Sequence stratigraphy, chronostratigraphy and zircon geochronology of the CIROS-1 drill core, Ross Sea, Antarctica: Implications for Cenozoic glacial and tectonic evolution

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### Abstract

Antarctica plays a central role in the global climate system. Understanding the continent's past climate interactions is key to predicting its future response to, and influence on, global climate change. In recent decades, sediment cores drilled on the Antarctic continental margin have provided direct evidence of past climatic and tectonic events. Drilled in 1986 from sea ice in western McMurdo Sound, the pioneering 702 m-long CIROS-1 core extended back to the Late Eocene and provided some of the first evidence of the antiquity and history of the Antarctic ice sheets. The CIROS-1 drill core recovered a depositional history of the western margin of the Victoria Land Basin adjacent to the Trans-Antarctic Mountains. It was located directly offshore from where the Ferrar Glacier, which drains the East Antarctic Ice Sheet, discharges into the Ross Sea. Consequently CIROS-1 contains a record of both the glacial and tectonic Cenozoic evolution of the Antarctic margin.

This thesis provides a timely re-evaluation of the CIROS-1 core with new analysis techniques that enable further insights into the glacial and tectonic history of the western Ross Sea region, and includes three key objectives:

(1) Re-examine CIROS-1 sedimentology and stratigraphy and provide a new facies and sequence stratigraphic analysis using modern methods developed from recent drilling projects (e.g. CRP, ANDRILL).

(2) Develop a new integrated chronostratigraphic model through an assessment and compilation of previous studies, which provides a context for the interpretation of detrital zircon data, climate and tectonic history.

(3) Undertake a detailed examination of the provenance of CIROS-1 sediments using cutting edge in situ analysis techniques of detrital zircons (U-Pb and trace element analysis using LA-ICP-MS).

Glaciomarine sequence stratigraphic analysis identifies 14 unconformity-bound sequences occurring in two distinctive stratigraphic motifs. The four sequences located beneath the 342 mbsf unconformity contain relatively complete vertical facies succession. They were deposited in shallow marine, fluvio-deltaic conditions with distal glaciers terminating on land, and possibly calving into the ocean in adjacent valleys as evidenced by occasional ice-rafted debris. The ten sequences located above ~342 mbsf have a fundamentally different architecture. They are incomplete (top-truncated), contain subglacial and ice proximal facies grading upsequence into distal glaciomarine and shelf conditions. Top truncation of these sequences represents overriding of the CIROS-1 site by the paleo-Ferrar Glacier during glacial phases.

A revised age model for CIROS-1 is presented that utilises new calibrations for Antarctic diatom zones and compiles three previously published age models for different sections of the core (Roberts et al., 2003; Wilson et al., 1998; Hannah et al., 1997). The new age model allows correlation of Late Oligocene cycles with coeval cycles in CRP-2/2A, 80 km to the north. A fundamental orbital control on the dynamics of these East Antarctic Ice Sheet outlet glaciers is evident from this comparison. Both glacier systems respond in-phase to longer-period orbital components (e.g. eccentricity 100 kyr and 400 kyr), but differ in their sensitivity to precession (20 kyr). It appears that during the Late Oligocene the Ferrar catchment responded to 20 kyr precession cycles, whilst the larger MacKay Glacier, which is more directly connected to the East Antarctic Ice Sheet, responded to longer duration 125 kyr (eccentricity) forcing. CIROS-1 zircons group into four distinct geochemical suites. Zircons formed in felsic igneous environments dominate the CIROS-1 population, with 89 % of zircons analysed showing geochemical characteristics inherent to granitic/rhyolitic zircons. Approximately 7 % of CIROS-1 zircons have a highly trace element enriched igneous provenance and were most probably sourced from enriched enclaves in granitic/rhyolitic units or from pegmatites. Approximately 3 % of CIROS-1 zircons show a metamorphic geochemical signature, and ~1 % formed in trace element depleted igneous environments. The zircons were sourced from the local basement (Koettlitz, Granite Harbour Groups), the Beacon Supergroup, and potentially, lithologies of the East Antarctic Craton located under the ice, or components of the Trans-Antarctic Mountains located under the current baseline of geologic exposure.

Large-scale, systematic temporal trends in zircon characteristics have been divided into three distinct climatic periods: Zone 1 (702-366 mbsf, Late Eocene), Zone 2 (366-250 mbsf, Late Oligocene) and Zone 3 (< 250 mbsf, Late Oligocene and Early Miocene). Zircons deposited during these periods show unique properties. During Zone 1, Antarctica experienced a relatively warm temperate climate and alpine style glaciers flowed eastwards through the Trans-Antarctic Mountains. Zircons in this zone contain a subtle record of unroofing of geochemically zoned Granite Harbour and Koettlitz units located in the Ferrar Valley. During Zone 2 deposition, glaciers flowed though the Trans-Antarctic Mountains draining a large and ephemeral EAIS, which oscillated on orbital time scales. Zircons in this interval show variable properties, high numbers and were most probably deposited as the paleo-Ferrar Glacier deeply incised the Ferrar Fiord. In contrast, Zone 3 is characterised by a flux of McMurdo Volcanic Complex derived sediments, together with systematic changes in zircon characteristics. These patterns indicate a Late Oligocene shift in ice flow to the site (above ~250 mbsf). Due to a cooling that culminated in the Mi-1 glaciation, ice flow to the site changed from an eastward to a northward flow, in response to an increased ice volume in the Ross embayment.

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Courtesy of Angie Fox, Scientific Illustrator at the University of Nebraska State Museum.

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# List of Acronyms

ANDRILL	Antarctic Geologic Drilling
BSE	Back scattered electron
CIROS	Cenozoic Investigations in western Ross Sea
CL	Cathodoluminescence
CRP	Cape Roberts Project
DSDP	Deep Sea Drilling Project
DVDP	Dry Valleys Drilling Project
EAC	East Antarctic Craton
EAIS	East Antarctic Ice Sheet
EAS	East Antarctic Shield
EPMA	Electron Probe Microanalyser
HREE	Heavy Rare Earth Elements
KES	Kukri Erosion Surface
LA-ICP-MS	Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry
LGM	Last Glacial Maximum
LREE	Light Rare Earth Elements
MREE	Medium Rare Earth Elements
MSSTS	McMurdo Sound Sediment and Tectonic Studies
MVG	McMurdo Volcanic Group
OPD	Ocean Drilling Project
REE	Rare Earth Element
SVL	Southern Victoria Land
TAM	Trans-Antarctic Mountains
VLB	Victoria Land Basin
WAIS	West Antarctic Ice Sheet

WARS West Antarctic Rift System

### **Chapter 1: Introduction**

Since. the climatic optimum in the Eocene the Earth's climate has experienced regular orbitally-paced glacial-interglacial fluctuations around a progressively cooling mean temperature (Zachos et al., 2001a). Superimposed onto this, large and abrupt shifts to a cooler climate have occurred during the Eocene-Oligocene boundary (~34 Ma; Kennett et al., 1975; DeConto and Pollard, 2003), the Oligocene-Miocene boundary (~23 Ma; Naish et al., 2001a; Pekar et al., 2006) and the Middle-Late Miocene climate transition (~13.8 Ma; Lewis et al., 2007) (Fig. 1.1). The marine oxygen isotope record from the deep ocean (Zachos et al., 2001a) arguably provides the most detailed and complete picture of the global cooling of Earth's climate during the Cenozoic and has allowed insights into past global ocean temperatures, ice volumes and sea water salinity.



Figure 1.1: Global temperature curve constructed from the composite  $CO_2$  isotopic ratios of benthic foraminifera in deep ocean sediments. Key climate events of the Cenozoic are annotated (source: Barrett, 2009).

It is known that Antarctica has played a pivotal role in the global climate system since the Cenozoic. The continent influences the Earth's albedo and ocean circulation and the Antarctic cryosphere contains enough water to raise global sea levels by  $\sim$ 65 m (IPCC, 2007). Nonetheless, there are still many questions regarding Antarctica's response to Cenozoic cooling (due to the continents remoteness and ice cover) and how the continents cryosphere may respond to the projected global warming from anthropogenic increases in atmospheric greenhouse gasses (IPPC, 2007; Naish et al., 2008a). In order to predict the future behaviour of the Antarctic cryosphere, it is first necessary to understand its past response to climate forcings.

A record of Antarctic's geological, tectonic, glaciological and climate past has been constructed in recent decades using a variety of ingenious sampling and modelling methods, possible despite the continent's extensive ice cover and isolation. These include integrated seismic and drill core basin analysis (e.g. Fielding et al., 2008) and analysis of the on-land geology (e.g. Siddoway and Fanning, 2009; Elliot and Fanning, 2008). Drilling continental shelf sediments eroded from the interior of the continent and deposited into sedimentary basins on the periphery provides direct evidence for the tectonic, climate and glaciological conditions present during sediment erosion and deposition.

The Victoria Land Basin (VLB) in the Ross Sea has been a hub of sediment drilling in the Antarctic over the last three decades. The basin is located adjacent to the Trans-Antarctic Mountains (TAM) in the West Antarctic Rift System (WARS) (Fig. 1.2) and has been the focus of extension in the WARS since the Late Eocene (or perhaps Cretaceous) (Fielding et al., 2008). The basin has accommodated an up to 10 km thickness of sediment supplied from the TAM and deposited by a variety of fluvial, glacial, volcanic and marine processes.

The McMurdo Sound area of the VLB (Fig. 1.2) has been the prime target for Antarctic sediment drilling over the last three decades for the following reasons (1) The high subsidence rates and high sediment accumulation rates means that, in this locality, the basin contains a fairly complete record of Antarctic climate and tectonism since the Late Eocene; (2) The location is proximal to pre-established bases and the McMurdo Station logistics hub; and (3) The region has the best understood sedimentary Cenozoic climate record in Antarctica (summarised in Barrett, 2009). Early sediment drilling in the VLB included the MSSTS-1 (late 1970's) and CIROS (1984 and 1986) projects (Barrett, 2009). Later, more advanced projects include the three-coring season Cape Roberts Project and, most recently, the two drill holes of the ANDRILL Project (Fig. 1.2).



Figure 1.2: Inset: A simplified overview of the tectonic and glacial components of Antarctica. Main picture: The tectonic configuration of the WARS in the Ross Sea embayment. The VLB is located in this basin adjacent to the TAM. The location of CIROS-1 is shown in red (modified from Fielding et al., 2008).

There is a large cost associated with obtaining new drill cores from the Antarctic periphery. This high cost, the value and relative paucity of direct evidence for Antarctica's past behaviour and recent advances in our ability to construct glaciological and tectonic histories from Antarctic sediments cores (e.g. Fielding et al., 2008; Dunbar et al., 2008) make it timely and beneficial to re-evaluate the early records obtained using modern techniques.

The CIROS-1 drill core was drilled into the VLB (Fig. 1.2) to a depth of 702 mbsf (Hambrey et al., 1989) and contains sediments of Late Eocene to Early Miocene age deposited as part of a glaciomarine deltaic complex fed from the Ferrar Valley (Barrett, 1989). The core contains a record of the Antarctic response to global climate events (e.g. the initiation of Antarctic glaciation and the Mi-1 glaciation) (Fig. 1.1) as well as a record of regionally-important tectonic events, such as the uplift of the TAM.

### 1.1. Objectives of this thesis

The objectives of this thesis are to re-evaluate the record of Antarctic climate and tectonism contained in the CIROS-1 core (Fig. 1.2). By analysing the core using modern techniques, fresh insights into the record contained in these sediments will be obtained.

More specifically, the two aims of this thesis are:

(1) Re-evaluate the sedimentology, lithofacies, sequence stratigraphy and chronology of CIROS-1 sediments using sediment analysis methods developed for the recent Antarctic drill cores (i.e. CRP and ANDRILL, e.g. Fielding et al., 2001; Dunbar et al., 2008; Naish et al., 2001b).

(2) Re-evaluate CIROS-1 sediment provenance (and any temporal variations therein) using modern in situ laser ablation inductively coupled (LA-ICP-MS) U-Pb and trace analysis of detrital zircons found in CIROS-1 sands. Such methods include those utilised and described by Chang et al. (2006); Kösler and Sylvester, (2003); and Veevers et al. (2008).

#### **1.2. Structure of this thesis**

This thesis comprises seven chapters and four appendices. The contents of these are as follows.

Chapter 2 describes the tectonic, climatic and glaciological history of the Antarctic continent with an emphasis on the depositional setting of CIROS-1 strata. This includes an overview of the zircon characteristics of known potential source units for CIROS-1 zircons.

Chapter 3 is a stand-alone paper that presents a revised sedimentology, lithofacies model, sequence stratigraphy and chronology for the CIROS-1 core. This paper is co-authored by Tim Naish, Chris Fielding and Mike Hannah and will be submitted to the journal *Sedimentary Geology*. Included in this paper are:

(1) A new stratigraphy of the CIROS-1 drill core, logged using the well-preserved, archived half of the core;

(2) A re-evaluated lithofacies scheme for the core, based on lithofacies models developed for CRP (Fielding et al., 1997; Fielding et al., 2001);

(3) A new composite sequence stratigraphic interpretation of CIROS-1 sediments based on recently developed sequence stratigraphic models for glaciomarine sedimentation on a wave-dominated coastline (Dunbar et al., 2008); and

(4) A new chronology for CIROS-1 sedimentation constructed by splicing of historical data (e.g. Roberts et al., 2003; Wilson et al., 1998) and newly developed chronologies.

Chapter 4 is a review of the use of zircons as an indicator of sediment provenance and an overview of the methods used in this thesis.

In Chapter 5, the geochronological and geochemical analytical techniques and data reduction methods used to obtain CIROS-1 zircon U-Pb and trace element characteristics by LA-ICP-MS are outlined. This includes an outline of samples analysed, a review of the operational parameters used during analysis and an overview of the detrital zircon-based tools used for CIROS-1 sediment provenance analysis.

Chapter 6 outlines the results of the dating and geochemical analyses of CIROS-1 zircons conducted in this project and a discussion of the implications of these results. This includes an overview of the provenance of CIROS-1 zircons and a discussion of the temporal trends observed down-core. The implications of these results for the Cenozoic evolution of the East Antarctic Ice Sheet and older tectonic evolution of the Antarctic Craton are outlined.

Appendix 1 presents detailed sedimentological descriptions for each of the 18 samples analysed. Appendix 2 contains the U-Pb isotopic data and the calculated ages for all analysed zircons. Appendix 3 contains the trace element data of the three samples analysed for zircon trace element composition. Appendix 4 contains CL images for all CIROS-1 zircons analysed (Appendix 4 is located in a CD disc at the back of the thesis).

### Chapter 2: Geological, glacial and climatic setting

### 2.1. Introduction

Antarctica is a particularly challenging continent for which to construct a tectonic and geologic history due to its extensive ice-cover, cold climate and isolation. However, a tectonic and geologic record has been constructed using various sampling and modelling methods which include integrated seismic and drill core basin analysis (e.g. Fielding et al., 2008; Fielding et al., 2006) and both direct (e.g. Siddoway and Fanning, 2009; Elliot and Fanning, 2008) and indirect sediment sampling. Sampling of sediments eroded from the interior of the continent and deposited on the periphery provides direct evidence for the tectonic and glacial conditions present during their deposition. This method provides the basis for this study and has been the focus of much research in the Ross Sea and other peripheral locations around the Antarctic continent (e.g. Harwood et al., 2008; Veevers et al., 2008).

The sedimentary strata that comprise the CIROS-1 drill core are part of a glaciomarine deltaic complex fed from the Ferrar Valley (Barrett, 1989). From the Late Eocene-Early Miocene (~38-21 Ma) these sediments were eroded from strata located in SVL (and potentially the EAC) and deposited into the VLB (Fig. 2.1). Sedimentation and deposition of detrital zircons at this site is influenced by three main factors; the geographical location of potential zircon source lithologies, tectonism during sediment deposition (e.g. exhumation of source lithologies and formation of accommodation space), and the climate and glacial dynamics during sediment deposition (e.g. erosional, depositional and sorting mechanisms). On the basis of these three factors, the present understanding of these depositional controls within the western Ross Sea are reviewed in this section, in order to provide a framework for CIROS-1 sedimentation dynamics discussed in later chapters.

## 2.2. Tectonic history of the West Antarctic Rift System and Trans-Antarctic Mountains

The Ross Sea is located above the WARS. The Sea is bounded by the TAM and the EAC in the west and the rocks of West Antarctica in the east (Fig. 1.2). The WARS and the TAM are the dominant tectonic features of the Ross Sea. The WARS separates East and West Antarctica (Fig. 1.2) and extends below the Ross Sea, the Ross Ice Shelf and part of the WAIS (Fitzgerald, 2002). The rift system formed in response to initial rifting between East and West Antarctica during the breakup of Gondwana and has had a complex history (Winberry and Anandakrishnan, 2004), with the main phase of extension and crustal thinning occurred in the late Cretaceous (105-85 Ma).

The system comprises a series of asymmetric basement grabens, separated by basement highs. CIROS-1 sediments were deposited into one such graben; the VLB. The VLB has been the focus of WARS extension since the Late Eocene or perhaps even Cretaceous, when rapid subsidence occurred due to crustal thinning and extension (Fitzgerald, 2002; Barrett, 2009). Slower rates of subsidence of the VLB occurred in the Miocene, when thermally controlled subsidence became the main driving mechanism, a process that has continued to present day (Fielding et al., 2008). The VLB is ~350 km long and has accumulated sediment thickness of up to 10 km.

