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**Microprobe studies of alteration, discordance and
metamictization of late Archean zircons from the Acasta
Gneiss Complex, Canada**

by

Nicole Marie Sanborn

**A thesis submitted to the Faculty of
Graduate Studies and Research in partial fulfillment
of the requirements for the degree of
Master of Science, Department of Earth Sciences**

Carleton University

Ottawa, Ontario

April 2000

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The undersigned hereby recommend to the Faculty of Graduate
Studies and Research the acceptance of the thesis
“Microprobe studies of alteration, discordance and metamictization
in zircons from the Acasta Gneiss Complex, Canada”
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April 28, 2000

ABSTRACT

In geochronology studies the interpretation of discordant U-Pb zircon data is commonly based on assumptions about Pb-loss mechanisms, although the processes and timing of Pb-loss are poorly understood. The aim of this thesis is to study Pb-loss on an intra-grain scale, and to directly examine its causes in a specific sample. U-Pb age and isotopic data were collected using the SHRIMP ion microprobe from 2.9 Ga zircons separated from a granitic dyke in the Acasta Gneiss Complex in the Slave Province. New growth of zircon rims and cross-cutting zircon “micro-dykes” are documented at 2.7 Ga. From the isotopic data it was concluded that alteration was predominantly responsible for Pb-loss. The age of alteration is interpreted to be ca. 2.2 Ga, and was constrained using the $^{207}\text{Pb}/^{206}\text{Pb}$ ages of thorite inclusions in the zircon. There is also evidence for a further, recent, Pb-loss episode.

The results of microstructural analyses by transmission electron microscopy and Raman spectroscopy, and geochemical analyses by electron and ion microprobes provide insight into the controls and characteristics of the alteration process. The individual zircon grains used in this study contain domains of both altered and unaltered zircon. Altered zircon domains are enriched in contaminants such as Ca, common Pb, light rare earth elements, and have a disturbed isotopic signature. This is in contrast to unaltered zircon domains, which are generally isotopically concordant, and poor in common Pb and other impurities. There is no evidence for a secondary phase, such as apatite, as a host for the Ca or rare earth elements. High Ca domains yield electron diffraction patterns that indicate an amorphous structure. Low Ca, unaltered zircon domains have a highly crystalline structure, which is interpreted to be a result of late-stage annealing. The concordant ages for the unaltered zircon domains suggest that exclusion of Pb did not accompany the recovery of the zircon crystal lattice.

A broad correlation exists between U content and degree of alteration. It appears that alteration is an important, but often overlooked, mechanism of Pb-loss that is controlled by a complex set of conditions that includes, but is not restricted to, the degree of metamictization.

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This project was carried out at the Geological Survey of Canada and at Carleton University under the supervision of Dr. Richard Stern and Dr. Sharon Carr. Funding was provided by an NSERC research grant to S. Carr, and an NSERC post-graduate scholarship and financial awards from Carleton University to N. Sanborn. I would like to thank Richard Stern for his interest, support and assistance in all aspects of this study. This thesis has been significantly improved by his wise advice concerning the development of the experiments and his constructive criticism during the writing stages. Our discussions have been invaluable to the formulation of the ideas presented in this thesis. I would also like to thank him for providing access to the GSC's analytical facilities including SHRIMP, electron microprobe and scanning electron microscope. I am grateful to Sharon Carr for the excellent advice and support she provided with respect to specific scientific issues that arose during study, and regarding general aspects of graduate work. Her accessibility and dedication to my success have meant a great deal to me. In a work such as this, where a great number of sophisticated instruments are employed, the help of the experts has been invaluable. Thanks go to W. Bleeker at the GSC for providing the rock sample. Natalie Morriset is thanked for ensuring that the SHRIMP instrument was always running smoothly, and for her enthusiasm in sharing her expertise. I thank Serge Desgreniers of the Physics Department at the University of Ottawa for his willingness to be a part of this project. He provided excellent training and assistance in the Raman microprobe technique, as well as in the interpretation of the Raman results. Rob Patterson's care and expertise in preparing zircon membranes for TEM analysis is greatly appreciated. I am grateful to Gianluigi Botton of CANMET for his interest in this project. His time, effort and expertise in transmission electron microscopy was vital in elucidating the complex crystallographic microstructures of the sample. I also appreciate his insightful comments on the data. I thank Pat Hunt for her assistance in collecting the back-scattered electron images. I gratefully acknowledge Katherine Venance of the GSC for the time and effort that she put into ensuring the quality of the zircon electron microprobe data. Synthetic zircon and hafnon electron microprobe standards were generously provided by Dr. J. Hanchar of Washington University. Mike Hamilton at the GSC is thanked for his thoughtful review of Chapter 4, which appears in a similar format as a GSC Current Research paper. The manuscript also benefited from a pre-defense review by John Blenkinsop of Carleton University. Many thanks to my colleagues at Carleton, especially Sarah McMullen and Dan Gibson for stimulating discussions, both geological and otherwise. Finally, I would like to extend my gratitude to Dave Rayner and to my family for their love, encouragement and support.

ORIGINAL CONTRIBUTION

This research focuses on further understanding the processes that lead to Pb-loss in zircon and the impact of these processes on the interpretation of discordant U-Pb geochronology data. It is a multi-disciplinary study that employs a number of techniques with micro-sampling capabilities. I was directly involved in the data collection using these techniques, however expert advice from specialists was utilized.

The rock from which the zircons were extracted was collected by W. Bleeker during the 1995 field season. Crushing, grinding and zircon separation was performed by the technicians at the Geological Survey of Canada. Previous SHRIMP geochronological work by R. Stern had roughly constrained the age of the sample, and highly discordant results had been obtained. I carried out further U-Pb geochronology to precisely determine the age of the sample and to constrain the cause of discordance. I prepared SHRIMP mounts IP82 and IP102, mount IP28 was already prepared at the time of this study. I carried out all SHRIMP U-Pb and REE analyses of zircons on IP102. As well, I performed the majority of the U-Pb SHRIMP analyses on IP82 and IP28, although some analyses were carried out by R. Stern and N. Morriset.

The SHRIMP results suggest that chemical alteration is the cause of discordance in the study sample. Further work, using micro-sampling techniques, was carried out to compare and contrast the properties altered and unaltered zircon domains, and to constrain the mechanisms and controls of alteration. I assisted K. Venance with electron microprobe analyses. I collected the Raman spectra and interpreted the data in consultation with S. Desgreniers, at the University of Ottawa's Physics department. I assisted G. Botton (CANMET) with the collection of the transmission electron microscopy (TEM) images and consulted with him on the interpretation of data. The TEM membrane was milled by J. Patterson at FIBICS, Inc.

I wrote and compiled each chapter of this thesis and received comments regarding content, style and format from Richard Stern, Sharon Carr and John Blenkinsop. Chapter 4 of this thesis was originally prepared as a contribution to the Geological Survey of Canada's Radiogenic Age and Isotopic Studies volume, with myself as first author and with Richard Stern, Gianluigi Botton and Serge Desgreniers as co-authors. This chapter was reviewed by all co-authors and internally refereed by Mike Hamilton. Chapter 4 and the remainder of the thesis incorporate critical comments as suggested by these reviewers.

TABLE OF CONTENTS

	PAGE
ACCEPTANCE SHEET	ii
ABSTRACT	iii
ACKNOWLEDGMENTS	iv
ORIGINAL CONTRIBUTION	v
TABLE OF CONTENTS	vi
LIST OF TABLES	vii
LIST OF FIGURES	vii
LIST OF APPENDICES	viii
 CHAPTER 1	
1.1 INTRODUCTION	1
1.2 STATEMENT OF THE PROBLEM	1
1.3 ORGANIZATION OF THE THESIS	2
 CHAPTER 2	
U-Pb ION PROBE GEOCHRONOLOGY AND Pb-LOSS MECHANISMS	
2.1 INTRODUCTION	4
2.1.1 Volume Diffusion	5
2.1.2 Recrystallization	7
2.1.3 Fast Transport Diffusion	8
2.1.4 Chemical Leaching	10
2.2 SAMPLE SELECTION	12
2.3 GEOLOGIC SETTING	12
2.4 SAMPLE DESCRIPTION	14
2.5 ANALYTICAL METHODS	15
2.6 RESULTS	17
2.6.1 Internal features of Sample BNB-95-110c	17
2.6.2 Zircon Geochronology of Sample BNB-95-110c	19
2.6.3 Thorite Geochronology of Sample BNB-95-110c	24
2.7 DISCUSSION	25
2.7.1 Timing of Pb-loss	25
2.7.2 Pb-loss mechanisms	28
2.8 CONCLUSIONS	30
 CHAPTER 3	
CHEMISTRY OF ALTERED AND UNALTERED ZIRCON	
3.1 INTRODUCTION	63
3.1.1 Aims of Study	64
3.2 ANALYTICAL METHODS	64
3.2.1 Electron Microprobe Analysis (EMPA)	64

3.2.2 Elemental Maps	65
3.2.3 REE Ion Probe	66
3.3 RESULTS.....	67
3.3.1 Electron Microprobe Major and Minor Element Analyses.....	67
3.3.2 Elemental Mapping.....	68
3.3.3 Ion Probe Trace and Rare Earth Element Analyses.....	69
3.4 DISCUSSION	71
3.5 CONCLUSIONS	72

CHAPTER 4

CRYSTAL STRUCTURE OF ALTERED AND UNALTERED ZIRCON

4.1 INTRODUCTION.....	96
4.1.1 Aims of Study	99
4.2 ANALYTICAL METHODS	99
4.2.1 Raman microscopy.....	99
4.2.2 Transmission Electron Microscopy (TEM)	102
4.3 RESULTS.....	103
4.3.1 Raman Results	103
4.3.2 TEM Results	107
4.4 DISCUSSION	110
4.5 CONCLUSIONS	115

CHAPTER 5

SUMMARY.....	135
---------------------	------------

REFERENCES.....	144
------------------------	------------

LIST OF TABLES

Table 2.1. Compilation of diffusion coefficients for Pb in zircon	7
Table 2.2. U-Pb isotopic data collected from sample BNB-95-110c	32
Table 2.3. Pb-Pb isotopic data from uranothorite inclusions.....	34
Table 3.1. Electron microprobe data from sample BNB-95-110c	74
Table 3.2. REE concentrations from sample BNB-95-110c.....	77
Table 4.1. Structural data for crystalline test zircons.....	105
Table 4.2. Comparison of radiation dose and Raman band widths for a given degree of crystallinity	105
Table 4.3. Radiation doses for selected grains from sample BNB-95-110c	106
Table 5.1. Ionic radii of cations commonly incorporated into zircon.....	138

LIST OF FIGURES

Figure 2.1. Graphical representation of closure temperature.....	36
Figure 2.2. Location map	38
Figure 2.3. Photographs of study sample BNB-95-110c	40

Figure 2.4. Thin section photomicrographs of zircons <i>in situ</i>	42
Figure 2.5. Transmitted light photomicrograph of zircons separated from BNB-95-110c.....	44
Figure 2.6. Back-scattered electron images of zircons separated from sample BNB-95-110c	46
Figure 2.7. Concordia diagram for low common Pb zircon domains.....	52
Figure 2.8. Concordia diagram for high common Pb zircon domains.....	54
Figure 2.9. Plot of discordancy vs. $^{204}\text{Pb}/^{206}\text{Pb}$	56
Figure 2.10. Concordia diagram for recrystallized tips, rims and micro-dykes	58
Figure 2.11. Probability density diagram of the distribution of uranothorite ages	60
Figure 2.12. Plots of discordance vs. U content and radiation dose	62
Figure 3.1. Plots of EMPA results	80
Figure 3.2. Plots of EMPA results	82
Figure 3.3. Element distribution maps for zircon grain e19	84
Figure 3.4. Plots of Lu and Dy vs. U concentrations.....	87
Figure 3.5. Plots of Ce and Sm vs. U concentrations	89
Figure 3.6. Plot of Ba vs. U concentrations	91
Figure 3.7. Plot of Ca vs. Ba concentrations.....	93
Figure 3.8. Plots of Ca and Ba vs. Eu concentrations.....	95
Figure 4.1. Schematic of a typical Raman experiment	118
Figure 4.2. Simple energy diagrams illustrating the origin of the Raman effect.....	120
Figure 4.3. Comparison of the Raman peak for variably crystalline zircons	122
Figure 4.4. Raman spectra of the altered and unaltered domains from sample BNB-95-110c.....	124
Figure 4.5. TEM results from BNB-95-110c.....	127
Figure 4.6. Schematic diagram of the transition from unaltered to altered zircon	130
Figure 4.7. Single grain X-ray diffraction pattern for zircon from sample BNB-95-110c.....	132
Figure 4.8. Cumulative radiation dose over time.....	134

LIST OF APPENDICES

Appendix A. Whole rock geochemistry of sample BNB-95-110c	152
Appendix B. Equation used to calculate radiation dose	154
Appendix C. Cameca SX-50 Electron Microprobe experimental setup	155
Appendix D. Masuda-Coryell diagrams for sample BNB-95-110c.....	156

CHAPTER 1

1.1 INTRODUCTION

One of the advantages of U-Pb geochronology is that it is based on two independent U decay schemes (decay of ^{235}U to ^{207}Pb and ^{238}U to ^{206}Pb). With these two independent radiometric "clocks" it is possible to determine if the system has remained closed to the loss or gain of the parent and daughter elements. In the case of zircon geochronology, the ^{235}U - ^{207}Pb and ^{238}U - ^{206}Pb systems are often in disagreement. This situation is referred to as "discordance", and is most often attributed to the loss of the daughter element, Pb. Discordant zircon data are mostly obstacles to the dating of rocks, but can be used to interpret the post-crystallization history of samples with complex geologic histories. However, these interpretations often rely upon a number of assumptions about zircon Pb-loss. The processes and timing of events that lead to zircon Pb-loss are often assumed or poorly constrained. Much of the existing zircon Pb-loss data come from bulk chemical analyses where there have been few direct attempts to understand the relative effects of trace element chemistry, crystal structure, degree of alteration or other mineralogical properties. Many proposed zircon Pb-loss mechanisms come from attempts to reconcile discordant data with the known geologic history of the sample.

1.2 STATEMENT OF THE PROBLEM

This study directly examines Pb-loss behaviour as it operates on the scale of individual zircon grains from a late Archean granitic dyke from the basement of the western Slave Province, Northwest Territories. Ion microprobe U-Pb geochronological data were collected from these high-U zircons, with the express purpose of determining

the cause of the discordance. From the isotopic data it is argued that chemical leaching is an important Pb-loss mechanism in these zircons.

In subsequent chapters the following questions are addressed, using a range of analytical techniques: What constraints can be placed on the timing of alteration relative to crystallization and other geologic events? How does zircon alteration manifest itself chemically? What crystal-chemical properties control alteration of zircon? What is the mechanism by which altered zircon domains lose Pb? How can the discordance patterns of altered zircons be interpreted?

In short, the aim of this thesis is to further our understanding of Pb-loss mechanisms by directly characterizing the isotopic, chemical and microstructural properties of complex zircons with intra-grain variations in Pb-loss behaviour. This is accomplished by employing a variety of techniques capable of sampling grain-scale domains.

1.3 ORGANIZATION OF THE THESIS

The three major chapters of this thesis (Chapters 2, 3, and 4) are subdivided on the basis of the type of data collected.

Chapter 2 addresses the geochronology and isotopic behaviour of the study zircons utilizing the SHRIMP ion microprobe. Chapter 3 presents the geochemical characterization of altered and unaltered portions of the study zircons. Major, minor and trace element chemistry was determined by electron microprobe analysis and using the SHRIMP ion probe. Chapter 4 presents the attempts to characterize the intra-grain crystal structures of the zircons. The crystallographic properties of the altered and unaltered zircon domains were examined using a laser Raman microprobe and with Transmission

Electron Microscopy (TEM). Correlations between microstructure and Pb-loss behaviour are discussed. Chapter 5 integrates the results of previous chapters addressing larger issues regarding the mechanisms by which alteration of zircon leads to Pb-loss, and the effect of alteration on the interpretation of the lower intercept ages. Possible solutions to these mechanistic and interpretation-related issues are presented, as well as suggestions for further research.

CHAPTER 2

U-Pb ION PROBE GEOCHRONOLOGY AND Pb-LOSS MECHANISMS

2.1 INTRODUCTION

Zircon (ZrSiO_4) is a common accessory mineral found in a wide variety of igneous, metamorphic and sedimentary rocks, and is one of the most commonly dated minerals in geochronological studies. The ideal stoichiometric formula for zircon is ZrSiO_4 (tetragonal crystal symmetry, ABO_4), although a number of different elements substitute into both the Zr (8-fold coordination) and Si (tetrahedral coordination) lattice sites. The most important substitution, is the incorporation of U^{+4} into the “A” site, normally occupied by Zr^{+4} . Although U fits readily into the crystal lattice during growth, any existing Pb in the growth medium is excluded, thus ensuring that virtually all Pb present at a later time will be radiogenic in origin. The fractionation of U from Pb is due to their differing ionic radii (1.00 and 1.29 Å, respectively) and charges (+4, +2 respectively) (Speer, 1982).

Zircon is also widely used in geochronology because of its resistance to destruction or complete isotopic resetting under most crustal conditions. For example, partial melts often contain inherited zircon grains, indicating that zircons can survive the very high temperatures required for crustal anatexis (Gulson and Krogh, 1973; Pankhurst and Pidgeon, 1976; Holzt et al., 1994). Similarly, zircons in rocks that have undergone granulite-facies metamorphism still partially retain the isotopic signature of the protolith, yielding age information for both crystallization and later metamorphism (e.g. Black et al., 1986). Surprisingly, the U-Pb systematics of some zircons may be drastically affected by low temperature events. For example it has been noted in several cases that

weathering, low-temperature metamorphism or metasomatism may lead to Pb-loss and discordant ages (Stern et al., 1966; Black, 1987). Discordant data are common in zircon analyses but are rarely observed in other U-bearing minerals such as monazite. The low temperature processes that lead to Pb-loss and discordance in zircon seem to have little effect on monazite and other U-bearing minerals despite their lower closure temperatures.

Discordant zircons, whose U-Pb systematics have been disturbed by either high or low temperature events, are critical to the interpretation of the post-crystallization history of a sample. However, to correctly interpret the geological significance of discordant data it is necessary to understand the processes that control Pb-loss. A number of studies have examined Pb-loss in zircon and from this large body of work, Pb-loss mechanisms can be grouped into 4 major categories (after Lee, 1993): (1) volume diffusion, (2) recrystallization, (3) fast transport diffusion, and (4) chemical leaching.

2.1.1 Volume Diffusion

Volume diffusion refers to the movement of atoms such as Pb or U through a pristine zircon lattice, relying on the concept of closure temperature, developed by Dodson (1973). Closure temperature (T_c) is graphically defined as the temperature of the system at the time of its apparent age (Dodson, 1973) as illustrated in Fig. 2.1. At high temperatures the radiogenic daughter atoms may not accumulate, as they diffuse out of the system as soon as they are formed. As the system cools, the rock eventually passes through the closure temperature, T_c , where accumulation of the daughter product begins, to where it is eventually fully retained. The apparent age, t_a , of the system is essentially an extrapolation of complete retention of the daughter element back to the time axis (x-

axis on Fig. 2.1). Estimates of the T_c of zircon range from 800 - 900°C (Heaman and Parrish, 1991; Cherniak and Watson, 2000)

Many studies have noted that the lower intercept of the discordia chord often corresponds to a geologically significant event, and in such cases it has been argued that if heat from metamorphism or nearby plutonism were to exceed the closure temperature of zircon, the system might become open to the diffusion of Pb. A linear array of discordant data on a Wetherill (1956) plot may result from a thermal event if different grains or parts of grains lose varying amounts of Pb by volume diffusion. This line is known as the discordia chord and its intercepts with concordia are used in the interpretation of the geologic history (see Faure, 1986). Typically, the upper intercept is interpreted as the age of crystallization of the sample. In the case of episodic diffusion, the lower intercept may be interpreted as the age of the second geologic event as it corresponds to the time-integrated isotopic composition of radiogenic Pb at the time of Pb-loss (Faure, 1986). Alternatively Tilton (1960) argued for continuous diffusion of Pb from the zircon which would result in a meaningless lower intercept. An understanding of the kinetics of Pb diffusion in zircon would contribute to a greater understanding of the geological significance of the lower intercept. Attempts to determine the activation energy and Pb diffusion coefficient, D , for zircon have resulted in a range of values over 10 orders of magnitude (see Table 2.1). The spread of values is the result of varying degrees of zircon crystallinity, different experimental conditions and unknown geologic parameters. Confirming that the observed loss of Pb is indeed due to volume diffusion, and not another mechanism such as decomposition of the experimental materials, is another challenge facing diffusion experiments (Cherniak and Watson, 2000). The most

recent study by Cherniak and Watson (2000), who employed special procedures to ensure that volume diffusion was the operative process, suggested that diffusion from pristine zircon is a process that operates on a time scale greater than the age of the earth. For example, calculations using the diffusion coefficients of Cherniak and Watson (2000) suggested that a pristine zircon held at 800°C would only lose 1% of radiogenic Pb over 1 Ga. Consequently, the contribution of volume diffusion to Pb-loss and discordance in pristine zircon is now considered negligible.

Table 2.1 Compilation of Diffusion Coefficients for Pb in zircon.

The range of D values is a result of the range of temperatures over which the diffusion experiments were carried out.

Diffusion Coefficient (D)	Temperature (°C)	Reference
2.5×10^{-19} to 1.6×10^{-24} m ² /s	1100-1300	Cherniak and Watson (2000)
6.3×10^{-21} to 4×10^{-25} m ² /s	1000-1100	Lee et al. (1997)
3.2×10^{-19} to 1.6×10^{-21} m ² /s	650-850	Cherniak et al. (1991)
2.5×10^{-16} to 1×10^{-21} m ² /s	1000-1300	Bogomolov (1991)
1×10^{-11} to 1×10^{-14} m ² /s	600-950	Shestakov (1972)

2.1.2 Recrystallization

Recrystallization of zircon, as defined by Lee (1993), involves the re-establishment of the zircon lattice in order to reduce the total free energy of the crystal. It manifests itself as irregular patches of unzoned zircon that may either cross-cut or parallel the original oscillatory zoning (Pidgeon, 1992). The trace element chemistry of recrystallized zircon differs from that of the original zircon, as Pb and perhaps U and Th, are excluded from the new lattice during the growth of the new crystal structure. The proportion of radiogenic Pb excluded from the new zircon will determine whether the recrystallized portions are concordant or discordant. In the case of complete isotopic resetting, a concordant age representing the time of recrystallization will result. If variable portions of the radiogenic Pb are lost, the upper and lower intercepts of discordia

are interpreted to record the ages of growth and recrystallization, respectively. The interpretation of the lower intercept as a distinct geologic event is identical to the interpretation of episodic loss by volume diffusion. A comprehensive study of recrystallized zircon by Pidgeon (1992) indicated that rates of recrystallization are independent of the degree of radiation damage. Recrystallization is believed to nucleate on inclusions within the zircon and is not restricted to areas where the lattice distortion is greatest. Pressure and temperature conditions, the presence of fluids and the composition of neighbouring minerals are all believed to be factors influencing the process of recrystallization.

The terms recrystallization and annealing are often used interchangeably in the literature regarding zircon, however there are fundamental differences between them. In the case of recrystallization, the restoration of the lattice is accompanied by a change in the trace element chemistry of the recrystallized zone, whereas annealing is an isochemical process. The processes of annealing and recrystallization appear to be separate, but not independent, of each other (Pidgeon, 1992). Further work is necessary to constrain the conditions that lead to each. The definition of annealing as an isochemical process, whereas recrystallization implies a change in chemistry, will be applied throughout this thesis.

2.1.3 Fast Transport Diffusion

Fast transport diffusion, as defined by Lee (1993), involves the movement of atoms along high-diffusivity paths such as cracks or dislocations. The radioactive decay of U and Th in a zircon results in damage to the crystal structure, a process known as metamictization. The damage caused during metamictization is almost exclusively the

result of recoil nuclei displacing neighbouring atoms (Holland and Gottfried, 1955; Nasdala et al., 1996; Murakami et al., 1991). If this damage is extensive enough, a network of pathways may exist that will facilitate Pb transport out of the crystal. As the uranium content of zircon is often heterogeneous, it follows that heterogeneous metamictization has been directly observed (Nasdala et al., 1996, 1998). Metamict zircon has an expanded unit cell and consequently it is less dense than pristine zircon (Holland and Gottfried, 1955). Zones of heterogeneous U content within a single crystal become metamict and expand at variable rates creating an internal stress that can induce fracturing. These metamictization-induced fractures have been observed in natural zircon (Chakoumakos et al., 1987) and their position and orientation have been predicted using mathematical models (Lee and Tromp, 1995). These fractures provide another pathway for fast-transport diffusion. The impact of metamictization has long been recognized as influencing Pb-loss and discordant ages in zircon (Silver and Deutsch, 1963). The lower intercept of a linear array of zircon analyses that have lost variable amounts of radiogenic Pb by fast-transport may reflect the age of a geologic event, such as regional or contact metamorphism or denudation (Goldich and Mudrey, 1972). However in the case of fast-transport, the rates of diffusion are assumed to be much higher than those occurring during volume diffusion. Experiments on zircons that have been doped with Pb using an ion implantation technique suggest rates of Pb loss on the order of 50% in 2 Ga if the zircons are held at 250°C (Cherniak and Watson, 2000). Pb-ion implantation mimics the damage incurred from natural metamictization, however the rate of damage accumulation is much faster (Cherniak et al., 1991). Diffusion by fast-transport is the model often implicitly invoked to explain episodic Pb-loss.

