Tracing the origins of refractory inclusions – the Solar System's oldest solids – a petrographic, geochemical and <sup>26</sup>Al-<sup>26</sup>Mg dating study of CV and CK refractory inclusions

by

#### Christopher Campbell Town

A thesis submitted to Victoria University of Wellington in partial fulfilment of the requirements for the degree of Master of Science in Geology.

Victoria University of Wellington 2008

#### Abstract

Refractory inclusions in carbonaceous chondrite meteorites are of particular interest because both long- and short-lived chronometers have shown that they are the oldest sampled material to have formed in the Solar System. The objective of this study was to establish high-precision petrographic, chemical and isotopic analyses of refractory inclusions and thus offer insights into the chemical and astrophysical environments present during the formation of the Solar System.

The former presence of the short-lived isotope <sup>26</sup>Al ( $T_{1/2} = ~730$  KYr) has been established in a majority of refractory inclusions. Recent studies using both solution-based and *in situ* methodologies have suggested that the initial <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> value of refractory inclusions is ~6 × 10<sup>-5</sup>, higher than the established "canonical" value of [5.00 ± 0.05] × 10<sup>-5</sup>. Knowing the initial concentration of <sup>26</sup>Al within the Solar System provides a useful anchor from which ancient materials can be dated.

Petrographic and trace element analyses were performed on nine newly-extracted refractory inclusions from CV3 and CK3 chondrites. These analyses revealed all but three refractory inclusions to have experienced multiple episodes of melting and evaporation prior to crystal closure.

Mg isotope analyses were performed on eight of the newly extracted refractory inclusions in addition to five inter-laboratory samples. All refractory inclusions shown to have remained unaltered following crystal-closure, regardless of thermal history prior to closure, yielded a model  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  of [4.89  $\pm$  0.265]  $\times$  10<sup>-5</sup>; within error of the canonical value. This result confirms that  ${}^{26}\text{Al}$  was homogenous and at canonical concentrations in the solar nebula. The results also suggest that chemical fractionation and crystal closure for the analysed refractory inclusions was completed within no more than 160 Kyr.

# Acknowledgments

Outrageous thanks go to my supervisor Dr Joel Baker for the work he's done to help me produce this thesis. My appreciation for his expertise and willingness to take me on as a student is well beyond my ability to express.

Thanks to Martin "Herman the German" Schiller whose extensive preliminary work for his own PhD research greatly benefited my research.

I'd like to extend my thanks to Dr Richard Wysoczanski for the help he's provided during the research section of this project.

Thanks to Benjamin Jacobsen and Dr Qing-zhu Yin from University of California at Davis for generously providing a suite of 5 digested CAIs from the Allende meteorite.

Thanks to my examiners, Dr Monica Handler and Dr Caroline Stirling, for their constructive criticism which has greatly improved the quality of this work.

To my office mates David "Thor" Murphy and Kimberly Andrews, thanks for making my thesis year not only bearable, but fun.

To my family, John, Vivian and Margaret, thanks for sticking by me as I decided to pack-in my IT career to do something I actually enjoy.

To my girlfriend Emma, thanks for brightening up my perspective on everything and changing my life for the better.

A special shout-out to Dhiresh Hansaraj, Joe Coyle, Oscar Clark, Aidan Allan, Julene Marr, Alex McCoy-West and all my other geology brothers and sisters for making the last five years simply fantastic.

Thanks to Damon Clarke for suggesting geology when I was heading back to university and for helping immensely in the editing of this thesis.

Financial resources were provided by the Marsden Fund.

# Contents

1	Intr	oduction	1
	1.1	Study overview	1
	1.2	Objectives of this study	2
	1.3	Meteorites: an introduction	2
	1.4	Chondritic meteorites	3
		1.4.1 Chondrite metamorphic types	4
		1.4.2 Carbonaceous chondrites	4
		1.4.3 Vigarano-like CV chondrites	5
		1.4.4 Karoonda-like CK chondrites	6
		1.4.5 Ivuna-like CI chondrites	6
	1.5	Refractory inclusions	7
		1.5.1 Refractory elements	8
		1.5.2 Petrology and mineralogy	3
	1.6	Calcium-aluminium rich inclusions	6
		1.6.1 Type A CAIs	7
		1.6.2 Type B CAIs	9
		1.6.3 Fine-grained CAIs	.0
	1.7	Amoeboid olivine aggregates	1
	1.8	Short-lived isotope dating of CAIs	1
		1.8.1 ${}^{26}$ Al- ${}^{26}$ Mg dating	2
		1.8.2 Canonical verses supra-canonical ${}^{26}Al/{}^{27}Al_0$ 2	3
2	Sam	ple Descriptions 2	5
	2.1	Sample acquisition	5

	2.2	Samp	les	25
		2.2.1	NWA 2364	26
		2.2.2	CAI 0	26
		2.2.3	CAI 1	27
		2.2.4	CAI 2	28
		2.2.5	CAI 3	28
		2.2.6	CAI 4	28
	2.3	NWA	760	30
		2.3.1	CAI 5	31
	2.4	NWA	1559	32
		2.4.1	CAI 8, AOA 1 and AOA 2	34
	2.5	Alleno	de	34
		2.5.1	A33, A39, A43, A44A and AJEF	35
3	Ana	lytical	Techniques	36
	3.1	Major	and trace element analysis	36
		3.1.1	Sample preparation	36
		3.1.2	Major element analysis	37
		3.1.3	Trace element analysis by LA–ICP–MS	37
	3.2	Al/M	g and Mg isotope analyses	41
		3.2.1	Sample preparation	41
		3.2.2	Acid digestion and column chemistry	42
		3.2.3	$^{27}$ Al/ $^{24}$ Mg measurements by solution ICP-MS $\ldots \ldots$	49
		3.2.4	Mg isotope ratio determinations by MC-ICP-MS $\ldots$	49
		3.2.5	Solution ICP-MS Al/Mg processing	52
		3.2.6	MC-ICP-MS Mg isotope analysis processing	53
		3.2.7	Calculation of ${}^{26}\text{Al}/{}^{27}\text{Al}_0$	54
4	Res	ults		55
	4.1	Miner	alogy and major element data for CAIs	55
		4.1.1	CAI 0 and CAI 1	57
		4.1.2	CAI 2	57
		4.1.3	CAI 3	58

5

	4.1.4	CAI 4	59
	4.1.5	CAI 5	60
	4.1.6	CAI 8	61
	4.1.7	AOA 1 and AOA 2	62
4.2	Trace e	elements	62
	4.2.1	Bulk trace element patterns	62
	4.2.2	Rare earth element patterns	66
4.3	<sup>27</sup> Al/ <sup>2</sup>	<sup>4</sup> Mg and $\delta^{26}$ Mg <sup>*</sup> values	73
	4.3.1	<sup>27</sup> Al/ <sup>24</sup> Mg and Mg isotope uncertainties	73
	4.3.2	Notes on stable $\delta^{25}$ Mg isotope values $\ldots \ldots \ldots$	73
	4.3.3	Notes on ${}^{27}\text{Al}/{}^{24}\text{Mg}$ and ${}^{26}\text{Mg}^*$ isochrons $\ldots \ldots \ldots$	74
	4.3.4	Overview of analytical results	74
	4.3.5	Inter-laboratory comparison - Allende CAIs	77
	4.3.6	Ion exchange chemistry and calcium	77
	4.3.7	NWA 2364	78
	4.3.8	NWA 760 - CAI 5	80
	4.3.9	NWA 1559	81
	4.3.10	All unaltered CAIs	81
Syn	thesis		83
5.1	Canon	lical vs supra-canonical ${}^{26}$ Al/ ${}^{27}$ Al <sub>0</sub>	83
	5.1.1	Non-canonical ${}^{26}\text{Al}/{}^{27}\text{Al}_0$	84
5.2	$^{26}Al^{-2}$	<sup>6</sup> Mg dating	85
	5.2.1	Allende inter-labratory comparison	87
	5.2.2	CAI 1 bulk and mineral separate chronology	88
5.3	Forma	tion and processing from major and trace element	
	compo	position and $\delta^{25}$ Mg values	88
	5.3.1	Group V REE patterns – CAI 0 and CAI 1	88
	5.3.2	Group III REE patterns – CAI 2	89
	5.3.3	Group II REE patterns	90
5.4	Summ	ary	91
	5.4.1	CAI residence time in the solar nebula	92
5.5	Future	ework	92

## CONTENTS

6	Conclusions				
	6.1	Petrology and trace elements	93		
	6.2	Canonical ${}^{26}\text{Al}/{}^{27}\text{Al}_0$	93		
Bi	Bibliography				

## Appendices

Α	Miscellaneous Appendix	100
	A.1 Meteorite purchase details	100
	A.2 Glossary of terms	101
B	ICP-MS operational settings	102
С	Analytical Sites	104
D	Major Element Data	116
E	Trace Element Data	133

# List of Tables

1.1	Data on the types of carbonaceous chondrites. Adapted	
	from Scott & Krot (2004) with additional data from	
	Greenwood et al. (2004). CAI: calcium aluminium-rich	
	inclusions, AOA: amoeboid olivine aggregates	5
1.2	Matrix petrology of CV3 chondrites. Adapted from Scott &	
	Krot (2004)	6
1.3	Mineral components of CV3 and CK3 CAIs and AOAs.	
	Adapted from Lodders (2003). Condensation temperatures	
	are those predicted in the solar nebula at a pressure of $10^{-4}$	
	atm	8
1.4	Equilibrium condensation temperatures (Tc) for trace	
	elements and their respective major phase hosts for 50%	
	trace element condensation in a Solar System composition	
	gas at $10^{-4}$ atm. Adapted from Lodders (2003). Only trace	
	elements analysed in this study are shown. Abbrevations:	
	Elmt: Element; Fel: Feldspar	9

1.5	Mineral phase types and frequency of occurrence in refractory inclusions. Abbreviations: a – an accessory mineral; p – mineral exists as a primary phase; m – mineral exists as a minor phase, either in small concentrations ( $\leq$ 5%) or as interstitial secondary phase ( $\leq$ 5%); r – mineral is rare; WL – appears in Wark-Lovering rims (not discussed); "–" indicates the mineral is not present. Percentages are volume percentages. Data from Brearley & Jones (1998) and MacPherson (2004). Chemical compositions for all minerals	
	can be found in Table 1.3.	10
2.1 2.2	List of the meteorites used in this study	26
	refractory inclusions is detailed in Sections 1.6 & 1.7	27
3.1	The data acquisition protocol for LA-ICP-MS trace element analyses	39
3.2	Symbols used in equations 3.1, 3.2 and 3.3	40
3.3	Measured trace element data (ppm) for BHVO-2G by LA-ICP-MS at Victoria University of Wellington versus the GeoRem recommended values (GeoRem, 2006). All values are concentrations in ppm. Abbreviation: Elmt: element	41
3.4	$\delta^{26}$ Mg* and $\delta^{25}$ Mg data for a solution of BDH Aristar Mg standard doped with 2% of different contaminant elements measured against a pure Aristar Mg solution. The effect of calcium is also shown at the 20% and 200% level. From Schiller et al. (In Submission)	42
	Schiller et al. (In Submission) $\ldots$	43

3.5	A typical analysis block used for measuring <sup>27</sup> Al/ <sup>24</sup> Mg	
	ratios in dissolved refractory inclusion samples. The Al/Mg	
	standard is a gravimetrically prepared standard with a	
	$^{27}\text{Al}/^{24}\text{Mg}$ ratio of 2.006. BCR-2 is a dissolved sample of the	
	Columbia River Basalt standard in dilute (0.5 %) HNO <sub>3</sub> . All	
	samples were analysed twice	50
3.6	$\delta^{26}Mg^*$ and $\delta^{25}Mg$ values for the BDH Aristar Mg ICP Multi-	
	element, BCR-2 and BHVO-2 standards from Schiller et al. (In	
	Submission). n is the number of repeat measurements. All	
	$\delta^{26}Mg^*$ values are within error of zero	52
3.7	Symbols used in equations 3.5, 3.6 & 3.7	53
3.8	Symbols used in equation 3.9	54
41	Typical oxide weight percentages for all minerals within	
1.1	refractory inclusions examined by electron microprobe	
	Numbers directly above mineral names are shortened	
	inclusion names followed by the analytical point e.g. CO	
	P302 is the point CAI 0, phase 3, analysis 2,	56
4.2	Appendix locations for analytical site maps, major element	00
	oxide and trace element results for all refractory inclusions	
	analysed in this study.	57
4.3	Mineral proportions for refractory inclusions. Values are	
	volume percentages.	59
4.4	Types of REE patterns exhibited by the studied refractory	
	inclusions. Abbreviations: FA - fluffy type A; CA - compact	
	type A; FG - fine-grained.	66

4.5	<sup>27</sup> Al/ <sup>24</sup> Mg and Mg isotope data obtained on refractory
	inclusions during this study. Abbreviations: n: number of
	measurements, Type: refractory inclusion type, CT:
	representative sample picked by Christopher Town, JB &
	JAB: representative sample picked by Joel Baker, WR: whole
	rock, FEL: feldspathic separate, PX: pyroxene separate,
	WRC: calculated whole rock weighted average. WRC for
	CAI 5 is the weighted average of the core and WR
	measurements. "-" denotes that a model <sup>26</sup> Al/ <sup>27</sup> Al <sub>0</sub> could
	not be calculated
4.6	<sup>27</sup> Al/ <sup>24</sup> Mg and Mg isotope data for Allende inter-laboratory
	samples, measured during this study and as reported in
	Jacobsen et al. (2008). Abbreviations: n: number of
	measurements, Type: refractory inclusion type
4.7	<sup>27</sup> Al/ <sup>24</sup> Mg and Mg isotope data for the Allende CAI sample
	A44A, before and after removal of Ca with the DGA column
	chemistry method. Abbreviations: n: number of repeat
	measurements
E 1	The isochron derived $\frac{26}{1}$ , $\frac{127}{1}$ from the Aller de seconds
5.1	The isochron-derived $-AI/-AI_0$ from the Allende sample
	values reported by Jacobsen et al. (2008) and this study. CAIs
	considered in this comparison are A33, A39, A43 A44A and
	AJEF
A.1	Glossary of terms used in this study
B.1	Typical settings for the Agilent 7500 octopole ICP MS and
	New Wave 193 nm deep UV laser ablation system used
	when determining trace element concentrations
B.2	Typical settings for the Agilent 7500 octopole ICP MS in
	solution mode when determining <sup>27</sup> Al/ <sup>24</sup> Mg ratios for
	digested refractory inclusion samples

#### LIST OF TABLES

D.1	Electron microprobe analyses for melilite, spinel,
	Ca-pyroxene and anorthite in CAI 0
D.2	Electron microprobe analyses for melilite in CAI 1 118
D.3	Electron microprobe analyses for melilite and Ca-pyroxene in
	CAI 1
D.4	Electron microprobe analyses for spinel and an orthitein CAI 1 $120$
D.5	Electron microprobe analyses for anorthite (phase 2) in CAI 1 121
D.6	Electron microprobe analyses for melilite, labradorite and
	pyroxene in CAI 2
D.7	Electron microprobe analyses for spinel and anorthite in CAI 2 123
D.8	Electron microprobe analyses for anorthite and Ca-poor
	pyroxene in CAI 3
D.9	Electron microprobe analyses for hedenbergite, nepheline
	and fassaite in CAI 3
D.10	Electron microprobe analyses for Fe-rich spinel and Ca-rich
	pyroxene in CAI 4
D.11	Electron microprobe analyses for Ca-pyroxene, nepheline
	and hedenbergite in CAI 4
D.12	Electron microprobe analyses for phases in CAI 5.
	Abbreviations: c: analytical site is in the core of the
	inclusion, r: analytical site is in the rim of the sample 128
D.13	Electron microprobe analyses for anorthite, olivine,
	Ca-pyroxene and feldspar in CAI 8
D.14	Electron microprobe analyses for olivine and feldspar in
	AOA 1
D.15	Electron microprobe analyses for Ca-pyroxene in AOA 1 131
D.16	Electron microprobe analyses for olivine, diopside and
	feldspar in AOA 2
E.1	CI chondrite trace element concentrations from Lodders (2003) 134
E.2	Trace element measurements in ppm for melilite in CAI 0 135
E.3	Trace element measurements in ppm for melilite (cont.) and
	pyroxene in CAI 0

E.4	Trace element measurements in ppm for spinel and anorthite
	in CAI 0
E.5	Average mineral and bulk trace element measurements in
	ppm for CAI 0
E.6	Trace element measurements in ppm for melilite and
	anorthite in CAI 1
E.7	Trace element measurements in ppm for pyroxene in CAI 1 140
E.8	Average mineral and bulk trace element measurements in
	ppm for CAI 1
E.9	Trace element measurements in ppm for melilite, anorthite,
	plagioclase and spinel in CAI 2
E.10	Average mineral and bulk trace element measurements in
	ppm for CAI 2
E.11	Trace element measurements in ppm for anorthite, pyroxene,
	hedenbergite, nepheline and fassaite in CAI 3
E.12	Average mineral and bulk trace element measurements in
	ppm for CAI 3
E.13	Trace element measurements in ppm for spinel, Ca-pyroxene
	and nepheline in CAI 4
E.14	Average mineral and bulk trace element measurements in
	ppm for CAI 4
E.15	Trace element measurements in ppm for melilite, an
	unknown phase and andradite in CAI 5. "r" and "c" denote
	the sample is from the rim or core, respectively
E.16	Average mineral and bulk trace element measurements in
	ppm for CAI 5
E.17	Trace element measurements in ppm for anorthite, feldspar,
	Ca-pyroxene and olivine in CAI 8
E.18	Average mineral and bulk trace element measurements in
	ppm for CAI 8
E.19	Trace element measurements in ppm for olivine and feldspar
	in AOA 1

#### LIST OF TABLES

E.20	Average mineral and bulk trace element measurements in	
	ppm for AOA 1	153
E.21	Trace element measurements in ppm for olivine, diopside	
	and feldspar in	
	AOA 2	154
E.22	Average mineral and bulk trace element measurements in	
	ppm for AOA 2	155

# **List of Figures**

Typical REE patterns from CAIs. Adapted from Taylor (2001).	11
CI normalised REE patterns for anorthite from type B CAIs	
(discussed in Section 1.6.2) from the CV3 chondrites Allende	
(CAIs 5241 & 3529Z) and Vigarano (CAI 1623-8). Data from	
Brearley & Jones (1998), normalised to CI values from	
Lodders (2003)	11
CI normalised REE patterns for melilite from the type B CAI	
"TS 23" from Allende. Data from Brearley & Jones (1998),	
normalised to CI values from Lodders (2003)	12
CI normalised REE patterns for Ca-pyroxene from the type B	
CAI 5241 from Allende. Data from Brearley & Jones (1998),	
normalised to CI values from Lodders (2003)	12
Bulk compositions for type A, type B and fine-grained,	
spinel-rich CAIs. Mineral compositions are in red.	
Abbreviations: An – anorthite; Cor – corundum; Di –	
diopside; Fo – forsterite; Geh – gehlenite; Gro – Grossite; Hib	
– hibonite; L – liquid; Mel – melilite; Mo – monticellite; Pyx –	
pyroxene; Åk – åkermanite. Adapted from MacPherson	
(2004). Chemical compositions for all minerals can be found	
in Table 1.3.	17
	Typical REE patterns from CAIs. Adapted from Taylor (2001). CI normalised REE patterns for anorthite from type B CAIs (discussed in Section 1.6.2) from the CV3 chondrites Allende (CAIs 5241 & 3529Z) and Vigarano (CAI 1623-8). Data from Brearley & Jones (1998), normalised to CI values from Lodders (2003)

1.6	Plain light photographs of some CAIs analysed in this study. The CAIs are the light white/pink material, while the surrounding meteorite matrix is dark grey/brown. (a) a fluffy type A CAI (CAI 2); (b) a type B CAI (CAI 1); (c) a zoned fine-grained CAI (CAI 5); (d) a fine-grained CAI (CAI 4). All refractory inclusions analysed in this study are discussed in detail in Chapter 2	18
2.1	A plain light photograph of both sides of the larger NWA 2364 slice. CAIs analysed in this study are outlined in red. (a) & (e) are the two sides of CAI 1, (b) is CAI 2, (c) is CAI 3 and (d) is CAI 4.	28
2.2	A plain light photograph of the smaller NWA 2364 slice. CAI	_0
	0 is outlined in red. $\ldots$	29
2.3	Plain light photographs of CAI 0, in situ (a), and mounted in epoxy resin and polished (b). The dashed red outline shows	
	the mounted portion of the inclusion.	29
2.4	Plain light photographs of CAI 1. (a) the inclusion from the side of its smallest exposure, (b) the side of its largest exposure, (c) the inclusion after being mounted in epoxy resin and polished. The dashed red outline in (b) denotes the	
	mounted portion of the inclusion in (c). $\ldots$	30
2.5	Plain light photographs of CAI 2 in situ (a) and mounted in epoxy resin and polished (b). The dashed red outline shows	
	the mounted portion of the inclusion.	30
2.6	Plain light photographs of CAI 3, in situ (a), and mounted in epoxy resin and polished (b). The dashed red outline shows	
	the mounted portion of the inclusion.	31
2.7	Plain light photographs of CAI 4, in situ (a), and mounted in	
	epoxy resin and polished (b). The dashed red outline shows	
	the mounted portion of the inclusion.	31
2.8	A plain light photograph of the NWA 760 end cut. CAI 5 is	
	outlined in red.	32

2.9	Photographs of CAI 5, in situ (a), and mounted in epoxy resin	
	and polished (b). The dashed red outline shows the mounted	
	portion of the inclusion.	32
2.10	A plain light photograph of the NWA 1559 slice, with studied	
	inclusions outlined in red: (a) AOA 1, (b) AOA 2, (c) CAI 8	33
2.11	Plain light photographs of CAI 8, both in situ (a) and	
	mounted in epoxy resin and polished (b). The dashed red	
	outline shows the mounted portion of the inclusion	33
2.12	Plain light photographs of AOA 1, both in situ (a) and	
	mounted in epoxy resin and polished (b). The dashed red	
	outline shows the mounted portion of the inclusion	34
2.13	Plain light photographs of AOA 2, both in situ (a) and	
	mounted in epoxy resin and polished (b). Th edashed red	
	line indicates the plane of the polished surface. The white	
	arrows indicate the portion of the divided inclusion that was	
	mounted and polished	34
3.1	A back scattered electron image of CAI 0. In this sample, the	
	lightest coloured mineral is melilite, followed by pyroxene,	
	anorthite and spinel. The large black areas are holes in the	
	mounted sample, filled with epoxy resin. Brightness is due	
	to the variation in X-ray wavelengths emitted by the chemical	
	element composition of each mineral	38
3.2	A schematic detailing the process of dissolution undertaken	
	for all refractory inclusions. This technique was also used in	
	Schiller et al. (2007) and Schiller et al. (In Submission) $\ldots$	44
3.3	Diagrams of the two types of exchange columns constructed	
	for use in all acid ion exchange chemistry. (a) An Eppendorf	
	EP Tip 1250 $\mu$ L pipette tip fashioned into an anion or DGA	
	exchange column. (b) A 1 mL pipette fashioned into a cation	
	exchange column	46
3.4	The anion exchange chemistry procedure (extraction step 1). $\ .$	47

3.5	The DGA ion exchange column chemistry procedure (extraction step 2)	47
3.6	The cation exchange column chemistry procedure (extraction	
0.0	step 3)	48
	step 0)	10
4.1	A mosaic of back-scattered electron photographs of	
	refractory inclusions analysed in this study. The blue bar in	
	each segment is = 1 mm. (a) CAI 0, (b) CAI 1, (c) CAI 2, (d)	
	CAI 3, (e) CAI 4, (f) CAI 5, (g) CAI 8, (h) AOA 1, (i) AOA 2	58
4.2	A back-scattered electron photograph of CAI 3 overlain with	
	a schematic of the mineral structure. The yellow borders	
	outline areas primarily consisting of hedenbegite and	
	nepheline. The blue border outlines the area primarily	
	consisting of anorthite and low-Ca-pyroxene. Abbreviations:	
	Hed: hedenbergite, Neph: nepheline, Low-Ca-Px:	
	low-Ca-Pyroxene	60
4.3	A highly magnified back-scattered electron photograph	
	displaying the crystal structure of CAI 4	61
4.4	CI-normalised bulk trace element patterns for CAIs 0, 1 & 2	63
4.5	CI-normalised bulk trace element patterns for CAIs 3 & 4	63
4.6	CI-normalised bulk trace element patterns for CAI 5	64
4.7	CI-normalised bulk trace element patterns for CAI 8 and	
	AOAs 1 & 2	64
4.8	CI-normalised REE patterns from CAI 0	67
4.9	CI-normalised REE patterns from CAI 1	68
4.10	CI-normalised REE patterns from CAI 2	68
4.11	CI-normalised REE patterns from CAI 3	69
4.12	CI-normalised REE patterns from CAI 4	70
4.13	CI-normalised Bulk REE patterns from CAI 5 core, rim &	
	"whole rock"	70
4.14	CI-normalised REE patterns for melilite from the core and	
	rim of CAI 5	71
4.15	CI-normalised REE patterns from CAI 8	71

4.16	CI-normalised REE patterns from AOA 1	72
4.17	CI-normalised REE patterns from AOA 2	72
4.18	An <sup>26</sup> Al- <sup>26</sup> Mg isochron for all Allende samples analysed in	
	this study. A dashed grey reference line has been added to	
	show the comparative data as reported in Jacobsen et al. (2008).	78
4.19	An isochron for all unaltered NWA 2364 samples analysed in	
	this study. The altered CAI 3 sits well below the ${}^{26}\text{Al}/{}^{27}\text{Al}_0$	
	line and is included for comparison only.	79
4.20	Internal <sup>26</sup> Al- <sup>26</sup> Mg isochron for mineral and whole-rock	
	samples of CAI 1	80
4.21	An <sup>26</sup> Al- <sup>26</sup> Mg isochron for all unaltered CAIs from Allende	
	(blue error ellipses) and NWA 2364 (red error ellipses). The	
	dashed grey reference line denotes the canonical value of 5	
	$ imes$ $10^{-5}$ and the solid green line denotes the supra-canonical	
	values as reported in Thrane et al. (2006)	82
5.1	Model <sup>26</sup> Al/ <sup>27</sup> Al <sub>0</sub> values for unaltered refractory inclusions	
	analysed in this study. The blue line and bounding box are	
	indicative of the final ${}^{26}\text{Al}/{}^{27}\text{Al}_0$ = [4.89 ± 0.265] × 10 <sup>-5</sup> . The	
	solid and bounding dashed red lines represent the canonical	
	value = $[5.00 \pm 0.05] \times 10^{-5}$	86
C.1	CAI 0 analytical sites. Circles denote EMP sites and squares	
	denote LA-ICP-MS sites	105
C.2	Electron microprobe and laser ablation analytical sites for	
	CAI 1. The yellow box encircles an example of a spinel	
	palisade as discussed in Chapter 1.5.2	106
C.3	Electron microprobe and laser ablation analytical sites for	
	CAI 2	107
C.4	Electron microprobe and laser ablation analytical sites for	
	CAI 3	108

C.5	Electron microprobe and laser ablation analytical sites for
	CAI 4. The yellow box denotes the location of the magnified
	inset (Fig. C.6)
C.6	A magnified inset of CAI 4
C.7	Analytical sites for CAI 5. Detailed inset maps follow in Fig.
	C.8
C.8	Electron microprobe and laser ablation analytical sites for the
	core and rim of CAI 5
C.9	Electron microprobe and laser ablation analytical sites for
	CAI 8
C.10	Electron microprobe and laser ablation analytical sites for
	AOA 1
C.11	Electron microprobe and laser ablation analytical sites for
	AOA 2. The white line denotes the boundary between AOA
	2 and its host groundmass

# Chapter 1

# Introduction

This chapter:

- Outlines the objectives of this study;
- Gives an overview of this study and the field of scientific concern;
- Describes the studied meteorites, their components and their chemical and mineralogical properties;
- Discusses current controversies within the field of cosmochemistry relevant to this study.

## 1.1 Study overview

The solar nebula was the flattened disk of gas, ice and dust from which the Solar System's planets, satellites and asteroids formed (Boss, 2004; Taylor, 2001). The solar nebula was the material remnant within the gravity well of the Sun, immediately following the accretion of sufficient mass into the young star to begin hydrogen burning (Taylor, 2001).

This study focuses on the timing and formation of mineral aggregates called refractory inclusions in the carbonaceous chondrite class of meteorites. Refractory inclusions and, specifically, calcium-aluminium rich inclusions (CAIs) are the oldest dated solids in the Solar System (Amelin et al., 2002) and due to their chemistry are likely to have been the first rock-like solids to have condensed from the solar nebula (MacPherson, 2004). Thus studies of refractory inclusions can reveal details about the physical and chemical environments present during the formation of the Solar System  $4.56 \times 10^9$  yr ago (Brearley & Jones, 1998; Taylor, 2001).

A glossary of terms used in this study is given in Appendix A.1.

## **1.2** Objectives of this study

The objectives of this study are as follows:

- 1. Petrographically describe a range of refractory inclusions.
- 2. Undertake major and trace element analyses of these refractory inclusions and, where possible, individual mineral phases.
- 3. Perform high precision <sup>26</sup>Al-<sup>26</sup>Mg relative dating of these refractory inclusions, including inter-laboratory samples provided by a US laboratory, using the chemical separation and mass spectrometric techniques developed by Schiller et al. (In Submission).

#### **1.3** Meteorites: an introduction

Meteorites are solid ejecta resulting from collisions and impacts suffered by source asteroids or planets known as meteorite "parent bodies" (Taylor, 2001), that have survived passage through the Earth's atmosphere and impact onto its surface (Krot et al., 2004). They provide a physical record of the processes that occurred within the solar nebula, planets, satellites and asteroids, prior to, contemporarily with and post planetary accretion (Taylor, 2001).

The majority of meteorites are sourced from the asteroid belt, located between the orbits of Mars and Jupiter and are divided into two major groups, chondrites and non-chondrites (Krot et al., 2004). Chondrites are primitive meteorites whose parent bodies have not suffered high enough temperatures to melt or differentiate (Taylor, 2001). Non-chondrites are meteorites sourced from parent bodies that have experienced sufficient heating to either melt (primitive non-chondrites) or differentiate (differentiated non-chondrites) (Krot et al., 2004). Examples of differentiated non-chondrites include the shergottite, nakhlite, chassignite and orthopyroxenite (SNC) meteorites, most likely sourced from Mars; the howardite-eucrite-diogenite (HED) clan of meteorites, most likely sourced from the asteroid belt object 4 Vesta (McCord et al., 1970); and the stony-iron mesosiderites, pallasites and iron meteorites. This study focuses on chondrites; a full review of all meteorite types can be found in Krot et al. (2004).

### **1.4** Chondritic meteorites

Chondrites are stony meteorites that are ultramafic in composition, comprising mostly iron, magnesium, silicon and oxygen (Scott & Krot, 2004). Chondrites were originally named for the high volumes of chondrules: mm-sized crystallised spherical droplets of melt consisting of silicates, glass, minor metals and sulphides (McKeegan & Davis, 2004).

The chondrite classification now refers to ancient meteorites from parent bodies that did not experience planetary differentiation or melting. Chondrites are therefore likely to have chemical and isotopic compositions representative of the original composition of their respective parent bodies (Palme & Jones, 2004). In addition to chondrules, chondrites contain a range of inclusions (Scott & Krot, 2004), including grains of pre-solar dust, such as micro-diamonds (Krot et al., 2004) that pre-date the formation of the Solar System (McKeegan & Davis, 2004). The study of these inclusions and the chondritic matrix provides a window into the conditions, processes and compositional variables involved in the formation of the Solar System (Scott & Krot, 2004; McKeegan & Davis, 2004).

#### **1.4.1** Chondrite metamorphic types

Chondrites are classified into six types using a scale that describes the degree to which metamorphism has affected the parent body. Types 1 and 2 represent degrees of aqueous alteration, with type 1 having a greater abundance of hydrous silicates and therefore alteration. The unequilibrated, textually unaltered type 3 through to the chemically equilibrated type 6 represent a continuum of increasing metamorphic grade (Krot et al., 2004). The type 3 class of chondrites are the least aqueously- and thermally-altered, undifferentiated meteorites.

Some type 3 chondrites, however, may have experienced thermal processing. Type 3 chondrites in the ordinary, K (Kakangari-like), CO (Ornans-like) and CV (Vigarano-like) groups contain kamacite and taenite, which equilibrate at temperatures of 670–870 K (Scott & Krot, 2004). These minerals suggest each of these chondrite groups were heated to those temperatures for more than 10<sup>6</sup> years and therefore cannot be considered pristine (Scott & Krot, 2004).

#### 1.4.2 Carbonaceous chondrites

The carbonaceous chondrite class of meteorites are defined as having refractory lithophile element concentrations (Section 1.5.1) that are equal to or exceed those of Ivuna-like (CI) chondrites (Section 1.4.5), and matrices that are predominately oxides, silicates, sulphides and metallic iron and nickel (Scott & Krot, 2004). Carbonaceous chondrites and more specifically Vigarano-like (CV) chondrites (Table 1.1) are notable in that they contain significant quantities of refractory inclusions.

Carbonaceous chondrites identified to date are dominated by the chemically unequilibrated type 3 samples (Table 1.1). Ordinary chondrites, by comparison, represent a continuum over the metamorphic types 1–6 (Greenwood et al., 2004). Whether this phenomenon is systematic of a sampling bias, representing meteorites most likely to survive transit through the Earth's atmosphere, or other conditions is not known (Scott &

Meteorite	CAI &	Chondrule	Ту	vpe (	no. d	of sa	mpl	es)
class	AOA (vol %)	(vol %)	1	2	3	4	5	6
CI	< 0.01	< 5	5					
СМ	5	20	4	44				
CO	13	40			31			
CV	10	45		1	35			
CR	0.5	50-60	1	13	1			
CH	0.1	70			7			
CBa	< 0.1	40			3			
CB <sub>b</sub>	< 0.1	30			2			
СК	4	17			8	13	6	1

**Table 1.1:** Data on the types of carbonaceous chondrites. Adapted from Scott & Krot (2004) with additional data from Greenwood et al. (2004). CAI: calcium aluminium-rich inclusions, AOA: amoeboid olivine aggregates

Krot, 2004). This study focuses on type 3 carbonaceous chondrites from the CV and CK groups.

#### 1.4.3 Vigarano-like CV chondrites

CV chondrites contain an appreciable volume (~10%) of refractory inclusions (Table 1.1). Up to 50% of the refractory elements (Section 1.5.1) in bulk CV chondrites can be contained solely within the refractory inclusions (Scott & Krot, 2004). The comparatively unaltered CV3 chondrites are divided into the CV3 reduced and CV3 oxidised subgroups, with the CV3 oxidised subgroup further divided into Bali-like and Allende-like oxidised CV3 subgroups (Krot et al., 2004). The petrographic properties of these CV3 meteorite matrices are given in Table 1.2.

The presence of metallic Fe and Ni and the lack of magnetite suggests that reduced CV3s are the least altered chondrites (Scott & Krot, 2004). CV matrices are normally dominated by iron-rich olivine, consisting of 30-60 % fayalite (Fa<sub>30-60</sub>) (Section 1.5.2; Scott & Krot, 2004).

Meteorite Type	Defining Matrix Petrology						
CV3 reduced	Abundant metallic Ni and Fe rather than						
	magnetite. Minor low-calcium pyroxene and						
	FeS.						
Bali-like CV3 oxidised	Abundant phyllosilicates, Fa>95, high-calcium						
	pyroxene, pentlandite and magnetite.						
Allende-like CV3 oxidised	Abundant Ca-Fe-rich pyroxene, nepheline,						
	pentlandite. Minor magnetite.						

Table 1.2: Matrix petrology of CV3 chondrites. Adapted from Scott & Krot (2004).

#### 1.4.4 Karoonda-like CK chondrites

CK chondrites represent a unique group within carbonaceous chondrites as known samples are predominantly metamorphosed, equilibrated types 4–6 (Table 1.1; Brandstatter et al., 2003; Greenwood et al., 2004). CK4–6 matrices consist primarily of olivine, low-calcium pyroxene and plagioclase with minor phases of magnetite and sulfide (Scott & Krot, 2004). In contrast, the CK3 and CK3-anomalous groups have matrices similar to the CV3 oxidised subgroup (Brandstatter et al., 2003; Scott & Krot, 2004), including large (>1 mm diameter) refractory inclusions. The similarities of CK3 and CK3-anomalous to CV3 oxidised subgroup chondrites, especially in terms of oxygen isotope ratios, has lead some to suggest they represent a sampling continuum from a single parent body (Greenwood et al., 2004).