The TAM are located at the western edge of the WARS (and VLB) (Figs. 1.2 and 2.1) and define a fundamental lithospheric boundary between the EAC and the WARS. They are 3500 km long, typically 100-200 km wide and <4500 m high (Fitzgerald, 2002). The TAM are divided by transverse structural features such as faults, grabens and accommodation zones through which major outlet glaciers typically run (Fitzgerald, 2002). The lithospheric boundary on which the TAM occurs has experienced numerous periods of exhumation, the most recent occurring in the Early Cenozoic. This episode caused the rock uplift associated with the formation of the TAM, which commenced ~55 Ma ago (Fitzgerald, 2002; Barrett, 2007). Average estimated exhumation rates for the TAM are relatively slow (100 m/Myr), and are hypothesised to have been quicker in the first 10-15 Ma of TAM uplift (Fitzgerald, 2002). By c. 36 Ma, when deposition of CIROS-1 sediments into the VLB had commenced, ~2 km of Ferrar and Beacon cover rocks had been eroded from the

TAM, which were approximately their current height (Stern et al., 2005). By this time the basement and overlying Beacon Supergroup were extensively exposed in the TAM (Barrett, 1999) and were being actively eroded (these units are extensively detected in the CIROS-1 drill core) (Barrett, 1989).



Figure 2.1: Cross-sectional view of the tectonic setting of the VLB, VLB stratigraphy and simplified geology of the TAM. Note the location of CIROS-1 proximal to the TAM and on the western margin of the Ross Sea and VLB (source: Naish et al., 2006).

## 2.3. Geology of the Trans-Antarctic Mountains in South Victoria Land

The geology of the TAM in SVL (Fig. 2.3) is a product of erosion, deposition and deformation of the geological units of the EAC margin. Many of the units in SVL formed in response to the Ross Orogeny, a series of events caused by collision of parts of West Gondwana along an internal suture (Tingey, 1991). This event caused widespread basement deformation, regional metamorphism, sedimentation of units and igneous intrusions and associated contact metamorphism. The orogeny may have started as early as ~590 Ma with the main period of Ross tectonism occurring post-Early Cambrian (Goodge et al., 2002).

The SVL basement consists of Proterozoic to Cambrian metamorphic and Cambrian-Ordovician intrusive units including granites formed during the Ross Orogeny (Granite Harbour Group) and metamorphic units (Skelton Group) (Fig. 2.2). The Granite Harbour intrusives are part of the numerous felsic plutons and smaller plugs and dykes (Allibone et al., 1993a) located along the length of the TAM. These (predominantly granite) plutons were intruded into a crystalline basement in two main phases between 590 and 455 Ma (Allibone et al., 1993b). The crystalline basement in SVL consists of the metamorphic units of the Skelton Group which formed during the early stages of the Ross Orogeny, when the basement underwent widespread deformation and metamorphism (700  $\pm$  50 °C and 4-5  $\pm$  1 kilo bar, upper amphibolite facies) (Allibone, 1992). The group includes multiply deformed marbles, calc-silicates, and pelitic, psammitic and amphibolitic schists (Grindely and Warren, 1964) that underwent variable episodes of deformation, metamorphism and intrusion of Ross granites. Denudation following the Ross Orogeny led to the formation of the Kukri Erosional Surface throughout the TAM in pre-Devonian times (Fitzgerald, 2002) (Fig. 2.3).

During the Devonian-Triassic, prior to rifting associated with the breakup of Gondwana, the Beacon Supergroup was deposited onto the Kukri Erosional Surface (Elliot and Fanning, 2008) (Fig. 2.2). During deposition of the Beacon Supergroup, an active magmatic arc was located at the paleo-Pacific boundary of the EAC. The Beacon Supergroup is divided into two units; the Taylor and Victoria Groups, separated by the Maya Erosional Surface. The Taylor Group, deposited on the Kukri Erosional Surface, is a voluminous (up to 1.4 km thick), dominantly sandstone unit, that outcrops predominantly in SVL (Elliot and Fanning, 2008).



Figure 2.2: Geology of SVL. The Ferrar Fiord is located between the McKay and Koettlitz glaciers, due west of the AND-1B site. The CIROS-1 site is located at the mouth of the Ferrar Fiord, approximately 20 km offshore. The most seaward geological unit located in the Ferrar Fiord are the metamorphic units of the Koettlitz and Skelton Groups. The Ross-aged Granite Harbour Group and the Beacon Supergroup are located progressively more inland. Annotations (ME, MB, MD etc) are annotated of the names of MVG volcanoes (source: Talarico et al., 2009).

The Victoria Group, the Permian-Triassic section of the Beacon Supergroup, was deposited into intra-cratonic basins whilst a magmatic arc was present and contributing large amounts sediments to the unit (Elliot and Fanning, 2008). The

group records the transition from a marine to terrestrial depositional environment, grading from marine sandstones to fluvial coal measures and then to Triassic flood plain sediments. Sedimentation of the Victoria Group ended in the Late Triassic (Savage, 2005; Elliot and Fanning, 2008).

The Ferrar Dolerite is a component of the Ferrar Large Igneous Province and was intruded into the Beacon Supergroup as a series of bedding-parallel, voluminous  $(1.7 \times 10^5 \text{ km}^3)$  sills and dykes (Elliot and Fleming, 2008; Fleming et al., 1997) in response to rifting between East and West Gondwana (Elliot and Fanning, 2008; Encarnación et al., 1996). Rifting commenced in the Jurassic and was punctuated by the deposition of siliclastic volcanic sediments into the early rift (Elliot and Fleming, 2008: Ross et al., 2008), followed by plume related magmatism at ~184 Ma (Encarnación et al., 1996). The Ferrar Large Igneous Province includes the Ferrar Diorite (dolerite sills and dykes) and the Kirkpatrick Basalt (erupted as pyroclastic rocks and lava flows) (Elliot and Fanning, 2008).

There is a c. 160 Myr gap in the stratigraphic record on land due to uplift and erosion of the rift margin (Fig. 2.3). Sediments have been deposited into the VLB since the Late Eocene, leaving an interval of time between 160-40 Myr unrepresented geologically in this part of Antarctica (Fig. 2.3).

		Age	Stratigrpahic unit	Description	Max thic	ckness (	metres)	Depostional environment	
					СТМ	SVL	NVL	an 1999 - Profil Indon House of Contract State House Dover Class House 1999	
Ferrar Group		<b>^</b>	Kirkpatrick flood basalt	Basaltic flows; glassy margins, scoriaceous tops, flow banding and pillows, with common amygdales and geodes of banded chalcedony, quartz, calcite and zeolite. Intercalated Mawson Formation tuff, lapilli-tuff and tuff-brecia, Carpace Sandstone, and Beacon Supergroup sandstone. Eroded channels in the surface of some flows have been infilled by succeeding flows	525	380	780	Sub-aerial and sub-aqueous; some flows coeval with fluvial and lacustrine sedimentation	
	olacem -		Ferrar intrusions	Tholeiitic basalt dikes and sills					
	ositionis/emp	184±1 Ma	Mawson Formation Exposure Hill Formation - NVL Prebble Formation - CTM	Heterolithologic, poorly - to unbedded basaltic tuff-breccia and lappili-tuff, minor bedded lapilli-tuff and tuff. Widespread peperite, hyaloclastite, swirly dikes	360	400+	100+	Subaerial	
	<ul> <li>Coeval dep</li> </ul>		Carapace Sandstone	Quartzose, quartz lithic and quartz-volcanic yellow or cream-coloured sandstones interbedded with siltstone, shale and chert horizons; hosts the richest and most diverse freshwater Jurassic biota recorded from Antarctica. Includes basaltic ash, increasing upsection, and accretionary lapilli-bearing beds		120		Sub-aerial and sub-lacustrine	
	↑ [	Unnamed men	nber - SVL; Hanson Formation - CTM	Silicic tuff, volcaniclastic sandstone, minor arkosic grit and sandstone, and lapilli tuff					
əergroup 		Jurassic	Lashly Formation	Arkosic and volcaniclastic sandstone, greenish grey and grey siltstone. Roots and stems common in lower part	1	520+ (34	40+)	ow-energy braided fluvial system on broad loodplain with low-lying mire complexes; periodic	
	- dnou	Triassic	Fleming Member	Quartzose sandstone with common pinkish grains, and yellowish-green siltstone. Clearly developed only north of the Taylor Glacier		(100)		large-volume nood events (metwater?)	
	ctoria G		 Feather Conglomerate 	Vein quartz pebble conglomerate, quartzose and arkose sandstone, siltstone and grit. Upper and lower 50m are mainly sst with scattered white and pinkish quartz pebbles	220 (120)		0)	Fluvial, lacustrine	
	5		Weller Coal Measures	Quartzose and minor arkoic sst and minor carbonaceous siltstone. Pebbles and boulders scattered and in lenses, especially near the base. Coals, logs and stems in upper part.	3	250 (110	)+)	Some small lakes (ponded thermokarst)	
		— — — — — — —		As for Weller, but lacks coal. Occurence local to Allan Hills area -	Pyramid	erosion	surface		
	Ļ	Lower Permian	Metschel Tillite	Tillite, conglomerate, sandstone, siltstone. locally slump-folded. A few striated surfaces. Clasts are mainly granitic and up to 1m across		70		Glacial, peri-glacial	
Sul	۸.			mainly granice and op to min across	Maya erosion surface				
Beacon —Taylor Group		Mid-Upper Devonian	Aztec Siltstone	Greyish red, greenish grey and grey siltstone and light coloured sandstone. Fish fossils, plant roots, mudcracks and ripplemarks common		220		New service	
			Beacon Heights Orhtoquartzite	Indurated quartz arenites with occasional quartz grit lenses. Rare lycopod stems		340		Non-marine	
		Devonian and ?Pre-Devonian	Arena Sandstone	Yellowish and light greenish grey quartz arenites and siltstones, ferruginous layers, burrows and trails		360			
	iroup		Altar Mountain Formation	Sandstone, siltstone, subarkose. Burrows and trails		240		Deltaic/coastal	
	ylor G		Odin Arkose	Arkose grit and conglomerate	Heimdall	(50) Lerosior	1 surface		
			New Mountain Sandstone	Quartzose sandstone, minor siltstone		270		Oballauranaina	
			Boreas Subgreywacke	Argillite, sandstone, conglomerate		(20)			
			Terra Cotta Siltstone	Siltstone, minor sandstone		60		Lagoonal?	
			Windy Gully Sandstone	Pebbly quartzose sandstone		50		Shallow marine	
3	↓				Kukri erc	osion su	rface	Marine transgression	
Basement		NeoProtoerozoic to Cambrian	Skelton Group North & South Hobbs Schist Salmon Marble	Upper amphibolite facies metasediments					
			Granite Harbour Intrusives	Undifferentiated granitoids					

Figure 2.3: Summary of the geology of the TAM in SVL including the names of units, unit descriptions, thicknesses, depositional environments and ages (source: McClintock, 2001).

### 2.4. Geology of the East Antarctic Craton

It is challenging to reconstruct the geology of the EAC due to extensive ice cover, poor petrological preservation, geochronological uncertainty due to isotopic resetting and debate over geological field relationships of exposed units (Goodge et al., 2001). However, it is understood that the geology of the Antarctic Shield is complex and composed of zones of mobile belts of Mid-Late Proterozoic metamorphic and igneous rocks that wrap around, separate and influence the edges of the older cratonic components (Tingey, 1991). The EAC is thought to be one of the oldest on Earth (Goodge et al., 2001) and includes Pan-African aged belts, Grenville aged provinces, Proterozoic domains and Archaean cratons (Fitzsimons, 2000; Harley, 2003). The growth of the EAC has been punctuated by a number of Archaean orogenic events including the Napier, (4.0 Ga), Rayner (3.5 Ga), Humboldt (3.0 Ga) and Insel (2.65 Ga) orogenies (Fitzsimons, 2000; Harley, 2003). The Proterozoic geological history of the EAC is dominated by three orogenic episodes, the Nimrod (1.73-1.72 Ga) (Goodge et al., 2001), Grenville (1.4-0.9 Ga), and Ross/Pan-African orogenies (600-400 Ma) (Fitzsimons, 2000; Laird, 1991).

#### 2.4.1. Geology of the Ross Sea sector of the East Antarctic Craton

There are no outcrops of the EAC in the Ross Sea region and most insights into the composition of the EAC near the Ross Sea are from investigations of the composition of sediments eroded from the craton and deposited on the periphery. Palmer (2008) presented detrital zircon ages for a variety of modern sediments located in numerous locations in the Ross Sea and TAM (Fig. 2.4). From this, it appears that the sector of the EAC underlying the section of the EAIS that drains into the Ross Sea may consists of:

- (1) 650-750 Ma Pan-African (?) units of igneous and metamorphic origin;
- (2) 0.9-1.3 Ga aged Grenvillian provinces of igneous and metamorphic origin; and
- (3) Numerous Archaean and Proterozoic igneous and metamorphic components.



Figure 2.4: Cumulative age probability diagram of modern sediments sourced from tills deposited by the Byrd Glacier and sediment samples in the Ross Sea. The age peaks herein are indicative of the ages of components that comprise the Ross Sea sector of the EAC (source: Palmer, 2008).

### 2.5. Potential source units for CIROS-1 zircons

Initial work on CIROS-1 sand provenance (Roser and Pyne, 1989; George, 1989) concluded that sand source units were confined to the basement of the Ferrar Fiord (Skelton and Granite Harbour groups) and the Beacon Supergroup. No evidence for direct contribution from the EAC was reported. The more advanced techniques used in this study allow detection of subtle aspects of sand provenance, such as a very minor input of zircons from a more distal lithology, that may have been undetectable using previous methods. With this consideration the following section has been constructed. In this section, the characteristics of all potential source lithologies for zircons found in the CIROS-1 core are reviewed. This includes lithologies not assessed to be contributing to sediments by earlier workers and includes proximal lithologies (such as those in the Ferrar Fiord) as well as distal units deemed to be within depositional distance of the core. No West Antarctic lithologies are reviewed, as modern day and reconstructed glacial ice flow lines indicate no West Antarctic input of sediments into the McMurdo Sound (Licht et al., 2005; McKay, 2008).

Potential lithologies reviewed in this section include both direct (igneous and metamorphic) and indirect (sedimentary) sources. Zircons with characteristics that cannot be tied to a known outcrop are assumed to be sourced from lithologies located under the ice or the current baseline of geologic exposure. To illustrate potential source lithologies and depositional pathways for CIROS-1 zircons, a map showing a generalised geology of the Ross Sea and paleo-ice flow lines for the LGM is included (Fig. 2.5).

#### 2.5.1. Descriptions of potential lithological sources for CIROS-1 zircons

#### 2.5.1.i. Direct sources

#### A. Granite Harbour Group

The Granite Harbour intrusive units are a dominant lithology in SVL and occur in the western Ross Sea border, the TAM, Dry Valleys and Ferrar Fiord. This group comprises the igneous units of the Ross Orogeny that formed through widespread intrusion of granites and numerous smaller plugs and dykes along the palaeo-Pacifc subduction zone of the EAC during the Ross Orogeny. These batholiths were emplaced during two periods: 589-490 Ma (syntectonic) and 486-477 Ma (post-tectonic). In the Dry Valleys, plutons are present in two forms. The older plutons are relatively undeformed, concordant, monzodiorite and granodiorite. They occur at deeper levels and were emplaced synchronously with the formation of the upper amphibolite facies Skelton Group. The younger plutons are discordant and consist of granodiorite and granite emplaced at higher crustal levels. The younger plutons formed in response to uplift and extension. Also present are younger mafic and felsic dykes (Allibone et al., 1993a).

#### B. Skelton Group

The Skelton Group occurs in the basement of SVL, and contains the oldest rocks in SVL. The group formed between 540-500 Ma, during metamorphism associated with the Ross Orogeny, and consists of regional and contact metamorphic units that formed from various protoliths. Units in the Skelton Group include metasediments, intercalated orthogneisses and pellitic schists, which experienced low pressure/high temperature deformation (700  $\pm$  50 °C and 4-5  $\pm$  1 kbar, upper amphibolite facies) and underwent variable episodes of deformation and metamorphism and

intrusion of Ross granites (Goodge et al., 2002; Rowell et al., 2001; Allibone, 1992; Allibone et al., 2003a and b; Findley et al., 1984).

#### C. Cotton Plateau Gabbro

The Cotton Plateau Gabbro is located within the Beardmore Group, a sedimentary unit located at the head of the Nimrod Glacier. It was emplaced ~668 Ma and consists of mafic metavolcanic units and includes greenschist facies pillow basalts, gabbro and plagiogranite. This unit produces zircons that yield concordant ages and are double prismatically terminated, equant to elongated in shape and contain abundant opaque inclusions (Goodge et al., 2002).

### D. 1.4 Ga Granitic Unit

This unit was inferred to be located under the EAIS (Fig. 2.5) based on studies of detrital zircons deposited in sediments located under the Ross Sea. It has an emplacement age of 1.4 Ga and a chemistry similar to A-type granites found in Laurentia. This unit is thought to be responsible for many of the detrital zircons of this age found around eastern Antarctica (Goodge et al., 2008).

### E. Nimrod Group

This group is located near the Upper Nimrod Glacier. It consists of a heterogeneous assemblage of gneisses, schists and orthogneisses that formed during multiple orogenic events from variable protoliths of Archaean age. The units of the Nimrod Group produce zircons that have recorded multiple events. Ages of zircon growth zones include 3 Ga, 2.9 Ga, 2.5 Ga, ~1.7 Ga and 530 Ma (Goodge et al., 2001; Goodge and Fanning, 1999; Grindley and McDougall, 1969; Grindley and Warren, 1964).



