Page 75) |
| c) Characterise the use of these modifications. | The reproducibility of these MFCs was proven. The bandwidth of tuning the cell was investigated. The effect of the total cell pressure was investigated. The speed of cell filling was considered. Long term calibration effects were considered. (Successful) | Section 4.3.1 (Page 79) |
| d) Develop tuning protocols a new user could implement | The concluding remarks include the protocol for filling the Xe-Ar cell which was refined over the course of the characterisation study. (Successful) | Section 4.4 (Page 92) |
2) To develop measurement and data reduction protocols.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a)</strong></td>
<td>To comprehend the data reduction system being used on the RELAX spectrometer data.</td>
<td>A comprehensive understanding of how the RELAX data reduction software reduces data and the corrections that must be applied for data validity was achieved. <strong>(Successful)</strong></td>
</tr>
<tr>
<td><strong>b)</strong></td>
<td>To assess differences in the data collection procedures between the RELAX and RIMSKI instruments.</td>
<td>The differences between the data collected for the RIMSKI instrument, and the RELAX instrument were understood and the required changes to the software were considered. <strong>(Successful)</strong></td>
</tr>
<tr>
<td><strong>c)</strong></td>
<td>To develop a method for the measurement of data, allowing the maximum scientific gain from any given sample analysis.</td>
<td>A proven method that upholds data validity was developed. Shown to be valid through the analysis of quarter air calibration aliquot standards. <strong>(Successful)</strong></td>
</tr>
<tr>
<td><strong>d)</strong></td>
<td>To produce a consistent and reproducible method of data handling, which accurately reduces the data and allows conclusions to be drawn with confidence.</td>
<td>The methods and software developed behave in an expected and predictable way. The software is capable of predicting the error of a measurement with accuracy in line with the standard deviation across a range of measurements over several days of analyses. <strong>(Successful)</strong></td>
</tr>
</tbody>
</table>

Section 5.3 (Page 96)

Section 5.4 (Page 101)

Section 5.5 (Page 104)

Section 5.5.1 (Page 105)
<table>
<thead>
<tr>
<th>3) To prove the function of both the modifications to the instrument, and the protocols developed.</th>
<th>a) Select a range of meteorite samples already measured using the RIMSKI instrument.</th>
<th>The Stannern and Bereba eucrites were used as standards that had previously been measured using the RIMSKI instrument. <strong>(Successful)</strong></th>
<th>Section 5.5.2 (Page 122)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b) Measure, and reduce the data collected using the new protocols.</td>
<td>Several fragments of the meteorites were subject to step pyrolysis and Kr systematics were collected for them. Arguments can be made both ways for whether step pyrolysis is a viable method for extracting cosmogenic Kr gas. <strong>(Successful)</strong></td>
<td>Section 5.5.3 (Page 125)</td>
</tr>
<tr>
<td></td>
<td>c) Compare data between previous analyses and the current instrument function.</td>
<td>The method of calculating the CRE age I developed appears to work well, however the previously applied method does not consistently produce similar numbers. Therefore, further validation for the measurement of extra-terrestrial samples should be carried out to ensure data validity. <strong>(Mostly Successful)</strong></td>
<td>Section 5.6 (Page 133)</td>
</tr>
<tr>
<td></td>
<td>d) Revise protocols if necessary.</td>
<td>An alternative method for the calculation of CRE ages based on the data produced by the RIMSKI instrument was devised and tested. The results are promising but further evaluation of this method must be carried out. <strong>(Mostly Successful)</strong></td>
<td>Section 5.5.4 (Page 126133)</td>
</tr>
</tbody>
</table>
To push the limits of samples that can be measured using the RIMSKI instrument.

<table>
<thead>
<tr>
<th>4)</th>
<th>Identify a range of CAIs from Allende thick sections.</th>
<th>Samples were identified using a series of Ion Microprobe and SEM element mapping techniques. However, not all samples were characterised before analysis, and characterisation of the samples without significant material loss was scarcely successful <em>(Mostly Successful)</em></th>
<th>Section 6.3.3 (Page 139)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b)</td>
<td>Extract material for analysis.</td>
<td>The technique used to extract the material was appropriate for a proof of concept experiment such as this one, but the method should be revised before further measurements are carried out. <em>(Mostly Successful)</em></td>
<td>Section 6.3.4 (Page 140)</td>
</tr>
<tr>
<td>c)</td>
<td>Measure the krypton gases within these inclusions.</td>
<td>The measurement and correct reduction of the data was successful, and the data faithfully reflects the Kr systematics of the CAIs measured. <em>(Successful)</em></td>
<td>Section 6.4 (Page 153)</td>
</tr>
<tr>
<td>d)</td>
<td>Constrain the krypton noble gas systems of Allende CAIs.</td>
<td>Steps have been made towards the interpretation and understanding of processes that have affected these inclusions, however, further work on a wider range of samples and source meteorites should be carried out in order to draw firm conclusions about these findings. <em>(Partly Successful)</em></td>
<td>Section 6.6 (Page 168)</td>
</tr>
</tbody>
</table>

Table 7.1 - A table outlining the successes and failures of achieving the aims and objectives laid out at the start of this thesis.
7.2 **STATE OF KNOWLEDGE AND FUTURE WORK**

Krypton has been widely used as a tool to calibrate a range of other cosmic ray exposure age calculation techniques. There is no doubt that the Kr technique has been well researched, but it seems odd that the geological understanding of samples used in researching the technique have been so poorly understood. It would seem logical that furthering understanding of the geology of these samples in conjunction with the noble gas systematics would only possibly increase our understanding of these systems.

We have demonstrated that there is good potential for the measurement of CAIs using this technique, and that there are grounds for further studies to be carried out. Perhaps most interesting is the potential for individual mineral separates from CAIs to be measured using the RIMSKI instrument.

The primary components of the CAI krypton systematics of Allende CAIs are, a trapped air/Q-Kr/Solar component, Br derived Kr from secondary neutron capture, and a heavy krypton component. There are also slight signs of a small cosmogenic component to the gases, although predominantly this component was not easily extricated from the other gas components.

### 7.2.1 FUTURE WORK

There remains a great deal to investigate with regards to the Kr systems of calcium-aluminium-rich inclusions. A multi-approach investigation, where samples were well characterised before analysis using non-destructive techniques would be greatly beneficial to achieving a maximum scientific output from such an endeavour.

I strongly advise the investigation of mineral separates from CAIs that have been gently separated by mechanical means only, using the RIMSKI instrument. The instrument has shown greatly improved sensitivity, and the capability to measure sub-milligram samples following the developments carried out throughout this thesis. Investigation of these separates will help constrain the source of the krypton components observed in the measurements reported here, as well as providing information towards the study of which mineral phases are best to target for krypton analyses.
8. REFERENCES


### Appendix 1 – Glossary of terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>4π / 2π Irradiation Exposure</td>
<td>A measure of the type of exposure an object may receive. This relates to the 3D geometry of the shielding conditions around the object in question. 4π exposure is spherical meaning shielding conditions allow exposure of the object from all directions. 2π exposure means that exposure only occurs from a hemispherical region centred around the object.</td>
</tr>
<tr>
<td>BBO</td>
<td>Beta Barium Borate - A crystal type used as a doubling crystal which halves the wavelength of laser light of a particular range of wavelengths. Within RIMSKI the BBO component converts ~505nm laser light to ~252.5nm laser light.</td>
</tr>
<tr>
<td>Calcium-Aluminium-rich Inclusion (CAI)</td>
<td>An agglomeration of the highest crystallisation temperature minerals to have formed in the solar system. Alongside chondrules, these are considered the oldest surviving solids within the solar system. They are found in most types of chondrite meteorites.</td>
</tr>
<tr>
<td>Chondrite</td>
<td>A broad classification for the meteorites that formed from parent body asteroids that did not achieve sufficient heat to allow total melting of their structure. These meteorites are considered representative of the materials that went on to melt and form the planetary bodies.</td>
</tr>
<tr>
<td>Chondrule</td>
<td>A crystalline spherical inclusion to chondritic meteorites, thought to have formed as one of the first surviving materials in the solar system.</td>
</tr>
<tr>
<td>Cosmogenic</td>
<td>Formed via interaction between high energy cosmic rays and a target element</td>
</tr>
<tr>
<td>CRE Age</td>
<td>Cosmic Ray Exposure Age - The amount of time an object has been exposed to the GCR flux of open space.</td>
</tr>
<tr>
<td>Delta (plot)</td>
<td>A plot to show the per mil deviation of a measured value from a reference value</td>
</tr>
<tr>
<td>DFMNIR</td>
<td>Difference Frequency Mixing - Near Infra-Red: A method of generating a third wavelength from the mixing of two wavelengths in a non-linear optical crystal.</td>
</tr>
<tr>
<td>Exotic</td>
<td>A noble gas component that does not fit the standard 'trapped' components</td>
</tr>
<tr>
<td>----------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>G-Kr</td>
<td>A Kr component which is thought to form as a result of s-process nucleosynthesis, predominantly in SiC grains from AGB stars</td>
</tr>
<tr>
<td>HL-Kr</td>
<td>High-low Kr: Usually denoting a relative enrichment of the heavy and light isotopes of an element, within the Kr system only an enrichment in heavy isotopes has been observed.</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>Lithium Niobate: The crystal used for DFMNIR on the RIMSKI system</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro Channel Plate - A component used for signal amplification</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller - A component used to control the flow of a gas or liquid through an aperture.</td>
</tr>
<tr>
<td>N0</td>
<td>The initial peak height for a given isotope (calculated via an extrapolation back to t=0)</td>
</tr>
<tr>
<td>Nano diamond</td>
<td>Nano meter sized particles of diamond, thought to have formed during super nova events which seeded this solar system with material.</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>Neodymium doped Yttrium Aluminium Garnet: The crystal optic through which a laser system can form a coherent laser light source.</td>
</tr>
<tr>
<td>Parent body alteration</td>
<td>This is alteration (thermal or hydrothermal) that occurs after the parent body has formed. The significant difference being the materials and isotope ratios that are available for redistribution between an inclusion of interest, and the surrounding matrix</td>
</tr>
<tr>
<td>P-Kr</td>
<td>A little understood component, thought to be related to HL-Kr and G-Kr. It can be found in either nano diamonds or SiC grains. It is unclear at present whether this is a distinct component or a mixing between other exotic components.</td>
</tr>
<tr>
<td>Pre-accretion alteration</td>
<td>This alteration takes place as an inclusion is forming, as a result of changing conditions in the formation environment</td>
</tr>
<tr>
<td>Pre-exposure</td>
<td>This is exposure to cosmic rays that has happened as a distinctly separate event to the final exposure the object receives during its transit to Earth. For example, a CAI may have been exposed during formation, then had exposure halted as it was incorporated into the chondrite parent body, before being exposed again following release from the parent body and subsequent transit to Earth.</td>
</tr>
</tbody>
</table>
| Pre-solar grain            | A range of very small grains found within unmelted meteorites. These are thought to
be extra solar in origin due to their abnormal isotopic composition.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Mineral</td>
<td>Defined here as a mineral that was present after the inclusion had formed but before incorporation into the parent body.</td>
</tr>
<tr>
<td>Q-Phase</td>
<td>A type of trapped component. The isotopic composition of this component is thought to represent a primordial asteroid composition.</td>
</tr>
<tr>
<td>Radiogenic</td>
<td>Formed via the radioactive decay of a parent atom</td>
</tr>
<tr>
<td>RIKSKI</td>
<td>The Resonance Ionisation Mass Spectrometer for Krypton Isotopes: An ultra-sensitive Kr mass spectrometer at the University of Manchester</td>
</tr>
<tr>
<td>RIMS</td>
<td>Resonance Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>SCCM</td>
<td>Standard cubic centimetres per minute- A measure of the rate of flow of a gas or liquid</td>
</tr>
<tr>
<td>Secondary Mineral</td>
<td>Defined here as a mineral that formed after incorporation into the parent body, as a result of alteration on the parent body</td>
</tr>
<tr>
<td>Shielding</td>
<td>A measure of how protected from radiation a given object is. In general, the greater the density of material between the radiation source and the target object, the greater the shielding is.</td>
</tr>
<tr>
<td>Solar wind (SW)</td>
<td>The trapped component that is expelled from the Sun. It is thought to be representative of the average solar system composition. This component is most commonly implanted in a sample after parent body formation.</td>
</tr>
<tr>
<td>Spallation</td>
<td>A nucleosynthetic mechanism by which a target nucleus is split into two subsequent atoms via the impact of a high-energy particle with the target atom nucleus</td>
</tr>
<tr>
<td>S-Process</td>
<td>A slow neutron capture nucleosynthetic process where by an atom nucleus captures a lone neutron increasing the atomic mass by 1. This neutron then undergoes beta decay to form a proton, thereby changing the atomic number by 1.</td>
</tr>
<tr>
<td>Terrestrial Air</td>
<td>The isotopic composition of an average sample of air on Earth. This is commonly used as a standard for noble gas analyses due to the homogenous distribution of noble gases throughout the Earth atmosphere reservoir</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of Flight - A method of separating isotopes according to their mass, and equivalent flight time when an equal acceleration is applied across all ions.</td>
</tr>
<tr>
<td>Trapped</td>
<td>Gases trapped within a meteorite that sample the reservoir the meteorite formed in. Within this thesis the term is used more generally to infer gases that were trapped at the point of</td>
</tr>
</tbody>
</table>
Appendix 2 – Tunable dye laser system details.