#### 1.4.5 Ivuna-like CI chondrites

CI chondrites are a unique group comprised almost entirely of matrix material. Due to high concentrations of hydrated minerals, all CI chondrites to date have been classified as type 1 (Table 1.1). CI chondrites are extensively aqueously altered, and thus cannot be considered primary, unprocessed material from the solar nebula, although they appear to have an unaltered bulk composition (Taylor, 2001). The refractory chemical

composition of CI chondrites is very similar to the calculated composition of the Sun's photosphere, with the Sun/CI ratio of 19 refractory lithophile elements (Al, Ca, Ti, V, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Lu) equal to  $1.004 \pm 0.12$  (Palme & Jones, 2004). This makes CI chondrites a unique proxy for solar composition and thus the composition of the solar nebula.

In this study, trace element data for refractory inclusions are normalised to the CI data in order to quantify the variation in concentration of an element from that of the bulk Solar System. When discussing the relative concentration of an element, this study adopts the notation of Brearley & Jones (1998), where "Y × CI" means an element or group of elements has a concentration Y times that found in bulk CI chondrites. Refractory elements are discussed in Section 1.5.1.

## 1.5 Refractory inclusions

Refractory inclusions are sub-millimetre- to centimetre-sized aggregates of minerals that can be thermodynamically predicted to have condensed first from, and free-floating in, hot solar nebula gas (Taylor, 2001; MacPherson, 2004; McKeegan & Davis, 2004). Refractory inclusions include calcium and aluminium-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs), both of which are analysed in this study (Chapter 2). AOAs are less refractory in chemical composition than CAIs (Taylor, 2001). Amelin et al. (2002) utilised Pb-Pb dating techniques to determine that CAIs from the CV chondrite Efremovka to be 4567.2  $\pm$  0.6 Myr in age, making CAIs the oldest dated material dated so far. Refractory inclusions most likely formed as free-floating objects in the inner solar nebula, and those inclusions that were not accreted into the Sun were sequestered into chondritic material in a region similar to the modern-day Asteroid Belt (McKeegan & Davis, 2004).

Major Mineral Phases						
Mineral	General Chemical Formula	Condensation				
		temperature (K)				
Hibonite	Ca(Al,Ti <sup>4+</sup> ,Mg) <sub>12</sub> O <sub>19</sub>	1659				
Perovskite	CaTiO <sub>3</sub>	1593				
Melilite	(Åkermanite) Ca <sub>2</sub> Mg(Si <sub>2</sub> O <sub>7</sub> ) –	1529				
	(Gehlenite) Ca2Al[AlSiO7]					
Spinel	(Mg,Fe)Al <sub>2</sub> O <sub>4</sub>	1397				
Anorthite	$CaAl_2Si_2O_8$	1387				
Ca-pyroxene	$CaMgSi_2O_6 - CaAl_2SiO_6 -$	1347				
	$CaTi^{4+}Al_2O_6 - CaTi^{3+}AlSiO_6$					
Olivine	(Fayalite) Mg <sub>2</sub> SiO <sub>4</sub> –	1354				
	(Forsterite) Fe <sub>2</sub> SiO <sub>4</sub>					
Less Common	Mineral Phases					
Mineral	General Chemical Formula					
Sodalite	NaAlSiO <sub>4</sub> ·NaCl					
Nepheline	NaAlSiO <sub>4</sub>					
Hedenbergite	CaFeSi <sub>2</sub> O <sub>6</sub>					
Andradite	$Ca_3Fe_2Si_3O_{12}$					
Grossular	$Ca_2Al_2Si_3O_{10}$					
Ilmenite	FeTiO <sub>3</sub>					

**Table 1.3:** *Mineral components of CV3 and CK3 CAIs and AOAs. Adapted from Lodders* (2003). Condensation temperatures are those predicted in the solar nebula at a pressure of  $10^{-4}$  atm.

#### 1.5.1 Refractory elements

Refractory chemical elements are those with relatively high melting and boiling temperatures. Refractory inclusions are comprised of minerals containing the most refractory of major (Table 1.3) and trace elements (Table 1.4; Davis & Richter, 2004) which appear in differing proportions depending on the type of refractory inclusion (Table 1.5). Refractory inclusions are universally enriched in refractory trace elements regardless of whether an element is of siderophile or lithophile character (Davis & Richter, 2004). Ca, Al and Ti oxides will condense at temperatures between

Elmt	50% Major phase(s)		Elmt	50%	Major phase(s)
	Tc (K)	or host(s)		Tc (K)	or host(s)
Sc	1659	Hibonite	Ce	1478	Hibonite + titanate
Ti	1582	Titanate	Pr	1582	Hibonite + titanate
V	1429	Titanate	Nd	1602	Hibonite
Cr	1296	Fe Alloy	Sm	1590	Hibonite + titanate
Mn	1158	Forsterite + enstatite	Eu	1356	Hibonite + titanate + fel
Co	1352	Fe Alloy	Gd	1659	Hibonite
Ni	1353	Fe Alloy	Tb	1659	Hibonite
Cu	1037	Fe Alloy	Dy	1659	Hibonite
Zn	726	Forsterite + enstatite	Но	1659	Hibonite
Ga	968	Fe Alloy + feldspar	Er	1659	Hibonite
Rb	800	Feldspar	Tm	1659	Hibonite
Sr	1464	Titanate	Yb	1487	Hibonite + titanate
Y	1659	Hibonite	Lu	1659	Hibonite
Zr	1741	ZrO <sub>2</sub>	Hf	1684	HfO <sub>2</sub>
Nb	1559	Titanate	Та	1573	Hibonite + titanate
Mo	1590	Refractory metal alloy	W	1789	Refractory metal alloy
Cs	799	Cs metal	Pb	727	Fe Alloy
Ba	1455	Titanate	Th	1659	Hibonite
La	1578	Hibonite + titanate	U	1610	Hibonite

**Table 1.4:** Equilibrium condensation temperatures (Tc) for trace elements and their respective major phase hosts for 50% trace element condensation in a Solar System composition gas at  $10^{-4}$  atm. Adapted from Lodders (2003). Only trace elements analysed in this study are shown. Abbrevations: Elmt: Element; Fel: Feldspar.

1700 and 1350 K within a nebula cloud with a density of  $10^{-4}$  atm (Lodders, 2003), as will refractory trace elements such as the rare earth elements (REE; Table 1.4) and platinum group metals (Ru, Rh, Pd, Os, Ir, and Pt) (Palme & Jones, 2004).

The REE are divided into the light rare earth elements (LREE; La, Ce, Pr Nd, Pm, Sm) and the heavy rare earth elements (HREE; Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The general trend for REE is the higher the atomic mass, the more refractory the element, with the exceptions of Eu and Yb, which are the most volatile REE (Table 1.4).

	CAIs					
			Fin			
Mineral	Type A	Туре В	Zoned		T	AOAs
			Core	Rim	Unzoned	
Hibonite	m	r	m	_	m	_
Perovskite	а	r	m	_	m	_
Melilite	р	5–20%	_	р	m	_
Spinel	р	15–30%	р	р	р	а
Ca-pyroxene	р	30–60%	m	_	р	а
Anorthite	р	5–25%	р	m	_	_
Sodalite	_	_	m	m	m	_
Nepheline	_	_	р	m	р	а
Hedenbergite	_	r	_	m	m	а
Andradite	_	_	_	m	m	_
Grossular	_	_	_	m	m	_
Ilmenite	_	_	m	m	m	_
Forsterite	WL	WL	m	_	_	р
Fayalite	WL	WL	m	_	_	р

**Table 1.5:** Mineral phase types and frequency of occurrence in refractory inclusions. Abbreviations: a - an accessory mineral; p - mineral exists as a primary phase; m - mineral exists as a minor phase, either in small concentrations ( $\leq$ 5%) or as interstitial secondary phase ( $\leq$ 5%); r - mineral is rare; WL – appears in Wark-Lovering rims (not discussed); "–" indicates the mineral is not present. Percentages are volume percentages. Data from Brearley & Jones (1998) and MacPherson (2004). Chemical compositions for all minerals can be found in Table 1.3.

#### **REE patterns**

The process(es) of formation for a refractory inclusion can be determined by analysing the chondrite-normalised concentration of one REE to another. Typical REE patterns for bulk CAIs are summarised in Figure 1.1. Group I patterns are enriched in the most volatile REE, Eu. Group II patterns are indicative of multistage evaporative and condensation events, the number and nature of which cannot be unequivocally estimated (Brearley & Jones, 1998; Taylor, 2001). Refractory inclusions with Group II



**Figure 1.2:** *CI* normalised REE patterns for anorthite from type B CAIs (discussed in Section 1.6.2) from the CV3 chondrites Allende (CAIs 5241 & 3529Z) and Vigarano (CAI 1623-8). Data from Brearley & Jones (1998), normalised to CI values from Lodders (2003).

REE patterns are not volatilisation residues due to the depletion of the refractory HREE and volatile REE, and have only been successfully modelled as fractional condensates (MacPherson, 2004). Group III and VI patterns are those expected through the loss or gain, respectively, of the most volatile REE (Eu and Yb). Group V inclusions have not lost or gained REE and have flat chondritic-normalised patterns, while "ultrarefractory"



**Figure 1.3:** *CI normalised REE patterns for melilite from the type B CAI "TS 23" from Allende. Data from Brearley & Jones (1998), normalised to CI values from Lodders (2003).* 



**Figure 1.4:** *CI normalised REE patterns for Ca-pyroxene from the type B CAI 5241 from Allende. Data from Brearley & Jones (1998), normalised to CI values from Lodders (2003).* 

patterns show a depletion of volatile REE and a surplus of the more refractory HREE (Taylor, 2001).

Relative REE concentrations can also vary as a result of petrology as much as thermal processing. Chondrite-normalised, individual mineral phase REE patterns for anorthite, melilite and Ca-pyroxene in type B CAIs from CV3 chondrites are shown in Figs. 1.2, 1.3 & 1.4 respectively. Figures 1.2, 1.3 & 1.4 show a positive Eu anomaly in the melilite and anorthite phases and a negative Eu anomaly in Ca-pyroxene. Type B CAIs show evidence for formation through the crystallisation of molten or semi-molten droplets (Brearley & Jones, 1998). In this case, the variation in Eu concentrations in relation to other REE is due to the mineral crystallisation sequence of spinel, melilite, and then anorthite and Ca-pyroxene in either order (MacPherson, 2004; Table 1.3; Section 1.6.2). Eu is highly compatible within plagioclase (Weill & Drake, 1973), producing a positive Eu anomaly in anorthite and melilite (Figs. 1.2 & 1.3 respectively), resulting in a Eu-depleted melt from which the Ca-pyroxene subsequently crystallised with a negative Eu anomaly (Fig. 1.4). A CAI consisting of primarily plagioclase, solidifying from a nebula of Solar-composition, will therefore produce a bulk Group I REE pattern (Fig. 1.1).

#### 1.5.2 Petrology and mineralogy

This study only examines those minerals that occur as major CAI phases (Table 1.3). Average microprobe-derived major element abundances for all minerals analysed in this study can be found in Chapter 4, Table 4.1. Refractory inclusion types mentioned in this section are discussed in Section 1.6.

#### Hibonite

Hibonite is the most common aluminate to occur in CAIs (Brearley & Jones, 1998) and is common in "fluffy" type A CAIs, but rare in type B CAIs. Its high condensation temperature (Table 1.3) allows for the study of solid formation in a hot solar nebula. Although corundum (Al<sub>2</sub>O<sub>3</sub>) is predicted to crystallise at higher temperatures than hibonite, it is exceptionally rare (Brearley & Jones, 1998; MacPherson, 2004) due to it readily reacting with nebula gas and forming melilite (Brearley & Jones, 1998).

Taylor (2001) noted that the highly refractory element patterns and the Ca and Ti abundances exhibited by hibonite in CAIs are indicative of formation through several episodes of melting of refractory dust particles. Hibonite displays extensive chemical variation, which is dominated by the coupled substitution of  $Ti^{4+} + Mg^{2+} \Leftrightarrow Al^{3+}$  (MacPherson, 2004). This

#### CHAPTER 1. INTRODUCTION

substitution leads to the incorporation of high concentrations of V, Fe, Si, Cr, Sc and other transition elements (Brearley & Jones, 1998).

#### Perovskite

Perovskite is a common accessory mineral in compact type A CAIs and occurs in association with hibonite, melilite and spinel in fluffy type A CAIs (Brearley & Jones, 1998), but is rare in type B CAIs (MacPherson, 2004). It occurs as a fine-grained mineral with most grains  $\leq 10 \ \mu m$  in diameter. REE patterns display a positive Eu anomaly (~200 × CI) but are otherwise flat (~1000 × CI) (Brearley & Jones, 1998) due to processes discussed in Section 1.5.1.

#### Spinel

Spinel is widespread in CAIs and often appears as octahedral crystals, 1  $\mu$ m – 100  $\mu$ m in diameter, poikilitically enclosed within phases such as melilite, anorthite and pyroxene. The magnesium phase of spinel (MgAl<sub>2</sub>O<sub>4</sub>) exists as a primary and dominant phase while the iron phase (FeAl<sub>2</sub>O<sub>4</sub>) is a minor secondary mineral (< 5 wt% of spinel) existing in altered zones (Brearley & Jones, 1998; MacPherson, 2004). Other elemental variations include the presence of CaO, V<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, which account for  $\leq$  1 wt% (Brearley & Jones, 1998). In some type B CAIs, spinel is present in the form of "palisades" - appearing as arcs or circles of loosely grouped spinel crystals in thin section or polished surface. These are likely cross-sections of spinel shells that formed around the edges of vesicles, which later filled with melt (Brearley & Jones, 1998). Spinel palisades are visible in the EMP image of CAI 1 (Appendix C, Fig. C.2).

#### Melilite

Melilite is present in CAIs as the binary solid-solution end members of  $a_2MgSi_2O_7$  and gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) (MacPherson, 2004). The proportion of each end member is a direct function of temperature,

giving a unique proxy for crystallisation temperatures of melilite. The thermal minimum exists with an åkermanite weight percentage of  $\sim$ 72% (MacPherson, 2004), denoted as Åk<sub>72</sub>, but the full range of values measured in melilite is Åk<sub>0-80</sub> (Brearley & Jones, 1998).

When present as a primary phase, normally in type B CAIs, individual melilite crystals exhibit a gehlenite-rich core ( $\sim$ Åk<sub>30</sub>), which gradually become enriched in magnesium, and thus åkermanite, towards the crystal edge ( $\sim$ Åk<sub>72</sub>) (Brearley & Jones, 1998). Melilite in compact type A CAIs exhibits reverse zoning with Al-rich (Åk<sub>10–15</sub>) rims and more Mg-bearing (Åk<sub>20–35</sub>) cores , but generally melilite in type A CAIs is  $\leq$  Åk<sub>20</sub> (Brearley & Jones, 1998). Despite the variation in Åk concentrations, melilite grains have smooth, consistent REE patterns independent of Åk content (Brearley & Jones, 1998). Generally, the REE patterns in melilite are reasonably flat (5–10 x CI) , with a trend of enrichment of the LREE ( $\sim$ 10 × CI at La to  $\sim$ 3 × CI at Sm) to depletion in the HREE ( $\sim$ 2 × CI at Gd to  $\leq$  1 × CI at Lu) and a positive Eu anomaly of 11 to 15 × CI (Section 1.5.1).

#### Ca-pyroxene

Pyroxene is a ubiquitous phase in most CAIs and exists as a primary igneous phase in type B CAIs and as a rare phase in type A CAIs (Brearley & Jones, 1998; MacPherson, 2004). Unlike terrestrial pyroxene, CAI-derived pyroxene does not commonly form iron-bearing end members such as hedenbergite (FeCaSi<sub>2</sub>O<sub>6</sub>), with  $Ti^{4+}$  and  $Ti^{3+}$  and aluminium dominating variation in the solid-solution end members (MacPherson, 2004). Trivalent and quadrivalent Ti requires an extremely reducing formation environment, such as one consisting of hot hydrogen gas (MacPherson, 2004). Ca-pyroxene appears in type B CAIs as predominantly large, blocky grains or as irregularly-shaped grains, poikilitically enclosed in melilite in inclusion interiors (Brearley & Jones, Minor textural occurences of rounded grains of pyroxene and 1998). inter-granular poikilitic grains appear in type B melilite mantles. REE patterns in igneous pyroxene have flat or depleted but gradually enriching

LREE ( $10 \times CI$  at La –  $50 \times CI$  at Sm) and flat ( $40-50 \times CI$ ) HREE patterns with a negative Eu anomaly of  $5 \times CI$  (Brearley & Jones, 1998).

#### Anorthite

Anorthite is a sodium-free plagioclase which occurs in type B CAIs as a coarse-grained primary phase (Brearley & Jones, 1998) and as a secondary phase replacing melilite in CAI interiors (MacPherson, 2004). REE patterns in anorthite in type B CAIs are similar in shape to those of melilite, with a generally flat ( $10-20 \times CI$ ) pattern and a positive Eu anomaly of  $20-50 \times CI$  (Brearley & Jones, 1998).

#### Olivine

Olivine exists as the iron and magnesium end-members of the solid solution  $Mg_2SiO_4 - Fe_2SiO_4$ . Forsterite bearing type B (FoB) CAIs contain the Mgrich solid-solution end-member forsterite (MacPherson, 2004), while AOAs consist of up to 60% of the Fe-bearing end member fayalite (Fa<sub>60</sub>) (Scott & Krot, 2004).

# 1.6 Calcium-aluminium rich inclusions

Calcium-aluminium rich inclusions (CAIs) are the major subgroup of refractory inclusions. The nature of the different CAI types is considered in depth here. CAIs have been dated through absolute Pb-Pb methods as having an age of 4567.2  $\pm$  0.6 Myr (Amelin et al., 2002). This makes CAIs the oldest known Solar System-derived material and a window into the most energetic period of Solar System formation (Scott & Krot, 2004). CAIs are divided into several types dependent on composition and formation processes. This study focuses on type A and type B CAIs, the comparative compositions of which can be found in Figure 1.5. This section will discuss the comparative differences and sub-types of type A and B CAIs.

16


**Figure 1.5:** Bulk compositions for type A, type B and fine-grained, spinel-rich CAIs. Mineral compositions are in red. Abbreviations: An – anorthite; Cor – corundum; Di – diopside; Fo – forsterite; Geh – gehlenite; Gro – Grossite; Hib – hibonite; L – liquid; Mel – melilite; Mo – monticellite; Pyx – pyroxene; Åk – åkermanite. Adapted from MacPherson (2004). Chemical compositions for all minerals can be found in Table 1.3.

### 1.6.1 Type A CAIs

On a bulk compositional diagram (Fig. 1.5), type A CAIs plot between the melilite end-members of the Ca-rich åkermanite and the Al-rich gehlinite, and tend to lie closer to the Al-rich gehlinite end-member. Al percentages in melilite are denoted as the percentage of the melilite phase which occurs as åkerminite ( $Åk_0-~Åk_{100}$ ). Type A CAIs are more widespread than type B, with the latter only occurring in CV chondrites, while the former occurs in CV, CO, CR, CM (Brearley & Jones, 1998) and CK3 (this study) chondrites. Type A CAIs are divided into two groups, "fluffy" and "compact", defined on the basis of composition and shape. With the possible exception of the extremely rare fractionation and unknown



**Figure 1.6:** Plain light photographs of some CAIs analysed in this study. The CAIs are the light white/pink material, while the surrounding meteorite matrix is dark grey/brown. (a) a fluffy type A CAI (CAI 2); (b) a type B CAI (CAI 1); (c) a zoned fine-grained CAI (CAI 5); (d) a fine-grained CAI (CAI 4). All refractory inclusions analysed in this study are discussed in detail in Chapter 2.

nuclear effects (FUN) CAIs (MacPherson et al., 2005), which are not discussed in this study, type A CAIs are generally considered the most primitive refractory inclusions (Brearley & Jones, 1998).

### Fluffy type A CAIs

Fluffy type A CAIs have contorted, highly-irregular outlines in section (Fig. 1.6a). The primary mineral assemblage of Al-rich melilite  $(Åk_0 - Åk_{35})$ , (Brearley & Jones, 1998), occurs as reverse-zoned crystals with Al-rich melilite on the rim of the crystal and Mg-rich melilite in the core (MacPherson, 2004). This is inconsistent with igneous crystallisation. Enclosed V-rich spinel, perovskite and hibonite are also common phases in

fluffy type A CAIs (Brearley & Jones, 1998). Pristine fluffy type A CAIs are considered to be aggregates of one or more irregular nodules consisting of the mineral phases mentioned above and do not exhibit the structure expected from the culmination of individual vapour-grown crystals (MacPherson, 2004). Rather, they display a structure more consistent with significant solid-state recrystallisation (Brearley & Jones, 1998).

#### **Compact type A CAIs**

Compact type A CAIs are spherical in shape, and contain more Mg-rich melilite ( $\leq Åk_{50}$ ) than fluffy type A CAIs. The melilite exhibits complex zoning not present in fluffy type A CAIs (MacPherson, 2004). Any hibonite present in compact type A CAIs is around the inclusion edge, rather than being enclosed in melilite in the inclusion body.

The primary difference in formation and processing history between fluffy and compact type A CAIs, is that compact inclusions have likely experienced melting, while the fluffy inclusions have never been melted (Brearley & Jones, 1998; MacPherson, 2004). Fluffy type A CAIs contain higher concentrations of refractory elements than compact type A CAIs and are therefore considered to be more primitive than compact type A CAIs (MacPherson, 2004).

### 1.6.2 Type B CAIs

Type B CAIs (Fig. 1.6 b) are large, cm-sized, coarse-grained inclusions which are igneous in nature and found exclusively in CV3 chondrites (MacPherson, 2004). They consist of melilite ( $\sim$ Åk<sub>10</sub>–Åk<sub>72</sub>), Al-Ti-rich Ca-pyroxene, anorthite and spinel (Brearley & Jones, 1998; MacPherson, 2004). Type B CAIs are divided into three subgroups: type B1, type B2 and type B3. Type B1 and type B2 CAIs are similar to one another. Type B1 CAIs have almost homogeneous melilite mantles surrounding cores containing pyroxene, anorthite, spinel, Ni-Fe metal, noble metal nuggets and xenolithic material (in oxidised CV3s) (MacPherson, 2004), while type

B2 CAIs lack melilite mantles. Type B3 CAIs, also known as FoB CAIs, are rare, contain large crystals of forsterite as a major phase and either contain anorthite as a minor phase, or not at all (MacPherson, 2004).

Type B CAIs show evidence for formation through the solidification of molten or semi-molten droplets (Brearley & Jones, 1998), which were in original, solar nebula-derived isotopic equilibrium (MacPherson, 2004). On a bulk compositional diagram (Fig. 1.5), type B CAIs plot within the primary phases of spinel + melilite and trend away from type A CAIs, toward a position between diopside and anorthite. Type B CAIs are not the products of a simple one-stage heating and cooling event. The sequence of mineral crystallisation starts with spinel, followed by melilite and then the kinetically driven solidification of pyroxene or anorthite in either order (MacPherson, 2004). This crystallisation sequence is a departure from the purely nebula-derived, thermally driven mineral condensation sequence shown in Table 1.3.

### 1.6.3 Fine-grained CAIs

Fine-grained spinel- and Ca-pyroxene-rich CAIs (Figs. 1.5, 1.6 c & d, & Table 1.5) are the most abundant type of CAIs present in chondrites (MacPherson, 2004). The fine-grained name is not uniquely descriptive, as inclusions with grains of comparable (1–20  $\mu$ m in diameter) or smaller size exist in most chondrite groups (MacPherson, 2004). Fine-grained, spinel-rich CAIs have the same basic structure of individual clusters or arcs of spinel enclosed in a thin layer of aluminium-rich Ca-pyroxene and contain an abundance of secondary minerals due to being heavily altered (Brearley & Jones, 1998). Nepheline, sodalite, hedenbergite and andradite (Table 1.5) are present in fine-grained inclusions from the Allende and other CV3 meteorites (MacPherson, 2004).

The fine-grained CAIs analysed in this study are either zoned into a core-rim configuration (Fig. 1.6c) or mineralogically unzoned (Fig. 1.6d). The mineral concentrations present in each type of CAI are displayed in Table 1.5. Zoned CAI cores are almost melilite-free, containing mostly

spinel grains (±perovskite and hibonite) enclosed by rims of anorthite and minor pyroxene. The rim components of zoned, fine-grained CAIs are comprised of melilite surrounding spinel grains with anorthite replacing the minor pyroxene (MacPherson, 2004). Unzoned, fine-grained CAIs contain little or no anorthite and tend to be smaller in size than the zoned examples. Fine-grained CAIs are universally depleted in the very refractory HREE and in the most volatile REE, Eu and Yb (MacPherson, 2004).

## 1.7 Amoeboid olivine aggregates

Amoeboid olivine aggregates (AOAs) are irregularly shaped aggregates of unmelted grains (MacPherson, 2004). In CV3 chondrites, AOAs are porous aggregates that show evidence for alteration through solid-state recrystallisation, that AOAs in less altered chondrites, such as types CR2, CB, CH and CO3, do not (Scott & Krot, 2004). Mineralogically they are dominated by fine-grained (1–20  $\mu$ m) olivine (Fa<sub>1–30</sub>), with Ca-pyroxene, spinel, anorthite, nepheline, hedenbergite and rare melilite as accessory minerals (Brearley & Jones, 1998; Scott & Krot, 2004).

Olivine in AOAs from CV chondrites is more fayalitic (containing more Fe) than olivine found in less-altered chondrite groups. This implies a greater degree of secondary alteration and thermal metamorphism within the meteoritic parent body (Scott & Krot, 2004). Olivine from AOAs in the altered Allende meteorite, for example, are Fa<sub>>4</sub>, with a majority being Fa<sub>>16</sub>, while unaltered groups like CH & CB have Fa<sub><2.5</sub> (Scott & Krot, 2004).

## **1.8 Short-lived isotope dating of CAIs**

The absolute age of CAIs in the CV chondrite Efremovka was measured, using the Pb-Pb chronometer, as  $4567.2 \pm 0.5$  Myr by Amelin et al. (2002). The same study measured the absolute date of chondrules in the CR

chondrite, Acfer 059, to be 4564.7  $\pm$  0.6 Myr. These dates therefore give an interval of 2.5  $\pm$  1.2 Myr between the formation of CAIs and the subsequent formation of chondrules (Amelin et al., 2002).

At the time of writing, the absolute dating measurements of Amelin et al. (2002) are the most precise performed on chondritic material, with a precision of ~1 Myr. Analyses using short-lived chronometers, such as the  $^{26}$ Al– $^{26}$ Mg system, are therefore required to establish high-resolution relative formation chronologies for CAIs during their brief (<±20 kyr) (Jacobsen et al., 2008) formation interval.

## 1.8.1 <sup>26</sup>Al-<sup>26</sup>Mg dating

Magnesium has three stable isotopes; <sup>24</sup>Mg, <sup>25</sup>Mg and <sup>26</sup>Mg, the proportional solar abundances of which are 78.992 %, 10.003 % and 11.005 %, respectively (Lodders, 2003). Aluminium has one stable isotope, <sup>27</sup>Al. <sup>26</sup>Al is an extinct, short-lived isotope which decays to its stable daughter isotope, <sup>26</sup>Mg, through the emission of a positron (<sup>26</sup>Al  $\rightarrow$  <sup>26</sup>Mg +  $\beta$ <sup>+</sup>), with a half-life (T<sub>1/2</sub>) of ~730 kyr (MacPherson, 2004). In the case of ancient material such as refractory inclusions, an excess of <sup>26</sup>Mg in alumino-silicate minerals is either evidence for stable Mg isotope fractionation, or a direct proxy for the presence of <sup>26</sup>Al at the time of mineral crystal closure.

A <sup>26</sup>Mg excess produced by the decay of <sup>26</sup>Al will correlate with the Al/Mg ratio of the mineral phases within a CAI. These <sup>26</sup>Mg excesses are denoted as  $\delta^{26}$ Mg\*. Stable Mg isotope fractionation is also accounted for when processing analytical data using the exponential mass fractionation law as detailed by Jacobsen et al. (2008) and in Section 3.2.6.

Lee et al. (1976) was one of the first studies to demonstrate the presence of an excess of <sup>26</sup>Mg in a type B CAI from the Allende meteorite. The excess of <sup>26</sup>Mg correlated with the Al/Mg ratio of the respective alumino-silicate minerals analysed. Lee et al. (1977) subsequently yielded a <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> value of  $[5.1 \pm 0.6] \times 10^{-5}$  at the time of CAI formation. Subsequent research on CAIs has established a "canonical" <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> value of ~5 × 10<sup>-5</sup> to be typical of many CAIs (MacPherson, 2004). The presence of <sup>26</sup>Al at or just prior to the formation of the Solar System is important, as <sup>26</sup>Al has such a short half-life, it must have been generated just prior to CAI formation. This has led to several suggestions for its origin: a.) <sup>26</sup>Al was produced by a nearby supernova, the shock-wave from which may also have been responsible for the collapse of the protosolar nebula into the Solar System (MacPherson et al., 2005); b.) <sup>26</sup>Al was injected into the protosolar nebula by interstellar winds from one to several nearby Wolf-Rayet stars prior to or contemporarily with the T Tauri phase of the Sun's formation (Dearborn & Blake, 1985; Vuissoza et al., 2003; Gaidos et al., 2007). c.) <sup>26</sup>Al was produced by the nucleosynthetic processes occurring in asymtotic giant branch stars and injected into the interstellar medium (Busso et al., 1999).

### **1.8.2** Canonical verses supra-canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>

Analyses of CAIs by Young et al. (2005) and Thrane et al. (2006) have yielded supra-canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values of  $[5.9 \pm 0.3] \times 10^{-5}$  and  $[5.85 \pm 0.05] \times 10^{-5}$  respectively. Young et al. (2005) surmised that the canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = ~4.5 \times 10^{-5}$ , as originally measured by Lee et al. (1976), did not mark the beginning of CAI formation, but recorded a near complete thermal resetting of the  ${}^{26}\text{Al}-{}^{26}\text{Mg}$  system within CAI precursors.

The temporal difference ( $\Delta$ t) between a <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>  $\approx$  6 × 10<sup>-5</sup> and one of 4.5 × 10<sup>-5</sup> is ~300 kyr (Young et al., 2005). If the supra-canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> value is accurate,  $\Delta$ t would be the residence time of CAI precursors within the solar nebula between initial Al/Mg fractionation from the magmatic source and final alumino-silicate crystallisation. Young et al. (2005) suggest CAI precursors experienced thousands of short heating events to >1600 K for >300 yrs, resulting in a homogenous Solar System-wide <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>  $\approx$  5 × 10<sup>-5</sup> at the time of crystal closure.

Jacobsen et al. (2008) challenged the supra-canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  as reported by Young et al. (2005), Thrane et al. (2006) and Bizzarro et al. (2004, 2005). Through a combination of absolute  ${}^{207}\text{Pb}-{}^{206}\text{Pb}$  and high precision  ${}^{26}\text{Al}-{}^{26}\text{Mg}$  dating, Jacobsen et al. (2008) reinstated a canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = ~5 \times 10^{-5}$  with an uncertainty corresponding to residence time of 20 kyr for two Allende CAIs (AJEF and A43). Jacobsen et al. (2008) attributed the discrepancy between studies yielding canonical or supra-canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values to variation in sampling techniques, such as the unknown effects of matrix and other material potentially present in analyses conducted with laser-ablation multi-collector inductively couple plasma mass-spectrometry (LA-MC-ICP-MS) as in Young et al. (2005), and artefacts of analytical procedure in Thrane et al. (2006) and Bizzarro et al. (2004, 2005).

Establishing a precise value for the initial  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  within the solar nebula is important if CAIs are to be used to define a "time zero" datum to guide future work with other short-lived chronometers (Jacobsen et al., 2008). The duration of the CAI forming event and their processing in the solar nebula is also important for understanding the earliest history of the Solar System. This study will present Al and Mg isotope data in order to establish a precise, accurate  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  value.

# Chapter 2

# **Sample Descriptions**

# 2.1 Sample acquisition

The meteorite samples used in this study were purchased from professional meteorite collectors (Appendix A). Meteorites selected for purchase:

- 1. were CV 3 or CK 3 carbonaceous chondrites, due to the high volume percentage of refractory inclusions;
- 2. contained large refractory inclusions,  $\geq$  3 mm in diameter, to allow a range of analytical techniques to be carried out on each sample.

In addition to the purchased samples, a suite of 5 digested CAIs from the Allende meteorite were provided by Dr Qing-zhu Yin and Benjamin Jacobsen from University of California at Davis. This was in order to perform inter-laboratory comparative Al/Mg ratio and Mg isotope analyses on the same samples studied in Jacobsen et al. (2008).

# 2.2 Samples

Refractory inclusions were sampled from 4 carbonaceous chondrites (Table 2.1). All samples, except those from Allende, required extraction from the host meteorite matrix as detailed in Chapter 3.

Meteorite	Туре	No. of analysed inclusions	First described
NWA 2364	CV 3	5	(Russell et al., 2005)
NWA 760	CV 3	1	(Grossman & Zipfel, 2001)
NWA 1559	CK 3	3	(Russell et al., 2003)
Allende	CV 3	6	(Brett et al., 1970)

**Table 2.1:** List of the meteorites used in this study.

The studied refractory inclusions encompassed a range of petrographic types as detailed in Table 2.2. Analysing a range of petrographic types is essential in order to determine differences in the timing and the physical and chemical processes involved during crystallisation and subsequent nebula and/or parent body processing.

### 2.2.1 NWA 2364

Northwest Africa (NWA) 2364 is a CV3 chrondrite purchased from Arizona Skies Meteorites (Appendix A). It was originally discovered in 18 pieces weighing a total of 1493 g, and purchased in Erfoud, Morocco, in 2000. Russell et al. (2005) noted that NWA 2364 has an Allende-like matrix. Two slices were purchased for this study and a total of 5 refractory inclusions (CAI 0 – CAI 4) were extracted (Figs. 2.1 & 2.2).

### 2.2.2 CAI 0

CAI 0 (Figs. 2.2 & 2.3) is a coarse-grained Type-B CAI with a black pyroxenerich core. The extracted inclusion was divided so as to include some of the core material in the mounted sample (Fig. 2.3) while keeping as much core material as possible in the piece intended for chemical and isotopic study. This was done so analyses of mineral separates could potentially be performed.

Inclusion	Туре	Meteorite
CAI 0	Туре-В САІ	NWA 2364
CAI 1	Туре-В САІ	NWA 2364
CAI 2	Fluffy Type-A CAI	NWA 2364
CAI 3	Compact Type-A CAI	NWA 2364
CAI 4	Fine-grained CAI	NWA 2364
CAI 5	Fine-grained CAI	NWA 760
AOA 1 (CAI 6)	AOA	NWA 1559
AOA 2 (CAI 7)	AOA	NWA 1559
CAI 8	Fine-grained CAI	NWA 1559
A33	Compact Type-A CAI	Allende
A39	Туре-В САІ	Allende
A43	Туре-В САІ	Allende
A44A	Туре-В САІ	Allende
AJEF	Туре-В САІ	Allende

**Table 2.2:** Details of the refractory inclusions that are the basis of this study. The terminology for classifying and describing refractory inclusions is detailed in Sections 1.6 & 1.7.

### 2.2.3 CAI 1

CAI 1 is sufficiently large to be exposed on both sides of the 5 mm slice (Fig. 2.1 a & e). CAI 1 is coarse-grained type-B CAI, which is 5 mm long across its maximum exposed axis. During extraction, the inclusion separated cleanly from its surrounding chondritic matrix. The mounted section (Fig. 2.4 c) is comprised almost entirely of the inclusion with a minimal shell of matrix material. The unmounted fragment contained enough material to allow for both mineral and duplicate whole rock separates to be subjected to <sup>26</sup>Al-<sup>26</sup>Mg study. CAI 1 displays an excellent example of a spinel palisade as discussed in Section 1.5.2, which is visible in Appendix C.2. When dividing CAI 1 into its two analytical portions, it was noted that the inclusion appeared to be partially hollow.



**Figure 2.1:** A plain light photograph of both sides of the larger NWA 2364 slice. CAIs analysed in this study are outlined in red. (a) & (e) are the two sides of CAI 1, (b) is CAI 2, (c) is CAI 3 and (d) is CAI 4.

## 2.2.4 CAI 2

CAI 2 (Fig. 2.1 b) is a fine-grained, fluffy type-A CAI, measuring 6 mm long across its longest axis. Figure 2.5a shows the inclusion prior to being mounted in epoxy resin and polished. An area of the exposed inclusion was a thin veneer which was removed during the polishing process. Hence the differences in apparent shape in Figures 2.5a & 2.5b. CAI 2 appeared slightly pink in plain light.

### 2.2.5 CAI 3

CAI 3 (Fig. 2.1c and Fig. 2.6) is a fine-grained, compact type-A CAI. Very little matrix material remained attached to the inclusion after extraction. CAI 3 is 5 mm long across its longest exposed axis.