2.1.4 Chemical Leaching

Zircon is regarded as a particularly stable mineral and it is this stability that makes it a very useful geochronometer. However zircon is prone to chemical leaching when fluids passing through the rock dissolve or alter the zircon. Chemical leaching of zircon and resulting Pb-loss has been noted for several years. Black (1987) has shown that recent Pb-loss is a natural phenomena and weathering was proposed as the likely mechanism. Similar results were reported by Hansen and Friderichsen (1989). Stern et al. (1966) reported large amounts of Pb-loss from zircons extracted from weathered clays of the Morton Gneiss. Krogh and Davis (1974, 1975) documented botryoidal alteration features along zircon surfaces adjacent to cracks. They suggested that zircon may be dissolved along these cracks, which act as paths for fluids, leaching Pb and U out of the grain, resulting in a discordant age. In their study, Krogh and Davis (1974, 1975) also noted an increase in the Ca, Al and Fe contents of altered zircon, as well as decreased oxide totals (95 to 88%). Similar results were documented by Gupta et al. (1998) who noted increased Ca, Al, Fe, and Mg contents and lowered oxide totals (98 to 89%) for zircon of variable “cloudiness”. The low oxide totals are believed to be due to the uptake of water in the crystal structure. The nature of the water has been subject of debate and the most recent studies have suggested that it is present as the hydroxide ion (Woodhead et al, 1991b).

A number of studies (Krogh and Davis, 1975; Scharer and Allegre, 1982; Mezger and Krogstad, 1997) have suggested that radiation damage is necessary but not sufficient to cause Pb-loss. Instead, chemical leaching or some other process may exploit metamict areas. It was suggested in these studies, that the pressure and temperature conditions and

the nature of the fluid determines whether a zircon becomes altered and loses Pb. A large body of work has dealt with the geological conditions under which zircons lose Pb by fluid alteration. Early hydrothermal experiments by Pidgeon et al. (1966) demonstrated that Pb can be leached from zircon at 500°C and 1 kbar in 2M NaCl. The behaviour of U under these conditions was variable, but losses were minimal. A study by Hansen and Friderichsen (1989) reported U- and Pb-loss of 17% and 15% respectively when unmetamict zircon was exposed to natural spring water at 180°C for 600 hours. Work by Sinha et al. (1992) also supports loss of Pb and U by leaching. They concluded that the severity of Pb- and U-loss depends on fluid composition with 2M NaCl being more reactive than 2% HNO₃. By examining the reacted zircon with backscattered electron images, Sinha et al. (1992) concluded that dissolution of zircon played a role in the removal of U. Levchenkov et al. (1998) documented that acidic, rather than carbonate, media resulted in increased Pb and U loss. Zircon dissolution is also attributed to having caused some of the U loss in the hydrothermal experiments of Levchenkov et al. (1998).

The studies cited above focus on high temperature alteration of zircon.

Experiments by Carroll (1953) simulated the effects of low-temperature weathering on zircon. Although the results were not conclusive, she demonstrated that zircon could be dissolved by alkaline solutions. Another study by Tole (1985) showed that radiation-damaged zircons dissolve in aqueous solution between 25°C and 80°C at a rate on the order of 10^{-13} moles/cm²/hr, while well-crystallized zircons have low solubility under the same conditions. Although the role of pressure, temperature and fluid composition is not well constrained, Pb-loss controlled by chemical leaching and alteration should be

considered an important process when interpreting the meaning of the lower intercept of the discordia chord.

2.2 SAMPLE SELECTION

The ultimate purpose of this study was to learn about the process of Pb-loss by relating isotopic behaviour to the chemical properties, microstructural properties and internal features of single zircon grains. The SHRIMP instrument analyses a tiny mass of material (1-10 ng) and this has implications for the precision of the isotopic measurements. The errors associated with SHRIMP analyses are large relative to the isotope dilution – thermal ionization mass spectrometry method (ID-TIMS), and therefore the amount of Pb lost from the system must be significant if we are to distinguish between a disturbed and undisturbed zircon using the SHRIMP. In order to have significant amounts of Pb-loss, the study sample must first contain considerable amounts of radiogenic Pb. Therefore the search for a suitable sample was restricted to Archean samples with U concentrations in excess of 100 ppm. A number of samples from the Acasta Gneiss Complex, Slave Province, roughly 300 km north of Yellowknife, were collected by R. Stern and W. Bleeker of the GSC. SHRIMP geochronology by R. Stern of a number of samples from this complex indicated a high degree of discordance in many of the samples. One particular sample, BNB-95-110c, a late granite dyke, showed a substantial range in Pb-loss and contained very high U contents. The dyke is one of the youngest units in the Acasta Gneiss Complex.

2.3 GEOLOGIC SETTING

The Slave Province in northwestern Canada is a relatively small Archean craton (Fig. 2.2). It is considered a typical granite-greenstone terrane, however, it contains

significant amounts of ancient sialic basement. Early Archean rocks, dated between 4.0 and 2.8 Ga, are preserved as gneisses that outcrop in the western half of the Slave Province (Padgham and Fyson, 1992). Nd studies of late Archean intrusions suggest that these ancient gneisses underlie most of the western Slave (Davis and Hegner, 1992). The basement rocks are unconformably overlain by a ca. 2.9 - 3.0 Ga, fuchsitic quartzite, and banded iron formation cover sequence (Central Slave Cover Group – CSCG). This cover sequence has been observed as far south as Yellowknife, as far east as the Sleepy Dragon Complex, and northwest to the western margin of the Acasta Gneiss Complex. Lateral correlation of these widely dispersed exposures of the CSCG suggests that the all Meso- and Paleoarchean basement of the Slave Province was a single cratonic nucleus by 2.8 Ga (Bleeker et al., 2000; Bleeker et al., 1999; Bleeker and Ketchum, 1998). The cover sequence is in turn overlain by the 2.73 - 2.65 Ga, volcanic-turbidite sequences of the Yellowknife Supergroup. Syn- to postvolcanic (2.70 - 2.58 Ga) granitic plutonism is extensive throughout the province (van Breemen et al., 1992). Regional polyphase deformation is believed to have occurred after ca. 2.66 Ga. High-temperature, low-pressure metamorphism characterizes the whole Slave Province, and is believed to be roughly syntectonic (Card and King, 1992).

The basement rocks of the Acasta Gneiss Complex (AGC) are exposed in structural culminations in the westernmost part of the Slave Province. The AGC gneisses are heterogeneous, comprising a number of different intrusive rock types, mainly tonalite, granodiorite, diorite and granite (R. Stern, unpubl. data, 1999). Each lithology appears to represent a separate phase of plutonism. The penetrative deformation of these various plutonic rocks is believed to be related to Late Archean events. Tonalite gneisses have

been dated using the SHRIMP and yield ages of 4.03 Ga, making them the oldest known terrestrial rocks (Stern and Bleeker, 1998; Bowring et al, 1989). They are in turn cut by intrusive rocks at 3.75, 3.6, 3.4, and 2.9 Ga (Bleeker and Stern, 1997, R. Stern, pers. comm., 1999). The study sample is representative of the 2.9 Ga intrusive event.

2.4 SAMPLE DESCRIPTION

Sample BNB-95-110c was collected from a foliated granitic dyke roughly 30 cm wide with contacts parallel with the gneissosity in the host rock (Fig. 2.3a). The specific location of the outcrop is UTM zone 11, 55450m E, 7228900m N on the Exmouth Lake 1:50,000 map sheet (86G/4). A moderate fabric defined by foliation of biotite and quartz is observed in hand specimen (2.3b). In a thin section cut perpendicular to the fabric, randomly-oriented, subhedral grains of microcline, quartz, minor biotite and minor plagioclase are observed, consistent with an igneous origin (Fig. 2.3c). Grain size distribution is bimodal, composed of coarse-grained phenocrysts (5-10 mm) and medium grained (1-3mm) interstitial grains. Grain boundaries are interlobate. There is little development of subgrains or deformation twins associated with the plagioclase. Quartz has straight extinction. The moderately developed foliation suggests some degree of deformation, however, the absence of deformation twins and undulose extinction suggest that it was not significant.

The granite is visibly altered at the outcrop scale, with the feldspars taking on a reddish tint. Petrographic study provides further evidence of alteration. Most plagioclase grains have been completely sericitized (Fig. 2.3c). Microcline has experienced a lesser degree of sericitization. Carbonate and epidote is present along cracks and grain boundaries.

Whole rock geochemistry for the sample is presented in Appendix A. The prominent europium anomaly on the rare earth element plot suggests that sample BNB-95-110c is a plagioclase cumulate. The dyke may have been emplaced as a crystal mush, with the solid and liquid phases partitioned during injection into the host rock.

Zircons separated from sample BNB-95-110c are prismatic with aspect ratios of 2:1 to 3:1, are light to dark brown in colour, with planar to curvilinear facets (Fig. 2.4a-c, Fig 2.5). The outer surfaces of the zircon grains are generally pitted. Most grains have a euhedral external morphology, although the margins of some grains are embayed which suggests a minor degree of dissolution and reprecipitation. Clarity varies from moderately turbid to opaque depending on magnetic susceptibility, and most grains contain numerous inclusions and fractures (Fig. 2.4a-c, Fig. 2.5). Areas of greater clarity and lighter colour are preserved within many individual grains (Fig. 2.5). Concentric zoning is visible under transmitted light in some crystals.

2.5 ANALYTICAL METHODS

A sample of granitic gneiss BNB-95-110c was pulverized at the Geological Survey of Canada (GSC). A heavy mineral concentrate was extracted using a Wilfley™ table, and heavy liquid separation, and magnetic separation was done using a Frantz™ isodynamic separator. The heavy mineral separate was further refined, using the Frantz™ instrument, into zircon concentrates of varying paramagnetism. Representative zircon populations from the 5 least-magnetic fractions were selected. Each magnetic fraction was mounted in three different 2.5cm epoxy pucks, two using Struers Epofix epoxy (lab # IP28 and IP82) and the third in Epo-tek 301 (lab # IP102). Fragments of the laboratory U-Pb standard (Kipawa zircon, 993 Ma) were also included in each mount. The

midpoints of the grains were exposed by polishing with a diamond compound. The zircons in all mounts were photographed in plane light, carefully cleaned, and coated with 6 to 8 nm of high purity gold.

A Cambridge Instruments S360 Scanning Electron Microscope at the Geological Survey of Canada was used to image the internal structure of the zircons prior to microanalysis. Most images were collected in back-scattered electron (BSE) mode, as these zircons do not exhibit a strong cathodoluminescence (CL). Highly metamict zircons are known to have suppressed CL emission. In order to increase contrast and highlight the internal features, the SEM was operated at its shortest possible working distance (1.6 mm). Mount IP102 was briefly etched with HF acid vapour to enhance the visibility of any zoning.

U-Pb isotopic data were collected using the Geological Survey of Canada's SHRIMP II ion microprobe (Sensitive High Resolution Ion MicroProbe). A detailed description of analytical procedures can be found in Stern (1997). Using the BSE images as guides, areas of the zircon grains were selected for analysis. The chosen spots were sputtered using a mass-filtered primary O⁺ beam with a current ranging from 0.5 to 5 nA. The resulting pits are elliptical with flat bottoms and shallowly sloping sides. Two spots sizes were used in the U-Pb SHRIMP work, depending on the size of the feature analyzed. The smaller of the two spots measure 7 x 9 µm while the larger pits measure 13 x 19 µm, and both are roughly 1 µm deep. Before analysis, the conductive gold coating and any accompanying common Pb was removed from the area immediately surrounding the analysis site by rastering with the ion beam for two to three minutes. Count rates for nine or ten Pb, U, Th and Zr isotopes were collected sequentially over five

or six scans for both the unknown and standard zircons. Any bias in the $^{206}\text{Pb}/^{238}\text{U}$ ratio of the unknown was corrected by comparison to the Kipawa standard. Using the standard Kipawa zircons on each mount, a unique calibration curve of $^{206}\text{Pb}/^{238}\text{U}$ vs UO/U was generated. There is an external error of roughly $\pm 2\%$ associated with the calibration plus an additional error attributed to counting statistics. Common Pb corrections were applied, using the Cummings and Richards (1975) Pb isotopic composition at 2.9 Ga. The ages for individual spots have been reported to the 1σ confidence level, unless otherwise noted. The decay constants of Steiger and Jäger (1977) were used.

2.6 RESULTS

2.6.1 Internal features of Sample BNB-95-110c

The zircon population from sample BNB-95-110c can be subdivided into two groups according to their internal features observed in BSE images. The first, volumetrically minor, class of zircons is uniformly dark in back-scattered mode (Fig. 2.6f). Primary zoning is still visible in these zircons and they contain few to no inclusions or fractures.

The second class, which comprises the majority of the zircons, contains variably dark and bright patches (Fig. 2.6a-e). The dark patches are irregularly shaped, and commonly preserve primary oscillatory zoning. The margins of these dark patches usually truncate any zoning. An exceptionally dark rim, roughly $3\text{ }\mu\text{m}$ thick, commonly defines the boundary between bright and dark zircon (Fig 2.6a). The contact between the rim and the bright zircon is sharp, while the transition from rim to dark zircon is gradational. The appearance of this rim is suggestive of a reaction front migrating through the zircon.

Bright patches are commonly enclosed by darker zircon, and are normally preserved in the interior of the grain. A dark patch generally separates the bright zircon domain from the grain boundary. BSE images of the bright zircon domains are devoid of zoning. However brief exposure to HF vapour was sufficient to enhance the visibility of oscillatory zoning in the bright zircon domains. The contrast level in the BSE images was chosen to maximize the difference between bright and dark zircon and may be responsible for obscuring the zoning in the unetched zircons. The appearance and context of the bright patches are identical to the patches which yielded the ages of the oldest terrestrial rocks (Stern and Bleeker, 1998). The extreme antiquity of these patches in the Stern and Bleeker study suggest that they consist of primary zircon. Therefore, we conclude that similar patches in the study sample have preserved the crystallization age of BNB-95-110c.

The patchy zircons in sample BNB-95-110c contain a variable number of inclusions. The zircons with the most inclusions generally have opaque cores where most of the inclusions are concentrated, while the inclusions are randomly dispersed in grains with fewer inclusions. Qualitative spot energy-dispersive x-ray spectra tentatively identify these inclusions as mainly uraninite, uranothorite, thorite, with minor feldspar, biotite, and epidote. A minor proportion of zircon grains contain large (~ 50 μm) inclusions of uranothorite (Fig. 2.6i, j, k).

There is evidence of later fracture sealing and new zircon growth in the sample. A number of grains have rims and tips that appear bright in BSE (Fig. 2.6e, g, h). A fewer number of zircon grains contain patches of bright zircon that cross cut the oscillatory zoning and the patchy zonation described above (Fig. 2.6g, h). Spot EDS

measurements confirm that this bright material is zircon. This younger growth that occurs as rims, tips and cross-cutting features, is likely the result of precipitation from an infiltrated fluid.

2.6.2 Zircon Geochronology of Sample BNB-95-110c

Fractions of sample BNB-95-110c on mounts IP28, IP82 and IP102 were dated using the SHRIMP ion microprobe. Examples of all of the internal features seen in BSE, and described above, were targeted for SHRIMP analysis. The complete data set, including a brief description of the internal structure sampled, is presented in Table 2.2. Each analysis is labeled according to its puck number, analytical session, magnetic susceptibility, grain number and spot number. See Table 2.2 caption for further explanation of the labeling system.

Zircon U-Pb geochronological data from sample BNB-95-110c can be divided into 4 distinct groups on the basis of isotopic behaviour. Group 1 includes zircon domains that record the crystallization age of the sample but do not record other ancient geological events. The matrix properties of this type of zircon are similar to that of the standard and therefore the U-Pb calibration is considered reliable. Group 2 contains zircon domains that are also well calibrated but do record ancient episodes of Pb-loss. Group 3 analyses can be normally or reversely discordant, however their U-Pb ages are unreliable due to calibration effects caused by differences in the matrices of the standard and the unknown. Their $^{207}\text{Pb}/^{206}\text{Pb}$ ages are unaffected by the calibration and are consistent with the age of crystallization determined from Group 1. These zircon domains may or may not record ancient Pb-loss. Group 4 consists of younger tips and

cross-cutting bands, believed to be reprecipitated from a fluid. These are also properly calibrated for U-Pb fractionation.

Group 1

The largest proportion of data, 43 of a total of 92 SHRIMP analyses, form a cluster of concordant to slightly discordant points. Analyses that lie within this cluster range from 0 to 16% discordant, however a few analyses are reversely discordant (up to -3%) points. The more discordant analyses define a discordia chord with a lower intercept near the origin. A York (1969) regression through 31 of these analyses yields an upper intercept of 2875 ± 3 Ma (2σ), on a conventional concordia diagram (Wetherill, 1956) (Fig. 2.7a, b). The upper intercept is interpreted as the crystallization age of the zircon. These analyses have similar $^{207}\text{Pb}/^{206}\text{Pb}$ ages, which, assuming a single zircon population, suggest that their isotopic systems have remained closed until recently. Group 1 zircon data were collected from domains that are distinct, with particular physical and geochemical properties. They occur as the bright zircon patches in back-scattered electron images described in Section 2.6.1 and illustrated in Figure 2.6. These bright patches will henceforth be referred to as the unaltered material. These patches of zircon have variable U contents but contain less than 50 ppb common Pb and have a $^{204}\text{Pb}/^{206}\text{Pb}$ ratio less than 10^{-4} .

Group 2

A smaller number of analyses (11 of 92) of material with common Pb content below 50 ppb and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios less than 10^{-4} are considerably more discordant, between 29 and 61% (Fig. 2.7a). These data were collected exclusively from a single grain. While some of the most discordant points from grain D9 are geochemically

indistinct from concordant zircon, a number of analyses have exceptionally low Th/U ratios. Although their common Pb contents and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios are within the range of the unaltered zircon domains, many of the values for grain D9 are at the upper end of this range. These more discordant data points do not form a simple discordia chord; the data fan out in a complex pattern suggesting both recent and ancient Pb-loss (Fig. 2.6a).

Group 3

The third group of U-Pb data (22 of 92 analyses) have ^{204}Pb concentrations greater than 50 ppb and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios greater than 10^{-4} . These high common-Pb-bearing domains within the zircons, which will henceforth be referred to as altered zircon, occur as either dark or, less commonly bright, patches in the BSE images. Group 3 data extend above and below concordia from the crystallization age of 2.87 Ga (Fig. 2.8). However, the U-Pb calibration of zircon with elevated common Pb contents can be problematic. Reverse discordance is often cited in ion microprobe studies and has in most cases been shown to be an analytical artifact (Wiedenbeck, 1995; Black et al, 1986). Wiedenbeck noted that reversely discordant analyses generally have elevated common Pb contents; the high common Pb content of the altered patches in sample BNB-95-110c is consistent with this observation. He suggested that reverse discordance is a result of enhanced Pb-ion yields from a labile Pb component. He concluded that the labile Pb was a mixture of local radiogenic and common Pb leached locally during a fluid event, then reintroduced into the sample. Enhanced Pb-ion yields from this labile component were not accounted for during calibration and therefore lead to exceptionally high U/Pb ages (Wiedenbeck, 1995). In an effort to normalize ion probe data with ID-TIMS data from the same sample, Wiedenbeck carried out “common Pb” corrections using slightly radiogenic $^{204}\text{Pb}/^{206}\text{Pb}$

and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, based on the $^{204}\text{Pb}/^{206}\text{Pb}$ of the most reversely concordant results, which he believed represented the isotopic character of the labile component. A similar calculation was carried out with the data from BNB-95-110c, but the data remained above concordia. It appears that matrix-related sputtering properties of high ^{204}Pb zircon, and not inaccurate isotopic ratios used in common Pb corrections, are responsible for reversely discordant ion probe data. These matrix-related sputtering effects are still not well understood and cannot be corrected for at this time.

The only means of coping with this difficulty is to screen out analyses that are subject to calibration errors. To determine the $^{204}\text{Pb}/^{206}\text{Pb}$ and ^{204}Pb concentration thresholds at which the zircon U-Pb calibration becomes suspect, a plot of discordance against $^{204}\text{Pb}/^{206}\text{Pb}$ was generated. There is a relationship between discordance and $^{204}\text{Pb}/^{206}\text{Pb}$ ratio (Fig. 2.9), with the reversely discordant data yielding the highest $^{204}\text{Pb}/^{206}\text{Pb}$ ratios. A $^{204}\text{Pb}/^{206}\text{Pb}$ ratio of 10^{-4} is considered a conservative estimate of the cutoff below which the zircon matrix is unaffected by the presence of common Pb, and where the U/Pb calibration can be considered reliable. A similar plot for discordance and ^{204}Pb concentrations was generated and we suggest that 50 ppb ^{204}Pb be used as a part of a dual threshold with $^{204}\text{Pb}/^{206}\text{Pb}$ ratios.

Due to the extreme discordance of the altered domains, and the difficulty in calibration, the U/Pb ages of the altered areas are difficult to interpret and cannot be assumed to yield reliable age information. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages however, are unaffected by these calibration difficulties and can be considered reliable estimates of the minimum age of the sample. The majority of the reversely discordant analyses from the altered domains have $^{207}\text{Pb}/^{206}\text{Pb}$ ages of ca. 2870 Ma, consistent with the age of crystallization

(see Table 2.2). Zircon domains that plot as reversely discordant are interpreted to have undergone a change in their crystalline matrix. For the $^{207}\text{Pb}/^{206}\text{Pb}$ ages to remain consistent with each other, this matrix change must have occurred recently, if we assume that the change took place under open system conditions. This assumption seems feasible as reversely discordant data often have high levels of common Pb which were likely added to the system some time after crystallization. A number of normally discordant analyses have $^{207}\text{Pb}/^{206}\text{Pb}$ ages that range from 2872 Ma down to 1850 Ma, a pattern that is consistent with a component of ancient Pb-loss.

Group 4

Due to the complex U-Pb systematics of the altered zircon domains, it was necessary to constrain the age(s) of alteration by other means. Featureless zircon overgrowths infill irregular relict interior zircon grain boundaries and appear to be the result of dissolution of igneous zircon, followed by reprecipitation. These overgrowths, both as tips and rims, are discordant with primary zoning, and their subhedral crystal form indicate that they grew after primary crystallization. Less commonly, zircons from the study sample contain what appear to be zircon “micro-dykes” (Fig. 2.6g, h). These features are likely the result of fracture healing through the precipitation of new zircon. The cross-cutting relationship between the micro-dykes and the “host” zircons argues strongly for a younger zircon-producing event. However, some areas of this new zircon growth have the darkened appearance in BSE that is characteristic of the altered zircon domains. This suggests that new zircon growth was followed by alteration and therefore the age of the new zircon growth constrains the maximum age of alteration. A beam roughly $7 \times 9 \mu$ in size was used to probe small, unaltered areas of new growth (16 of 92

analyses). The results are presented in Table 2.2 and on a concordia diagram (Fig. 2.10). Concordant to slightly discordant $^{207}\text{Pb}/^{206}\text{Pb}$ ages range from 2600 Ma to 2700 Ma. The best estimate of the age of the overgrowths is 2697 ± 14 Ma (2σ), the upper intercept of a linear array of five concordant and discordant analyses from two grains. This constrains the maximum age of alteration at ca. 2700 Ma. There are a number of discordant analyses with $^{207}\text{Pb}/^{206}\text{Pb}$ ages ranging from 2200 Ma to 2700 Ma. These discordant data points form a roughly linear array that trends along a shallow slope suggesting a Pb-loss event in the early Proterozoic.