Figure 2.5: Geology of the TAM and inferred geology of the EAC combined with LGM reconstructed ice flow lines. Note the location of the CIROS-1 core, which is marked by the black oval. The Beacon Supergroup in the Ferrar Fiord consists of both Taylor and Victoria Groups. (Ice flow lines and TAM geology from Licht et al., 2005; Savage, 2005 and McKay, 2008. Vostok core location from Delmonte et al., 2004. Proterozoic granite complex located under the ice from Goodge et al., 2008).
## 2.5.1.ii Recycled sources

Most siliclastic rocks in Antarctica contain large (but generally not dominant) populations of ~1.8- to 1.6 Ga detrital zircons in addition to relatively sparse Mesoproterozoic (1.2 to 0.9 Ga) and Archaean populations. These are generally assumed to be sourced from the EAC under the ice (Goodge et al., 2008), which indicates paleo-Proterozoic igneous and/or metamorphic rocks are a substantial crustal component within the composite EAC, as well as minor Archaean rocks.

## A. Beacon Supergroup

The Beacon Supergroup is subdivided into two units, the older Taylor Group and younger Victoria Group.

The Taylor Group, which outcrops predominantly in SVL, was deposited onto the KES during the Devonian. It is a voluminous unit (up to 1.4 km thick) consisting mainly of well sorted sandstones that outcrop in the Sperm Bluff near the MacKay Glacier and on the southern side of the Ferrar Fiord (Elliot and Fanning, 2008; Savage, 2005). The zircons in the Taylor Group are dominated by a ~500 Ma age peak and older subordinate age peaks (Fig. 2.7). No age peaks younger than ~450 Ma have been reported in any Taylor Group localities.

The Late Proterozoic-Early Cambrian zircons (490-560 Ma) found in the Taylor Group are inferred to have a Granite Harbour Group provenance. Proterozoic and older grains (~650-3300 Ma) are inferred to be sourced from either erosion of older units (e.g. Skelton Group or the units of the EAC) or from the inherited component of Granite Harbour igneous units (Bassett et al., 2009; Savage, 2005; Bradshaw and Harmsen, 2007).



Figure 2.6: Examples of age probability diagrams for zircons obtained for the Taylor Group at Sperm Bluff, SVL. The top age probability, from a granulite conglomerate, is dominated by a ~500 Ma age peak. The bottom diagram is the age probability diagram constructed from a granulitic conglomerate at a different locality on Sperm Bluff. As with the top diagram, this shows a dominant age peak at ~500 Ma with additional subordinate peaks at ~700-2200 Ma and ~3.3 Ga (source: Savage, 2005).

The Victoria Group was deposited into intra-cratonic basins during the Permian and Triassic in association with a magmatic arc. The group records a transition from marine to terrestrial depositional settings from marine sandstones to fluvial coal measures to Triassic flood plain sediments. Victoria Group sediments were derived from both the EAC and volcaniclastic sandstones derived from this magmatic arc present during deposition. The characteristics of zircons in the Victoria Group are highly variable dependent on the spatial and temporal location of sampling (Fig. 2.7).



Figure 2.7: Examples of age probability diagrams constructed using detrital zircons from the Victoria Group of the Beacon Supergroup. Note the ~200 Ma peak, the pronounced Early Cambrian peak and the older 'cratonic' component (source: Elliot and Fanning, 2008).

Late Permian (267  $\pm$  3 Ma and 249  $\pm$  3 Ma) zircons found in the Victoria Group are hypothesized to be from a magmatic source of Permian age, potentially the active magmatic arc present at the paleo-Pacific boundary of the EAC. Late Devonian zircons (~370 Ma) found in the group were potentially sourced from the Ford Granodiorite in Marie Byrd Land or 'from an uncertain extension of that belt eastward toward the Antarctic Peninsula' (Elliot and Fanning, 2008). The ~460-510 Ma zircons located in the Victoria Group were sourced from post-tectonic Ross granitoids, whilst Early Cambrian grains (560-510 Ma) were sourced from Ross or late Pan-African units. Late Neoproterozoic aged grains (~640 Ma) are inferred to be sourced from unknown early Pan-African units located in the EAC and Proterozoic and older grains from other unknown units in the EAC (Elliot and Fanning, 2008).

#### B. Beardmore Group

The Beardmore Group was deposited during the Late Precambrian, syntectonic with the Ross Orogeny. The group comprises pelitic schists, hornfels, metagreywackes, argillites and contains two assemblages, one which is located nearer the paleocoastline that the other.

The Beardmore Group inboard assemblage was deposited during the Late Proterozoic ( $\leq 670$  Ma) in a platform to shoreline setting along an existing rift margin. The assemblage contains zircons from mixed cratonic sources that are dominated by 2.8 Ga and 1.9 to 2.4 Ga ages (Fig. 2.8). All zircons in this assemblage are thought to have been sourced from unknown units located under the ice in the EAC (Goodge et al., 2002).



Figure 2.8: Age probability diagrams produced for zircons from the Beardmore Group inboard assemblage (source: Goodge et al., 2002).

The volumetrically dominant outboard assemblage (Byrd Group) was deposited during the Early Cambrian ( $\leq$ 520 Ma) in a continental margin volcanic arc setting. Detrital zircon ages in this group show a heavy dominance of Ross Orogeny aged strata (~500 Ma) and with minor 1.4 Ga, 1.1-0.94 Ga and 825 Ma age peaks (Fig. 2.9).



Figure 2.9: Detrital zircon age probability diagram for the Byrd Group. Note the presence of a Ross aged peak and the presence of various cratonic-sourced and Grenvillian-aged zircons (source: Goodge et al., 2002).

The Late Proterozoic-Early Cambrian (500-600 Ma) zircons located in the Byrd Group are thought to be sourced from the Ross granitoids in the TAM. Zircons of ~668 Ma in age are thought to be sourced from the Cotton Plateau Gabbro. Zircons in the Byrd Group ~830 Ma and 1.1-1.2 Ma in age are thought to have been sourced from an unknown igneous source and asyet unknown Grenvillian aged belts. The zircons in the ~1.4 Ga age peak are hypothesised to be sourced from the igneous province inferred to be under

the EAIS by Goodge et al. (2008), whist older grains (1.5-2.8 Ga) were sourced from unknown cratonic components (Goodge et al., 2002).

## 2.6. Climatic and glacial influence on CIROS-1 deposition

CIROS-1 sediments were deposited as part of a glaciomarine deltaic system fed by the Ferrar fiord (Barrett, 1989) between  $\sim$ 38-22 Ma. The fluctuation of ice sheets and the dynamics of glaciers played a critical role in the erosion, transportation and deposition of sediments present in CIROS-1. In order to provide a framework for investigations into CIROS-1 sediments that occur in later chapters, the current knowledge of Antarctic and global climate conditions during CIROS-1 sedimentation are outlined in this section.

#### 2.6.1. Cenozoic global ice volumes

The isotopic composition of oxygen in sea water changes in response to variances in global ice volume, local deep-sea temperature and salinity of seawater (Zachos et al., 2001a).  $\delta^{18}$ O of sea water increases during cold periods, whilst it decreases when global and/or local temperatures increase. Benthic foraminifera live on the sea floor. In some species, the  $\delta^{18}$ O composition of foraminifera tests directly reflects that of the seawater in which they lived. Thus, by measuring the  $\delta^{18}$ O of foraminifera tests, the global ice volume, sea water temperature and salinity in which it grew may be inferred. It is estimated that a 1 ‰ increase in  $\delta^{18}$ O is reflects a 110 m fall in sea level or 4 °C decrease in global temperature (Barrett, 1999; Kennett, 1982)

The Cenozoic ice volume and temperature record (Fig. 2.10) can be divided into 4 broad periods (Barrett, 1999; McKay et al., 2009; Barrett, 2009):

(1) 100-34 Ma; 'Greenhouse world'-preglacial times in Antarctica.

(2) 34-14 Ma; 'Transition world'- first occurrence of continental glaciation of

Antarctica, ephemeral and large ice sheets that extended to the continental margin.

(3) 14-2.6 Ma; 'Icehouse world'- persistent ice sheets on Antarctica, the variability of size much debated.

(4) 2.6 Ma-present: 'Icehouse world'- current Antarctic regime with large and constant ice sheets.

The deep-sea benthic record shows an increase in  $\delta^{18}$ O of 5.4 ‰, reflecting a cooling trend during the Cenozoic (Zachos et al., 2001a). Approximately 3.1 ‰ of this is

attributed to deep-sea cooling and 2.3 % to increases in global ice volume (~1.2 % in Antarctica and ~1.1 % in the Arctic) (Zachos et al., 2001a).

Long-term trends in the Cenozoic climate record include gradual warming during the Late Paleozoic (~59 Ma to 52 Ma) expressed as ~1.5 ‰ decrease in benthic  $\delta^{18}$ O. This warming culminated in the Eocene Climatic Optimum at ~52-50 Ma (Fig. 2.11). Superimposed on the trend of this period is the aberration of the Late Palaeocene thermal maximum. During this event deep-sea temperatures increased by 5-6 °C (decrease in  $\delta^{18}$ O of > 1 ‰) in less than 10 kyr. The warming trend in the Eocene was followed by ~17 Myr of cooling (expressed as a ~3 ‰ increase in  $\delta^{18}$ O) and a 'transitional world' climatic state was entered into (Barrett, 1999) (Fig. 2.11). This cooling culminated with the Oi-1 glaciation, a large glaciation in Early Oligocene which lasted ~400 kyr, during which benthic  $\delta^{18}$ O increased by ~1 ‰ and bottom water temperatures decreased by ~4 °C. During the Oi-1 glaciation, Antarctic ice volume increased to present day volumes and permanent, yet dynamic ice sheets formed in Antarctica (Barrett, 2009; Zachos et al., 2001a; Pekar and Christie-Blick, 2008).

The cold conditions remained more or less constant until the Late Oligocene, when global oceans warmed and the extent of glaciation decreased. The records presented by Zachos et al. (2001a) show a significant drop in  $\delta^{18}$ O in the Late Oligocene, which was attributed to a marked increase in bottom water temperatures and a decrease in global ice volumes at this time. On the record presented by Zachos et al. (2001a), the warming of the Late Oligocene lasted~2-3 Myr and was followed by a period of cooling, represented by a  $\delta^{18}$ O decrease of ~0.4 ‰. This relatively cool climate was argued to have lasted until ~20 Ma, when temperatures increased again and culminated in the Mid-Miocene Climatic Optimum (Fig. 2.10).

The period of increased warmth during the Late Oligocene presented by Zachos et al. (2001a) is inconsistent with the findings from Antarctic margin sediment cores, such as CRP (Barrett, 2007). These direct proxies suggest a much smaller degree of warming during the Late Oligocene than was suggested by Zachos et al. (2001a). This inconsistency was accounted for by Pekar et al. (2006) who found that, during the period of  $\delta^{18}$ O decrease in the Late Oligocene presented by Zachos et al. (2001a), a splicing of two deep ocean records from vastly different latitudes had occurred.

Thus the change in isotopic composition was strongly influenced by the meridional difference in deep ocean temperature between the equator and the polar regions.



Figure 2.10: The deep sea benthic oxygen isotope record from Zachos et al. (2001a) showing both the accepted general cooling over the Eocene, abrupt cooling of the Oi-1 glaciation and the more contentious Late Oligocene warming and deglaciation.

In an attempt to constrain ice volume and extract temperature from the oxygen isotope record in the Late Oligocene, Pekar and Christie-Blick (2008) conducted backstripping of the New Jersey continental margin sea level record to constrain the size of eustatic change and thus the size of the Antarctic ice sheet during the Late Oligocene-Early Miocene. This investigation indicated that though a decrease in size of the EAIS occurred from the Late Oligocene to Early Miocene, warming was not as pronounced as appeared in the Zachos  $\delta^{18}$ O record (Fig. 2.10). Rather, this showed that during the Late Oligocene-Early Miocene the EAIS decreased in size from ~30 % greater than present to no less than ~40 % of its present size.



Figure 2.11: Global temperature curve constructed using oxygen isotopic concentrations of benthic foraminifera. Shown are key climate events that occurred in the Cenozoic (source: Barrett, 2009).

The Mi-1 glaciation, which occurred at the Oligocene-Miocene boundary (~23 Ma), was a short-lived (~200 kyr) but intense glacial event (Zachos et al., 2001a) during which the EAIS reached ~120 % of its current size (Naish et al., 2001a; Pekar et al., 2006). The Mi-1 glaciation was followed by warming that resulted in the Mid-Miocene Climatic Optimum (Fig. 2.10), the culmination of the trend of decreasing  $\delta^{18}$ O that had occurred since the Late Oligocene. The Mid-Miocene Climatic Optimum lasted ~2 Myr (from ~17-15 Ma) and was followed by a gradual cooling (represented by an increase in  $\delta^{18}$ O of ~2.6 ‰) during which an 'Icehouse world' state was entered (Barrett, 2009) (Figs. 2.10 and 2.11). This cooling has continued to the present day and was punctuated by the establishment of permanent ice sheets in Antarctica (~14 Ma) and the initiation of northern hemisphere ice sheets (~3 Ma) (Figs. 2.10 and 2.11).

Though the benthic oxygen isotope record allows insights into global temperatures and ice volumes during the Cenozoic, it does not allow direct and unambiguous assessment of the glacial state of Antarctica during this interval. To construct the Cenozoic glacial history of Antarctica direct records of Antarctic glaciology must be used. These are discussed in the following section.

#### 2.6.2. Cenozoic Antarctic glaciology

Drilling of Antarctic sediments located in peripheral basins started in the 1970's and includes deep sea drilling (ODP and DSDP), cores drilled on the sea ice and onshore cores (DVDP).

DSDP Leg 28 (1970-1973) initiated drilling of sediments, some of which were eroded from the Antarctic Continent. An aim of this leg was to obtain a climate and ocean record from the Southern Ocean and the Ross Sea continental shelf. This project produced the first record of Antarctic glaciation from the Quaternary to the Oligocene in the form of glacial marine debris (Barrett, 2009) and contained the first evidence of Antarctic glaciation as early as 30 Ma and the presence of ice sheets since 14 Ma (Barrett, 2009). This record demonstrated that the Antarctic ice sheet, first thought to have been only 3 Ma old, had in fact been in existence since the Late Oligocene.

Subsequent  $\delta^{18}$ O studies of calcareous microfossils in the Southern Ocean (e.g. DSDP Leg 29) showed that the Cretaceous was warm and that the climate cooled and ice volume increased dramatically at the Eocene-Oligocene boundary and after the Mid-Miocene Climatic Optimum (Shackelton and Kennett, 1974). However, these records did not give direct evidence of Antarctica's glacial state during these times.

The DVDP project, initiated in 1973, yielded the first direct evidence of Antarctic glaciation from the terrestrial continental margin. These cores were drilled in various locations in the Dry Valleys (Fig. 2.12). Recovered strata contained glacial sediments and gave evidence for glaciation in this sector of Antarctic from the Late Miocene to present (Barrett, 2009). The first Antarctic offshore hole to be drilled on sea ice was DVDP-15, which was drilled into the sediments of the VLB (Fig. 2.12). Although this core only reached a depth of 62 mbsf, it proved the feasibility and scientific potential of drilling on sea ice and initiated a new era in Antarctic margin drilling.

Following DVDP-15, the MSSTS project was developed in the late 1970's. MSSTS-1 hole (Fig. 2.12), drilled in 1979, reached a depth of 227 mbsf and included Oligocene aged strata that contained cyclic packages of diamicts, sands and mud interpreted to reflect cycles of glacial advance and retreat. Further investigations (e.g. seismics) showed that these cycles of advance and retreat mainly occurred from the Oligocene onwards (Barrett, 2009).

Drilling for the CIROS project was initiated in 1984 with the aim to investigate the record of Antarctic glaciology and tectonism contained in sediments in the western margin of the VLB. Due to unforeseen circumstances, CIROS-2 was the first of these cores to be drilled in the Ferrar Fiord, 20 km inland from the future CIROS-1 site (Fig. 2.13). This core revealed Quaternary and Pliocene sediment cycles caused by: (1) The advance and retreat of inland ice in the Pliocene; and (2) Westward flow of the Ross Ice Shelf into the site during major Quaternary glacial events (Barrett, 2009).

Two years later, in 1986, CIROS-1 was drilled 20 km to the east of CIROS-2 (Fig. 2.13). This core reached a depth of 702 mbsf (Late Eocene to Early Oligocene age), had a recovery of 98 % (Hambrey et al., 1989) and gave the first direct evidence that the dynamic Antarctic ice sheet reached the Victoria Land coast from the Earliest Oligocene (Barrett, 1989; Barrett, 2009). It also gave direct evidence for the expansion and contraction of the EAIS during the Late Eocene to Early Miocene, which was found to be relatively synchronous with temperature fluctuations observed in the global deep sea  $\delta^{18}$ O record (e.g. Zachos et al., 2001a; Figs. 2.10 and 2.11).

DSDP Leg 113 and ODP Leg 119 were drilled to gain insights into the initiation of the East Antarctic Ice Sheet and history of glaciation in other sectors of Antarctica (Barrett, 2009). DSDP 113, drilled in the Weddell Sea, contained Palaeogene to Oligocene aged sediments that showed a cooling from the warmer Cretaceous to the Oligocene and the presence of some ice on land during the Oligocene (Barrett, 2009). ODP 119, drilled in Prydz Bay, recovered Cretaceous aged terrestrial sediments and thick Late Eocene-Early Oligocene aged diamicts. These diamicts gave the first evidence that 'continental scale ice sheets on Antarctica were delivering ice to the shelf edge beyond the limits of the modern ice sheet at least from Early Oligocene times' (Barrett, 2009).



Figure 2.12: Map of the McMurdo Sound area showing the locations of various sediment cores drilled in and near the VLB (source: Naish et al., 2008a).