Sirah Tuneable Dye Lasers

A dye laser is a common commercially available laser used to tune a pump beam (in this case formed by the Powerlite 9010 Nd:YAG) via excitation of a large organic molecule. The decay of which, back to the ground state, releases a wide bandwidth of laser light wavelengths. Diffraction gratings are used to split out a distinct wavelength, the angle between the gratings governs the wavelength of the beam outputted from the laser.

A series of three tunable dye lasers are implemented to allow control of the specific wavelengths used in the ionisation scheme. Each dye laser runs on a specific laser dye, and each is pumped by one of the Powerlite 9010 Nd:YAG beams.

The dye within each laser system is capable of outputting a wide range of wavelengths, roughly centred on the theoretical optimum wavelength required for krypton ionisation via the scheme employed on the RIMSKI system.

The wavelengths of each dye laser are roughly guided by a graphical user interface, however, hysteresis effects from motor systems within each laser can mean differences in performance with each iteration of tuning. When tuning wavelengths to specific atomic transitions, it is impractical to use an overall instrument signal to reflect individual wavelength tuning. This is due to the way each wavelength can affect the others in the ionisation sequence after it. Therefore, for accurate and reproducible tuning, two detector cells are used. These cells are standard con-flat 40mm internal diameter stainless steel UHV parts, with an electrode either side of the beam path. Each end of the cell is isolated from the rest of the spectrometer system by an MgF₂ viewport (internal MgF₂ diameter - 15 mm). They are filled with a known amount of particular gases, which will be detailed for each wavelength in the following section. Each laser is passed through the cell, between two electrodes. The resulting voltage decrease is measured after amplification via charge sensitive amplifiers. Mentions of ‘detector cells’ from this point, follow this standardised design.

Sirah Cobra
A Sirah Cobra laser is used to form the 558.1935 nm wavelength from a 532 nm pump beam. The laser dye is pyrromethene 580, with a peak energy output at 557 nm.

This wavelength is tuned to the appropriate transition using a detector cell filled with pure krypton gas (1.5 x 10^{-2} mbar). This is carried out after all other beams have been tuned. Because the green beam forms the intermediate step in the resonance transition, in order to be visible in a signal profile, all other beams must be tuned and aligned properly.

**Sirah Cobra Stretch with DFMNIR**

Another Sirah Cobra Stretch dye laser, pumped by a 532 nm beam from the Powerlite 9010 Nd:YAG, is used to form a 623 nm beam. The beam is then directed into a LiNbO$_3$ crystal, where it is overlapped with a 1064 nm pump beam from the Powerlite 9010 Nd:YAG and dual frequency mixed (DFM) to form a 1507.331 nm beam. The laser dye used in the cobra stretch laser is DCM.

Difference Frequency Mixing Near Infrared (DFMNIR), allows the resulting red wavelength beam to be combined with a 1064 nm beam from the Powerlite 9010 Nd:YAG. The beams require delay lines to ensure the pulses from each beam reach the LiNbO$_3$ crystal at the same time.

**Sirah Cobra Stretch with FCU**

A Sirah Cobra Stretch dye laser is used to tune a pump beam of 355 nm to a 504.971 nm wavelength. The laser dye used in the oscillator and amplifier of the cobra stretch is coumarin 503 (also referred to as coumarin 307), with a peak output at 505 nm. This is then passed through a frequency doubling beta barium borate (BBO) crystal to produce a 252.4855 nm beam.

The oscillator and amplifier cells are quartz cuvette cells.

In order to properly tune this beam to the required wavelength, a detector cell is filled with ~1.5x10^{-1} mbar of pure xenon gas. Adjustment of the UV wavelength is carried out until a maximum signal is achieved, in practice, this signal varies on a day to day basis, making constraining the value of the signal a complex problem, fortunately the shape of the tuning curve remains constant and thus can reproducibly be used to tune the UV wavelength to a maximum coupling with the $5p^7(3/2)^26p^2(3/2)^2$ transition within xenon. In theory, and accounting for the two-photon nature of the transition, this should correspond to a combined wavenumber of 79212.464 cm$^{-1}$, or a wavelength per photon of 252.4855 nm. Due to hysteresis effects of the motors within the dye laser, the reproducibility of this exact wavelength is
imperfect, adding to this, the calibration of the wavelength produced against the wavelength reported on the laser software is known to drift over time. Therefore, it is more reproducible to use the detector cell filled with xenon as a means of tuning the UV beam to the transition.

With the detector cell setup, it is possible to locate the correct transition for xenon by observing the peak in signal output from the xenon gas, relative to the location of other peaks associated with xenon.

Peaks that are accessible to this method, and are commonly used in tuning include:

<table>
<thead>
<tr>
<th>Electronic Transition Configuration</th>
<th>J</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Single photon wavelength (nm)</th>
<th>Distance to Theoretical ideal wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p$^5$(2p$^3/2$)6p$^2[3/2]$</td>
<td>2</td>
<td>79212.464</td>
<td>252.4855</td>
<td>N/A</td>
</tr>
<tr>
<td>5p$^5$(2p$^3/2$)6p$^2[3/2]$</td>
<td>1</td>
<td>78956.031</td>
<td>253.3055</td>
<td>0.8200</td>
</tr>
<tr>
<td>5p$^5$(2p$^3/2$)5d$^2[1/2]$</td>
<td>0</td>
<td>79771.268</td>
<td>250.7168</td>
<td>1.7687</td>
</tr>
<tr>
<td>5p$^5$(2p$^3/2$)5d$^2[1/2]$</td>
<td>1</td>
<td>79986.619</td>
<td>250.0418</td>
<td>2.4437</td>
</tr>
</tbody>
</table>

*Table 9.1 – Transitions surrounding the theoretical ideal wavelength setting for the UV cobra stretch laser system.*
Appendix 3 – Photographs of Allende thick sections provided by J. Wasson and A. Rubin. Taken with a DSLR camera, prior to any work on the samples

<table>
<thead>
<tr>
<th>Sample Slides</th>
<th>Front</th>
<th>Back</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slide 1a+1b</td>
<td><img src="slide1a.png" alt="Image" /></td>
<td><img src="slide1b.png" alt="Image" /></td>
</tr>
<tr>
<td>Slide 2a+2b</td>
<td><img src="slide2a.png" alt="Image" /></td>
<td><img src="slide2b.png" alt="Image" /></td>
</tr>
<tr>
<td>Slide 3a+3b</td>
<td><img src="slide3a.png" alt="Image" /></td>
<td><img src="slide3b.png" alt="Image" /></td>
</tr>
<tr>
<td>Slide 6a+6b</td>
<td><img src="slide6a.png" alt="Image" /></td>
<td><img src="slide6b.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Appendix 4 - Scans of the Allende thick sections provided by J. Wasson and A. Rubin. Scans at 600dpi using Canonscan scanner.
Appendix 5- SEM EDS element maps from the two example CAIs shown in Chapter 2. (scale bars apply across all EDS maps for that sample).
<table>
<thead>
<tr>
<th>Al</th>
<th>Slide 10a +10b Melted CAI</th>
<th>280 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Slide 10a+10b Fluffy CAI</td>
<td>800 µm</td>
</tr>
</tbody>
</table>
Appendix 6 – A schematic diagram of the RIMSKI instrument.
Appendix 7 – Excerpts from the standard user protocol manual for RIMSKI- all protocols were developed over the duration of this thesis.

Turning On

Before starting the instrument up, check the electronics unit is powered and the temperature control unit for the DFMIIR and UV Cobra Stretch are powered. The crystal in the DFMIIR unit is hygroscopic- if the unit is turned off then it must be left on for 24 hours before a beam is let through the crystal to prevent damage to the optics. Laser goggles must be worn for the entire procedure.