2.6.3 Thorite Geochronology of Sample BNB-95-110c

Although the age of the cross-cutting features places a maximum age on the timing of alteration, it is still necessary to determine if the alteration was a recent or ancient event. The trend of highly discordant data from unaltered patches (Fig. 2.7), and overgrowths/cross-cutting features (Fig. 2.10) suggests that the alteration occurred in the early Proterozoic. As was previously mentioned, uranothorite inclusions are common in zircons from sample BNB-95-110c (Fig. 2.6). These inclusions truncate the primary oscillatory zoning and are found exclusively in the dark patches, which suggest that they are related to the alteration event. SHRIMP analyses were carried out on the inclusions to further constrain the age of alteration. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages from the uranothorite inclusions are presented in Table 2.3 and as a probability density diagram in Fig. 2.11. A probability density diagram is generated by calculating the probability of a given age using the 2σ error associated with each $^{207}\text{Pb}/^{206}\text{Pb}$ age. The probabilities for each 1 Ma interval are summed and the total is plotted against age. U-Pb ages are unobtainable as a calibration standard was unavailable to correct for the fractionation of U-Pb in

uranothorite during secondary ion generation. Without U-Pb data to constrain concordancy, the $^{207}\text{Pb}/^{206}\text{Pb}$ ages can only be considered the minimum age of the inclusions. The analyses yield $^{207}\text{Pb}/^{206}\text{Pb}$ ages ranging from 300 Ma to 2400 Ma. A cluster of analyses lies at 2204 Ma while another significant cluster occurs at 1420 Ma.

The coexistence of uranothorite inclusions and altered zircon domains suggests that alteration and uranothorite growth were synchronous. However, in some cases the textures can be considered ambiguous and therefore the age of the inclusions cannot be considered to directly date the alteration event. In one particularly dramatic case (IP102, grain e19), uranothorite is present as a mineral corroding and replacing zircon at a grain margin (Fig. 2.6i). Veins of secondary uranothorite penetrate several microns into the grain. This zircon grain provides us with a “snapshot” of the process of alteration, and is a more direct means of dating the alteration than simply determining the age of the inclusions. The textural relationship between the zircon and uranothorite in this grain is consistent with an alteration mechanism that involves fluid attack and precipitation of secondary uranothorite. The uranothorite was probed in three nearby spots. Two of these spots yielded $^{207}\text{Pb}/^{206}\text{Pb}$ ages of ca. 2200 Ma, consistent with the age obtained from a number of other inclusions. The third spot was dated at 2400 Ma, the oldest uranothorite age obtained (Table 2.3).

2.7 DISCUSSION

2.7.1 Timing of Pb-loss

The regression through the cluster of concordant and slightly discordant unaltered zircon data, shown in Fig. 2.7 a, b, constrains the age of primary crystallization at 2875 Ma. Sample BNB-95-110c is interpreted as part of the basement rocks of the Slave

Province, as they pre-date the 2.71-2.65 Ma, volcanic-turbidite assemblages of the Yellowknife Supergroup (van Breemen et al, 1992; Padgham and Fyson, 1992). The unaltered zircon data, excluding analyses from grain D9, form a roughly linear array, trending towards the origin, consistent with recent Pb-loss. Analyses from grain D9, however, form a complex, fan-shaped array (Fig. 2.7a) that suggests the influence of both ancient and recent Pb-loss events.

A York (1969) regression through a linear array of concordant and discordant analyses of new zircon tips and cross-cutting micro-dykes suggests that new zircon growth occurred at ca. 2.7 Ga (Fig. 2.10). These features are present along irregular grain margins (Fig. 2.6g) and suggest a process of dissolution of existing zircon followed by precipitation of new zircon. The younger zircon is also present as cross-cutting features (Fig. 2.6g, h) which likely represent the sealing of fractures by the precipitation of new zircon. Both features strongly suggest the involvement of fluids in new zircon growth. Zircon growth at ca. 2700 Ma is coincident with large-scale magmatism in the Slave Province. The intrusion of granitoid plutons between 2.70 and 2.58 Ga into the Yellowknife Supergroup is well documented (van Breemen et al, 1992) and perhaps new zircon growth is related to the circulation of magmatic fluids during this period.

Both linear (see Figs. 2.7a,b, 2.8, and 2.10) and fan-shaped (see Fig. 2.7a - grain D9, and Fig. 2.8) patterns of discordant data have been observed in sample BNB-95-110c. In order to interpret these patterns it is necessary to clarify the nature and timing of the alteration event(s) that affected the isotopic system of the sample. The uranothorite isotopic data offer one means of determining the timing of alteration in zircon. The numerous peaks on the probability density plot (Fig. 2.11) make the interpretation of the

timing difficult. There are two end-member scenarios which could lead to this distribution of data. All the uranothorite inclusions can be considered as a single generation, in which case the maximum thorite $^{207}\text{Pb}/^{206}\text{Pb}$ age would represent the minimum age at which alteration could have occurred. In this scenario, the younger $^{207}\text{Pb}/^{206}\text{Pb}$ ages are the result of multiple episodes of Pb-loss from the single population of uranothorite inclusions. Therefore, the minimum age of alteration would be 2400 Ma, the age of the oldest uranothorite (Table 2.3). The maximum age is constrained by the age of the recrystallized tips at 2700 Ma, as BSE images suggest that they have been altered.

An alternate end-member possibility is that each $^{207}\text{Pb}/^{206}\text{Pb}$ age represents a separate episode of uranothorite growth or recrystallization. It is also possible that a small number of uranothorite growth episodes, followed by ancient and recent Pb-loss, accounts for the multiple $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Due to their prominence on the probability density plot, there are likely significant episodes of growth at 2200 Ma and 1400 Ma. An earlier episode must have also occurred to generate the single data point at 2400 Ma. However, it seems unlikely that this was a significant event, as this age was not replicated elsewhere.

A major episode of alteration and uranothorite growth at 2200 Ma would have been coincident with emplacement of the MacKay dyke swarm, which was intruded into the western margin of the Slave Province at 2.1-2.2 Ga (Lecheminant et al., 1996). Metamorphic zircons from mafic granulite xenoliths from the Lac de Gras area record an event at 2.1-2.2 Ga (Davis, 1997). The study by Davis (1997) suggests that the heat required to grow these metamorphic zircons in the lower crust was provided by the lateral

injection, at deep crustal levels, of mafic magma from the MacKay swarm. Davis suggests that the magma traveled laterally, hundreds of kilometers from the centre of the plume. The injection of magma and the circulation of corresponding magmatic fluids may be responsible for uranothorite growth and hydrothermal alteration of the zircons. There is no indication of any alteration ca. 1270 Ma, the time of the Mackenzie dyke swarm, despite the fact that this was a much more significant mafic intrusive event.

There is evidence of recent Pb-loss from a number of different lines of reasoning. The data from unaltered zircon domains (excluding analyses from grain D9) have a lower intercept near the origin, which suggests that sample BNB-95-110c has undergone minor amounts of recent Pb-loss (Fig. 2.7 a, b). The consistent $^{207}\text{Pb}/^{206}\text{Pb}$ ages for reversely discordant, altered, zircon imply that a recent event was responsible for a change in the zircon matrix (Table 2.2, Fig. 2.8). Recent Pb-loss is also suggested by the clustering of uranothorite $^{207}\text{Pb}/^{206}\text{Pb}$ data at 2200 Ma (Fig. 2.11). It seems most likely that this cluster is the result of variably discordant, 2200 Ma old uranothorites that are affected by a recent Pb-loss event similar to that which affected the unaltered zircon domains.

2.7.2 Pb-loss mechanisms

In order to learn more about the nature of the discordance in this sample, a number of plots were generated to highlight relationships between discordance and other chemical or mineralogical properties of zircon. Plots of discordance versus U content were generated, as well as plots of discordance versus radiation dose (Fig. 2.12a, b). Radiation dose is a measure of the radiation damage that a mineral has accumulated over time. The age, U concentrations and Th concentrations are used to calculate radiation dose, which is reported as alpha-events per milligram of zircon. The equation used in this

calculation is presented in Appendix B. The calculated total radiation dose for zircons from sample BNB-95-110c analyzed by the SHRIMP are given in Table 2.2. Between 0.4×10^{16} and 0.8×10^{16} alpha events/mg are thought to be sufficient to render a zircon “completely metamict” (Woodhead et al. 1991; Chakoumakos et al., 1987). Applying the threshold of 0.4×10^{16} alpha events/mg (Woodhead et al., 1991), all the zircon analysed in this study should now be completely metamict. Plots of U content and radiation dose compared to discordance can be used to test the fast-transport Pb-loss hypothesis, where the damage incurred during metamictization controls Pb mobility. Figures 2.12a and 2.12b do not illustrate a simple correlation between discordance with respect to U content or radiation dose. This suggests that metamictization alone is not enough to induce Pb-loss and that a process other than simple fast-transport diffusion was at work.

On the other hand, there is a relationship, although not a linear correlation, between common Pb content and discordance (Fig. 2.9). Once the ratio of $^{204}\text{Pb}/^{206}\text{Pb}$ increases above a threshold value of roughly 10^{-5} , the amount of discordance (normal and reverse) increases greatly. Due to incompatibility in ionic radii and valence state, Pb is not normally incorporated into zircon during growth. The high levels of common Pb measured in discordant zircon from sample BNB-95-110c were likely added to the system at some time during its history, perhaps by exchange with the radiogenic Pb in the zircon lattice (Watson et al., 1997). A similar Pb exchange mechanism was suggested by Scharer and Allegre (1982) for highly discordant zircon. We believe that a process of chemical leaching or alteration is responsible for both the ancient and recent Pb-loss in the study sample. High common Pb contents (up to 10's of ppm) are often cited in studies with discordant results (Black, 1987; Williams et al., 1984; Scharer and Allegre,

1982); and alteration may be a common but overlooked cause of discordance in many cases.

2.8 CONCLUSIONS

The following points summarize the main findings from the U-Pb age and isotopic data collected using the SHRIMP ion microprobe.

1. The crystallization age of sample BNB-95-110c is 2875 ± 3 Ma.
2. Secondary zircon growth, present as thin overgrowths and cross-cutting zircon "micro-dykes", occurred at 2697 ± 14 Ma.
3. Pb-loss and discordance in this sample are related to the alteration of select zircon domains, recognized as having high $^{204}\text{Pb}/^{206}\text{Pb}$ values relative to unaltered domains.
4. Alteration resulted in changes to the zircon matrix that rendered the U-Pb isotopic values unreliable. The thresholds for proper calibration of sample BNB-95-110c are values of ^{204}Pb concentration less than 50 ppb and $^{204}\text{Pb}/^{206}\text{Pb}$ less than 10^{-4} .
5. Pb-loss occurred during multiple events, both recent and ancient. One ancient event, related to the growth of some uranorthorite inclusions, is believed to have occurred at ca. 2200 Ma. The age of other ancient events are not well constrained.

Table 2.2. U-Pb isotopic data for sample BNB-95-110c collected using the GSC's SHRIMP II. See text for discussion.

Spot labels for grains from IP28 include the following information:

IP number.session number magnetic susceptibility – grain number.SHRIMP spot number
magnetic susceptibility is reported as:

NM1 or NM = non –magnetic at 1° side slope

M1 = magnetic at 1° side slope

M2 = magnetic at 2° side slope

for example 28.2NM1 -6.1 refers to a puck number IP28, session number 2, non mag at 1° , grain number 6, spot 1

Spot labels for grains from IP82 and 102 include the following information:

IP number.session number - magnetic susceptibility grain number. SHRIMP spot number
magnetic susceptibility is reported as:

A = non –magnetic at 1° side slope

B = magnetic at 1° side slope

C = magnetic at 2° side slope

D = magnetic at 5° side slope

E = magnetic at 10° side slope

for example 82.1-A4.1 refers to a puck number IP82, session number 1, non mag at 1° , grain number 4, spot 1

or 102-c7.1 refers to puck number 102, magnetic at 2° side slope, grain 7, spot 1

Pb* - radiogenic Pb

All errors are reported at the 1 sigma level.

** concordancy of measured $^{206}\text{Pb}/^{238}\text{U}$ from expected $^{206}\text{Pb}/^{238}\text{U}$ of a concordant analysis.
i.e. concordancy = $(^{206}\text{Pb}/^{238}\text{U}_{\text{measured}} / ^{206}\text{Pb}/^{238}\text{U}_{\text{expected}}) * 100$

Table 2.2

LABELS	FEATURES	U (ppm)	Th (ppm)	Pb ⁺ ThU	Pb ⁺ (ppm)	²⁰⁶ Pb (ppb)	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb
low common Pb zircons													
IP28 session 1, O ⁺ beam													
28.1M-5.1	bright patch	936	43	0.05	524	4	1.00E-05	1.00E-05	0.00016	0.00016	0.0008	0.0270	0.012
28.2NM-18.1	bright patch	894	35	0.04	454	19	5.23E-05	1.17E-05	0.00081	0.00018	0.0044	0.0447	0.036
28.1NM-8.3	bright patch	1192	54	0.05	713	11	1.98E-05	2.14E-05	0.00031	0.00033	0.0015	0.0304	0.022
28.1M2-5.1	bright patch	1997	147	0.07	1161	40	4.24E-05	5.98E-05	0.00086	0.00009	0.0031	0.0702	0.019
28.1M2-5.3	bright patch	1093	49	0.04	627	6	1.25E-05	4.40E-05	0.00019	0.00007	0.0010	0.0350	0.012
28.1M2-5.4	bright patch	924	42	0.05	530	4	9.28E-05	4.79E-05	0.00014	0.00007	0.0007	0.0282	0.012
28.1NM-5.5	bright patch	571	34	0.08	316	4	1.47E-05	9.71E-05	0.00023	0.00015	0.0011	0.0320	0.015
IP28 session 2, O ⁺ beam													
28.2NM1-5.1	bright patch	1174	59	0.05	638	31	5.67E-05	9.02E-05	0.00087	0.00013	0.0045	0.1136	0.015
28.2M11-20.1	bright patch	943	46	0.05	568	1	3.28E-05	8.65E-05	0.00005	0.00013	0.0002	0.0055	0.020
28.2NM1-8.8	bright patch	775	39	0.05	443	1	2.05E-05	3.88E-05	0.00003	0.00006	0.0002	0.0061	0.013
28.2NM1-8.9	bright patch	868	54	0.06	477	4	1.00E-05	4.19E-05	0.00015	0.00008	0.0007	0.0212	0.016
28.2NM1-8.10	bright patch	811	48	0.06	467	0	1.00E-05	1.00E-05	0.00001	0.00001	0.0001	0.0022	0.015
28.2NM1-14.1	bright patch	2072	90	0.04	1251	1	1.00E-05	1.00E-05	0.00001	0.00001	0.0001	0.0029	0.012
28.2NM1-14.2	bright patch	1513	57	0.04	893	0	4.20E-07	2.20E-05	0.00001	0.00033	0.0000	0.0014	0.010
28.2NM1-14.5	bright patch	2981	158	0.05	1742	3	2.35E-05	5.68E-05	0.00004	0.00009	0.0002	0.0067	0.014
28.2NM1-14.9	bright patch	1315	47	0.04	798	7	1.03E-05	1.28E-05	0.00015	0.00019	0.0008	0.0378	0.009
28.2NM1-14.10	bright patch	1704	65	0.04	1023	1	1.00E-05	1.00E-05	0.00001	0.00001	0.0001	0.0033	0.010
28.2NM1-14.13	bright patch	1853	72	0.04	1005	1	1.00E-05	1.00E-05	0.00001	0.00001	0.0001	0.0030	0.011
IP82 session 2, O ₂ ⁺ beam													
82.2-C10.1	bright patch	1813	144	0.08	1110	29	3.25E-05	4.91E-05	0.00050	0.00008	0.0024	0.0343	0.032
82.2-C10.2	bright patch	3934	235	0.08	2394	1	3.50E-07	4.42E-05	0.00001	0.00007	0.0000	0.0006	0.016
82.2-C10.3	bright patch	3909	231	0.08	2316	1	5.00E-07	6.70E-07	0.00001	0.00001	0.0000	0.0012	0.015
82.2-C10.4	bright patch	3817	221	0.08	2320	2	1.00E-05	1.00E-05	0.00002	0.00002	0.0001	0.0024	0.015
82.2-C10.5	bright patch	4002	232	0.08	2416	2	1.00E-05	1.00E-05	0.00002	0.00002	0.0001	0.0024	0.015
82.2-C10.6	bright patch	3482	218	0.08	2089	3	1.87E-05	1.85E-05	0.00003	0.00003	0.0001	0.0041	0.016
82.2-C10.7	bright patch	2732	204	0.07	1651	2	1.31E-05	4.50E-05	0.00002	0.00006	0.0001	0.0024	0.020
82.2-C10.13	bright patch	3487	187	0.05	2125	2	1.00E-05	1.00E-05	0.00002	0.00002	0.0001	0.0026	0.014
82.2-C10.11	bright patch	2992	306	0.10	1739	3	2.42E-05	2.25E-05	0.00004	0.00004	0.0002	0.0024	0.036
82.2-C10.12	bright patch	3720	224	0.08	2270	18	9.70E-05	3.13E-05	0.00017	0.00005	0.0007	0.0212	0.016
82.2-C10.14	bright patch	3980	228	0.08	2211	24	1.32E-05	7.11E-05	0.00023	0.00012	0.0010	0.0296	0.016
IP82 session 1, O ₂ ⁺ beam													
82.1-A4.1	bright patch	959	45	0.05	534	6	1.39E-05	7.29E-05	0.00022	0.00011	0.0011	0.0144	0.033
82.1-C6.1	bright patch	1451	77	0.05	821	2	2.90E-05	5.00E-05	0.00004	0.00008	0.0002	0.0068	0.014
82.1-D35.1	bright patch	1647	135	0.08	953	3	4.03E-05	4.26E-05	0.00006	0.00007	0.0003	0.0085	0.021
82.1-D17.1	bright patch	807	37	0.05	451	4	1.00E-05	1.00E-05	0.00016	0.00016	0.0008	0.0285	0.012
82.1-D23.1	bright patch	1537	113	0.07	932	1	6.70E-07	2.73E-05	0.00001	0.00004	0.0001	0.0011	0.020
82.1-B11.1	bright patch	1201	102	0.08	705	4	7.81E-05	3.86E-05	0.00012	0.00006	0.0006	0.0086	0.026
82.1-D12.1	bright assume	1093	52	0.05	598	1	1.33E-05	1.05E-05	0.00002	0.00016	0.0001	0.0031	0.015
GRAIN D9 - low common Pb, discordant													
82.1-D8.1	bright patch	632	10	0.02	215	14	7.48E-05	2.58E-05	0.00116	0.00040	0.0063	0.0739	0.033
82.1-D8.2	bright patch	738	12	0.02	283	9	3.89E-05	1.42E-05	0.00057	0.00022	0.0037	0.0837	0.014
82.1-D8.5	bright patch	951	35	0.04	248	18	8.43E-05	3.20E-05	0.00131	0.00060	0.0114	0.0824	0.029
82.1-D8.7	bright patch	1484	71	0.05	542	38	8.14E-05	2.08E-05	0.00128	0.00032	0.0101	0.0819	0.043
82.1-D8.8	bright patch	1213	17	0.01	357	15	4.97E-05	2.58E-05	0.00077	0.00040	0.0052	0.0741	0.021
82.1-D8.10	bright patch	1287	58	0.05	411	5	1.50E-05	9.88E-05	0.00023	0.00015	0.0013	0.0100	0.052
82.1-D8.11	bright patch	1130	15	0.01	345	23	7.93E-05	2.88E-05	0.00123	0.00045	0.0084	0.0769	0.033
82.1-D8.38	bright patch	938	35	0.04	207	5	2.88E-05	1.88E-05	0.00045	0.00028	0.0039	0.0675	0.014
82.1-D8.108	bright patch	1907	113	0.06	444	10	2.88E-05	1.70E-05	0.00044	0.00028	0.0027	0.0130	0.076
82.1-D8.9	bright patch	1659	95	0.06	701	45	7.98E-05	1.54E-05	0.00124	0.00024	0.0084	0.0580	0.044
82.1-D8.4	bright patch	781	8	0.01	286	9	3.60E-05	8.05E-05	0.00058	0.00012	0.0033	0.0480	0.024
IP102, O ⁺ beam													
102-C7.1	bright patch	754	33	0.04	361	3	1.00E-05	1.00E-05	0.00017	0.00017	0.0007	0.0287	0.012
102-C22.1	bright patch	954	52	0.06	538	4	1.00E-05	1.00E-05	0.00017	0.00017	0.0008	0.0173	0.021
102-C18.1	bright patch	805	48	0.08	489	5	1.24E-05	1.58E-05	0.00021	0.00027	0.0009	0.0252	0.017
102-E24.1	bright patch	789	39	0.05	422	14	3.91E-05	3.04E-05	0.00088	0.00053	0.0030	0.0886	0.014
102-D19.1	bright patch	799	42	0.05	444	2	5.00E-05	8.78E-05	0.00009	0.00015	0.0004	0.0122	0.016
102-E28.2	bright patch	768	38	0.05	433	13	3.75E-05	4.87E-05	0.00085	0.00081	0.0029	0.0836	0.013
102-E19.1	bright patch	1071	43	0.04	615	10	1.91E-05	1.61E-05	0.00033	0.00028	0.0014	0.0489	0.013