From 1997 to 1999, the CRP was drilled as three holes 70 km north of CIROS-1 (Fig. 2.12) (Barrett, 2007). These holes penetrated a near continuous sequence of VLB strata from Quaternary to Oligocene which terminated at the Beacon Supergroup basement. The CRP cores showed that continental ice reached beyond present ice limits in earliest Oligocene times, glaciers calved at sea level as early as 34 Ma, and that grounded ice started extending into the Victoria Land Coast periodically from the 33 Ma and continued to do so until the Early Miocene (Barrett, 2007). The cores yielded high resolution information on orbitally-forced fluctuations in ice volume and sea level from 34-17 Ma (Naish et al., 2001b; Barrett, 2009) however, no evidence to support extreme warming in the Late Oligocene, as hypothesised by Zachos et al. (2001a).

Most recently, the two cores of the ANDRILL program were drilled in Miocene and younger sediments of the VLB, to obtain information on the climate, volcanic and tectonic history of the Ross Sea region during the Neogene (Naish et al., 2008a; Harwood et al., 2008). In 2006, AND-1 (MIS) was drilled south of Ross Island on the Ross Ice Shelf to a depth of 1285 mbsf with a 95 % core recovery (Fig. 2.12) (Naish et al., 2006; Krissek et al., 2007; Barrett, 2009). The core is located in the middle of the VLB and contains sediments of Late Neogene age that are a record of the Ross Ice Shelf and WAIS behaviour during the Neogene. A key finding of this core is the presence of a large diatomite unit between 350-460 mbsf (Scherer et al., 2007), indicating an extended period of open water in the Ross Embayment between 4.6-3.4 Ma (Barrett, 2009; Naish et al., 2008a).

AND-2/2A (SMS) was drilled in 2007 in the southern end of the McMurdo Sound (Fig. 2.12) to a depth of 1139 mbsf with a core recovery of 98 %. This core includes sediments of Early Miocene and younger age, a period long held as one of the fundamental time intervals in development of the modern Antarctic ice sheets. These strata hold the first physical evidence of the behaviour of the EAIS and the Ross Ice Shelf during the Mid-Miocene Climatic Optimum (Harwood et al., 2008) and Miocene sediments in the core show evidence of glacial advance and retreat. Palynomorphs from Mid-Miocene sediments in the SMS core show 'a sudden remarkably warm Antarctica' (Warney et al., 2009).

## 2.7. Summary of conditions during CIROS-1 sedimentation

During CIROS-1 sedimentation, the EAIS was dynamic, large and ice volume oscillated on orbital timescales (Fig. 2.12). The EAIS was wet-based for the entire duration of CIROS-1 sedimentation and had much more erosional power than the current EAIS, which has been cold-based for the past ~14 Myr.

When CIROS-1 sedimentation initiated (Late Eocene,  $\sim 37$  Ma), the VLB was the focus of extension in the WARS and was rapidly subsiding in response to crustal thinning and extension (Fitzgerald, 2002; Barrett, 2009). The TAM, which had been exhumed since perhaps the Early Cretaceous, were approximately their current height, being uplifted at  $\sim 100$  m / Myr (Fitzgerald, 2002) and had been eroded enough to expose the Granite Harbour Group (Barrett, 1989; Stern et al., 2005).

During early CIROS-1 sedimentation (Later Eocene and Early Oligocene), the EAIS was ephemeral, oscillated on orbital time scales and had a low ice volume. EAIS outlet glaciers flowed westward through the TAM and terminated on-land (Barrett, 2009). Late Eocene to Early Oligocene aged sediments occur below ~366 mbsf in

CIROS-1. These strata were deposited by glacial fluvial and shallow-marine depositional systems and include muds, sands and conglomerate and a minor iceberg rafted component. During this initial stage of CIROS-1 sedimentation, chemical weathering mechanisms were more significant that mechanical weathering, due to the warmer climate that prevailed (Barrett, 2007; Ehrmann, 1998).

Ice volume increased dramatically during the cooling of the Early Oligocene, during which the EAIS may have become  $\sim 30$  % bigger than its present size (Zachos et al., 2001a). The  $\sim 9$  Myr unconformity located at  $\sim 366$  mbsf in CIROS-1 (Roberts et al., 2003; Chapter 3, Fig 3.9), may have been caused by the overriding of the CIROS-1 site by an expanded EAIS. Ice volume remained high for the duration of the Oligocene and Early Miocene; with the EAIS no less than  $\sim 40$  % of its current size (Pekar et al., 2006). During this time the ephemeral EAIS fluctuated on orbital time scales and flowed though outlet glaciers into the Ross Sea. CIROS-1 sediments deposited after the Early Oligocene cooling (above  $\sim 366$  mbsf) include diamicts, muds and sands, which are typically interspersed with drop stones, and record regular cycles of ice advance-retreat-readvance across the CIROS-1 drill site (as discussed in Chapter 3).

During the latest stages of CIROS-1 sedimentation (Latest Oligocene and Early Miocene), deposition of CIROS-1 strata was associated with proximal glaciers and glacial/fluvial systems (Fig. 2.13). During glacial times, an expanded ice sheet passed though the Ferrar Fiord and grounded on the continental shelf, whilst during interglacials, a reduced ice sheet with terrestrial margins caused sediments to be deposited by glacially fed fluvial systems (Barrett, 2007; Fig. 2.13). Due to the cooling of the climate from the Early Oligocene, mechanical weathering was the dominant erosional mechanism in the Late Oligocene and Early Miocene (Barrett, 2007; Ehrmann, 1998). By the Miocene, thermal subsidence became the dominant subsidence mechanism in the VLB and subsidence rates decreased to present day rates (Fielding et al., 2006). The EAIS increased in size significantly in response to the Mi-1 glaciation (~22 Ma) (Naish et al., 2008a) during which the WAIS became established. Due to the increased volume of the EAIS and the presence of a WAIS, ice flow to the CIROS-1 site likely changed from an eastward (onshore-offshore) flow direction to a southern flow (e.g. as illustrated by McKay, 2008; Licht et al., 2005).



Figure 2.13: Glacial conditions of the Victoria Land coast from the Mid-Oligocene to Early Miocene. Estimated conditions during both glacial and interglacial periods are shown. This figure illustrates the types of depositional (and erosional) environments thought to have been present during CIROS-1 sediment deposition. During glacial times the EAIS overrode the site, most likely causing erosion of sediments and/or diamict deposition. During interglacial periods, sand, mud and conglomerate, interspersed with drop stones would have been deposited (source: Dunbar et al., 2008, modified from Barrett, 2007).

By ~14 Ma, when CIROS-1 sedimentation had ceased, the EAIS was cold-based and non-erosive. This caused significant reduction in wet-based glacial reworking and may have lowered TAM exhumation rates. As a result, the landscape formed during the Eocene to Mid-Miocene from fluvial activity, uplift, escarpment retreat and fluvial down-cutting, has remained relatively unaltered for the past ~14 Myr (Fitzgerald, 2002). Tectonism that has altered the landscape since includes minor faulting, localised uplift and subsidence and formation of the MVG (Raymond, 1976).

## Chapter 3: A re-evaluation of the Cenozoic record of East Antarctic glacial history from the CIROS-1 drill core: implications for Late Oligocene ice volume change

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## 3.1. Introduction

The marine oxygen isotope records from the deep ocean (e.g. Zachos et al., 2001a), arguably provide the most detailed and complete picture of the stepwise global climate cooling during the Cenozoic. From an Eocene climatic optimum (~50 Ma), the Earth has experienced regular orbitally-paced glacial-interglacial fluctuations around a stepwise cooling climatic mean. The mean climate state has also experienced abrupt permanent shifts to cooler climates at:

(1) The Eocene-Oligocene boundary (~ 34 Ma), when Earth cooled by 3-4 °C and the first large ice sheets are inferred to have developed on Antarctica (e.g. Kennett et al., 1975; DeConto and Pollard, 2003);

(2) The Oligocene-Miocene boundary ( $\sim$ 23 Ma) when a major transient glaciation is inferred to have grown the Antarctic ice sheet to 120 % of its present day size (Naish et al., 2001; Pekar et al., 2006);

(3) The Middle-Late Miocene climate transition (~13.8 Ma) when the East Antarctic Ice Sheet (EAIS) attained its present size and the West Antarctic Ice Sheet began to form (e.g. Lewis et al., 2007); and

(4) The Pliocene-Pleistocene boundary (~2.6 Ma) when Earth experienced bi-polar glaciation with the development of a relatively stable cold polar WAIS (McKay et al., 2009) and a highly dynamic ice sheet on Northern Hemisphere continents (Maslin et al., 1999).

Owing to Antarctica's remoteness, its extensive sea ice apron and its extended ice sheet cover for the last 34 Myr, the Antarctic response to these Cenozoic climate changes inferred from deep-ocean sediment cores is only now being evaluated, through the recovery of well-constrained marine sedimentary records that directly sample past ice sheet oscillations from the Antarctic continental shelf. A drilling approach based on a closed-circulation, continuous wireline coring system used by the mineral industry has been applied from land and sea ice platforms in the McMurdo Sound region over the last 30 yrs. The first attempts at drilling from sea ice were made in the late 1970's with limited success and core recoveries of 50-60 % (DVDP-15; Barrett and Treves, 1981; MSSTS-1; Barrett, 1986). During the 1980's and 1990's, progressively more sophisticated sea-riser technology was employed by the CIROS project (CIROS-1; Barrett, 1989) and CRP (CRST, 1999), which enabled the first deep Cenozoic records to be recovered (95-98 % core recovery). The results from sea ice-based drilling in the Ross Sea and McMurdo Sound have provided a framework for the Cenozoic (Late Eocene to Miocene) history of the Antarctic Ice Sheet.

CIROS-1 was drilled in the western margin of the VLB and recovered 702 m of glaciomarine strata (Figs. 3.1 and 3.2). Since the initial interpretation of the CIROS-1 core (Barrett et al., 1989) new evidence from both high-resolution deep-ocean climate proxies (e.g. Zachos et al., 1997; Pagani et al., 2005), and well-dated glaciomarine sedimentary cycles recovered by CRP (Naish et al., 2001, 2008a), 90 km north of CIROS-1 (Fig. 3.1), have revolutionised our understanding of Antarctic Ice Sheet behaviour during the Oligocene and Early Miocene. During this time, atmospheric carbon dioxide levels were as high as double pre-industrial levels (Pagani et al., 2005) and the Earth's average surface temperature was 3-4 °C warmer than present (Billups and Schrag, 2002). The Antarctic ice sheets were highly unstable, oscillating in response to orbital forcing (DeConto and Pollard, 2003; Naish et al., 2001) and driving global sea level change of up to 40 m amplitude (Naish et al., 2008a; Pekar et al., 2006). Moreover, the chronology of the CIROS-1 core has received a number of revisions as new-generation cryogenic magnetometers have enabled more detailed magnetostratigraphies to be developed (e.g. Wilson et al., 1998; Roberts et al., 2003) and high-latitude biochronologic schemes continue to improve (e.g. Hannah et al., 1997; Bohaty et al., 1998).

This paper presents a revised glaciomarine sequence stratigraphy for identifying ice advance and retreat cycles in the CIROS-1 drill core. This is based on approaches recently applied by Fielding et al. (2001) and Dunbar et al. (2008) to strata in the Cape Roberts core of similar age. The chronostratigraphic framework for the evaluation of Late Eocene to Early Miocene environmental changes in the core is revised by combining recently published improvements to the chronology and changes to the Geomagnetic Polarity Timescale (e.g. Gradstein et al., 2004). Finally, the new CIROS-1 chronostratigraphy is used to correlate orbitally-paced sequences of glacial advance and retreat during the Late Oligocene with the CRP-2A core and the global oxygen isotope record. This shows that both the Ferrar and McKay outlet glacier systems responded in phase to Milankovitch-scale climate cycles during cooling leading up to major ice expansion during the Mi-1 glaciation.

## 3.2. Geological and glaciological setting

CIROS-1 penetrated numerous unconformity-bound Late Eocene to Early Miocene sedimentary cycles (Barrett, 1986). These record the advance and retreat of a laterally-continuous ice margin across the western Ross Sea continental shelf. The strata accumulated some kilometres off the coast as part of a laterally-extensive seaward-thickening wedge in the VLB (Fig. 3.1); a structural half-graben, approximately 350 km long, hinged on its western side at the TAM front (Fig. 3.2). Major rifting in the VLB has occurred since the latest Eocene, perhaps having been initiated in the Cretaceous, and has accommodated up to 10 km of sediment (Cooper and Davey, 1985; Brancolini, 1995).



Figure 3.1: Key geographical and structural features of the VLB. CIROS-1 is located 20 km offshore at the mouth of the Ferrar Fiord. Note the location of the CRP drill cores off the McKay Glacier (source: Naish et al., 2006).



Figure 3.2: Cross-sectional view of the tectonic setting of the VLB, VLB stratigraphy and simplified geology of the TAM in SVL. Note the location of CIROS-1 proximal to the TAM and on the western margin of the Ross Sea and VLB (source: Naish et al., 2006).



Figure 3.3: Glacial conditions of the Victoria Land coast from the Mid-Oligocene to Early Miocene. Estimated conditions during both glacial and interglacial periods are shown. This figure illustrates the types of depositional (and erosional) environments thought to have been present during CIROS-1 sediment deposition. During glacial times the EAIS overrode the TAM and terminated over the site, causing erosion of sediments and/or deposition of grounding-line proximal facies. During interglacial periods, sand, mud and conglomerates, interspersed with iceberg rafted drop stones were deposited (source: Dunbar et al. (2008) modified from Barrett, (2007)).

The geometry of the strata is evident in seismic data (e.g. Fielding et al., 2006) oriented parallel to the coast (Fig. 3.2). During the Late Oligocene-Early Miocene periods of glacial advance, an interior ice sheet (the EAIS) fed through outlet glaciers to a laterally extensive ice terminus which extended well out onto the continental shelf east of the CIROS-1 drill site. In periods of ice retreat, the drill site lay off an open, wave-dominated, coast, with deposition of mud and occasional debris from floating ice (Fig. 3.3). Thus cycles of ice margin advance and retreat across the continental shelf have been viewed as cycles of expansion and contraction of the EAIS recorded as unconformity bound sequences (e.g. Dunbar et al., 2008).

## 3.3. Previous stratigraphic and facies descriptions

A variety of sedimentological, facies and environmental interpretations of the CIROS-1 core have been proposed since publication of the initial science report volume in 1989, which drew heavily on procedures established for previous and ice proximal drill holes in southern McMurdo Sound (MSSTS-1, Barrett, 1986; CIROS-2, Pyne et al., 1985). Hambrey et al. (1989) presented a detailed sedimentological and stratigraphic description of the core, utilising Robinson's original descriptions (Barrett, 1989). The strata were considered to show a strongly cyclical glacial influence throughout. Conglomerates, diamictites, sandstones and mudstones were reported in varying amounts along the length of the core, and were interpreted to represent fluctuations in the relative proximity of the East Antarctic ice margin to the drill site. Most notably, diamicts, though more common in the upper section (Barrett, 1989), were reported through the entire length of the core, suggesting proximal continental glaciation for the entire duration of deposition (Hambrey et al., 1989). A number of unconformities underlay ice proximal diamictites, and were interpreted as the result of erosion by an advancing glacier or ice sheet terminus, with a major unconformity identified at 366 mbsf (Hambrey et al., 1989), that may have resulted from both glacial and longer term tectonic influences.

Fourteen lithofacies were recognised in the CIROS-1 core (Hambrey et al., 1989) including massive, weakly- and well-stratified diamicts, sandstones, mudstones, conglomerates and breccias, associated with a spectrum of glaciomarine environments from ice contact/grounding line proximal to open marine. In addition, the ice proximity and water depth during deposition were constrained using both the facies analysis and grainsize characteristics of a wave-graded shelf (Barrett, 1989).

The latter was only appropriate when glaciers were terminating on land during interglacial times and the coastline and shelf were wave-dominated.

There is a marked unconformity located at ~366 mbsf. The presence of breccias and diamicts representing regular advances of the grounding line over the drill site in the sediments above this unconformity, and their lesser occurrence below 366 mbsf, led Fielding et al. (1997) to hypothesise that this unconformity represented a major shift in depositional environment, associated with a fundamental change involving climate cooling and an increase in the size of the EAIS. However, the presence of icebergrafted debris though the entire length of the core implied that coastal outlet glaciers (e.g. paleo-Ferrar or adjacent fjiordal glaciers) were calving at the coastline throughout deposition of the core. The deposition of the sub-366 mbsf section was reported to have occurred in relatively deep water setting (mid to outer shelf), whilst the water depth during deposition of the upper section was variable (shelf to emergent; Barrett, 1989). This implied that a major shoaling of the basin occurred across the (then) Mid-Oligocene unconformity due to tectonic, glacial and/or eustatic influences. While glaciomarine sediments dominated above 366 mbsf, sediment gravity flow sediments were inferred to have been deposited directly from coastal fan-deltas during the sedimentation of the lower interval of the section with significantly less ice-proximal influence.

Fielding et al. (1997) re-logged the CIROS-1 strata using the heavily degraded and sampled working half of the core. This in part may explain the considerable reduction in the number of diamicts identified above the 366 mbsf unconformity, and the absence of diamicts reported beneath it. Rather, these sections were logged as (potentially) fluvially-derived conglomerates or mudstones and sandstones with dropstones. Fielding et al. (1997) removed all breccias below 366 mbsf and reported the occurrence of these exclusively above 366 mbsf. The revised facies model for CIROS-1 core presented by Fielding et al. (1997) consisted of seven lithofacies and four facies associations. These included sandstone, siltstone, mudstone, breccia, diamict and conglomerate facies. Lithofacies were interpreted in terms of deposition in a range of environments from coastal fluvial plain, delta, wave-dominated coastline and shelf, with significantly less influence from glaciomarine, groundingline-proximal deposition. The sedimentary characteristics of the strata show that changes in lithofacies-stacking patterns through time primarily reflect the proximity of the ice sheet grounding zone and changes in relative sea level driven by associated mass changes in the EAIS.