### 2.2.6 CAI 4

CAI 4 (Figs. 2.1d & 2.7) is a fine grained Type-A CAI which is 5 mm across its longest axis. It has a wispy contact with the chondritic matrix which is visible both *in situ* (Fig. 2.7a) and after mounting and polishing (Fig. 2.7b).

### CHAPTER 2. SAMPLE DESCRIPTIONS



**Figure 2.2:** *A plain light photograph of the smaller NWA 2364 slice. CAI 0 is outlined in red.* 



**Figure 2.3:** *Plain light photographs of CAI 0, in situ (a), and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 

The inclusion is grey/white and speckled with a black mineral, most likely spinel.



**Figure 2.4:** Plain light photographs of CAI 1. (*a*) the inclusion from the side of its smallest exposure, (*b*) the side of its largest exposure, (*c*) the inclusion after being mounted in epoxy resin and polished. The dashed red outline in (*b*) denotes the mounted portion of the inclusion in (*c*).



**Figure 2.5:** *Plain light photographs of CAI 2 in situ (a) and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 

# 2.3 NWA 760

NWA 760 is a CV3 carbonaceous chondrite which was first purchased in Erfoud, Morocco in September 2000 with a total sample size of 1,581 g (Komatsu et al., 2004; Grossman & Zipfel, 2001). A 10 g end cut (Fig. 2.8) was purchased from The Earth's Memory LLC (Appendix A), as it contained a single large, zoned refractory inclusion. NWA 760 contains chondrules (65% vol%), AOAs (5 vol%), CAIs (1 vol%) and fine-grained matrix (28 vol%) (Komatsu et al., 2004).



**Figure 2.6:** *Plain light photographs of CAI 3, in situ (a), and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 



**Figure 2.7:** *Plain light photographs of CAI 4, in situ (a), and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 

# 2.3.1 CAI 5

CAI 5 is a fine-grained, white-pink inclusion with marked zoning (Fig. 2.9). The zoning represents differences in petrographic composition, likely due to a sequence of fractional condensation within the solar nebula (MacPherson, 2004 & Section 1.6.3). Once extracted, a small section representing both zones was removed (Fig. 2.9 b), leaving a majority of the inclusion for use in the  ${}^{26}$ Al/ ${}^{26}$ Mg dating study. This was to allow independent whole-rock and individual zone separate analyses.



Figure 2.8: A plain light photograph of the NWA 760 end cut. CAI 5 is outlined in red.



**Figure 2.9:** *Photographs of CAI 5, in situ (a), and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 

# 2.4 NWA 1559

NWA 1559 was purchased from The Earth's Memory LLC (Appendix A) as a 4 mm slice measuring 5 mm by 10 mm (Fig. 2.10). This meteorite was originally purchased in the Zagora region of Morocco in 2000 as a 284 g fragment (Russell et al., 2003). NWA 1559 has been described as an



**Figure 2.10:** *A plain light photograph of the NWA 1559 slice, with studied inclusions outlined in red: (a) AOA 1, (b) AOA 2, (c) CAI 8.* 



**Figure 2.11:** *Plain light photographs of CAI 8, both in situ (a) and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 

anomalous CK3 (Brandstatter et al., 2003), due to its unmetamorphosed, unshocked appearance.



**Figure 2.12:** *Plain light photographs of AOA 1, both in situ (a) and mounted in epoxy resin and polished (b). The dashed red outline shows the mounted portion of the inclusion.* 



**Figure 2.13:** *Plain light photographs of AOA 2, both in situ (a) and mounted in epoxy resin and polished (b). Th edashed red line indicates the plane of the polished surface. The white arrows indicate the portion of the divided inclusion that was mounted and polished.* 

# 2.4.1 CAI 8, AOA 1 and AOA 2

CAI 8 is a fine grained CAI (Fig. 2.11). AOA 1 (Fig 2.12) and AOA 2 (Fig 2.13), were revealed to be AOAs following electron microprobe analyses as detailed in Section 3.1.

# 2.5 Allende

The Allende meteorite was an observed fall and came to ground on the 8th of February, 1969 near the Mexican village Pueblito de Allende (Brett et al.,

1970). The Allende fall has yielded several metric tons in recovered samples.

# 2.5.1 A33, A39, A43, A44A and AJEF

The Allende CAIs used in this study were supplied as digested aliquots by Dr Qing-zhu Yin and Benjamin Jacobsen from University of California at Davis. As these CAIs have been described and studied (Jacobsen et al., 2008), only a brief description of the samples is provided here and in Table 2.2. Jacobsen et al. (2008) describe the A33, A39, A43, A44A and AJEF CAIs as being composed of melilite, fassaite and anorthite, which all poikilitically enclose euhedral spinel grains. Perovskite is present as a minor phase. Minor alteration was noted with melilite being cross-cut or pseudomorphed by grossular, monticellite, forsterite and wollastonite.

# **Chapter 3**

# **Analytical Techniques**

This chapter describes the analytical techniques used in this study including details of:

- 1. Sample preparation;
- 2. Analyses of the mineral major element compositions by electronprobe microanalyser (EMPA);
- 3. Determination of mineral trace element compositions by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS);
- 4. Measurement of Al/Mg ratios by solution-based ICP-MS;
- 5. Analyses of Mg isotope ratios by multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).

# 3.1 Major and trace element analysis

### 3.1.1 Sample preparation

All refractory inclusions used in this study were cut away from the surrounding chondritic matrix with a slow diamond saw. Each inclusion was removed in a manner so as to retain the inclusion in its entirety, while leaving as little matrix material as possible, although small quantities of matrix remained attached to some extracted inclusions.

Each sample was then divided into two pieces using a diamond saw or gently broken into 2–3 pieces using an agate mortar and pestle. One piece of each sample was mounted in epoxy resin and polished. The mounted samples were used for electron microprobe analysis of mineral major elemental compositions and LA-ICP-MS analyses of trace element compositions.

### 3.1.2 Major element analysis

A JEOL 733 electronprobe microanalyser (EMPA) at Victoria University of Wellington was used to determine the major elemental and petrographic profiles of all selected inclusions. The epoxy-mounted samples were carbon coated and then photographed by electron backscattered imaging. Individual minerals were identified by back scattered intensity, i.e., the recorded brightness in the image (e.g. Fig. 3.1). The EMPA was calibrated using the VG-A99 basalt glass standard and used an accelerating voltage of 15 kV, a Faraday cup current of 12 nA and a defocused beam diameter of 20  $\mu$ m.

The oxide weight percentages of major elements were measured using the EMPA in spot mode. Locations of the probe points were recorded on the back scattered electron image. Subsequent identification of these points was essential as CaO from the EMPA analysis was used as an internal standard when processing trace element data from the LA-ICP-MS analyses. Where possible, at least 10 probe analyses of each mineral phase were made so as to reduce sampling bias and give a greater choice of location for subsequent laser ablation trace element analysis.

### 3.1.3 Trace element analysis by LA–ICP–MS

Mineral phases in each inclusion were analysed *in situ* for 38 trace elements with a New Wave 193 nm deep UV laser ablation system coupled to an

### CHAPTER 3. ANALYTICAL TECHNIQUES



**Figure 3.1:** *A back scattered electron image of CAI 0. In this sample, the lightest coloured mineral is melilite, followed by pyroxene, anorthite and spinel. The large black areas are holes in the mounted sample, filled with epoxy resin. Brightness is due to the variation in X-ray wavelengths emitted by the chemical element composition of each mineral.* 

Agilent 7500 octopole ICP-MS. The Columbia River Basalt standard (BCR-2) was used to bracket all sample analyses, allowing for correction of any trace element fractionation during analysis. CaO concentrations were monitored by the measurement of <sup>43</sup>Ca in LA-ICP-MS analyses, and were used as an internal normalising standard as described in Allan et al. (2008). Data acquisition parameters are given in Table 3.1. Laser and ICP-MS operational settings are detailed in Appendix B.1.

### LA-ICP-MS analytical processing

Statistical processing of collected data was performed in order to generate absolute concentrations of the selected trace elements in ppm. Machinederived drift in recorded measurements during analysis was corrected to

Elements analysed	<sup>45</sup> Sc, <sup>47</sup> Ti, <sup>51</sup> V, <sup>53</sup> Cr, <sup>55</sup> Mn, <sup>59</sup> Co,			
	<sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>71</sup> Ga, <sup>85</sup> Rb,			
	<sup>88</sup> Sr, <sup>89</sup> Y, <sup>90</sup> Zr, <sup>93</sup> Nb, <sup>95</sup> Mo, <sup>133</sup> Cs,			
	<sup>137</sup> Ba, <sup>139</sup> La, <sup>140</sup> Ce, <sup>141</sup> Pr, <sup>146</sup> Nd,			
	<sup>147</sup> Sm, <sup>153</sup> Eu, <sup>157</sup> Gd, <sup>159</sup> Tb, <sup>163</sup> Dy,			
	<sup>165</sup> Ho, <sup>166</sup> Er, <sup>169</sup> Tm, <sup>172</sup> Yb, <sup>175</sup> Lu,			
	<sup>178</sup> Hf, <sup>181</sup> Ta, <sup>182</sup> W, <sup>208</sup> Pb, <sup>232</sup> Th,			
	238U			
Background measurements	10			
and repetitions	40 s			
Dwell time	100			
and repetitions	100 S			
Counting mode	Pulse			

**Table 3.1:** The data acquisition protocol for LA-ICP-MS trace element analyses.

the bracketing BCR-2 standards. Absolute concentrations were calculated using CaO, as measured with EMPA, as an internal standard. The use of CaO as an internal standard meant only mineral phase locations previously analysed during the EMPA survey were suitable for analysis by LA-ICP-MS.

The average absolute counts per second (CPS) of each element was calculated using equation 3.1. The averaged CPS measurement for each element was then converted to ppm concentrations as given in equation 3.2. Absolute concentrations were then calculated by normalising the concentration of CaO as measured by EMPA to that measured by LA-ICP-MS, as detailed in equation 3.3.

$$X_{cps_{av}} = \sum (X_{cpsscan} - X_{cpsbg}) \times \frac{1}{\sum scan}$$
(3.1)

$$X_{ppm(sample)} = \left(\frac{X_{ppm_{std}}}{X_{cps_{std}}}\right) \times X_{cps_{av}} (sample)$$
(3.2)

$$X_{ppm_{cor}} = \left(\frac{Ca_{real}}{Ca_{meas.}}\right) \times X_{ppm}$$
(3.3)

X/Ca	:	element X isotope / EMPA corrected <sup>43</sup> Ca
bg	:	background measurement
cps	:	counts per second of the isotope
ppm	:	parts per million concentration of the element
scan	:	one integration on the isotope
std	:	concentration/cps in the standard
av	:	average of all scans
cor	:	Ca corrected isotope concentration

Table 3.2: Symbols used in equations 3.1, 3.2 and 3.3

#### LA-ICP-MS accuracy and reproducibility

In addition to the measurements of refractory inclusions, analyses were also performed on a sample of the Hawaiian Volcanic Observatory basalt glass standard (BHVO-2G), so as to assess the accuracy and reproducibility of the LA-ICP-MS trace element data. Three LA-ICP-MS analyses were performed on a single BHVO-2G sample and bracketed by analyses of the BCR-2 standard. LA-ICP-MS settings and data processing were kept consistent with those used on refractory inclusions samples (Section 3.1.3). The processed BHVO-2G analyses were checked against the preferred standard values from GeoRem (GeoRem, 2006). Measured values were generally within error of GeoRem preferred values for BHVO-2G (Table 3.3).

Elements which produced values outside of error of the GeoRem (2006) recommended values were Sc (-0.32 %), Cu (+6.5 %), Y (-0.54 %), Ce (+0.29 %) and U (+8.4 %). Of the measured elements with >1 % variance from the recommended values, Cu has a large recommended  $2\sigma$  error (± 8.7 %) and U has very low measured concentrations. The low repetition of measurements may also have resulted in an underestimate of the measured  $2\sigma$ . Despite these outliers, the reproducibility and accuracy of LA-ICP-MS measurements was deemed acceptable.

Elmt	BHVO-2G	2σ	BHVO 01	BHVO 02	BHVO 03	Measured	Meas.	Within
	Preferred					Average	<b>2</b> σ	error?
Sc	33.0	2.0	30.0	29.4	28.9	29.5	1.0	Ν
Ti	2.79	0.02	2.75	2.74	2.67	2.72	0.09	Y
V	308	19.0	327	329	323	326	6.4	Y
Cr	293	12.0	300	296	315	303	20.2	Y
Mn	1317	300	1208	1184	1228	1207	44	Y
Co	44.0	2.0	46.5	47.0	49.0	47.5	2.6	Y
Ni	116	7.0	130	139	151	140	20.3	Y
Cu	127	11.0	152	152	157	153	6.1	Ν
Zn	102	6.0	105	102	102	103	3.2	Y
Ga	22.0	3.0	22.9	22.1	23.0	22.6	1.0	Y
Rb	9.20	0.04	9.17	9.31	9.31	9.26	0.16	Y
Sr	396	1.0	405	397	401	401	7.9	Y
Y	26.0	2.0	23.1	23.2	23.6	23.3	0.6	Ν
Zr	170	7.0	159	159	154	158	5.9	Y
Nb	18.3	0.80	17.9	17.7	17.8	17.8	0.16	Y
Мо	3.80	0.2	4.60	4.43	4.19	4.40	0.4	Y
Cs	0.10	0.02	0.12	0.10	0.08	0.10	0.04	Y
Ва	131	2.0	134	133	133	133	1.8	Y
La	15.2	0.2	15.3	15.0	14.1	14.8	1.3	Y
Ce	37.6	0.2	38.7	39.7	38.9	39.1	1.1	Ν
Pr	5.35	0.22	5.22	5.00	5.28	5.17	0.29	Y
Nd	24.5	0.20	24.4	24.3	23.8	24.2	0.67	Y
Sm	6.10	0.03	6.10	5.99	5.68	5.92	0.43	Y
Eu	2.07	0.01	2.10	2.14	2.06	2.10	0.07	Y
Gd	6.16	0.05	6.40	5.58	6.14	6.04	0.84	Y
Dy	5.28	0.05	5.13	5.08	4.91	5.04	0.24	Y
Er	2.56	0.02	2.54	2.39	2.46	2.46	0.16	Y
Yb	2.01	0.02	1.98	2.06	1.89	1.97	0.17	Y
Lu	0.28	0.003	0.24	0.24	0.27	0.25	0.04	Y
Hf	4.32	0.18	4.30	4.34	4.14	4.26	0.20	Y
Та	1.15	0.10	1.10	1.09	1.09	1.09	0.01	Y
W	0.23	0.04	0.22	0.22	0.25	0.23	0.04	Y
Pb	1.70	0.20	1.95	1.81	1.94	1.90	0.16	Y
Th	1.22	0.05	1.13	1.24	1.10	1.16	0.14	Y
U	0.40	0.003	0.44	0.45	0.45	0.45	0.01	Ν

**Table 3.3:** Measured trace element data (ppm) for BHVO-2G by LA-ICP-MS at Victoria University of Wellington versus the GeoRem recommended values (GeoRem, 2006). All values are concentrations in ppm. Abbreviation: Elmt: element.

# 3.2 Al/Mg and Mg isotope analyses

### 3.2.1 Sample preparation

Sample fragments not used in the major and trace element analyses were used for the <sup>26</sup>Al-<sup>26</sup>Mg dating study. After being lightly crushed with an

agate mortar and pestle, samples were hand-picked in order to remove unwanted matrix material and extract "representative" bulk samples and individual mineral separates where possible. It was only possible to hand-pick bulk samples of fine grained and small refractory inclusions. CAI 1, a coarse-grained sample, was of sufficient size to allow feldspathic (anorthite and melilite) and pyroxene mineral separates to be picked in addition to whole rock samples. Hand-picking of CAI 5, a fine grained, zoned inclusion (Section 2.3.1), produced separate whole-rock samples of the pink coloured core zone and the white coloured rim zone, in addition to a representative whole rock sample including both the core and the rim.

The hand-picked samples were placed in 3 mL teflon Savillex capsules and labelled. Each separate sample was weighed using a high precision Sarrtorius balance and the approximate amount of magnesium in each sample was calculated (Eq. 3.4) to ensure there was sufficient material to conduct the Mg isotope analyses. In equation 3.4, 24.35 is the atomic weight of Mg and 40.35 is the atomic weight of MgO.

$$Mg(mg) \text{ in sample} = Wt \text{ sample} (mg) \times Wt \% MgO \times \frac{24.35}{40.35}$$
(3.4)

### 3.2.2 Acid digestion and column chemistry

All acid digestion and ion exchange column chemistry steps were conducted in class 10 laminar flow hoods located in a class 100 clean laboratory at Victoria University of Wellington. Ultrapure SeaStar (SS) acids were used in all of the column chemistry steps described in this section. Mg chemical yield at the conclusion of the three ion exchange column chemistry was >99%.

Samples were taken into solution in order to determine the Al/Mg ratio and separate Mg from other elements within the samples for Mg isotope analysis. The digestion process was designed to avoid incomplete dissolution of either Al or Mg phases and to avoid mass dependent Mg isotope fractionation.

Sample	$\delta^{26}$ Mg*	$\pm$ 2 $\sigma$ (‰)	$\delta^{25}$ Mg	$\pm$ 2 $\sigma$ (‰)	n
Ca/Mg	+0.0102	$\pm 0.0080$	+0.67	$\pm 0.15$	4
Ca/Mg (= 0.2)	+0.0294	$\pm \ 0.0142$	+0.80	$\pm 0.13$	1
Ca/Mg (= 2.0)	+0.2425	$\pm 0.0240$	+0.76	$\pm 0.18$	1
Mn/Mg	-0.0022	$\pm 0.0089$	+0.64	$\pm 0.05$	3
Ti/Mg	+0.0074	$\pm 0.0094$	+0.30	$\pm 0.01$	3
Ni/Mg	-0.0008	$\pm 0.0074$	+0.16	$\pm 0.03$	5
Fe/Mg	+0.0095	$\pm 0.0081$	+0.24	$\pm 0.05$	4
Cr/Mg	-0.0036	$\pm 0.0096$	+0.35	$\pm 0.20$	3
Al/Mg	-0.0072	$\pm 0.0083$	+0.27	$\pm 0.01$	3
Na/Mg	-0.0002	$\pm \ 0.0120$	+0.05	$\pm 0.01$	2

**Table 3.4:**  $\delta^{26}Mg^*$  and  $\delta^{25}Mg$  data for a solution of BDH Aristar Mg standard doped with 2% of different contaminant elements measured against a pure Aristar Mg solution. The effect of calcium is also shown at the 20% and 200% level. From Schiller et al. (In Submission)

Weighed samples, typically 1–10 mg, were placed in Savillex Teflon beakers and 300  $\mu$ L of concentrated SS HF acid and 50  $\mu$ L of concentrated SS HNO<sub>3</sub> acid were added. The beaker was placed on a hotplate for 24-48 hours at approximately 125 °C. The digestion procedure then progressed as detailed in Figure 3.2 until each sample had been fully dissolved. In addition to processing samples of refractory inclusions, an analytical blank was also chemically processed in order to measure the presence of any analytical contamination or contamination during the dissolution process.

The acquisition of accurate Mg isotope data can be compromised by the presence of elements such as Ti, Na, Cr, Al, Fe and Ca. Using the same analytical instruments as in this study, Schiller et al. (In Submission) produced data illustrating the influence of contaminations of Ti, Na, Cr, Al, Fe and Ca when measuring Mg isotopic ratios via MC-ICP-MS (Table 3.4). At a 2% concentration, Ca (<sup>48</sup>Ca<sup>2+</sup>) will inflate a  $\delta^{26}$ Mg\* measurement by 0.8% (Table 3.4; Schiller et al. (In Submission)). Ca is the most problematic



**Figure 3.2:** A schematic detailing the process of dissolution undertaken for all refractory inclusions. This technique was also used in Schiller et al. (2007) and Schiller et al. (In Submission)

element present in CAIs, as the constituent minerals (Section 1.5.2) can contain many hundreds of percent more Ca than Mg (Table 1.3 & Fig. 1.5), as well as high concentrations of Ti, Na, Cr, Al and Fe.

The presence of these elements in the dissolved refractory inclusions meant special care needed to be taken during chemical processing in order to produce a >99 % Mg solution, which is essential for isotopic measurements using MC-ICP-MS (Schiller et al., 2007). The chemical processing employed to prepare and purify the sample involved a series of column-based ion-exchange chemical techniques. Three steps using anion, diglycolamine (DGA) and cation exchange resins were utilised. Matrix elements were progressively eluted from the dissolved samples with each exchange column step.

Anion and DGA columns were fashioned from Eppendorf EP Tip 1250  $\mu$ L pipette tips. After removing 2 mm from the point of the pipette tip in order to enhance fluid flow, a porous polypropylene frit was pushed into the tapered end of each column and an appropriate quantity of anion or DGA exchange resin was then placed in the column chamber (Fig. 3.3 a). Cation exchange columns were fashioned from 1 mL squeezable pipettes. Each pipette had its domed top removed and a porous polypropylene frit pushed flat into the tapered end and 1 mL of cation exchange resin was then placed in the column state placed in the column state placed in the column chamber (Fig. 3.3 b).

In all column chemistry steps, the ability of liquid to flow through the loaded exchange resin was checked using distilled, ultra clean (>18.2 M $\Omega$ ) H<sub>2</sub>O. Any air bubbles that may have been present in the exchange resin were removed. Prior to loading any sample material, each column was washed three times with a two-step sequence of distilled water and an appropriate acid (concentrated HCl for the anion columns, 3 M HNO<sub>3</sub> for the DGA columns, 1 M HNO<sub>3</sub>/0.1 M HF solution for the cation columns).

#### Anion exchange column chemistry

Anion exchange chemistry was performed in order to totally remove Fe from the dissolved samples (Fig. 3.4). The anion exchange resin used was



**Figure 3.3:** Diagrams of the two types of exchange columns constructed for use in all acid ion exchange chemistry. (a) An Eppendorf EP Tip 1250  $\mu$ L pipette tip fashioned into an anion or DGA exchange column. (b) A 1 mL pipette fashioned into a cation exchange column.

Bio-Rad AG 1-X8 100-200 mesh chloride form resin, and elution of Mg was performed using concentrated HCl. 0.5 mL of resin was used in each column. Samples were loaded onto labelled columns in 1 mL of concentrated HCl. Four complete washes of concentrated HCl were performed whereby each column was filled to the very top with acid, and then allowed to drain completely. The eluted concentrated HCl containing Mg was then evaporated on a hot-plate. Following evaporation, samples were converted to nitrates by adding and then evaporating 1 mL of concentrated HNO<sub>3</sub>.

#### DGA ion exchange column chemistry

In the second ion exchange step, Eichrom DGA resin was used to remove Ca (Fig. 3.5). 0.5 mL of resin was loaded into each column, samples were loaded onto the columns in 1 mL of 3 M HNO<sub>3</sub> and elution was performed with 3 M HNO<sub>3</sub>. Four complete washes of 3 M HNO<sub>3</sub> were passed through each column, collected, evaporated and then taken up into concentrated



Figure 3.4: The anion exchange chemistry procedure (extraction step 1).

HNO<sub>3</sub>. This column chemistry step was conducted twice in order to remove the high concentrations of Ca present in refractory inclusions. Following the second round of evaporation, samples were taken up in a solution of 1 M HNO<sub>3</sub> and 0.1 M HF.



Figure 3.5: The DGA ion exchange column chemistry procedure (extraction step 2).

#### Cation exchange column chemistry

Cation exchange chemistry was conducted in order to remove Ti, Na, Cr and Al from the CAI and AOA samples (Fig. 3.6). The resin used in this step was Bio-Rad AG 50W-X8 200-400 mesh hydrogen form resin with 1 mL in each column (Fig. 3.3a). Samples were loaded onto the resin in 1 mL of 1 M HNO<sub>3</sub>/0.1 M HF solution. A 6 mL elution using a 1 M HNO<sub>3</sub> and 0.1 M HF solution was conducted first and discarded. A 16 mL wash of the same acid mix was then collected and evaporated prior to a second column pass-through using the same procedure. The resultant dried samples were taken up into 0.1 M HNO<sub>3</sub> for Mg isotope analysis by MC-ICP-MS.



Figure 3.6: The cation exchange column chemistry procedure (extraction step 3).

The presence of Ca (<sup>48</sup>Ca<sup>2+</sup>) can generate erroneous  $\delta^{26}$ Mg\* measurements (Schiller et al., In Submission). In order to ensure purity of the Mg samples at the conclusion of all the column chemistry steps, a small aliquot of each sample was taken into solution as described in Section 3.2.4, in order to test for the presence of Ca. Any sample that recorded Ca above background measurements was reprocessed through DGA and cation

chemistry in order to properly purify the sample.

### 3.2.3 <sup>27</sup>Al/<sup>24</sup>Mg measurements by solution ICP-MS

Following the digestion of whole-rock and mineral separates, each solution was aliquoted in order to determine the <sup>27</sup>Al/<sup>24</sup>Mg ratio by way of solution ICP-MS. An Agilent 7500 ICP-MS in solution mode was used in this analysis, the settings of which are given in Appendix B.2. Two solutions were employed as standards during the sample analyses.

The first standard was a gravimetrically prepared solution produced by mixing a weighed 2:1 solution of BDH Aristar Al and BDH Aristar Mg ICP Multi-element standard solutions, using a high precision Sartorius balance. Each standard solution contained 1000 ppm pure (99.999%) Al or Mg in dilute (0.5 %) HNO<sub>3</sub>. The resulting solution had a  ${}^{27}$ Al/ ${}^{24}$ Mg value of 2.006.

The second standard was a sample of BCR-2 dissolved in HNO<sub>3</sub>. BCR-2 has a recommended  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  value of 3.76 ± 4.0 % (GeoRem, 2006; Schiller et al., In Submission). Between the analysis of each sample or standard aliquot, a 0.2 M HNO<sub>3</sub> wash step was performed in order to avoid sample cross-comtamination. Each sample aliquot was analysed twice for a total of 90-100 seconds per analysis. The gravimetric and BCR-2 standard analyses bracketed sample aliquot blocks, comprised a sequence of 5 analyses (Table 3.5). The bracketing scheme was required to remove machine-derived analytical drift over the course of the analyses and to correct for elemental/isotopic fractionation.

Isotope dilution was not employed, or considered in order to increase isotopic precision, as synthetic samples of <sup>26</sup>Al are too radioactive to be used in New Zealand.

### 3.2.4 Mg isotope ratio determinations by MC-ICP-MS

Samples were analysed for the proportions of <sup>24</sup>Mg, <sup>25</sup>Mg & <sup>26</sup>Mg isotopes using a Nu Plasma high resolution MC-ICP-MS at Victoria University of Wellington. <sup>24</sup>Mg, <sup>25</sup>Mg & <sup>26</sup>Mg were monitored using the L5, Ax and H6

Chara #	Solution		
Step #	Analysed		
1	HNO <sub>3</sub> Blank		
2	Al/Mg Standard		
3	Wash		
4	BCR-2		
5	Wash		
6	Sample 1		
7	Wash		
8	Sample 2		
9	Wash		
10	Sample 3		
11	Wash		
12	Sample 4		
13	Wash		
14	Sample 5		
15	Wash		
16	HNO <sub>3</sub> Blank		
17	Al/Mg Standard		

**Table 3.5:** A typical analysis block used for measuring <sup>27</sup>Al/<sup>24</sup>Mg ratios in dissolved refractory inclusion samples. The Al/Mg standard is a gravimetrically prepared standard with a <sup>27</sup>Al/<sup>24</sup>Mg ratio of 2.006. BCR-2 is a dissolved sample of the Columbia River Basalt standard in dilute (0.5 %) HNO<sub>3</sub>. All samples were analysed twice.

Faraday collectors, respectively. All Faraday collectors were equipped with 10<sup>11</sup> Ohm resistors. Samples were introduced to the argon plasma torch using a desolvating nebulizer system.

A portion of each sample was placed into a clean 7 mL Teflon beaker and diluted with 0.1 M HNO<sub>3</sub>. After dilution, each sample was checked to ensure the presence of Mg at a concentration of 1–2 ppm. This would result in measurements of 8–9 ×  $10^{-11}$  A on the Faraday collector monitoring <sup>24</sup>Mg. Samples that did not produce the desired amperage were either diluted with 0.1 M HNO<sub>3</sub>, or additional sample was added until an adequate amperage was recorded on the MC-ICP-MS.

Analyses were conducted continuously over several 24 hour periods to

ensure machine stability and consistency. Each individual sample analysis involved a total of four blocks, each of which was comprised of 120 seconds of baseline measurements followed by 400 seconds of data acquisition. This totalled 480 seconds of baseline and 1600 seconds of sample data acquisition for each analysis. Machine-related drift was corrected by bracketing each sample measurement with a similar measurement of Dead Sea Magnesium Ltd (DSM-3) standard (Galy et al., 2003). A wash of 0.1 M HNO<sub>3</sub> was run for several minutes between each sample and standard analysis in order to remove any remaining material from the MC-ICP-MS, as this eliminates any effects of sample cross-contamination. Multiple, replicate measurements were conducted on all samples in this study.

The chemical techniques employed in this study are designed to produce almost pure (>99 %) Mg samples, and as such, some minor contaminates will remain in solution. Pseudo-high-resolution mode was therefore used during all Mg isotope analyses. This gives an effective mass resolution of 2000–2500 which enables a 100 % resolution of all molecular interferences on the high mass side from Mg (e.g.,  ${}^{12}C^{2+}$  and  ${}^{12}C^{14}N^{+}$ ), with the exception of  ${}^{24}Mg^{1}H^{+}$ , which is resolved at the 70 % level and affects both samples and standards equally (Schiller et al., In Submission). The pseudo-highresolution method cannot resolve interferences on the low mass side of Mg, such as divalent cation  ${}^{48}Ca^{2+}$ . However, using doping tests with exactly the same equipment and chemical techniques as this study, Schiller et al. (In Submission) demonstrated that at the level of purity of the Mg in this study, low mass interferences are lower than analytical precision.

Repeat analyses by Schiller et al. (In Submission) showed the chemical processing methodologies described here were effective in eliminating contaminants in samples before MC-ICP-MS Mg isotope analyses, and introduced no undesirable analytical artefacts. Repeat measurements of BDH Aristar Mg ICP Multi-element standard, and BCR-2 and BHVO-2 standards yielded  $\delta^{26}$ Mg\* within error of zero (Table 3.6). These standards are all terrestrial and a  $\delta^{26}$ Mg\* value of zero is therefore expected.

Sample	δ <sup>26</sup> Mg*	$\pm$ 2 $\sigma$ (‰)	$\delta^{25}$ Mg	$\pm$ 2 $\sigma$ (‰)	n
Aristar	+0.0010	$\pm 0.0062$	+0.071	$\pm 0.034$	9
BCR-2	+0.0017	$\pm 0.0044$	-0.017	$\pm 0.095$	18
BHVO-2	+0.0017	$\pm 0.0034$	-0.153	$\pm 0.049$	42

**Table 3.6:**  $\delta^{26}Mg^*$  and  $\delta^{25}Mg$  values for the BDH Aristar Mg ICP Multi-element, BCR-2 and BHVO-2 standards from Schiller et al. (In Submission). *n* is the number of repeat measurements. All  $\delta^{26}Mg^*$  values are within error of zero.

# 3.2.5 Solution ICP-MS Al/Mg processing

Processing of data acquired during Al/Mg analyses involved:

- 1. Correcting measured data to account for background measurements.
- 2. Calculating the mean measured  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  ratio (Equation 3.5).
- 3. Normalising the mean measured ratio to the gravimetrically prepared (Al/Mg = 2.006) standards (Equation 3.6).
- 4. Determining the  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  atomic ratio (Equation 3.7).

This series of calculations (Equations 3.5 - 3.7) gave the final atomic ratio value required for the calculation of  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  for each sample.

$$\frac{{}^{27}\text{Al}}{{}^{24}\text{Mg}}_{\text{measured}} = \frac{{}^{27}\text{Al}_{\text{msrmnt }av} - {}^{27}\text{Al}_{\text{bg }av}}{{}^{24}\text{Mg}_{\text{msrmnt }av} - {}^{24}\text{Mg}_{\text{bg }av}}$$
(3.5)

$$\frac{\text{Al}}{\text{Mg}}_{\text{sample(corr)}} = 2.006 \times \frac{\frac{27 \text{Al}}{24 \text{Mg}}_{\text{msrd sample}}}{\frac{27 \text{Al}}{24 \text{Mg}}_{\text{msrd standard}}}$$
(3.6)

$$\frac{{}^{27}\text{Al}}{{}^{24}\text{Mg}}_{sample(corr)} = \frac{\frac{\text{Al}}{\text{Mg}_{sample(corr)}} \times \frac{\text{Mg}_{at wt}}{\text{Al}_{at wt}}}{{}^{24}\text{Mg}_{abundance}}$$
(3.7)
$^{27}\mathrm{Al}/^{24}\mathrm{Mg}_{\mathrm{atomic}}$	:	The ratio of the atomic weights of $^{27}$ Al & $^{24}$ Mg
$^{24}\mathrm{Mg}$ abundance	:	The abundance of <sup>24</sup> Mg in comparison
		to <sup>25</sup> Mg and <sup>26</sup> Mg (=0.7899)
msrmnt	:	A single <sup>27</sup> Al/ <sup>24</sup> Mg measurement
msrd	:	Measured
av	:	Average
bg	:	Background measurement
msrd	:	The measured value
std	:	The gravimetrically prepared Al/Mg standard
		(A1/Mg=2.006).
sample(corr)	:	Corrected sample
at wt	:	Atomic weight

Table 3.7: Symbols used in equations 3.5, 3.6 & 3.7

# 3.2.6 MC-ICP-MS Mg isotope analysis processing

 $δ^{26}$ Mg values for all samples were calculated by internally normalising measured  ${}^{26}$ Mg/ ${}^{24}$ Mg to  ${}^{25}$ Mg/ ${}^{24}$ Mg = 0.12663, using the exponential mass fractionation law (Eq. 3.8; Schiller et al., In Submission; Jacobsen et al., 2008). In Equation 3.8 the symbols m1, m2, and m3 are masses of isotopes  ${}^{24}$ Mg,  ${}^{25}$ Mg and  ${}^{26}$ Mg, respectively. CAIs have very fractionated Mg isotope compositions and the choice of using the exponential mass fractionation law (β = 0.511) was taken in order to remain consistent with the studies of Jacobsen et al. (2008) and Bizzarro et al. (2004). Jacobsen et al. (2008) noted that the exponential mass fractionation law gives the best fit to CAI data and that using a consistent β value is essential when discussing canonical vs. supra-canonical  ${}^{26}$ Al/ ${}^{27}$ Al<sub>0</sub> ratios.  $δ^{26}$ Mg\* denotes the radiogenic component of  ${}^{26}$ Mg for each sample which was determined by calculating the difference between the value for the sample and the average value of the bracketing DSM-3 standards in per mil (‰) notation (Eq. 3.9 and Table 3.8).

$$\beta = \frac{\ln(m1/m2)}{\ln(m1/m3)} = 0.511 \tag{3.8}$$

$$\delta^{26} Mg^*_{sample} = \left( \frac{\frac{26}{Mg}/24}{Mg_{sample}}{\left(\frac{(26}{Mg}/24}{Mg_{std1}}) + (26}{Mg/24}{Mg_{std2}}) - 1 \right) \times 10^3 \quad (3.9)$$

**Table 3.8:** Symbols used in equation 3.9

$\delta^{26}Mg^*_{sample}$	:	The $\delta^{26}$ Mg* of the sample
$^{26}Mg/^{24}Mg_x$	:	The fractionation corrected ${}^{26}Mg/{}^{24}Mg$ measurement
		as recorded and processed by the MC-ICP-MS for sample
		or standard x
std1	:	bracketing standard run before the sample
std2	:	bracketing standard run after the sample

# **3.2.7** Calculation of <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>

Model <sup>26</sup>Al/<sup>27</sup>Al values were calculated for individual samples by plotting an isochron of the measured sample <sup>27</sup>Al/<sup>24</sup>Mg and  $\delta^{26}$ Mg\* values through the chondritic values of 0.1 and 0, respectively. However, none of the reported multi-CAI isochrons were forced through the chondritic value.

Equation 3.10 is used to calculate relative ages of analysed inclusions and convert isochron slope error values into date errors. In Equation 3.10,  $\lambda = 9.50 \times 10^{-7} \text{ year}^{-1}$  (corresponding to a T<sub>1/2</sub> for <sup>26</sup>Al of 730 kyr) and the <sup>26</sup>Al/<sup>27</sup>Al value of *sample 1* > *sample 2*.

$$\Delta t = \frac{1}{\lambda} \times \ln \left( \frac{{}^{26}\text{Al}/{}^{27}\text{Al}_{sample 1}}{{}^{26}\text{Al}/{}^{27}\text{Al}_{sample 2}} \right)$$
(3.10)

# Chapter 4

# Results

# 4.1 Mineralogy and major element data for CAIs

Minerals were identified by major element oxide proportions. Typical major element oxide compositions of all minerals encountered are given in Table 4.1. Table 4.2 details the Appendices where full major and trace element data, as well as maps of analysed points for each inclusion are located. A summary of petrographic compositions of all refractory inclusions analysed in this study can be found in Table 4.3. Petrographic descriptions for all Allende refractory inclusions can be found in Section 2.5. Maps of all analytical points and all major element analytical data can be found in Appendices C and D respectively. Mineral compositions were those of mounted sample sections and assumed to represent the composition of the entire refractory inclusion.