				±		±		±		±	AGE (Ma)	± age (Ma)	AGE (Ma)
²³⁸ U	²³⁵ U	²³² Th	²³⁸ U/ ²³⁵ U	²³⁸ U/ ²³² Th	²³⁵ U/ ²³² Th	²³⁸ U/ ²³⁵ U	²³⁸ U/ ²³² Th	²³⁵ U/ ²³² Th	²³⁸ U/ ²³² Th	²³⁸ U/ ²³⁵ U	²³⁸ U/ ²³² Th	²³⁸ U/ ²³² Th	²³⁸ U/ ²³² Th
0.00016	0.0008	0.0270	0.0127	0.0004	0.5348	0.0080	15.0610	0.2453	0.2041	0.0010	2761.5	33.6	2818.5
0.00018	0.0044	0.0447	0.0394	0.0021	0.4836	0.0109	12.2120	0.2853	0.1831	0.0007	2543.0	47.6	2620.5
0.00033	0.0015	0.0304	0.0222	0.0012	0.5655	0.0089	16.1980	0.4016	0.2076	0.0032	2886.3	41.1	2886.3
0.00009	0.0031	0.0702	0.0198	0.0003	0.5511	0.0083	15.6740	0.2470	0.2063	0.0006	2829.7	34.6	2857.7
0.00007	0.0010	0.0350	0.0122	0.0002	0.5488	0.0084	15.3420	0.2485	0.2027	0.0006	2820.3	34.8	2836.7
0.00007	0.0007	0.0262	0.0121	0.0003	0.5477	0.0082	15.4800	0.2470	0.2050	0.0009	2815.5	34.1	2845.5
0.00015	0.0011	0.0320	0.0157	0.0006	0.5287	0.0081	14.8430	0.2545	0.2044	0.0012	2727.7	34.3	2805.2
0.00013	0.0045	0.1138	0.0158	0.0004	0.5213	0.0072	14.1710	0.2052	0.1972	0.0006	2704.6	30.6	2761.2
0.00013	0.0002	0.0055	0.0205	0.0005	0.5614	0.0085	15.7530	0.2900	0.2035	0.0011	2872.4	38.4	2861.2
0.00006	0.0002	0.0051	0.0138	0.0003	0.5454	0.0082	15.4920	0.2581	0.2080	0.0011	2805.8	34.2	2846.5
0.00006	0.0007	0.0212	0.0180	0.0003	0.5237	0.0081	14.8080	0.2755	0.2051	0.0010	2714.9	38.7	2802.2
0.00001	0.0001	0.0022	0.0159	0.0003	0.5483	0.0112	15.5390	0.3298	0.2056	0.0006	2818.1	46.6	2848.5
0.00001	0.0001	0.0029	0.0121	0.0004	0.5738	0.0098	16.7380	0.3432	0.2116	0.0020	2923.2	40.3	2919.2
0.00033	0.0000	0.0014	0.0104	0.0014	0.5631	0.0114	16.1410	0.5043	0.2079	0.0045	2879.4	47.0	2885.2
0.00009	0.0002	0.0057	0.0141	0.0004	0.5586	0.0085	15.8550	0.2701	0.2086	0.0012	2852.7	35.2	2868.5
0.00019	0.0008	0.0378	0.0081	0.0007	0.5795	0.0102	16.8180	0.3756	0.2080	0.0028	2946.7	41.6	2912.2
0.00001	0.0001	0.0033	0.0104	0.0004	0.5745	0.0100	16.2240	0.3232	0.2048	0.0016	2826.1	41.2	2880.2
0.00001	0.0001	0.0030	0.0113	0.0006	0.5181	0.0098	14.7040	0.3205	0.2058	0.0018	2891.1	41.8	2796.5
0.00008	0.0024	0.0343	0.0322	0.0004	0.5745	0.0084	16.3980	0.2482	0.2070	0.0005	2826.4	34.5	2900.2
0.00007	0.0000	0.0008	0.0163	0.0006	0.5787	0.0130	16.4900	0.4185	0.2087	0.0019	2943.4	53.4	2905.2
0.00001	0.0000	0.0012	0.0157	0.0001	0.5635	0.0102	16.0920	0.3010	0.2071	0.0007	2881.2	42.0	2882.2
0.00002	0.0001	0.0024	0.0154	0.0002	0.5780	0.0112	16.5070	0.3303	0.2071	0.0006	2940.8	46.1	2906.5
0.00002	0.0001	0.0024	0.0157	0.0004	0.5738	0.0117	16.4180	0.3585	0.2075	0.0012	2923.3	46.0	2901.2
0.00003	0.0001	0.0041	0.0167	0.0001	0.5652	0.0102	16.0250	0.2950	0.2067	0.0004	2887.9	42.3	2878.5
0.00006	0.0001	0.0024	0.0202	0.0005	0.5728	0.0110	16.3110	0.3401	0.2065	0.0013	2919.1	45.2	2895.2
0.00002	0.0001	0.0026	0.0144	0.0002	0.5803	0.0098	16.5580	0.2818	0.2070	0.0005	2850.0	39.4	2909.2
0.00004	0.0002	0.0024	0.0389	0.0004	0.5440	0.0095	15.3730	0.2764	0.2060	0.0006	2799.9	39.6	2838.5
0.00005	0.0007	0.0212	0.0188	0.0002	0.5814	0.0118	16.3340	0.3380	0.2038	0.0005	2954.5	48.1	2886.5
0.00012	0.0010	0.0298	0.0180	0.0005	0.5486	0.0109	15.0110	0.3259	0.1985	0.0014	2819.2	45.4	2815.5
0.00011	0.0011	0.0144	0.0335	0.0005	0.5237	0.0085	14.6400	0.2481	0.2027	0.0007	2714.9	36.1	2792.2
0.00008	0.0002	0.0088	0.0149	0.0003	0.5388	0.0084	15.2800	0.2547	0.2058	0.0009	2779.0	35.3	2832.2
0.00007	0.0003	0.0085	0.0216	0.0004	0.5481	0.0087	15.5350	0.2891	0.2058	0.0011	2817.4	36.3	2848.5
0.00016	0.0008	0.0285	0.0120	0.0004	0.5337	0.0080	15.1080	0.2335	0.2053	0.0005	2756.9	33.8	2822.2
0.00004	0.0001	0.0011	0.0204	0.0003	0.5752	0.0085	16.3380	0.2542	0.2080	0.0007	2929.0	34.8	2898.5
0.00006	0.0006	0.0086	0.0285	0.0003	0.5546	0.0084	15.4480	0.2436	0.2020	0.0005	2844.4	35.1	2843.5
0.00016	0.0001	0.0031	0.0152	0.0007	0.5224	0.0092	14.6080	0.2845	0.2028	0.0013	2709.4	39.1	2790.2
0.00040	0.0063	0.0739	0.0331	0.0013	0.3385	0.0056	6.4384	0.1211	0.1380	0.0010	1679.6	26.9	2037.2
0.00022	0.0037	0.0837	0.0142	0.0007	0.3822	0.0073	8.1221	0.1687	0.1541	0.0010	2086.7	33.9	2244.2
0.00050	0.0114	0.0824	0.0292	0.0016	0.2633	0.0048	4.0540	0.0886	0.1117	0.0011	1506.8	24.4	1645.2
0.00032	0.0101	0.0619	0.0435	0.0010	0.3638	0.0080	6.1467	0.1146	0.1226	0.0009	2000.3	26.2	1987.2
0.00040	0.0052	0.0741	0.0219	0.0012	0.2825	0.0063	5.9383	0.1229	0.1472	0.0011	1854.0	26.7	1986.2
0.00015	0.0013	0.0100	0.0525	0.0009	0.3028	0.0071	7.2885	0.1871	0.1741	0.0015	1705.1	35.0	2145.2
0.00045	0.0084	0.0789	0.0335	0.0017	0.3018	0.0083	5.9857	0.2019	0.1439	0.0015	1700.0	46.3	1973.2
0.00028	0.0039	0.0875	0.0141	0.0008	0.2282	0.0039	3.5508	0.0715	0.1129	0.0010	1324.8	20.7	1538.2
0.00026	0.0027	0.0130	0.0763	0.0012	0.2188	0.0043	4.8148	0.0898	0.1598	0.0008	1275.6	22.7	1767.2
0.00024	0.0084	0.0680	0.0448	0.0008	0.3983	0.0067	10.3530	0.1918	0.1885	0.0011	2161.1	31.1	2486.2
0.00012	0.0033	0.0480	0.0246	0.0006	0.3888	0.0063	8.5410	0.1570	0.1680	0.0008	2013.2	30.0	2290.2
0.00017	0.0007	0.0297	0.0121	0.0011	0.4555	0.0313	13.1480	0.9258	0.2094	0.0019	2419.5	140.2	2680.2
0.00017	0.0008	0.0173	0.0211	0.0006	0.5378	0.0143	14.7770	0.4158	0.1894	0.0013	2773.4	60.0	2801.2
0.00027	0.0009	0.0252	0.0177	0.0008	0.5550	0.0127	15.5510	0.3941	0.2032	0.0017	2845.8	52.8	2849.2
0.00053	0.0030	0.0886	0.0147	0.0012	0.5100	0.0130	14.4290	0.4148	0.2052	0.0021	2856.8	55.8	2778.2
0.00015	0.0004	0.0122	0.0150	0.0013	0.5319	0.0155	14.6880	0.4673	0.2003	0.0020	2748.6	65.4	2785.2
0.00081	0.0029	0.0836	0.0135	0.0018	0.5400	0.0138	14.9820	0.4641	0.2014	0.0030	2783.4	57.8	2814.2
0.00028	0.0014	0.0489	0.0138	0.0008	0.5478	0.0158	15.5220	0.4702	0.2055	0.0014	2815.9	65.9	2847.2

$^{232}\text{Pu}/^{232}\text{Pu}$	$\pm$ $^{232}\text{Pu}/^{232}\text{Pu}$	AGE (Ma) $^{232}\text{Pu}/^{232}\text{U}$	$\pm$ age (Ma) $^{232}\text{Pu}/^{232}\text{U}$	AGE (Ma) $^{232}\text{Pu}/^{232}\text{U}$	$\pm$ age (Ma) $^{232}\text{Pu}/^{232}\text{U}$	AGE (Ma) $^{232}\text{Pu}/^{232}\text{Pu}$	$\pm$ age (Ma) $^{232}\text{Pu}/^{232}\text{Pu}$	CONC. TO ORIGIN (%)	CONC. TO 6/30 (%)	RADIATION DOSE (alpha-events/mg)
0.2041	0.0010	2761.5	33.6	2818.5	15.6	2859.5	8.0	96.6	95.0	1.29E+16
0.1831	0.0007	2543.0	47.6	2620.9	22.2	2681.5	6.3	94.8	85.9	1.20E+16
0.2076	0.0032	2690.3	41.1	2688.1	24.0	2687.1	25.3	100.1	100.4	1.60E+16
0.2063	0.0008	2829.7	34.6	2857.1	15.2	2878.5	5.0	98.4	97.8	2.69E+16
0.2027	0.0008	2820.3	34.8	2836.7	15.6	2848.3	6.5	99.0	97.5	1.47E+16
0.2050	0.0009	2815.5	34.1	2845.3	15.3	2866.4	6.8	98.2	97.2	1.24E+16
0.2044	0.0012	2727.7	34.3	2905.2	16.4	2861.4	9.6	95.3	93.5	7.67E+15
0.1972	0.0008	2704.6	30.6	2761.2	13.8	2802.9	4.8	98.5	92.6	1.58E+16
0.2036	0.0011	2872.4	38.4	2861.9	17.7	2854.6	8.8	100.6	99.7	1.27E+16
0.2060	0.0011	2805.8	34.2	2846.0	15.9	2874.6	8.8	97.6	96.8	1.04E+16
0.2061	0.0010	2714.9	38.7	2802.9	17.9	2866.6	7.8	94.7	93.0	1.17E+16
0.2056	0.0008	2818.1	46.6	2848.9	20.5	2870.6	6.5	98.2	97.4	1.09E+16
0.2116	0.0020	2923.2	40.3	2919.8	19.8	2917.4	15.3	100.2	101.9	2.78E+16
0.2079	0.0045	2879.4	47.0	2885.2	30.3	2889.2	35.3	99.7	100.0	2.03E+16
0.2088	0.0012	2852.7	35.2	2868.1	16.4	2878.9	9.8	99.1	98.8	4.00E+16
0.2080	0.0026	2946.7	41.6	2912.9	21.9	2889.7	20.0	102.0	102.9	1.76E+16
0.2048	0.0016	2828.1	41.2	2890.1	19.2	2865.1	12.5	102.1	102.0	2.26E+16
0.2058	0.0018	2691.1	41.8	2798.2	20.9	2873.0	14.2	93.7	92.0	2.48E+16
0.2070	0.0005	2926.4	34.5	2900.3	14.6	2882.3	4.0	101.5	102.0	2.45E+16
0.2067	0.0019	2943.4	53.4	2906.7	24.6	2879.7	15.2	102.2	102.8	5.29E+16
0.2071	0.0007	2881.2	42.0	2882.3	18.0	2883.1	5.2	99.9	100.1	5.28E+16
0.2071	0.0006	2940.8	46.1	2906.6	19.3	2883.1	4.7	102.0	102.6	5.13E+16
0.2075	0.0012	2923.3	48.0	2901.4	21.2	2886.2	9.6	101.3	101.9	5.38E+16
0.2057	0.0004	2887.9	42.3	2878.3	17.8	2871.6	3.0	100.6	100.4	4.68E+16
0.2085	0.0013	2919.1	45.2	2895.2	20.2	2878.6	10.0	101.4	101.7	3.68E+16
0.2070	0.0005	2950.0	38.4	2906.6	16.4	2881.8	3.7	102.4	103.0	4.68E+16
0.2060	0.0006	2799.9	39.6	2838.7	17.3	2886.3	4.7	97.7	96.6	4.05E+16
0.2038	0.0006	2954.5	48.1	2896.6	20.0	2856.5	4.3	103.4	103.2	5.00E+16
0.1985	0.0014	2819.2	45.4	2815.9	20.9	2813.6	11.1	100.2	97.4	5.19E+16
0.2027	0.0007	2714.9	36.1	2792.1	16.2	2848.4	5.2	95.3	93.0	1.29E+16
0.2056	0.0009	2779.0	35.3	2832.9	16.0	2871.4	6.9	96.8	95.7	1.95E+16
0.2066	0.0011	2817.4	36.3	2848.6	16.7	2870.6	8.6	98.1	97.3	2.22E+16
0.2063	0.0006	2756.9	33.8	2822.0	14.8	2866.9	3.7	96.1	94.6	1.09E+16
0.2060	0.0007	2829.0	34.8	2896.7	15.0	2874.3	5.6	101.9	102.1	2.07E+16
0.2020	0.0006	2844.4	35.1	2843.2	15.2	2842.3	4.3	100.1	96.5	1.62E+16
0.2028	0.0013	2708.4	39.1	2790.1	16.7	2848.9	10.5	95.1	92.6	1.47E+16
0.1380	0.0010	1879.6	26.9	2037.7	16.7	2201.7	12.6	85.4	80.1	8.43E+15
0.1541	0.0010	2086.7	33.9	2244.7	19.0	2392.1	10.9	87.2	67.9	9.86E+15
0.1117	0.0011	1506.8	24.4	1645.1	18.0	1826.7	18.6	82.5	46.8	1.27E+16
0.1226	0.0009	2000.3	28.2	1997.3	16.4	1994.2	12.6	100.3	64.6	1.99E+16
0.1472	0.0011	1654.0	26.7	1998.8	18.2	2314.1	13.3	71.5	51.9	1.62E+16
0.1741	0.0015	1705.1	35.0	2145.0	23.2	2597.6	14.1	65.6	53.8	1.73E+16
0.1439	0.0015	1700.0	46.3	1973.8	29.6	2274.2	17.8	74.8	53.6	1.51E+16
0.1129	0.0010	1324.8	20.7	1538.6	16.1	1846.1	15.4	71.8	40.5	1.26E+16
0.1586	0.0008	1275.6	22.7	1767.5	17.6	2451.4	8.3	52.0	38.9	2.59E+16
0.1885	0.0011	2161.1	31.1	2468.9	17.3	2729.3	9.6	79.2	70.7	2.23E+16
0.1680	0.0008	2013.2	30.0	2290.3	16.6	2547.7	7.5	79.0	65.1	1.01E+16
0.2084	0.0019	2419.5	140.2	2690.3	68.7	2900.6	14.4	83.4	80.9	1.01E+16
0.1984	0.0013	2773.4	60.0	2801.0	27.1	2821.0	10.9	98.3	95.5	1.29E+16
0.2032	0.0017	2845.8	52.8	2848.6	24.5	2852.4	13.8	99.8	96.5	1.09E+16
0.2062	0.0021	2666.8	55.8	2778.4	27.7	2867.9	17.0	92.6	90.6	1.08E+16
0.2003	0.0020	2748.6	65.4	2795.2	30.7	2828.3	16.0	97.2	94.5	1.07E+16
0.2014	0.0030	2763.4	57.8	2814.7	28.9	2837.2	24.2	98.1	95.9	1.03E+16
0.2065	0.0014	2815.9	65.9	2847.8	29.3	2870.5	10.8	98.1	97.3	1.44E+16

Table 2.2 cont'd.

LABELS	FEATURES	U (ppm)	Th (ppm)	Th/U	Pb [*] (ppm)	²⁰⁶ Pb (ppb)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁸ Pb	²⁰⁷ Pb/ ²⁰⁸ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁸ Pb	²⁰⁷ Pb/ ²⁰⁸ Pb
high common Pb zircons														
28.2NM1-14.3	dark patch	4554	330	0.07	3231	590	2.38E-04	7.13E-05	0.00356	0.00108	0.0180	0.0715	0.1074	
28.2NM1-14.4	dark patch	3908	313	0.08	3763	1785	8.85E-04	4.19E-05	0.01022	0.00062	0.0489	0.0880	0.2480	
28.2NM1-14.6	dark patch	3283	197	0.06	2060	219	1.34E-04	1.91E-05	0.00200	0.00029	0.0099	0.0897	0.0470	
28.2NM1-14.7	dark patch	4450	286	0.06	3935	2830	1.08E-03	4.09E-05	0.01575	0.00081	0.0807	0.1105	0.2983	
28.2NM1-14.8	bright patch	2235	103	0.05	1594	451	3.84E-04	2.59E-05	0.00642	0.00039	0.0269	0.1282	0.0859	
28.2NM1-14.11	dark patch	4976	382	0.08	4440	1904	6.01E-04	2.43E-05	0.00897	0.00036	0.0426	0.0843	0.2015	
28.2NM1-14.12	dark patch	4201	277	0.07	5529	4307	1.23E-03	4.27E-05	0.01831	0.00064	0.0887	0.0971	0.4019	
28.2NM1-14.16	dark patch	3124	199	0.06	3423	1896	8.02E-04	3.68E-05	0.01390	0.00064	0.0577	0.1080	0.2544	
82.1-D4.1	bright patch	730	36	0.05	418	58	1.70E-04	1.46E-05	0.00263	0.00023	0.0126	0.3051	0.0136	
82.1-D2.1	bright patch	1157	87	0.07	670	97	1.78E-04	9.28E-06	0.00277	0.00014	0.0132	0.1962	0.0259	
82.1-E9.1	dark patch	2971	161	0.05	1933	513	3.27E-04	1.94E-05	0.00607	0.00030	0.0253	0.2293	0.0388	
82.1-E8.1	dark patch	2687	175	0.07	536	899	1.98E-03	6.60E-05	0.03072	0.00102	0.1783	0.5080	0.0886	
82.1-D8.3	bright patch	829	31	0.04	201	25	1.40E-04	2.98E-05	0.00218	0.00046	0.0187	0.2204	0.0175	
82.1-D8.6	bright patch	485	1	0.00	191	21	1.31E-04	4.77E-05	0.00204	0.00074	0.0146	0.0835	0.0449	
82.1-D8.13	bright patch	2507	157	0.06	1746	486	3.81E-04	3.91E-05	0.00691	0.00061	0.0306	0.0625	0.2433	
82.1-D8.14	bright patch	1013	56	0.06	644	41	8.08E-05	2.08E-05	0.00125	0.00032	0.0080	0.0528	0.0509	
82.1-D8.16	bright patch	2242	101	0.04	1126	197	2.31E-04	7.36E-05	0.00356	0.00114	0.0232	0.0458	0.1897	
82.1-D8.17	bright patch	1933	102	0.05	1084	246	3.05E-04	2.02E-05	0.00473	0.00031	0.0309	0.0592	0.1714	
82.1-D8.15	bright patch	2823	124	0.04	706	154	2.57E-04	4.39E-05	0.00399	0.00068	0.0334	0.1221	0.0853	
82.1-D2.2	bright patch	1221	87	0.07	717	63	1.08E-04	8.32E-06	0.00188	0.00013	0.0081	0.1424	0.0230	
82.2-C10.9	bright patch	1270	90	0.07	934	212	3.01E-04	2.37E-05	0.00621	0.00041	0.0225	0.0840	0.1222	
82.2-C10.8	bright patch	3599	360	0.10	2811	55	2.55E-05	2.49E-06	0.00044	0.00004	0.0019	0.0094	0.0993	
reprecipitated tips and microdykes IP102, O ⁺ beam														
102-C16.1	dyke	970	32	0.03	379	3	1.10E-05	4.20E-05	0.00019	0.00073	0.0010	0.0332	0.0119	
102-C23.1	tip	806	1	0.00	241	1	6.62E-06	4.35E-05	0.00011	0.00075	0.0009	0.2297	0.0006	
102-E3.1	tip	711	18	0.03	329	3	1.00E-05	1.00E-05	0.00017	0.00017	0.0009	0.0192	0.0190	
102-E3.3	tip	680	20	0.03	351	2	8.14E-06	2.17E-05	0.00014	0.00038	0.0007	0.0284	0.0103	
102-D6.1	tip	720	9	0.01	222	2	1.00E-05	1.00E-05	0.00017	0.00017	0.0009	0.0169	0.0215	
102-D5.2	tip	963	27	0.03	303	2	1.00E-05	4.70E-05	0.00017	0.00081	0.0008	0.0291	0.0124	
102-D6.3	tip	612	20	0.03	214	18	1.01E-04	4.66E-05	0.00175	0.00081	0.0085	0.1355	0.0240	
102-C23.4	tip	614	26	0.03	301	19	7.27E-05	2.88E-05	0.00128	0.00050	0.0072	0.2772	0.0070	
102-C23.5	tip	632	22	0.04	247	44	2.13E-04	7.00E-05	0.00370	0.00121	0.0191	0.2872	0.0197	
102-E3.5	tip	1074	52	0.05	630	30	6.11E-05	1.90E-05	0.00106	0.00033	0.0051	0.0207	0.1072	
102-E3.7	tip	705	26	0.04	341	6	2.10E-05	2.35E-05	0.00038	0.00041	0.0018	0.0389	0.0192	
102-E26.1	tip	807	32	0.04	426	4	1.00E-05	1.00E-05	0.00017	0.00017	0.0008	0.0300	0.0120	
102-C19.1	tip	718	9	0.01	315	39	1.43E-04	3.86E-05	0.00248	0.00067	0.0146	0.9840	0.0002	
102-C19.2	tip	868	29	0.03	411	15	4.37E-05	5.89E-05	0.00078	0.00102	0.0042	0.1549	0.0089	
82.2-C10.10	tip	708	19	0.03	344	3	9.88E-06	9.71E-06	0.00017	0.00017	0.0009	0.0179	0.0201	
102-E3.4	tip	748	291	0.40	481	230	6.33E-04	4.46E-05	0.01086	0.00077	0.0525	0.1346	0.1527	

	$^{238}\text{Pu}/^{239}\text{Pu}$	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$	$^{243}\text{Pu}/^{239}\text{Pu}$	$^{244}\text{Pu}/^{239}\text{Pu}$	$^{245}\text{Pu}/^{239}\text{Pu}$	$^{246}\text{Pu}/^{239}\text{Pu}$	$^{247}\text{Pu}/^{239}\text{Pu}$	AGE (Ma)	$\pm$ age (Ma)	AGE (Ma)	$\pm$ age (Ma)
(200)										$^{238}\text{Pu}/^{239}\text{Pu}$	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$
0	0.0715	0.1074	0.0040	0.6317	0.0131	17.2370	0.5024	0.1979	0.0036	3156.2	52.1	2948.1	
9	0.0880	0.2480	0.0025	0.7699	0.0104	21.6640	0.3329	0.2041	0.0012	3680.5	37.8	3168.8	
9	0.0897	0.0470	0.0011	0.5800	0.0081	16.3450	0.2593	0.2044	0.0012	2948.7	33.2	2897.2	
7	0.1105	0.2963	0.0022	0.6919	0.0104	17.6810	0.3337	0.1854	0.0018	3389.7	39.9	2972.6	
9	0.1282	0.0859	0.0012	0.6447	0.0112	17.8090	0.3405	0.2003	0.0012	3207.6	44.0	2979.5	
8	0.0943	0.2015	0.0017	0.7358	0.0109	21.0110	0.3395	0.2071	0.0010	3554.9	40.4	3139.1	
7	0.0971	0.4019	0.0023	0.9564	0.0130	25.7010	0.3917	0.1949	0.0011	4328.1	42.9	3335.2	
7	0.1080	0.2544	0.0016	0.8712	0.0179	24.7800	0.5279	0.2081	0.0008	4039.1	61.8	3298.8	
5	0.3051	0.0136	0.0006	0.5459	0.0084	15.4140	0.2442	0.2048	0.0005	2806.1	35.0	2841.2	
2	0.1952	0.0259	0.0004	0.5486	0.0080	15.4860	0.2331	0.2055	0.0005	2811.2	33.3	2845.6	
3	0.2293	0.0388	0.0009	0.6138	0.0097	18.3590	0.2729	0.1833	0.0007	3085.1	38.8	2898.0	
3	0.5080	0.0686	0.0025	0.1913	0.0030	3.8000	0.0702	0.1441	0.0012	1128.2	16.0	1592.7	
7	0.2204	0.0175	0.0012	0.2490	0.0046	3.8879	0.0820	0.1133	0.0010	1433.2	23.5	1611.2	
3	0.0935	0.0449	0.0022	0.3885	0.0077	7.3023	0.1732	0.1363	0.0015	2115.9	35.9	2149.1	
3	0.0625	0.2433	0.0025	0.5659	0.0094	14.4990	0.2782	0.1858	0.0015	2891.1	38.7	2782.9	
0	0.0528	0.0509	0.0012	0.5892	0.0121	16.5490	0.3572	0.2037	0.0009	2986.1	49.3	2909.1	
2	0.0458	0.1697	0.0052	0.4426	0.0087	9.1084	0.2599	0.1493	0.0027	2362.1	39.0	2349.0	
9	0.0592	0.1714	0.0014	0.4850	0.0074	9.8526	0.1608	0.1473	0.0008	2549.1	32.4	2421.1	
1	0.1221	0.0653	0.0019	0.2467	0.0039	3.8884	0.0736	0.1143	0.0010	1421.3	19.9	1611.3	
4	0.1424	0.0230	0.0004	0.5560	0.0083	15.9680	0.2401	0.2044	0.0005	2850.3	34.4	2856.8	
5	0.0840	0.1222	0.0016	0.6438	0.0116	18.1190	0.3382	0.2041	0.0007	3203.9	45.5	2996.1	
9	0.0094	0.0993	0.0006	0.6952	0.0114	19.7940	0.3304	0.2065	0.0004	3402.4	43.5	3081.4	
0	0.0332	0.0119	0.0024	0.3620	0.0392	9.2780	1.0551	0.1761	0.0067	2086.8	185.5	2365.9	1
9	0.2297	0.0008	0.0016	0.3118	0.0335	5.0519	0.7053	0.1175	0.0090	1749.3	168.9	1828.1	1
9	0.0192	0.0190	0.0007	0.4479	0.0109	11.2870	0.3097	0.1824	0.0019	2386.0	48.5	2545.5	
7	0.0284	0.0103	0.0009	0.4941	0.0098	12.6810	0.3064	0.1859	0.0023	2586.3	41.4	2654.8	
9	0.0189	0.0215	0.0007	0.2971	0.0105	7.4769	0.2945	0.1825	0.0024	1676.8	52.5	2170.2	
3	0.0291	0.0124	0.0019	0.2996	0.0095	8.5885	0.2858	0.2079	0.0014	1689.2	47.4	2295.1	
5	0.1355	0.0240	0.0031	0.3368	0.0110	8.4985	0.5010	0.1831	0.0083	1870.3	53.1	2285.6	
2	0.2772	0.0070	0.0015	0.3683	0.0094	7.9882	0.2290	0.1569	0.0016	2026.0	44.4	2229.5	
1	0.2872	0.0197	0.0028	0.3826	0.0149	8.9764	0.4709	0.1702	0.0052	2088.2	69.8	2335.6	
1	0.0207	0.1072	0.0016	0.5279	0.0109	13.4640	0.2936	0.1850	0.0009	2732.4	46.1	2712.7	
3	0.0389	0.0192	0.0010	0.4675	0.0101	11.7280	0.2891	0.1819	0.0010	2472.4	44.4	2582.8	
3	0.0300	0.0120	0.0011	0.5122	0.0124	13.0420	0.3296	0.1847	0.0009	2865.8	53.0	2682.7	
5	0.9840	0.0002	0.0016	0.4432	0.0088	9.2205	0.2090	0.1509	0.0013	2364.9	39.4	2360.2	
2	0.1549	0.0089	0.0022	0.4703	0.0123	10.5080	0.3245	0.1621	0.0022	2484.7	54.3	2480.6	
9	0.0179	0.0201	0.0007	0.4725	0.0090	11.4290	0.2435	0.1754	0.0013	2494.5	39.4	2558.6	
5	0.1346	0.1527	0.0033	0.5805	0.0127	13.8550	0.3803	0.1793	0.0018	2888.8	52.7	2739.9	