1. Turn on the water supplies to the lasers and cryogenerator (the two red valves and the lower green valve found on the central column)
2. Turn the Continuum YAG on:
   i. On the Mains power unit there are three breakers, set the lower right one to the on position, followed by the middle and finally the top most breaker
   ii. Turn the key to the on position; the YAG should beep and start a warm up test sequence. This will appear on the remote control panel. Once the startup count down has ended, proceed to the next step
   iii. Before going any further check that the external shutter to the YAG is closed. These are the black stops on top of the left end of the YAG.
   iv. Ensure the program display on the remote control is set to program 1, you can do this by using the program up/down arrows and the ‘activate’ button
   v. Press the charge button, then the fire button; do this three times or until the simmer lights are all lit (on the mains power supply)
   vi. Press the automatic/manual toggle button on the remote
   vii. Press the start button. The YAG should now be set to its automated flash lamp mode and should be firing continuously.
3. Turn on the Seeder:
   i. Turn the key to the on position
   ii. Switch the toggle to the auto position
4. Turn on the QC boxes, both the RIMSKI composer (Found next to the Mini YAG power supply; push the power button on) and the RELAX composer (Found above the RELAX compressor; turn the power on and then press run. The circle in the top right of the display should start flashing rapidly)
5. Turn the Cryogenerator on; The electronics stack houses the control unit. Turn the power on (right switch), allow the temperature control unit to go through its warm up procedure. Once the display is stable use the small arrow buttons to set the target temperature to 65K. Flip the switch on the left to enable cooling.
6. Turn the compressor on, this is under the laser table housing the mirror assembly.
7. Turn on the Mini YAG:
   i. Cycle the key on the power supply unit.
ii. Press the start button; the Q-switch LED should start flashing
iii. Check a beam is going into the ion source using the IR detection card

8. Turn on the two getter power supplies and set them to 5.5A.

9. **Leave the instrument to warm up for 30 minutes**

10. Switch the YAG to external triggering:
    i. Press stop on the remote control panel
    ii. Change the program to program 2, making sure to press activate.
    iii. Check the external Q-switch toggle is set to external triggering
    iv. Attach the BNC cables to the relevant ports on the side of the laser
        (These are labeled). The laser should start triggering and the Seeder
        pulse LED should start flashing.
    v. Open the internal shutter using the button on the remote control unit
        (ensuring all external black plunger shutters are closed)

11. Leave the instrument for 30 minutes or until the Cryogenerator has reached a stable
    low temperature.

**Turning on for Sample Analysis**

*The extra steps when setting up the instrument for sample analysis should only be
 carried out after all the previous steps are completed. These steps are not required
 when a sample is not being measured:*

1. Cycle the key switch
2. Push the power on button and wait for the display to prompt the next step
3. Push the pump power button and give the laser time to activate the pump
   and get the water flowing
4. Check the shutter is closed (the toggle is in the down position) and then
   press the flash lamps power button
5. The laser should now be ready to use when required.

Once you are ready to use the instrument and the temperature is constant and low, proceed to
the final stage of turning on:

12. Turn the electronics unit on, cycle the key and turn the dials so that they are set to the
    value displayed on the unit. Turn up the two accelerating plate voltages at the same
    time and roughly the same speed, this prevents a large potential difference building up
    and discharging across the ion source.
13. Open the shutters on the YAG to let the beams through the dye lasers.

The instrument is now ready to use. Please refer to the normal operating procedure section for
guidance on how to run analyses on the instrument.

**Running Analyses**
This section is subdivided into types of analyses that are commonly run. Deviation from these protocols should only be carried out under the supervision of an experienced and authorized user. For all these procedures there is an assumed initial set up. Please check this is true before continuing on to carry out any of the below procedures.

**Basic Assumed Setup**

The setup below is how the instrument should be left at any point when a user is not present for extended periods of time (unless otherwise specified by an experienced authorized user or when it is explicitly stated in a procedure detailed in this document).

Where red highlighting indicated a closed valve and green indicates an open valve. Further to this, if the instrument will be unattended for extended periods of time, the accelerating plates and einzel lens must be turned down to 0 and turned off.
Suggested Analysis Protocol

There are no strict reasons that analyses should be run in any particular order but the order laid out in this section aims to provide the maximum useful data from a sample and lowering the error as much as possible.

After turning on, it is suggested a series of air calibrations and blank assessments are carried out. This is particularly important if the spectrometer has undergone baking since the last time it was used. It is suggested that the time taken for each analysis type should be the same for any given sample. This prevents instrument bias or an inaccurate measurement of the instrument blank.

Suggested Protocol:

1x Air calibration analysis
   This is to check the instrument is functioning and producing the vuv wavelength required.

1x Air side blank analysis
1x Sample side blank analysis
   These are primarily to check for any residual contamination but are also useful for detecting leaks before a sample analysis is carried out

From here, the protocol varies depending on the sample you are analyzing. For a sample that will be step heated follow section A, for a complete single stage melting analysis follow section B. In the situation where a sample contains an unknown gas quantity it is often worth running a stepped heating method on the first grain (or in situation where the grain is suspected of being contaminated by a resin). This however is at the prerogative of the sample holder and the user.

Suggested Protocol (A):

1. 3x Air calibration analysis
2. 1x Air side blank analysis
3. 1x Sample side blank analysis
4. 1x Air calibration analysis
5. 3x Sample step analysis

Repeat steps 4 &5 as necessary. But when leaving the instrument (or after 3 cycles) it is worth running through steps 1, 2 & 3 again. The blanks must be carried out before turning the instrument off.

Suggested Protocol (B):

1. 3x Air calibration analysis
2. 2x Air side blank analysis
3. 2x Sample side blank analysis
4. 3x Air calibration analysis
5. 1x Sample analysis

Repeat steps 4 &5 as necessary. But when leaving the instrument (or after 3 cycles) it is worth running through steps 1, 2 & 3 again. The blanks must be carried out before turning the instrument off.

Air Calibration Analysis
These are the primary standard of this noble gas mass spectrometer.

1. Set the spectrometer up as shown in the diagram. Green highlighted valves should be open and red should be shut.
2. Close the Ion pump valve (1) on the air calibration side of the spectrometer.
3. Check that the dual valve (2) of the lower air calibration bottle has both aliquot stage valves shut.
4. Open the Right hand valve of the dual valve (3) of the upper air calibration bottle. Count to 5 then shut the valve.
5. Open the Left hand valve of the dual valve (3) of the upper air calibration bottle. Count to 5 and then shut the valve.
6. Close valve (4) to divide the air aliquot in two.
7. Open the ion pump valve (1) and count to 10. Close the ion pump valve.
8. Open the dividing valve (4) and count to 10. Close the dividing valve.
9. Open the ion pump valve (1).
10. Close the valve to the sample port side (5).
11. Open the valve to the flight tube (6) and count to 10.
12. On the data acquisition software, press stop and then clear, check the save box is ticked and then press start.
13. Check the details in the diary log are correct and watch the software.
14. Once it has completed the 3000 spectra it will begin counting again. When it does this, press stop, uncheck the save box and press start.
15. Close valve (6) and open valves (5) and (4).
Blank Analysis (Air Calibration Side)

The blank measurement for the air calibrations uses four times the amount of build up as would normally be present. This enhances the ability to detect it but must be taken into account for any data reduction and analysis.

1. Set the spectrometer up as shown in the diagram. Green highlighted valves should be open and red should be shut.
2. Close the Ion pump valve (1) on the air calibration side of the spectrometer.
3. Wait 2 minutes.
4. Close the valve to the sample port side (5).
5. Open the valve to the flight tube (6) and count to 10.
6. On the data acquisition software, press stop and then clear, check the save box and the 81Kr box are ticked and then press start.
7. Check the details in the diary log are correct and watch the software.
8. Once it has completed the 3000 spectra it will begin counting again. When it does this, press stop, uncheck the save and the 81Kr boxes and press start.
9. Close valve (6) and open valves (5) and (1).
Sample Analysis

For this procedure the sample heating CW laser must have been turned on during the turn on procedure.

1. Set the spectrometer up as shown in the diagram. Green highlighted valves should be open and red should be shut.
2. Close the valve to the flight tube from the sample port side (3) and open the valve between the flight tube and air cal side (2).
3. Make sure the air cal dividing valve is open (4).
4. Close the ion pump valve on the sample port side (5).
5. Laser heating section needs to be checked and added
6. On the data acquisition software, press stop and then clear, check the save box and the 81Kr box are ticked and then press start.
7. Check the details in the diary log are correct and watch the software.
8. Once it has completed the 3000 spectra it will begin counting again. When it does this, press stop, uncheck the save and the 81Kr boxes and press start.
9. Close valve (2) and open valve (5).
Blank Analysis (Sample Side)

The blank measurement for the Sample side uses the same amount of build up as would normally be present. It may also be used to check a sample port has been connected properly before sample analysis. If prominent peaks are seen on this type of blank it is normally indicative of a leak. If a leak is suspected, an authorized and experienced user should be called to assess the problem.

1. Set the spectrometer up as shown in the diagram. Green highlighted valves should be open and red should be shut.
2. Close the valve from the flight tube to the sample side (1) and open the valve from the flight tube to the air cal side (3)
3. Close the valve to the ion pump on the sample port side (2).
4. Wait 2 minutes.
5. Close the valve to the air cal side (3).
6. Open the valve to the flight tube from the sample side port (1) and count to 10
7. On the data acquisition software, press stop and then clear, check the save box and the 81Kr box are ticked and then press start.
8. Check the details in the diary log are correct and watch the software.
9. Once it has completed the 3000 spectra it will begin counting again. When it does this, press stop, uncheck the save and the 81Kr boxes and press start.
10. Close valve (3) and open valves (2) and (1)
Turning Off

1. Turn the electronics dials to 0 and turn off the unit, removing the key.
2. Turn the getter power supply dials to 0 and turn them off.
3. Close the external shutters on the YAG then press the stop button on the remote control for the YAG and disconnect the BNC cables.
4. Press the stop button on the Mini YAG power unit.

5. Turn the compressor unit off using the power switch on the compressor. Then turn the cooling button (left) on the control panel off, followed by the main power switch to the unit.