# CHAPTER 4. RESULTS

C4 P301	ənilənqə <sup>N</sup>		48.5	0.02	37.9	0.38	0.01	0.06	1.78	10.2	1.58	100.44
C2 6404	əfibsıbnA		36.1	0.08	0.46	32.7	0.29	4.25	25.7	0.06	0.14	9.99
C3 L303	Hedenbergite		50.3	0.32	1.47	19.6	0.72	4.75	22.8	0.19	0.06	100.18
42 P206	əbieqoiU	xene	54.1	0.09	0.07	5.13	0.28	16.1	24.6	0.04	0.01	100.51
CI 1309	dəir-iT & -sO	Pyro	38.2	8.84	18.5	0.00	0.00	9.79	25.1	0.04	0.04	100.18
C3 6515	Ca-poor		48.5	5.17	13.4	0.32	0.08	32.2	0.47	0.00	0.04	100.34
C8 6 <del>7</del> 02	ənivilO		36.2	0.05	0.07	31.3	0.19	31.9	0.49	0.09	0.02	101.13
C2 F404	ləniqZ		0.19	0.29	71.5	1.00	0.00	27.8	0.08	0.00	0.00	100.47
CI 1136	( <sub>8</sub> ÅÅ) əfililəM		24.2	0.07	34.4	0.05	0.14	1.69	40.8	0.09	0.01	101.45
C0 F102	( <sub>88</sub> ¥Å) əfililəM		35.1	0.01	15.9	0.04	0.04	8.76	40.2	0.19	0.04	100.18
C8 F208	Feldspar	oclase	57.9	0.03	26.7	0.20	0.00	0.02	8.28	6.74	0.21	100.04
C0 L304	Anorthite	Plagic	42.7	0.03	36.2	0.09	0.05	0.05	20.9	0.08	0.03	100.00
		Oxide	$SiO_2$	$TiO_2$	$Al_2O_3$	FeO	MnO	MgO	CaO	$Na_2O$	$K_2O$	Total
	L											

Table 4.1: Typical oxide weight percentages for all minerals within refractory inclusions examined by electron microprobe. Numbers directly above mineral names are shortened inclusion names followed by the analytical point e.g. C0 P302 is the point CAI 0, phase 3, analysis 2.

Inclusion	Analytical	Major element	Trace element
name	site map(s)	analyses	analyses
CAI 0	C.1	D.1	E.2 – E.4
CAI 1	C.2	D.2 – D.5	E.6 – E.8
CAI 2	C.3	D.7	E.9 & E.10
CAI 3	C.4	D.8 & D.9	E.11 & E.12
CAI 4	C.5 & C.6	D.10 & D.11	E.13 & E.3
CAI 5	C.7 – C.8	D.12	E.15 & E.3
CAI 8	C.9	D	E.17 & E.18
AOA 1	C.10	D	E.19 & E.20
AOA 2	C.11	D	E.21 & E.22

**Table 4.2:** Appendix locations for analytical site maps, major element oxide and trace element results for all refractory inclusions analysed in this study.

# 4.1.1 CAI 0 and CAI 1

CAI 0 is a type B2 CAI and CAI 1 is a type B1 CAI. Both are comprised of melilite (CAI 0:  $Åk_{20-40}$ , CAI 1:  $Åk_{17}$ ), Ca-pyroxene, anorthite and iron-free spinel (Table 4.3). The petrology of CAI 0 is indicative of mineral crystallisation occurring in an environment at a lower temperature than that of CAI 1. CAI 0 contains twice the volume of anorthite as CAI 1 (Table 4.3), with the condensation temperature of anorthite at 1387 K (Table 1.3). The most refractory mineral phase analysed in these type B CAIs was melilite. Åkermanite values of Åk <sub>28</sub> (CAI 0) and Åk <sub>17</sub> (CAI 1) indicate a lower mineral condensation temperature for CAI 0 (Section 1.5.2).

# 4.1.2 CAI 2

The fluffy type A CAI 2 is composed of plagioclase, anorthite, spinel, Ca-pyroxene and minor melilite (Åk <sub>3</sub>; Table 4.3). Analysed plagioclase contains significant Na<sub>2</sub>O (7–9 wt %), very low FeO (1 wt %) and variable MgO (1 – 5 wt %). This can be described as a member of the plagioclase solid-solution of albite (NaAlSi<sub>3</sub>O<sub>8</sub>) – anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). Albite



**Figure 4.1:** A mosaic of back-scattered electron photographs of refractory inclusions analysed in this study. The blue bar in each segment is = 1 mm. (a) CAI 0, (b) CAI 1, (c) CAI 2, (d) CAI 3, (e) CAI 4, (f) CAI 5, (g) CAI 8, (h) AOA 1, (i) AOA 2.

concentrations of 30–50 %, with a corresponding anorthite concentration of 50–70 % are indicative of the mineral labradorite. Albite concentrations in the plagioclase phase of CAI 2 are within the range of 37–50 %.

# 4.1.3 CAI 3

CAI 3 is a compact type A CAI comprised of low-Ca-pyroxene, anorthite, nepheline and Ca-pyroxene (hedenbergite) (Table 4.3). Areas consisting primarily of the secondary mineral hedenbergite and nepheline are enclosed by anorthite and low-Ca pyroxene phases (Fig. 4.2). Fassaite is present across the entire inclusion.

	I	Plagio	oclas	e	Ру	roxe	ne	Spi	nel				
Sample	Anorthite	Melilite	Feldspar	Labradorite	Ca rich	Ca poor	Hedenbergite	Fe free	Fe-bearing	Nepheline	Andradite	Olivine	Unknown
CAI 0	21	33			35			11					
CAI 1	9	37			39			15					
CAI 2	34	6		38	10			13					
CAI 3	25					24	21			30			
CAI 4					39		6		40	15			
CAI 5 (core)		23		19					10		1		47
CAI 5 (rim)		31		27					14				29
CAI 5 (bulk)		29		26					13		0.2		32
CAI 8	62		33									5	
AOA 1			25		34							41	
AOA 2			31		34							35	

**Table 4.3:** Mineral proportions for refractory inclusions. Values are volume percentages.

# 4.1.4 CAI 4

CAI 4 is a fine-grained CAI containing Ca-pyroxene, nepheline, Fe-rich spinel and minor hedenbergite (Table 4.3). CAI 4 has a zoned crystal structure (Fig. 4.3). Spinel cores, 10–30  $\mu$ m in diameter, are fully enclosed by 5–10  $\mu$ m thick Ca-pyroxene mantles. Hedenbergite is present as a non-enclosing crust in direct contact with the Ca-pyroxene. Nepheline fills the inter-crystal areas. Ca-pyroxene occurs as the solid solution CaMgSi<sub>2</sub>O<sub>6</sub>–CaAl<sub>2</sub>SiO<sub>6</sub> (Appendix D.10 & D.11). A traverse across the Ca-pyroxene mantle and an estimate of the proportions of each end member was not possible due to grain size. This is the structure expected in a fine-grained CAI (Brearley & Jones, 1998).



**Figure 4.2:** A back-scattered electron photograph of CAI 3 overlain with a schematic of the mineral structure. The yellow borders outline areas primarily consisting of hedenbegite and nepheline. The blue border outlines the area primarily consisting of anorthite and low-Ca-pyroxene. Abbreviations: Hed: hedenbergite, Neph: nepheline, Low-Ca-Px: low-Ca-Pyroxene.

# 4.1.5 CAI 5

CAI 5 is a fine-grained, zoned CAI. The rim–core proportions in the exposed surface of the in situ sample (Fig. 2.9) were 83% and 17% respectively. Both core and rim comprise melilite, plagioclase, Fe-bearing spinel and an unidentified mineral (phase 3) (Table 4.3). The core region also contains andradite as an accessory mineral. The rim contains an unknown proportion of clinopyroxene (P5 in Appendix D.12 & P109 in Fig. C.8 rim). The unidentified mineral phase 3 has an oxide component, comprising  $\leq$  50% volume, missing from all EMP spots. SO<sub>3</sub> and Cl were added in analyses of this phase, both yielded  $\leq$  1 wt %. Back-scattered electron photographs of CAI 5 (Appendix C.7 and C.8), show phase 3 as



**Figure 4.3:** *A highly magnified back-scattered electron photograph displaying the crystal structure of CAI 4.* 

being close to black in colour, indicative of low mass elements. All spinel in CAI 5 is Fe-bearing and therefore secondary.

Mineral oxide weight percentages of  $Al_2O_3$ , MgO and TiO<sub>2</sub> vary in phase 3. Analyses of phase 3 from the core region of CAI 5 consistently contain 2–4 times the  $Al_2O_3$ , half the MgO, and over an order of magnitude more TiO<sub>2</sub> than the same phase in the rim. There is no identifiable internal variation between sites within the core, or sites within the rim.

# 4.1.6 CAI 8

CAI 8 is a fine-grained CAI consisting of anorthite, feldspar and minor amounts of olivine. Internal mineral oxide weight percentages were consistent (Appendix D.13).

# 4.1.7 AOA 1 and AOA 2

The inclusions identified as AOAs showed little variation in structure, petrology or oxide chemistry. Both inclusions contained relatively equal volumes of olivine, feldspar and pyroxene as end member proportions of the hedenbergite–diopside solid solution. Pyroxene in AOA 1 consisted of  $21 \pm 8$  % hedenbergite, AOA 2 consisted of  $25 \pm 6$  %. There was no trend in solid-solution variation related to crystal location within the inclusion.

# 4.2 Trace elements

A suite of trace elements (Table 3.1) were analysed by LA-ICP-MS (Section 3.1.3) for all refractory inclusions. The bulk CI normalised trace element patterns are discussed in Section 4.2.1 and CI normalised REE patterns are discussed in depth in Section 4.2.2. All values presented and discussed in this section have been normalised to CI chondrite values from Lodders (2003). Processed ppm values for all analyses and CI chondrite values from Lodders (2003) can be found in Appendix E.

## 4.2.1 Bulk trace element patterns

Bulk trace element concentrations were calculated for each refractory inclusion by normalising each individual, targeted mineral's trace element concentration to its volume percentage. For example, melilite comprises 33 % of the volume of CAI 0 (Table 4.3). Concentrations of trace elements for melilite were normalised to 33 % and then added to the bulk total. Analyses that did not target all minerals within a refractory inclusion (e.g, spinel was not analysed for CAI 1), were normalised to 100 %.

CI-normalised trace element patterns for all analysed refractory inclusions are displayed in Figures 4.4 - 4.7. Elements are plotted in order of atomic number, from <sup>45</sup>Sc to <sup>238</sup>U. CI normalised trace element patterns for all analysed refractory inclusions can be divided into three major categories, A (CAIs 0, 1 and 2), B (CAIs 3 and 4) and C (CAIs 5 and 8 and

62



Figure 4.4: CI-normalised bulk trace element patterns for CAIs 0, 1 & 2.



**Figure 4.5:** *CI-normalised bulk trace element patterns for CAIs 3 & 4.* 

AOAs 1 and 2). Category A and B refractory inclusions have very similar patterns of CI normalised values between Sc and Ga, with flat super-chondritic LREE values and similar Th and U values. Category A inclusions have flat HREE patterns with negative Eu and Yb anomalies in CAI 2 (Fig. 4.4; Section 4.2.2). Category B and C inclusions display Group II REE patterns with negative HREE values and a positive Yb anomaly (Fig. 4.5).



Figure 4.6: CI-normalised bulk trace element patterns for CAI 5.



Figure 4.7: CI-normalised bulk trace element patterns for CAI 8 and AOAs 1 & 2.

#### CAIs 0, 1 and 2

CI normalised bulk trace element analyses for CAIs 0 and 1 are presented in Figure 4.4. The volatile element Cs in CAI 0 was below detection of the LA-ICP-MS technique. Tb, Ho, and Tm were not analysed in CAIs 0 and 1. CAIs 1 and 2 display negative Rb and Cs anomalies, and CI-depleted values for Mn, Co, Ni, Cu, Zn and Ga. CAIs 0 and 1 display Group V generalised REE patterns, with flat LREE and HREE, CAI 2 displays a Group III REE pattern (Section 4.2.2). Pb in these CAIs is sub-chondritic and Th and U values are flat between 10 and 100 x CI. CAI 1 displays a positive Nb anomaly not present in CAIs 0 or 2.

The CI normalised bulk trace element patterns for CAI 2 are presented in Figure 4.4. CAI 2 displays positive Ti, Zn and Ta anomalies but the general pattern is otherwise similar to CAIs 0 and 1 with CI-depleted values for Mn, Co, Ni, Cu and Ga. The Group III REE pattern of CAI 2 is discussed in Section 4.2.2.

## CAIs 3 and 4

CAIs 3 and 4 display almost identical bulk trace element patterns (Fig. 4.5). Both show negative Cs anomalies and positive Sr, Nb, Yb and Ta anomalies. The CI normalised trace elements of the two inclusions notably vary only in the relative concentrations of Ti with values of 40.8 (CAI 3) and 4.40 (CAI 4)  $\times$  CI. Both CAIs display a Group II REE pattern.

## CAI 5 core, rim and bulk

Trace elements analyses for representative core and rim samples of CAI 5, in addition to a calculated bulk trace element pattern, are displayed in Figure 4.6. The shapes of CI-normalised patterns for the core and rim are very similar, varying only in CI normalised concentration. CAI 5 displays positive Ti, Sr, Nb, Tm, Yb and Ta anomalies, negative Cr and Cu anomalies and a Group II REE pattern. Differences in core and rim measurements were not due to analytical proceses, as targeted melilite in the core and rim yielded trace element patterns which differed consistently with calculated bulk concentrations (Fig. 4.14; Section 4.2.2)

#### CAI 8, AOA 1 and AOA 2

CI normalised bulk trace element values for CAI 8, AOA 1 and AOA 2 are shown in Figure 4.7. All three refractory inclusions from the CK3 chondrite NWA 1559 have the same CI normalised trace element pattern. All inclusions display positive Ti, Sr, Nb, Ba, Eu, Tm, Yb and Ta anomalies, negative Cu, La, Lu and Hf anomalies and exhibit marked Group II REE patterns. The variation from Th to U is an order of magnitude for CAI 8

Inclusion	Inclusion	Generalised bulk
Inclusion	type	REE pattern
CAI 0	B1	V
CAI 1	B1	V
CAI 2	FA	III
CAI 3	CA	II
CAI 4	FG	II
CAI 5	FG	II
CAI 8	FG	II
AOA 1	AOA	II
AOA 2	AOA	II

**Table 4.4:** Types of REE patterns exhibited by the studied refractory inclusions.

 Abbreviations: FA - fluffy type A; CA - compact type A; FG - fine-grained.

(1.7 and 28.2  $\times$  CI), AOA 1 (0.1 and 1.7  $\times$  CI) and AOA 2 (1.2 and 16.4  $\times$  CI). These are the only bulk values to display this Th–U variation.

# 4.2.2 Rare earth element patterns

The general REE patterns for all analysed inclusions are summarised in Table 4.4. In addition to graphing CI-normalised bulk concentrations, average individual mineral phases are analysed and represented in Figs. 4.8 - 4.17. Full tables of all trace-element data are available in Appendix E. All REE data are representative of the mineral phases tested, and calculated bulk patterns may be biased due to minor minerals being omitted from analysis due to them being too fine-grained to analyse (see the CI-normalised spinel phase in CAI 0 as seen in Figure 4.8). A Group II generalised REE pattern is typical for analysed CAIs, except for CAI 0 and 1 (Group V) and CAI 2 (Group III).

## CAI 0

CAI 0 has a calculated flat, Group V, bulk REE pattern with slight enrichments of Eu and Lu (Fig. 4.8). Anorthite in CAI 0 displays a general

downward trend of LREE to HREE (5 × CI at La through to 0.5 × CI at Er), with a positive Eu anomaly of 50 × CI. Yb and Lu diverge from the general trend with 1 and 40 × CI concentration respectively. The melilite phase displays a similar LREE to HREE trend, with a positive Eu anomaly (22 × CI). Yb and Lu concentrations do not diverge from the general downward HREE trend in melilite. Ca-pyroxene has a trend of LREE enrichment (19 × CI at La to 39 × CI at Sm), a negative Eu anomaly (9 × CI) and a flat trend of HREE (~40 × CI). The spinel phase of CAI 0 yielded poor REE data.



Figure 4.8: CI-normalised REE patterns from CAI 0.

#### CAI 1

CAI 1 has a flat Group V bulk REE pattern (Fig. 4.9). Analysed anorthite has a downward LREE trend ( $20 \times CI$  at La to  $9 \times CI$  at Sm), a positive Eu anomaly ( $70 \times CI$ ) and an upwards trend of HREE ( $7 \times CI$  at Gd to  $17 \times CI$  at Lu). Melilite has a flat REE trend ( $24 \times CI$  at La to  $13 \times CI$  at Lu) and positive Eu anomaly ( $29 \times CI$ ). Ca-pyroxene has an upwards trending LREE–HREE pattern ( $18 \times CI$  at La to  $60 \times CI$  at Lu) and a negative Eu anomaly ( $8 \times CI$ ). Such Group V patterns are typical for type B CAIs (Brearley & Jones, 1998).



Figure 4.9: CI-normalised REE patterns from CAI 1.



Figure 4.10: CI-normalised REE patterns from CAI 2.

# CAI 2

Anorthite, melilite and pyroxene in CAI 2 display Group III REE patterns, as does the calculated bulk composition (Fig. 4.10). The bulk REE pattern is

68



Figure 4.11: CI-normalised REE patterns from CAI 3.

flat (40–60  $\times$  CI) with negative Eu (18  $\times$  CI) and Yb (13  $\times$  CI) anomalies.

## CAI 3 and CAI 4

All mineral phases of CAIs 3 and 4 (Figs. 4.11 and 4.12 respectively) display Group II-like REE patterns. In bulk, LREE are enriched and display a flat pattern (30–40 × CI in CAI 3, 13–18 × CI in CAI 4) and HREE display a general downward trend (5 × CI at Eu to < 1 × CI at Lu in both CAIs) with a positive Yb anomaly (9 × CI for CAI 3, 3 × CI for CAI 4).

# CAI 5

The small average grain size of CAI 5 ( $\leq$  20 µm in diameter), only allowed for whole rock trace element analyses. The bulk REE pattern of CAI 5 displays a volatile-enriched Group II-like pattern with a relative enrichment of LREE over HREE, positive volatile element (Ce, Eu and Yb) anomalies and a positive Tm anomaly (Fig. 4.13). Comparative CI normalised analyses centred on melilite phases from the core and rim are displayed in Figure 4.14. In the core and rim, Eu (36 and 45 × CI



Figure 4.13: CI-normalised Bulk REE patterns from CAI 5 core, rim & "whole rock".

respectively), Yb (66 and 88  $\times$  CI respectively) and Tm (20 and 53  $\times$  CI respectively) diverge by less than an order of magnitude. Normalised Ce values diverge by an order of magnitude between core (22  $\times$  CI) and rim (148  $\times$  CI) (Fig. 4.14).



Figure 4.14: CI-normalised REE patterns for melilite from the core and rim of CAI 5.



Figure 4.15: CI-normalised REE patterns from CAI 8.

# CAI 8, AOA 1 and AOA 2

CAI 8, AOA 1 and AOA 2 from the CK3 chondrite NWA 1559 display a volatile enriched Group II-like REE pattern (Figs. 4.15, 4.16 & 4.17, respectively). The average grain size of these inclusions ( $\leq$  20  $\mu$ m in



Figure 4.17: CI-normalised REE patterns from AOA 2.

diameter) precluded individual mineral phase analysis, therefore analytical data is bulk. REE patterns in these refractory inclusions are very similar to the bulk REE pattern seen in CAI 5, with positive anomalies in volatile REE (Ce, Eu and Yb) and a positive Tm anomaly.

# 4.3 ${}^{27}\text{Al}/{}^{24}\text{Mg}$ and $\delta^{26}\text{Mg}^*$ values

Al and Mg isotope data are reported in Table 4.5. All  $\delta^{25}$ Mg,  $\delta^{26}$ Mg and fractionation corrected  $\delta^{26}$ Mg<sup>\*</sup> data (where \* denotes the radiogenic excess), are reported in parts per mil (‰) relative to the bracketing DSM-3 terrestrial standard, as in Galy et al. (2003), Jacobsen et al. (2008) and Schiller et al. (In Submission).

# 4.3.1 <sup>27</sup>Al/<sup>24</sup>Mg and Mg isotope uncertainties

Uncertainties for all reported Mg isotope compositions (Table 4.5) are derived from the calculated weighted mean of replicated sample analyses that incorporate the errors of sample and bracketing standard analyses (Schiller et al., In Submission). Analyses where the number of repeat analyses (n) is 2–3, have uncertainties (2 $\sigma$ ) on mass-bias-corrected  $\delta^{26}$ Mg\* of  $\pm 0.049\%$  (CAI 8b JB) to  $\pm 0.011\%$  (multiple samples). Analyses with n = 5–9 have weighted means with uncertainties of  $\pm 0.014\%$  (CAI 0 WR CT) to  $\pm 0.007\%$  (multiple samples). These uncertainties are consistent with those reported by Schiller et al. (In Submission).

A 2% error was assigned to all  ${}^{27}$ Al/ ${}^{24}$ Mg measurements (Table 4.5). This error is based on repeated analyses of the USGS BHVO-2 and BCR-2 basalt standards, which yielded values of 1.91 ± 0.02 (2 sd) and 3.80 ś 0.05 (2 sd), respectively, both within error of the preferred values of 1.87 ± 4.4% and 3.76 ± 4.0% (GeoRem, 2006). Repeated analyses in this study and Schiller et al. (In Submission), yield values within 2%, and therefore the conservative 2% margin of error is applied to all  ${}^{27}$ Al/ ${}^{24}$ Mg measurements.

# **4.3.2** Notes on stable $\delta^{25}$ Mg isotope values

The terrestrial J11 olivine standard analysed in this study has a  $\delta^{25}$ Mg value = -0.161 ± 0.068 ‰. All CAIs from NWA 2364 (CAI 0, CAI 1, CAI 2, CAI 3 and CAI 4; Table 4.5), NWA 1559 (CAI 5; Table 4.5) and Allende (A39, A43, A44A, AJEF; Table 4.6) have heavy (0.028 ± 0.006 ‰ for CAI 4) to very

heavy (6.816 ± 0.005 ‰ for CAI 1 WR 1)  $\delta^{25}$ Mg value. This is evidence for evaporative processes causing Mg isotope fractionation, evaporating light <sup>24</sup>Mg from the bulk composition of each CAI, thus enriching it in heavier <sup>25</sup>Mg. Likely formation and processing histories pertaining to  $\delta^{25}$ Mg and REE patterns for each CAI are discussed in Section 5.3.

# **4.3.3** Notes on ${}^{27}$ Al/ ${}^{24}$ Mg and ${}^{\delta^{26}}$ Mg\* isochrons

On plotted isochrons (Figs. 4.18–4.21), a mean standard weight distribution (MSWD) >1 (Figs. 4.19 and 4.21) is indicative of genuine variability in data outside of analytical uncertainty (Young et al., 2005). Non-zero initial  $\delta^{26}$ Mg\* values would be represented where the intercept of an isochron is > 0, and would be indicative of the presence of <sup>26</sup>Mg\* prior to Al/Mg fractionation from source and final crystal closure (Young et al., 2005). This would be evidence for potential thermal resetting of the <sup>26</sup>Al/<sup>26</sup>Mg system after primary CAI formation. None of the plotted isochrons in this study display evidence for thermal resetting of the <sup>26</sup>Al/<sup>26</sup>Mg chronometer.

# 4.3.4 Overview of analytical results

Bulk inclusions from CV3 chondrites have  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  ratios from 1.70 – 4.03 and  $\delta^{26}\text{Mg}^*$  ranged from 0.591 – 1.397 ‰. Inclusions from the CK chondrite NWA 1559 yielded  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  values of 0.09 – 0.77 and  $\delta^{26}\text{Mg}^*$  ranging from 0.045 – 0.151 ‰. Individual whole-rock model  ${}^{26}\text{Al}/{}^{27}\text{Al}_{O}$  values for all unaltered CAIs were within error of the "canonical" value of 5 × 10<sup>-5</sup> (MacPherson, 2004). All values for altered samples CAI 3 ([3.49 ± 0.851] × 10<sup>-5</sup>), CAI 5 Rim ([5.50 ± 0.128] × 10<sup>-5</sup>), and CAI 8 ([2.55 ± 0.706] – [4.84 ± 0.147] × 10<sup>-5</sup>) were non-canonical.

11.04         0.005         5.060           10.58         0.008         4.700	0.014 11.04 0.005 5.060	1329 0.014 11.04 0.005 5.050	0.075 1.329 0.014 11.04 0.005 5.060	
C CUUU +U.II P C0008 + 10.58	C CUUU TUTI TUTU		C   CUU.0 40.11   410.0 620.1   CUU.0	
5 900.0 QC.01	10 10 0 000			3.741 0.075 1.329 0.014 11.04 0.005 5
4	4 4	+ 000.0 00.01 /00.0 +00.1 +	+ 000.0 00.01 /00.0 +00.1 070.0	+ 000.0 00.01 /00.0 +00.1 070.0 +20.0
15.14 0.005 6.71	0.008 15.14 0.005 6.71	1.942 0.008 15.14 0.005 6.71	0.115 1.942 0.008 15.14 0.005 6.71	5.756         0.115         1.942         0.008         15.14         0.005         6.71
13.92 0.005 6.720	0.007 13.92 0.005 6.720	0.860 0.007 13.92 0.005 6.720	0.051 0.860 0.007 13.92 0.005 6.720	2.542 0.051 0.860 0.007 13.92 0.005 6.720
14.62 0.004 6.800	0.007 14.62 0.004 6.800	1.318 0.007 14.62 0.004 6.800	0.076 1.318 0.007 14.62 0.004 6.800	3.824 0.076 1.318 0.007 14.62 0.004 6.800
14.53 0.009 6.712	0.012 14.53 0.009 6.712	1.055 0.012 14.53 0.009 6.712	0.063 1.055 0.012 14.53 0.009 6.712	3.126 0.063 1.055 0.012 14.53 0.009 6.712
6.73	6.73	6.73	6.73	6.73
3.002 0.016 1.000	0.012 3.002 0.016 1.000	1.040 0.012 3.002 0.016 1.000	0.061 1.040 0.012 3.002 0.016 1.000	3.026 0.061 1.040 0.012 3.002 0.016 1.000
3.124 0.007 1.050	0.007 3.124 0.007 1.050	1.023 0.007 3.124 0.007 1.050	0.061 1.023 0.007 3.124 0.007 1.050	3.035 0.061 1.023 0.007 3.124 0.007 1.050
1.03	1.03	1.03	1.03	1.03
3.124 0.007 0.280	0.011 3.124 0.007 0.280	0.796 0.011 3.124 0.007 0.280	0.066 0.796 0.011 3.124 0.007 0.280	3.285 0.066 0.796 0.011 3.124 0.007 0.280
0.675 0.007 0.040 0.	0.007 0.675 0.007 0.040 0.	0.591 0.007 0.675 0.007 0.040 0.	0.034 0.591 0.007 0.675 0.007 0.040 0.	1.696         0.034         0.591         0.007         0.675         0.007         0.040         0.
-1.386 0.016 -0.670 0.270	0.034 -1.386 0.016 -0.670 0.270	0.045 0.034 -1.386 0.016 -0.670 0.270	0.004 0.045 0.034 -1.386 0.016 -0.670 0.270	0.175 0.004 0.045 0.034 -1.386 0.016 -0.670 0.270
-1.260 0.010 -0.740 0.430	0.011 -1.260 0.010 -0.740 0.430	0.047 0.011 -1.260 0.010 -0.740 0.430	0.002 0.047 0.011 -1.260 0.010 -0.740 0.430	0.108 0.002 0.047 0.011 -1.260 0.010 -0.740 0.430
007.1 07.10- 010.0 007.1-				0.0100 0.0101 0.0101 0.00000 0.00000 0.0000 0.00000 0.00000 0.00000 0.000000
			_	
0.675 0.007 0.040 -1.386 0.016 -0.670 -1.260 0.010 -0.740	0.007         0.675         0.007         0.040           0.034         -1.386         0.016         -0.670           0.011         -1.260         0.010         -0.740	0.591         0.007         0.675         0.007         0.040           0.045         0.034         -1.386         0.016         -0.670           0.047         0.011         -1.260         0.010         -0.740	0.034         0.591         0.007         0.675         0.007         0.040           0.004         0.045         0.034         -1.386         0.016         -0.670           0.002         0.047         0.011         -1.260         0.010         -0.740	1.696         0.034         0.591         0.007         0.675         0.007         0.040           0.175         0.004         0.045         0.034         -1.386         0.016         -0.670           0.108         0.002         0.047         0.011         -1.260         0.010         -0.740
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
14.62         0.00           14.53         0.00           3.002         0.01           3.124         0.00           3.124         0.00           0.675         0.00           -1.386         0.01	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	0.076         1.318         0.007         14.62         0.0           0.063         1.055         0.012         14.53         0.0           0.061         1.040         0.012         3.022         0.01           0.061         1.023         0.007         3.124         0.00           0.066         0.796         0.011         3.124         0.00           0.066         0.796         0.011         3.124         0.00           0.034         0.591         0.007         3.124         0.00           0.034         0.591         0.007         0.675         0.00           0.004         0.591         0.007         0.675         0.00           0.004         0.047         0.011         -1.386         0.01	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
13.92 14.62 14.53 3.002 3.124 3.124 0.675 -1.386 -1.260	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.051         0.860         0.007         13.92           0.076         1.318         0.007         14.62           0.063         1.055         0.012         14.53           0.061         1.040         0.012         3.002           0.061         1.023         0.007         3.124           0.064         0.796         0.011         3.124           0.034         0.591         0.007         3.124           0.034         0.591         0.007         3.124           0.034         0.591         0.007         3.124           0.034         0.591         0.011         3.124           0.034         0.591         0.011         3.124           0.034         0.591         0.011         3.124           0.034         0.591         0.011         1.560	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
	0.008 0.007 0.007 0.012 0.012 0.012 0.011 0.007 0.007 0.001 0.007	1.942       0.008         0.860       0.007         1.318       0.007         1.318       0.007         1.055       0.012         1.023       0.007         1.023       0.007         0.796       0.011         0.591       0.007         0.591       0.007         0.047       0.011	0.115         1.942         0.008           0.051         0.860         0.007           0.076         1.318         0.007           0.063         1.055         0.012           0.061         1.040         0.012           0.061         1.023         0.007           0.064         1.023         0.007           0.064         0.796         0.011           0.064         0.796         0.011           0.063         1.023         0.007           0.064         0.796         0.011           0.034         0.591         0.007           0.004         0.047         0.034	5.756     0.115     1.942     0.008       2.542     0.051     0.860     0.007       3.824     0.076     1.318     0.007       3.824     0.063     1.055     0.012       3.126     0.061     1.040     0.012       3.035     0.061     1.040     0.012       3.285     0.064     1.023     0.007       3.126     0.054     0.012       3.035     0.064     1.023     0.012       1.056     0.034     0.796     0.011       1.696     0.034     0.591     0.007       0.175     0.004     0.045     0.034       0.108     0.002     0.047     0.011
B     5.756     0.115     1.942       B     2.542     0.051     0.860       B     3.824     0.076     1.318       B     3.126     0.063     1.055       FA     3.026     0.061     1.040       FA     3.035     0.061     1.040       FA     3.035     0.061     1.040       FA     3.035     0.061     1.023       FA     3.035     0.061     1.023       FA     3.036     0.061     1.040       FA     3.035     0.061     1.040       FA     3.036     0.061     1.040       A     0.175     0.034     0.591       AOA     0.108     0.002     0.045	B     3.824     0.076       B     5.756     0.115       B     5.756     0.115       B     2.542     0.051       B     3.824     0.076       FA     3.126     0.063       FA     3.026     0.061       FA     3.035     0.061       FA     3.035     0.061       FA     3.035     0.061       AOA     0.175     0.034	B         3.824           B         5.756           B         5.756           B         5.756           B         5.756           B         2.542           B         3.824           B         3.824           B         3.325           FA         3.026           FA         3.026           FA         3.035           FA         3.035           AOA         0.175           AOA         0.108	B B B B B B F A C A O A O A O A	
7         B         5.756         0.115         1.942           7         B         5.542         0.051         0.860           8         B         3.824         0.076         1.318           9         B         3.126         0.063         1.040           3         FA         3.026         0.061         1.040           9         FA         3.035         0.061         1.023           9         FA         3.035         0.061         1.023           7         CA         3.285         0.064         0.796           3         CA         3.285         0.064         0.796           4         0.034         0.344         0.591	9     B     3.824     0.076       7     B     5.756     0.115       7     B     5.756     0.115       8     B     3.824     0.076       9     B     3.126     0.061       9     FA     3.026     0.061       3     CA     3.035     0.061       9     FA     3.035     0.061       3     CA     3.285     0.061       3     A     0.175     0.034	0     B     3.824       7     B     5.756       7     B     5.756       8     B     3.824       9     B     3.324       9     B     3.126       3     FA     3.026       9     FA     3.035       9     FA     3.035       9     FA     3.035       3     CA     3.285       9     FG     1.696       3     AOA     0.175	9 B 7 B 8 B 9 FA 9 FA 9 FA 3 AOA	и <u>о и о 88 7 7 о</u> 9

**Table 4.5:** <sup>27</sup>Al/<sup>24</sup>Mg and Mg isotope data obtained on refractory inclusions during this study. Abbreviations: n: number of measurements, Type: refractory inclusion type, CT: representative sample picked by Christopher Town, JB & JAB: representative sample picked by Joel Baker, WR: whole rock, FEL: feldspathic separate, PX: pyroxene separate, WRC: calculated whole rock weighted average. WRC for CAI 5 is the weighted average of the core and WR measurements. "-" denotes that a model  $^{26}$ Al/ $^{27}$ Al<sub>0</sub> could not be calculated.

## CHAPTER 4. RESULTS

	Tuno	ş	27 A1/24 Mr~	2%	0-0 IMB.	ť	0-~ INI 8	5	0 IMB	5	Model	5
	adkı	-	SIM IN	error	( %)	40mean	(%)	4 Umean	( ‰ )	4 Umean	$[^{26}$ Al / $^{27}$ Al] <sub>0</sub>	<b>z</b> umean
Allende	e - Jacob	sen e	t al. (2008)									
A33	A	9	4.07	0.08	1.468	0.019	10.81	0.27	4.47	0.13	$5.152 \times 10^{-5}$	$0.120 \times 10^{-5}$
A39	В	9	2.22	0.04	0.789	0.018	10.62	0.12	5.00	0.07	$5.185  imes 10^{-5}$	$0.153 \times 10^{-5}$
A43	В	4	2.54	0.05	0.924	0.018	6.27	0.24	2.73	0.12	$5.276 \times 10^{-5}$	$0.139 \times 10^{-5}$
A44A	В	9	2.24	0.04	0.817	0.017	3.53	0.28	1.39	0.15	$5.319 \times 10^{-5}$	$0.139 \times 10^{-5}$
AJEF	В	9	3.07	0.06	1.086	0.017	5.45	0.13	2.22	0.06	$5.095 \times 10^{-5}$	$0.127 \times 10^{-5}$
Allend	e - This (	Study										
A33	A	ю	4.03	0.08	1.397	0.021	10.27	0.44	4.51	0.24	$4.958 \times 10^{-5}$	$0.124 \times 10^{-5}$
A39	В	ю	2.18	0.04	0.767	0.017	11.74	0.50	5.61	0.30	$5.149 \times 10^{-5}$	$0.153 \times 10^{-5}$
A43	В	ю	2.61	0.05	0.924	0.014	7.11	0.28	3.17	0.17	$5.140 \times 10^{-5}$	$0.130 \times 10^{-5}$
A44A	В	7	2.29	0.05	0.781	0.044	3.46	0.16	1.36	0.02	$4.974 \times 10^{-5}$	$0.293 \times 10^{-5}$
AJEF	В	Ŋ	3.14	0.06	1.085	0.012	4.97	0.10	1.99	0.05	$4.975 \times 10^{-5}$	$0.114 \times 10^{-5}$

l during this study and as reported in Jacobser	
tory samples, measured	ctory inclusion type.
Allende inter-labora	urements, Type: refru
Mg isotope data for	n: number of meas
<b>6:</b> ${}^{27}Al/{}^{24}Mg$ and $i$	08). Abbreviations:
Table 4.	<i>et al.</i> (20

ł	<b>L</b> Umean	$0.167 \times 10^{-5}$	$0.293 \times 10^{-5}$	
Model	[ <sup>26</sup> Al / <sup>27</sup> Al] <sub>0</sub>	$6.294 \times 10^{-5}$	$4.974 \times 10^{-5}$	
ţ	<b>4</b> 0mean	0.66	0.02	
$\delta^{25}$ Mg	(%)	2.99	1.36	
ţ	<b>2</b> 0mean	0.02	0.16	
$\delta^{26}$ Mg	(%)	6.87	3.46	
ć	<b>2</b> 0mean	0.017	0.044	
$\delta^{26} Mg^*$	(%)	0.988	0.781	
2%	error	0.05	0.05	
27 41124 142		2.29	2.29	
1	-	2	7	
43 C-124 MC		0.05	I	
		A44A	A44A	

 

 Table 4.7:  $^{27}Al/^{24}Mg$  and Mg isotope data for the Allende CAI sample A44A, before and after removal of Ca with the DGA column

 chemistry method. Abbreviations: n: number of repeat measurements.