	$^{232}\text{Pu}/^{232}\text{Pu}$	$\pm$ $^{232}\text{Pu}/^{232}\text{Pu}$	AGE (Ma) $^{232}\text{Pu}/^{232}\text{U}$	$\pm$ age (Ma) $^{232}\text{Pu}/^{232}\text{U}$	AGE (Ma) $^{232}\text{Pu}/^{232}\text{U}$	$\pm$ age (Ma) $^{232}\text{Pu}/^{232}\text{U}$	AGE (Ma) $^{232}\text{Pu}/^{232}\text{Pu}$	$\pm$ age (Ma) $^{232}\text{Pu}/^{232}\text{Pu}$	CONC. TO ORIGIN (%)	CONC. TO 6/38 (%)**	RADIATION DOSE (alpha-events/mg)
24	0.1879	0.0036	3158.2	52.1	2948.1	28.4	2808.1	28.7	112.4	112.2	6.14E+16
29	0.2041	0.0012	3680.5	37.8	3168.8	15.0	2859.0	9.7	128.7	136.7	5.27E+16
33	0.2044	0.0012	2948.7	33.2	2897.2	15.3	2861.6	9.6	103.0	103.0	4.42E+16
37	0.1854	0.0018	3389.7	39.9	2972.6	18.3	2701.4	16.0	125.5	122.8	5.98E+16
505	0.2003	0.0012	3207.6	44.0	2979.5	18.6	2828.9	10.1	113.4	114.5	3.00E+16
95	0.2071	0.0010	3554.9	40.4	3139.1	15.8	2883.0	8.2	123.3	130.6	6.71E+16
117	0.1949	0.0011	4326.1	42.9	3335.2	15.0	2784.0	9.0	155.4	169.8	5.65E+16
179	0.2081	0.0008	4039.1	61.8	3298.8	21.0	2875.4	6.3	140.5	154.7	4.20E+16
42	0.2048	0.0005	2808.1	35.0	2841.2	15.2	2864.8	4.1	98.0	98.9	9.80E+15
131	0.2055	0.0005	2811.2	33.3	2845.6	14.5	2870.1	3.7	97.9	97.1	1.58E+16
29	0.1933	0.0007	3085.1	38.8	2898.0	16.1	2770.4	6.3	111.4	109.0	3.99E+16
02	0.1441	0.0012	1128.2	18.0	1592.7	15.0	2277.0	14.5	49.5	34.0	3.62E+16
20	0.1133	0.0010	1433.2	23.5	1611.2	17.2	1852.3	15.4	77.4	44.2	1.11E+16
32	0.1363	0.0015	2115.9	35.9	2149.1	21.4	2180.9	18.8	87.0	69.0	6.45E+15
92	0.1858	0.0015	2891.1	38.7	2782.9	18.5	2705.4	13.3	108.9	100.5	3.37E+16
72	0.2037	0.0009	2986.1	49.3	2908.1	20.9	2856.2	7.5	104.6	104.6	1.38E+16
99	0.1493	0.0027	2382.1	39.0	2349.0	26.5	2337.6	31.7	101.0	78.6	3.01E+16
08	0.1473	0.0008	2549.1	32.4	2421.1	15.2	2315.1	6.9	110.1	86.1	2.60E+16
36	0.1143	0.0010	1421.3	19.9	1611.3	15.4	1869.3	16.2	76.0	43.8	3.79E+16
01	0.2044	0.0005	2850.3	34.4	2856.8	14.7	2861.4	3.7	98.6	98.7	1.65E+16
92	0.2041	0.0007	3203.9	45.5	2986.1	18.2	2859.4	5.8	112.0	114.3	1.71E+16
04	0.2085	0.0004	3402.4	43.5	3081.4	16.3	2878.3	2.7	116.2	123.4	4.87E+16
51	0.1761	0.0067	2085.8	185.5	2365.9	110.0	2618.8	64.4	79.7	67.8	1.19E+16
53	0.1175	0.0090	1749.3	168.9	1828.1	125.8	1919.0	144.3	91.2	55.4	9.79E+15
97	0.1824	0.0019	2386.0	48.5	2545.5	26.0	2675.2	17.2	89.2	79.5	8.67E+15
84	0.1859	0.0023	2588.3	41.4	2654.8	23.0	2705.8	20.5	95.7	87.7	8.42E+15
45	0.1825	0.0024	1676.8	52.5	2170.2	35.9	2678.0	22.3	62.7	52.7	8.77E+15
58	0.2079	0.0014	1689.2	47.4	2295.1	30.7	2689.1	11.0	58.5	53.2	1.17E+16
10	0.1831	0.0083	1870.3	53.1	2285.6	55.0	2680.9	76.8	69.8	59.8	7.47E+15
80	0.1589	0.0016	2026.0	44.4	2229.5	26.1	2422.0	17.3	83.7	65.6	9.94E+15
09	0.1702	0.0052	2088.2	69.8	2335.6	49.1	2559.4	52.3	81.6	67.9	7.73E+15
36	0.1850	0.0009	2732.4	46.1	2712.7	20.8	2698.1	8.3	101.3	93.7	1.32E+16
91	0.1819	0.0010	2472.4	44.4	2582.8	21.7	2670.5	9.5	92.6	83.0	8.62E+15
86	0.1847	0.0009	2885.8	53.0	2882.7	24.0	2695.5	7.8	98.9	90.9	9.88E+15
90	0.1509	0.0013	2384.9	39.4	2390.2	21.0	2356.1	15.0	100.4	78.7	8.73E+15
45	0.1821	0.0022	2484.7	54.3	2480.6	29.0	2477.4	22.7	100.3	83.5	1.08E+16
35	0.1754	0.0013	2484.5	39.4	2558.6	20.1	2609.7	12.7	95.6	83.9	6.63E+15
03	0.1793	0.0018	2888.8	52.7	2739.9	24.9	2648.1	17.0	108.4	99.5	9.73E+15

Labels	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{204}\text{Pb}/^{206}\text{Pb}$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	AGE (Ma)	$\pm$ age (Ma)
<i>IP28.2</i>										
20TH1.1A	3.28E-05	8.00E-06	0.00049	0.00012	0.0037	0.0014	0.1327	0.0010	2134.0	13.1
20TH1.1B	3.84E-05	4.26E-05	0.00057	0.00064	0.0043	0.0017	0.1352	0.0041	2166.5	54.0
20TH1.2A	2.90E-05	1.91E-05	0.00043	0.00028	0.0034	0.0015	0.1281	0.0019	2072.1	26.0
21TH1.1A	3.21E-06	4.32E-06	0.00005	0.00006	0.0007	0.0001	0.0743	0.0007	1049.3	18.9
21TH1.2A	4.90E-06	5.44E-06	0.00007	0.00008	0.0010	0.0002	0.0720	0.0008	985.7	21.3
33TH1.1A	7.01E-05	2.88E-05	0.00105	0.00043	0.0092	0.0359	0.1150	0.0017	1879.5	26.4
20TH1.3A	2.70E-05	1.70E-05	0.00040	0.00025	0.0033	0.0013	0.1257	0.0015	2038.3	21.2
20TH1.3B	3.13E-05	2.04E-05	0.00047	0.00030	0.0037	0.0015	0.1292	0.0016	2087.6	22.3
20TH1.3C	2.84E-05	1.85E-05	0.00042	0.00028	0.0032	0.0013	0.1329	0.0019	2136.6	24.9
20TH1.2B	3.36E-05	2.35E-06	0.00050	0.00004	0.0038	0.0018	0.1342	0.0003	2153.6	3.5
20TH1.2C	3.16E-05	2.64E-06	0.00047	0.00004	0.0035	0.0017	0.1384	0.0002	2207.0	2.1
20TH1.1C	3.45E-05	2.50E-05	0.00051	0.00037	0.0039	0.0015	0.1332	0.0022	2140.0	28.8
20TH2.1A	3.14E-05	1.10E-05	0.00047	0.00016	0.0065	0.0006	0.0726	0.0006	1002.5	16.0
23TH1.1A	1.12E-04	1.28E-04	0.00167	0.00191	0.0182	0.0043	0.0918	0.0047	1463.5	101.1
13TH1.1A	1.60E-04	5.18E-05	0.00238	0.00077	0.0322	0.0031	0.0731	0.0012	1015.7	33.8
13TH1.2A	1.29E-04	5.42E-05	0.00192	0.00081	0.0313	0.0017	0.0606	0.0013	624.2	48.0
<i>IP82.1</i>										
D20.1TH	2.06E-04	8.16E-06	0.00307	0.00012	0.0281	0.0085	0.1083	0.0003	1771.7	5.0
D21.1TH	4.36E-05	5.15E-06	0.00065	0.00008	0.0091	0.0022	0.0720	0.0002	985.6	6.6
D29.1TH	2.06E-04	1.49E-05	0.00307	0.00022	0.0315	0.0083	0.0961	0.0003	1550.5	6.7
D30.1TH	6.81E-05	2.53E-06	0.00102	0.00004	0.0114	0.0057	0.0896	0.0002	1417.7	3.2
D30.2TH	6.18E-05	3.44E-06	0.00092	0.00005	0.0103	0.0052	0.0900	0.0002	1426.4	3.5
D30.3TH	6.27E-05	5.68E-06	0.00093	0.00008	0.0098	0.0057	0.0965	0.0003	1557.8	6.4
E8.1TH	2.54E-05	4.83E-06	0.00038	0.00007	0.0069	0.0010	0.0551	0.0002	416.8	9.9
E2.1TH	3.43E-06	1.49E-06	0.00005	0.00002	0.0010	0.0002	0.0524	0.0006	302.9	24.9
D20.2TH	1.95E-04	1.07E-05	0.00291	0.00016	0.0262	0.0090	0.1106	0.0003	1809.5	4.7
D20.3TH	1.90E-04	9.66E-06	0.00284	0.00014	0.0254	0.0088	0.1110	0.0003	1816.5	5.4
C1.1TH	2.54E-06	2.38E-06	0.00004	0.00004	0.0006	0.0001	0.0642	0.0003	746.6	8.2
C1.2TH	2.16E-06	2.94E-06	0.00003	0.00004	0.0005	0.0000	0.0702	0.0004	934.3	11.9
C1.3TH	4.55E-06	2.62E-06	0.00007	0.00004	0.0011	0.0001	0.0644	0.0002	754.6	7.8
D9.1TH	1.02E-06	1.26E-05	0.00002	0.00019	0.0003	0.0000	0.0544	0.0018	387.2	77.1
C1.4TH	6.33E-06	2.26E-06	0.00009	0.00003	0.0015	0.0002	0.0657	0.0003	795.9	8.6
C1.5TH	1.41E-06	1.40E-06	0.00002	0.00002	0.0003	0.0000	0.0662	0.0003	811.6	8.0
D9.2TH	4.30E-07	7.90E-07	0.00001	0.00001	0.0001	0.0000	0.0553	0.0003	423.1	10.1
D15.1TH	1.00E-05	1.00E-05	0.00015	0.00015	0.0017	0.0006	0.0901	0.0009	1427.8	18.2
D15.2TH	3.00E-06	2.54E-06	0.00004	0.00004	0.0006	0.0001	0.0832	0.0004	1274.9	9.8
D18.1TH	1.45E-06	2.46E-06	0.00002	0.00004	0.0003	0.0000	0.0894	0.0004	1413.2	7.7
<i>IP 102</i>										
E19TH.1	2.59E-03	3.42E-05	0.04487	0.00059	0.2322	0.0480	0.1391	0.0012	2215.4	15.4
E19TH.2	3.53E-03	1.37E-04	0.06118	0.00237	0.2710	0.1204	0.1569	0.0038	2422.5	41.9
E19TH.3	3.06E-03	1.64E-04	0.05305	0.00284	0.2655	0.0581	0.1388	0.0033	2211.6	41.9

Table 2.3 Thorite Data

Analyses from pucks IP 82 and 102 are labelled with the grain number of the zircon that contains the thorite (i.e. D20) and the spot number on that thorite inclusion (i.e. d20.1), the initials TH are to distinguish thorite from zircon analyses.

All errors given at the 1 sigma level.

Fig. 2.1 Graphical representation of the concept of closure temperature and apparent age (modified from Dodson, 1973). The extrapolation (shown by the dashed line) of the D/P growth curve back to the time axis represents the apparent age. T_c is the temperature that existed at the apparent age. The curved portion of the D/P growth curve represents the time/temperature range over which there is only partial retention of the daughter isotope.

Fig 2.1

Fig. 2.2 Location map. **a)** Map of Canada showing the location of the Slave Province. **b)** Simplified geological map of the Slave Province, showing the location of the Acasta Gneiss Complex. Adapted from Stern and Bleeker (1998).

Fig 2.2

Fig. 2.3 **a)** Granite dyke (sample BNB-95-110c) hosted by tonalite gneiss. The foliation within the dyke and the contacts are parallel to foliation in the host rock. Sledgehammer for scale is 1m long. **b)** Hand specimen of BNB-95-110c, the fabric defined by foliation of biotite and quartz-rich bands is easily observed. **c)** Photomicrograph of BNB-95-110c in thin section, crossed Nicols. Composed of tartan-twinned microcline, quartz and minor plagioclase. Grains are randomly oriented, with roughly 120° boundaries, consistent with an igneous origin. The lobate grain boundaries suggest some degree of strain recovery. Note sericitized plagioclase in the lower right corner. Field of view is 2 mm.

Fig 2.4 Thin section photomicrographs of zircons *in situ*. **a)** Relatively euhedral, clear, and inclusion-free zircon at grain boundary between quartz and feldspar, viewed under crossed Nichols. Field of view is 0.5 mm. **b)** Plane-polarized light image of a subhedral rust-coloured, turbid, highly included zircon, surrounded by a thick rim of calcite. Field of view is 1 mm. **c)** Crossed Nicols image of zircon shown in (b). Field of view is 1 mm.

(a)

(b)

Fig. 2.4

(c)

Fig 2.5 Transmitted light photomicrograph of zircons separated from BNB-95-110c. Zircons are faceted and are interpreted to be of igneous origin. The cores of some crystals contain a number of inclusions.

Fig. 2.5

Fig. 2.6 Back-scattered electron images of zircons separated from sample BNB-95-110c. (a) Grain e26; A typical example of patchy zircon composed of lighter grey, unaltered regions and darker grey, altered regions. (b) Grain C22; patchy zircon lightly etched with HF, composed of altered and unaltered domains. Strong zoning observed in altered domains and faint zoning observed in the unaltered domains. (c) Grain d5; patchy zircon, unetched. (d) Grain d5; etched.

Fig. 2.6 cont'd (e) Grain c7; patchy zircon, etched. (f) Grain d15; uniformly altered zircon, unetched. (g) Grain e3; note the irregular light grey rim and patches (top edge of grain) and cross-cutting zircon "micro-dyke". (h) Grain c16; contains a zircon "micro-dyke" that cross-cuts oscillatory zoning

Fig 2.6 cont'd.

Fig 2.6 cont'd (i) Grain e19; uranothorite replacing margin of zircon, note the penetration of bright veins into the zircon. (j) Grain e20; zircon containing large, bright uranothorite inclusion. (k) Grain c1; zircon containing large, bright uranothorite inclusion.

Fig. 2.6 cont'd.

Fig 2.7 (a) Concordia diagram for zircon with less than 50 ppm ^{204}Pb , and $^{204}\text{Pb}/^{206}\text{Pb} < 10^{-4}$ (see Groups 1 and 2 in text). Error reported at the 2σ level. **(b)** Detail of concordia curve showing SHRIMP results for zircon with low common Pb (see Group 1 in text). Error reported at the 1σ level.

Fig. 2.7

Fig 2.8 Concordia diagram of SHRIMP results for zircon with greater than 50 ppm ^{204}Pb , and $^{204}\text{Pb}/^{206}\text{Pb} > 10^{-4}$ (see Group 3 in text). Error reported at the 2σ level.

Fig. 2.8

Fig 2.9 Plot of discordancy vs. $^{204}\text{Pb}/^{206}\text{Pb}$. In this case discordancy refers to the disagreement between the measured $^{206}\text{Pb}/^{238}\text{U}$ ratio with the expected $^{206}\text{Pb}/^{238}\text{U}$ ratio for a 2.87 Ga rock ($^{206}\text{Pb}/^{238}\text{U}_{\text{expected}}$) at 2.87 Ga = 0.5632). It is calculated using the following equation.

$$\text{Discordancy} = 100 - (^{206}\text{Pb}/^{238}\text{U}_{\text{measured}} / ^{206}\text{Pb}/^{238}\text{U}_{\text{expected}}) * 100$$

Such a calculation considers the discordance along the y-axis only. See text for explanation.

Fig. 2.9

Fig 2.10 Concordia diagram for SHRIMP analyses collected from recrystallized tips, rims and crystal-scale dykes (see Group 4 in text). Error reported at the 2σ level.

Fig. 2.10

Fig 2.11 Probability density diagram of the distribution of uranothorite ages. See text for discussion.

Fig. 2.11

Fig 2.12 (a) Plot of discordance vs. U content. **(b)** Plot of discordance vs. radiation dose. The dashed line represents the dosage threshold where partially metamict zircon becomes completely metamict (from Murakami et al., 1991). See text for discussion.

Fig. 2.12

CHAPTER 3

CHEMISTRY OF UNALTERED AND ALTERED ZIRCON

3.1 INTRODUCTION

Ideal zircon contains 67.1 wt% ZrO₂ and 32.9 wt% SiO₂ but more than 50 different minor and trace elements have been reported (Speer, 1982). The most common substitutions in the Zr site are tetravalent U and Hf. Rare earth elements (REE) are also common trace constituents in zircon. They are incorporated in eight-fold coordination in the Zr site of the zircon structure (Speer, 1982). Within the REE group, the ionic radii of the atoms become progressively smaller, and more similar to the radius of Zr⁺⁴, with increased atomic number, a trend known as the lanthanide contraction. The typical zircon REE pattern on a Masuda-Coryell chondrite-normalized diagram, depicting depletion in the larger light REE (LREE) and significant enrichment of smaller heavy REE (HREE), is due to the lanthanide contraction (Murali et al., 1983; Hinton and Upton, 1991; Nagasawa, 1975; Heaman et al., 1990; Gromet and Silver, 1983).

There is a charge disparity between Zr⁺⁴ and the REE, which are generally trivalent in nature, therefore an accompanying charge-balancing substitution is required. The most often cited substitution mechanism is the "xenotime replacement" where phosphorus and silicon are the charge balancing species according to the following reaction (Speer, 1982, Romans et al., 1975):

However studies on REE in zircon by Cherniak et al. (1997) have suggested that natural zircons rarely contain adequate P to compensate for the charge disparity and that defects such as oxygen centers are created to neutralize the charge imbalance.

A number of impurities, including Hf, Th, U, minor REE and P, are variably incorporated in all natural zircons during primary crystallization. However other, more extreme, variations in chemistry have been observed and have been attributed to chemical alteration. Steiger and Wasserburg (1969) were the first to suggest that discordant zircon are composed of concordant domains and highly discordant "hot spots". Krogh and Davis (1974, 1975) expanded on the concept of mixing concordant and discordant domains. Through HF dissolution experiments, they suggested that chemical alteration was the cause of discordance in their study sample. The alteration in these samples was confined to discrete zones and was characterized by a decrease in Si and Zr, a pattern which is suggestive of hydration. As well, increased Fe, Al and Ca concentrations were observed in the altered zones (Krogh and Davis; 1974, 1975). Similar results were observed by Gupta et al., (1998) from chemical analyses of altered zircon.

3.1.1 Aims of Study

The purpose of this chapter is to characterize and compare the chemistry of altered and unaltered portions of zircon from sample BNB-95-110c. Electron microprobe analyses yielded information about the major and minor element chemistry. Trace and rare earth element chemistry was established using the SHRIMP. The geochemical patterns are used to place constraints on the mechanism of alteration.

3.2 ANALYTICAL METHODS

3.2.1 Electron Microprobe Analysis (EMPA)

Major and trace element chemical data for sample BNB-95-110c were obtained by wavelength-dispersive analysis using a Cameca SX50 instrument at the Geological Survey of Canada, Mineralogy Division. Mount IP102, (preparation of this mount is

described in Chapter 2) was carefully cleaned and carbon-coated before analysis. Concentrations of both major (Zr, Si) and minor (U, Th, Hf, Ca, Fe, P, Mn, Al and Y) elements were obtained. Care was taken to ensure that all internal domains of sample BNB-95-110c, described in Chapter 2, were targeted for analysis. An accelerating voltage of 20 keV and a beam current of 10nA was used for these analyses. Synthetic zircon was used as the Zr and Si standard, and synthetic hafnon was used as the Hf standard, both of which were provided by Dr. J. Hanchar (George Washington University). Natural minerals and pure metals were used as standards for the other elements. ZAF (atomic number-absorption-fluorescence) matrix corrections were applied on-line to the raw data. Analytical uncertainties (2σ) for major (elemental wt.% > 1, excluding Ca) and minor elements (elemental wt.% < 1, including Ca) are reported at 2% and 20%, respectively. A complete table of the electron microprobe experimental setup, including detection limits, is presented in Appendix C.

3.2.2 Elemental Maps

Qualitative elemental maps were generated using the Cambridge Instruments SEM on a select number of grains. The electron beam was rastered over the entire grain, and an energy-dispersive detector was used to collect the secondary x-rays. The elements mapped were Si, Zr, U, Th, Hf, Ca, and Al. It was hoped that the distribution of elements in the zircon would generate patterns that would elucidate the processes that are responsible for the observed internal structures, alteration and isotopic behaviour of the sample.

3.2.3 REE Ion Probe

Mount IP 102 was used for REE analyses and was prepared according to the description given in chapter 2. A coating of 8 nm of high purity gold was applied to prevent charging. Sputtering of the sample employs a mass-filtered O_2^- primary ion beam with beam current of roughly 4 nA. The beam was rastered across the analysis area for 1 minute to remove the gold coating and any associated contamination. Twenty-five isotopes (listed below) were collected over 4 scans. The large radius SHRIMP II ion microprobe uses the high mass resolution of the instrument to resolve isobaric interferences between the isotopes, permitting the highest possible secondary ion signal strengths. The mass resolution (1% definition) under these conditions is 7000, and the flat-tops on the peaks are 0.010 atomic mass units wide at mass 208. This working mass resolution eliminates all known isobaric interferences for the particular isotope species analyzed: ^{89}Y , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{147}Sm , ^{151}Eu , ^{155}Gd , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{175}TbO , ^{175}Lu , ^{185}TmO , ^{189}YbO , $^{196}Zr_2O$, ^{196}HfO , ^{248}ThO , ^{254}UO (Stern, 1999).

Calibration was done using BR266, a gem quality zircon believed to originate from Sri Lanka, which is embedded on a separate "set-up" mount with other standards. From extensive testing, the standard is reported to be homogeneous in trace elements to $\pm 2\%$ (Stern, 1999). The absolute abundances of the major, minor and trace elements in the zircon standard were determined using laser ablation ICP-MS at MacQuarie University, in Sydney, Australia. With this information, the absolute abundances in unknown zircon samples can be calculated from the measured ratios (Stern, 1999).

The analytical uncertainties reported for trace element concentrations from BNB-95-110c vary from 0.6% to 6.9% depending on the element, and take into consideration

the counting errors, and analytical scatter in the standard data. The error associated with the LA-ICP-MS measurement of the absolute abundances of the trace elements from the standard is not considered. The detection limit of the trace elements using this technique is ~2 ppb.

3.3 RESULTS

3.3.1 Electron Microprobe Major and Minor Element Analyses

Electron microprobe (EMPA) results are presented as elemental weight percents in Table 3.1. The labeling system for EMPA data is similar to that of the geochronology data, and includes the mount number, magnetic susceptibility, grain number and spot number. However, each spot number is given the prefix “e” to distinguish it from ion probe spots. Most analyses were obtained close to areas that had been analyzed by other techniques such as ion probe and Raman microprobe, and the corresponding ion microprobe U-Pb and REE spots are noted.