6. Turn off the two QC units

7. Cycle the key in the mini YAG power supply and remove it

8. Cycle the key in the YAG power supply, remove it and then turn the breakers to their off position, starting with the top, then the middle and finally the bottom. (The last breaker may cause a discharge within the power supply which will sound like an audible ping, this is normal)

9. Switch the seeder to manual and then cycle the key

11. **It should now be safe to remove laser goggles, only if RELAX is not on.**

10. **Turn off the water supplies (only turn off the red valves if RELAX is not on)**

12. Check the sample side valve is open to the flight tube and that the ion pump to that side is open.

13. Check that the air calibration side valve is shut to the flight tube and that the ion pump for that side is open

*The instrument is now safe to leave over night or over the weekend.*
### Appendix 8 – Bereba Eucrite Reduced Data

<table>
<thead>
<tr>
<th>Step</th>
<th>Atoms $^{84}_{Kr}$ x10^15</th>
<th>Atoms $^{81}_{Kr}$ x10^-18</th>
<th>$^{84}<em>{Kr}$/$^{84}</em>{Kr}$</th>
<th>$^{81}<em>{Kr}$/$^{81}</em>{Kr}$</th>
<th>$^{82}<em>{Kr}$/$^{82}</em>{Kr}$</th>
<th>$^{83}<em>{Kr}$/$^{83}</em>{Kr}$</th>
<th>$^{86}<em>{Kr}$/$^{86}</em>{Kr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bereba 1.45mg</td>
<td>16.35</td>
<td>0.1181</td>
<td>0.0527 (±0.0033)</td>
<td>0.00516 (±0.00045)</td>
<td>0.2504 (±0.0072)</td>
<td>0.2713 (±0.00247)</td>
<td>0.3313 (±0.0087)</td>
</tr>
<tr>
<td>Bereba 1.45mg</td>
<td>58.71</td>
<td>2.1849</td>
<td>0.2475 (±0.0083)</td>
<td>0.00588 (±0.00052)</td>
<td>0.472 (±0.0129)</td>
<td>0.7034 (±0.063)</td>
<td>0.2376 (±0.0097)</td>
</tr>
<tr>
<td>Bereba 1.45mg</td>
<td>32.17</td>
<td>1.1973</td>
<td>0.2888 (±0.0081)</td>
<td>0.00558 (±0.00049)</td>
<td>0.5115 (±0.0121)</td>
<td>0.7741 (±0.0683)</td>
<td>0.2415 (±0.0088)</td>
</tr>
<tr>
<td>Bereba 1.45mg</td>
<td>24.58</td>
<td>0.9148</td>
<td>0.4163 (±0.0113)</td>
<td>0.00325 (±0.00028)</td>
<td>0.675 (±0.0164)</td>
<td>1.1504 (±0.1014)</td>
<td>0.2195 (±0.0095)</td>
</tr>
<tr>
<td>Bereba 1.45mg</td>
<td>75.41</td>
<td>2.8064</td>
<td>0.3052 (±0.0069)</td>
<td>0.00725 (±0.00064)</td>
<td>0.5308 (±0.0101)</td>
<td>0.7118 (±0.0623)</td>
<td>0.2352 (±0.007)</td>
</tr>
<tr>
<td>Bereba 1.45mg</td>
<td>39.05</td>
<td>1.4532</td>
<td>0.2592 (±0.0059)</td>
<td>0.00541 (±0.00048)</td>
<td>0.4902 (±0.0092)</td>
<td>0.663 (±0.0578)</td>
<td>0.2464 (±0.0068)</td>
</tr>
<tr>
<td>Bereba 7.96mg</td>
<td>672.94</td>
<td>25.0442</td>
<td>0.3999 (±0.0024)</td>
<td>0.0047 (±0.00025)</td>
<td>0.6606 (±0.0034)</td>
<td>0.8172 (±0.0394)</td>
<td>0.2065 (±0.0017)</td>
</tr>
<tr>
<td>Bereba 7.96mg</td>
<td>223.98</td>
<td>8.3357</td>
<td>0.5283 (±0.0064)</td>
<td>0.00756 (±0.0004)</td>
<td>0.8318 (±0.0088)</td>
<td>1.0977 (±0.0539)</td>
<td>0.1637 (±0.0036)</td>
</tr>
<tr>
<td>Bereba 8.28mg</td>
<td>344.45</td>
<td>12.8190</td>
<td>0.5999 (±0.0086)</td>
<td>0.00689 (±0.00043)</td>
<td>0.922 (±0.0116)</td>
<td>1.0977 (±0.0641)</td>
<td>0.1519 (±0.004)</td>
</tr>
<tr>
<td>Bereba 8.28mg</td>
<td>191.62</td>
<td>7.1312</td>
<td>0.2298 (±0.0035)</td>
<td>0.00692 (±0.00041)</td>
<td>0.444 (±0.0052)</td>
<td>0.5239 (±0.0303)</td>
<td>0.2329 (±0.0037)</td>
</tr>
<tr>
<td>Bereba 8.28mg</td>
<td>145.83</td>
<td>5.4271</td>
<td>0.4218 (±0.0077)</td>
<td>0.00661 (±0.00041)</td>
<td>0.6824 (±0.0107)</td>
<td>0.8997 (±0.0529)</td>
<td>0.1954 (±0.0055)</td>
</tr>
<tr>
<td>Bereba 8.28mg</td>
<td>322.43</td>
<td>11.9994</td>
<td>0.5398 (±0.0085)</td>
<td>0.00797 (±0.0005)</td>
<td>0.8419 (±0.0115)</td>
<td>1.021 (±0.0599)</td>
<td>0.1902 (±0.0048)</td>
</tr>
</tbody>
</table>
### Appendix 9 – Stannern Eucrite Reduced Data

<table>
<thead>
<tr>
<th>Step</th>
<th>Atoms $^{84}$Kr</th>
<th>Atoms $^{81}$Kr</th>
<th>$^{84}$ccSTP x10^-15</th>
<th>$^{81}$ccSTP x10^-18</th>
<th>$^{80}$Kr /$^{84}$Kr</th>
<th>$^{81}$Kr /$^{84}$Kr</th>
<th>$^{82}$Kr /$^{84}$Kr</th>
<th>$^{83}$Kr /$^{84}$Kr</th>
<th>$^{86}$Kr /$^{84}$Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannern 3.19mg CW 15% (~9W)</td>
<td>21822.64</td>
<td>39.60</td>
<td>0.8122</td>
<td>1.4736</td>
<td>0.4566 (±0.013)</td>
<td>0.00181 (±0.00011)</td>
<td>0.7701 (±0.0185)</td>
<td>1.1095 (±0.0682)</td>
<td>0.1698 (±0.0086)</td>
</tr>
<tr>
<td>Stannern 3.19mg Pulsed 35µs 10% (~1.5W)</td>
<td>111427.64</td>
<td>218.35</td>
<td>4.1469</td>
<td>8.1260</td>
<td>0.2084 (±0.002)</td>
<td>0.00196 (±0.00012)</td>
<td>0.4288 (±0.0031)</td>
<td>0.4991 (±0.0285)</td>
<td>0.2467 (±0.0023)</td>
</tr>
<tr>
<td>Stannern 3.19mg Pulsed 45µs 10% (~2.5W)</td>
<td>52029.56</td>
<td>192.67</td>
<td>1.9363</td>
<td>7.1706</td>
<td>0.6151 (±0.0101)</td>
<td>0.0037 (±0.00023)</td>
<td>0.9599 (±0.014)</td>
<td>1.3258 (±0.0777)</td>
<td>0.1802 (±0.0054)</td>
</tr>
<tr>
<td>Stannern 3.19mg Pulsed 80µs 10% (~5W)</td>
<td>53079.76</td>
<td>215.45</td>
<td>1.9754</td>
<td>8.0180</td>
<td>0.6169 (±0.0092)</td>
<td>0.00406 (±0.00025)</td>
<td>0.9626 (±0.0126)</td>
<td>1.3226 (±0.0771)</td>
<td>0.1605 (±0.0046)</td>
</tr>
<tr>
<td>Stannern 5.18mg CW 20% (~12W)</td>
<td>395100.47</td>
<td>1734.34</td>
<td>14.7040</td>
<td>64.5452</td>
<td>0.6288 (±0.0177)</td>
<td>0.00439 (±0.0003)</td>
<td>0.9156 (±0.0153)</td>
<td>1.0529 (±0.0665)</td>
<td>0.1854 (±0.0035)</td>
</tr>
<tr>
<td>Stannern 5.18mg CW 25% (~14W)</td>
<td>41791.95</td>
<td>984.31</td>
<td>1.5553</td>
<td>36.6322</td>
<td>0.2328 (±0.0104)</td>
<td>0.02355 (±0.00165)</td>
<td>0.4355 (±0.0141)</td>
<td>0.6325 (±0.0431)</td>
<td>0.2143 (±0.0104)</td>
</tr>
</tbody>
</table>
## Appendix 10 – Bereba Eucrite CRE Age Data

<table>
<thead>
<tr>
<th>Step</th>
<th>$81 \text{ ccSTP \times 10^{-18}}$</th>
<th>Prod Rate</th>
<th>Error</th>
<th>CRE</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bereba 1.45mg &lt;1W</td>
<td>0.6086</td>
<td>0.366781</td>
<td>0.247985</td>
<td>1.23783</td>
<td>0.759293</td>
<td>61.34%</td>
</tr>
<tr>
<td>Bereba 1.45mg 1W</td>
<td>2.1849</td>
<td>0.46167</td>
<td>0.069594</td>
<td>14.15416</td>
<td>2.672724</td>
<td>18.88%</td>
</tr>
<tr>
<td>Bereba 1.45mg 1.5W</td>
<td>1.1973</td>
<td>0.47058</td>
<td>0.06553</td>
<td>17.10731</td>
<td>3.08775</td>
<td>18.05%</td>
</tr>
<tr>
<td>Bereba 1.45mg 2.5W</td>
<td>0.9148</td>
<td>0.433353</td>
<td>0.057395</td>
<td>44.29468</td>
<td>7.550106</td>
<td>17.05%</td>
</tr>
<tr>
<td>Bereba 1.45mg 5W</td>
<td>2.8064</td>
<td>0.5544</td>
<td>0.073211</td>
<td>14.05306</td>
<td>2.587957</td>
<td>18.42%</td>
</tr>
<tr>
<td>Bereba 1.45mg 7W</td>
<td>1.4532</td>
<td>0.525958</td>
<td>0.071227</td>
<td>16.06338</td>
<td>2.953988</td>
<td>18.39%</td>
</tr>
<tr>
<td>Bereba 7.96mg 5W*</td>
<td>25.0442</td>
<td>0.625626</td>
<td>0.038948</td>
<td>29.93754</td>
<td>2.930873</td>
<td>9.79%</td>
</tr>
<tr>
<td>Bereba 7.96mg 9W*</td>
<td>8.3357</td>
<td>0.590575</td>
<td>0.040376</td>
<td>25.52188</td>
<td>2.588377</td>
<td>10.14%</td>
</tr>
<tr>
<td>Bereba 8.28mg 14W</td>
<td>12.8190</td>
<td>0.667425</td>
<td>0.053979</td>
<td>31.88822</td>
<td>4.002678</td>
<td>12.55%</td>
</tr>
<tr>
<td>Bereba 8.28mg 1.5W</td>
<td>7.1312</td>
<td>0.62771</td>
<td>0.058697</td>
<td>11.09133</td>
<td>1.500905</td>
<td>13.53%</td>
</tr>
<tr>
<td>Bereba 8.28mg 2.5W</td>
<td>5.4271</td>
<td>0.585073</td>
<td>0.052019</td>
<td>22.52509</td>
<td>2.858602</td>
<td>12.69%</td>
</tr>
<tr>
<td>Bereba 8.28mg 5W</td>
<td>11.9994</td>
<td>0.65299</td>
<td>0.05409</td>
<td>24.22204</td>
<td>3.064185</td>
<td>12.65%</td>
</tr>
</tbody>
</table>
## Appendix 11 – Stannern Eucrite CRE Age Data