# 4.3.5 Inter-laboratory comparison - Allende CAIs

Some CAI samples from the Allende meteorite analysed in Jacobsen et al. (2008) have been analysed in this study. Both sets of data are reported in Table 4.6. The  $\delta^{26}$ Mg\* and model  ${}^{26}$ Al/ ${}^{27}$ Al<sub>O</sub> values for all individual CAIs, as well as calculated isochrons for data from each study, [4.72 ± 0.28] × 10<sup>-5</sup>, intercept = (0.029 ± 0.057) ‰ (this study) and [4.97 ± 0.27] × 10<sup>-5</sup>, intercept = (0.007 ± 0.051) ‰ (Jacobsen et al., 2008), are within error and canonical. Figure 4.18 is an isochron created using data attained in this study with a reference line denoting the isochron using data reported in Jacobsen et al. (2008).

Variations in the data attained from the inter-laboratory samples might be explained through differences in the number of repeat measurements (n) and chemical processing. Due to the quantity of material available for analyses in this study, each sample measurement was repeated  $\leq$  3 times. The same measurements were repeated  $\geq$  4 in Jacobsen et al. (2008). As n increases so too does precision.

## 4.3.6 Ion exchange chemistry and calcium

Ion exchange column processing of samples in this study involved cation, anion and DGA exchange-column chemistry (Section 3.2.1), while Jacobsen et al. (2008) only employed cation exchange column chemistry. DGA exchange chemistry was employed to completely eliminate Ca<sup>2+</sup> from processed samples, as the presence of Ca<sup>2+</sup> results in erroneously high measurements of  $\delta^{26}$ Mg\* (Schiller et al., In Submission). Table 4.7 shows measurements of the Allende sample A44A prior to and post DGA column chemistry processing when it contained <sup>43</sup>Ca/<sup>24</sup>Mg = 0.05.  $\delta^{26}$ Mg\* measurements from the sample containing Ca were inflated by 0.207 ‰, resulting in a supra-canonical model <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> of [6.294 ± 0.167] × 10<sup>-5</sup>, 21 % greater than the sample of A44A after being processed through DGA ion exchange chemistry ([4.974 ± 0.293] × 10<sup>-5</sup>).



**Figure 4.18:** An <sup>26</sup>Al-<sup>26</sup>Mg isochron for all Allende samples analysed in this study. A dashed grey reference line has been added to show the comparative data as reported in Jacobsen et al. (2008).

# 4.3.7 NWA 2364

The unaltered CAIs from NWA 2364 plot on a forced single isochron at  $2\sigma$  (95%) confidence, with  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.86 \pm 0.26] \times 10^{-5}$  and an intercept = (-0.009 ± 0.054) ‰ (Fig. 4.19). This value is within error of the canonical value. The unaltered CAIs from NWA 2364 do not define a statistically significant single isochron due to resolvable age differences between different CAIs.



**Figure 4.19:** An isochron for all unaltered NWA 2364 samples analysed in this study. The altered CAI 3 sits well below the  ${}^{26}Al/{}^{27}Al_0$  line and is included for comparison only.

#### CAI 1 internal mineral isochron

Al-Mg analyses were conducted on a separate containing melilite and anorthite, a pyroxene separate and representative whole-rock samples. Al-Mg values from CAI 1 plot and on internal isochron with a  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.74 \pm 0.18] \times 10^{-5}$  (Fig. 4.20) with a 2 $\sigma$  confidence. The internal value is not within error of the canonical value by <1 %, but both whole-rock samples yield model canonical values. The tightly constrained internal  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  value strongly suggests a consistent crystallisation date for all minerals in CAI 1.



Figure 4.20: Internal <sup>26</sup>Al-<sup>26</sup>Mg isochron for mineral and whole-rock samples of CAI 1.

#### CAI 3

The bulk analysis of CAI 3 gives a model  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [3.482 \pm 0.085] \times 10^{-5}$ . This model value does not fall within error of the canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  value ( $\sim 5 \times 10^{-5}$ ) and sits well outside of error in comparison to all other analysed inclusions from NWA 2364. Given that CAI 3 is petrographically altered it has been omitted from the initial  ${}^{26}\text{Al}$  calculations for NWA 2364.

## 4.3.8 NWA 760 - CAI 5

Analyses for CAI 5 were conducted for representative samples of the rim, core and whole-rock (Table 4.5). An internal isochron at  $2\sigma$  confidence is not possible, as the rim sample analysed is comparatively enriched in  $\delta^{26}$ Mg\*. The occurrence of Fe-bearing spinel and andradite, both of which

are secondary minerals, the Group II-like REE patterns and the comparative enrichment of  $\delta^{26}$ Mg\*, suggest CAI 5 experienced post-crystallisation alteration. The model  ${}^{26}$ Al/ ${}^{27}$ Al<sub>0</sub> for the whole-rock ([4.99 ± 0.11] × 10<sup>-5</sup>) and core ([5.05 ± 0.11] × 10<sup>-5</sup>) samples are canonical. Analysis of a representative sample of the rim section of CAI 5 yielded a supra-canonical model value of [5.50 ± 0.13] × 10<sup>-5</sup>.

# 4.3.9 NWA 1559

Individual analyses of AOA 1 and CAI 8 from the CK3 chondrite NWA 1559 resulted in varied and inconsistent model  ${}^{26}A1/{}^{27}Al_0$  values.  $\delta^{26}Mg$  measurements were of the same magnitude as analytical error (Table 4.5). AOA 2 was not subjected to Al and Mg isotope analysis.

# 4.3.10 All unaltered CAIs

An isochron was plotted without considering the altered refractory inclusions (AOA 1, CAI 3, CAI 5 & CAI 8). Analyses of Allende and NWA 2364 do not plot on a likely isochron, but can be forced with  $2\sigma$  confidence (Fig. 4.21) onto an isochron with a  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.89 \pm 0.26] \times 10^{-5}$ , intercept = (-0.014 ± 0.059) ‰. This is within error of the canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  and represents data for 9 refractory inclusions from two separate CV3 chondrites.



**Figure 4.21:** An <sup>26</sup>Al-<sup>26</sup>Mg isochron for all unaltered CAIs from Allende (blue error ellipses) and NWA 2364 (red error ellipses). The dashed grey reference line denotes the canonical value of  $5 \times 10^{-5}$  and the solid green line denotes the supra-canonical values as reported in Thrane et al. (2006)

# Chapter 5

# **Synthesis**

Of the three sets of analytical results reported in this thesis, the first to consider is resolvable temporal variation as evident from the <sup>26</sup>Al–<sup>26</sup>Mg isotopic system. This chapter will first discuss these measurements and then consider the reported variations in analyses of petrographic or trace element concentrations.

# 5.1 Canonical vs supra-canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>

Recent studies (Young et al., 2005; Thrane et al., 2006; Cosarinsky et al., 2007) of CAIs using a variety of techniques have yielded supra-canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values of ~6 × 10<sup>-5</sup> (Section 1.8.2). Subsequent analyses of CAIs by Teng et al. (2007), Jacobsen et al. (2008) and this study have yielded only canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values of ~5 × 10<sup>-5</sup>.

Analyses of three refractory inclusions, which were from an altered parent body (CAI 8 & AOA 1) or exhibited partial or complete mineralogical alteration (CAI 3) resulted in sub-canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> values. All three sub-canonical refractory inclusions display petrographic evidence for post-formation alteration, due to the high volume percentage of secondary minerals (63 % secondary anorthite in CAI 8, 25 % feldspar and 41 % olivine in AOA 1, 21 % hedenbergite and 30 % nepheline in CAI 3; Table 4.3). The altered rim portion of CAI 5 yielded a supra-canonical

 $^{26}$ Al/ $^{27}$ Al<sub>0</sub> value = [5.50 ± 0.80] × 10<sup>-5</sup>.

This study has failed to produce supra-canonical  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values for bulk CAIs from four different meteorites: Allende, NWA 2364, NWA 760 or NWA 1559. With the exception of the altered inclusions from the CK3 chondrite NWA 1559, all  $\delta^{26}$ Mg\* intercepts are within error of 0, indicating an absence of detectable (within analytical uncertainty)  ${}^{26}$ Mg\* at the time of initial Al/Mg fractionation or final crystal closure.

# 5.1.1 Non-canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>

The following refractory inclusions are not considered as representative in regards to the Solar System  ${}^{26}\text{Al}/{}^{27}\text{Al}_{0}$ .

#### CAI 3

The model <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> of CAI 3 ([ $3.48 \pm 0.09$ ] ×  $10^{-5}$ ) is 21 % lower than the whole rock isochron value for the pristine CAIs (CAIs 0, 1, 2 & 4; [ $4.86 \pm 0.36$ ] ×  $10^{-5}$ ; Fig. 4.19) of NWA 2364. The thermal processing experienced by CAI 3, which produced its group II REE pattern (Section 5.3.3), may have prevented final crystal closure until  $352^{+103}_{-108}$ Kyr after the the prisitine CAIs of NWA 2364. Late closure is consistent with CAI 3's classification, as compact type A CAIs have experienced melting (Section 1.6.1).

### CAI 5

CAI 5 has experienced post formation alteration. The whole-rock and core samples yield canonical model  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values ([5.00 ± 0.11] × 10<sup>-5</sup> and [5.04 ± 0.11] × 10<sup>-5</sup> respectively). Analysis of a representative sample of the rim section of CAI 5, however, yielded a supra-canonical value of [5.50 ± 0.13] × 10<sup>-5</sup>. This is consistent with the variability of Al<sub>2</sub>O<sub>3</sub> and MgO concentrations between the core and rim portions of CAI 5 (Section 4.1.5).

#### CAI 8 and AOA 1

The low  $\delta^{26}$ Mg\* values and resulting sub-canonical isochron ( ${}^{26}$ Al/ ${}^{27}$ Al<sub>O</sub> = [2.44 ± 0.36] × 10<sup>-5</sup>) of CAI 8 and AOA 1 are not unexpected. CK3 chondrites show evidence for aqueous alteration within the meteorite parent body (Section 1.4.4). A positive  $\delta^{26}$ Mg\* intercept ([0.028 ± 0.009] ‰), is evidence for the presence of  ${}^{26}$ Mg\*, and therefore a history of  ${}^{26}$ Al radioactive decay, prior to final crystal closure.

# 5.2 <sup>26</sup>Al–<sup>26</sup>Mg dating

Despite agreement between canonical and model <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> values, the reported analytical precision precludes all pristine CAIs from plotting on a statistically significant isochron. Model relative differences in formation chronology may, however, be resolved.

## Range of model bulk <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> values

Figure 5.1 illustrates the range of model  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  values for all pristine CAIs and CAI 5. The measured values of the pristine CAIs do not plot on a statistically significant isochron, however forcing the values onto an isochron produces a  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.89 \pm 0.265] \times 10^{-5}$  with a MSWD=2.8 (Fig. 4.21). This gives an age uncertainty of <±58 Kyr. This is the temporal range for Al and Mg fractionation from the source material in the solar nebula for the plotted CAIs.

The maximum and minimum model  ${}^{26}$ Al/ ${}^{27}$ Al<sub>0</sub> values, measured on the NWA 2364 samples CAI 4 ([5.158 ± 0.121] × 10<sup>-5</sup>) and CAI 1 ([4.897 ± 0.074] × 10<sup>-5</sup>) (Table 4.5) give a maximum model temporal variation of <±96 Kyr.

#### **Resolvable model temporal variation in NWA 2364**

The values for CAIs from NWA 2364 cannot be plotted on a probable isochron. A forced, model 2 fit isochron yields a  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.86 \pm 0.36] \times 10^{-5}$ , MSWD=4.4 (Fig. 4.19). The error produced from a forced isochron



**Figure 5.1:** Model  ${}^{26}Al/{}^{27}Al_0$  values for unaltered refractory inclusions analysed in this study. The blue line and bounding box are indicative of the final  ${}^{26}Al/{}^{27}Al_0 = [4.89 \pm 0.265] \times 10^{-5}$ . The solid and bounding dashed red lines represent the canonical value =  $[5.00 \pm 0.05] \times 10^{-5}$ .

for whole rock analyses of CAIs from NWA 2364 produces a temporal uncertainty of  $<\pm79$  Kyr.

Model temporal variation in individual inclusions can be resolved with samples from NWA 2364. CAI 4 has the highest model  ${}^{26}A1/{}^{27}Al_0$  value ([5.16 ± 0.121] × 10<sup>-5</sup>; Table 4.5) and CAI 1 WRC has the lowest model  ${}^{26}A1/{}^{27}Al_0$  value ([4.897 ± 0.074] × 10<sup>-5</sup>). Both model values are within error of the canonical value ([5.00 ± 0.05] × 10<sup>-5</sup>). CAI 1 WRC is, however, outside of the model  ${}^{26}A1/{}^{27}Al_0$  value of CAI 4 by >1.3%. This difference equates to a relative temporal variation of at least 14 Kyr between CAI 1 WRC and CAI 4.

Ctudy	$^{26}\text{Al}/^{27}\text{Al}_0$ from	Age
Study	multi-CAI isochron	uncertainty
Jacobsen et al. (2008)	$[4.97 \pm 0.27]  imes 10^{-5}$	<± 57 Kyr
This study	$[4.72 \pm 0.28]  imes 10^{-5}$	$<\pm$ 63 Kyr

**Table 5.1:** The isochron-derived <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> from the Allende sample values reported by Jacobsen et al. (2008) and this study. CAIs considered in this comparison are A33, A39, A43 A44A and AJEF.

# 5.2.1 Allende inter-labratory comparison

Inter-laboratory analyses of five in-solution CAI samples from the Allende meteorite yielded model <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> and a multi-CAI isochron within error of values reported by Jacobsen et al. (2008) (Table 4.6). Errors from analyses reported in this study were comparatively smaller than those reported in Jacobsen et al. (2008), and produced a  ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.72 \pm 0.28] \times 10^{-5}$ . The resulting formation date uncertainty of the analysed Allende CAIs is  $<\pm$  66 Kyr, an uncertainty ~9 % greater than that calculated from the values reported in Jacobsen et al. (2008) (Table 5.1). The uncertainty in this study is higher due to measurements being of (mostly) greater accuracy, therefore producing an increased uncertainty of sample values plotting on the same The consistently lower  $\delta^{26}$ Mg\* values measured on the isochron. inter-laboratory samples in this study compared to Jacobsen et al. (2008) can be attributed to the addition of the anion exchange column chemistry and the DGA column chemistry step which removed the possibility of Ca inflating measured <sup>26</sup>Mg values (Section 4.3.6). Analytical techniques for solution-based MC-ICP-MS analyses between the two studies were otherwise identical. Multi-CAI isochron values from this study and Jacobsen et al. (2008) are canonical.

# 5.2.2 CAI 1 bulk and mineral separate chronology

 $^{26}$ Al/ $^{27}$ Al<sub>0</sub> values were determined for both whole rock and mineral constituents of CAI 1. The isochron of the combined bulk and individual mineral samples from CAI 1 ( $^{26}$ Al/ $^{27}$ Al<sub>0</sub> = [4.74 ± 0.18] × 10<sup>-5</sup>), translates to chronological uncertainty of ±40 Kyr. This is interpreted as the temporal variation between initial bulk Al and Mg fractionation from the solar nebula and the final crystallisation or thermal resetting of the constituent minerals of CAI 1.

# 5.3 Formation and processing from major and trace element composition and $\delta^{25}$ Mg values

The petrographic and trace element compositions of analysed refractory inclusions show a variety of formation histories.  $\delta^{25}$ Mg values and REE patterns can be used to constrain the evaporative histories of refractory inclusions, allowing model maximum evaporative temperatures to be established.

## 5.3.1 Group V REE patterns – CAI 0 and CAI 1

The type B CAIs 0 & 1 display a bulk, flat Group V REE pattern. Group V patterns display relative REE concentrations in equilibrium with, but enriched from, solar nebula composition. This is consistent with a history of crystallisation through condensation without a relative depletion of volatile REE through subsequent thermal processing. Type B CAIs are presumably crystallised molten or semi-molten condensates (Section 1.6.2).

 $\delta^{25}$ Mg values for CAI 0 (4.70 ± 1.40 ‰) and CAI 1 (6.73 ± 0.47 ‰; Table 4.5) are very enriched in the heavy <sup>25</sup>Mg. This is indicative of extensive evaporation events, but due to the flat REE patterns, we can constrain the upper limit of these events. The condensation temperature of Mg (T<sub>c</sub>(50 %) = 1336 K; Lodders,2003), is slightly lower than that of Eu and Yb (1356 K and 1487 K respectively; Table 1.4). It is assumed that in order to enriched
the heavy Mg isotopes, CAI 0 and CAI 1 must have reached a temperature where Mg could evaporate. The flat Group V bulk REE pattern suggests CAI 0 and CAI 1 did not reach temperatures high enough to fractionate the most volatile REE (Eu and Yb). This gives a temperature range of >1336 K to <1356 K. The magnitude of the  $\delta^{25}$ Mg values suggests this temperature was sustained for an extensive period in order to fractionate the light and heavy Mg isotopes. Though REE patterns are not available, a similar petrology and  $\delta^{25}$ Mg enrichment (Table 4.5) in the type B CAIs from Allende (A39, A43, A44A and AJEF) suggests a similar thermal history.

### 5.3.2 Group III REE patterns – CAI 2

CAI 2 exhibits a Group III REE pattern. This indicates the loss of the most volatile elements Eu and Yb through a process of evaporation. CAI 2 is a volatilisation residue, i.e, the remains of an evaporative process which removed the more volatile elements, leaving the bulk composition more refractory than Group V inclusions.

The  $\delta^{25}$ Mg value for CAI 2 (1.03 ± 0.11 ‰; Table 4.5) is enriched in the heavy <sup>25</sup>Mg, but not to the extent of CAI 0 or CAI 1. This is indicative of extensive evaporation events, but due to the flat REE patterns, we can constrain the upper limit of these events. The Group III bulk REE pattern of CAI 2 (Section 4.2.2) can be used to limit the temperature of post fractionation thermal processing. The T<sub>c</sub> of Yb and Ce as given by (Lodders, 2003) are 1487 K and 1478 K respectively. This is not consistent with Ce being less volatile than Yb. Taylor (2001) gives T<sub>c</sub> of Yb and Ce as 1420 K and 1440 K respectively, and adds that though T<sub>c</sub> values are normally given to 4 significant figures, they should only be used as a rough guide. As such, a depletion in Yb suggests an lower thermal limit of ~1420 K, and an upper limit of ~1440 K (Taylor, 2001) due to there being no CI-normalised negative anomaly for the next most volatile REE, Ce.

# 5.3.3 Group II REE patterns

A majority of the refractory inclusions analysed in this study exhibit a Group II REE pattern. This suggests a history of high temperature thermal alteration, including multiple evaporative and condensation events (Section 1.5.1). These histories of thermal alteration are also supported by the  $\delta^{25}$ Mg values for CAI 3 (0.028 ± 0.006 ‰) and CAI 4 (0.040 ± 0.110 ‰; Table 4.5), which yield <1 ‰ enrichments in heavy Mg isotopes over those of the terrestrial J11.

# CAI 3

The petrology of CAI 3 is indicative of mineral alteration. Hedenbergite is rare in a highly reducing formation environment, such as the hot hydrogen gas (Section 1.5.2). A concentration of ~21 % hedenbergite in CAI 3 suggests aqueous alteration of Ca-pyroxene or crystal closure in an oxidising environment. Anorthite occurs as a secondary mineral, presumably replacing a primary melilite phase (Section 1.5.2).

### CAI 4

CAI 4 displays a group II REE pattern and has a major petrographic composition (~85 % volume) consisting of secondary, Fe-bearing spinel cores enclosed in pyroxene. This is consistent with thermal bulk alteration. Of all the CAIs which display a type II pattern, however, CAI 4 is unique with a bulk composition which has not experienced Mg isotopic fractionation away from the canonical value (Section 5.2).

### CAI 5 core-rim variation

The rim and core of CAI 5 differ in CI normalised REE concentrations (Fig. 4.13) in addition to  $\delta^{26}$ Mg\* values (Table 4.5). The core section of CAI 5 has an internal relative enrichment of volatiles in comparison to the rim. This is indicative of a thermal event that affected the inclusion but did not propagate through its entirety. This event was most likely a nebula event

rather than a parent body event as the heat involved did not persist for long enough to affect the entire (<6 mm diameter) inclusion. A full analysis of the petrology of CAI 5 is not possible due to the large percentage of an unknown mineral (Section 4.1.5).

The  $\delta^{25}$ Mg value for the rim section of CAI 5 (0.214 ± 0.07 ‰) is higher than the  $\delta^{25}$ Mg values for the core (-0.333 ± 0.004 ‰) and whole-rock (0.007 ± 0.005 ‰) samples of CAI 5. An enrichment in the more volatile light <sup>24</sup>Mg in the core and rim and a heavy <sup>25</sup>Mg surplus in the rim section is consistent with a thermal event which failed to affect the entire inclusion.

### CAI 8 and AOAs 1 and 2

A group II pattern for all analysed inclusions from NWA 1559 is consistent with a series of high temperature thermal alteration events. Negative  $\delta^{25}$ Mg values for CAI 8 (-0.15 ± 0.13 ‰) and AOA 1 (-0.84 ± 0.34 ‰) are also indicative of these refractory inclusions having a surplus of light Mg isotopes, most likely the result of crystallising as fractional condensates.

# 5.4 Summary

Though the model age of the fine-grained CAI 4 is outside of error of the type B1 CAI 1, it is inside of error of the type B2 CAI 0 and all type B CAIs from Allende (A39, A43, A44A & AJEF) (Fig. 5.1). There is no temporal variation which correlates with trace element pattern groups. Group V CAIs 1 & 2, the group III CAI 2 and the group II CAI 4 all have canonical model  ${}^{26}A1/{}^{27}Al_0$  values. Temporal and petrographic variation in analysed CAIs is therefore decoupled. The only refractory inclusions with non-canonical  ${}^{26}A1/{}^{27}Al_0$  values are those which display petrographic evidence for post-formation Mg isotope fractionation or thermal alteration (CAIs 3, 5 & 8 and AOA 1). Variation in the consistent, canonical  ${}^{26}A1/{}^{27}Al_0$  values of all pristine CAIs suggests a history of Al and Mg fractionation from the solar nebula, with a homogenous  ${}^{26}Al$  concentration, over a period of <160 Kyr.

### 5.4.1 CAI residence time in the solar nebula

The plotted internal  ${}^{26}\text{Al}/{}^{27}\text{Al}_0$  isochron of CAI 1 ( ${}^{26}\text{Al}/{}^{27}\text{Al}_0 = [4.74 \pm 0.18] \times 10^{-5}$ ) gives an error equal to ±40 Kyr. CAI 1 has a flat, REE composition which is in equilibrium with the solar system composition and so therefore does not exhibit evidence of any significant post-crystallisation thermal processing. The residence time of CAI 1 following fractionation and final closure of the  ${}^{26}\text{Al}-{}^{26}\text{Mg}^*$  system is therefore no more than 80 Kyr. The intercept of the internal isochron is within error of 0, and so precludes the presence of  ${}^{26}\text{Mg}^*$  at the time of initial fractionation of CAI 1. A residence time of 80 Kyr is inconsistent with the 300 Kyr as reported by Young et al. (2005).

There is no temporal variation based on classified CAI types. Measured <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> concentrations in pristine whole rock CAI samples do not diverge from the canonical value. In explaining the differences in inclusion formation models, temporal and chemical variations are therefore unlikely. In the analysed samples of this study there the only possible explanations remaining to explain chemical and petrographic differences in pristine refractory inclusions is temperature, which can be modelled with spacial variation in formation and subsequent alteration.

# 5.5 Future work

Portions of all refractory inclusions analysed in this study remain as epoxy mounted, polished fragments. Future work on <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> values reported in this study is possible, through either LA-MC-ICP-MS based analysis (as in Young et al. (2005)) or micro-drilled, chemically processed MC-ICP-MS analyses (as in Jacobsen et al. (2008)). Further inter-laboratory analyses, as was performed in this study, is required to reach a consensus on the initial isotopic composition of the solar nebula.

# Chapter 6

# Conclusions

# 6.1 Petrology and trace elements

Resolvable temporal variation in CAIs are decoupled from petrographic and trace element compositions. There is no identifiable temporal trend in normalised trace element concentrations or mineral and textural classification in refractory inclusions. Variation in trace element data is best described as limited, with all but CAIs 0, 1 & 2 displaying a Group II pattern.

Variation in normalised trace element concentrations is reliant on the style of CAI formation and thermal or aqueous alteration following initial element fractionation from the solar nebula. This can be solely attributed to variability of heating events within the solar nebula after the fractionation of refractory elements from the source material.

# 6.2 Canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub>

Non-canonical values were only recorded for refractory inclusions that were either petrographically altered (CAIs 3 & 5), or yielded  $\delta^{26}$ Mg<sup>\*</sup> measurements with analytical error of >20 % (CAI 8b JB and all AOA 1 whole-rock samples).  ${}^{26}$ Al/ ${}^{27}$ Al<sub>0</sub> values from pristine CAIs are uniformally within error of the canonical value of [5 ± 0.05] × 10<sup>-5</sup>. Despite some

variation in analytical techniques, inter-laberatory samples of CAIs from the Allende meteorite produced a multi-CAI isochron within error of values reported by Jacobsen et al. (2008).

This study did not produce results that ranged as greatly as those reported by Young et al. (2005) or Cosarinsky et al. (2007), and did not produce a consistently supra-canonical <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> values (~6 × 10<sup>-5</sup>) as reported in Thrane et al. (2006). Young et al. (2005) utilised LA-MC-ICP-MS methodologies to analyse individual crystals within CAIs, but as shown by Schiller et al. (In Submission) and discussed in Section 3.2.2, small quantities of elements commonly contained in CAIs can greatly vary measured  $\delta^{26}$ Mg\* values in MC-ICP-MS analyses. The <sup>26</sup>Al/<sup>27</sup>Al<sub>0</sub> values reported by Thrane et al. (2006) and Cosarinsky et al. (2007) can be attributed to analytical artefacts.

It was not possible to produce statistically significant isochrons when considering all pristine refractory inclusions, as the accuracy produced during analysis (a date error of  $\pm 40$  Kyr for the internal CAI 1 isochron, for example), is enough to resolve genuine temporal variation in the Al and Mg fractionation events. Temporal differences, however, all occur within <1 % of the canonical  ${}^{26}$ Al/ ${}^{27}$ Al<sub>0</sub> value. Errors in plotted isochrons suggest the initial Al/Mg fractionation event for CAIs from the solar nebula occurred over <160 Kyr.

Initial <sup>26</sup>Al was homogenous in the solar nebula. As <sup>26</sup>Al was most probably introduced from an external stellar source (Brearley & Jones, 1998; Taylor, 2001; MacPherson, 2004) and then subsequently mixed to either full or close-to-full homogeneity in the solar nebula, it is unreasonable to assume that other elements did not experience the same mixing event. Variation in petrology and trace element compositions are the result of thermal variation within the solar nebula during the period between initial fractionation and final crystal closure.

# References

Allan, A. S., Baker, J. A., Carter, L., & Wysoczanksi, R. J. (2008). Reconstructing the quaternary evolution of the world's most active f silicic volcanic system: insights from an 1.65 ma deep ocean tephra record sourced from taupo volcanic zone, new zealand. *Quaternary Science Reviews*.

Amelin, Y., Krot, A. N., Hutcheon, I. D., & Ulyanov, A. A. (2002). Lead Isotopic Ages of Chondrules and Calcium-Aluminium-Rich Inclusions. *Science*, 297, 1678–1683.

Bizzarro, M., Baker, J. A., & Haack, H. (2004). Mg isotope evidence for contemporaneous formation of chondrules and refractory inclusions. *Nature*, 431, 275–278.

Bizzarro, M., Baker, J. A., Haack, H., & Lunigaard, K. L. (2005). Rapid timescales for accretion and melting of differentiated planetesimals inferred from <sup>26</sup>Al–<sup>26</sup>Mg chronometry. *The Astrophysical Journal*, 632, 41–44.

Boss, A. (2004). The solar nebula. In A. Davis (Ed.) *Treatise on Geochemistry*, vol. 1: Meteorites, Comets and Planets, chap. 1.04, (pp. 63–80). Elsevier Ltd.

Brandstatter, M., Bukovanska, M., & Kurat, G. (2003). Nwa 1559: Another anomalous ck3 chondrite? *66th Annual Meteoritical Society Meeting*.

### REFERENCES

Brearley, A. J., & Jones, R. H. (1998). Reviews in mineralogy. InJ. J. Papike (Ed.) *Planetary Materials*, chap. 3: Chondritic Meteorites.Mineralogical Society of America.

Brett, R., Guppy, D. J., & Milton, D. J. (1970). The Meteoritical Bulletin, No. 45. Meteoritics, 5, 101. URL http://adsbit.harvard.edu/cgi-bin/nph-iarticle\_

query?1970Metic...5...85.

Busso, M., Gallino, R., & Wasserburg, G. J. (1999). Nucleosynthesis in asymptotic giant branch stars: Relevance for galactic enrichment and solar system formation. *Annual Reviews of Astronomy and Astrophysics*, *37*, 239–309.

Cosarinsky, M., Taylor, D. J., Liu, M. C., McKeegan, K. D., & Krot, A. N. (2007). Distribution of aluminium-26 in refractory inclusions from CV chondrites. In *Workshop on Chronology of Meteorites*.

Davis, A. M., & Richter, F. M. (2004). Condensation and Evaporation of Solar System Materials. In A. M. Davis (Ed.) *Treatise on Geochemistry*, vol. 1, chap. 1.16, (pp. 431–460). Elsevier Ltd.

Dearborn, D. S. P., & Blake, J. B. (1985). On the source of the <sup>26</sup>Al observed in the interstellar medium. *Astrophysical Journal*, 288, L21–L24.

Gaidos, E., Moskovitz, N., Williams, J., & Rogers, D. (2007). Extinct <sup>26</sup>Al from wolf-rayet stars: Accumulation, variation, and implications. In *Workshop on Chronology of Meteorites*.

Galy, A., Yoffe, O., Janney, P. E., Williams, R. W., Cloquet, C., Alard, O., Halicz, L., Wadhwa, M., Hutcheon, I. D., Ramond, E., & Carignane, J. (2003). Magnesium isotope heterogeneity of the isotopic standard srm980 and new reference materials for magnesium-isotoperatio measurements. *Journal of Analytical Atomic Spectrometry*, (18), 1352–1356.

GeoRem (2006). BHVO-2G: GeoReM preferred values http://georem.mpch-mainz.gwdg.de. URL http://georem.mpch-mainz.gwdg.de

Greenwood, R., Franchi, I. A., Kearsley, A. T., & Alard, O. (2004). The relationship between ck and cv chondrites: A single parent body source? *Lunar and Planetary Science*, XXXV.

Grossman, J. N., & Zipfel, J. (2001). The Meteoritical Bulletin, No. 85. *Meteoritics & Planetary Science*, 36, A293–A322. URL http://tin.er.usgs.gov/meteor/docs/mb89.pdf

Jacobsen, B., zhu Yin, Q., Moynier, F., Amelin, Y., Krot, A. N., Nagashima, K., Hutcheon, I. D., & Palme, H. (2008). Al-Mg and Pb-Pb systematics of Allende CAIs: Canonical solar initial <sup>26</sup>Al/<sup>27</sup>Al ratio reinstated. *Lunar and Planetary Science*, XXXVIII(1491).

Komatsu, M., Krot, A. N., Mikouchi, T., Tagai, T., Miyamoto, M., & Keil, K. (2004). Amoeboid olivine aggregates in the nwa 760 cv3 chondrite. *Lunar and Planetary Science*.

Krot, A. N., Keil, K., Goodrich, C. A., Scott, E. R. D., & Weisberg, M. K. (2004). Classification of meteorites. In A. M. Davis (Ed.) *Treatise on Geochemistry*, vol. 1, chap. 1.05, (pp. 83–120). Elsevier Ltd.

Lee, T., Papanastassiou, D. A., & Wasserbug, G. J. (1976). Demonstration of <sup>26</sup>Mg in allende and evidence for <sup>26</sup>Al. *Geophysical Research Letters*, 3(1), 41–44.

Lee, T., Papanastassiou, D. A., & Wasserbug, G. J. (1977). Aluminium -26 in the early solar system: Fossil or fuel? *The Astrophysical Journal*, *211*, L107–L110.

Lodders, K. (2003). Solar system abundances and condensation temperatures of the elements. *The Astrophysical Journal*, *591*, 1220–1247.

MacPherson, G. J. (2004). Calcium–Aluminum-rich Inclusions in Chondritic Meteorites. In A. Davis (Ed.) *Treatise on Geochemistry*, vol. 1: Meteorites, Comets and Planets, chap. 1.08, (pp. 201–246). Elsevier Ltd.

MacPherson, G. J., Simon, S. B., Davis, A. M., Grossman, L., & Krot, A. N. (2005). Calcium-Aluminium-rich Inclusions: Major Unanswered Questions. *ASP Conference Series*, 341, 225–250.

McCord, T. B., Adams, J. B., & Johnson, T. V. (1970). Asteroid Vesta: spectral reflectivity and compositional implications. *Science*, *168*, 1445–1447.

McKeegan, K. D., & Davis, A. M. (2004). Early Solar System Chronology. In A. M. Davis (Ed.) *Treatise on Geochemistry*, vol. 1, chap. 1.16, (pp. 431–460). Elsevier Ltd.

Palme, H., & Jones, A. (2004). Solar system abundances of the elements. In A. Davis (Ed.) *Treatise on Geochemistry*, vol. 1: Meteorites, Comets and Planets, chap. 1.03, (pp. 41–60). Elsevier Ltd.

Russell, S. S., Zipfel, J., Folco, L., Jones, R., Grady, M. M., McCoy, T., & Grossman, J. N. (2003). The Meteoritical Bulletin, No. 87. *Meteoritics & Planetary Science*, *38*, A189–A248.

URL http://tin.er.usgs.gov/meteor/docs/mb87.pdf

Russell, S. S., Zolensky, M., Righter, K., Folco, L., Jones, R., Connolly, H. C., Jr., Grady, M. M., & Grossman, J. N. (2005). The Meteoritical Bulletin, No. 89. *Meteoritics & Planetary Science*, 40, A201–A263. URL http://tin.er.usgs.gov/meteor/docs/mb89.pdf

Schiller, M., Baker, J. A., & Bizzarro, M. (In Submission). <sup>26</sup>Al-<sup>26</sup>Mg dating asteroidal magmatism in the young solar system. *Earth and Planetary Science Letters*.

Schiller, M., Bizzarro, M., & Baker, J. A. (2007). Development of precise and accurate magnesium isotope measurements by multiple-

### REFERENCES

collector inductively coupled plasma mass spectrometry. In *Workshop* on *Chronology of Meteorites*.

Scott, E. R. D., & Krot, A. N. (2004). Chondrites and their Components. In A. Davis (Ed.) *Treatise on Geochemistry*, vol. 1: Meteorites, Comets and Planets, chap. 1.07, (pp. 143–200). Elsevier Ltd.

Taylor, S. R. (2001). *Solar System Evolution A New Perspective*. Cambridge University Press, 2 ed.

Teng, F. Z., Wadhwa, M., Janney, P. E., Grossman, L., Simon, S., & Dauphas, N. (2007). Magnesium isotopic systemat ics of chondrules and cais from allende, murchison, murray and bjurbole. In *Workshop* on Chronology of Meteorites.

Thrane, K., Bizzarro, M., & Baker, J. A. (2006). Extremely brief formation interval for refractory inclusions and uniform distribution of <sup>26</sup>Al in the early solar system. *The Astrophysical Journal*, 646, L159–L162.