The total sums of the oxides vary from 102.11% to roughly 95%. The Zr and Si contents of unaltered zircon domains (bright in BSE) cluster near the stoichiometric values of 15.32 wt% Si and 49.76 wt% Zr. However, altered zircon domains (dark in BSE) have lower Si and Zr contents (Fig. 3.1a). A similar trend would be anticipated with increased substitution of Hf for Zr; however, such a trend is not observed, as low Zr is accompanied by lower Hf contents (Fig. 3.1b). The low Zr and Si contents correspond with low combined oxide totals (Fig. 3.1c). This suggests that altered zircon domains have incorporated a hydrous component and that the lower Si and Zr concentrations result from the constant sum effect.

The only other major or minor element detectable by EMPA to show significant variation is Ca. Altered zircon domains generally contains higher concentrations of Ca than unaltered domains, as Ca contents increase with decreasing values of Si and with increasing U content (Fig. 3.2a, b respectively). Although Pb isotopic data was not collected from specific grains analyzed for Ca by EMPA, elevated concentrations of both Ca and ^{204}Pb are observed in dark (in BSE) domains. From this observation we suggest concomitant addition of Ca and Pb during alteration. This result is not unexpected as both Ca and Pb are divalent cations, and have comparable ionic radii (1.12Å for Ca and 1.29Å for Pb, both in 8-fold coordination).

Despite the incorporation of Ca, Pb, and a hydrous component, altered and unaltered zircon domains maintain a constant Si/Zr ratio (Fig. 3.2c). The dashed line on Figure 3.2c represents the Si/Zr ratio of perfect ZrSiO_4 . The data for the BNB-95-110c zircons fall slightly above this line due to the incorporation of Hf, U, and Th during crystallization. The constant Si/Zr ratio demonstrates that zircon stoichiometry is maintained, and that alteration does not produce a distinct secondary phase.

3.3.2 Elemental Mapping

The elemental maps of Si, Zr, Hf, U, Th, Al, and Ca for grain BNB-95-110c-e19 are presented in Figure 3.3. Figure 3.3a is the backscattered electron image of the crystal. This is a patchy zircon, with a high density of inclusions in the centre of the crystal. Some of the primary oscillatory zoning is preserved in the intact tip of the crystal. The broken end of the crystal is characterized by much brighter back-scattered electrons than the majority of the grain, indicating the presence of a secondary phase. The elemental maps indicate that this bright phase is rich in U, Th and Ca and these three elements form

a network of channels within the zircon. Apart from the U and Th- rich veins that penetrate the broken end of the grain, U, Th, Hf, and Zr appear to be homogeneously distributed in the bulk of zircon grain 110c-E19. However, elemental mapping by electron microprobe is a relatively insensitive technique, and apparent homogeneity will result in cases where the variations in chemistry are small. Consequently, this technique is only useful for identifying large-scale variations in chemistry. The Si and Ca maps are heterogeneous, indicating dramatic differences in the distribution of these elements. The bright, Si-rich domain in the centre of the grain is cross cut by a series of darker veins (lower in Si). Low Si is a characteristic of the alteration seen in these zircons (see the EMPA data) and it appears that alteration occurs as a network of channels or as large domains within parts of the grain. The Ca distribution is the most dramatic of all the elements mapped for this grain. The pattern visible in the Ca X-ray map corresponds inversely with the back scattered image (areas that are bright in BSE are dark in the X-ray map). The decrease in average atomic number or density that leads to dark BSE images is correlated with the presence of Ca in the zircon.

3.3.3 Ion Probe Trace and Rare Earth Element Analyses

Table 3.2 presents trace element data from selected zircon domains. The same labeling system was used for the trace element analyses as for the SHRIMP U-Pb analyses (see Table 2.1 for explanation). Most spots are spatially correlated with EMPA analyses.

Appendix D contains Masuda-Coryell diagrams for each grain, and multiple spots from a single grain are present on a single diagram for comparison. The C1 chondrite values of Sun and McDonough (1989) were used for normalization. All spots have

positive Ce anomalies, consistent with incorporation of Ce^{+4} during the growth of the zircons. With few exceptions, domains of both bright and dark zircon yield typical REE patterns with depletion in the LREEs and enrichment in the HREEs. Four altered areas (spots d6.1, c5.2, c24.1, and e19.1) as well as two spots on new zircon overgrowths (e3.1 and c7.1) are exceptional as they are highly enriched in the LREEs whereas the HREEs remain consistent with the other spots. A number of the plots in Appendix D contrast the REE patterns from analyses of altered and unaltered spots. The altered areas generally have higher LREEs than corresponding bright areas on the same grain, while the HREEs remain consistent. HREEs content, from Gd to Lu is strongly correlated with the U content for each spot as illustrated in Figure 3.4. There is also an excellent correlation between the LREE and U for all but the six spots listed above which are particularly enriched in the LREE (Fig. 3.5).

In addition to REEs, other trace elements analyzed using the SHRIMP II include P and Ba. Ion probe analyses of phosphorus on sample BNB-95-110c range from 38 - 683 ppm, with a median of ~150 ppm. This is inadequate to account for the total REE content and it is likely that the charge imbalance is accounted for by oxygen centres, as suggested by Cherniak et al. (1997).

Ba contents are variable, ranging from 9 ppb to 583 ppm, however 70% of analyses have Ba concentrations less than 100 ppm. There is little correlation between Ba content and REE content, however, there is a moderate correlation with U content (Fig. 3.6). There is also a strong correlation between the Ba content measured by ion probe and the Ca content determined by electron microprobe (Fig. 3.7). This correlation is expected, as the two elements are both divalent, alkali earth metals.

3.4 DISCUSSION

A critical question is whether the higher LREE content in the altered areas is primary or a result of alteration. For example, did the alteration occur preferentially in zones of high primary LREE, and accompanying high U because they would have a more distorted lattice making them more susceptible to alteration, or was there input of LREEs during alteration? The excellent positive correlation between U, a primary element in zircon, and the REE, is compatible with a primary REE signature. However, the shapes of the Masuda-Coryell diagram argue otherwise. The shape of the REE profile is controlled by the configuration of the crystallographic site which houses the REE. The size of this site is not affected by the temperature or chemistry of the magma (Gromet and Silver, 1983). Consequently the profile of REEs incorporated during primary crystallization is consistent. The altered zircon domains display an enrichment in the LREE elements compared with unaltered zircon domains. Consequently we conclude that the enriched LREE signatures of altered zircon domains are due to a secondary process such as alteration. This conclusion is similar to that reached by Heaman et al. (1990) who found, by analyses of entire zircon grains with differing magnetic susceptibility, a gradual increase in REE content with increasing magnetic susceptibility. They also suggested that an external influence such as alteration lead to the increase in REE content.

As with Ba, Ca is weakly correlated with U. Domains with high U contents are generally enriched in Ca, however there is a large degree of scatter in the Ca concentrations (Fig. 3.2b). There is no correlation between Ba or Ca content and Eu content, a divalent rare earth element, (Fig. 3.8 a, b) that is incorporated into the crystal

during growth. This suggests that the zircon was enriched in Ba and Ca during a secondary process such as alteration. The presence of Ca in discordant zircon has been noted by other workers and is also attributed to an alteration process (Krogh and Davis, 1974, 1975; Gupta et al., 1998).

The lack of correlation between Ca, Ba and other elements such as P argue against the presence of secondary phases hosting those elements. For example if the Ca was present as apatite intergrowths then there should be a strong correlation with P. The relationship of Ca to the zircon structure is further examined with transmission electron microscopy (Chapter 4).

3.5 CONCLUSIONS

1. Altered zircon domains (dark in BSE) are characterized by a depletion in Zr and Si content and low totals for the sum of the oxides, but stoichiometric Zr/Si is maintained.
2. Altered zircon domains are characterized by enrichments in Ca, Ba and the LREEs as compared to unaltered zircon domains.
3. Ca, Ba and LREE are believed to have been introduced into the zircon system during solid state alteration, rather than during primary igneous crystallization.

Table 3.1

Electron microprobe data for sample BNB-95-110c, puck IP102.

- signifies analysis below the detection limit for that element.

The labeling system used is the same as that described for Table 2.1.

Concentrations are presented as elemental weight percent (wt%).

The final two rows indicate corresponding label for REE and U-Pb analyses from the same grain

Table 3.1

Labels feature	c11-e1 dark	c22-e1 bright	c22-e2 bright	c22-e4 dark	c7-e1 bright	c7-e2 bright	c7-e3 bright	c7-e4 bright	c5-e1 bright	c2-e1 dark	c16-e2 dyke	c16-e3 dyke	c16-e5 dyke	c17-e1 dyke	c19-e2 tip
Al	0.08	-	0.02	-	-	0.03	-	-	-	0.07	-	0.11	-	0.05	-
Si	14.66	15.54	15.58	14.94	15.61	14.61	15.14	15.5	15.57	14.27	14.99	15.02	15.5	15.55	15.46
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca	2.03	-	-	0.08	-	0.42	-	-	-	2.28	-	0.12	-	0.1	-
Mn	0.05	-	-	-	-	-	-	0.07	-	-	-	-	0.05	-	-
Fe	-	-	-	-	-	-	-	-	-	-	-	0.08	-	-	-
Y	0.11	-	-	-	-	-	-	-	-	0.13	-	0.11	-	-	-
Hf	1.4	1.48	1.6	1.4	1.69	1.4	1.44	1.46	1.59	1.33	1.46	1.6	1.67	1.9	1.62
Zr	44.87	48.36	48.53	46.97	48.31	46.56	49.9	48.09	48.14	44.09	47.06	48.84	49.08	48.42	47.03
U	0.33	0.13	0.08	0.2	0.14	0.28	0.14	0.08	0.09	0.37	0.11	0.12	0.12	-	0.09
Th	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
oxide totals	97.16	100.47	100.91	97.42	100.80	96.76	101.67	100.04	100.32	95.56	97.47	100.73	101.62	101.16	98.62
REE spot	c11.1	c22.1		c22.2	c7.2	c7.3	c7.1,4.5	c7.1,4.5		c2.1					
UPb spot							c7.1	c7.1			c16.2	c16.3		c17.1	c19.2

Labels feature	c23-e1 tip	c23-e2 tip	c23-e3 tip	c24-e2 dark	c24-e1 dark	d28-e1 bright	d28-e2 dark	d5-e1 bright	d5-e2 tip	d5-e3 tip	d5-e4 tip	d7-e1 bright	d7-e2 tip	d7-e3 tip	d15-e1 dark
Al	0.18	-	-	0.1	0.04	-	0.05	-	-	-	-	-	-	-	-
Si	15.06	15.73	15.55	14.68	14.44	15.64	14.89	15.54	16.05	15.4	15.7	15.61	15.52	15.52	14.42
P	-	-	-	-	0.05	-	-	-	-	-	-	-	-	-	-
Ca	0.32	-	-	0.74	1.89	-	0.82	-	-	-	-	-	0.02	0.04	1.92
Mn	-	-	0.06	0.08	-	-	-	-	-	-	-	-	0.04	-	-
Fe	0.07	-	-	-	-	-	0.08	-	-	-	-	-	-	-	0.08
Y	-	-	-	0.14	0.15	-	-	-	-	-	-	-	-	-	0.12
Hf	2.39	1.74	1.89	1.45	1.42	1.44	1.47	1.45	1.68	1.59	1.96	1.38	1.84	1.85	1.37
Zr	44.75	48.14	49.18	45.72	45.46	48.32	45.77	48.72	47.37	47.95	48.29	48.25	47.64	47.74	44.01
U	0.13	0.09	0.1	0.34	0.3	0.13	0.23	0.16	0.07	0.1	0.08	0.19	0.12	0.08	0.34
Th	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
oxide totals	96.53	100.84	102.11	96.77	97.35	100.58	97.00	100.95	100.38	99.70	101.23	100.42	99.95	100.02	95.23
REE spot				c24.2	c24.1	d28.1	d28.2	d5.1				d7.1			d15.1
UPb spot	c23.1	c23.2,4	c23.2						d5.3	d5.1	d5.2		d7.1	d7.2	

Table 3.1 cont.

Labels feature	d6-e1 dark	d12-e1 dark	e26-e1 bright	e26-e2 dark	e26-e3 tip	e26-e4 bright	e19-e1 dark	e19-e3 nr. incl	e19-e2 bright	e3-e1 dark	e3-e2 tip	e3-e3 tip	e3-e4 tip	e3-e6 tip	e3-e7 tip
Al	0.08	0.05	-	-	-	-	-	-	-	0.07	-	-	0.23	-	-
Si	14.86	14.69	15.52	14.77	15.51	15.71	14.43	15.25	15.58	14.34	15.66	15.6	15.44	16.01	15.98
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca	1.37	1.21	-	0.68	-	-	1.13	0.75	-	2.11	0.02	-	0.42	-	-
Mn	-	-	-	0.06	0.07	-	-	-	0.06	-	-	-	-	-	-
Fe	-	-	-	0.08	-	-	0.52	0.09	-	0.54	-	-	0.16	-	-
V	-	-	-	0.09	-	-	0.1	-	-	0.13	-	-	-	-	-
Mg	1.3	1.44	1.48	1.37	1.68	1.65	1.35	1.44	1.72	1.3	1.45	1.43	1.39	1.63	1.48
Zr	45.12	46.2	48.36	47.64	49.37	47.82	46.34	47.13	46.57	44.43	48.08	48.53	45.03	48.31	46.87
U	0.31	0.3	0.18	0.21	0.09	0.1	0.35	0.29	0.11	0.33	0.08	0.1	0.13	0.07	0.11
Th	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
oxide totals	96.69	97.64	100.49	99.05	102.06	100.28	97.83	99.46	98.47	96.54	100.27	100.73	96.88	101.52	99.38
REE spot	d6.1	d12.1	e26.1	e26.2	e26.1	e26.2	e19.1			e3.2	e3.12	e3.11	e3.9	e3.13	e3.13
U/Pb spot					e26.1	e26.2	e26.2			e3.4	e3.3	e3.8	e3.5	e3.17	e3.4

Table 3.2 REE concentrations for sample BNB-95-110c, puck IP102.

The labeling system used is the same as that described for Table 2.1.

EMPA results are given for corresponding analyses.

REE and major/minor element concentrations are presented in ppm.

***Percentage error, accounts for uncertainties in the counting statistics and reproducibility of the standard.**

- signifies analyses below the detection limit of 2 ppb.

Table 3.2 cont.

Element (ppm)	A8.1 dark	B24.1 dark	B8.1 bright	E3.1 tip	E8.1 bright	E20.1 dark	C16.1 dark	C7.1 tip	C7.2 bright	C7.3 dark	C11.1 v.dark	C24.1 v.dark	C24.2 dark	D7.2 dark	D5.2 dark	E19.1 v.dark	E8.2 dark	E3.2 dark
Ba	193	249	0.051	9.0	0.32	21	8.0	4.4	0.41	39	290	258	6.4	3.2	2.4	51	1.0	208
La	0.053	0.086	0.038	3.5	0.010	0.034	0.003	2.4	0.084	0.025	0.23	4.9	0.16	0.35	0.11	2.3	0.002	0.61
Ce	13	21	4.8	24	11	8.3	9.5	15	4.5	8.4	10.3	33.2	6.4	6.0	8.4	30	11	11
Pr	0.012	0.028	0.005	3.1	0.019	0.035	0.010	0.88	0.14	0.020	0.021	4.8	0.054	0.020	0.060	2.4	0.019	0.16
Nd	0.14	0.48	0.062	17	0.29	0.32	0.20	7.8	1.0	0.21	0.22	23.0	0.28	0.22	0.40	13	0.48	0.85
Sm	1.3	2.4	0.34	5.6	1.4	1.1	1.0	5.2	0.71	0.94	1.3	5.4	0.83	0.54	0.94	4.8	1.3	1.7
Eu	0.32	0.45	0.084	1.4	0.25	0.30	0.17	0.49	0.18	0.24	0.25	1.0	0.13	0.13	0.20	5.0	0.24	0.33
Gd	23	34.8	4.6	8.3	20.5	12.4	20	9.0	4.1	14	16	20	13	7.8	14	19	22	16
Tb	3.9	3.6	1.3	1.1	4.3	4.1	4.0	2.2	1.3	3.7	4.4	4.4	3.2	2.4	3.4	5.0	4.1	4.5
Dy	139	195	37	16	132	76	120	31	28	76	101	97	81	50	85	90	130	107
Ho	65	91	18	9	59	33	58	13	13	33	47	43	37	23	40	40	58	48
Er	380	548	112	72	342	185	345	85	77	181	273	239	215	134	233	225	327	275
Tm	49	40	18	22	47	42	43	24	17	39	50	45	38	28	39	52	39	49
Yb	565	453	221	332	519	492	512	318	208	438	591	541	433	329	445	637	452	590
Lu	290	415	82	117	243	108	254	82	56	111	182	150	148	93	159	144	230	180
Y	2376	3471	644	371	2080	1136	2032	543	435	1129	1703	1529	1353	857	1473	1432	2144	1645
Hf	21777	33123	17689	17826	24263	17139	23632	20428	20283	17392	17530	18135	19896	16596	17967	18301	23938	18432
Th	306	479	72	30	302	254	231	33	48	249	277	201	132	128	217	217	306	297
U	4439	4923	1106	810	3838	3218	3764	772	1013	3064	3965	3393	1875	1917	2924	3922	3952	3743
P	122	39	69	121	87	227	137	291	125	156	271	260	121	154	164	443	77	242
Corresponding EMPA analyses																		
Al											800		1000					700
Si								151400	156100	146100	146600	144400	146800			144300		143400
P												500						
Ca										4200	20300	18900	7400			11300		21100
Mn																		
Fe																		
Y																		
Hf								14400	16900	14000	1100	1500	1400			5200		5400
Zr								499000	483100	465600	448700	454600	457200			1000		1300
U								1400	1400	2800	3300	3000	3400			463400		444300
Th																3500		3300

Fig. 3.1 Plots of EMPA results. **a)** Zr vs. Si. **b)** Hf vs. Zr. **c)** Oxide totals vs. Si. Open circles (○) represent analyses from unaltered zircon domains that appear bright in BSE images, closed circles (●) represent analyses from altered zircon domains that appear dark in BSE images, open triangles (Δ) represent analyses from zircon dykes or tips. Error bars represent the average 2% uncertainties in the Zr, Si, and Hf concentrations and sum of the oxides. See text for discussion.

Fig 3.1

Fig. 3.2 Plots of EMPA results. **a)** Si vs. Ca. Error bars represent average 2% uncertainty for Si concentrations and 20% uncertainty for Ca. **b)** U vs. Ca. Error bars represent average 20% uncertainties for U and Ca concentrations. **c)** Si/Zr vs Si. Error bar represents average 4% uncertainty for Si/Zr ratio. This plot illustrates that zircon stoichiometry is retained during alteration and that the decreasing Zr and Si concentrations are the result of dilution. The dashed line represents the Si/Zr of perfect ZrSiO_4 . $\bigcirc$ = unaltered zircon domains; $\bullet$ = altered zircon domains; Δ = dykes or tips. See text for discussion.

Fig. 3.2

Fig. 3.3 Element distribution maps for zircon grain e19. **a)** BSE image of grain e19.
b-h) Elemental maps; the specific element is noted in the top-left corner of the image.
See text for discussion.

Fig. 3.3

Fig. 3.3 cont'd.

Fig. 3.4 Plot of two HREE (Dy and Lu) concentrations vs. U, as measured by SHRIMP.
a) Dy analyses are represented by squares: □ = unaltered zircon domains (bright in BSE); ● = altered zircon domains (dark in BSE); ⊞ = tips. **b)** Lu analyses are represented by circles: ○ = unaltered zircon domains (bright in BSE); ● = altered zircon domains (dark in BSE); ⊙ = tips. Error limits are within the symbols.

Fig. 3.4

Fig. 3.5 Plot of two LREE (Ce and Sm) concentrations vs. U, as measured by SHRIMP.
a) Ce analyses are represented by circles: ● = unaltered zircon domains (bright in BSE); ● = altered zircon domains (dark in BSE); ⊙ = tips. **b)** Sm analyses are represented by squares: □ = unaltered zircon domains (bright in BSE); ● = altered zircon domains (dark in BSE); ⊞ = tips. Error limits are within the symbols.

Fig. 3.5

Fig 3.6 Plot of SHRIMP results. Ba vs. U. $\bigcirc$ = unaltered zircon domains; $\bullet$ = altered zircon domains; Δ = dykes or tips. Error limits are within the symbols. See text for discussion.

Fig. 3.6

Fig. 3.7 Plot of Ca (as measured by EMPA) vs. Ba (as measured by SHRIMP) for select spots analysed by both methods. Error bar represents average uncertainty of 20% for Ca concentrations, errors for Ba concentrations are within the limits of the symbols. ● = unaltered zircon domains; ● = altered zircon domains; Δ = dykes or tips. See text for discussion.

Fig. 3.7

Fig. 3.8 Plot of Ca (as measured by EMPA) and Eu, Ba (as measured by SHRIMP). **a)** Ba vs. Eu. Inset is a detail of the cluster of data near origin. **b)** Ca vs. Eu. **○** = unaltered zircon domains; **●** = altered zircon domains; **Δ** = dykes or tips. See text for discussion.

Fig. 3.8

CHAPTER 4

CRYSTAL STRUCTURE OF ALTERED AND UNALTERED ZIRCON

4.1 INTRODUCTION

As was mentioned in previous chapters, the U-Th-Pb systematics of zircon are subject to disturbance, most commonly the loss of radiogenic Pb. Early in the study of geochronology, the correlation between the concentration of radioactive elements and discordant isotopic systematics was noted. It was therefore suggested that metamictization, crystal lattice damage caused by the decay of the radioactive elements, was related to discordance by facilitating the loss of radiogenic Pb (Silver and Deutsch, 1963). It has been proposed that radiation damage results in a network of pathways and that these channels facilitate the transport of Pb out of the crystal.

Metamictization of zircon has been studied extensively, as it has serious implications for geochronology and is of concern to scientists addressing the issue of radioactive waste storage. The zircon structure has been proposed as a host phase for nuclear waste (Harker and Flintoff, 1984). In order to avoid environmental contamination by radionuclides leached from the storage material, it is necessary to understand the effects of radiation damage on the crystal lattice.

Metamictization is largely caused by the nucleic recoil of U and Th during alpha decay. The bombardment of the crystal lattice by large nuclei progressively distorts and eventually destroys the crystal lattice (Holland and Gottfried, 1955; Chakoumakos et al., 1987; Murakami et al., 1991). More recently it has been shown that the degree of metamictization is heterogeneously distributed on the microscale due to intra-grain

variations in U and Th concentrations (Nasdala et al., 1996; Chakoumakos et al., 1987). Consequently, the Pb-loss behaviour can vary on the scale of a single zircon grain.

Although the cause of metamictization is believed to be well-constrained, the nature of metamict zircon has been the subject of debate. Early workers suggested that the structure of metamict zircon consisted of misoriented zircon crystallites (Bursill and McLaren, 1966), or a mixture of SiO_2 and ZrO_2 (Wasilewski et al., 1973, Ellsworth et al., 1994). More recent studies of laboratory annealed zircon suggest that heating of metamict zircon results in breakdown of the silicate structure to the oxides (McLaren et al., 1994). X-ray diffraction and high resolution transmission electron microscopy (HRTEM) studies are not consistent with either of these models, however (Farges and Calas, 1991). A structure composed of mixed crystalline and amorphous microdomains (Chakoumakos et al., 1987) or amorphous ZrSiO_4 (Holland and Gottfried, 1955) is more compatible with these studies.

Geochronologists often describe zircons as metamict, as though it is an observable physical characteristic, like its colour. However the definition of metamict zircon is much more complicated. A zircon is said to be metamict when a certain well-defined radiation dose results in changes to the physical or x-ray (or electron) diffraction behaviour of the mineral. Radiation dose is calculated as the number of alpha-events that occurred per mg of sample. The calculation, as given in Holland and Gottfried (1955), factors in the age, and U and Th concentrations of the sample (Appendix B). In their classic paper, Holland and Gottfried (1955) state that at or above a dose of 0.45×10^{16} α -events/mg zircon no longer yields X-ray diffraction peaks and the expansion of the zircon lattice ceases. At this point a zircon is considered metamict. Three stages of

metamictization are defined by Murakami et al (1991), each defined by a specific dose and electron diffraction pattern. According to their study, complete loss of electron diffraction spots and X-ray diffraction maxima, and hence complete metamictization occurs at a dose of 0.8×10^{16} α -events/mg. However even these definitions are too simple. X-ray diffraction intensity decreases asymptotically with increasing radiation dose (Salje et al., 1999). For this reason there is no single dose at which diffraction patterns disappear and consequently the transition to amorphous zircon cannot be considered a sharp phase change. The difficulty in defining metamictization is exacerbated by the fact that the sensitivity with which X-ray diffraction patterns are detected depends upon sometimes poorly defined experimental conditions. In their study, Salje et al. (1999) are able to observe clear X-ray diffraction peaks from samples originally characterized as completely metamict. Indeed the transition to metamict zircon should be considered a "percolation" phase change, where the transition occurs when the minor component, in this case the volume of amorphous zircon, becomes the major component of the grain (Salje et al., 1999). The percolation transition is proposed to occur at 0.35×10^{16} α -events/mg (Salje et al., 1999), roughly the same radiation dose reached by Holland and Gottfried (1955) and Murakami et al. (1991). These studies illustrate complications often overlooked by geochronologists. The term "metamict" has quantitative implications and does not imply a clear phase transition to a completely amorphous state. An understanding of the limitations on our definition of the metamict state is necessary if we are going to draw conclusions about the effect of metamictization on geochronology. For the remainder of this chapter I intend to use the dose thresholds of

Holland and Gottfried (1955) and Murakami et al. (1991) when referring to metamict or non-metamict zircon.