<table>
<thead>
<tr>
<th>Step</th>
<th>81 ccSTP x10^-18</th>
<th>Prod Rate</th>
<th>Error</th>
<th>CRE</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannern 3.19mg CW 15% (~9W)</td>
<td>1.4736</td>
<td>0.520059</td>
<td>0.059723</td>
<td>94.35119</td>
<td>13.88711</td>
<td>14.72%</td>
</tr>
<tr>
<td>Stannern 3.19mg Pulsed 35µs 10% (~1.5W)</td>
<td>8.1260</td>
<td>0.623895</td>
<td>0.057248</td>
<td>35.33844</td>
<td>4.748893</td>
<td>13.44%</td>
</tr>
<tr>
<td>Stannern 3.19mg Pulsed 45µs 10% (~2.5W)</td>
<td>7.1706</td>
<td>0.563677</td>
<td>0.04784</td>
<td>60.62727</td>
<td>7.367132</td>
<td>12.15%</td>
</tr>
<tr>
<td>Stannern 3.19mg Pulsed 80µs 10% (~5W)</td>
<td>8.0180</td>
<td>0.567053</td>
<td>0.046369</td>
<td>56.09223</td>
<td>6.672615</td>
<td>11.90%</td>
</tr>
<tr>
<td>Stannern 5.18mg CW 20% (~12W)</td>
<td>64.5452</td>
<td>0.713381</td>
<td>0.059861</td>
<td>49.90606</td>
<td>6.743386</td>
<td>13.51%</td>
</tr>
<tr>
<td>Stannern 5.18mg CW 25% (~14W)</td>
<td>36.6322</td>
<td>0.482303</td>
<td>0.068226</td>
<td>3.318959</td>
<td>0.561411</td>
<td>16.92%</td>
</tr>
</tbody>
</table>
## Appendix 12 – Alternative Method CRE Age Calculation Data

<table>
<thead>
<tr>
<th>Heating step (W)</th>
<th>1.5</th>
<th>2.5</th>
<th>5</th>
<th>9</th>
<th>1.5</th>
<th>2.5</th>
<th>5</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>int Age at t=0</td>
<td>29.63786</td>
<td>35.26345</td>
<td>38.8966</td>
<td>43.2292</td>
<td>14.8277</td>
<td>46.615</td>
<td>23.69348</td>
<td>26.31617</td>
</tr>
<tr>
<td>int err Error on Age</td>
<td>10.07298</td>
<td>3.640828</td>
<td>12.42279</td>
<td>10.09054</td>
<td>2.199168</td>
<td>7.177081</td>
<td>4.26313</td>
<td>4.936185</td>
</tr>
<tr>
<td>grad Decrease per pulse</td>
<td>-0.00705</td>
<td>-0.00994</td>
<td>-0.0107</td>
<td>-0.01109</td>
<td>-0.00378</td>
<td>-0.01322</td>
<td>-0.00407</td>
<td>-0.00585</td>
</tr>
<tr>
<td>grad err</td>
<td>0.004518</td>
<td>0.001446</td>
<td>0.006579</td>
<td>0.004411</td>
<td>0.001009</td>
<td>0.003596</td>
<td>0.002204</td>
<td>0.002351</td>
</tr>
<tr>
<td>cov</td>
<td>-0.04181</td>
<td>-0.00498</td>
<td>-0.07619</td>
<td>-0.04139</td>
<td>-0.00208</td>
<td>-0.02438</td>
<td>-0.00822</td>
<td>-0.01046</td>
</tr>
<tr>
<td>chi</td>
<td>1.89938</td>
<td>16.45658</td>
<td>2.31018</td>
<td>15.18964</td>
<td>12.34805</td>
<td>22.32262</td>
<td>4.348051</td>
<td>3.185556</td>
</tr>
<tr>
<td>Sample Mass</td>
<td>3.19</td>
<td>3.19</td>
<td>3.19</td>
<td>3.19</td>
<td>8.28</td>
<td>8.28</td>
<td>8.28</td>
<td>8.28</td>
</tr>
<tr>
<td>Mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Amount Monitor</td>
<td>84 initial</td>
<td>136529</td>
<td>62028</td>
<td>63165.5</td>
<td>64157</td>
<td>37094</td>
<td>67039</td>
<td>53924.62</td>
</tr>
<tr>
<td>Monitor 83 Initial</td>
<td>52332</td>
<td>57258.99</td>
<td>60045.01</td>
<td>46602</td>
<td>13606</td>
<td>41663.01</td>
<td>39840.98</td>
<td>50028.99</td>
</tr>
<tr>
<td>Monitor 86 Initial</td>
<td>33063.59</td>
<td>11634.59</td>
<td>10441.21</td>
<td>11090</td>
<td>8633.205</td>
<td>12859.21</td>
<td>10173.97</td>
<td>9572.795</td>
</tr>
<tr>
<td>83/84</td>
<td>0.383303</td>
<td>0.923115</td>
<td>0.950598</td>
<td>0.726374</td>
<td>0.366798</td>
<td>0.621474</td>
<td>0.738827</td>
<td>0.803014</td>
</tr>
<tr>
<td>86/84</td>
<td>0.242173</td>
<td>0.18757</td>
<td>0.165299</td>
<td>0.172857</td>
<td>0.232739</td>
<td>0.191817</td>
<td>0.18867</td>
<td>0.153653</td>
</tr>
<tr>
<td>83/86</td>
<td>1.582768</td>
<td>4.921445</td>
<td>5.750774</td>
<td>4.202164</td>
<td>1.576008</td>
<td>3.239936</td>
<td>3.91597</td>
<td>5.226164</td>
</tr>
<tr>
<td>cosmogenic 83</td>
<td>0.923068</td>
<td>4.261745</td>
<td>5.091074</td>
<td>3.542464</td>
<td>0.916308</td>
<td>2.580236</td>
<td>3.25627</td>
<td>4.566464</td>
</tr>
</tbody>
</table>