Vuissoza, C., Meynet, G., Knodlseder, J., Cervinod, M., Schaererb, D., Palaciose, A., & Mowlavif, N. (2003). <sup>26</sup>al yields from rotating Wolf–Rayet star models. *New Astronomy Reviews*, 48, 7–11.

Weill, D. F., & Drake, M. J. (1973). Europium anomaly in plagioclase feldspar: Experimental results and semiquantitative model. *Science*, *180*, 1059–1060.

Young, E. D., Simon, J. I., Galy, A., Russell, S. S., Tonui, E., & Lovera, O. (2005). Supra-canonical <sup>26</sup>Al/<sup>27</sup>Al and the residence time of CAIs in the solar protoplanetary disk. *Science*, *308*, 223–227.

# Appendix A

# **Miscellaneous** Appendix

# A.1 Meteorite purchase details

The CV3 chondrite NWA 2364 was purchased from:

### **Arizona Skies Meteorites**

John and Dawn Birdsell P.O. Box 2412 Flagstaff, Arizona 86003 http://www.arizonaskiesmeteorites.com

The CV3 chondrite NWA 760 and the CK3 chondrite NWA 1559 were purchased from:

# **Bruno and Carine**

La Memoire de la Terre Sarl The Earth's Memory LLC France http://www.meteorite.fr

# A.2 Glossary of terms.

Term or	Description
Acronym	Description
AOA	amoeboid olivine aggregate
CAI	calcium-aluminium rich inclusion
Chondrite	An undifferentiated, primitive meteorite
EMPA	electronprobe microanalyser
LA-ICP-MS	laser-ablation inductively coupled plasma
	mass spectrometer
MC-ICP-MS	multi-collector inductively coupled plasma
	mass spectrometer
Nonchondrite	A meteorite from a parent body that has experienced
	petrographic differentiation
REE	Rare earth elements, the elements confined to the
	lanthanide region of the periodic table
Solar nebula	The cloud of gas, dust and ice from which the Solar
	System planets formed
wt%	Weight percent

**Table A.1:** Glossary of terms used in this study.

# Appendix **B**

# **ICP-MS** operational settings

Tuning Parameters	i	Ion Lenses	
Plasma Condition		Extract 1	5 V
RF Power	1500 W	Extract 2	-140 V
RF matching	1.72 V	Omega Bias-cs	-38 V
Smpl depth	4mm	Omega Lens-cs	8.8 V
Torch-H	0.3mm	Cell entrance	-40 V
Torch V	0.1mm	Qp Focus	+3 V
Carrier Gas (Ar)	0.9 L/Min	Cell exit	-40 V
Optional Gas (He)	80%	Octopole Param	eters
Detector Parameter	rs	OctP RF	170 V
Discriminator	8 mV	OctP Bia	-6 V
Analogue HV	1640 V	Q-Pole Paramet	ers
Pulse HV	1080 V	AMU Gain	130
Laser Settings		AMU Offset	122
Beam wavelength	193 nm	Axis Gain	1
Dwell time	100 seconds	Axis offset	-0.04
Power output	65%	QP Bias	-3 V
Spot size	35 µm	Reaction Cell	
Repetition rate	5 Hz	Reaction Mode	Off

**Table B.1:** Typical settings for the Agilent 7500 octopole ICP MS and New Wave 193 nmdeep UV laser ablation system used when determining trace element concentrations.

Tuning Parameters		Ion Lenses	
Plasma Condition		Extract 1	5 V
RF Power	1500 W	Extract 2	-140 V
RF matching	1.72 V	Omega Bias-cs	-38 V
Smpl depth	7mm	Omega Lens-cs	8.8 V
Torch-H	0.3mm	Cell entrance	-40 V
Torch V	0.1mm	Qp Focus	-8 V
Carrier Gas (Ar)	0.64 L/Min	Cell exit	-40 V
Makeup Gas	0.45 L/min	Octopole Param	eters
Optional Gas (He)	0%	OctP RF	170 V
Reaction Cell		OctP Bia	-18 V
Reaction Mode	On	Q-Pole Paramet	ers
He flow rate	0.8 L/min	AMU Gain	130
Detector Parameter	rs	AMU Offset	122
Discriminator	8 mV	Axis Gain	1
Analogue HV	1640 V	Axis offset	-0.04
Pulse HV	1080 V	QP Bias	-16 V

**Table B.2:** Typical settings for the Agilent 7500 octopole ICP MS in solution mode when determining  ${}^{27}Al/{}^{24}Mg$  ratios for digested refractory inclusion samples.

# Appendix C

# **Analytical Sites**

All mounted refractory inclusion samples were photographed using an electron microprobe. Site maps were produced by recording all analytical point locations on the electron back scatter images. This section contains all site maps for refractory inclusions analysed in this study. The labelled analytical sites are used for both major and trace element analyses (Appendices D & E respectively).







Figure C.2: Electron microprobe and laser ablation analytical sites for CAI 1. The yellow box encircles an example of a spinel palisade as discussed in Chapter 1.5.2



**Figure C.3:** *Electron microprobe and laser ablation analytical sites for CAI 2.* 



**Figure C.4:** *Electron microprobe and laser ablation analytical sites for CAI 3.* 







# APPENDIX C. ANALYTICAL SITES



**Figure C.7:** *Analytical sites for CAI 5. Detailed inset maps follow in Fig. C.8* 



**Figure C.8:** *Electron microprobe and laser ablation analytical sites for the core and rim of CAI 5.* Town 2008



Figure C.9: Electron microprobe and laser ablation analytical sites for CAI 8.



Figure C.10: Electron microprobe and laser ablation analytical sites for AOA 1.



**Figure C.11:** Electron microprobe and laser ablation analytical sites for AOA 2. The white line denotes the boundary between AOA 2 and its host groundmass.

# Appendix D

# **Major Element Data**

This section contains major element analyses for all analytical points displayed in Appendix C. Minerals were identified using oxide weight percentage ratios and matched to analyses published in Brearley & Jones (1998). Due to the process of identifying mineral phases by comparative brightness on an electron microprobe, the phase of some sites was originally misidentified. All analyses retain their originally identified phase and site number, but are displayed below according to petrology. All measurements are oxide weight percentages. Abbreviations used in this chapter: Hdn - hedenbergite; Ca-px- Ca-pyroxene; Lbdr - labradorite

Ŏ	ide					[] Me	lilite						Spi	nel	
Wt	t %	0	1	7	Э	-	4	ß	9	7		æ	1	6	
SiO	<b>)</b> <sub>2</sub> 3!	5.7 3	36.7	35.1	36.7	7 32	2.5	31.8	31.5	31.0	ς.	1.7	0.16	1.15	
TiO	0. 0.	.13 (	D.04	0.01	0.0	5 0.	03	0.03	0.09	0.05	0	.05	0.34	0.38	
$AI_2$	0 <sub>3</sub> 1(	5.6 1	14.6	15.9	15.(	0 2	1.9	22.6	23.0	24.2	0	3.3	70.7	66.0	-
FeC	0.	.10 (	0.08	0.04	0.0	5 0.	.05	0.16	0.16	0.04	0	.01	0.03	0.19	
Мn	0. 0.	00	D.01	0.04	0.0	5 0.	10	0.07	0.02	0.03	0	.06	0.00	0.00	
Mg	0 8.	39 5	9.13	8.76	9.2	2 6.	39	6.00	6.13	5.65	ß	.82	28.3	26.0	-
CaC	0	).6 4	40.5	40.2	40.2	2 4	1.0	40.2	40.4	41.1	4	0.7	0.06	0.29	
Na	2 <b>0</b> 0.	25 (	0.19	0.19	0.25	5 0.	08	0.08	0.17	0.00	0	.12	0.00	0.05	
$\mathbf{K}_2$	0.	02 (	0.02	0.04	0.0	5 O.	02	0.02	0.02	0.02	0	.04	0.00	0.02	
Tot	al 10:	1.76 1(	01.22	100.18	101.6	53 10.	1.97	100.92	101.52	102.1	0 10	1.70	99.58	94.02	,1
:			0					-							
Oxide			ġ	-pyroxei	ne						Anor	thite			
Wt %	9	5	8	•	6	10	11		19	Э	4	ю	9		5
$SiO_2$	40.2	40.6	40.	3 41	1.3	41.3	40.5	9 42	2.0	46.6	42.7	41.1	45	8.	12.1
$TiO_2$	6.29	5.53	4.7	5 4.	73	4.74	5.64	4 0.	54	0.02	0.03	0.11	0.1	11 (	.04
$AI_2O_3$	21.5	21.8	20.	8 22	2.1	21.3	20.6	3	5.0	38.7	36.2	36.4	37	Ŀ.	36.5
FeO	0.12	0.03	0.1	2 0.	.08	0.09	0.0	3 0.	.01	0.04	0.09	0.0	0.1	0	).13
MnO	0.00	0.00	0.0	0. 0.	02	0.10	0.0	8 0.	08	0.00	0.05	0.00	0.(	5 (	.14
MgO	9.18	9.39	9.5	5 9.	32	9.53	9.8	0.	49	0.08	0.05	0.04	0.0	33 (	.15
CaO	25.9	25.7	25.	3 2(	5.5	26.4	26.7	7 2(	J.8	20.5	20.9	21.0	20	.9	9.3
$Na_2O$	0.08	0.01	0.0	8 0.	.05	0.07	0.0	4 0.	08	0.11	0.08	0.10	0.0	) (	.15
$\mathbf{K}_2\mathbf{O}$	0.01	0.01	0.0	1 0.	.05	0.03	0.02	2 0.	05	0.02	0.03	0.02	0.(	)4 (	40.0
Total	103.22	103.13	101.0	00 104	4.12	103.60	104.]	11 100	0.08 1	06.11	100.00	98.8	4 104	.56 9	8.60

**Table D.1:** Electron microprobe analyses for melilite, spinel, Ca-pyroxene and anorthite in CAI 0

Oxide								Melilite							
Wt %	1	7	4	ß	9	7	8	6	10	11	12	13	14	15	16
$SiO_2$	34.7	36.2	36.7	36.5	34.7	34.6	33.1	31.8	26.2	31.9	28.0	28.6	32.1	27.3	25.7
$TiO_2$	0.04	0.07	0.13	0.05	0.01	0.08	0.10	0.00	0.04	0.01	0.05	0.01	0.07	0.53	0.09
$Al_2O_3$	16.2	15.9	15.3	14.8	17.9	16.2	19.9	21.4	27.7	23.0	28.4	25.9	20.8	29.4	31.9
FeO	0.02	0.0	0.07	0.06	0.11	0.04	pu	0.06	0.14	0.09	0.10	0.21	0.02	0.05	0.09
MnO	pu	0.10	0.05	pu	0.01	pu	0.139	pu	pu	pu	pu	0.19	pu	pu	0.06
MgO	8.57	8.70	8.84	9.24	7.87	8.47	6.93	6.20	3.99	6.04	3.64	4.71	6.63	3.44	2.35
CaO	42.9	43.0	40.9	40.9	41.3	40.1	41.2	40.6	40.9	41.6	40.1	40.7	40.4	40.5	41.2
$Na_2O$	0.18	0.25	0.23	0.21	0.24	0.20	0.19	0.13	0.06	0.25	0.07	0.16	0.19	0.00	0.09
$\mathbf{K}_2\mathbf{O}$	pu	0.01	0.02	0.02	pu	pu	0.02	0.02	0.03	0.04	0.04	0.06	0.05	0.02	0.01
Total	102.61	104.30	102.24	101.78	102.13	69.66	101.57	100.22	99.05	102.94	100.40	100.53	100.26	101.24	101.49
Oxide								Melilite							
Wt %	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
$SiO_2$	27.6	30.3	24.7	28.9	32.7	32	30.4	28.1	30.6	31.8	28.3	25.0	26.3	29.0	27.0
$TiO_2$	0.01	0.03	0.11	0.07	0.03	0.06	0.11	0.01	0.07	0.05	0.03	0.02	0.06	0.11	0.06
$AI_2O_3$	29.0	25.1	32.5	28.9	21.6	22.8	25.5	28.7	25.4	22.6	27.6	33.1	31.8	28.2	30.0
FeO	0.04	0.05	0.14	0.06	0.12	0.10	0.09	0.04	0.05	0.02	0.10	0.02	0.08	0.10	0.06
MnO	0.03	0.07	0.11	0.01	0.06	0.08	pu	pu	pu	0.01	pu	0.01	pu	0.06	0.18
MgO	3.61	5.27	1.88	3.87	6.91	6.46	5.37	3.76	5.53	6.38	4.28	1.93	2.50	4.48	3.49
CaO	40.8	41.7	40.3	41.4	41.1	41.3	41.4	41.4	41.3	41.1	40.4	40.6	40.7	41.1	40.6
$Na_2O$	0.01	0.05	0.03	0.12	0.12	0.09	0.11	pu	0.13	0.12	0.04	pu	0.07	0.08	0.05
<b>K</b> <sub>2</sub> <b>O</b>	0.03	0.01	0.01	0.01	0.05	0.02	0.03	0.03	0.01	0.02	0.01	pu	0.04	0.02	0.04
Total	101.13	102.58	99.78	103.34	102.69	102.91	103.01	102.04	103.10	102.09	100.75	100.68	101.54	103.14	101.47

 Table D.2: Electron microprobe analyses for melilite in CAI 1

Oxide					Mel	ilite							5	Ca-pyrox	ene		
Wt %	32	33	5	34	35	36	37	38	39	41	0	1	7	3	4	ю	9
SiO <sub>2</sub>	28.1	31.1	26.	.6 2	5.5 2	14.2	27.7	27.5	28.5	25.5	5 42	2.5	37.0	39.3	39.7	35.9	38.2
$TiO_2$	0.05	0.05	0.0	11	) pu	.07	0.06	0.05	0.05	0.0	9 5.	86	11.1	8.39	7.27	12.5	8.84
$Al_2O_3$	30.3	23.1	30.	.5 3.	3.5 3	34.4	29.3	29.4	28.2	34.0	3 16	5.0	19.1	20.8	21.1	19.4	18.5
FeO	0.00	0.04	0.0	0.0	.06 (	.05	0.12	0.08	0.12	0.0	9 0.	01 (	0.05	0.00	0.02	0.04	0.00
MnO	1.00	0.12	1.0	0.00	.03 (	.14	0.10	1.00	pu	0.0	1	) pu	0.01	0.03	0.11	0.11	0.00
MgO	3.64	6.22	3.1	19 2.	.14 1	69.	3.69	3.82	4.35	2.0	6 11	5 6.1	€.22	9.7	9.71	8.54	9.79
CaO	40.9	40.4	40.	9 4	1.4 4	10.8	40.6	40.9	41.1	41.5	2 25	5.2	24.6	25.3	25.1	24.8	25.1
$Na_2O$	0.07	0.11	0.0	.0 0.	.03 (	60.(	pu	0.08	0.07	лс	ط 0.	01 (	0.07	pu	0.06	0.06	0.04
$\mathbf{K}_2\mathbf{O}$	pu	0.07	ä	id 0.	.02 (	.01	pu	0.03	0.04	0.0	4 0.	03 (	0.05	pu	0.02	pu	0.04
Total	104.06	101.21	102.2	<u> 102.</u>	.68 101	.45 1(	01.58	102.86	102.43	103.3	1 101.	51 10	1.19 10	3.52 1(	03.09	101.34	100.51
	Oxic	de							a-pyroxe	ne							
	Wt	%	8	6	10	11	1	10	13	14	16	17	18	19		20	
	SiO	~	35.3	39.3	38.8	38.3	40.	2	36.5	33.6	33.2	40.6	34.5	33.4	č	4.3	
	TiO	~	13.4	7.71	9.10	9.82	8.6	9 1	11.7	17.8	17.4	7.73	14.4	14.0	1,	4.0	
	$Al_2$	<b>J</b> <sup>3</sup>	18.9	18.5	18.6	20.2	17	4 1	19.2	20.7	20.0	16.9	21.1	21.0	5(	.08	
	FeO		0.00	0.10	0.07	1.00	0.1	1 0	).12	0.07	0.11	0.05	0.03	2.00	0.	08	
	MnC		0.05	0.11	pu	0.05	0.0	5 (	00.0	0.16	0.06	0.08	0.03	0.00	0	04	
	MgC		8.26	10.3	9.64	9.24	10.	5 8	3.81	6.55	6.56	11.0	7.39	7.35	7.	81	
	CaO		24.6	25.2	25.2	25.3	25.	4	24.7	24.6	24.7	25.7	25.2	24.5	5	5.3	
	$Na_{2}^{\dagger}$	0	0.01	0.00	0.03	0.01	0.0	7 (	00.0	0.06	pu	0.01	0.01	0.05	0.	01	
	$K_2C$		0.02	0.04	0.01	pu	0.0	3 1	00.1	0.01	0.01	0.07	0.04	0.01	0.	00	
	Tota	1 10	0.54	101.26	101.44	103.92	102.4	4 102	2.04 10	3.56 1	102.05	102.14	102.70	102.31	102.	34	

 Table D.3: Electron microprobe analyses for melilite and Ca-pyroxene in CAI 1

Oxide								Spin	el							
Wt %	1	7	3	4	ß	9		-	8	6	10	11	12	13	14	15
$SiO_2$	0.12	0.11	0.09	0.17	0.13	0.08	0.0	8 0.1	6 0.	12 (	0.11	0.11	0.16	0.11	0.13	0.14
$TiO_2$	0:30	0.31	0.25	0.24	0.20	0.21	0.9	8 0.3	5 0.	66 1	1.14	0.29	06.0	0.75	0.35	0.88
$AI_2O_3$	74.3	73.7	74.5	72.4	72.2	74.8	72.	3 72.	.5 74	1.2 5	70.9	71.6	72.1	72.9	72.8	72.6
FeO	0.06	0.08	0.04	0.05	0.06	pu	0.0	2 0.C	)3 O.	07	pu	0.01	0.10	0.07	0.03	0.07
MnO	0.05	0.07	0.02	0.01	0.00	pu	0.1	3 n	d 0.	04 (	0.07	0.08	0.07	0.03	0.04	pu
MgO	28.4	28.1	28.7	28.3	28.8	28.6	28.	2 28.	.5 26	3.8	28.6	28.5	28.3	28.7	28.4	28.3
CaO	0.08	0.12	0.08	0.12	0.09	0.08	0.0	4 0.C	.0 0.	08 (	).03	0.08	0.07	0.03	0.16	0.05
$Na_2O$	0.03	0.01	0.03	0.03	0.04	0.03	0.0	4 0.C	0.	05 (	0.01	0.01	0.01	0.03	pu	0.04
$\mathbf{K}_2\mathbf{O}$	0.07	0.01	0.00	0.04	0.03	pu	'n	4 0.C	0.1	02 (	).03	0.01	0.02	pu	pu	0.03
Total	103.41	102.50	103.70 10	1.36 1	101.55	103.81	101.7	9 101.6	3 104.	02 100	).89 1(	69.0C	101.74	102.62	101.90	102.10
													[			
			Oxide					Anortl	nite							
			Wt %		1	6	e	4	ы	9	8	1	0			
			$SiO_2$	43.		44.0	44.4	44.7	44.1	42.8	42.6	43.	4.			
			$TiO_2$	0.0	6	0.02	0.05	0.07	0.15	0.12	pu	0.0	33			
			$AI_2O_3$	37.	9	37.1	37.6	38.1	37.3	36.2	37.0	37.	4.			
			FeO	0.0	11	0.20	pu	0.00	0.09	0.09	0.12	0.0	5			
			MnO	0.0	0	0.08	0.10	0.02	0.07	0.03	0.00	0.0	9			
			MgO	0.1	0	0.08	0.11	0.25	0.23	0.21	0.14	0.1	8			
			CaO	20.	0	19.7	20.5	20.3	19.9	19.8	20.1	20.	0.			
			$Na_2O$	0.1	0	0.12	0.14	0.18	0.13	0.13	0.14	0.1	1			
			$K_2O$	0.0	4	0.01	0.01	0.01	0.00	0.04	0.02	0.0	33			
			Total	101.1	4 10	1.31 1	02.90	103.63	101.97	99.43	100.13	101.2	9			

# Table D.4: Electron microprobe analyses for spinel and anorthitein CAI 1

Oxide				Anorthi	te (P2)			
Wt %	1	6	Э	4	υ	9	8	10
$SiO_2$	43.2	44.0	44.4	44.7	44.1	42.8	42.6	43.4
$TiO_2$	0.09	0.02	0.05	0.07	0.15	0.12	pu	0.03
$AI_2O_3$	37.6	37.1	37.6	38.1	37.3	36.2	37.0	37.4
FeO	0.01	0.20	pu	0.00	0.09	0.09	0.12	0.05
MnO	0.00	0.08	0.10	0.02	0.07	0.03	0.00	0.06
MgO	0.10	0.08	0.11	0.25	0.23	0.21	0.14	0.18
CaO	20.0	19.7	20.5	20.3	19.9	19.8	20.1	20
$\mathbf{Na}_2\mathbf{O}$	0.10	0.12	0.14	0.18	0.13	0.13	0.14	0.11
$\mathbf{K}_2\mathbf{O}$	0.04	0.01	0.01	0.01	0.00	0.04	0.02	0.03
Total	101.20	101.22	102.93	103.61	102.00	99.47	100.16	101.23

 Table D.5: Electron microprobe analyses for anorthite (phase 2) in CAI 1

Oxide			Melili	te					La	bradorit	e		
Wt %	18	20	21	22	23	24	25	6	10	14	16	21	22
SiO <sub>2</sub>	23.2	22.9	24.4	24.3	23.8	24.9	21.9	37.3	40.6	39.5	39.5	38.9	43.8
$TiO_2$	0.01	0.06	0.05	3.23	0.10	0.126	0.16	0.07	0.07	0.06	0.03	0.08	0.06
$AI_2O_3$	33.8	34.9	34.2	32.7	35.8	35.8	53.7	41.2	40.1	39.7	40.0	43.5	39.4
FeO	0.10	0.09	0.03	0.17	0.12	0.123	4.55	1.07	0.81	0.93	0.99	0.67	0.31
MnO	0.06	0.05	0.04	0.09	0.07	0	0.02	0.06	0.07	0.03	0.14	0.11	0.01
MgO	1.41	1.11	1.36	1.38	0.94	0.828	10.3	2.90	1.28	1.56	2.20	3.31	0.66
CaO	42.4	41.8	42.7	38.8	41.7	44	5.52	9.41	9.56	9.83	8.51	9.56	11.6
$Na_2O$	0.09	0.11	0.09	0.17	0.10	0.09	3.33	8.20	8.45	7.93	8.28	7.62	8.97
$\mathbf{K}_2\mathbf{O}$	0.01	0.01	0.01	0.05	0.06	0.005	0.11	0.06	0.06	0.03	0.05	0.08	0.02
Total	101.07	101.04	102.83 1	00.93	102.74	105.832	99.635	100.29	101.02	99.56	69.66	103.82	104.84
			Oxide		Labra	dorite		Pyrox	ene				
			Wt %		23	24	25	1	2	6			
			$SiO_2$	6	2.1 3	6.3 3	8.5 41	.5 39.	6 52.(	0			
			$TiO_2$	0	.21 0	0.10 0	.13 1.8	37 4.5	3 0.05	6			
			$AI_2O_3$	4	6.5 4	1.0 4	0.5 25	.3 33.	3 5.19	6			
			FeO	6	.23 1	.67 1	.61 2.2	20 0.3	2 3.84	4			
			MnO	0	.14 0	.03	0.(	J3 0.0	6 0.0	10			
			MgO		.32 3	.53 3	.68 6.7	75 2.4	.3 15.(				
			CaO	6	.19 8	.77 7	.23 18	.5 22.	1 25.	1			
			$Na_2O$	ß	.50 8	8.72 8	.73 3.5	52 0.1	8 0.12	5			
			$\mathbf{K}_2\mathbf{O}$	0	.05 0	0.03 0	).0 60.	<b>34 0.0</b>	4 0.0				

 Table D.6:
 Electron microprobe analyses for melilite, labradorite and pyroxene in CAI 2

101.44

102.57

99.72

100.52

100.11

103.21

Total

Oxide			Spi	nel					7	Anorthit	e		
Wt %	7	æ	4	9	4	8	13	14	15	19	23	24	25
$SiO_2$	0.09	0.17	0.19	0.15	5.04	0.10	38.9	35.5	42.5	42.5	39.8	35.3	39.8
$TiO_2$	0.29	0.24	0.29	0.27	0.22	0.31	0.12	0.06	0.41	0.08	0.07	0.11	0.07
$\mathbf{AI}_{2}\mathbf{O}_{3}$	71.1	70.1	71.5	72.0	67.9	72.1	39.9	40.4	37.0	36.6	42.3	47.0	42.3
FeO	3.30	2.93	1.00	1.18	8.22	2.40	0.61	0.60	0.36	0.10	pu	2.39	0.32
MnO	1.00	0.04	pu	0.08	0.13	0.00	0.01	0.07	0.02	0.02	0.03	0.00	0.03
MgO	26.2	25.7	27.8	27.0	16.3	26.6	2.72	3.47	0.89	0.07	2.34	4.85	2.34
CaO	0.04	0.10	0.08	0.08	1.11	0.08	18.4	17.5	19.8	20.1	17.9	8.19	17.9
$Na_2O$	0.08	0.04	0.00	0.03	0.42	pu	0.54	0.57	0.53	0.10	pu	8.03	0.87
$\mathbf{K}_2\mathbf{O}$	0.03	0.02	0.00	0.05	0.10	0.01	0.05	0.03	0.09	0.02	pu	0.03	0.01
Total	101.21	99.41	100.47	100.85	99.41	101.64	101.19	98.23	101.65	99.59	103.67	105.99	103.67

 Table D.7: Electron microprobe analyses for spinel and anorthite in CAI 2

Oxide							Anor	thite						
Wt %	1	7	3	4	ъ	9	4	8	6	10	11	12	14	15
$SiO_2$	43.6	43.9	43.8	45.6	41.7	44.2	43.4	44.8	43.2	42.1	43.2	43.7	44.8	45.3
$TiO_2$	0.13	0.10	0.13	1.35	0.20	0.14	0.14	0.20	0.24	0.42	0.13	0.20	0.16	0.22
$AI_2O_3$	36.8	36.1	36.8	30.5	36.5	36.0	35.8	37.5	33.9	35.3	37.5	37.1	35.4	36.5
FeO	0.17	0.08	0.19	0.29	0.23	0.17	0.14	0.13	0.31	0.14	0.44	0.15	0.25	0.12
MnO	0.06	0.07	0.00	0.05	0.00	0.03	0.02	0.05	0.12	0.09	0.03	0.00	0.00	0.09
MgO	0.66	0.18	0.24	7.67	0.35	0.27	0.67	0.18	1.03	1.62	0.10	0.26	0.41	0.88
CaO	20.9	19.5	20.6	15.0	20.5	20.5	20.2	20.9	20.0	19.4	20.9	19.6	19.5	19.9
$Na_2O$	0.10	0.86	0.32	0.40	0.11	0.59	0.31	0.23	0.48	0.22	0.20	0.54	0.67	0.38
$\mathbf{K}_2\mathbf{O}$	0.03	0.00	0.00	0.03	0.04	0.03	0.00	0.06	0.09	0.01	0.04	0.03	0.01	0.04
Total	102.47	100.83	102.12	100.88	99.68	101.97	100.64	103.99	99.42	99.21	102.53	101.58	101.24	103.53
	Oxide						Ca-poor p	yroxene						
	Wt %	1	7	ю	υ	9	8	6	10	11	12	13	14	
I	$SiO_2$	50.2	49.4	48.7	48.5	49.4	49.1	47.5	48.1	48.7	48.5	50.3	48.4	
	$TiO_2$	4.05	4.55	5.52	4.67	4.90	2.78	7.40	5.36	4.79	5.17	4.21	6.25	
	<b>Al</b> <sub>2</sub> <b>O</b> <sub>3</sub>	13.4	13.5	15.2	14.3	13.9	21.6	15.3	15.2	13.2	13.4	13.0	14.6	
	FeO	0.44	0.38	0.46	0.58	0.52	0.57	0.75	0.91	0.37	0.32	0.36	0.45	
	MnO	0.08	0.16	0.17	0.17	0.14	0.03	0.11	0.08	0.18	0.08	0.05	0.04	
	MgO	32.7	32.2	31.3	31.5	32.2	23.4	30.3	30.5	31.3	32.2	33.3	32.0	
	CaO	0.58	0.50	0.46	0.65	09.0	6.36	0.65	0.87	0.42	0.47	0.51	0.34	
	$Na_2O$	0.01	pu	0.01	0.06	0.05	0.13	0.03	0.25	0.05	pu	0.04	0.01	
	$\mathbf{K}_2\mathbf{O}$	0.02	pu	pu	0.01	0.00	0.08	0.04	0.05	0.00	0.04	0.02	0.02	
	Total	101.47	100.66	101.91	100.41	101.70	104.01	102.12	101.35	90.66	100.18	101.79	102.16	
1														


Oxide		Hε	edenbergi	te			Neph	ıline		Fas	saite
Wt %	1	7	Э	ъ	9	1	3	4	7	1	2
$SiO_2$	48.2	48.9	50.3	48.4	47.5	48.2	46.8	43.1	49.2	48.3	48.8
$TiO_2$	0.05	0.09	0.32	0.24	0.19	0.05	0.08	0.16	0.06	0.86	1.88
$\mathbf{AI}_{2}\mathbf{O}_{3}$	0.28	0.25	1.47	1.36	0.78	37.9	36.6	36.0	37.7	4.73	7.09
FeO	22.7	17.3	19.6	24.1	26.9	0.42	0.40	0.46	0.35	9.30	9.56
MnO	0.78	0.80	0.72	0.18	0.45	pu	0.07	pu	0.05	0.10	0.07
MgO	0.72	1.11	4.75	2.35	0.83	0.05	0.32	0.41	0.23	11.0	10.3
CaO	26.4	31.6	22.8	23.1	22.5	3.54	3.10	18.80	2.48	23.1	24.0
$Na_2O$	0.08	0.06	0.19	nd	0.08	15.9	14.9	0.86	13.1	0.19	0.27
$\mathbf{K}_2\mathbf{O}$	0.03	pu	0.06	0.02	0.07	1.43	1.44	0.03	1.21	0.04	0.03
Total	99.29	100.03	100.18	99.68	99.32	107.60	103.72	99.79	104.32	97.65	101.97

 Table D.9: Electron microprobe analyses for hedenbergite, nepheline and fassaite in CAI 3

Oxide							Fe	-rich spin	lel						
Wt %	1	7	3	ß	9	7	6	10	11	13	14	15	16	17	18
$SiO_2$	0.36	2.88	0.15	0.27	0.21	1.98	0.51	1.75	0.15	0.18	0.13	0.18	7.40	0.68	0.27
$TiO_2$	0.31	0.34	0.27	0.16	0.18	0.38	0.24	0.65	0.31	0.48	0.27	0.24	0.27	0.35	0.50
$\mathbf{AI}_{2}\mathbf{O}_{3}$	67.5	62.7	68.0	67.6	66.1	64.8	66.7	65.8	65.8	67.1	65.9	68.3	59.5	66.6	6.69
FeO	15.5	16.8	14.5	15.3	16.5	15.2	13.1	15.9	15.2	13.6	17.1	17.1	14.1	15.3	10.8
MnO	0.09	0.06	0.04	0.08	0.04	0.10	0.07	0.16	0.11	0.13	0.03	0.18	0.07	0.07	0.00
MgO	18.1	16.6	19.0	18.3	17.3	17.8	18.9	17.3	18.4	19.8	17.0	17.2	22.6	17.8	21.5
CaO	0.25	1.10	0.12	0.24	0.15	0.72	0.31	1.14	0.13	0.10	0.15	0.11	0.14	0.51	0.13
$Na_2O$	0.03	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.06	0.05	0.01	0.00	0.08	0.01	0.00
$\mathbf{K}_2\mathbf{O}$	0.00	0.00	0.03	0.02	0.01	0.03	0.01	0.01	0.00	0.01	0.03	0.00	0.06	0.01	0.01
Total	102.13	100.51	102.19	101.94	100.53	101.00	99.88	102.73	100.12	101.40	100.54	103.34	104.17	101.43	103.13
Oxide		Fe-rich	ı spinel						Ca	-pyroxene	0				
Wt %	19	20	21	22	1	6	4	ю	9	œ	6	10	12	13	14
$SiO_2$	0.26	5.29	1.25	0.21	48.2	51.5	48.2	48.8	51.4	51.7	51.3	52.8	48.4	47.8	51.9
$TiO_2$	0.48	0.66	0.22	0.19	3.23	0.92	0.37	0.06	0.76	0.50	0.80	0.26	0.69	0.71	0.36
$\mathbf{AI}_{2}\mathbf{O}_{3}$	68.5	61.1	64.7	62.9	9.43	3.84	9.90	12.91	4.04	4.33	4.69	2.86	8.88	5.58	2.97
FeO	15.8	16.5	19.6	14.1	0.53	1.08	5.69	0.69	1.27	0.51	0.61	0.53	1.58	3.74	0.35
MnO	0.05	0.17	0.09	pu	pu	0.09	0.27	pu	0.08	0.15	0.04	0.04	0.00	0.11	0.06
MgO	18.3	15.6	15.8	19.0	15.5	18.0	15.2	13.4	17.9	17.3	17.4	18.4	14.3	15.9	18.0
CaO	0.16	3.07	0.35	0.20	25.6	24.6	22.0	23.7	26.0	26.8	26.2	27.2	24.7	23.9	26.4
$Na_2O$	pu	0.39	0.06	0.00	0.01	0.09	0.28	1.13	0.16	0.23	0.16	0.00	0.50	0.24	0.06
$\mathbf{K}_2\mathbf{O}$	0.03	0.03	0	0.03	0.03	0.03	0.06	0.09	0.06	0.02	0.04	0.02	0.05	0.01	0.04
Total	103.51	102.80	102.00	99.73	102.59	100.14	101.89	100.70	101.65	101.53	101.25	102.06	99.01	97.94	100.09

4
Ц
Ú
ц
61
цэ
х <i>о</i> ,
ıћ
44
101
1-1
C
рı
а
lel
hi
l S
ich
1-
$F_{\ell}$
01
sf
ISC
aly
ш
e i
ťo'
ŀd
СЛС
m
n 1
10
ect
Εľ
ö
.1
Ω
le
ab
Ĥ

Oxide			Ca-py	roxene					Neph	eline			Hdn.
Wt %	15	16	17	19	20	21	1	7	ю	4	9	8	1
$SiO_2$	51.9	51.3	51.8	53.9	53.1	49.1	48.5	41.0	51.4	43.4	47.3	41.1	46.9
$TiO_2$	0.31	0.18	0.06	0.12	0.81	0.03	0.02	0.06	pu	0.07	0.04	0.06	0.05
$Al_2O_3$	3.17	4.57	3.67	3.61	5.50	9.52	37.9	34.6	39.5	33.7	35.1	34.5	0.21
FeO	0.35	0.53	0.36	0.46	0.24	2.37	0.38	0.42	0.28	2.38	0.50	0.42	27.8
MnO	0.09	0.04	0.00	0.00	0.07	0.03	0.01	0.08	0.00	0.06	0.00	0.00	0.83
MgO	18.6	17.6	17.9	18.4	17.7	15.2	0.06	0.83	0.01	6.48	0.13	0.04	0.13
CaO	27.6	27.4	27.2	26.0	25.6	25.2	1.78	2.39	1.75	7.00	1.66	0.22	22.0
$Na_2O$	0.16	0.23	0.00	0.05	0.01	0.19	10.2	15.6	15.7	5.51	17.6	20.8	0.00
$\mathbf{K}_2\mathbf{O}$	0.03	0.02	0.01	0.06	0.03	0.02	1.58	0.04	1.80	0.16	1.91	0.02	0.03
Total	102.15	101.77	100.99	102.63	103.04	101.96	100.44	94.96	110.44	98.82	104.33	97.10	98.02

 Table D.11: Electron microprobe analyses for Ca-pyroxene, nepheline and hedenbergite in CAI 4