Based on these lithofacies-stacking relationships, the associations and cycle-bounding unconformities, Fielding et al. (1997) undertook the first sequence stratigraphic analysis of the core. Sequence boundaries were identified by abrupt facies dislocations. At least six cycles were recognised in the upper section of the core (< 366 mbsf). These sequences consisted of inconsistent but prevalent groupings of diamict, breccia and conglomerate deposited in ice proximal and ice contact glaciomarine environments during advance and withdrawal of the grounding line over the drill site. Mud-dominated facies represent deposition in more ice-distal marine environments during interglacial ice minima. Sharp erosional surfaces at the base of diamictites truncating underlying shelf facies were termed glacial surfaces of erosion, and represented erosion by the glacier entering the marine environment. Diamictite, conglomerate and breccia facies overlying the glacial surface of erosion represented ice contact (lodgement till) or grounding zone deposition. Typically facies successions fined upwards into interstratified sandstones and siltsones with iceberg rafting and massive biotrubated mudstones as the grounding line progressively retreated from the drill site. These fining upwards and progressively less ice influenced cycles were considered to represent retreat of the grounding-line in concert with rising eustatic sea level. Periods of glacial advance are generally marked by glacial surfaces of erosion and occasionally, a shallowing-upwards regressive facies succession is preserved below the overlying glacial surface of erosion. The latter represents shallowing from shelf to shoreline water depths and relative sea level fall prior to glacial over-riding during the next advance. Only two sequences were recognised by Fielding et al. (1997) in the sub-366 mbsf section of the core. These consist of packages of conglomerate and mudstone, the conglomerate having been deposited during glacial advances as outwash from a relatively distal, land-terminating glacier.

Below we present a revised stratigraphy and facies model for the CIROS-1 drill core, based on a redescription of the better preserved archived half of the core stored at the Florida State University Antarctic Core Repository.

## 3.4. Revised lithofacies analysis of the CIROS-1 Core

Facies analysis of CIROS-1 strata was conducted using the facies scheme developed for CRP-3 (Fielding et al., 2001) which was based on previous schemes used for CRP 1 (CRST, 1998) and CRP2/2A (CRST, 1999). The facies scheme, including lithological description and interpretation, is summarised in Table 1, and more details

of facies and inferred deposition environments are available in the above references. In this revised scheme, seven facies are identified. They are numbered in an order that spans a 'deepest water and/or most ice-distal' to 'shallowest water and/or most ice-proximal' depositional spectrum. The vertical occurrence of the lithofacies in the CIROS-1 core is shown in Figure 3.4.

Facies	Lithology	Facies characteristics	Interpretation		
1	Fine-grained siltstone, locally interlaminated with very fine- to fine- grained sandstone	Horizontal stratification, sparse-to-common bioturbation, sedimentary intrusions, invertebrate shells, dispersed gravel	Offshore marine to glaciomarine (shelfal, below storm wave base)		
2	Sandy siltstone	Kare stratification, abundant bioturbation, sedimentary intrusions, invertebrate shells, dispersed gravel	(between storm and fair-weather wave base), with iceberg and/or sea ice rafting		
3	Muddy (interstratified), very fine to fine-grained sandstone	Rare-to-common stratification (flat and low-angle lamination, hummocky cross-stratification, ripple cross-lamination), abundant bioturbation, soft- sediment deformation, invertebrate shells, dispersed gravel	Distal lower shoreface, with iceberg and/or sea ice rafting		
4	Well-sorted, stratified sandstone	Pervasive stratification (flat lamination, cross-bedding, ripple cross-lamination), bioturbation absent-to-sparse, invertebrate shells, dispersed or layers of gravel	Middle to upper shoreface, possibly on delta fronts, minimal iceberg and/or sea ice influence		
5	Sandy conglomerate and clast-rich sandstone	As for Facies 4	As for Facies 4, plus possible delta platform		
6	Intraformational mudstone clast breccia	Sparse stratification, sedimentary intrusions, no bioturbation, sparse shell debris	Sedimentary gravity flow deposits triggered by seafloor failures		
7	Diamictite	Weak (particularly in fine- grained partings) stratification to massive, soft-sediment deformation, sedimentary intrusions, dropstone textures, sparse shell debris	Grounding zone to subglacial associated with tidewater glaciers		

Table 3.1: Lithofacies scheme developed for CIROS-1 core glaciomarine sediments and their interpreted depositional processes and environments (modified after Fielding et al., 1997 and Fielding et al., 2001).











Figure 3.4 (previous 3 pages): Revised lithologic log for the CIROS-1 drill core. Facies are annotated using numbers from Table 3.1. Sequence boundaries (SB) predominantly representing glacial surfaces of erosion (GSE), bound facies cycles of ice advance retreat and readvance across the drill site in concert with eustatic sea level fluctuations. Sequences are noted.

# 3.5. Sequence stratigraphy of sediments deposited on an open, wave-dominated glaciated continental margin

Dunbar et al. (2008) presented a sequence stratigraphic model for sediments deposited on a glaciated continental margin (Fig. 3.5), based on an analysis of the CPR cores, which is applied here to stratigraphic interpretation of the CIROS-1 lithofacies. A complete and idealised motif for a cycle of glacial advance and retreat and coupled sea level rise and fall is given in Figure 3.6 (Motif A). It contains repetitive and predictable facies successions that are stacked vertically and bounded by unconformities (Fielding et al., 2001). At the base is the sequence boundary, the glacial surface of erosion (GSE), which forms as the glacier advances over the site (Fig. 3.5D and E; Fig. 3.6). Above the GSE, stratified and massive diamicts are deposited in association with graded conglomerates and interstratified mudstone and sandstone in ice-proximal and grounding zone environments. As the glacier retreats and sea level rises, progressively finer-grained sediments are deposited in this glacial transgressive systems tract (Fig. 3.5A and B; Fig. 3.6). At the sea level maximum and interglacial ice volume minima, the glacial highstand systems tract is deposited, consisting of sandstones and mudstones and condensed shell beds with the lowest abundance of ice-rafted debris (Fig. 3.5 C; Fig. 3.6). During glacial periods, relative sea level falls, the glacier terminus advances and a progressively coarsening-upwards regressive, wave-influenced shelf-to-shoreline facies succession is deposited as a glacial regressive systems tract (Figs. 3.5 and 3.6). Superposed onto this, the GSE marks erosional truncation of underlying regressive and highstand facies during ice advance, with deposition of sub-glacial diamictite immediately overlying the GSE (Figs. 3.5 E and 3.6 Motif A). The idealised sequence described above is not always fully preserved. Preservation is dependent on rate of subsidence, sediment supply, glacial erosion and base-level change. Additionally, the stratigraphic architecture of a glaciomarine sequence is strongly controlled by the environment in which the glacier terminates. For example the above architecture represents deposition by a marineterminating ice sheet (Fig. 3.6 Motif A). For glaciomarine sequences influenced by a land-terminating glacier feeding a fluvial deltaic system, the resulting facies succession is different. Such sequences are dominated by fluvially-derived conglomerates and shallow-marine sandstones (with or without ice rafting) deposited during glacial periods, and shallow shelf sandstones and sandy-mudstones deposited during interglacial periods. Sequence boundaries are controlled by wave-base erosion due to base-level changes rather than by the proximity of the grounding line (Fig. 3.6 Motif B).



Figure 3.5: Sequence stratigraphical model for glaciomarine deposition on a wave dominated coastline and shelf during the advance and retreat of a glacier. This image shows the development of facies and sequences as discussed in the text (source: Dunbar et al., 2008).

#### IDEALISED SEQUENCE MOTIF A



IDEALISED SEQUENCE MOTIF B



Figure 3.6: Typical glaciomarine sequence stratigraphic architecture shown with respect to a cycle of relative sea level and local ice influence. In Motif A the grounding line advances into the marine environment and passes across the drill site producing a GSE at the sequence boundary. In Motif B the grounding line remains on land and issues sub-glacial sediment into a fluvio-deltaic system. The sequence boundary represents subaerial exposure during base-level fall and/or wave base erosion during ensuing transgression of the shoreline (source: Fielding et al., 2001).

## 3.6. New sequence stratigraphic analysis of the CIROS-1 core

The revised sequence stratigraphy of the CIROS-1 drillhole is based on a redescription of the better-preserved archived half of the core, and utilises the facies scheme in Table 3.1 and the glaciomarine sequence stratigraphic model of Dunbar et al. (2008) (Fig. 3.5). The succession has been divided into 14 sequences (Fig. 3.7). There are two major "motifs" or sequence styles represented in the core, with sequences 1-4 (below 342 mbsf) showing a fundamentally different style from

sequences 5-14 (above 342 mbsf). It is therefore possible that the fundamental discontinuity in the core may not be at 366 but at 342 mbsf.

Sequences 1-4 are relatively complete (in terms of systems tracts), containing both fining-upward and overlying coarsening-upward facies successions. These sequences are typically thick and bounded by packages of well-washed sandy conglomerates deposited as distal outwash and displaying no direct evidence of ice contact (Figs 3.4 and 3.7). For this reason, we do not use the term "Glacial Surface of Erosion" to describe sequence boundaries in this part of the core. Rather, such sequence boundaries represent erosion during base level changes associated with subaerial exposure and/or transgressive wave base erosion. These sequences resemble aspects of Motif B sequences in CRP-3 (Fig. 3.6), in that they preserve well-developed regressive shoreline facies assemblages in their upper parts. They also preserve abundant bioturbation and shell fossils

Sequences 5-14 are incomplete, strongly top-truncated, thin, and contain finingupward trends but not overlying coarsening-upward trends (Fig. 3.7). These sequences are bounded by diamictites representing ice-proximal proglacial to possibly subglacial settings and show direct evidence of glacial influence. Sequences 5-14 resemble those in CRP-2 and-1 (Fig. 3.6 Motif A) and do not preserve a regressive shoreline facies assemblage, only intermittently preserve bioturbation, and have sparse shell fossils.



Figure 3.7: Composite sequence stratigraphic interpretation of the CIROS-1 log showing sequence boundaries, facies and interpretations. Fluctuations in relative sea level inferred from these are shown.

### 3.7. Previous chronostratigraphy for the CIROS-1 Core

The original chronostratigraphic analysis of CIROS-1 core inferred that the sediments were deposited during the Early Oligocene to the Early Miocene (Fig. 3.8). The age of the sub-366 mbsf section of the core has been problematic due to generally poorly-preserved fossils, their generally low abundance and diversity and the presence of older reworked fossils. Harwood (1989) used siliceous (diatom) microfossils to constrain the depositional age, and reported an Early Oligocene age for the base of the core, whilst the top was at least Middle Miocene. Above 502 mbsf, the presence of well-preserved and rich Oligocene and Miocene species made the age determination relatively robust for sections therein.

However, between 702-502 mbsf the siliceous microfossils were particularly poorlypreserved due to diagenetic dissolution of the diatoms. Both Eocene and Oligocene siliceous microfossils were found in this section, and as no age-diagnostic Eocene species were found, an Early Oligocene age was attributed and a hiatus of 4 Myr was estimated for the 366 mbsf unconformity.

Webb (1989) used benthic foraminifera to constrain the age of the core. Like Harwood (1989), Webb (1989) concluded a Late Oligocene-Early Miocene age for the upper half of the core. An Early Oligocene age was assigned to the section below 366 mbsf, despite the presence of Eocene foraminifera, which were assumed to be reworked. Terrestrial (Mildenhall, 1989) and marine palynology (Wilson, 1989) both showed low recovery and diversity of taxa, with a high degree of reworking. Wilson (1989) found many dinoflagellate cysts of Eocene age below 366 mbsf of the core, which were attributed to reworking. Thus an Early Oligocene age was assigned to the lower section which was consistent with <sup>87</sup>Sr/<sup>86</sup>Sr ages from mollusca providing a minimum age of earliest Oligocene for the very lowest section of the core (679 mbsf) (Barrera, 1989).

Edwards and Waghorn (1989) used calcareous nannofossils to constrain the core's chronology. Similarly to previous studies, a low species occurrence and diversity was noted. Based on the presence of potentially in situ Eocene-age species in the lower section of the core, a Late-Middle Eocene age was assigned to the sub-366 mbsf section, and an Early Miocene age was inferred for the upper section. In addition, the shift from diamict-poor sediments to diamict-dominant sediments at 366 mbsf was attributed to abrupt cooling associated with growth of the EAIS across the

Eocene-Oligocene boundary. Rieck (1989) constructed an initial magnetic polarity zonation for the core. A number of processes were reported to have masked the detrital magnetisation and thus a partial polarity zonation was constructed. As with Hambrey et al. (1989), Rieck (1989) assigned an Early Oligocene-Early Miocene chronology to the core, producing a magnetostratigraphic interpretation that was consistent with the available biostratigraphic data.

Owing to the considerable amount of ambiguity associated with the early chronology of CIROS-1, a substantial amount of effort has been invested to further constrain the core's chronology. Wei (1992) used calcareous nannofossils to constrain the age model for the sub-366 mbsf section of the core. As the assemblages were of similar composition to other 'presumed coeval assemblages of ODP legs 113 and 119' and 'consistent with other Southern Ocean sites' (Watkins, 2007), Wei (1992) concluded the nannofossils were not reworked and assigned a Late Eocene age to the studied interval.

Hannah (1994) presented a chronology with similar ages to those assigned by previous workers to the upper 366 mbsf. A Mid-Eocene age was assigned to the very bottom section. Hannah (1994) put the Eocene-Oligocene boundary at  $\sim$ 500 mbsf, with a section of Early Oligocene strata below the 366 mbsf unconformity.

In 1997, a volume on new studies conducted on CIROS-1 was published in the journal *Terra Antarctica*. In it, Hannah et al. (1997) further developed the dinoflagellate-based chronology of Hannah (1994) with a focus on the sub-366 mbsf section. In this section dinoflagellates are moderately diverse and abundant and are of Eocene and Oligocene age. Originally, the presence of Eocene dinoflagellates was attributed to reworking (Wilson, 1989). However, a strong relationship between glacial proximity and melt-water influence, and the distribution of dinoflagellate assemblages, led Hannah et al. (1997) to consider the Eocene microfossils as in situ. A Late Eocene age was assigned to the lower section of the core, and an Early Oligocene age was reported for the sediments directly below the 366 mbsf unconformity. The Eocene-Oligocene (E-O) boundary was reported to be located at  $\sim$ 460 mbsf (Figs. 3.8 and 3.9).

	AGE									
	Siliceous microfossils	Calcareous nannofossils	Dinoflagellates	Foramnifera	Dinoflagellates	Calcareous nannofossils	Magneto- biostratigraphic	Magneto- piostratigraphic		
	Harwood et al, (1989)	Edwards & Waghorn (1989)	Hannah (1994)	Coccioni & Galeotti (1997)	Hannah et al, (1997)	Monechi & Reale (1997)	Wilson (1998)	Roberts et al, (2003) & Naish et al, (2008)		
25	MIOCENE		EARLY MIOCENE	OLIGOCENE- Y MIOCENE			ED	EARLY MIOCENE		
	?			LATE ( EARL						
150					IED		IDN.			
175	ШZ		ШN		TUD	<u>ر.</u>	T ST	Ш N		
200	DCE	<u>с</u> .	OCE	ш	DT S		NO	OCE		
225	LIG(		PLIG	CEN	N			LIG(		
250	о Ш		о Ш	lGO				о Ц		
275	LAT		LAJ	, oL				LAT		
300		MIDDLE EOCENE LATE CLIGOCENE	EARLY OLIGOCENE	RLY						
350	?			ΕA		EARL-LATE	EARLY OLIGOCENE			
375					FARIY					
400					OLIGOCENE	EARLY OLIGOCENE				
425										
450	EARLY OLIGOCENE						LATE EOCENE	NOT STUDIED		
475										
500			DLE EOCENE		LATE EOCENE					
525				IE EOCENE		LATE EOCENE				
575										
600										
625										
650			AIDE	LAJ						
675			2							
700 ₹ 5 2 ₹										

ਰ ਂ ੱ ਨੂੰ ਛੂ Figure 3.8: A summary of previous chronostratigraphic schemes for the CIROS-1 core.

In the same volume, Monechi and Reale (1997) used calcareous nannofossils too constrain depositional age and assigned a Late Eocene age to the lowermost section of the core. Similarly to Hannah et al. (1997), Monechi and Reale (1997) estimated the Eocene-Oligocene boundary as lying between 468-455 mbsf (Fig. 3.8). Coccioni and Galeotti (1997) re-evaluated the foraminiferal content of CIROS-1 and produced a revised chronology and, like the above workers, found that the lowermost section of the core was of late Eocene age and that the Eocene-Oligocene boundary was located between 468-455 mbsf. Above the Eocene-Oligocene boundary an Early Oligocene age was assigned, and the Miocene-Oligocene boundary was placed at ~150 mbsf (Fig. 3.8). Coccioni and Galeotti (1997) estimated that the unconformity at 366 mbsf encompassed about 4 Myr.

The magnetobiostratigraphic chronology of the section below 366 mbsf was revised by Wilson et al. (1998) (Figs. 3.8 and 3.9), who analysed paleomagnetic samples taken every 1-2 m, and made a new correlation to the geomagnetic polarity timescale (Cande and Kent, 1995). The results of this were combined with previously established biostratigraphic horizons and Sr isotope age data. Wilson et al. (1998) assigned an age of Early-Late Eocene ( $\sim$ 36.5 Ma) to the base of the core, whilst an Earliest Oligocene (~33 Ma) age was assigned to the sediments directly below the 366 mbsf unconformity. Wilson et al. (1998) inferred the Eocene-Oligocene boundary to be located between 410-420 mbsf, within a sandy mudstone and not incidental with an unconformity. This was established by combining the age models presented in Reick (1989) and Harwood (1989) and the chronology established for the sub-366 mbsf section presented in Wilson et al. (1998). As Rieck (1989) and Harwood (1989) assigned an Early-Late Oligocene age (ca. 28 Ma) to the sediments directly above the 366 mbsf unconformity, and Wilson et al. (1998) dated the sediments directly below as Earliest Eocene (ca. 33 Ma), Wilson et al. (1998) estimated the 366 mbsf unconformity to cover 4 Myr and suggested this time may have been distributed amongst the suite of unconformities located between ~366-250 mbsf.