211
Appendix 13 – A table of measurements carried out for the CAI measurements.
<table>
<thead>
<tr>
<th>Slide Number</th>
<th>CAI ID</th>
<th>Fragment Number</th>
<th>Mass (mg)</th>
<th>Analysis Date</th>
<th>File Number</th>
<th>Laser Power (W)</th>
<th>Laser Type</th>
<th>Laser Power (%)</th>
<th>Laser Pulse duration (µs)</th>
<th>Measurement Scale (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>15/04/2016</td>
<td>1115</td>
<td>7</td>
<td>CW</td>
<td>10</td>
<td>50</td>
<td>2.0</td>
</tr>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>07/04/2016</td>
<td>1116</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>06/04/2016</td>
<td>1116</td>
<td>&lt;1</td>
<td>Pulsed</td>
<td>10</td>
<td>55</td>
<td>1.0</td>
</tr>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>06/04/2016</td>
<td>1117</td>
<td>1</td>
<td>Pulsed</td>
<td>10</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>06/04/2016</td>
<td>1119</td>
<td>1.5</td>
<td>Pulsed</td>
<td>10</td>
<td>35</td>
<td>1.0</td>
</tr>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>06/04/2016</td>
<td>1120</td>
<td>2</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td>10a</td>
<td>CAI</td>
<td>~</td>
<td>0.79</td>
<td>06/04/2016</td>
<td>1121</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>45</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>1</td>
<td>2.11</td>
<td>02/02/2016</td>
<td>1128</td>
<td>19</td>
<td>CW</td>
<td>35</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>2</td>
<td>4.09</td>
<td>02/02/2016</td>
<td>1119</td>
<td>12</td>
<td>CW</td>
<td>20</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>2</td>
<td>4.09</td>
<td>02/02/2016</td>
<td>1124</td>
<td>14</td>
<td>CW</td>
<td>25</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>2</td>
<td>4.09</td>
<td>02/02/2016</td>
<td>1126</td>
<td>19</td>
<td>CW</td>
<td>35</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1115</td>
<td>&lt;1</td>
<td>Pulsed</td>
<td>10</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1116</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1116</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>80</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1117</td>
<td>5.5</td>
<td>Pulsed</td>
<td>10</td>
<td>85</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>05/02/2016</td>
<td>1117</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>05/02/2016</td>
<td>1118</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1118</td>
<td>6</td>
<td>Pulsed</td>
<td>10</td>
<td>90</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1118</td>
<td>1.5</td>
<td>Pulsed</td>
<td>10</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>05/02/2016</td>
<td>1119</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1119</td>
<td>4</td>
<td>Pulsed</td>
<td>10</td>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1120</td>
<td>4</td>
<td>Pulsed</td>
<td>10</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1120</td>
<td>6.5</td>
<td>Pulsed</td>
<td>10</td>
<td>95</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1120</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>05/02/2016</td>
<td>1121</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1121</td>
<td>4.5</td>
<td>Pulsed</td>
<td>10</td>
<td>65</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1121</td>
<td>7</td>
<td>CW</td>
<td>10</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-------</td>
<td>----</td>
<td>------</td>
<td>------------</td>
<td>------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>05/02/2016</td>
<td>1122</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>80</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1122</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1122</td>
<td>9</td>
<td>CW</td>
<td>15</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1123</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1123</td>
<td>4.5</td>
<td>Pulsed</td>
<td>10</td>
<td>70</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1124</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1124</td>
<td>4.5</td>
<td>Pulsed</td>
<td>10</td>
<td>70</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1124</td>
<td>9</td>
<td>CW</td>
<td>15</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>02/08/2016</td>
<td>1125</td>
<td>9</td>
<td>CW</td>
<td>15</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>04/02/2016</td>
<td>1125</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1126</td>
<td>12</td>
<td>CW</td>
<td>20</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1126</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1127</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>08/02/2016</td>
<td>1128</td>
<td>17</td>
<td>CW</td>
<td>30</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>CAI 3</td>
<td>4</td>
<td>5.68</td>
<td>03/02/2016</td>
<td>1128</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>18/04/2016</td>
<td>1115</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>80</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>18/04/2016</td>
<td>1116</td>
<td>7</td>
<td>CW</td>
<td>10</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1116</td>
<td>1</td>
<td>Pulsed</td>
<td>10</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1118</td>
<td>2</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1119</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>45</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1120</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1122</td>
<td>3.5</td>
<td>Pulsed</td>
<td>10</td>
<td>55</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1123</td>
<td>4</td>
<td>Pulsed</td>
<td>10</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>3a</td>
<td>Matrix</td>
<td>~</td>
<td>0.99</td>
<td>15/04/2016</td>
<td>1124</td>
<td>4.5</td>
<td>Pulsed</td>
<td>10</td>
<td>65</td>
<td>0.5</td>
</tr>
<tr>
<td>6a</td>
<td>CAI 3</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1117</td>
<td>&lt;1</td>
<td>Pulsed</td>
<td>10</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>CAI 3</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1118</td>
<td>1</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>6a</td>
<td>CAI 3</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1119</td>
<td>1</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>6a</td>
<td>CAI 3</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1124</td>
<td>1.5</td>
<td>Pulsed</td>
<td>10</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>6a</td>
<td>CAI 3</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1125</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>6a</td>
<td>CAI 3</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1126</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1128</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1129</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1130</td>
<td>3.5</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1131</td>
<td>3.5</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1133</td>
<td>6</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1134</td>
<td>6</td>
<td>Pulsed</td>
<td>10</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>6a</td>
<td>CAI</td>
<td>~</td>
<td>0.54</td>
<td>17/03/2016</td>
<td>1135</td>
<td>7</td>
<td>CW</td>
<td>10</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>7a</td>
<td>CAI</td>
<td>r</td>
<td>0.67</td>
<td>16/03/2016</td>
<td>1116</td>
<td>14</td>
<td>CW</td>
<td>25</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>7a</td>
<td>CAI</td>
<td>r</td>
<td>0.67</td>
<td>16/03/2016</td>
<td>1117</td>
<td>14</td>
<td>CW</td>
<td>25</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>7a</td>
<td>CAI</td>
<td>r</td>
<td>0.67</td>
<td>16/03/2016</td>
<td>1118</td>
<td>17</td>
<td>CW</td>
<td>30</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1119</td>
<td>&lt;1</td>
<td>Pulsed</td>
<td>10</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1121</td>
<td>1</td>
<td>Pulsed</td>
<td>10</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1122</td>
<td>1.5</td>
<td>Pulsed</td>
<td>10</td>
<td>35</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1123</td>
<td>2</td>
<td>Pulsed</td>
<td>10</td>
<td>40</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1124</td>
<td>2.5</td>
<td>Pulsed</td>
<td>10</td>
<td>45</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1125</td>
<td>2.75</td>
<td>Pulsed</td>
<td>10</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1127</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>55</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1129</td>
<td>3.5</td>
<td>Pulsed</td>
<td>10</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1130</td>
<td>5</td>
<td>Pulsed</td>
<td>10</td>
<td>80</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 2</td>
<td>~</td>
<td>0.72</td>
<td>22/03/2016</td>
<td>1131</td>
<td>7</td>
<td>CW</td>
<td>10</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 1</td>
<td>~</td>
<td>0.55</td>
<td>16/03/2016</td>
<td>1125</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 1</td>
<td>~</td>
<td>0.55</td>
<td>16/03/2016</td>
<td>1126</td>
<td>3</td>
<td>Pulsed</td>
<td>10</td>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 1</td>
<td>~</td>
<td>0.55</td>
<td>16/03/2016</td>
<td>1128</td>
<td>4</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>0.5</td>
</tr>
<tr>
<td>8a</td>
<td>CAI 1</td>
<td>~</td>
<td>0.55</td>
<td>16/03/2016</td>
<td>1129</td>
<td>4</td>
<td>Pulsed</td>
<td>10</td>
<td>75</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Appendix 14 – A table of reduced CAI sample data. All ratios have been corrected for instrument mass discrimination, as well as instrument signal dependent mass discrimination.
<table>
<thead>
<tr>
<th>Step</th>
<th>Atoms $^{84}$Kr</th>
<th>Atoms $^{83}$Kr</th>
<th>$^{80}$Kr $^{84}$Kr</th>
<th>$^{81}$Kr $^{84}$Kr</th>
<th>$^{82}$Kr $^{84}$Kr</th>
<th>$^{83}$Kr $^{84}$Kr</th>