4.1.1 Aims of Study

It should be mentioned that metamictization only enhances the likelihood of Pb-loss, but it does not cause Pb-loss. Another driving mechanism, such as diffusion, alteration or recrystallization, is required to mobilize the Pb. Zircons from sample BNB-95-110c have been extensively altered and it is believed that the alteration is largely responsible for the observed Pb-loss. This portion of the study is an attempt to understand the relationship between metamictization, alteration and Pb-loss in BNB-95-110c. By combining SHRIMP geochronology data with Raman spectroscopy and transmission electron microscopy (TEM) we examine the nature and degree of crystallinity of variably concordant zircons. The high spatial resolution of the instruments used makes them ideal to address questions regarding the effect of microstructure on Pb-loss. With the increased use of microsampling techniques in geochronology, such as ID-TIMS analysis of fragments of single grains, SHRIMP, and laser ablation ICP-MS, an understanding of the grain scale processes that lead to Pb-loss and discordance is necessary. With this study, we hope to clarify the role of microstructure in zircon alteration and Pb-loss processes.

4.2 ANALYTICAL METHODS

4.2.1 Raman microscopy

The Raman microprobe is a vibrational spectroscopic tool used primarily by geologists in the identification of mineral and fluid inclusions. However recent works by Nasdala et al. (1995, 1996, 1998) and Wopenka et al. (1996) have shown its usefulness in

quantifying the degree of metamictization of zircon. A typical Raman apparatus consists of a laser source, the sample and a high stray-light-rejection spectrometer. Intense monochromatic light from the laser is focused through a series of lenses or mirrors onto the sample. While the majority of the light is transmitted through a non-opaque sample, a small portion of it is scattered. Of the scattered component, most maintains the same wavelength as the incident light, known as Rayleigh scattered light. However a small component is scattered at a wavelength slightly higher or lower than that of the incident light. The change in wavelength of scattered light is known as the Raman effect and is illustrated in Figure 4.1. The scattered light is collected and its wavelength recorded by the spectrometer, and the data are presented as a plot of relative change in wavenumbers (the difference between the reciprocal of wavelengths of Rayleigh and Raman scattered light) against intensity.

The basis of the Raman effect can be explained using simple energy diagrams (Fig. 4.2). The vibrations of atoms within the crystal lattice of a mineral are quantized. A quantum of vibrational energy is known as a phonon. As light interacts with the vibrations of the crystal lattice, some of the energy from the photon may be transferred to one of the phonons, exciting the system to a higher vibrational state. The photon is therefore scattered at a lower frequency having lost some of its energy to the vibrational excitation. The reverse process is also possible, where an excited vibrational state transfers a phonon to the incoming photon and the scattered light is thus more energetic. Not all vibrational modes of a molecule or crystal-lattice contribute to the Raman effect. For a vibration to be “Raman active” the vibration must lead to a change in the polarizability of the molecule or crystal lattice.

Although the Raman spectrum of each mineral is distinct, that pattern is subject to modification. With increased metamictization, two changes occur: 1) there is a shift of peak position to lower wavenumbers and 2) there is a systematic peak-broadening (Nasdala et al., 1995). The first effect can be explained by the lengthening of inter-atomic bonds during the process of metamictization. Longer bonds vibrate at a lower frequency, and consequently the scattered light is shifted to lower wavenumbers. The second effect is the result of the distortion of the crystal lattice during metamictization. A distorted crystal lattice no longer has a unique frequency of vibration, as it varies with the degree of distortion. Light interacting with phonons of slightly varying frequencies will be scattered correspondingly and the result is a broadened peak. Complete metamictization leads to a loss of long-range atomic ordering characterized by an ill-defined vibrational spectrum. Raman spectroscopy is a non-destructive technique. Consequently, any subsequent ion probe analyses are unaffected by the Raman analysis (Nasdala et al. 1998). This makes it an excellent method to use to pre-screen samples before geochronological study. By assessing the degree of crystallinity, the most robust portions of zircon can be selected for analysis.

Sample preparation for Raman analysis is very simple, as the style of epoxy mounts used for SHRIMP work (described in Stern, 1997) is adequate. Because fluorescence from the sample or the epoxy can mask the Raman signal, zircon mount IP102 was made specifically for the Raman analysis using Epo-tek 301®, a low-fluorescing epoxy. The Raman work was carried out at the High Pressure Physics Laboratory in the Physics Department of the University of Ottawa. Micro-Raman spectra were recorded on a Jobin-Yvon S3000 subtractive triple spectrometer equipped with a

liquid nitrogen-cooled charge coupled device detector. Samples at room temperature were excited with the 514.53-nm line of the Ar⁺ laser at a power less than 200 mW at the source, in a near 180° scattering geometry using an Olympus 50X microscope objective. The Raman analysis sampled a cylindrical volume of mineral roughly 20µm in diameter and 100µm deep. A field aperture was also used to reduce the depth of field and consequently to enhance the Raman signal-to-background ratio. The instrumental spectral line width was kept smaller than 4 cm⁻¹. Following Nasdala et al. (1996, 1998), the degree of metamictization is estimated from the full width at half the maximum intensity (FWHM) of the Raman peak at 1000 cm⁻¹ which is measured using an in-house line profile analysis (Desgreniers and Lagarec, 1994). A Lorentzian curve is fitted to the data and the measured peak width, also known as a band width (b_s), is derived from the equation of the curve. A further calculation is needed to determine the true band width (b). True band widths do not correlate directly with b_s and are strongly influenced by instrumental conditions. The conversion to true band width is necessary to more rigorously quantify the degree of metamictization and is calculated from the measured band width and the spectral resolution of the instrument (s) using the equation of Irmer (1985):

$$b = b_s \cdot \sqrt{1 - 2(s/b_s)^2}.$$

4.2.2 *Transmission Electron Microscopy (TEM)*

Thin membranes of zircon, appropriate for TEM studies, were prepared by Rob Patterson at Fibics Inc., Ottawa, via the “lift-out” technique described below. Two zircon grains were selected for analysis, grain D23 on SHRIMP mount IP82, and grain TEM 11 on a mount made specifically for the TEM analysis. SHRIMP ion probe analysis on a

large bright patch from grain D23 yielded a concordant U-Pb age and detected only trace amounts of common Pb. Both these properties are typical of unaltered zircon from this sample. Using the BSE images as a guide, an area from grain D23 composed of an unaltered zone, a very dark transition zone and an adjacent altered patch was selected for study. Using a Micrion 2500 focused ion beam instrument, a Ga^+ ion beam, with an accelerating voltage of 50kV, was used to excavate two adjacent trenches, roughly 15 μm long and 10 μm deep, leaving a thin vertical slice of zircon between them. The slice of zircon is a cross-section through the selected area, exposing the contact between bright and dark zircon. This vertical slice was further thinned using the focused ion beam to a thickness of roughly 80 nm. After thinning was completed, the Ga^+ ion beam was used to cut through the edges and bottom of the membrane to free it from the grain. The electrostatic charge on the tip of a very fine needle was used to transfer the membrane onto a copper grid for analysis. The TEM instrument used was a Philips CM20FEG operated at 200keV, located at the CANMET facility. The system is equipped with a field emission gun, making it possible to obtain electron probe sizes in the order of 1-2 nm. An energy dispersive x-ray detector and a scanning unit are also available on the microscope so that elemental maps at high spatial resolution (with 1-2 nm probe sizes) and scanning annular dark field images can be obtained.

4.3 RESULTS

4.3.1 Raman Results

As a zircon becomes metamict the long-range order of the crystal structure is lost and the width of vibrational bands increases (Nasdala et al., 1995). Stacked spectra of two variably crystalline zircons are used to illustrate this effect (Fig. 4.3, Table 4.1). The

upper spectrum corresponds to Archean sample FG2, from the Abitibi Subprovince in Quebec (Mortensen, 1993), while the lower spectrum is from the Mud Tank zircon, a late-Proterozoic, gem-quality zircon from Australia (Black and Gulson, 1978). The band at roughly 1000 cm^{-1} is characteristic of zircon and this vibrational mode (SiO_4 asymmetric stretch) is most affected by metamictization (Nasdala et al. 1995). Raman data are presented in Table 4.1. The measured FWHM of the 1000cm^{-1} band of the Mud Tank zircon is 2.5 cm^{-1} . In cases such as this, where the measured band width (2.5 cm^{-1}) is comparable to or less than the spectral slit width (4 cm^{-1}), the half width is measured with great uncertainty even after mathematical correction. Despite the uncertainty in the calculation of the exact band width, the scheme outlined by Nasdala et al. (1998) in Table 4.2, indicates that this band width corresponds to the structure of a very well-crystallized zircon.

The true FWHM of the $\sim 1000\text{ cm}^{-1}$ band for the sample FG2 is $5\text{-}8.5\text{ cm}^{-1}$ depending on the U content of the area selected for analysis. According to the scheme presented in Table 4.1, this band width is consistent with a well crystallized zircon. The wider band width suggests a more damaged structure, which is consistent with the greater age and U content of sample FG2.

Dose calculations are another means of predicting the extent of structural damage in a crystal. The net radiation dose for the Mud Tank zircon is calculated to be 0.01×10^{16} alpha-events/mg, calculated using an age of 732 Ma and average U and Th concentrations (Black and Gulson, 1978). Murakami et al. (1991) compared radiation dosages to TEM diffraction patterns and outlined three stages of zircon structure, from highly crystalline to completely amorphous, and defined each stage by a range of

radiation doses. According to that scheme, the dose experienced by the Mud Tank zircon is consistent with a highly crystalline zircon. The net average radiation dose estimated for sample FG2 is 0.09×10^{16} alpha-events/mg. This dose is also consistent with well-crystallized zircon according to the stages of metamictization outlined by Murakami et al. (1991).

Table 4.1. Structural data for crystalline test zircons

<i>Sample</i>	<i>Raman band width (cm^{-1})</i>	<i>Radiation Dose (alpha-events/mg)</i>
Mud Tank	2.5*	0.01×10^{16}
FG2	5*-8.5**	0.09×10^{16}

* $b_s < \text{or } \cong s$; therefore true band width b is not given (Irmer; 1985)

** $b_s \gg s$; therefore true band width b is given (Irmer; 1985)

Table 4.2. Comparison of radiation dose and Raman band widths for a given degree of crystallinity.

<i>Degree of crystallinity*</i>	<i>Raman band width*</i>	<i>Dose** (alpha events/mg)</i>	<i>Electron Diffraction Pattern**</i>
very well crystallized to well crystallized	1-5 cm^{-1} 5-10 cm^{-1}	Stage I less than 0.3×10^{16}	sharp, pin-point diffraction spots
intermediate to metamict	10-20 cm^{-1} 20-30 cm^{-1}	Stage II $0.3 - 0.8 \times 10^{16}$	diffuse, elliptical diffraction spots
highly metamict (complete amorphization)	greater than 30 cm^{-1}	Stage III greater than 0.8×10^{16}	diffuse halos

*Nasdala et al. (1998)

**Murakami et al. (1991)

Raman spectra for sample BNB-95-110c were obtained for both bright, unaltered and dark, altered patches from single grains. The results for three grains, d5, c7 and c22, which are representative of all zircons analyzed, are presented as spectra with identical vertical and horizontal scales for comparison (Fig. 4.4). Figure 4.4a contains the Raman spectra for the unaltered portions of three different zircon grains. In each case a large, bright patch, similar to those that yield concordant results, was selected for analysis. Care

was taken to ensure that there was no overlap with adjacent dark patches. The characteristic band at $\sim 1000\text{ cm}^{-1}$ was not observed for any of the bright zircon domains. This suggests a complete loss of crystallinity.

Raman spectra for the dark, altered areas adjacent to the bright patches of the same three grains are presented in Figure 4.4b. The band at 1000 cm^{-1} is not present, similar to the unaltered zircon, again suggesting complete metamictization. The intensity of background noise of the altered zircon domains is significantly greater than that of the unaltered material. High Raman background has been previously observed for trace element-rich zircons and has been attributed to rare-earth element induced fluorescence (Wopenka et al., 1996). Trace element analyses carried out on the study samples using the SHRIMP II indicate that dark, altered patches have consistently higher light rare earth element concentrations than corresponding bright patches on the sample grain. These results are consistent with the observations of Wopenka et al. (1996) and support a similar origin for the high background noise of altered domains of BNB-95-110c.

U and Th concentrations used in the radiation dose calculation for sample BNB-95-110c were taken from SHRIMP analyses of specific unaltered and altered domains. An age of 2.87 Ga was assumed in the radiation dose calculations presented in Table 4.3. In all cases the total accumulated doses exceed the threshold needed to reach amorphization according to Murakami et al. (1991).

Table 4.3. Radiation dose for selected grains from sample BNB-95-110c

<i>Sample</i>	<i>Feature in BSE</i>	<i>Radiation Dose (alpha-event/mg)</i>
82.1-D23.1*	bright	2.1×10^{16}
102-C22.1	bright	1.28×10^{16}
102-C7	bright	1.01×10^{16}

*grain used in TEM analysis

4.3.2 TEM Results

Bright field diffraction contrast (BF) images and selected area diffraction patterns (SAD) were collected from TEM membranes from two separate zircon grains. The brightness in the diffraction contrast images is controlled by the degree to which an area diffracts incoming electrons. In bright field images of these samples, increased brightness is due to the poor electron diffraction properties of damaged or non-crystalline material (i.e. brighter = more metamict, as less scattering of the objective aperture occurs). The electron diffraction patterns offer another qualitative means of determining the crystallinity of an area with a diameter on the order of 200 nm, limited by a selected area aperture.

The membrane collected from grain d23 is composed of an unaltered zone, a very dark transition zone and an adjacent altered patch, as observed in BSE imaging. A BF image of the entire membrane is given in Fig. 4.5a. The membrane can be divided into three sections, divided by the intersection of three linear features. The membrane is oriented such that the darker, irregular speckled portion in the top-left half of the image corresponds to the unaltered patch observed in the BSE image. SAD patterns were collected along a transect across both sides of the linear feature in the lower left side of the membrane. The SAD patterns, collected in the zone believed to be the unaltered zircon, display diffuse elliptical electron diffraction spots as shown by example in Fig. 4.5b, spot 1. This type of pattern is consistent with a distorted but crystalline lattice. The mottled appearance of the unaltered zircon in the BF image is interpreted to be due to 3-5 nm microcrystals misoriented by less than 1° with respect to its neighbour. The absence

of halos in this electron diffraction pattern suggests that there is a negligible component of amorphous material in the unaltered zircon domains.

SAD patterns collected from both sides of the lower left boundary show that each is composed of diffuse but distinct diffraction spots, though the distribution of spots around the central beam varies for each analysis (spots 2 and 3, Fig. 4.5 c, d). This suggests that the sharp linear feature is in fact a grain boundary between two crystalline grains of zircon that are slightly misoriented with respect to each other. The bright, rectilinear features along the junction are tiny holes, likely the result of the accumulation of defects.

Subsequent SAD patterns were collected further below the lower left grain boundary. The SAD pattern from spot 4 (Fig. 4.5e) contains both weak diffraction spots and diffuse halos, indicating a mixture of crystalline and amorphous material. Further from the boundary, the SAD pattern is dominated by the diffuse halos, with a few faint spots, suggesting a greater degree of metamictization (Fig. 4.5f - spot 5). This suggests that the transition from crystalline to amorphous zircon is progressive. The electron diffraction behaviour, illustrated by the brightness in the BF image, also changes gradually from a dark speckled appearance for the unaltered zircon domains to a brighter more homogeneous appearance for the altered zircon domains.

Energy dispersive (EDS) maps of a number of elements (Si, Zr, U, Pb, Ca, O, Ga), counted for 4 hours were collected from the membrane. Ca is the only element to show any detectable heterogeneity (Fig. 4.5h). As expected from previous electron probe analyses, the unaltered (top left) area of the membrane has no detectable Ca. The SAD pattern from Spot 1 was collected from this low Ca domain and is characterized by a

sharp electron diffraction pattern. The sharp lower left boundary, believed to be a grain boundary and not a sharp transition to amorphous zircon, corresponds with only a moderate increase in Ca. Spot 4 within this moderate Ca zone has a mixed diffraction pattern. A more significant increase in Ca occurs in the lower central portion of the EDS map. Although the location of the amorphous domain (spot 5) is not within the field sampled by the EDS map, examination of the BSE image suggests that the position of spot 5 is in the zone characterized by high Ca content. A gradual transition to increasing Ca contents appears to be mirrored by a gradual transition to a more amorphous structure (Fig. 4.6). Prior EMPA analyses suggest that the darkest zones in BSE have the highest Ca, on the order of 2wt %. The boundary between bright and dark zircon in this membrane is defined by an exceptionally dark rim. Therefore the area of highest Ca content in the EDS map (Fig. 4.5h) is interpreted to correspond to the transition to the altered zircon domain observed in the BSE image. The other two branches of the triple junction (upper and lower right) are diffuse and are defined by an increase in Ca content. Though the boundary between altered and unaltered zircon domains is very distinct in BSE images, the same boundary is less distinct in the EDS map and BF image due to the smaller sampling scale of these images.

Another membrane was milled entirely from an altered patch of grain TEM11. A BF image of a portion of the membrane is shown in Fig. 4.5i. The majority of the membrane consists of speckled patches of variable brightness. The SAD pattern from these patches is composed of distinct spots, again indicating a distorted microcrystalline structure. EDS maps indicate lesser Ca content in these regions. The most prominent feature observed in the BF image of this membrane is a very bright, T-shaped vein. EDS

maps show an even wider band of high Ca material centred on the vein but extending into the surrounding zircon. SAD patterns from the bright vein are composed of diffuse halos, indicating a total loss of short-range order (Fig. 4.5j). At the scale of the TEM analyses, altered zircon (a dark patch in BSE images) appears to be composed of domains of high Ca, amorphous material and low Ca, partially crystalline material.

In summary, for both membranes the amorphous domains are the most enriched in Ca. There are no signs of other crystalline phases in the diffraction patterns of the high Ca zircon, and energy dispersive spectra do not indicate other elements, such as P, in sufficient abundance to account for the Ca as an intergrowth of another discrete mineral phase, such as apatite. Therefore we conclude that the Ca in the zircon structure is found as interstitial atoms in the distorted crystal lattice.

4.4 DISCUSSION

The transition of zircon to a largely glassy state, such as that achieved by complete metamictization, is the simplest interpretation for the absence of Raman peaks in both altered and unaltered zircon domains from sample 110c. Total metamictization is also predicted by the calculated radiation doses for both types of domains, which greatly exceed the thresholds for amorphization proposed by x-ray diffraction, infra-red, and TEM studies (Holland and Gottfried, 1955; Woodhead et al., 1991; Chakoumakos et al., 1987; Murakami et al., 1991).

The Raman data, however, are not consistent with the TEM observations of the unaltered zircon, the latter indicating the presence of crystallinity. Clearly it is necessary to reconcile the differences between these measures of crystal structure. The TEM diffraction patterns convincingly demonstrate the crystallinity of the unaltered zircon.

The observed crystallinity is inherent to the zircon and could not have been induced during membrane milling as only a transition to an amorphous structure has been attributed to interactions with the focussed Ga^+ ion beam. Amorphization occurs mainly in extreme cases of very thin samples (20-30 nm) and in implantation conditions, rather than polishing, as was done in our work. The absence of the Raman signal from unaltered microcrystalline zircon is curious and requires explanation. The defects associated with the boundaries between the slightly misaligned microcrystals thought to comprise the unaltered zircon should result in a broadened and weakened Raman signal. Photoluminescence from impurities such as U, REE or mineral inclusions will increase the background noise, which could overwhelm an already weak Raman signal. The area sampled by the Raman beam is roughly $20 \times 100\mu\text{m}$ (width x depth). This relatively poor control on the depth of analysis makes it likely that there is some interference from domains of altered zircon which underlie the unaltered lenses. The most likely result of interaction with altered zircon would be increased photoluminescence due to Ca- and REE-enrichment. Further systematic experiments would be necessary to constrain the effect of the microcrystalline structure and to confirm that the loss of Raman peaks was the result of a very high background. The sampling volume of the Raman technique appears to be large with respect to the internal features observed in BSE. As both altered and unaltered zircon domains have likely been sampled in a single analysis, the Raman data may be considered a measure of the bulk structure of the grain. Single grain X-ray diffraction analyses yield the bulk structure of a crystal. The X-ray diffraction pattern from a single zircon grain from sample BNB-95-110c shows diffuse rings, which is

interpreted as a largely amorphous structure, also consistent with the absence of Raman peaks (Fig. 4.7).

Although it is possible to reconcile the Raman data with the diffraction patterns, we are still left with radiation dose calculations well above the thresholds for complete metamictization, illustrated by the plot of cumulative radiation dose versus time (Fig. 4.8). The diffuse elliptical electron diffraction spots from low Ca zircon in both unaltered and weakly altered domains correspond with a distorted but not amorphous structure (Fig. 4.5b). The BF image is consistent with a structure composed of a mosaic of misaligned 3-5 nm microcrystals. The electron diffraction pattern observed for these spots is similar to the type of diffraction pattern that Chakoumakos et al. (1987) and Murakami et al. (1991) relate to a radiation dose of $0.3 - 0.8 \times 10^{16}$ alpha-events/mg, an intermediate crystal state. However, the radiation dose calculated using the age and U content of grain d23 is 2.1×10^{16} alpha-events/mg, well above the threshold for metamictization. At this dose an electron diffraction pattern composed of diffuse halos would be expected (Woodhead et al., 1991, Holland and Gottfried, 1955, Chakoumakos et al., 1987, Murakami et al., 1991).

A mechanism is needed to account for the discrepancy between the radiation dose calculations, which are consistent with complete metamictization, and the TEM diffraction patterns, which reveal a distorted, but crystalline structure. Crystal structure can be recovered by one of two mechanisms, annealing or recrystallization (see section 2.1.2). In the case of BNB-95-110c, the recovery of the structure is interpreted to have been isochemical. U-Pb analyses from the unaltered areas, similar to the area where the TEM data was collected, are concordant, indicating that radiogenic Pb was not excluded

from the newly formed lattice. Similarly, the U concentrations of the unaltered zircon domains (crystalline) are comparable to the U concentrations of altered zircon domains (amorphous). Consequently, it is inferred that a process of annealing is responsible for the recovery of a zircon lattice.

It is difficult to place constraints on the temperature, duration, and time of annealing. A number of studies, using both natural and synthetic zircon, cite temperatures required for annealing that vary from 360°C to 600°C (Mezger and Krogstad, 1997; Weber et al., 1994; Weber, 1990; Meldrum et al., 1998). Murakami et al. (1991) have shown that rapid recovery of the lattice during intense, accelerated heating, is associated with the exclusion of Pb from the structure. Regardless of the exact temperature of annealing, the thermal regime must change slowly and the elevated temperature must be maintained for an extended period of time (~1Ma).

The observed crystallinity in BNB-95-110c, corresponds to a radiation dose of roughly 0.3 to 0.4×10^{16} alpha-events/mg. To have accumulated this minor amount of damage, annealing must have occurred at a considerable time after primary growth. Assuming average U and Th concentrations of 1000 ppm and 100 ppm respectively, annealing at ~1000 Ma ago would result in a current radiation dose of 0.4×10^{16} alpha-events/mg, comparable to the observed electron diffraction pattern (Fig. 4.8). Very large errors are associated with this calculation, due to uncertainty in the U and Th concentrations used and in the actual dose represented by the diffraction pattern from sample BNB-95-110c. However, the intention of this calculation is to give a first-order reference to the earliest time of annealing. The lack of control on the thermal history of the sample further complicates our ability to assess the time of annealing. Although the

temperatures required for annealing (between 400°C and 600°C) are poorly constrained, they do imply a significant thermal event. No such protracted, thermal event is recorded as late as 1.0 Ga in the Slave Province. The most recent, major thermal events are the Early Proterozoic Wopmay Orogen that occurred at *ca.* 2.0-1.8 Ga (Hoffman, 1998), and potential underplating of the lithosphere by a spreading mantle plume during the emplacement of the MacKenzie dykes *ca.* 1.27 Ga (LeCheminant et al., 1996). Calculations using the age of Wopmay orogenesis or MacKenzie dykes in the radiation dose equation result in a dose that exceeds the threshold for metamictization. If orogenesis and/or dyke emplacement provided the heat necessary for the observed annealing of the zircon structure, the only means of reducing the total accumulated radiation dose is to invoke a protracted period of moderate to high temperatures following these events. Studies by Meldrum et al. (1998) suggest that radiation damage will not begin to accumulate until the sample temperature has dropped below 360°C, the temperature above which the recoil tracks are healed as soon as they are formed. Sample BNB-95-110c could have been heated above the annealing temperature (360°C to 600°C) at 1.9 Ga or 1.27 Ga (orogenesis or dyke emplacement respectively), at which time pre-existing damage may have been annealed. As long as the sample remained above 360°C, no new damage would have accumulated. If BNB-95-110c cooled below 360°C by 1.0 Ga or later, damage could begin to accumulate anew and this would possibly account for the crystalline structure. The scenario of protracted moderate to high temperatures presented above is plausible but unsubstantiated, and a number of other options are available. The purpose of introducing one possible sequence of events serves to illustrate the complexities of annealing mechanisms, and to highlight the difficulties in assessing

the significance of zircon microstructure. Without a greater understanding of the process of annealing, the significance of TEM patterns from Archean zircons, and the thermal history of the sample, it is difficult to place constraints on the mechanism that lead to annealing of the lattice. Based on the microstructural data, the only statement that can be made with certainty is that the sample records a complex thermal history.