Roberts et al. (2003) re-evaluated the magnetostratigraphy of the uppermost section of the core. Roberts et al. (2003) analysed 231 samples at  $\sim$ 0.5-1 m intervals for their magnetic polarity stratigraphy. These were plotted relative to the geomagnetic polarity time scale from Cande and Kent (1995). In addition to these new data, Roberts et al. (2003) re-evaluated published diatom biostratigraphic data for the upper section of the core. These zones were correlated to a high-precision age model constructed for CRP 2/2A based on the biostratigraphic zonation scheme of Scherer et al. (2000), which was calibrated by Wilson et al. (2002) using two  $^{40}$ Ar/ $^{39}$ Ar ages for two ash horizons near the Oligocene-Miocene boundary in the CRP2/2A core. The results differ significantly from the original paleomagnetic work done by Rieck (1989) (Fig. 3.8), being much simpler and with fewer polarity intervals. This, combined with the updated diatom zonation created for CRP 2/2A, enabled Roberts et al. (2003) to significantly revise the chronology for the uppermost 366 mbsf of the core (Figs. 3.8 and 3.9). The ~24.3 Ma age for the sediments directly above the 366 mbsf unconformity reported by Wilson et al. (2002) is significantly younger than the initial age of ~29 Ma presented by Rieck (1989) and Harwood (1989). As such, Roberts et al. (2003) concluded that the time lost in the 366 mbsf unconformity is ~9 Myr, rather than the 4 Myr originally believed. Roberts et al. (2003), report that the Miocene-Oligocene boundary is located in an unconformity in sediments at 249 mbsf. A Lower Miocene age of ~23.7 Ma was assigned to sediments at 80 mbsf.

In spite of burgeoning amounts of chronostratigraphic data, Watkins (2007) reported strong doubts about an Eocene age for the sub-366 mbsf section of the core. Watkins (2007) argued that many of the Eocene ages for this section were derived from potentially reworked nannofossils that were reported by the authors as being in situ. It was argued that, as global proxies (such as deep-ocean sediment cores) imply no significant glaciation in Antarctica until the earliest Oligocene, the Eocene age assigned to the sub-366 mbsf section of the CIROS-1 drill core must be incorrect, as sediments in the section show signs of significant glaciation (e.g. diamicts and the presence of ice-rafted debris reported in Hambrey et al, 1989). Consequently, Watkins (2007) assigned an Early Oligocene age to sub-366 mbsf section.

## 3.8. Revised chronology for the CIROS-1 core

The composite age model for CIROS-1 (Fig. 3.9) presented here, was constructed by re-evaluating the historical data and selectively splicing previously published and newly-developed chronologies for different sections of the core (Tables 3.2 and 3.3). The age for the section down to 100 mbsf is based on the integrated biomagnetostratigraphy developed by Roberts et al. (2003). The chronology for the section between 100-366 mbsf has been revised based on Roberts et al. (2003), following the recalibration of diatom zones in correlative strata in the CRP-2/2A core by Naish et al. (2008b). Two  $^{40}$ Ar/ $^{39}$ Ar ages on ash layers in the CRP-2/2A core
(e.g. Wilson et al., 2002) allow detailed correlation of the *Hemiaulus sp. A* and *Pterotheca reticulata* diatom zones to short-lived subchrons within Chron C7, consistent with the astronomically-tuned timescale of Billups et al. (2004). This recalibration constrains the Oligocene-Miocene boundary at ~100 mbsf in the CIROS-1 core (Fig. 3.9). A consequence of this is that the beech leaf identified by Hill (1989) sits in Late Oligocene strata. It is not possible, with the available chronostratigraphic data, to determine what percentage of the ~9 Myr time interval between 35 and 26 Ma is lost at the 366 mbsf or 342 mbsf unconformities, as illustrated by the error boxes (in light yellow, Fig. 3.9). The chronology for the lower section reflects two main options from published work.

A strength of the Wilson et al. (1998) chronology is that it is based on correlation of a revised magnetostratigraphy to the magnetic polarity timescale and is supported by the available biostratigraphic data. Moreover, the accumulation rate of 100 m / Myr implied by the slope of the curve on the age depth plot in Figure 3.9 is consistent with typical rates of glaciomarine successions on the western margin of the VLB. To this end, a third option for the age of sediments between 366-425 mbsf is offered which is consistent with the biostratigraphic data and the accumulation rates of Wilson et al. (1998). In this model (coloured red in Fig. 3.9), this normal-polarity stratigraphic interval has been correlated with C15n instead of C13n. A Late Eocene age for the sediments in the lower section of the core is consistent with the higher occurrence of clay minerals, such as smectite, associated with relatively more chemical weathering and a warmer, wetter climate regime than that of the earliest Oligocene (Ehrmann, 1998).



Figure 3.9: An integrated chronological framework for the CIROS-1 core. Above 366 mbsf the chronology is based on Roberts et al. (2003) which has been recalibrated using Naish et al. (2008b). Three possible chronologies have been given for the sub-366 mbsf section of the core (Wilson et al., 1998; Hannah et al., 1997). An alternative chronology for the upper part of the sub-366 mbsf section of the core, suggested in this work, is shown in red. The light yellow zone indicates the uncertainty associated with the chronology of the sub-366 mbsf section and shows that the time missing in the  $\sim$ 9 Myr hiatus (traditionally thought to be located at  $\sim$ 366 mbsf), may be partially of wholly distributed at the unconformity located at 342 mbsf. The magnetochronology used is based on Gradstein et al. (2004). For definitions of biostratigraphic datums and paleomagnetic chrons used refer to Tables 3.2 and 3.3.

Table 3.2: Chronostratigraphic datums used to construct the revised CIROS-1 age model (Fig. 3.9).								
Roberts et al. (2003) (Above 366 mbsf)								
Datum	Occurrer	ice (mbsf)	Paleo chronology		References			
	Base	Тор	Base	Тор	Occurrence	Chronology		
Kisseleviella sp. A	145.21-139.35	296.68-290.78	C7n.1n	C6Cn.2n	Harwood (1989) presented in Roberts et al. (2003)	Scherer et al. (2000) calibrated by Wilson et al. (2002)		
Pterotheca reticulata	296.68-290.78	309.38-304.95	C7n.1n C7n.1n		"	Scherer et al. (2000) recalibrated based on Naish et al. (2008)		
Hemiaulus sp. A	309 38-304 95	~342	C7n 2n	C7n 2n	"	"		
		012	07111211	07111211				
		Wilson et	al, (1998)	(Below 366	δ mbsf)			
Datum	First Occurrence / Last Occurrence	Occurrence (mbsf)	Paleo ch	ronology	References			
					Occurrence	Chronology		
Diamtoms								
Consistent Pyxilla reticulata	LO	367	C1	2.n	Harwood and Maruyama (1992) presented in Wilson et al. (1998)	Harwood and Maruyama (1992) callibrated based on Berggren et al.		
Hemiaulus caracterusticus	LO	375	C11	n.2n	64	(1995) presented in Wilson et al. (1998)		
Sphynctolethus pacificus	LO	383	C11	n.2n	α.			
Rhizosolenia oligocaenica	LO	383	C1	2n	u			
Rhizosolenia oligocaenica	FO	438	C13r/C15	.n or older	41			
Stephanopyxis splendidus	FO	500	C13r/	C15.n	**			
Asterolampra punctifera	FO	438	C13r/	C15.n	a -			
Foramnifera								
Epistominella exigua	FO	558	N	D.	Coccioni and Monechi (1996, pers coms), presented in Wilson et al. (1998)	Webb (1996, Pers comms) presented in Wilson et al. (1998)		
Nonion cf. graniferum	LO	669	C13r c	or older	Webb (1989), presented in Wilson	Webb (1989) presented in Wilson		
Alabamina dissonata	LO	669	C13r c	or older	et al. (1998) "	et al. (1998) "		
Pseudogloboguadrina	LO	690	C16r or poss	siblv vounaer	• "	Couch and Hollis (1996) and Evitt and Pierce		
Calcareous nannofossils	6			,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		(1979) preasined in Wildon (1990)		
Isthmolithus recurvus	LO	392	C,	12r	Wei (1992) presented in Wilson et al. (1998)	Wei (1992), callibrated using Cande and Kent (1992, 1995) and Barragen et al. (1995)		
Isthmolithus recurvus	FO	681	C16	n 2n	"	(1992, 1995) and beiggien et al. (1995)		
Marine Palynomorphs		001	0.10					
Enneadocysta partridgei	LO	455	С	10	Wilson (1989) presented in Wilson et al.	Stover and Williams (1995), presented in		
Deflandrea antarctica	LO	455	С	10	(1998)	Mohr (1990), presented in Wilson		
Spinidinium macmurdoense	10	455	C	10	"	et al. (1998) Wilson (1967) presented in Wilson et al.		
Tubiosphaera filosa	LO	455	C	10	"	(1998) Couch and Hollis (1996) and Evitt and Pierce		
Arachaodinium anaroticum	10	172	C10	/012	Harwood et al. (1989) and references	Harwood et al. (1989) and references		
Arachhouinium anarcticum	LO	473	010	/012	there-in, presented in Wilson et al. (1998)	therein, presented in Wilson et al. (1998)		
		Hannah et	al (1997)	(Below 366	S mbsf)			
Diatoms		Thanhalf of			5 111501)			
Pyxilla reticulata	LO	367	C1	2.r	Harwood (1989) presented in Hannah	Harwood (pers comm.) presented in Hannah et al. (1997)		
Sphynctolethus pacificus	LO	383	C11	n.2n	"	Wilson et al. (1998) presented in Hannah		
Rhizosolenia oligocaenica	LO	383	C	12r	"	et al. (1997)		
Rhizosolenia oligocaenica	FO	438	C1	3n	44	Harwood and Maruyama (1992) presented in		
Stephanopyxis splendidus	FO	500	C1	5n		Wilson et al, (1998) presented in Hannah		
Asterolampra punctifera	FO	500	C1	5n		et al. (1997)		
F irregularis	FO	438	C1	5n	66			
Hemiaulus caracterusticus	10	375			56			
	EO	694	011n.2n		C17n 1n			
Forompiforo	10	004	CH					
	10	559	unkr	NOWD	Coccioni and Galeotti (1997),	N/A		
	E0	000		C19n	presented in Hannah et al. (1997) Webb (1989) presented in Hannah	Berggren et al. (1995) presented in		
A. primiuva	10	000	iviid-	0 1011	et al. (1997)	Hannah et al. (1997)		
Calcareous nannotossils				0.10	Wei (1992) presented in Hannah et al	Berggren et al. (1995) presented in		
R. umbilica	LO	392	late	C12r	(1997)	Hannah et al. (1997)		
Isthmolithus recurvus	LO	407	Mid-la	te C12r	in Hannah et al. (1997) in Hannah et al.			
Isthmolithus recurvus	FO	681	C16	n.2n	Wei (1992), presented in Hannah et al, (1997)			
O. oamaruensis	LO	468	Late	C13r	Monechi and Reale (1997) presented in Hannah et al. (1997)	ь.		
O oamaruensis	FO	673	Late C	16n 1n		"		

Tabl +h CIROS 1 del (Eig. 3.9) L 1 1

Chron	Depth	(mbsf)	Reference	
	Base	Тор		
Magnetostratigraphic				
C6Cn.2n	92	27	Roberts et al, (2003) recallibrated	
C6Cn.2r	111	92	based on Naish et al, (2008)	
C6Cn.3n	244	111	"	
C6Cn.3r	254	244	"	
C7n.2n (+ C7n1n?)	338	254	"	
C6Cr	366??	338	**	
C13n	405	366	Wilson et al, (1998)	
C13r	435	405	"	
C15n	543	435	"	
C15r	570	543	"	
C16n.1n	595	570	"	
C16n.1r	602	595	"	
C16n.2n	692	602	"	
Strontium isotope ratio				
<sup>87</sup> Sr/ <sup>86</sup> Sr = 0.707764 ± 20 (NBS-987)	679	13n or older	Barrera (1989), Harwood et al, (1989) presented in Wilson et al, (1998)	

Table 3.3: Magnetostratigraphical and chemical chronological datums used to construct the revised CIROS-1 age model (Fig. 3.9).

## 3.9. Implications for Late Oligocene ice volume change and the Mi-1 Glaciation

In Figure 3.10B, Late Oligocene sedimentary cycles of grounding-line advance and retreat along the Victoria Land coastline of Western Ross Sea are correlated with the astronomically-tuned benthic  $\delta^{18}$ O record. This has been done using the new chronostratigraphy for the CIROS-1 drill core. Figure 3.10A shows a similar correlation for age-equivalent sedimentary cycles to that of the CRP-2/2A drill core, 80 km to the north, as reported in previous studies (Naish et al., 2008b; Naish et al., 2001). The chronostratigraphic constraints on both drill cores allow one-to-one correlation between sedimentary cycles and the  $\delta^{18}$ O cycles. This implies an orbital control on Late Oligocene EAIS volume changes. A noteworthy point is that the new chronostratigraphy allows the orbital response of two different EAIS outlet glaciers, the McKay and the Ferrar, to be evaluated and compared prior to and during a major cooling event that culminated in the Mi-1 glaciation at the Oligocene-Miocene boundary.

Ice-volume estimates for the Late Oligocene and Early Miocene have been determined by Pekar and DeConto (2006) and Pekar et al. (2006) by applying  $\delta^{18}$ O-

to-sea level calibrations to the high-resolution  $\delta^{18}$ O record from ODP Site 1090 (Billups et al., 2004). These calibrations are based on reconstructions of "apparent sea level" (eustasy + water loading effects on the crust) fluctuations recorded in the New Jersey Shelf margin using a two-dimensional flexural backstripping approach (Pekar, et al., 2002).



Figure 3.10: Correlation of Late Oligocene sequences in the CIROS-1 core (B) and age-equivalent sediments in CRP-2/2A (A) to the astronomically-tuned benthic  $\delta^{18}$ O record (A is from Naish et al., 2008a).

These calibrated records indicate that ice volume ranged between 50 % and 125 % of

the present day EAIS during the Late Oligocene and most of the Early Miocene (23-

17 Ma). Maximum ice volume occurred at the Early Miocene Mi-1 event (125 % of the present day ice sheet), and implies a glaciated WAIS, with grounding-lines well beyond their present day position and an ice extent similar to that of Late Quaternary glacial periods (EAIS 15-20 % greater than present) (Denton and Hughes, 2002; Huybrechts, 2002). Using this approach, individual 41 kyr- and 100 kyr  $\delta^{18}$ O ice volume cycles during the Late Oligocene and Early Miocene are inferred to represent global eustatic fluctuations of 10-30 m with a minimum sea level of -50 m at the peak of the Mi-1 glaciation.

Naish et al. (2008a) attempted to measure a direct record of eustatic sea level from the Antarctic continental shelf sedimentary sequences in the CRP-2/2A core utilising a grainsize-derived paleobathymetry curve (Dunbar et al., 2008). This approach estimated the eustatic sea level contribution to the paleobathymetry curve by placing constraints on total subsidence, decompacted sediment accumulation and glacioisostasy. In close agreement with Pekar et al. (2006), these authors showed that eustatic sea level fluctuated at orbital frequencies by between 10 m and 40 m. These fluctuations represented ice volume variances involving 15 % to 60 % of the present day Antarctic Ice Sheet. The estimates of Naish et al. (2008a) for the Mi-1 glacial excursion support a significant expansion of ice on Antarctica, perhaps equivalent to 120 % of the present day EAIS, with an attendant fall in global sea level of ~50 m.

This and other major glacial events (Mi and Oi events) have been attributed to times of comparatively-rare orbital congruence between 400 kyr-duration eccentricity and obliquity minima (e.g. Zachos et al., 2001b). These anomalies, which consist of low-amplitude variance in obliquity (a node) and a minimum in eccentricity, produce extended periods (200 kyr) of low-seasonality orbits favourable to ice sheet expansion (Palike et al., 2006). The record from CIROS-1 for this time interval provides further insights into the dynamics of the TAM outlet glaciers through which the EAIS discharged. Three short-lived Oligocene diatom zones *Hemiaulus sp. A*, *Pterotheca reticulata* and *Kisseleviella sp A*. are recognised in both drill core records. The fortuitous occurrence of two silicic volcanic ashes with high-precision <sup>39</sup>Ar/<sup>40</sup>Ar numeric ages occurring within short-duration normal polarity zones in Late Oligocene sequences 10 and 11 in CRP-2/2A has allowed the diatom zones and sequences to be accurately correlated with the astronomically-tuned timescale (Fig. 3.10A). Recognition of the same diatom zones associated within normal polarity

Subchrons C7n.2n, C7n.1n C6Cn.2n in the CIROS-1 drill core allows direct comparison of the cycles of glacial advance and retreat.

The first observation of note is that both drill core records preserve sequences of similar age and have similar times of erosion during the Late Oligocene. This implies a first-order regional response of the EAIS outlet glaciers to orbital climate cycles. However, there are significant differences between the records in terms of the detailed response to orbital influences. While the paleo-McKay Glacier (CRP) experiences a single eccentricity-paced ~125 kyr-duration cycle of advance-retreat-readvance spanning Subchron C6Cn.2n, the grounding-line of the paleo-Ferrar Glacier oscillated 5 times across the CIROS-1 drill site at ~20 kyr-duration. Correlation with the oxygen isotope record shows a prominent eccentricity cycle modulating five precession cycles at this time. Moreover the paleo-Ferrar appears to oscillate at a ~20 kyr frequency during subchrons C7n.1n and C7n.2n, whereas the paleo-McKay cycles correlate with the longer-period obliquity components.