Oxide				Me	lilite					AI	northite				Spinel	
Wt %	1	7	e.	4	ю	9	7	10	5	сл (л)		9	11	1	7	ŝ
$SiO_2$	24.2	24.0	24.5	24.2	23.7	24.6	21.9	33.6	41.6	38.9	41.	5 3	6.1	0.25	0.66	0.17
$TiO_2$	0.10	0.02	0.13	0.01	0.11	0.12	0.13	0.14	0.13	3 0.04	0.3	9	60.	0.48	1.06	0.61
$AI_2O_3$	32.3	32.7	32.7	32.8	33.9	35.9	39.6	28.2	37.7	7 35.9	35.8	8 4	0.5	71.1	71.3	70.6
FeO	0.40	0.27	0.56	0.56	0.20	0.30	2.87	0.53	0.70	0.45	0.3	7 2	.40	5.31	3.14	7.78
MnO	0.08	0.01	0.08	0.00	0.05	0.07	0.06	0.01	0.05	5 0.10	0.0	0	00.	0.00	0.14	0.06
MgO	1.94	1.61	1.56	1.49	2.74	2.90	6.07	2.01	1.07	7 0.93	2.1	4 3.	.94	25.8	26.9	24.3
CaO	40.0	41.2	40.7	41.1	39.7	41.7	34.0	32.9	19.0	) 21.3	21.	3 1	7.6	0.16	0.68	0.27
$Na_2O$	0.21	0.10	0.18	0.21	0.07	0.12	0.25	4.78	0.06	0.12	0.0	9 0.	.17	0.01	0.00	0.01
$\mathbf{K}_2\mathbf{O}$	0.01	pu	0.03	0.02	0.01	0.01	0.06	0.11	0.04	0.06	0.0	4 0	.17	0.02	0.06	0.01
Total	99.27	96.66	100.45	100.45	100.48	105.67	104.95	102.22	100.27	97.82	101.6	7 101	.01	03.09	104.01	103.81
	L	Oxide		Andre	adite		Ca-px	Lbdr			Unkne	uwc				
		Wt %	1	6	3	4	1	1	1	ß	4	ю	9	7		
		$SiO_2$	33.4	36.5	36.8	36.1	33.2	45.8	27.2	25.3	19.8	14.2	18.0	28.7		
		$TiO_2$	0.07	0.14	0.22	0.08	12.18	0.06	0.22	0.40	6.08	7.54	2.62	0.86		
		$\mathbf{AI}_{2}\mathbf{O}_{3}$	0.24	0.23	0.51	0.46	22.7	38.0	5.31	5.20	15.9	9.11	11.3	22.0		
		FeO	36.90	17.30	35.20	32.70	0.38	0.23	0.32	0.28	0.91	0.67	0.36	0.49		
		MnO	0.44	0.17	0.18	0.29	0.01	0.04	0.04	0.02	0.02	pu	0.07	0.07		
		MgO	1.16	14.80	4.87	4.25	8.05	0.34	9.75	7.88	5.55	3.53	3.66	2.22		
		CaO	30.6	34.8	22.5	25.7	25.5	1.67	11.4	12.4	12.6	12.6	9.47	16.1		
		$Na_2O$	0.05	0.05	0.25	0.06	0.01	10.62	0.01	0.01	0.23	0.15	0.12	0.22		
		<b>K</b> <sub>2</sub> <b>O</b>	0.03	0.04	0.18	0.14	0.07	1.63	0.02	0.08	0.08	0.08	0.04	0.17		
		Total	103.00	104.00	101.00	99.90	102.07	98.38	54.25	51.54	61.25	48.99	45.70	70.75		
	L														٦	



## APPENDIX D. MAJOR ELEMENT DATA

Oxide					Anorthit	e				Ca-px		oli	vine	
Wt %	ß	9	7	8	6	10	11	12	13	1	1	3	3	4
$SiO_2$	42.6	42.7	42.4	42.4	44.3	42.7	43.5	43.2	44.0	49.2	37.2	37.8	37.5	37.3
$TiO_2$	0.05	0.02	0.02	0.09	0.08	0.10	0.03	0.05	0.08	0.15	0.02	0.03	0.12	0.04
$\mathbf{Al}_2\mathbf{O}_3$	37.6	37.8	37.2	37.5	34.5	36.6	35.6	36.4	34.6	4.01	0.53	0.06	0.04	0.07
FeO	0.22	0.14	0.23	0.20	0.47	0.13	0.19	0.19	0.52	5.43	28.2	31.6	28.8	26.8
MnO	0.19	0.06	0.14	0.00	0.15	0.00	0.00	0.05	0.18	0.14	0.21	0.23	0.17	0:30
MgO	0.01	0.00	0.03	0.06	0.89	0.01	0.05	0.01	2.06	15.0	30.5	33.2	35.0	36.2
CaO	20.7	20.1	19.9	19.6	18.9	19.3	19.1	19.3	20.5	24.9	0.37	0.14	0.23	0.29
$Na_2O$	0.14	0.27	0.27	0.29	0.96	0.63	0.65	0.88	0.31	0.13	0.10	0.04	0.17	0.05
$\mathbf{K}_2\mathbf{O}$	0.02	0.05	0.00	0.02	0.03	0.03	0.01	0.02	0.04	0.14	0.02	0.00	0.00	0.00
Total	101.56	101.11	100.16	100.14	100.27	, 99.53	99.15	100.01	102.30	99.07	97.17	103.13	102.06	101.13
Oxide		Oliv	ine						Felds	spar				
Wt%	ъ	9	4	8	1	7	Э	4	υ	9	4	80	6	10
$SiO_2$	37.1	35.9	36.2	34.6	65.5	64.8	56.5	58.3	65.3	61.4	55.4	57.9	58.9	64.9
$TiO_2$	0.09	0.01	0.05	0.04	0.01	0.02	0.06	0.05	0.03	0.00	0.02	0.03	0.03	0.01
$Al_2O_3$	0.05	0.06	0.07	0.06	24.8	26.5	29.1	28.2	24.9	26.7	27.7	26.7	26.4	23.8
FeO	31.6	26.6	31.3	30.8	0.21	0.14	0.05	0.20	0.13	0.14	0.18	0.20	0.29	0.16
MnO	0.25	0.24	0.19	0.29	0.03	0.08	0.02	0.07	0.03	0.12	0.02	0.00	0.03	0.01
MgO	33.4	35.9	31.9	31.8	0.06	0.04	0.06	0.07	0.01	0.02	0.02	0.02	0.00	0.01
CaO	0.15	0.32	0.49	0.13	4.00	5.20	10.27	9.02	4.99	7.60	9.84	8.28	7.82	3.86
$Na_2O$	0.12	0.10	0.09	0.11	8.00	8.04	5.95	6.57	8.48	7.33	6.26	6.74	7.18	7.42
$\mathbf{K}_2\mathbf{O}$	0.01	0.05	0.02	0.02	0.37	0.28	0.15	0.26	0.32	0.29	0.17	0.21	0.24	0.55
Total	102.68	99.10	100.34	97.82	102.89	105.07	102.16	102.65	104.21	103.61	99.62	100.04	100.85	100.70

 Table D.13:
 Electron microprobe analyses for anorthite, olivine, Ca-pyroxene and feldspar in CAI 8
 <thCAI 8</th>
 <thCAI 8</th>
 CAI 8<

Oxide							Olivine						
Wt %	1	7	3	4	ß	9	7	8	6	10	11	12	15
$SiO_2$	37.7	39.2	38.1	38.2	38.7	38.6	37.2	38.6	38.4	37.8	38.9	37.5	37.5
$TiO_2$	0.01	0.09	0.03	0.01	0.05	0.04	0.06	0.35	0.03	0.11	0.11	0.05	0.15
$\mathbf{AI}_{2}\mathbf{O}_{3}$	0.26	0.06	0.17	0.33	0.12	0.05	0.42	0.24	0.06	0.10	0.05	0.70	0.16
FeO	29.2	29.7	29.2	30.2	29.5	30.7	29.4	30.2	30.1	30.4	31.3	29.8	30.4
MnO	0.29	0.23	0.23	0.31	0.19	0.20	0.26	0.25	0.29	0.39	0.26	0.28	0.24
MgO	34.2	35.1	33.8	35.3	35.2	34.9	33.3	34.6	34.4	33.3	34.4	34.8	34.1
CaO	0.04	0.05	0.07	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.04
$Na_2O$	0.00	0.06	0.02	0.00	0.00	0.02	0.05	0.02	0.00	0.07	0.00	0.02	0.00
$\mathbf{K}_2\mathbf{O}$	0.04	0.01	0.02	0.03	0.02	0.00	0.02	0.01	0.00	0.02	0.03	0.02	0.06
Total	101.79	104.51	101.65	104.35	103.74	104.44	100.63	104.24	103.28	102.16	105.02	103.11	102.71
Oxide		Oliv	vine						Feldspar				
Wt %	16	17	18	19	1	3	4	5	9	7	8	9	10
$SiO_2$	38.3	38.1	37.8	38.4	64.2	68.7	65.1	68.1	65.4	69.2	58.0	62.1	58.5
$TiO_2$	0.05	0.14	0.07	0.10	0.04	0.02	0.03	0.00	0.00	0.09	0.04	0.09	0.07
$Al_2O_3$	0.04	0.05	0.07	0.13	24.3	24.6	25.9	24.0	24.8	23.8	28.5	26.9	27.7
FeO	32.5	31.3	30.5	31.5	0.72	0.25	0.58	0.50	0.63	0.20	0.42	0.61	0.41
MnO	0.32	0.26	0.26	0.25	0.04	0.01	0.00	0.13	0.03	0.09	0.02	0.09	0.03
MgO	32.5	33.8	33.5	33.7	0.32	0.01	0.04	0.38	0.03	0.03	0.06	0.03	0.07
CaO	0.01	0.06	0.00	0.01	4.90	4.15	6.07	3.85	5.07	2.50	9.62	6.64	8.71
$Na_2O$	0.05	0.02	0.00	0.04	7.85	7.69	7.19	7.95	8.06	7.98	6.13	7.33	6.41
$\mathbf{K}_2\mathbf{O}$	0.01	0.01	0.06	0.04	0.44	0.05	0.31	0.52	0.38	0.50	0.14	0.37	0.15
Total	103.73	103.76	102.26	104.22	102.72	105.92	105.19	105.38	104.35	105.40	103.01	104.14	102.04

 Table D.14: Electron microprobe analyses for olivine and feldspar in AOA 1

Oxide				U	a-pyroxei	Je			
Wt %	2	œ	6	10	11	12	13	14	15
$SiO_2$	55.1	55.0	55.2	53.8	55.4	55.2	54.5	53.5	54.6
$TiO_2$	0.09	0.16	0.05	0.04	0.09	0.02	0.00	0.13	0.04
$AI_2O_3$	0.18	0.31	0.11	0.31	0.50	0.06	0.05	0.85	0.10
FeO	3.38	3.61	3.42	4.63	4.70	5.16	5.50	5.45	5.36
MnO	0.04	0.04	0.06	0.08	0.09	0.10	0.03	0.08	0.25
MgO	17.9	17.5	17.7	16.6	16.5	15.9	16.2	16.3	15.5
CaO	25.3	25.7	25.8	25.2	24.9	25.1	25.2	24.1	25.6
$Na_2O$	0.06	0.14	0.05	0.14	0.37	0.07	0.01	0.09	0.01
$\mathbf{K}_2\mathbf{O}$	0.00	0.00	0.00	0.04	0.03	0.02	0.01	0.02	0.00
Total	102.06	102.42	102.34	100.72	102.64	101.67	101.45	100.53	101.37

 Table D.15: Electron microprobe analyses for Ca-pyroxene in AOA 1.
 Particular Statement
 Particular Statement

 <th Part

Oxide					Oliv	rine							Diopsid	e	
Wt%	1	7	Э	4	ъ	9	5	8	6	10	1	5	3	ю	9
$SiO_2$	36.7	37.8	36.4	37.0	36.3	36.7	37.8	36.8	37.0	38.0	53.2	53.5	54.0	53.3	54.1
$TiO_2$	0.07	0.07	0.03	0.00	0.06	0.02	0.18	0.01	0.02	0.01	0.05	0.03	0.12	0.14	0.0
$Al_2O_3$	0.04	0.02	0.04	0.04	0.11	0.11	0.01	0.09	0.08	0.04	0.18	0.01	0.21	0.35	0.07
FeO	29.8	29.9	30.0	29.4	29.2	30.0	29.9	29.5	29.5	29.6	6.20	5.54	4.46	5.47	5.13
MnO	0.19	0.36	0.26	0.31	0.20	0.29	0:30	0.20	0.43	0.20	0.08	0.12	0.15	0.02	0.28
MgO	32.5	33.2	32.3	32.4	31.9	32.4	32.4	32.2	32.8	33.3	14.9	15.8	16.3	16.7	16.1
CaO	0.05	0.05	0.06	0.10	0.13	0.08	0.05	0.10	0.06	0.08	24.0	24.6	24.4	22.4	24.6
$Na_2O$	0.05	0.04	0.00	0.00	0.04	0.01	0.00	0.01	0.01	0.00	0.14	0.06	0.07	0.21	0.04
$\mathbf{K}_2\mathbf{O}$	0.03	0.02	0.02	0.00	0.02	0.01	0.02	0.04	0.02	0.04	0.02	0.05	0.00	0.01	0.01
Total	99.48	101.50	99.03	99.32	97.99	99.63	100.79	60.66	96.66	101.37	98.83	99.75	99.81	98.63	100.43
	Oxide	(P2) (	cont.)					Fel	dspar (	(P3)					
	Wt %	~	8	1	6	ι (ή)		4	ы	9	~	æ	6	10	
I	$SiO_2$	53.3	54.4	67.4	63.7	. 64.9	64.	1 68	8.1	66.3	67.3	64.9	64.4	62.8	
	$TiO_2$	0.07	0.07	0.05	0.01	0.00	0.0	3 0.(	64	0.03	0.04	0.02	0.03	0.04	
	$\mathbf{AI}_{2}\mathbf{O}_{3}$	0.14	0.05	23.4	24.2	23.7	22.4	9 21	6.1	24.5	23.7	23.2	23.4	23.9	
	FeO	6.11	5.01	0.52	0.46	0.63	1.00	3 0.	57	0.50	0.50	0.73	0.46	0.72	
	MnO	0.24	0.15	0.03	0.03	0.04	0.0	3 0.(	64	0.04	0.01	0.09	0.13	0.06	
	MgO	14.9	16.2	0.01	0.00	0.01	0.5	7 0.(	03	0.00	0.05	0.00	0.07	0.22	
	CaO	24.7	24.8	3.29	4.51	4.35	4.8	7 2.3	32	4.55	3.97	3.64	4.37	4.88	
	$Na_2O$	0.08	0.01	7.88	7.38	7.71	8.0	5 8.0	30	7.14	7.46	8.19	6.93	7.46	
	$\mathbf{K}_2\mathbf{O}$	0.03	0.01	0.31	0.28	0.34	0.3	5 0.3	37	0.33	0.43	0.37	0.35	0.34	
	Total	99.55	100.71	102.93	100.71	101.86	101.8	9 101.	71 1(	03.52	103.63	101.18	100.16	100.43	
L															_

 Table D.16: Electron microprobe analyses for olivine, diopside and feldspar in AOA 2

## Appendix E

## **Trace Element Data**

All values given in this chapter are parts per million (ppm). Abbreviations used in this chapter: Elmt - element; Mel - melilite; Px -pyroxene; Neph - nepheline; Ca-px- Ca-pyroxene; Anor - anorthite; Spnl- spinel; Plag-plagioclase; Hed - hedenbergite; Fass - fassaite; Fe-sp - Fe-spinel; Unk - unknown; And - andradite; Olvn - olivine; Diop - diopside; nm - not measured; nd - not detected.

Elmt	ppm	1 σ	Elmt	ppm	1 σ
Sc	5.83	0.06	Pr	0.0928	0.0005
Ti	440	3	Nd	0.457	0.011
V	55.7	1.3	Sm	0.145	0.002
Cr	2590	80	Eu	0.0546	0.001
Mn	1910	40	Gd	0.198	0.006
Со	502	17	Tb	0.0356	0.0031
Ni	10640	210	Dy	0.238	0.002
Cu	127	6	Но	0.0562	0.0012
Zn	310	12	Er	0.162	0.008
Ga	9.51	0.31	Tm	0.0237	0.0014
Rb	2.13	0.02	Yb	0.163	0.005
Sr	7.74	0.10	Lu	0.0237	0.0002
Y	1.53	0.12	Hf	0.115	0.006
Zr	3.96	0.11	Ta	0.0144	0.0001
Nb	0.265	0.016	W	0.089	0.007
Mo	1.02	0.11	Pb	2.56	0.03
Cs	0.185	0.002	Th	0.0309	0.003
Ba	2.31	0.03	U	0.0084	0.008
La	0.232	0.01			

**Table E.1:** Concentrations of trace elements from CI chondrites from Lodders (2003). These were the values used in converting ppm concentrations to CI normalised values in this study.

Elmt					Mel	ilite				
EIMt	01	02	03	04	05	06	07	08	09	10
Sc	2.51	9.51	9.53	1.50	2.62	1.92	4.13	1.66	2.35	2.04
Ti	15053	57012	57109	8988	15678	11519	24772	9967	14086	12210
V	36.2	43.4	43.1	8.84	29.9	7.36	140	3.76	4.68	12.8
Cr	6.88	19.3	23.3	4.17	7.90	1.19	6.49	nd	nd	1.53
Mn	5.44	14.1	14.5	3.09	2.68	2.75	5.75	5.55	3.88	3.65
Co	6.84	0.469	0.471	0.124	0.161	0.530	7.23	7.00	0.922	nd
Ni	175	1.22	1.22	nd	0.280	22.8	395	190	29.7	0.455
Cu	nd	3.66	3.90	nd	0.434	0.603	4.65	2.01	1.76	nd
Zn	nd	19.1	18.8	1.23	1.04	nd	4.63	3.01	5.57	0.018
Ga	0.048	0.152	0.154	0.108	nd	0.103	0.099	0.288	0.242	0.005
Rb	0.014	0.088	0.084	nd	0.038	nd	0.052	nd	0.016	0.015
Sr	262	259	252	210	179	213	245	323	379	240
Y	3.29	1.39	1.37	2.58	3.91	3.50	5.81	2.37	5.62	1.04
Zr	0.238	0.143	0.140	0.007	0.055	0.094	0.914	0.017	0.124	0.300
Nb	0.112	0.164	0.156	0.022	0.025	0.126	0.870	0.222	0.644	0.310
Мо	0.342	0.028	0.027	nd	nd	0.019	0.688	0.194	0.080	0.036
Cs	nd	0.043	0.040	0.006	nd	0.011	0.000	nd	nd	nd
Ba	43.0	25.6	24.6	31.5	30.4	31.7	34.9	46.2	62.8	26.2
La	2.77	1.53	1.47	2.08	1.75	3.53	3.56	5.64	18.0	1.94
Ce	5.80	3.21	3.06	4.85	4.97	7.78	7.46	11.0	31.6	3.78
Pr	0.702	0.393	0.378	0.688	0.635	0.945	0.968	1.12	3.47	0.515
Nd	2.84	1.62	1.58	2.82	3.20	4.02	3.92	4.47	12.0	2.10
Sm	0.722	0.378	0.374	0.693	0.792	0.828	1.00	0.851	1.91	0.429
Eu	1.22	0.791	0.767	1.18	0.947	1.07	1.52	1.13	1.99	0.884
Gd	0.614	0.413	0.396	0.582	0.781	0.942	0.810	0.713	1.60	0.435
Tb	nm									
Dy	0.533	0.289	0.287	0.525	0.871	0.673	1.02	0.571	1.30	0.334
Но	nm									
Er	0.364	0.126	0.123	0.251	0.452	0.355	0.648	0.292	0.629	0.095
Tm	nm									
Yb	0.537	0.205	0.205	0.261	0.552	0.246	0.827	0.236	0.429	0.097
Lu	0.036	0.024	0.023	0.017	0.050	0.023	0.085	0.021	0.029	0.006
Hf	0.013	0.012	0.012	0.010	0.007	0.015	0.031	nd	0.008	nd
Та	0.002	0.004	0.004	nd	nd	0.007	0.001	0.003	0.007	0.004
W	0.012	0.005	0.005	nd	nd	0.008	3.48	0.166	0.113	0.001
Pb	0.162	0.534	0.495	0.009	0.031	0.052	0.217	0.053	0.142	0.031
Th	0.121	0.181	0.173	0.038	0.013	0.091	0.291	0.054	0.233	0.092
U	0.032	0.068	0.062	0.009	0.025	0.016	0.062	0.006	0.025	0.013

**Table E.2:** Trace element measurements in ppm for melilite in CAI 0

Elmt		Melilit	e (cont.)				Pyroxene		
EIIIIt	11	12	13	14	04	05	06	08	09
Sc	2.02	0.702	2.22	2.63	263	76.9	362	484	586
Ti	12116	4211	13329	15746	1574650	461187	2169403	2902413	3515844
V	4.48	14.7	16.5	12.6	803	244	1110	1337	1847
Cr	nd	nd	3.97	nd	659	782	634	544	490
Mn	6.21	4.19	4.21	2.63	0.631	3.65	0.845	0.516	0.474
Со	0.383	0.149	0.094	0.117	1.68	10.5	2.73	32.1	0.173
Ni	7.71	0.666	nd	0.417	82.0	289	77.9	1645	0.497
Cu	0.898	0.637	0.983	0.269	0.755	2.69	0.111	1.83	0.212
Zn	5.91	1.62	0.447	0.137	1.00	0.483	0.815	0.052	1.65
Ga	0.196	0.045	0.040	0.188	0.406	0.965	0.205	0.225	0.162
Rb	nd	nd	nd	0.028	nd	nd	0.004	0.017	0.029
Sr	259	252	243	236	28.4	47.4	25.9	23.3	23.6
Y	4.27	1.37	0.588	1.71	54.0	129	48.9	46.2	45.1
Zr	0.039	0.152	0.082	0.123	207	203	207	236	253
Nb	0.160	0.112	0.049	0.012	5.56	13.1	5.11	2.64	1.96
Мо	0.072	0.032	nd	0.018	0.198	0.873	0.252	176	0.029
Cs	0.018	nd	0.025	0.000	nd	nd	nd	nd	nd
Ba	38.5	23.7	24.8	31.9	10.8	1.96	8.49	0.305	0.524
La	3.29	1.76	1.33	2.43	4.19	12.5	3.67	2.17	2.22
Ce	7.41	3.81	2.83	5.60	12.3	41.0	11.9	8.35	8.37
Pr	0.906	0.473	0.377	0.668	2.41	7.59	2.22	1.75	1.64
Nd	3.65	1.88	1.37	2.65	13.5	41.6	13.3	11.8	11.3
Sm	0.901	0.272	0.360	0.706	5.75	13.9	5.23	4.37	4.69
Eu	2.34	0.932	0.874	1.06	0.343	1.02	0.262	0.263	0.263
Gd	0.824	0.289	0.360	0.555	6.67	17.1	6.87	6.56	6.45
Tb	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dy	0.784	0.265	0.153	0.361	8.98	22.6	8.55	7.98	7.64
Но	nm	nm	nm	nm	nm	nm	nm	nm	nm
Er	0.314	0.128	0.064	0.205	5.95	14.8	5.34	5.03	5.00
Tm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Yb	0.476	0.147	0.080	0.126	6.43	16.1	5.68	5.14	5.11
Lu	0.037	0.005	0.005	0.023	0.940	2.41	0.801	0.801	0.837
Hf	0.014	nd	0.006	nd	6.05	3.29	7.05	7.53	8.53
Ta	0.012	nd	0.001	nd	0.397	1.11	0.335	0.269	0.247
W	0.074	0.011	0.002	0.005	nd	0.204	0.032	32.6	0.011
Pb	0.017	nd	0.050	0.119	0.253	1.19	0.205	0.101	0.086
Th	0.043	0.081	0.033	0.051	0.492	2.18	0.372	0.144	0.155
U	0.001	0.014	0.001	0.012	0.123	0.612	0.073	0.022	0.032

**Table E.3:** Trace element measurements in ppm for melilite (cont.) and pyroxene in CAI 0

Elmit	Spnl				Anorthite	5		
EIIII	01	01	02	03	04	05	06	07
Sc	1.30	5.07	5.54	4.40	4.08	4.41	4.14	3.11
Ti	7809	30386	33232	26378	24484	26414	24806	18621
V	1405	14.1	1024	16.3	10.8	9.52	8.83	7.77
Cr	860	1.93	601	3.79	6.36	2.85	2.62	nd
Mn	16.5	0.501	12.1	24.2	0.769	0.359	0.331	0.614
Co	nd	0.101	4.58	2.46	5.44	1.40	1.30	0.148
Ni	3.33	1.08	44.0	138	372	89.1	86.3	0.328
Cu	1.44	0.407	nd	1.22	3.17	0.760	0.697	nd
Zn	5.02	0.260	0.691	0.817	1.39	nd	nd	1.66
Ga	0.053	0.039	0.056	0.104	0.036	nd	nd	nd
Rb	0.065	0.003	0.064	nd	0.046	0.027	0.025	0.048
Sr	nd	525	518	400	483	471	433	393
Y	nd	0.842	0.800	1.34	0.724	0.552	0.513	0.392
Zr	0.220	0.592	0.729	0.328	0.296	0.116	0.107	0.226
Nb	nd	0.460	0.523	0.478	0.135	0.060	0.056	0.053
Mo	nd	0.053	0.916	0.591	0.431	0.338	0.313	nd
Cs	nd	nd	nd	nd	0.017	nd	nd	0.017
Ba	0.403	176	182	119	126	73.5	68.5	56.1
La	nd	1.16	1.14	1.69	0.906	1.02	0.960	0.968
Ce	nd	1.80	1.82	2.95	1.73	1.91	1.77	1.66
Pr	0.025	0.204	0.181	0.377	0.206	0.238	0.218	0.201
Nd	0.087	0.790	0.762	1.40	0.727	0.911	0.841	0.681
Sm	nd	0.140	0.077	0.277	0.100	0.091	0.085	0.180
Eu	0.007	3.19	3.00	2.22	2.79	2.53	2.36	2.17
Gd	nd	0.088	0.166	0.304	0.196	0.132	0.121	0.139
Tb	nm	nm	nm	nm	nm	nm	nm	nm
Dy	nd	0.146	0.083	0.165	0.128	0.068	0.062	0.101
Но	nm	nm	nm	nm	nm	nm	nm	nm
Er	nd	0.089	0.034	0.134	0.046	0.103	0.096	0.048
Tm	nm	nm	nm	nm	nm	nm	nm	nm
Yb	0.076	0.240	0.241	0.262	0.140	0.115	0.104	0.044
Lu	0.047	0.015	0.010	0.013	0.003	0.003	0.003	0.002
Hf	nd	0.022	0.034	0.007	0.003	nd	nd	0.020
Ta	nd	0.026	0.028	0.009	0.001	0.001	0.001	0.008
W	0.084	nd	0.250	0.548	0.054	0.061	0.058	0.016
Pb	0.295	0.025	0.079	0.034	0.215	0.004	0.004	0.003
Th	0.025	0.074	0.082	0.075	0.052	0.008	0.007	0.004
U	0.004	0.020	0.022	0.015	0.013	nd	nd	0.008

**Table E.4:** Trace element measurements in ppm for spinel and anorthite in CAI 0

Elast			]	B11.		
EIMt	Mel 3.24	Ca-px	Anor	Spnl	1	BUIK
Sc	3.24	296	4.39	1.30	1	107
Ti	19414	1772134	491	7809		11153
V	27.1	892	156	1405		512
Cr	4.62	519	88.0	860		299
Mn	5.61	1.87	5.54	16.5		5.48
Co	1.75	8.18	2.21	nd		3.91
Ni	58.9	363	104	3.33		170
Cu	1.04	1.20	0.775	1.44		1.09
Zn	4.30	0.745	0.531	5.02		2.34
Ga	0.114	0.345	0.030	0.053		0.172
Rb	0.007	0.011	0.028	0.065		0.019
Sr	254	51.5	460	nd		197
Y	2.77	54.1	0.738	nd		20.2
Zr	0.173	184	0.342	0.220		65.4
Nb	0.213	4.75	0.252	nd		1.66
Мо	0.099	29.6	0.372	nd		10.6
Cs	0.004	nd	nd	nd		nd
Ba	34.0	7.05	115	0.403		37.4
La	3.65	4.34	1.12	nd	1	2.96
Ce	7.36	14.1	1.95	nd		7.81
Pr	0.874	2.66	0.232	0.025		1.28
Nd	3.44	15.5	0.873	0.087		6.80
Sm	0.730	5.71	0.136	nd		2.28
Eu	1.19	0.495	2.61	0.007		1.11
Gd	0.665	7.33	0.164	nd		2.84
Tb	nm	nm	nm	nm		nm
Dy	0.569	9.34	0.108	nd		3.49
Но	nm	nm	nm	nm		nm
Er	0.289	6.04	0.078	nd		2.24
Tm	nm	nm	nm	nm		nm
Yb	0.316	6.44	0.164	0.076		2.42
Lu	0.027	0.965	0.007	0.047		0.357
Hf	0.008	5.41	0.012	nd	1	1.90
Ta	0.003	0.393	0.011	nd		0.138
W	0.277	5.47	0.139	0.084		2.06
Pb	0.137	0.309	0.052	0.295		0.198
Th	0.107	0.561	0.043	0.025		0.245
U	0.025	0.142	0.011	0.004		0.061

**Table E.5:** Average mineral and bulk trace element measurements in ppm for CAI 0

				Melilite					Anorthite	9
Eimt	10	17	22	31	34	37	40	08	10	05
Sc	4.48	1.89	1.49	36.2	1.99	0.905	46.1	2.56	1.92	2.01
Ti	26859	11303	8918	216986	11918	5427	276522	15360	11522	12039
V	315	4.03	53.1	79.4	32.2	2.66	56.2	1.57	145	5.98
Cr	302	nd	45.3	13.6	46.9	3.74	7.13	4.56	438	11.9
Mn	10.5	4.47	27.0	9.67	2.18	2.08	0.607	63.2	26.0	33.8
Co	38.9	41.1	165	184	45.9	2.70	0.480	179	85.7	126
Ni	1794	1815	6308	7558	2169	135	14.6	6053	3070	3440
Cu	10.7	4.92	28.9	43.5	10.5	0.799	nd	26.9	16.6	4.50
Zn	1.87	0.378	4.10	4.19	1.38	0.053	0.292	4.79	2.89	3.22
Ga	0.126	0.196	0.195	0.219	0.518	0.243	0.007	0.009	nd	0.116
Rb	0.141	nd	0.104	0.396	0.116	0.007	nd	0.110	0.090	nd
Sr	287	211	254	224	188	212	228	644	634	793
Y	8.39	16.9	15.8	15.7	22.5	18.3	12.8	1.41	1.13	1.78
Zr	0.396	0.160	1.90	30.6	0.225	0.028	5.08	0.321	0.064	0.263
Nb	0.334	0.065	13.6	2.98	0.734	0.206	0.257	1.06	1.79	3.03
Мо	1.66	0.370	23.8	1.26	0.078	0.048	6.02	2.16	1.60	1.40
Cs	0.034	0.025	0.006	0.004	nd	0.003	nd	nd	0.000	0.021
Ba	41.4	36.8	52.9	32.4	22.0	29.4	49.6	168	256	353
La	5.13	5.40	6.21	3.53	5.80	5.35	1.95	1.82	2.10	3.23
Ce	12.6	15.3	15.8	9.73	16.8	14.7	5.50	3.18	3.73	5.33
Pr	1.60	2.14	2.13	1.44	2.24	2.14	0.770	0.359	0.303	0.535
Nd	7.69	8.98	9.32	6.51	10.7	9.38	3.47	1.46	1.37	2.03
Sm	1.86	2.68	2.41	1.97	3.02	2.57	1.46	0.223	0.276	0.438
Eu	1.87	1.77	1.83	1.41	1.32	1.60	1.45	4.05	3.88	4.22
Gd	1.64	2.44	2.48	2.08	3.26	2.53	1.58	0.160	0.085	0.333
Tb	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dy	1.76	3.11	3.17	2.74	4.16	3.64	1.97	0.319	0.084	0.240
Но	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Er	0.850	1.77	2.02	1.54	2.46	2.08	1.39	0.120	0.092	0.252
Tm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Yb	0.831	1.71	1.99	1.96	2.51	1.58	1.68	0.439	0.280	0.402
Lu	0.083	0.127	0.157	0.208	0.277	0.176	0.185	0.023	0.016	0.027
Hf	0.035	nd	nd	0.446	nd	nd	0.076	0.004	nd	nd
Та	0.007	0.006	0.125	0.264	0.040	0.014	nd	0.021	0.010	0.053
W	0.109	0.000	3.20	0.313	0.021	0.013	0.912	0.085	0.117	0.039
Pb	0.127	0.073	0.346	0.287	0.461	0.227	0.109	0.225	0.321	0.300
Th	0.137	0.108	0.494	0.421	0.380	0.290	nd	0.215	0.100	0.253
U	0.043	0.048	0.191	0.109	0.169	0.071	0.015	0.079	0.047	0.092

**Table E.6:** Trace element measurements in ppm for melilite and anorthite in CAI 1

Elect			Ру	roxene		
EIMt	04	05	10	12	15	20
Sc	0.980	901	130	76.9	1583	1899
Ti	5875	5401021	778957	460786	9489320	11383998
V	0.628	995	208	406	1543	1975
Cr	2.07	347	468	651	289	595
Mn	16.5	0.103	40.4	11.7	2.49	4.41
Co	46.1	2.52	93.5	61.6	13.9	25.6
Ni	1161	125	2816	2715	480	1040
Cu	2.61	1.74	15.8	27.5	7.62	14.8
Zn	0.730	1.80	3.71	10.7	3.74	5.17
Ga	0.117	0.222	0.257	0.630	0.228	0.424
Rb	0.015	0.061	0.033	0.109	0.026	0.256
Sr	222	26.5	36.7	93.3	25.3	26.4
Y	3.12	78.3	144	134	50.8	52.1
Zr	nd	563	475	288	401	442
Nb	0.488	4.82	12.9	43.2	2.83	3.21
Мо	1.05	0.031	2.15	2.90	0.505	1.54
Cs	nd	0.011	nd	0.027	0.034	0.018
Ba	30.5	0.112	3.42	51.8	3.62	1.90
La	3.42	2.89	5.83	9.85	2.06	2.11
Ce	7.08	11.0	22.7	36.1	9.27	8.91
Pr	0.770	2.44	4.48	5.77	1.82	1.92
Nd	3.33	14.5	27.4	30.5	11.2	10.9
Sm	0.597	6.65	10.9	12.4	4.85	4.48
Eu	0.633	0.267	0.399	0.921	0.208	0.255
Gd	0.612	9.74	16.7	15.9	6.87	7.47
Tb	nm	nm	nm	nm	nm	nm
Dy	0.621	12.9	23.1	22.1	10.3	9.84
Но	nm	nm	nm	nm	nm	nm
Er	0.357	8.14	16.3	15.6	6.09	6.03
Tm	nm	nm	nm	nm	nm	nm
Yb	0.404	8.60	16.1	16.0	6.46	6.26
Lu	0.031	1.49	2.55	2.65	0.878	0.943
Hf	nd	16.1	6.67	2.96	16.1	17.3
Ta	0.009	0.402	1.25	2.97	0.179	0.260
W	0.042	0.065	0.152	0.528	0.144	0.364
Pb	0.124	0.161	0.477	2.20	0.136	0.227
Th	0.196	0.243	0.787	3.97	0.124	0.198
U	0.018	0.070	0.247	1.28	0.035	0.084

**Table E.7:** Trace element measurements in ppm for pyroxene in CAI 1

	<b>F1</b> (		s	D 11	
	Elmt	Mel	Anor	Ca-px	Bulk
	Sc	25.9	2.95	765	361
	Ti	155011	17659	4586659	2164523
	V	117	987	855	546
	Cr	103	3466	392	591
	Mn	12.7	137	12.6	25.8
	Co	71.5	309	40.6	82.5
	Ni	2916	8914	1390	2854
	Cu	15.6	74.5	11.7	20.1
	Zn	2.43	47.5	4.31	8.07
	Ga	0.267	0.319	0.313	0.293
	Rb	0.105	0.357	0.083	0.122
	Sr	233	578	71.8	196
	Y	20.6	15.6	77.0	45.9
	Zr	26.6	5.71	361	177
	Nb	14.4	42.8	11.3	16.0
	Mo	4.31	5.44	1.36	3.08
	Cs	0.009	0.008	0.012	0.011
	Ba	37.4	351	15.2	60.4
1	La	5.65	4.84	4.36	4.98
	Ce	15.4	9.61	15.8	15.0
	Pr	2.14	1.31	2.86	2.38
	Nd	9.66	5.35	16.3	12.2
	Sm	2.90	1.34	6.66	4.45
	Eu	1.56	3.75	0.447	1.29
	Gd	2.93	1.45	9.54	5.79
	Tb	nm	nm	nm	nm
	Dy	3.84	2.39	13.2	7.94
	Но	nm	nm	nm	nm
	Er	2.47	2.44	8.76	5.34
	Tm	nm	nm	nm	nm
	Yb	2.45	2.52	8.97	5.44
	Lu	0.328	0.415	1.42	0.837
ĺ	Hf	0.327	0.054	9.86	4.65
	Ta	2.21	0.778	0.845	1.44
	W	0.545	0.433	0.216	0.383
	Pb	1.90	1.38	0.554	1.23
	Th	3.57	1.98	0.920	2.19
	U	1.35	0.583	0.290	0.785