<th>$^{86}$Kr $^{84}$Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a CAI 3 (2) 4.09mg CW 20% (~12W)</td>
<td>424923.64</td>
<td>-36.87</td>
<td>0.0896 (±0.004)</td>
<td>-0.00009 (±0.00002)</td>
<td>0.3013 (±0.0145)</td>
<td>0.3156 (±0.0152)</td>
<td>0.531 (±0.0194)</td>
</tr>
<tr>
<td>3a CAI 3 (2) 4.09mg CW 25% (~14W)</td>
<td>1603901.92</td>
<td>526.36</td>
<td>0.0666 (±0.0043)</td>
<td>0</td>
<td>0.2871 (±0.0131)</td>
<td>0.276 (±0.0126)</td>
<td>0.2687 (±0.0141)</td>
</tr>
<tr>
<td>3a CAI 3 (2) 4.09mg CW 35% (~19W)</td>
<td>157106.94</td>
<td>223.82</td>
<td>0.0437 (±0.0014)</td>
<td>0.00142 (±0.00063)</td>
<td>0.1833 (±0.0038)</td>
<td>0.1766 (±0.0047)</td>
<td>0.3419 (±0.0059)</td>
</tr>
<tr>
<td>3a CAI 3 (1) 2.11mg CW 35% (~19W)</td>
<td>432933.56</td>
<td>455.03</td>
<td>0.1391 (±0.0025)</td>
<td>0.00105 (±0.00055)</td>
<td>0.2555 (±0.0041)</td>
<td>0.2077 (±0.0048)</td>
<td>0.2758 (±0.0037)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 20µs Pulsed 10% (~&lt;1W)</td>
<td>7714.74</td>
<td>94.75</td>
<td>0.0438 (±0.0032)</td>
<td>0.01228 (±0.00443)</td>
<td>0.1963 (±0.0071)</td>
<td>0.1699 (±0.0096)</td>
<td>0.3648 (±0.0112)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 30µs Pulsed 10% (~1.5W)</td>
<td>450212.11</td>
<td>124.77</td>
<td>0.1325 (±0.0025)</td>
<td>0.00028 (±0.00014)</td>
<td>0.2264 (±0.0034)</td>
<td>0.1915 (±0.0078)</td>
<td>0.2937 (±0.0033)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (first heating)</td>
<td>1752081.55</td>
<td>-192.08</td>
<td>0.1295 (±0.0106)</td>
<td>0</td>
<td>0.2454 (±0.0146)</td>
<td>0.2237 (±0.0163)</td>
<td>0.2817 (±0.0209)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (second heating)</td>
<td>990725.64</td>
<td>-61.25</td>
<td>0.0922 (±0.0061)</td>
<td>0</td>
<td>0.1977 (±0.0088)</td>
<td>0.1936 (±0.0108)</td>
<td>0.3341 (±0.0147)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (third heating)</td>
<td>442378.21</td>
<td>111.38</td>
<td>0.1046 (±0.0024)</td>
<td>0.00025 (±0.00009)</td>
<td>0.1996 (±0.0036)</td>
<td>0.1835 (±0.0078)</td>
<td>0.3278 (±0.0048)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (fourth heating)</td>
<td>320253.08</td>
<td>63.51</td>
<td>0.1082 (±0.0024)</td>
<td>0.0002 (±0.00007)</td>
<td>0.2078 (±0.0034)</td>
<td>0.1827 (±0.0077)</td>
<td>0.3351 (±0.0047)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (fifth heating)</td>
<td>357936.48</td>
<td>38.80</td>
<td>0.1052 (±0.0023)</td>
<td>0.00011 (±0.00004)</td>
<td>0.2036 (±0.0035)</td>
<td>0.1866 (±0.0078)</td>
<td>0.3319 (±0.0044)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (sixth heating, 2 mins +1 getter)</td>
<td>442840.28</td>
<td>34.95</td>
<td>0.0913 (±0.0022)</td>
<td>0.00008 (±0.00003)</td>
<td>0.1998 (±0.0036)</td>
<td>0.1817 (±0.0077)</td>
<td>0.3234 (±0.0048)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (seventh heating, 2 mins +1 getter)</td>
<td>291554.74</td>
<td>52.20</td>
<td>0.1 (±0.0024)</td>
<td>0.00018 (±0.00006)</td>
<td>0.1999 (±0.0037)</td>
<td>0.1809 (±0.0077)</td>
<td>0.3343 (±0.0049)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 40µs Pulsed 10% (~2.5W)  (eightth heating, 5mins +1 getter)</td>
<td>420985.24</td>
<td>-106.10</td>
<td>0.1042 (±0.003)</td>
<td>-0.00025 (±0.00008)</td>
<td>0.2159 (±0.0044)</td>
<td>0.1875 (±0.0056)</td>
<td>0.3179 (±0.0044)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 50µs Pulsed 10% (~3W)</td>
<td>1655083.66</td>
<td>-291.94</td>
<td>0.0875 (±0.0048)</td>
<td>0</td>
<td>0.199 (±0.0076)</td>
<td>0.1951 (±0.0067)</td>
<td>0.3204 (±0.0123)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 60µs Pulsed 10% (~4W)</td>
<td>2977829.33</td>
<td>-427.19</td>
<td>0.0804 (±0.0081)</td>
<td>-0.00009 (±0.00006)</td>
<td>0.2318 (±0.0172)</td>
<td>0.2357 (±0.0195)</td>
<td>0.2833 (±0.0307)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 60µs Pulsed 10% (~4W)  (second heating)</td>
<td>1056354.81</td>
<td>-49.08</td>
<td>0.0604 (±0.0051)</td>
<td>0</td>
<td>0.1887 (±0.0105)</td>
<td>0.1883 (±0.0107)</td>
<td>0.3121 (±0.0161)</td>
</tr>
<tr>
<td>Test Description</td>
<td>Current (μA)</td>
<td>Voltage (V)</td>
<td>P (W)</td>
<td>T (°C)</td>
<td>LF (μs)</td>
<td>SF (μs)</td>
<td>Analyte (ppm)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------------</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 65µs Pulsed 10% (~4.5W)</td>
<td>1259191.80</td>
<td>-32.52</td>
<td>0.053 (±0.0036)</td>
<td>0</td>
<td>0.1913 (±0.0086)</td>
<td>0.1931 (±0.0089)</td>
<td>0.3229 (±0.014)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 70µs Pulsed 10% (~4.5W) (first heating)</td>
<td>1403942.23</td>
<td>-179.27</td>
<td>0.0479 (±0.0028)</td>
<td>0</td>
<td>0.1868 (±0.0072)</td>
<td>0.1903 (±0.007)</td>
<td>0.3221 (±0.0121)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 75µs Pulsed 10% (~5W) (first heating)</td>
<td>384821.29</td>
<td>74.54</td>
<td>0.0485 (±0.0016)</td>
<td>0.00019 (±0.00005)</td>
<td>0.1946 (±0.0039)</td>
<td>0.1929 (±0.0054)</td>
<td>0.3221 (±0.0041)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 75µs Pulsed 10% (~5W) (second heating)</td>
<td>941724.04</td>
<td>50.59</td>
<td>0.0437 (±0.0041)</td>
<td>0</td>
<td>0.193 (±0.0117)</td>
<td>0.1878 (±0.0116)</td>
<td>0.3221 (±0.0178)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 75µs Pulsed 10% (~5W) (third heating 2mins +1 getter)</td>
<td>769258.76</td>
<td>28.56</td>
<td>0.0389 (±0.0038)</td>
<td>0.00003 (±0.00001)</td>
<td>0.187 (±0.0131)</td>
<td>0.1856 (±0.0154)</td>
<td>0.3275 (±0.0192)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 75µs Pulsed 10% (~5W) (fourth heating 2mins +1 getter)</td>
<td>591501.21</td>
<td>93.37</td>
<td>0.0413 (±0.0013)</td>
<td>0.00016 (±0.00001)</td>
<td>0.187 (±0.0071)</td>
<td>0.1762 (±0.0107)</td>
<td>0.3178 (±0.0065)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 75µs Pulsed 10% (~5W) (fifth heating 2mins +1 getter)</td>
<td>372453.86</td>
<td>190.27</td>
<td>0.0435 (±0.0014)</td>
<td>0.00051 (±0.00017)</td>
<td>0.1888 (±0.0071)</td>
<td>0.1744 (±0.0106)</td>
<td>0.3233 (±0.0067)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 80µs Pulsed 10% (~5W)</td>
<td>1130241.86</td>
<td>114.70</td>
<td>0.0401 (±0.0025)</td>
<td>0</td>
<td>0.1825 (±0.0095)</td>
<td>0.1794 (±0.0121)</td>
<td>0.3264 (±0.014)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 80µs Pulsed 10% (~5W) (Second heating ~10mins)</td>
<td>1656441.12</td>
<td>-1.12</td>
<td>0.0366 (±0.0037)</td>
<td>0</td>
<td>0.1789 (±0.0126)</td>
<td>0.1982 (±0.0201)</td>
<td>0.3399 (±0.0295)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 85µs Pulsed 10% (~5.5W)</td>
<td>332868.12</td>
<td>93.54</td>
<td>0.0379 (±0.0023)</td>
<td>0.00028 (±0.00013)</td>
<td>0.1754 (±0.0067)</td>
<td>0.1968 (±0.0158)</td>
<td>0.3426 (±0.0105)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 90µs Pulsed 10% (~6W)</td>
<td>83416.03</td>
<td>150.21</td>
<td>0.0366 (±0.0028)</td>
<td>0</td>
<td>0.1716 (±0.0087)</td>
<td>0.1884 (±0.0159)</td>
<td>0.3456 (±0.0164)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg 95µs Pulsed 10% (~6.5W)</td>
<td>1356218.90</td>
<td>169.25</td>
<td>0.0364 (±0.0031)</td>
<td>0</td>
<td>0.1723 (±0.0101)</td>
<td>0.1825 (±0.0167)</td>
<td>0.3525 (±0.0224)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg CW 10% (~7W)</td>
<td>1684770.06</td>
<td>45.49</td>
<td>0.0377 (±0.0038)</td>
<td>0</td>
<td>0.1767 (±0.0126)</td>
<td>0.1835 (±0.0188)</td>
<td>0.3432 (±0.0304)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg CW 15% (~9W) (first heating) (saturated)</td>
<td>330082.34</td>
<td>-155.59</td>
<td>0.0387 (±0.0049)</td>
<td>-0.00002 (±0.00002)</td>
<td>0.1792 (±0.0176)</td>
<td>0.2216 (±0.0295)</td>
<td>0.3798 (±0.0862)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg CW 15% (~9W) (second heating) (saturated)</td>
<td>289070.87</td>
<td>11.79</td>
<td>0.0418 (±0.0053)</td>
<td>0 (±0)</td>
<td>0.2042 (±0.0195)</td>
<td>0.2326 (±0.0302)</td>
<td>0.3111 (±0.0594)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg CW 15% (~9W) (third heating) (saturated)</td>
<td>418399.51</td>
<td>46.09</td>
<td>0.0389 (±0.0019)</td>
<td>0.00011 (±0.00007)</td>
<td>0.1877 (±0.0062)</td>
<td>0.179 (±0.0139)</td>
<td>0.3331 (±0.0085)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg CW 20% (~12W)</td>
<td>45338.82</td>
<td>71.67</td>
<td>0.0497 (±0.0025)</td>
<td>0.00158 (±0.00074)</td>
<td>0.1794 (±0.0064)</td>
<td>0.1806 (±0.0142)</td>
<td>0.3551 (±0.0099)</td>
</tr>
<tr>
<td>3a CAI 3 (4) 5.68mg CW 30% (~17W)</td>
<td>120021.44</td>
<td>104.05</td>
<td>0.0373 (±0.002)</td>
<td>0.00087 (±0.00032)</td>
<td>0.174 (±0.0061)</td>
<td>0.1767 (±0.0139)</td>
<td>0.348 (±0.0095)</td>
</tr>
<tr>
<td>7a CAI (round CAI) 0.67mg CW 25% (~14W) (Saturation problems)</td>
<td>511505.46</td>
<td>-34.82</td>
<td>0.0592 (±0.0059)</td>
<td>-0.0001 (±0.00003)</td>
<td>0.2227 (±0.0159)</td>
<td>0.2033 (±0.0221)</td>
<td>0.2942 (±0.0302)</td>
</tr>
<tr>
<td>Sample</td>
<td>Power (W)</td>
<td>Energy (mJ)</td>
<td>Time (us)</td>
<td>FWHM (pm)</td>
<td>Damping (ps)</td>
<td>Recovery (ps)</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>-------------</td>
<td>-----------</td>
<td>-----------</td>
<td>-------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>7a CAI (round CAI) 0.67mg CW 25% (~14W) (second heating)</td>
<td>113102.82</td>
<td>39.58</td>
<td>0.0461 (±0.0017)</td>
<td>0.00035 (±0.00015)</td>
<td>0.2048 (±0.0035)</td>
<td>0.2027 (±0.0143)</td>
<td>0.3011 (±0.0045)</td>
</tr>
<tr>
<td>7a CAI (round CAI) 0.67mg CW 30% (~17W)</td>
<td>10034.93</td>
<td>54.45</td>
<td>0.043 (±0.0027)</td>
<td>0.00543 (±0.00251)</td>
<td>0.2182 (±0.006)</td>
<td>0.2145 (±0.016)</td>
<td>0.3257 (±0.0077)</td>
</tr>
<tr>
<td>8a CAI 0.55mg 50µs Pulsed 10% (~3W) (Small Aliquot)</td>
<td>27567.27</td>
<td>24.86</td>
<td>0.2105 (±0.0045)</td>
<td>0.0009 (±0.00035)</td>
<td>0.2714 (±0.0055)</td>
<td>0.225 (±0.0162)</td>
<td>0.3162 (±0.0062)</td>
</tr>
<tr>