The differing orbital responses may reflect major differences in the glaciology of these quite different outlet glacier systems. Today the McKay Glacier is one of the major outlet glaciers along the TAM – third-largest after the Byrd and Beardmore glaciers. Moreover it has the most direct connection to the EAIS, discharging through a wide gap in the TAM. In contrast, the Ferrar Glacier is a more restricted, steeper-gradient glacier incised deeply within the TAM, and fed from Taylor Dome at the edge of the EAIS. During the Late Oligocene, prior to the Mi-1 glaciation, sea level-calibrated oxygen isotope records imply a significantly smaller ice sheet on East Antarctica – 50 % of present day (Pekar et al., 2006) during the warmest climate Earth had experienced since the Eocene (Zachos et al., 2001a).

It is proposed here that under such climatic conditions, the paleo-Ferrar Glacier behaved in a similar manner to the Alpine-style temperate glaciers of Patagonia or New Zealand. Numerical ice sheet models show the occurrence of an isolated ice cap on the TAM during warmer climates when ice volume was half that of present day (DeConto and Pollard, 2003). Its mass-balance would have been fundamentally sensitive to surface ablation controlled by local insolation; over long timescales the intensity of summer insolation, and thus the number of positive-degree-days, is controlled by precession. In contrast, the paleo-McKay glacier's mass-balance would have reflected the overall behaviour of the EAIS, given its direct connection to the interior ice sheet which is maintained at 50 % present day volume (DeConto and Pollard, 2003). It is proposed that the continental EAIS remained colder because of its higher elevation and height-mass balance feedbacks and may have been less sensitive to seasonal insolation. Rather, it may have only responded during times of extremely favourable orbital geometries for ice ablation or accumulation. For example, times when high eccentricity coincided with extremes in precession or obliquity values. This might explain the sensitivity of the paleo-McKay Glacier to the longer-period orbital components. Notwithstanding the apparently different behaviour during major longer-duration periods of ice advance and retreat, such as the Mi-1 glaciation, which is recorded as a major unconformity of regional extent, presumably associated with widespread expansion of the EAIS into Ross Embayment.

### 3.10. Conclusions

(1) CIROS-1 sediments occur as seven facies, including muds, sands, conglomerates and diamicts.

(2) A revised stratigraphy for the CIROS-1 core, based on descriptions of the wellpreserved archived half, contains no diamicts beneath 366 mbsf. Rather, large clasts are deposited as conglomerates or by ice rafting.

(3) Sequence stratigraphic analysis of the CIROS-1 core shows two fundamentally different sequence motifs are preserved in CIROS-1. Sequences 1-4 (702-342 mbsf) are reasonably complete and were deposited during advance and retreat of fairly distal glaciers that terminated on land. Sequences 5-14 (342-25 mbsf) are incomplete, top-truncated and were deposited in glacial proximal conditions.

(4) CIROS-1 sediments were deposited between the Late Eocene-Early Miocene. Strata below  $\sim$ 366 mbsf were deposited during the Latest Eocene. Strata between 342 and 100 mbsf are of Late Oligocene age and strata above 100 mbsf were deposited during the Early Miocene. The age of the strata between 366-342 mbsf may be between 31-22 Ma. The  $\sim$ 9 Myr hiatus in the core may be wholly or partially distributed in the 342 mbsf unconformity in addition to the 366 mbsf unconformity.

(5) The revision of CIROS-1 facies and chronology has enabled a correlation between CIROS-1 and CRP-2/2A for the sedimentary cycles spanning the Late Oligocene-Miocene and the high-resolution oxygen isotope curve. The chronostratigraphic constraints of both drill cores allow one-to-one correlation between sedimentary cycles and the  $\delta^{18}$ O cycles, and imply an orbital control on Late Oligocene EAIS volume changes. The new chronostratigraphy allows the orbital response of two different EAIS outlet glaciers, the McKay and the Ferrar, to be evaluated and compared prior to and during a major cooling event that culminated in the Mi-1 glaciation at the Oligocene-Miocene boundary. While the paleo-McKay Glacier experiences a single eccentricity paced ~125 kyr-duration cycle of advanceretreat-readvance spanning Subchron C6Cn.2n in the Late Oligocene, the groundingline of the paleo-Ferrar Glacier oscillated five times across the drill site at ~20 kyrduration during this same interval. This contrasting style of behaviour represents a fundamentally different sensitivity to orbital forcing between the two glacier systems.

## Chapter 4: Zircons as indicators of sediment provenance

### 4.1. Introduction

The properties of zircons that make them useful tracers of sediment provenance are reviewed in this chapter, which provides a framework for the methods used in this thesis to constrain CIROS-1 zircon provenance. The major element chemistry, physical characteristics and formation environments of zircons are reviewed first. This is followed by: (1) An overview of tools currently used to investigate zircon compositions and the advantages and shortfalls of each; (2) An outline of the systematics of U-Th-Pb zircon dating and applications of detrital zircon geochronology in sediment provenance studies; and (3) An outline of other tools used to constrain detrital zircon provenance, including minor and trace element compositions and internal zonation.

## 4.2. Properties of zircons

Zircon has an orthosilicate structure and a general formula of  $ATO_4$  (Finch and Hanchar, 2003). It is comprised of silicon atoms which are surrounded by a tetragonal group of four oxygen atoms (distance 1.61 Å) and a zirconium atom located between two groups of four oxygen atoms (distance 2.15 Å and 2.29 Å, respectively) (Deer et al., 1997). To this end, the principle structure of this mineral is a chain of alternating edge and corner sharing SiO<sub>4</sub> tetrahedra and ZrO<sub>8</sub> triangular dodecahedra extending parallel to the z axis (Deer et al., 1997). The average major element chemistry of three zircon is outlined in Table 4.1.

	1	2	3
SiO <sub>2</sub>	32.51	31.45	27.13
$ZrO_2$	67.02	64.03	51.68
HfO <sub>2</sub>			1.18
TiO <sub>2</sub>		0.04	tr
AlO <sub>2</sub>	0.21	1.36	0.48
Fe <sub>2</sub> O <sub>3</sub>	0.08	0.09	0.45
$REE_2O_3$	0.04	1.18	10.51
MgO	0.01	0.04	tr
CaO	0.22	0.13	tr
ThO		0.01	1.03
$P_2O_5$			3.37
$H_2O^+$	0.03		3.12
$H_2O^-$		0.17	0.32
Total	100.12	99.81	99.84

Table 4.1: Major and minor element chemistry of three zircon suites: (1) Dark red-brown zircons, North Burgess, Ontario, Canada; (2) Zircon, China; and (3) Greyish green to brown zircon from pegmatite, Japan (source: Deer et al., 1997).

Zircon is part of the zircon group minerals. The only naturally occurring polymorph of zircon is the high-pressure reidite, found in shocked zircons formed during meteorite impacts or high pressure metamorphic events (Glass and Lui, 2001; Glass et al., 2002). The physical properties of a zircon grain are governed by its chemistry and the degree of metamictisation it has experienced (Speer, 1982a; Deer et al., 1997). Distinguishing features of zircon crystals include straight extinction, high refractive indices and birefringence, and common prismatic habit (Fig. 4.1; Table 4.2) (Deer et al., 1997).

Table 4.2: Physical and	l optical characteristics	of zircon	(source: Deer	et al., 1997).
-------------------------	---------------------------	-----------	---------------	----------------

Optical character	Tetragonal positive		
Dispersion	Very strong (nearly equal to diamond)		
D*	4.6-4.7		
Н	7.5		
Twinning	Rare		
Colour	Reddish brown, yellow, grey green,		
	colourless. In thin section colourless		
	to pale brown.		
Pleochroism	Very weak		
* These values are for fresh materials. Metamict materials may have values outside these ranges.			

Generally, zircon major element chemistry allows few insights into its provenance (i.e. Table 4.1) and trace element chemistry and isotope ratios must be analysed to constrain its formation history. The small voids between the tetrahedra and dodecahedra and open channels parallel to cause the zircon structure to be relatively open and prone to trace element incorporation (Finch and Hanchar, 2003). Trace elements are substituted into the zircon lattice in either the Zr<sup>4+</sup> or Si<sup>4+</sup> sites via reactions governed by the ionic radii and charge of the substituting cation relative to the one it is replacing. Trace elements incorporated into the zircon lattice generally have high closure temperatures (~900 °C) (Pettke et al., 2005).



Figure 4.1: A zircon crystal under plain (left) and cross-polarised (right) light. These photomicrographs show common double terminated prismatic habit, high relief and high order interference colours (source: http://www.ucl.ac.uk/~ucfbrxs/PLM/zircon.html).

## 4.3. Zircon formation environments

The environments in which zircons can form are many and varied and there is considerable ambiguity as to the boundaries that separate their classification. Zircon crystallisation environments require silicate melts (or aqueous fluids) with intermediate to high degrees of zirconium saturation. Zirconium saturation may be caused by high initial whole rock zirconium concentrations and saturation due to differentiation, the introduction of zirconium-saturated fluids and the dissolution of zirconium-rich sources.

Most commonly, zircon forms in intermediate to felsic igneous units (Hoskin and Schaltegger, 2003) and low grade metamorphic rocks. Zircons occur in lesser abundances in high grade metamorphic rocks and mafic (ophiolites), mantle affinity igneous units (kimberlites, carbonatites) and rocks that formed by hydrothermal processes (Grimes et al., 2009). It has been suggested that zircons can form from

authigenic processes (Hoskin and Schaltegger, 2003 and references therein). Due to the overlap in many of these environments, there may be considerable ambiguity regarding the identification of detrital zircon provenance. For example, should a zircon that formed in a late-stage, aqueous fluid-rich magma be classified as magmatic or a hydrothermal? And should a zircon formed in a closed system metamorphic environment in the presence of metamorphic aqueous fluids be classified as metamorphic or hydrothermal?

#### 4.4. Trace element and U-Pb analytical methods

The techniques used to investigate zircon elemental and isotopic compositions are outlined in Table 4.3.

For this study, a LA-ICP-MS was utilised. This tool allows rapid, relatively high precision (to ~0.5 %, 1  $\sigma$ ) in situ analyses, but it has the advantage that instrumentation is much cheaper. LA-ICP-MS uses a laser to ablate the zircon, after which elements and isotopes are ionised in an inductively coupled plasma source. These are then analysed by mass in a mass spectrometer (Davis et al., 2003).

The characteristics of LA-ICP-MS make it an ideal tool for zircon-based sediment provenance studies. The lesser degree of precision offered by LA-ICP-MS is, if mitigated properly, offset by the advantages of the high sample throughput offered by this technique.

Table 4.3: Tools for geochemical analysis of zircons (sources: Stern and Amelin, 2003; Davis et al., 2003; Dickin, 2003; Bernet et al., 2004).

Method	Method overview	Precision	Sample
name			through-put

ID-TIMS	Isotope dilution-thermal ionisation mass spectrometry- one of the most accurate and precise methods of obtaining isotopic and concentrations, however this method requires a large amount of preparation work and is largely restricted to bulk analysis	< 1 % (2se)	Low
SIMS	Secondary ionisation mass spectrometry- SIMS uses a high energy ion beam to transport the sample to a mass spectrometer. Allows for in situ isotopic measurements of zircon zones. High cost of instrumentation.	~1 % (1se)	Intermediate
MC-ICP- MS	Multi-collector inductively coupled mass spectrometry- utilises a double focusing mechanism to obtain isotopic compositions and is the most precise MS method. Cost of instrumentation is high.	~1 % (1se)	Intermediate
LA-ICP- MS	Laser ablation inductively coupled mass spectrometry- offers less precision and accuracy than double focusing ICP-MS. However, the instrumentation is cheap, sample through-put is high and sample preparation is short. This method allows in situ analysis of zones by the attachment of a laser for sample introduction.	> 1 % (2se)	High
Fission Track	Often a complementary method to U-Pb dating- fission track allows for insights into sediment provenance and by investigating the length of fission tracks. These are the results of radioactive (primarily $\alpha$ decay) of <sup>235</sup> U, <sup>238</sup> U and <sup>232</sup> Th.	N/A	Low

## 4.5. Detrital zircon ages and their use for provenance analysis

The analysis of sediment provenance using detrital zircon ages includes two steps:

(1) Individual zircons are radiometrically dated (by LA-ICP-MS).

(2) Suites of zircon ages from a sample are analysed for age populations which are tied to potential known sources of appropriate ages.

## 4.5.1. Radiometric U-Th-Pb dating of zircons using LA-ICP-MS

Radiometric zircon age dating is the cornerstone for many zircon provenance studies. It is based on the long-lived radioisotopes of U and the U-Th-Pb decay scheme. Tetravalent U<sup>4+</sup> and Th<sup>4+</sup> are incorporated into the zircon lattice by simple substitution for  $Zr^{4+}$  (i.e.  $Th^{4+} = Zr^{4+}$ ). As this reaction does not require additional substitutions for charge balance, U and Th occur in zircons (Grimes et al., 2007;

Hoskin and Schaltegger, 2003; Belousova et al., 2002) (Table 4.1). Pb is the daughter isotope of U and Th. It is too large to be readily substituted for  $Hf^{4+}$  or  $Si^{4+}$  during zircon formation or alteration thus, any Pb measured in zircons is presumed to have formed as a result of radioactive decay of U<sup>4+</sup> or Th<sup>4+</sup>. Assuming no lead loss, an age of the last time the zircon was above the closure temperature of this system can be calculated.

#### 4.5.1.i. Discordant versus concordant zircons

U-Pb dating comprises two U-Pb decay chains,  ${}^{235}U \rightarrow {}^{207}Pb$  (t<sub>1/2</sub> 704 Ma) and,  ${}^{238}U \rightarrow {}^{206}Pb$  (t<sub>1/2</sub> 4.47 Ga). The presence of two distinct dating schemes allows two U-Pb-based ages to be obtained for a single grain (or spot on a crystal). These ages can be plotted against one another on a concordia diagram (Fig. 4.2) which is used to the assessment of the robustness of ages obtained from individual ratios.

On the y-axis of a concordia diagram, the  $^{238}U/^{206}Pb$  ratio is plotted and on the x-axis is the <sup>235</sup>U/<sup>207</sup>Pb. The concordia line represents the shift in respective ratios with changing zircon age. If data from both schemes plot as a point on this line, the zircon is concordant. This concordancy means that the zircon has remained pristine since its formation and that the ages obtained from it are robust. If the data from the two dating systems do not fall on the concordancy line, the zircon is discordant. Discordancy is mainly caused by lead loss from the zircon, which may be catalysed by metamorphic events and radiation damage and discordant zircons are often discounted from further age analysis (e.g. are not used in age probability diagrams). However, discordant zircons can allow valuable insights into a zircon's history. Discordant zircons from an individual suite may plot on a straight line, their position on this reflecting their initial uranium content. The upper intersect of this line and the concordia line indicates the age of initial crystallisation of the suite, the lower intercept represents the age of the event that caused discordancy. Thus, although significantly discordant zircons are not be used to construct age probability diagrams, they can yield insights into the events that formed them.



Figure 4.2: U-Pb concordia diagram. Note the differing decay schemes on the x and y-axes and the curved concordia line. Concordant samples will fall within error of the concordia line. Discordant samples (black dots) are those that are not within error of the concordia line. If these are from the same suite and fall in a straight line, the lower intersect of this discordancy line with the concordia line indicates timing of the event which caused discordancy (most often a metamorphic episode), whilst the upper intersect indicates the time of crystallisation (source: http://www.tulane.edu/~sanelson/images/Discordia Pbleakage.jpg).

#### 4.5.2. Sediment provenance analysis using zircon ages

The focus of detrital zircon-based sediment provenance studies is to gain insights into the ages (and compositions) and relative input of lithologies that contributed to the sediment. To do this, clusters of radiometric ages of zircon found in the sediment are analysed. Age probability diagrams (Fig. 4.3) are an effective way to present age data obtained from detrital zircons of a single sediment sample. They allow easy interpretation of the age range of lithologies contributing to the sediment and their relative importance. By linking the age peaks to known lithologies (using age data and other provenance information), inferences about the conditions in past sedimentary systems, minimum deposition age of the sediment and the timing and relative importance of geological events may be made. Data representation on an age probability diagram is often two-fold; the numbers of zircons that have ages within certain age bins are plotted as a bar graph (Fig. 4.3) and an age probability line is calculated to account for the errors associated with each age. These lines, calculated using Gaussian kernels that vary with each individual age (Fedo et al., 2003), depict a probability distribution of the ages of detrital zircon populations found in the sediment.



Figure 4.3: Combined age probability diagrams and age distribution histograms for sediments from a range of ages. These show variations in sediment source which may allow interpretations into the conditions present during sediment deposition (source: DeGraaf-Surpless et al., 2003).

The amount of zircons (n) needed to construct a robust age probability diagram was investigated by Dodson et al. (1988) who found that in a typical case of a provenance component comprising of 1 in 20 of the total sediment, there is a 95 % probability that all provenance sources are includes if 59 grains are analysed (Dodson et al., 1988; Fedo et al., 2003).

Analysis of sediment provenance using age probability diagrams is often two-fold. Potential source lithologies for a sediment sample are constrained by comparison of age peaks in the sediment to those of known potential source lithologies. This is made easier and more reliable with the use of complementary trace element and morphological information, as discussed later in this chapter. Also, changes in the system that deposited the sediments may be quantified by comparison of age probability diagrams of spatially and/or temporally proximal samples (e.g. Veevers et al., 2008).