**Table E.8:** Average mineral and bulk trace element measurements in ppm for CAI 1

Elmit		Melillite	!	A	nor	Pl	ag	Spnl
EIMt	20	21	23	12	15	17	22	20
Sc	590	1377	775	95.3	162	20.1	159	0.183
Ti	14588	30644	14645	2727	7095	982	2674	4.32
V	1812	786	756	579	1145	1023	142	2.21
Cr	374	153	128	140	151	113	29.4	0.602
Mn	257	159	215	59.8	131	151	36.4	0.684
Со	794	35.3	278	128	258	70.9	9.17	0.430
Ni	24033	316	12101	4167	21834	5993	293	28.3
Cu	160	84.7	49.7	31.4	102	13.8	10.0	0.157
Zn	1720	137	85.4	478	1226	1137	61.5	1.33
Ga	5.45	4.01	3.95	1.82	6.36	3.02	1.19	0.012
Rb	4.06	2.98	2.39	0.841	3.21	2.06	0.559	0.006
Sr	418	202	110	137	318	989	94.5	0.257
Y	213	282	133	56.4	162	93.4	23.4	0.180
Zr	552	1047	536	61.9	241	4.56	89.6	0.026
Nb	2.60	3.86	1.56	0.84	2.29	0.788	0.459	0.004
Mo	15.2	5.04	7.90	39.7	6.17	2.55	1.53	0.012
Cs	0.848	0.838	1.04	0.30	0.64	0.397	0.18	0.002
Ва	162	69.9	14.7	51.8	105	143.5	48.2	0.071
La	27.2	23.0	15.4	8.11	17.9	19.8	2.13	0.029
Ce	67.5	62.0	38.3	19.4	55.8	38.0	5.07	0.078
Pr	10.5	11.8	6.54	3.19	7.98	6.94	0.873	0.011
Nd	58.7	72.4	34.4	16.0	40.9	41.4	5.10	0.057
Sm	18.1	27.4	12.2	5.23	13.7	9.42	2.28	0.023
Eu	1.99	1.55	1.38	0.807	1.27	1.26	0.349	0.004
Gd	26.6	43.3	16.2	7.29	17.7	18.7	2.56	0.021
Tb	5.01	8.99	3.23	1.34	3.54	3.26	0.518	0.005
Dy	34.7	56.6	22.2	9.09	26.3	19.3	3.90	0.030
Но	7.98	11.3	5.17	2.06	6.13	3.64	0.854	0.006
Er	23.8	30.0	15.0	5.81	16.9	8.88	2.86	0.020
Tm	3.44	3.74	2.28	0.88	2.18	1.11	0.429	0.003
Yb	4.98	3.60	3.19	1.58	3.44	2.40	0.833	0.007
Lu	3.69	4.29	3.19	0.887	3.44	0.799	0.583	0.003
Hf	18.7	34.4	17.9	2.07	3.44	1.26	2.23	0.008
Та	1.20	1.79	0.933	0.385	1.20	0.384	0.190	0.002
W	2.23	2.36	3.02	1.69	2.26	0.861	0.578	0.004
Pb	2.23	4.48	3.02	1.46	2.26	2.18	0.781	0.009
Th	2.95	5.53	1.63	1.00	2.68	3.15	0.473	0.003
U	1.06	0.641	0.671	0.271	0.595	0.239	0.162	0.002

**Table E.9:** Trace element measurements in ppm for melilite, anorthite, plagioclase andspinel in CAI 2

<b>F1</b> (		Aver	ages	Averages							
Elmt	Mel	Anor	Plag	Spnl		Bulk					
Sc	914	171	89.4	0.183		138					
Ti	19959	6077	1828	4.32		3650					
V	1118	968	583	2.21		630					
Cr	218	119	71.2	0.602		95.3					
Mn	210	120	93.5	0.684		88.5					
Со	369	200	40.0	0.430		105					
Ni	12150	14164	3143	28.3		6552					
Cu	98.1	48.1	11.9	0.157		33.6					
Zn	647	894	599	1.33		608					
Ga	4.47	4.19	2.10	0.012		2.63					
Rb	3.14	2.37	1.31	0.006		1.48					
Sr	243	426	542	0.006		348					
Y	209	111	58.4	0.180		76.3					
Zr	712	177	47.1	0.026		114					
Nb	2.67	1.45	0.624	0.004		0.973					
Мо	9.36	16.3	2.04	0.012		9.21					
Cs	0.910	0.458	0.289	0.002		0.348					
Ba	82.1	88.5	95.8	0.071		76.7					
La	21.8	15.1	11.0	0.029		10.8					
Ce	55.9	36.2	21.5	0.078		26.0					
Pr	9.58	5.97	3.90	0.011		4.28					
Nd	55.2	32.5	23.3	0.057		23.8					
Sm	19.2	10.1	5.85	0.023		7.06					
Eu	1.64	1.16	0.806	0.004		0.826					
Gd	28.7	14.5	10.6	0.021		10.9					
Tb	5.75	2.79	1.89	0.005		2.04					
Dy	37.8	19.3	11.6	0.030		13.6					
Но	8.14	4.29	2.25	0.006		2.91					
Er	22.9	11.5	5.87	0.020		7.91					
Tm	3.16	1.49	0.770	0.003		1.06					
Yb	3.92	2.79	1.62	0.007		1.84					
Lu	3.50	1.35	0.691	0.003		0.98					
Hf	23.7	6.48	1.74	0.008		3.94					
Ta	1.31	0.703	0.287	0.002		0.476					
W	2.53	1.65	0.719	0.004		1.15					
Pb	4.20	2.14	1.48	0.009		1.70					
Th	3.37	2.01	1.81	0.003		1.67					
U	0.791	0.379	0.201	0.002		0.286					

**Table E.10:** Average mineral and bulk trace element measurements in ppm for CAI 2

Elmit	Anor	Px		Hedenbergite			Neph		Fassaite	
EIMt	14	14	02	03	05	06	01	03	01	02
Sc	109	0.389	38.0	6.24	24.0	10.0	6.86	2.95	12.1	37.1
Ti	57113	229	18523	4635	12736	7487	3143	1695	11078	18115
v	281	1.62	148	42.5	147	52.9	21.1	10.1	90.0	147
Cr	12071	85.2	8667	3280	16664	2893	1161	691	5595	10542
Mn	2574	12.3	5455	6501	2453	6097	450	315	2818	2522
Co	4.37	0.521	279	91.9	498	121	41.6	38.2	274	127
Ni	44.0	35.2	23928	6529	40893	10234	3527	3385	27575	10158
Cu	2.33	0.176	197	55.4	358	125	35.5	30.6	247	96.8
Zn	39.4	3.76	2797	1277	4406	781	128	143	1185	1376
Ga	0.944	0.045	84.2	36.7	174	18.6	5.20	6.66	58.2	27.9
Rb	5.25	0.129	12.7	4.90	67.1	5.93	4.45	4.26	25.2	9.19
Sr	71.9	1.76	112	31.5	122	59.7	22.4	19.3	111	156
Y	1.20	0.023	0.564	0.513	1.43	0.873	0.218	0.129	2.12	1.26
Zr	5.00	0.056	0.996	1.33	1.21	1.46	0.418	0.230	6.35	7.68
Nb	5.02	0.097	8.67	3.61	8.19	4.81	0.919	1.04	9.54	5.63
Мо	0.117	0.001	0.634	0.390	1.47	0.718	0.200	0.124	0.844	0.335
Cs	0.105	0.017	0.317	0.198	0.844	0.148	0.121	0.063	0.453	0.201
Ва	53.6	0.777	22.6	52.1	20.7	37.4	13.8	2.66	46.0	53.3
La	10.7	0.280	9.25	6.67	12.5	8.29	1.27	1.85	20.2	12.3
Ce	43.6	1.09	30.6	22.4	45.7	27.8	4.38	6.44	74.2	43.5
Pr	5.43	0.139	4.10	2.98	6.58	3.60	0.532	0.845	9.46	5.58
Nd	25.6	0.640	16.3	13.5	26.5	16.2	2.80	4.01	44.4	27.6
Sm	9.58	0.236	5.66	4.86	9.56	5.44	1.07	1.26	15.1	10.2
Eu	0.412	0.006	0.628	0.163	0.524	0.380	0.085	0.092	0.846	0.553
Gd	2.23	0.042	1.34	0.895	1.30	1.15	0.138	0.207	2.47	1.93
Tb	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dy	1.77	0.028	1.06	0.723	1.64	0.777	0.164	0.179	1.96	1.50
Но	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Er	0.273	0.001	0.109	0.039	0.097	0.168	0.029	0.014	0.297	0.233
Tm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Yb	3.96	0.051	1.74	0.790	2.28	1.02	0.340	0.217	2.40	2.26
Lu	0.021	0.000	0.014	0.010	0.036	0.015	0.006	nd	nd	0.036
Hf	0.059	0.001	0.001	0.007	nd	0.004	0.023	0.003	0.120	0.181
Та	1.13	0.024	0.666	0.559	0.907	0.880	0.187	0.175	2.94	1.15
w	nd	0.000	0.371	0.158	0.270	0.094	0.027	0.033	0.394	0.209
Pb	0.440	0.011	1.02	0.541	1.79	0.523	0.169	0.175	4.31	3.56
Th	0.771	0.022	0.536	0.480	1.17	0.432	0.097	0.075	1.23	0.806
U	0.132	0.002	0.031	0.041	0.095	0.037	0.013	0.004	0.162	0.058

**Table E.11:** Trace element measurements in ppm for anorthite, pyroxene, hedenbergite,nepheline and fassaite in CAI 3

			D 11			
Elmt	Anor	Px	Hed	Neph	Fass	Bulk
Sc	109	0.389	19.6	4.90	24.6	33.7
Ti	57113	229	10845	2419	14596	17961
V	281	1.62	97.7	15.6	118	99.0
Cr	12071	85.2	7876	926	8069	4972
Mn	2574	12.3	5127	383	2670	1382
Со	4.37	0.521	248	39.9	200	55.8
Ni	44.0	35.2	20396	3456	18867	4987
Cu	2.33	0.176	184	33.0	172	46.3
Zn	39.4	3.76	2315	135	1280	345
Ga	0.944	0.045	78.4	5.93	43.1	11.9
Rb	5.25	0.129	22.6	4.35	17.2	6.35
Sr	71.9	1.76	81.4	20.8	133	50.7
Y	1.20	0.023	0.844	0.174	1.69	0.680
Zr	5.00	0.056	1.25	0.324	7.02	2.64
Nb	5.02	0.097	6.32	0.979	7.59	3.10
Мо	0.117	0.001	0.803	0.162	0.589	0.206
Cs	0.105	0.017	0.377	0.092	0.327	0.127
Ва	53.6	0.777	33.2	8.24	49.6	25.8
La	10.7	0.280	9.19	1.56	16.2	6.36
Ce	43.6	1.09	31.6	5.41	58.8	24.1
Pr	5.43	0.139	4.31	0.689	7.52	3.05
Nd	25.6	0.640	18.1	3.41	36.0	14.5
Sm	9.58	0.236	6.38	1.17	12.7	5.23
Eu	0.412	0.006	0.424	0.088	0.699	0.267
Gd	2.23	0.042	1.17	0.172	2.20	1.04
Tb	nm	nm	nm	nm	nm	nm
Dy	1.77	0.028	1.05	0.172	1.73	0.836
Но	nm	nm	nm	nm	nm	nm
Er	0.273	0.001	0.103	0.022	0.265	0.125
Tm	nm	nm	nm	nm	nm	nm
Yb	3.96	0.051	1.46	0.279	2.33	1.54
Lu	0.021	0.000	0.019	0.003	0.017	0.010
Hf	0.059	0.001	nd	0.013	0.151	0.045
Ta	1.13	0.024	0.753	0.181	2.05	0.727
W	nd	0.000	0.223	0.030	0.301	0.061
Pb	0.440	0.011	0.968	0.172	3.94	0.888
Th	0.771	0.022	0.654	0.086	1.02	0.423
U	0.132	0.002	0.051	0.008	0.110	0.057

**Table E.12:** Average mineral and bulk trace element measurements in ppm for CAI 3

<b>F1</b>	Spinel			C	a-pyroxe	ne	Nepheline			
Elmt	05	09	16	18	08	09	15	02	07	08
Sc	0.474	0.333	0.216	0.391	46.1	28.8	35.3	5.57	0.117	0.215
Ti	55.8	41.4	28.4	79.0	6271	2655	4489	695	18.7	36.5
V	14.7	12.0	7.12	16.5	805	301	1237	116	4.57	11.1
Cr	72.8	60.2	31.8	70.5	3458	892	4046	507	19.6	55.2
Mn	11.8	18.1	10.3	7.88	1236	1779	943	168	3.88	16.5
Co	2.62	1.14	0.872	0.987	129	56.6	62.8	7.44	1.49	1.87
Ni	129	58.6	35.4	43.9	8300	4020	2667	350	78.9	155
Cu	0.502	0.288	0.107	0.260	58.7	31.7	14.3	1.07	0.410	0.671
Zn	29.7	16.7	9.80	26.1	706	178	962	170	10.4	22.9
Ga	0.229	0.089	0.050	0.195	5.87	5.69	3.92	0.448	0.134	0.140
Rb	0.121	0.128	0.017	0.030	5.81	27.8	1.67	1.21	0.021	0.046
Sr	2.60	1.16	0.486	0.537	155	93.5	134	14.6	0.523	1.96
Y	0.020	0.008	0.007	0.010	1.29	0.650	1.15	0.151	0.006	0.009
Zr	0.039	0.034	0.016	0.099	7.86	4.96	3.54	1.50	0.011	0.015
Nb	0.017	0.012	0.006	0.016	2.15	1.01	1.49	0.188	0.006	0.014
Mo	0.011	0.006	0.006	0.006	1.08	0.261	0.087	0.075	0.004	0.011
Cs	0.006	0.002	0.002	0.001	0.847	0.193	0.168	0.035	0.003	0.005
Ва	0.411	0.152	0.096	0.106	35.7	9.33	13.5	2.14	0.071	0.221
La	0.131	0.087	0.053	0.081	11.2	6.88	7.52	0.842	0.035	0.071
Ce	0.265	0.161	0.099	0.188	26.0	14.5	16.5	2.38	0.072	0.153
Pr	0.057	0.032	0.022	0.037	4.96	2.60	3.00	0.377	0.014	0.030
Nd	0.327	0.165	0.113	0.181	23.4	12.6	15.3	1.79	0.095	0.152
Sm	0.086	0.049	0.035	0.062	8.45	3.88	5.52	0.619	0.022	0.053
Eu	0.005	0.007	0.003	0.004	0.524	0.927	0.859	0.081	0.002	0.004
Gd	0.051	0.028	0.018	0.032	3.30	1.50	2.72	0.305	0.015	0.026
Tb	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dy	0.038	0.017	0.013	0.022	3.22	1.19	1.86	0.211	0.012	0.023
Но	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Er	0.003	0.001	0.000	0.002	0.126	0.102	0.177	0.025	0.001	0.002
Tm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Yb	0.016	0.008	0.005	0.006	1.30	0.665	1.04	0.100	0.005	0.006
Lu	nd	0.000	0.000	nd	0.010	0.004	0.023	0.003	nd	nd
Hf	0.001	0.000	nd	0.001	0.099	0.122	0.075	0.027	0.000	nd
Ta	0.008	0.002	0.004	0.019	0.842	0.225	0.217	0.056	0.002	0.003
W	0.005	0.004	0.001	0.000	0.457	0.123	0.066	0.016	0.001	0.004
Pb	0.005	0.003	0.002	0.007	0.546	0.221	0.267	0.027	0.003	0.004
Th	0.009	0.003	0.003	0.006	0.532	0.247	0.272	0.036	0.002	0.004
U	0.001	0.001	0.000	0.000	0.032	0.059	0.063	0.006	nd	nd

**Table E.13:** Trace element measurements in ppm for spinel, Ca-pyroxene and nepheline inCAI 4

Elmit		D.,11.		
EIMt	Fe-sp	Ca-px	Neph	DUIK
Sc	0.354	36.8	1.97	15.9
Ti	51	4472	250	1938
V	12.6	781	43.8	339
Cr	58.8	2799	194	1233
Mn	12.0	1319	62.8	567
Co	1.40	83.0	3.60	35.7
Ni	66.7	4996	195	2136
Cu	0.289	34.9	0.715	14.6
Zn	20.6	615	67.8	282
Ga	0.141	5.16	0.241	2.24
Rb	0.074	11.7	0.425	4.99
Sr	1.20	128	5.68	54.7
Y	0.011	1.03	0.055	0.446
Zr	0.047	5.45	0.508	2.44
Nb	0.013	1.55	0.070	0.664
Мо	0.007	0.475	0.030	0.208
Cs	0.003	0.403	0.014	0.171
Ba	0.191	19.5	0.809	8.34
La	0.088	8.52	0.316	3.63
Ce	0.178	19.0	0.869	8.17
Pr	0.037	3.52	0.140	1.50
Nd	0.197	17.1	0.679	7.31
Sm	0.058	5.95	0.231	2.54
Eu	0.005	0.770	0.029	0.328
Gd	0.032	2.51	0.115	1.08
Tb	nm	nm	nm	nm
Dy	0.022	2.09	0.082	0.892
Но	nm	nm	nm	nm
Er	0.002	0.135	0.009	0.059
Tm	nm	nm	nm	nm
Yb	0.009	1.00	0.037	0.426
Lu	nd	0.012	0.001	0.005
Hf	0.001	0.098	0.009	0.044
Та	0.008	0.428	0.021	0.185
W	0.003	0.215	0.007	0.092
Pb	0.004	0.345	0.011	0.147
Th	0.005	0.350	0.014	0.150
U	0.001	0.051	0.002	0.022

**Table E.14:** Average mineral and bulk trace element measurements in ppm for CAI 4

Elmt		Mellilite	:	Uı	ık.		Andradite		
EIMU	01 r	03 r	10 c	01 r	03 r	01 c	02 c	03 c	
Sc	66.3	67.4	18.9	18.9	20.5	17.6	20.0	14.8	
Ti	39977	40676	17744	11393	12393	16503	18769	13861	
V	837	852	517	239	260	481	547	404	
Cr	90.6	92.1	241	25.8	28.1	224	255	188	
Mn	493	502	310	141	153	289	328	242	
Со	438	445	680	125	136	632	719	531	
Ni	18034	18349	28088	5140	5590	26125	29711	21941	
Cu	8.76	8.92	9.07	2.50	2.72	8.44	9.60	7.09	
Zn	204	208	236	58.2	63.3	219	249	184	
Ga	14.4	14.6	9.74	4.09	4.45	9.06	10.3	7.61	
Rb	14.4	14.6	1.55	4.10	4.46	1.44	1.64	1.21	
Sr	890	906	204	254	276	190	216	159	
Υ	29.7	30.3	2.95	8.48	9.22	2.75	3.12	2.31	
Zr	92.2	93.8	5.02	26.3	28.6	4.66	5.30	3.92	
Nb	38.8	39.4	17.1	11.0	12.0	15.9	18.0	13.3	
Мо	37.5	38.1	1.84	10.7	11.6	1.71	1.94	1.44	
Cs	1.87	1.90	0.149	0.532	0.578	0.138	0.157	0.116	
Ba	419	426	52.5	119	130	48.9	55.6	41.0	
La	31.2	31.7	1.41	8.88	9.66	1.31	1.49	1.10	
Ce	90.6	92.2	14.0	25.8	28.1	13.0	14.8	10.9	
Pr	8.32	8.46	0.979	2.37	2.58	0.911	1.04	0.765	
Nd	36.9	37.6	3.23	10.5	11.4	3.00	3.41	2.52	
Sm	11.1	11.3	2.00	3.16	3.44	1.86	2.11	1.56	
Eu	4.74	4.82	1.99	1.35	1.47	1.85	2.10	1.55	
Gd	3.54	3.60	0.422	1.01	1.10	0.392	0.446	0.330	
Tb	0.719	0.731	0.086	0.205	0.223	0.080	0.091	0.067	
Dy	6.32	6.43	0.584	1.80	1.96	0.543	0.618	0.456	
Но	0.825	0.840	0.096	0.235	0.256	0.089	0.101	0.075	
Er	3.53	3.59	0.427	1.01	1.09	0.397	0.451	0.333	
Tm	1.24	1.26	0.487	0.354	0.385	0.453	0.515	0.380	
Yb	10.7	10.9	7.49	3.05	3.32	6.97	7.93	5.85	
Lu	0.445	0.453	0.087	0.127	0.138	0.081	0.092	0.068	
Hf	1.70	1.73	0.174	0.484	0.526	0.162	0.184	0.136	
Та	1.80	1.83	0.419	0.513	0.558	0.390	0.443	0.327	
W	0.569	0.579	0.348	0.162	0.176	0.323	0.368	0.272	
Pb	4.21	4.28	0.903	1.20	1.30	0.840	0.955	0.705	
Th	3.02	3.08	0.087	0.862	0.938	0.081	0.092	0.068	
U	3.05	3.10	0.355	0.868	0.944	0.330	0.376	0.277	

**Table E.15:** *Trace element measurements in ppm for melilite, an unknown phase and andradite in CAI 5. "r" and "c" denote the sample is from the rim or core, respectively.* 

Elmt		Bull		
EIMU	Mel	Unk	And	Duik
Sc	41.8	19.7	17.4	18.6
Ti	28037	11893	16378	12024
V	652	249	478	271
Cr	153	26.9	222	53.6
Mn	386	147	286	160
Co	522	130	628	195
Ni	21561	5365	25926	8065
Cu	8.45	2.61	8.37	3.32
Zn	208	60.8	217	80.5
Ga	11.6	4.27	8.99	4.76
Rb	7.95	4.28	1.43	3.69
Sr	539	265	188	243
Y	16.3	8.85	2.73	7.60
Zr	48.7	27.4	4.63	23.0
Nb	27.1	11.5	15.7	11.6
Мо	19.7	11.2	1.70	9.33
Cs	1.01	0.555	0.137	0.472
Ba	234	125	48.5	108
La	16.3	9.27	1.30	7.74
Ce	51.9	27.0	12.9	23.8
Pr	4.63	2.47	0.904	2.15
Nd	20.1	11.0	2.98	9.38
Sm	6.48	3.30	1.84	2.95
Eu	3.27	1.41	1.84	1.41
Gd	1.97	1.05	0.389	0.913
Tb	0.401	0.214	0.079	0.185
Dy	3.45	1.88	0.539	1.61
Но	0.459	0.246	0.088	0.213
Er	1.97	1.05	0.394	0.912
Tm	0.842	0.369	0.449	0.365
Yb	8.72	3.18	6.92	3.58
Lu	0.263	0.132	0.080	0.119
Hf	0.933	0.505	0.161	0.434
Та	1.09	0.536	0.387	0.492
W	0.441	0.169	0.321	0.184
Pb	2.52	1.25	0.833	1.14
Th	1.56	0.900	0.080	0.745
U	1.24	0.906	0.328	0.653

**Table E.16:** Average mineral and bulk trace element measurements in ppm for CAI 5

Elmit	Anorthite		Feldspar		Ca-px	Ca-px Olivine		
EIMt	09	10	13	03	04	1	07	08
Sc	13.7	14.0	14.9	7.46	6.55	18.1	0.355	0.092
Ti	10123	10326	10994	5504	4830	13338	261	67.5
V	306	313	333	167	146	404	7.91	2.04
Cr	430	438	467	234	205	566	11.1	2.87
Mn	254	259	275	138	121	334	6.55	1.69
Со	472	482	513	257	225	622	12.2	3.15
Ni	23425	23894	25441	12735	11176	30863	605	156
Cu	7.70	7.85	8.36	4.18	3.67	10.1	0.199	0.051
Zn	174	177	189	94.5	82.9	229	4.49	1.16
Ga	6.63	6.77	7.20	3.61	3.16	8.74	0.171	0.044
Rb	1.09	1.11	1.18	0.591	0.519	1.43	0.028	0.007
Sr	139	142	151	75.5	66.3	183	3.59	0.926
Y	1.99	2.03	2.16	1.08	0.950	2.62	0.051	0.013
Zr	3.33	3.40	3.62	1.81	1.59	4.39	0.086	0.022
Nb	11.7	12.0	12.7	6.38	5.59	15.5	0.303	0.078
Мо	1.30	1.33	1.42	0.709	0.622	1.72	0.034	0.009
Cs	0.118	0.120	0.128	0.064	0.056	0.155	0.003	0.001
Ba	239	244	260	130	114	315	6.18	1.59
La	0.987	1.01	1.07	0.537	0.471	1.30	0.025	0.007
Ce	10.2	10.4	11.0	5.52	4.85	13.4	0.262	0.068
Pr	0.686	0.700	0.745	0.373	0.327	0.904	0.018	0.005
Nd	2.31	2.36	2.51	1.26	1.10	3.05	0.060	0.015
Sm	1.53	1.56	1.67	0.834	0.732	2.02	0.040	0.010
Eu	1.52	1.55	1.65	0.825	0.724	2.00	0.039	0.010
Gd	0.317	0.323	0.344	0.172	0.151	0.417	0.008	0.002
Tb	0.060	0.061	0.065	0.033	0.029	0.079	0.002	0.000
Dy	0.420	0.429	0.456	0.228	0.201	0.554	0.011	0.003
Но	0.072	0.074	0.078	0.039	0.034	0.095	0.002	0.000
Er	0.302	0.308	0.328	0.164	0.144	0.398	0.008	0.002
Tm	0.391	0.399	0.424	0.212	0.186	0.515	0.010	0.003
Yb	5.37	5.48	5.83	2.92	2.56	7.07	0.139	0.036
Lu	0.060	0.062	0.066	0.033	0.029	0.080	0.002	0.000
Hf	0.129	0.131	0.140	0.070	0.061	0.169	0.003	0.001
Та	0.318	0.324	0.345	0.173	0.152	0.418	0.008	0.002
W	0.301	0.307	0.327	0.164	0.144	0.397	0.008	0.002
Pb	0.753	0.768	0.818	0.410	0.359	0.993	0.019	0.005
Th	0.062	0.064	0.068	0.034	0.030	0.082	0.002	0.000
U	0.270	0.276	0.294	0.147	0.129	0.356	0.007	0.002

**Table E.17:** Trace element measurements in ppm for anorthite, feldspar, Ca-pyroxene and olivine in CAI 8

Elmit	Averages					B11.
Linu	Anor	Feld	Ca-px	Olvn	1	BUIK
Sc	14.2	7.01	18.1	0.223		12.0
Ti	10481	5167	13338	164		8877
V	317.3	156	404	4.98		269
Cr	445.0	219	566	6.98		377
Mn	262.7	129	334	4.12		222
Со	489.0	241	622	7.67		414
Ni	24253	11955	30863	381		20540
Cu	7.97	3.93	10.1	0.125		6.75
Zn	180	88.7	229	2.82		152
Ga	6.87	3.39	8.74	0.108		5.82
Rb	1.13	0.555	1.43	0.018		0.954
Sr	144	70.9	183	2.26		122
Y	2.06	1.02	2.62	0.032		1.75
Zr	3.45	1.02	4.39	0.054		2.92
Nb	12.1	5.99	15.5	0.191		10.3
Мо	1.35	0.666	1.72	0.021		1.14
Cs	0.122	0.060	0.155	0.002		0.103
Ba	247.7	122	315	3.89		210
La	1.02	0.504	1.30	0.016	1	0.866
Ce	10.5	5.19	13.4	0.165		8.91
Pr	0.710	0.35	0.904	0.011		0.602
Nd	2.39	1.18	3.05	0.038		2.03
Sm	1.59	0.783	2.02	0.025		1.34
Eu	1.57	0.774	2.00	0.025		1.33
Gd	0.328	0.162	0.417	0.005		0.278
Tb	0.405	0.199	0.515	0.006		0.343
Dy	0.435	0.215	0.554	0.007		0.369
Но	0.075	0.037	0.095	0.001		0.063
Er	0.313	0.154	0.398	0.005		0.265
Tm	0.405	0.199	0.515	0.006		0.343
Yb	5.56	2.74	7.07	0.087		4.71
Lu	0.063	0.031	0.080	0.001		0.053
Hf	0.133	0.066	0.169	0.002		0.113
Та	0.329	0.162	0.418	0.005		0.278
W	0.312	0.154	0.397	0.005		0.264
Pb	0.780	0.384	0.993	0.012		0.661
Th	0.065	0.032	0.082	0.001		0.055
U	0.280	0.138	0.356	0.004		0.237

**Table E.18:** Average mineral and bulk trace element measurements in ppm for CAI 8

Elmit		Olivine	Feldspar		
EIMT	02	08	19	04	07
Sc	0.040	0.006	0.005	4.61	1.90
Ti	27.7	4.27	3.73	3234	1333
V	0.789	0.121	0.106	92.0	37.9
Cr	0.960	0.148	0.129	112	46.1
Mn	0.682	0.105	0.092	79.6	32.8
Co	1.21	0.186	0.163	141	58.2
Ni	55.8	8.59	7.52	6514	2685
Cu	0.017	0.003	0.002	2.03	0.837
Zn	0.338	0.052	0.045	39.4	16.2
Ga	0.014	0.002	0.002	1.67	0.690
Rb	0.002	0.000	0.000	0.289	0.119
Sr	0.324	0.050	0.044	37.8	15.6
Y	0.005	0.001	0.001	0.574	0.236
Zr	0.008	0.001	0.001	0.973	0.401
Nb	0.029	0.004	0.004	3.34	1.38
Mo	0.003	0.000	0.000	0.348	0.144
Cs	0.000	0.000	0.000	0.028	0.012
Ва	0.079	0.012	0.011	9.22	3.80
La	0.002	0.000	0.000	0.264	0.109
Ce	0.021	0.003	0.003	2.45	1.01
Pr	0.001	0.000	0.000	0.175	0.072
Nd	0.005	0.001	0.001	0.593	0.244
Sm	0.003	0.001	0.000	0.391	0.161
Eu	0.003	0.000	0.000	0.357	0.147
Gd	0.001	0.000	0.000	0.084	0.035
Tb	0.000	0.000	0.000	0.015	0.006
Dy	0.001	0.000	0.000	0.107	0.044
Но	0.000	0.000	0.000	0.018	0.008
Er	0.001	0.000	0.000	0.075	0.031
Tm	0.001	0.000	0.000	0.095	0.039
Yb	0.011	0.002	0.002	1.30	0.537
Lu	0.000	0.000	0.000	0.017	0.007
Hf	0.000	0.000	0.000	0.031	0.013
Ta	0.001	0.000	0.000	0.079	0.033
W	0.001	0.000	0.000	0.063	0.026
Pb	0.001	0.000	0.000	0.149	0.062
Th	0.000	0.000	0.000	0.014	0.006
U	0.000	0.000	0.000	0.054	0.022

**Table E.19:** Trace element measurements in ppm for olivine and feldspar in AOA 1

Flmt	Aver	ages		Bull	
Linu	Olvn Feld		]	DUIK	
Sc	0.017	3.26	1	1.24	
Ti	11.9	2283		871	
V	0.339	64.9		24.8	
Cr	0.412	79.1		30.2	
Mn	0.293	56.2		21.4	
Со	0.520	99.7		38.0	
Ni	24.0	4600		1754	
Cu	0.007	1.43		0.547	
Zn	0.145	27.8		10.6	
Ga	0.006	1.18		0.451	
Rb	0.001	0.204		0.078	
Sr	0.139	26.7		10.2	
Y	0.002	0.405		0.154	
Zr	0.004	0.687		0.262	
Nb	0.012	2.36		0.900	
Мо	0.001	0.246		0.094	
Cs	nd	0.02		0.008	
Ва	0.034	6.51		2.48	
La	0.001	0.186	]	0.071	
Ce	0.009	1.73		0.661	
Pr	0.001	0.123		0.047	
Nd	0.002	0.418		0.160	
Sm	0.001	0.276		0.105	
Eu	0.001	0.252		0.096	
Gd	nd	0.059		0.023	
Tb	nd	0.067		0.004	
Dy	nd	0.076		0.029	
Но	nd	0.013		0.005	
Er	nd	0.053		0.020	
Tm	nd	0.067		0.026	
Yb	0.005	0.921		0.351	
Lu	nd	0.012		0.005	
Hf	nd	0.022	]	0.008	
Ta	nd	0.056		0.021	
W	nd	0.045		0.017	
Pb	0.001	0.105		0.040	
Th	nd	0.010		0.004	
U	nd	0.038		0.014	

**Table E.20:** Average mineral and bulk trace element measurements in ppm for AOA 1

<b>F</b> (	Olivine		Diopside		Feldspar	
Emt	09	01	07	04	09	05
Sc	0.030	0.033	14.0	14.6	1.37	2.59
Ti	28.9	32.4	13714	14256	1343	2527
V	0.834	0.934	396	411	38.7	72.9
Cr	0.606	0.679	287	299	28.2	53.0
Mn	0.581	0.651	276	286	27.0	50.8
Co	1.11	1.24	526	547	51.5	96.9
Ni	47.4	53.1	22510	23399	2204	4148
Cu	0.016	0.018	7.57	7.87	0.741	1.40
Zn	0.504	0.564	239	249	23.4	44.1
Ga	0.016	0.018	7.67	7.97	0.751	1.41
Rb	0.003	0.003	1.39	1.45	0.136	0.256
Sr	0.409	0.458	194	202	19.0	35.8
Y	0.006	0.007	2.97	3.09	0.291	0.547
Zr	0.011	0.012	5.03	5.23	0.493	0.927
Nb	0.035	0.039	16.6	17.3	1.63	3.06
Mo	0.004	0.004	1.70	1.77	0.166	0.313
Cs	0.000	0.000	0.144	0.150	0.014	0.027
Ba	0.706	0.790	335	348	32.8	61.7
La	0.003	0.004	1.52	1.58	0.149	0.281
Ce	0.031	0.034	14.6	15.1	1.43	2.68
Pr	0.002	0.002	0.970	1.01	0.095	0.179
Nd	0.007	0.008	3.36	3.49	0.329	0.619
Sm	0.005	0.005	2.17	2.25	0.212	0.399
Eu	0.004	0.005	2.03	2.11	0.198	0.373
Gd	0.001	0.001	0.451	0.469	0.044	0.083
Tb	0.000	0.000	0.086	0.089	0.008	0.016
Dy	0.001	0.001	0.605	0.629	0.059	0.112
Но	0.000	0.000	0.104	0.108	0.010	0.019
Er	0.001	0.001	0.427	0.444	0.042	0.079
Tm	0.001	0.001	0.554	0.576	0.054	0.102
Yb	0.016	0.017	7.40	7.69	0.725	1.36
Lu	0.000	0.000	0.093	0.097	0.009	0.017
Hf	0.000	0.000	0.194	0.202	0.019	0.036
Ta	0.001	0.001	0.452	0.470	0.044	0.083
W	0.001	0.001	0.361	0.375	0.035	0.067
Pb	0.002	0.002	0.884	0.919	0.087	0.163
Th	0.000	0.000	0.093	0.096	0.009	0.017
U	0.001	0.001	0.355	0.369	0.035	0.065

**Table E.21:** Trace element measurements in ppm for olivine, diopside and feldspar inAOA 2

Elmit		D11.		
EIMt	Olvn	Diop	Feld	BUIK
Sc	0.031	14.3	1.98	5.46
Ti	30.6	13985	1935	5334
V	0.884	404	55.8	154
Cr	0.642	293	40.6	112
Mn	0.616	281	38.9	107
Со	1.17	536	74.2	205
Ni	50.3	22954	3176	8755
Cu	0.017	7.72	1.07	2.94
Zn	0.534	244	33.7	93.0
Ga	0.017	7.82	1.08	2.98
Rb	0.003	1.42	0.196	0.541
Sr	0.434	198	27.4	75.5
Y	0.007	3.03	0.419	1.16
Zr	0.011	5.13	0.710	1.96
Nb	0.037	17.0	2.35	6.47
Мо	0.004	1.73	0.240	0.661
Cs	0.000	0.147	0.020	0.056
Ва	0.748	341	47.3	130
La	0.003	1.55	0.215	0.592
Ce	0.033	14.8	2.05	5.66
Pr	0.002	0.989	0.137	0.377
Nd	0.008	3.42	0.474	1.31
Sm	0.005	2.21	0.306	0.843
Eu	0.005	2.07	0.286	0.788
Gd	0.001	0.460	0.064	0.175
Tb	0.000	0.088	0.012	0.033
Dy	0.001	0.617	0.085	0.235
Но	0.000	0.106	0.015	0.041
Er	0.001	0.435	0.060	0.166
Tm	0.001	0.565	0.078	0.215
Yb	0.017	7.55	1.04	2.88
Lu	0.000	0.095	0.013	0.036
Hf	0.000	0.198	0.027	0.076
Ta	0.001	0.461	0.064	0.176
W	0.001	0.368	0.051	0.140
Pb	0.002	0.901	0.125	0.344
Th	0.000	0.095	0.013	0.036
U	0.001	0.362	0.050	0.138

**Table E.22:** Average mineral and bulk trace element measurements in ppm for AOA 2