<td>8a CAI 0.55mg 75µs Pulsed 10% (~4W) (Small Aliquot)</td>
<td>39949.89</td>
<td>29.65</td>
<td>0.0787 (±0.0027)</td>
<td>0.00074 (±0.00029)</td>
<td>0.2182 (±0.006)</td>
<td>0.2145 (±0.0162)</td>
<td>0.3088 (±0.0059)</td>
</tr>
<tr>
<td>8a CAI 0.55mg 75µs Pulsed 10% (~4W) (Small Aliquot)</td>
<td>7485.47</td>
<td>25.37</td>
<td>0.0657 (±0.0036)</td>
<td>0.00339 (±0.00156)</td>
<td>0.2238 (±0.0068)</td>
<td>0.2151 (±0.0166)</td>
<td>0.3047 (±0.0085)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 20 µs Pulsed 10% (~&lt;1W) (Small Aliquot)</td>
<td>7994.93</td>
<td>2.96</td>
<td>0.0801 (±0.0035)</td>
<td>0.00037 (±0.00014)</td>
<td>0.2218 (±0.0063)</td>
<td>0.2149 (±0.024)</td>
<td>0.3141 (±0.0078)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 30 µs Pulsed 10% (~1W) (Small Aliquot)</td>
<td>83602.01</td>
<td>-4.54</td>
<td>0.2162 (±0.0016)</td>
<td>-0.00005 (±0.00002)</td>
<td>0.2616 (±0.0019)</td>
<td>0.1974 (±0.021)</td>
<td>0.3051 (±0.0021)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 35 µs Pulsed 10% (~1.5W) (Small Aliquot)</td>
<td>21736.67</td>
<td>24.96</td>
<td>0.1203 (±0.0045)</td>
<td>0.00115 (±0.00056)</td>
<td>0.2395 (±0.007)</td>
<td>0.246 (±0.0275)</td>
<td>0.3109 (±0.0084)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 45 µs Pulsed 10% (~2.5W) (Small Aliquot)</td>
<td>168805.55</td>
<td>44.82</td>
<td>0.0699 (±0.0072)</td>
<td>0.00023 (±0.00009)</td>
<td>0.2102 (±0.0138)</td>
<td>0.199 (±0.0247)</td>
<td>0.2911 (±0.0173)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 50 µs Pulsed 10% (~3W) (Small Aliquot)</td>
<td>31520.86</td>
<td>66.29</td>
<td>0.0635 (±0.003)</td>
<td>0.0021 (±0.00018)</td>
<td>0.2099 (±0.0058)</td>
<td>0.235 (±0.026)</td>
<td>0.3038 (±0.0073)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 50 µs Pulsed 10% (~3W) (Small Aliquot)</td>
<td>129181.10</td>
<td>39.01</td>
<td>0.053 (±0.0016)</td>
<td>0.0003 (±0.00012)</td>
<td>0.2148 (±0.0032)</td>
<td>0.2186 (±0.0236)</td>
<td>0.3007 (±0.0041)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 60 µs Pulsed 10% (~3.5W) (Small Aliquot)</td>
<td>22656.41</td>
<td>74.42</td>
<td>0.0498 (±0.0027)</td>
<td>0.00328 (±0.00157)</td>
<td>0.2062 (±0.0057)</td>
<td>0.2402 (±0.0266)</td>
<td>0.3058 (±0.0074)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 60 µs Pulsed 10% (~3.5W) (Small Aliquot)</td>
<td>127007.43</td>
<td>51.67</td>
<td>0.0496 (±0.0017)</td>
<td>0.00041 (±0.00018)</td>
<td>0.2133 (±0.0035)</td>
<td>0.2133 (±0.0231)</td>
<td>0.3006 (±0.0043)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 60 µs Pulsed 10% (~3.5W) (Small Aliquot)</td>
<td>22790.21</td>
<td>86.65</td>
<td>0.0454 (±0.0024)</td>
<td>0.0038 (±0.0018)</td>
<td>0.2103 (±0.0054)</td>
<td>0.2381 (±0.0262)</td>
<td>0.3111 (±0.007)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 80 µs Pulsed 10% (~6W) (Small Aliquot)</td>
<td>167173.33</td>
<td>21.85</td>
<td>0.0504 (±0.0053)</td>
<td>0.00011 (±0.00005)</td>
<td>0.206 (±0.0136)</td>
<td>0.1949 (±0.0242)</td>
<td>0.2922 (±0.0174)</td>
</tr>
<tr>
<td>6a CAI 0.54mg 80 µs Pulsed 10% (~6W) (Small Aliquot)</td>
<td>30173.09</td>
<td>58.84</td>
<td>0.0429 (±0.0017)</td>
<td>0.00195 (±0.00087)</td>
<td>0.1998 (±0.0038)</td>
<td>0.2154 (±0.0233)</td>
<td>0.3012 (±0.0049)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-------</td>
<td>-----</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>6a CAI 0.54mg CW 10% (~7W)</td>
<td>6312.90</td>
<td>94.68</td>
<td>0.0449 (±0.0028)</td>
<td>0.015 (±0.00737)</td>
<td>0.2217 (±0.0066)</td>
<td>0.2192 (±0.0244)</td>
<td>0.322 (±0.0078)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 20µs pulsed 10% (~&lt;1W)</td>
<td>15909.76</td>
<td>91.72</td>
<td>0.1143 (±0.0041)</td>
<td>0.00577 (±0.00327)</td>
<td>0.249 (±0.0067)</td>
<td>0.1822 (±0.015)</td>
<td>0.305 (±0.0076)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 30µs pulsed 10% (~&lt;1W)</td>
<td>109211.66</td>
<td>29.95</td>
<td>0.4731 (±0.0055)</td>
<td>0.00027 (±0.00016)</td>
<td>0.3612 (±0.0048)</td>
<td>0.2064 (±0.016)</td>
<td>0.2865 (±0.0044)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 35µs pulsed 10% (~1.5W)</td>
<td>96174.88</td>
<td>92.85</td>
<td>0.3815 (±0.0069)</td>
<td>0.00097 (±0.00053)</td>
<td>0.3299 (±0.0066)</td>
<td>0.1952 (±0.0158)</td>
<td>0.3013 (±0.0066)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 40µs pulsed 10% (~2W)</td>
<td>121073.91</td>
<td>44.68</td>
<td>0.2138 (±0.0041)</td>
<td>0.00037 (±0.00019)</td>
<td>0.2673 (±0.0049)</td>
<td>0.1929 (±0.0153)</td>
<td>0.2946 (±0.0054)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 45µs pulsed 10% (~2.5W)</td>
<td>90721.92</td>
<td>112.31</td>
<td>0.1514 (±0.004)</td>
<td>0.00124 (±0.00068)</td>
<td>0.2443 (±0.0055)</td>
<td>0.1959 (±0.0158)</td>
<td>0.3049 (±0.0065)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 50µs pulsed 10% (~2.75W)</td>
<td>115908.17</td>
<td>121.78</td>
<td>0.1038 (±0.0029)</td>
<td>0.00105 (±0.00056)</td>
<td>0.2294 (±0.0047)</td>
<td>0.188 (±0.015)</td>
<td>0.2959 (±0.0056)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 55µs pulsed 10% (~3W)</td>
<td>97776.70</td>
<td>141.69</td>
<td>0.0849 (±0.003)</td>
<td>0.00145 (±0.00078)</td>
<td>0.2273 (±0.0051)</td>
<td>0.2025 (±0.0162)</td>
<td>0.2971 (±0.0062)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 60µs pulsed 10% (~3.5W)</td>
<td>55879.09</td>
<td>120.50</td>
<td>0.0584 (±0.0029)</td>
<td>0.00216 (±0.00115)</td>
<td>0.2167 (±0.0058)</td>
<td>0.2105 (±0.0171)</td>
<td>0.3104 (±0.0073)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg 60µs pulsed 10% (~5W)</td>
<td>142505.62</td>
<td>91.62</td>
<td>0.0746 (±0.0015)</td>
<td>0.00064 (±0.00033)</td>
<td>0.2238 (±0.0027)</td>
<td>0.1845 (±0.0141)</td>
<td>0.29 (±0.0032)</td>
</tr>
<tr>
<td>8a CAI 2 0.72mg CW 10% (~7W)</td>
<td>17507.62</td>
<td>137.38</td>
<td>0.0699 (±0.0027)</td>
<td>0.00785 (±0.000438)</td>
<td>0.2231 (±0.005)</td>
<td>0.2066 (±0.0163)</td>
<td>0.3098 (±0.0063)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 20µs 10% (~&lt;1W)</td>
<td>37413.27</td>
<td>211.86</td>
<td>0.1006 (±0.0021)</td>
<td>0.00566 (±0.000321)</td>
<td>0.2281 (±0.0033)</td>
<td>0.2017 (±0.0074)</td>
<td>0.3042 (±0.0039)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 30µs 10% (~&lt;1W)</td>
<td>234572.06</td>
<td>-256.79</td>
<td>0.6718 (±0.0037)</td>
<td>-0.000109 (±0.000064)</td>
<td>0.4303 (±0.0028)</td>
<td>0.1899 (±0.0065)</td>
<td>0.2875 (±0.0022)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 35µs 10% (~1.5W)</td>
<td>227531.41</td>
<td>-154.70</td>
<td>0.2224 (±0.0018)</td>
<td>-0.00068 (±0.000029)</td>
<td>0.2698 (±0.0002)</td>
<td>0.196 (±0.0066)</td>
<td>0.2931 (±0.0021)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 40µs 10% (~2W)</td>
<td>353301.11</td>
<td>-225.23</td>
<td>0.1847 (±0.0153)</td>
<td>0</td>
<td>0.2565 (±0.0139)</td>
<td>0.1948 (±0.012)</td>
<td>0.2979 (±0.0154)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 45µs 10% (~2.5W)</td>
<td>175592.84</td>
<td>-55.08</td>
<td>0.2263 (±0.0019)</td>
<td>-0.00031 (±0.00001)</td>
<td>0.2698 (±0.0021)</td>
<td>0.1954 (±0.0066)</td>
<td>0.2936 (±0.0023)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 50µs 10% (~3W)</td>
<td>322266.89</td>
<td>-66.48</td>
<td>0.1335 (±0.0013)</td>
<td>-0.00021 (±0.00008)</td>
<td>0.2375 (±0.0018)</td>
<td>0.186 (±0.0299)</td>
<td>0.2919 (±0.0021)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg Pulsed 55µs 10% (~3.5W)</td>
<td>372564.44</td>
<td>-146.16</td>
<td>0.0908 (±0.0095)</td>
<td>-0.00034 (±0.00013)</td>
<td>0.2167 (±0.0144)</td>
<td>0.1823 (±0.0316)</td>
<td>0.2883 (±0.0172)</td>
</tr>
<tr>
<td>10a Fluffy CAI 0.79mg CW 10% (~7W)</td>
<td>804287.73</td>
<td>-65.08</td>
<td>0.0561 (±0.0038)</td>
<td>0</td>
<td>0.2212 (±0.0103)</td>
<td>0.2261 (±0.0114)</td>
<td>0.2798 (±0.0153)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 30μs pulsed 10% (~1W)</td>
<td>306033.56</td>
<td>17.05</td>
<td>0.0916 (±0.0011)</td>
<td>0.00006 (±0.00002)</td>
<td>0.2232 (±0.0018)</td>
<td>0.2086 (±0.0049)</td>
<td>0.2909 (±0.0022)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 40μs pulsed 10% (~2W)</td>
<td>620825.94</td>
<td>-40.32</td>
<td>0.0604 (±0.0029)</td>
<td>0</td>
<td>0.2142 (±0.0069)</td>
<td>#NUM!</td>
<td>0.2926 (±0.0101)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 45μs pulsed 10% (~2.5W)</td>
<td>307928.00</td>
<td>-8.25</td>
<td>0.0496 (±0.0007)</td>
<td>-0.00003 (±-0.00001)</td>
<td>0.2123 (±0.0016)</td>
<td>0.2047 (±0.0047)</td>
<td>0.2883 (±0.002)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 50μs pulsed 10% (~3W)</td>
<td>213133.82</td>
<td>65.43</td>
<td>0.0495 (±0.0007)</td>
<td>0.00031 (±0.00011)</td>
<td>0.2083 (±0.0016)</td>
<td>0.2045 (±0.0047)</td>
<td>0.2899 (±0.002)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 55μs pulsed 10% (~3.5W)</td>
<td>114961.73</td>
<td>14.48</td>
<td>0.0478 (±0.0012)</td>
<td>0.00013 (±0.00004)</td>
<td>0.2133 (±0.0026)</td>
<td>0.2022 (±0.0052)</td>
<td>0.3014 (±0.0032)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 60μs pulsed 10% (~4W)</td>
<td>235581.20</td>
<td>#VALUE!</td>
<td>0.0472 (±0.0015)</td>
<td>0</td>
<td>0.1905 (±0.0032)</td>
<td>0.189 (±0.0119)</td>
<td>0.3014 (±0.0035)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg 65μs pulsed 10% (~4.5W)</td>
<td>160230.95</td>
<td>#VALUE!</td>
<td>0.0482 (±0.0016)</td>
<td>0</td>
<td>0.1918 (±0.0034)</td>
<td>0.1837 (±0.0117)</td>
<td>0.3103 (±0.0039)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg Pulsed 80μs 10% (~5W)</td>
<td>104145.43</td>
<td>26.85</td>
<td>0.0554 (±0.0013)</td>
<td>0.00026 (±0.00008)</td>
<td>0.4359 (±0.0052)</td>
<td>0.2055 (±0.0055)</td>
<td>0.3154 (±0.0032)</td>
</tr>
<tr>
<td>3a Matrix 0.99mg CW 10% (~7W) (2mins heating 1 getter)</td>
<td>67736.45</td>
<td>138.45</td>
<td>0.0605 (±0.0013)</td>
<td>0.00204 (±0.00071)</td>
<td>0.4394 (±0.0049)</td>
<td>0.2135 (±0.0055)</td>
<td>0.3123 (±0.0031)</td>
</tr>
</tbody>
</table>