Although rare, the preservation of concordant ages from a zircon whose crystallinity has been recovered has been observed. One of the samples characterized by Nasdala et al. (1998) has U or Th concentrations and ages comparable to those of sample BNB-95-110c. In that study, zircons from Jack Hills, Australia are composed of zoned and unzoned domains, and both types meet or exceed the radiation dose required for metamictization (Nasdala et al. 1998). However, the unzoned zircon domains still preserve a narrow Raman peak consistent with intermediate crystallinity and yield concordant age data. Nasdala et al. (1998) account for the difference between Raman peak width and radiation dose by invoking annealing/ recrystallization later in the geologic history of the sample. A similar annealing mechanism is proposed here for sample BNB-95-110c.

4.5 CONCLUSIONS

Comparison of Raman spectroscopic spectra, TEM diffraction patterns and calculated radiation doses have allowed us to characterize the microstructure of zircon from a high U, late Archean rock sample. SHRIMP isotopic data for this sample suggest that alteration is responsible for Pb loss in this sample and the microstructural data presented here shed some light on the alteration mechanism. The following points summarize the key observations of this study:

1. Unaltered zircon, which appears bright in BSE images, is composed of a mosaic of slightly misaligned microcrystals and contains a negligible amorphous component.
2. Altered zircon, which appears dark in BSE images, has a heterogeneous microstructure, composed of domains of both crystalline and amorphous zircon.
3. Low Ca-domains in zircons from BNB-95-110c experienced at least one thermal event which resulted in the recovery of the zircon lattice.
4. Pb-loss did not accompany the re-establishment of the lattice therefore a process of annealing is responsible for the recovery of the structure.
5. There is a qualitative correlation between amount of Ca in the structure and the extent of amorphous structure.
6. The Ca is restricted to discrete veins or patches. There is no indication of secondary Ca- rich phases, such as apatite. We conclude that the Ca added during alteration is present as cations housed in lattice vacancies.

Fig. 4.1. Schematic of a typical Raman experiment (after Roberts and Beattie, 1995). See text for further explanation.

Fig. 4.1

Fig. 4.2 Simple energy diagrams illustrating the origin of the Raman effect (after Roberts and Beattie, 1995). See text for further explanation.

Fig. 4.2

Fig. 4.3 Stacked spectra comparing the Raman peak at 1000 cm^{-1} for two variably crystalline zircons. The lower spectrum is that of a low U, highly crystalline early Proterozoic zircon. The upper spectrum is that of a partially metamict, Archean zircon. Intensity is given in counts/s. The vertical scale of the upper spectrum is exaggerated 2.5x compared to the lower spectrum.

Fig. 4.3

Fig. 4.4 (a) Raman spectra of the unaltered domains (bright in BSE) of three typical zircons from sample 110c. There is no indication of the SiO_4 stretching peak at roughly 1000 cm^{-1} , which suggests that these zircon domains are completely metamict. **(b)** Raman spectra of the altered domains (dark in BSE) of three typical zircons from sample 110c. There is no indication of the SiO_4 stretching peak at roughly 1000 cm^{-1} , which suggests that these zircon domains are completely metamict. The higher backgrounds for the altered zircon domains are accounted for by increased rare earth element fluorescence.

Fig. 4.4a

Fig. 4.4b

Fig. 4.5 TEM results from BNB-95-110c. See text for complete description of results. (a) Bright field image of zircon membrane from grain d23. Metamict areas appear bright. Numbers 1 to 5 represent the locations of the selected area diffraction analyses (b) Diffraction pattern from spot 1, illustrating a distorted but crystalline structure in the unaltered zircon domains. (c) Diffraction pattern from spot 2 (d) Diffraction pattern for spot 3. (e) Diffraction pattern for spot 4, interpreted as representing a mixture of crystalline and amorphous zircon. (f) Diffraction pattern for spot 5, interpreted as representing a metamict structure. (g) Bright field image of zircon membrane from grain 23 (same image as 4.5a) with a rectangle outlining the boundary of the EDS map. (h) EDS map of Ca for a portion of the membrane. Note the enrichment of Ca in the lower right side of the map. (i) Bright field image of grain 11. (j) Diffraction pattern from the bright, Ca-rich vein.

Fig. 4.5

Fig. 4.5 cont'd.

Fig. 4.6 Schematic diagram of the transition from unaltered to altered zircon.

Fig. 4.6

Fig. 4.7 Single grain X-ray diffraction pattern for zircon from BNB-95-110c. Diffuse halos indicate a largely amorphous structure.

Fig. 4.7

Fig. 4.8 Cumulative radiation dose over time. Dark areas illustrate the accumulation of alpha-events/mg since ~2880 Ma (time of primary crystallization). The light grey zone represents the cumulative radiation dose since ~2700 Ma (time of new zircon growth as tips and dykes). The medium grey zone represents the cumulative radiation damage since 1000 Ma, (accumulation since annealing stopped). Upper and lower limits determined using the maximum and minimum U and Th concentrations measured using SHRIMP. Horizontal band represents the range of doses over which the transition to completely metamict zircon is believed to occur (Murakami et al., 1991). Note that accumulation of new damage at 1000 Ma results in a present total dose below the threshold for metamictization, which is consistent with the TEM results (see text for discussion).

Fig. 4.8

CHAPTER 5

SUMMARY

In this chapter, the central questions proposed in Chapter 1 are evaluated. To review, these questions were: 1) What caused the discordance in zircons from sample BNB-95-110c? 2) What constraints can be placed on the timing of alteration relative to crystallization and other geologic events? 3) How does zircon alteration manifest itself chemically? 4) What crystal-chemical properties control alteration of zircon? 5) What is the mechanism by which altered zircon domains lose Pb? 6) How can the discordance patterns of altered zircons be interpreted?

What caused the discordance in zircons from sample BNB-95-110c?

Based on U-Pb isotopic evidence presented in Chapter 2, the largest amounts of discordance in this sample appear to be related to fluid alteration of select zircon domains. This research suggests that alteration is an important mechanism of Pb-loss. Pb-loss by other mechanisms cannot be excluded, but appear to be of lesser importance than fluid alteration.

What constraints can be placed on the timing of alteration relative to crystallization and other geologic events?

From the isotopic data (Chapter 2), it is possible to suggest the following order of events affecting zircons in the study sample. Zircon from sample BNB-95-110c crystallized from a magma at 2875 ± 3 Ma. Crystallization was followed by secondary zircon growth at 2697 ± 14 Ma, manifested as thin overgrowths and cross-cutting zircon "micro-dykes". SHRIMP U-Pb analyses of uranothorite inclusions suggest that alteration and concomitant addition of Ca and LREE occurred at ca. 2200 Ma. By this time, the

primary, 2.88 Ga zircons were already significantly damaged, having accumulated between 0.25 and 1.8×10^{16} alpha-events/mg, depending on local U contents (see Fig. 4.8). The accumulated defects may have been sufficient to accommodate large Ca and LREE ions introduced at 2200 Ma. Annealing, the repair of a radiation-damaged lattice, affected low Ca (i.e. least-altered) regions of zircons. Extreme distortion in the high Ca/high LREE domains may have prohibited reorganisation of the altered zircon lattice into a true zircon structure during annealing. This is in contrast to the unaltered zircon; though radiation damage had occurred, the degree of distortion was not as great as in the altered zircon and recovery of the lattice was possible. The cause of annealing is proposed to be a protracted moderate-temperature event, such as Wopmay orogenesis or Mackenzie dyke emplacement. From first-order calculations it seems unlikely that annealing ended significantly before 1000 Ma. No Pb-loss was associated with this annealing event.

Recent Pb-loss was the last event to affect sample BNB-95-110c. The details of this recent loss of Pb are unknown. Previous studies have suggested that recent Pb-loss can be attributed to weathering of the zircons while exposed at the surface of the earth (Stern et al, 1966).

How does zircon alteration manifest itself chemically?

Chapters 2, 3, and 4 document a number of chemical and microstructural traits for unaltered and altered zircon. The following is a summary of the observations recorded in these chapters.

From back-scattered electron images, it is noted that single zircon grains contain both altered and unaltered domains. Unaltered zircon domains from sample BNB-95-

110c appear bright in BSE images, while altered zircon domains are dark. Alteration results in changes to the zircon matrix that renders the calibration of U-Pb fractionation unreliable. The thresholds for proper calibration of sample BNB-95-110c are values of ^{204}Pb concentration less than 50 ppb and $^{204}\text{Pb}/^{206}\text{Pb}$ less than 10^{-4} .

Altered zircon domains are characterized by depleted Zr and Si contents and have low combined oxide totals. Altered zircon domains are also characterized by enrichment in Ca, Ba and the LREE as compared to unaltered zircon domains. Ca, Ba and LREE are believed to be introduced into the zircon lattice during alteration, not during primary crystallization from a magma.

Unaltered zircon domains are composed of a mosaic of slightly misaligned microcrystals and contain a negligible amorphous component. Altered zircon domains have a heterogeneous microstructure, composed of domains of both crystalline and amorphous zircon.

There is a qualitative correlation between Ca concentrations and the extent of amorphous structure. High Ca contents are observed both in discrete veins and large altered patches. There is no chemical or microstructural evidence for secondary Ca- rich phases, such as apatite. We conclude that the Ca is present as lattice impurities.

What crystal-chemical properties control alteration of zircon?

Why did only some parts of the zircon crystals become altered while other areas remain pristine? There is a correlation between the proportion of amorphous structure, as measured by TEM, and high concentrations of impurities such as Ca, LREE and common Pb, which can be considered as a measure of the extent of alteration. However these correlations do not provide us with an insight into the cause-and-effect relationship.

For example, was a distorted lattice necessary to accommodate Ca, LREE and Pb, or did the addition of these impurities lead to the destruction of the crystal structure? There is a correlation between LREE and U, which at first glance suggests that the altered areas contained higher primary U contents and therefore are more metamict. Ca, Pb and LREE all have ionic radii much larger than the usual constituents of zircon (See Table 5.1).

The prevailing interpretation would be that metamict zircon was necessary to accommodate these alteration-related atoms. However, other evidence suggests that metamictization does not entirely control the distribution of alteration. The boundaries between altered and unaltered zircon are not concordant with primary oscillatory zoning and presumed variation in U content. If U content were the sole control on alteration we would expect the altered/unaltered boundaries to be parallel with the zoning.

Alternatively, the altered/unaltered boundaries may represent the reaction front of chemically active fluids. Their placement may be controlled by the availability of fluid pathways such as cracks, and/or ambient temperature and pressure conditions that favour the existence of the fluids.

Table 5.1 Ionic radii of cations commonly incorporated into zircon. All ionic radii are given assuming the cation is in 8-fold coordination, unless otherwise noted.
From Shannon (1976)

Cation	Ionic Radii (Å)	Cation	Ionic Radii (Å)
Zr ⁺⁴	0.84	La ⁺³	1.16
Si ⁺⁴	0.26 (4-fold coor.)	Lu ⁺³	0.98
Hf ⁺⁴	0.83	Pb ⁺²	1.29
U ⁺⁴	1.00	Ca ⁺²	1.12
Th ⁺⁴	1.05	Ba ⁺²	1.42

To determine if the loss of crystal structure controls, or is controlled by, alteration, it is necessary to constrain the nature of the microstructure at the time of alteration. In the

case of BNB-95-110c, it is unclear whether pre-existing crystal defects were responsible for controlling which parts of the zircons were altered, as the structural state of the lattice at 2200 Ma is unknown. Without more information on the prevalence of annealing of natural zircon in geologically-reasonable environments, it is difficult to consider alteration of an annealed zircon. In short, this research suggests that Pb-loss is controlled by a complex set of conditions that includes, but is not restricted to, the degree of metamictization. Exploitation of crystal-structural weaknesses, such as cracks, seems to be a more important process.

What is the mechanism by which altered zircon domains lose Pb?

The textural relationship between zircon and uranothorite, dramatically illustrated by grain e19 (Fig 2.6i), suggests that fluids are the vehicle for alteration. The presence of Ca, LREE and Pb in the altered zircon domains suggests a fluid composition rich in these elements. Other studies have suggested that Ca-rich brines play an important role in the mobilization of Pb and U (Kurz and Hansen, 1999; Hansen and Friderichsen, 1989). Hansen and Friderichsen (1989) have suggested that the fluids are Ca-dominated basement brines. In the case of the fluids responsible for 2.2 Ga alteration of sample BNB-95-110c, it is proposed that they are related to the mafic magmatism of the MacKay dyke swarm.

A correlation between discordancy in the U-Pb isotopic systems and high common Pb contents is observed for sample BNB-95-110c. High common Pb concentrations are not unusual for discordant zircons (Black, 1987; Williams et al., 1984; Scharer and Allegre, 1982). Watson et al. (1997) proposed that a "Pb exchange" mechanism may be necessary for radiogenic Pb-loss. The decay of U^{+4} to Pb^{+2} leads to a

charge imbalance in zircon. Without the addition of some charge-compensating species, loss of the radiogenic Pb would lead to an even greater charge imbalance in the system. The exchange of radiogenic Pb (found within the zircon crystal) with common Pb (found in the surrounding rock), perhaps coupled with Ca^{+2} or H^+ , provides a means of overcoming the discrepancy in charge. The relationship between discordancy and common Pb content observed in BNB-95-110c is consistent with a mechanism where radiogenic Pb is partially leached from the sample and common Pb is introduced.

How can the discordance patterns of altered zircons be interpreted?

Very few, if any, studies have deliberately sought out discordant zircon for analysis. The goal of this thesis was to find highly discordant zircons and determine what processes lead to their extreme discordance.

Discordant data from sample BNB-95-110c (where discordance is defined as the percent discrepancy between the observed $^{206}\text{Pb}/^{238}\text{U}$ ratio for an analysis and the expected $^{206}\text{Pb}/^{238}\text{U}$ ratio for a 2.87 Ga rock) can be divided into two groups. One group of analyses has $^{207}\text{Pb}/^{206}\text{Pb}$ ages consistent with the age of crystallization. These data points form a linear array with a lower intercept near the origin and are at most 4% discordant. This linear pattern is interpreted to indicate that the sample has undergone recent Pb-loss. Recent Pb-loss only accounts for a small percentage of total discordance observed in BNB-95-110c.

Analyses that fall into the second group have a wide range of $^{207}\text{Pb}/^{206}\text{Pb}$ ages, form a complex fan-shaped array on a concordia diagram and are substantially more discordant, up to 60%. I propose that alteration causes this extreme discordance, and that

the mechanism of Pb-loss by alteration likely differs from the process that leads to recent Pb-loss.

The complexity of the fan of discordant data makes a unique estimate of the timing of alteration event impossible. Through indirect methods, such as the dating of uranothorite inclusions, one ancient Pb-loss event is proposed during the Paleoproterozoic, although multiple alteration events cannot be completely ruled out. Irregularities with the U-Pb fractionation calibration for SHRIMP is another major obstacle in constraining the age of alteration. Differences between the matrices of the Kipawa standard zircon and altered zircon make it difficult to reliably calibrate the degree of U-Pb fractionation during sputtering. Without this calibration it is impossible to accurately determine U-Pb ages from altered zircon. U-Pb ages can only be determined if a suitable standard, with sputtering properties similar to altered zircon is found, or if a correction factor to account for the sputtering differences can be established.

The extreme levels of discordance (greater than ~10%) observed in sample BNB-95-110c are attributed to alteration. Highly discordant analyses do not plot along a simple linear discordia but instead form a complex fan of data. Such a complex distribution of data makes it very difficult to uniquely interpret the post-crystallization history of the sample. From this research it is proposed that at least one alteration event occurred in the early Proterozoic. However, the distribution of zircon U-Pb ages may have resulted from multiple episodes of open-system behaviour. Until the nature and timing of each open-system episode is isolated, it will be difficult to confidently interpret these highly discordant results. The ability to interpret analyses with a high degree of Pb-

loss is further complicated by the analytical difficulties in calibrating the U-Pb fractionation of the altered material.

ISSUES FOR FURTHER STUDY

Alteration is still a little-studied phenomenon despite its effect on measured isotopic ages. Further characterization of altered zircons from a number of geologic environments and of a variety of ages with known, simple, geologic histories is needed. By examining the relationships between microstructure and chemistry from simple samples, using techniques that may include TEM, EMPA and SHRIMP, it may be possible to further define the role of microstructure on alteration. From back-scattered electron images of a number of samples, we know that alteration in ancient zircon is widespread. By studying samples from a variety of geologic settings, it may be possible to determine if there is a singular chemical signature for altered zircon or if alteration varies with geologic environment.

A greater understanding of the microstructure of early Proterozoic and Archean zircons is also needed. Little work has been done to characterize the microstructure of zircons as ancient as that of the Acasta sample BNB-95-110c. Most TEM studies concerned with the metamict structure of natural zircon to date have examined the ca. 570 Ma or younger Sri Lankan megacrysts. Further TEM studies into the microstructure of zircons with a range of types and ages are needed to generate a baseline against which the microstructure of other ancient zircons can be compared. Such a study might reveal patterns or behaviours such as annealing unaccompanied by Pb-loss, as observed in this study, but not observed in younger zircons.

To evaluate the effects of annealing on the Acasta sample, additional research into its pressure-temperature-time path is required. However, further radiation dose calculations that take into account the amount of time spent below the annealing temperature threshold would still be subject to a large degree of uncertainty. Even with a known pressure-temperature-time path for the sample, the conditions for annealing of natural zircon are not well constrained, and the role of fluids is unknown (Meldrum et al., 1998). The study by Meldrum et al, (1998) examined annealing in synthetic zircon free of impurities, therefore, it is difficult to extrapolate their results to the natural zircon with high levels of impurities (U, Th, Hf, Ca, REE, and Pb) used in this study. To fully evaluate the role of microstructure in facilitating or hindering Pb-loss, further study into the annealing of natural samples is needed.

This work has potential scientific applications outside of geochronology. Synthetic zircon is proposed as a host phase for the radioactive actinide isotopes. To determine if zircon is suitable to safely contain high-level radioactive waste, many studies have sought to determine the effects of radiation damage on the structure of zircon (Chakoumakos et al., 1987; Farges and Calas, 1991; Meldrum et al., 1998; Murakami et al., 1991; Weber, 1990; Weber et al., 1994). This study of fluid alteration of zircon, and its effects on element mobility, may have applications to researchers interested in the consequences of groundwater percolation through the waste repository.

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Appendix A Whole rock geochemistry for sample BNB-95-110c

	Abundance (%)			Abundance (ppm)		Abundance/Chondrite	
	(1)	(2)		(1)	(2)	(1)	(2)
SiO ₂	75.7	76.7	La	1.2	1.3	3.3	3.5
TiO ₂	0.04	0.01	Ce	1.7	2.1	1.8	2.2
Al ₂ O ₃	13.8	14.2	Pr	0.2	0.22	1.5	1.6
Fe ₂ O ₃ T	0.5	0.3	Nd	0.7	0.8	1.0	1.1
Fe ₂ O ₃	nd	nd	Sm	0.15	0.16	0.6	0.7
FeO	nd	nd	Eu	0.43	0.43	4.9	4.9
MnO	0	0	Gd	0.17	0.13	0.6	0.4
MgO	0.13	0.15	Tb	0.03	nd	0.5	nd
CaO	1.94	2.54	Dy	0.16	0.15	0.4	0.4
Na ₂ O	3.4	4	Ho	0.04	0.03	0.5	0.4
K ₂ O	4.24	2.67	Er	0.13	0.13	0.5	0.5
CO ₂ T	nd	nd	Tm	0.03	0.02	0.8	0.6
P ₂ O ₅	0.01	0.01	Yb	0.2	0.21	0.8	0.8
St	nd	nd	Lu	0.05	0.04	1.3	1.0
Ba	0.12	0.077	Y	1.2	1.2		
TOTAL	99.7	100.5	La/Lu			2.5	3.4

	Abundance (ppm)	
LOI	0.1	0.2
Ag	nd	nd
Be	0.8	1.1
Bi	nd	nd
Cd	nd	nd
Co	19	nd
Cr	nd	10
Cs	1.3	1.1
Cu	nd	nd
Ga	15	16
Hf	3.5	3.5
In	nd	0.07
Mo	0.8	0.5
Nb	0.93	0.55
Ni	13	nd
Pb	33	30
Rb	72	46
Sb	nd	nd
Sc	nd	nd
Sn	nd	nd
Sr	320	330
Ta	0.11	0.07
Te	nd	nd
Th	45	36
Tl	0.55	0.39
U	5.4	5.1
V	19	nd
Zn	8	7
Zr	100	99

nd = not detected

Appendix B Equation used to calculate radiation dose

$$D = [(M_{238}^0 - M_{238}) \times N_A \times 8 \times 10^{-3}] + [(M_{235}^0 - M_{235}) \times N_A \times 7 \times 10^{-3}] + [(M_{232}^0 - M_{232}) \times N_A \times 6 \times 10^{-3}]$$

D = radiation dose in α -events/mg

$M_{238, 235, 232}^0$ = number of moles of isotope per gram of mineral present at time t = time of growth of mineral; e.g. for ^{238}U : $(^{238}\text{U} \text{ (ppm)} \times 10^{-6} \times \text{abundance of } ^{238}\text{U} / \text{atomic weight of } ^{238}\text{U})e^{\lambda_{238}t}$

$M_{238, 235, 232}$ = number of moles of isotope per gram of mineral present today; e.g. ^{238}U (ppm) $\times 10^{-6} \times$ abundance of ^{238}U /atomic weight of ^{238}U ;

t = time of growth of mineral

$\lambda_{238, 235, 232}$ = decay constant for ^{238}U , ^{235}U and ^{232}Th respectively

N_A = Avogadro's number

Appendix C Cameca SX-50 Electron Microprobe Experimental Setup

Element	X-Ray Line	X-Ray line (Å)	Crystal Spectrometer	Standard	Count time (s) on Unknown	Peak (Sin Theta)	Background (+) (Sin Theta)	Background(-) (Sin Theta)	Interference	Detection Limit
Al	ka	8.339	TAP	Al ₂ O ₃	10	0.32467		0.32167		0.06
Si	ka	7.125	TAP	ZrSiO ₄	20	0.27735		0.27235		
P	ka	6.157	PET	(synthetic) GaP	300	0.70378	0.70778		Zr	0.03
Ca	ka	3.358	PET	Wollastonite	900	0.38383	0.38783			0.01
Mn	ka	2.102	LiF	Mn	10	0.52199	0.52799			0.2
Fe	ka	1.936	LiF	Fe	300	0.48078	0.48678			0.04
Y	la	6.449	PET	Y	300	0.73710	0.74210			0.1
Zr	la	6.071	PET	ZrSiO ₄	20	0.69371	0.69971			
Hf	ma	7.539	TAP	(synthetic) HfSiO ₄	600	0.29333	0.29933			
Th	ma	4.138	PET	(synthetic) ThO ₂	600	0.47264	0.47964	0.46264		0.07
U	ma	3.91	PET	(synthetic) UO ₂	600	0.44660	0.45660			0.07

Synthetic zircon and hafnon standards were generously provided by Dr. John Hanchar at Washington University.

Operating conditions 20 keV, 10nA

Standard calibration data acquired using 10s on peak

Off-peak count times are half that of on-peak count times

LiF 2d (A) 4.0267

PET 2d (A) 8.75

TAP 2d (A) 25.745

ZAF (atomic number-absorption-fluorescence) matrix correction

Appendix D Masuda-Coryell diagrams for sample BNB-95-110c.

Multiple REE analyses on individual grains are presented on the same diagram for comparison. The internal feature (i.e. bright patch, dark patch, tip) sampled by each analysis is noted.