### 4.6. Trace element based constraints on zircon provenance

In situ trace element analysis of detrital zircons is often successfully used in conjunction with radiometric dating to discern sediment provenance (e.g. Veevers et al., 2008). This dual approach to constraining detrital zircon provenance was used in this research and the chemistry-based provenancing tools used in this study are outlined in this section.

#### 4.6.1. Rare earth elements in zircon

A zircon's REE composition reflects that of its formation environment. Zircons are resistant to chemical and physical weathering and REE are essentially immobile in zircons under most geologic conditions (Cherniak et al., 1997). Thus, REE in zircons form a unique archive of the environment within which the zircon formed (Hanchar and van Westrenen, 2007).

#### 4.6.1.i. REE incorporation into zircons

Rare earth elements are trivalent cations that have relatively large ionic radii, high charge and are commonly substituted into a zircon crystal lattice for  $Zr^{4+}$  (Hanchar and van Westrenen, 2007). The incorporation of REE into the zircon lattice is governed by REE size relative to  $Zr^{4+}$  (0.84 Å) and the pressure, temperature and composition of their growth environment (Hanchar and van Westrenen, 2007). Thus the zircon lattice can better accommodate ions of decreasing size and REE profiles in zircons are generally depleted in LREE relative to smaller HREE (Whitehouse, 2003).

#### 4.6.1.ii. Total REE concentrations in zircons

A zircons total REE concentration ( $\Sigma REE$ ) reflects the  $\Sigma REE$  of its formation environment. Belousova et al. (2002) found it is possible to constrain the composition of the melt in which an igneous zircon formed based on its  $\Sigma REE$  with higher total concentrations occurring in zircons formed in evolved melts. Zircons formed in pegmatites and granitoids were found to have  $\Sigma REE < 1.5-2$  wt %. Kimberlitic and carbonatitic zircons were found to have  $\Sigma REE \sim 90-480$  ppm and mantle affinity zircons had  $\Sigma REE$  of < 50 ppm (Belousova et al., 2002).

#### 4.6.1.iii. Chondrite-normalised REE patterns

Chondrite-normalised REE profiles are used to distinguish zircons from a variety of formation environments. To construct a REE profile, the concentration of rare earth elements in a zircon are divided by chondritic REE values (McDonough, 2000) and plotted adjacent to one another in ascending atomic mass on the x-axis (Fig. 4.4).

It is difficult to pin-point the formation environment for a single detrital zircon based on its REE profile alone. However, it is possible to distinguish between REE profiles from zircons formed in distinctly different environments. At present, based solely on chondrite-normalised REE patterns, it is possible to resolve between:

(1) Igneous zircons formed in the crust;

(2) Igneous zircons formed in the mantle;

(3) Zircons formed in high pressure metamorphic environments;

(4) Zircons formed in low pressure metamorphic environments; and

(5) Hydrothermal zircons.

It is not yet possible to resolve finer scale variation in sources for zircons (e.g. the resolution of different granite sources) based on REE profiles alone (Rubbato, pers. comm., 2009).

#### Chondrite-normalised REE profiles for igneous zircons

Two broad groups of igneous zircons are distinguishable based on chondritenormalised REE plots alone:

(1) Mantle affinity (carbonatite and kimberlite).

(2) Crustal affinity (e.g. gabbro, granite).

As some ambiguity remains regarding the role of fluids during the formation of zircons in pegmatites and the mantle (van Lichtervelde et al., 2009; Schaltegger, 2007), zircons from such environments may be arguably classified as hydrothermal.

Zircons are a common minor mineral in kimberlites, carbonatite, peridotites and pyroxenites. Two types of mantle affinity zircons are known to exist, those that are xenolithic and those that crystallised in the mantle. Zircons that formed in situ in the mantle are very rare. Such zircons are commonly very depleted in trace elements, have steep chondrite-normalised REE profiles, have variable degrees of enrichment and concavity of HREE and have positive Ce anomalies and no Eu anomalies (Fig. 4.4) (e.g. Siebel et al., 2009; Schmidberger et al., 2005; Belousova et al., 1998).



Figure 4.4: Chondrite-normalised REE profiles for rare 'primary' mantle affinity zircons, hypothesised to have crystallised in the mantle. Note the variable amplitude Eu and Ce anomalies and the relatively depleted concentrations of HREE (source: Hoskin and Schaltegger, 2003).

The REE profiles of mantle xenolith zircons are commonly a result of partial overprinting of inherited REE signatures whilst the crystal resided in the mantle. To this end, mantle xenolith zircons are generally more trace element enriched than those that formed in situ in the mantle and show variable REE profiles (Fig. 4.5). REE profiles may include a lack of Eu anomalies, a pronounced Ce anomaly and high HREE concentrations (Fig. 4.5; Siebel et al., 2009).



Figure 4.5: Chondrite-normalised REE profiles for xenolithic mantle affinity zircons. Note the characteristically high HREE and the pronounced Ce anomaly discussed in the text (source: Siebel et al., 2009).

A crustal formation environment is most common for zircons. Crustal affinity zircons display large intra- and inter- crystal chemical heterogeneity (e.g. Gagnevin et al., 2010), which reflects the high degree of chemical variability present in the crust. Zircons formed in crustal igneous environments generally have overlapping REE profiles (Fig. 4.6) and it is not possible to distinguish between different crustal sources for zircons based on chondrite-normalised REE profiles alone (Grimes et al., 2009). Zircons formed in crustal igneous environments have REE profiles that are distinct from those formed in mantle, metamorphic and hydrothermal environments. To this end it is possible to constrain a crustal igneous province for a detrital zircon based on its REE profile alone.

Typical crustal affinity igneous zircon have REE profiles with steep positive slopes (HREE enrichment) and a pervasive prominent positive Ce and negative Eu anomalies (Fig. 4.6) (Whitehouse, 2003). Steep positive trends from LREE to HREE are caused by the increasing ability of zircon lattice to incorporate the elements as their atomic radii decreases with increasing atomic number (the lanthanide contraction effect) (Whitehouse, 2003). The

negative Eu anomaly can be accounted for due to the presence of coexisting feldspars that crystalised before the zircon, which have strong positive Eu anomalies (Rubatto and Herman, 2007). The magnitude of the Ce anomaly reflects variations in redox state during zircon growth. The total concentrations of REE in crustal affinity zircons is caused by the enrichments of the source units (increases with increasing differentiation, as discussed above) and the distribution coefficients during crystallisation.



Figure 4.6: Typical REE profiles from crustal affinity zircons which are reasonably reproducible and therefore easily distinguishable from those from other broad formation groups. However, inter- and intra- grain chemical heterogeneity within this group of zircons is large making it challenging to distinguish between zircons from within this group based on REE profiles alone (source: Grimes et al., 2007).

Chondrite-normalised REE profiles of metamorphic zircons

Based on a zircon's chondrite-normalised REE profile, two broad metamorphic environments are distinguishable:

(1) Low pressure metamorphic environments (e.g. greenschists).

(2) High pressure metamorphic environments (e.g. eclogites and granulites).

High grade metamorphic zircons are known to occur in eclogites and granulites, but are generally quite rare. If such a zircon forms in equilibrium with an anatectic melt its trace element composition and REE profile will be very similar to that of igneous zircon (Figs. 4.7 and 4.8). However, if the zircon grows in subsolidus conditions in equilibrium with garnet it will have a distinctive trace element composition and REE profile (Figs. 4.7 and 4.8).



Figure 4.7: REE profiles for high pressure metamorphic zircons. Crystals formed in equilibrium with an anatectic melt (black dots) have REE profiles comparable to those of crustal affinity igneous zircon (e.g. igneous cores in Figure 4.8). Zircons formed in subsolidus conditions in a high grade metamorphic rock (white dots) have distinctive REE profiles, which may be distinguishable from those of other broad formation groups (source: Hoskin and Schaltegger, 2003).

High grade metamorphic zircons that formed in subsolidus conditions have extremely variable REE profiles which may include: (1) Depletion of HREE relative to Mid REE (MREE) or flat HREE slopes (Figs. 4.7 and 4.8). This pervasive trait is due to the co-crystallisation of garnet (Rubatto and Hermann, 2007); (2) Weak Eu anomalies, which is due to the zircons crystallising prior to feldspars in high grade metamorphic rocks (Rubatto and Hermann, 2007); and (3) Variable Ce anomalies, the cause of which are poorly understood (perhaps oxidation states).



Figure 4.8: REE profiles of high pressure metamorphic zircon (granulite grade rims) and igneous cores. The HREE depletion in the metamorphic zircon is due to the presence of garnet during crystallisation (Rubatto and Herman, 2007). Note the similarity between the REE profiles of the igneous cores and that of the zircon formed in equilibrium with a melt (black dots) in Figure 4.7. (source: Whitehouse, 2003).

Zircons formed in low grade metamorphic environments have REE profiles distinct from those formed in high grade metamorphic, igneous and hydrothermal environments (Fig. 4.9). Fluids expelled during metamorphic reactions may cause hydrothermal growth or alteration of pre-existing zircons. However, as these fluids are usually expelled in a closed system, such zircons may generally be classified as metamorphic.

In low grade metamorphic environments new zircon growth is rare and zircons are commonly formed from the recrystallisation of protolith zircons. Thus the chemical compositions of low-grade metamorphic zircons are often a result of the partial overprinting of the protolith zircon in the metamorphic environment. Though sections that retain the characteristics of the protolith zircons will be chemically indistinguishable from the protolith, sections of zircons formed from the complete recrystallising of the protolith will show distinct REE patterns (Fig. 4.9).



Figure 4.9: Completely re-crystallised, low grade metamorphic zircon REE profiles (black) for zircons found in a metapelite. Inherited igneous core REE profiles (shown in grey) are significantly different. Note the exceedingly low MREE and LREE concentrations found in the metamorphic overgrowths (source: Martin et al., 2008).

During complete recrystallisation of a protolith zircon in a low pressure metamorphic environment, cations with ionic radii significantly larger than Si, Zr and Hf are expelled. As a result, entirely recrystallised protolith zircons will show depletions in LREE and MREE, as these are larger than HREE (Fig. 4.9). Low grade metamorphic zircons commonly show variable Eu and Ce anomalies.

## Chondrite-normalised REE profiles of zircons formed in association with aqueous fluids

Due to the large amount of overlap in zircon formation environments, it is ambiguous whether hydrothermal zircons are a distinct group or whether they should be classified as igneous and/or metamorphic (Schaltegger, 2007). Recently, much research has been conducted into hydrothermal zircon characteristics (e.g. Pelleter et al., 2007) that suggest hydrothermal REE (and other trace element) characteristics are often distinct from those formed in other environments (e.g. Grimes et al., 2009). Thus, for completeness, the current understanding of the REE characteristics of hydrothermal zircon is briefly reviewed. It is difficult constrain the shape of hydrothermal zircon REE profiles (and trace element concentrations) due to the extreme variability of the composition of hydrothermal zircons (e.g. Pettke et al., 2005), which reflects the high degree of chemical heterogeneity in hydrothermal environments. The geochemical characteristics of zircons formed from or altered by fluids are controlled by an interplay of the crystallisation sequence of accessory minerals (Schaltegger, 2007), the composition of the aqueous fluid, the redox state in which the zircon formed, and the composition of the pre-exiting, altered zircon (Pelleter et al., 2007).



Figure 4.10: Variable REE compositions obtained from hydrothermal zircons from a single source. The variability is attributed to a number of factors including: the evolution of fluid composition (from Eu enriched to depleted, causing variations in Eu anomalies) and variations in altered magmatic zircon composition and redox state. This illustrates how variable zircon chemistry from a single suite can be if fluid interaction occurs (source: Pelleter et al., 2007).

A pervasive characteristic of hydrothermal zircons is an enrichment in REE (and other trace elements) relative to magmatic zircons from the same rock (Fig. 4.10) (Hoskin, 2004; Pettke et al., 2005) which reflects the elemental enrichment common in many hydrothermal fluids. Other reported characteristics include elevated LREE, hypothesised to be a product of zircon interaction with saline aqueous fluids (Hoskin, 2004; Grimes et al., 2009). Depletion of LREE in hydrothermal zircons has also been reported

(Schaltegger, 2007). Coupled variation in Eu and Ce anomalies have also been reported for hydrothermal zircons (Pelleter et al., 2007), with a strong positive correlation between the magnitudes of negative Eu anomalies and positive Ce anomalies.

#### 4.6.2. The Ti-in-zircon geothermometer

Ti-in-zircon saturation geothermometry allows Ti concentration-based zircon formation temperatures to be estimated. This system has been widely applied to rocks from a variety of genesis (e.g. Watson and Harrison, 2005) but recently it has been found that this system may not be as reliable as initially thought and may be influenced by a variety of factors, such as the presence of co-crystallising Ti incorporating phases (Fu et al., 2008). It appears the formation temperatures for zircons formed in a variety of host rocks are generally considerably lower than expected and it is understood that Ti-in-zircon temperatures alone are not sufficient to identify parental melt compositions (Fu et al., 2008).

The premise of this system is the increased ability of  $Ti^{4+}$  to replace  $Zr^{4+}$  and  $Si^{4+}$  in the zircon lattice with increased temperature. The dominant substitution in this reaction is  $Ti^{4+} = Si^{4+}$  or  $Zr^{4+}$ , which is isovalent and relatively insensitive to pressure. This replacement relationship (Equation 4.1) is logarithmic with concentrations of 0.3-50 ppm yielding temperatures between ~600-1,450 °C (Watson et al., 2006).

 $Log (Ti_{zircon}) = (6.01 \pm 0.03) - ((5080\pm 30) / (T (K)))$ Equation 4.1: Ti-in-zircon geothermometer (source: Watson et al., 2006).

The geothermometer assumes Ti saturation in a host rock. For in situ zircons saturation may be confirmed by the co-existence of a Ti-bearing accessory phase. However, as this cannot be confirmed for detrital zircons, Ti-in-zircon values for detrital zircons are minimum formation temperatures.

#### 4.6.3. Li concentrations and zircon provenance

The lithium concentration of a zircon may give information on the Li content of its parent rock, the degree of surface material incorporated into the parent rock, and the amount and duration of heating the zircon experienced since its formation. High Li concentrations within zircons indicate highly evolved magmatic sources or contamination by surface material (Cherniak and Watson, 2010). Lower concentrations indicate no surficial contamination and/or low degrees of magma differentiation. As such, mantle derived zircons have Li concentrations of the order of parts per billion, whilst evolved melts such as granites and pegmatites, and pelitic metasediments have Li concentrations up to 250 ppm (Ushikubo et al., 2008).

Ushikubo et al. (2008) measured the lithium concentrations of Jack Hills (Australia) zircons, to constrain the amount of surficial contamination and/or differentiation in the parent melt. It was assumed that, similarly to other elements, Li diffusion in zircon was slow and that Li concentrations in a zircon were generally unaltered since formation. The Jack Hills zircons were found to have high Li concentrations (10-60 ppm) which was hypothesised to indicate a low temperature interaction of the Jack Hills zircon parental melt with liquid water.

More recently, Cherniak and Watson (2010) found diffusion of Li in zircon is relatively rapid and requires lower activation energy than other trace elements (such as U, Th and REE). It was calculated that the Li concentrations from the centre of a 100 µm grain are lost in 2000 yr if a temperature of 750 °C is sustained and are lost in 60 Myr if the zircon is heated to 500 °C. To this end, the closure temperature for Li in zircon is much lower than those for other trace elements (e.g. Pb; Cherniak and Watson, 2000). This indicates that a xenolith zircon that experienced high temperature metamorphic conditions would experience a decoupling of its elemental compositions; the zircon's Li concentrations would be reset and whilst concentrations of other element with higher activation energies would be maintained.

Thus, a decoupling of Li and other trace elements may be observed if a detrital zircon was once a xenolith in high grade metamorphic, mafic igneous and/or mantle environment. However, this decoupling is less likely to occur in zircons that were once xenoliths in lower grade metamorphic or felsic igneous environments.

#### 4.6.4. Zr/Hf and Hf concentrations

Zircon Zr/Hf ratios allow insights into the amount of differentiation of the parental melt, regardless of the temperature at which the zircons formed. Zircon is the prime

reservoir for both Zr and Hf (Grimes et al., 2009), which are substituted into the zircon lattice for Si<sup>4+</sup> by a reaction that requires no charge compensation (Grimes et al., 2007). Due to its slightly smaller size, Zr is slightly more compatible than Hf<sup>4+</sup> in zircon (Grimes et al., 2007; Hoskin and Schaltegger, 2003). Thus, when zircon crystallisation occurs, the Zr/Hf of the melt will decrease as Zr is preferentially incorporated into the crystal. Subsequent zircon crystallised from this melt have lower Zr/Hf ratios and their crystallisation will serve to further lower Zr/Hf in the residual melt. Thus, high Hf concentrations (low Zr/Hf ratios) indicate highly differentiated formation environments, whereas low Hf concentrations (high Zr/Hf ratios) indicate a lesser degree of differentiation has occurred.

As their incorporation characteristics are so similar, any appreciable variances in Hf and Zr concentrations in zircons requires a high degree of melt differentiation. Most crustal rocks maintain near chondritic whole rock ratios with only rhyolitic and granitic melts displaying whole rock Zr/Hf that deviate significantly from chondritic values (Grimes et al., 2009). Generally Zr/Hf ratios in calc-alkaline rocks decrease from 60 for mafic, early formed rocks, such as gabbros to about 30-40 for granites (Gulson, 1969). This well established trend in Zr/Hf ratios allows large-scale investigations into the amount of differentiation an igneous rock has experienced However, it does not allow more detailed insights into the degrees of differentiation experienced (e.g. it is not possible to distinguish between granites with variable amounts of differentiation based solely on Zr/Hf ratios) (Grimes et al., 2009).

#### 4.6.5. U and Th compositions and the Th/U ratio

U and Th concentrations in zircon reflect parental melt enrichment. Crustal zircons are generally most enriched in U and Th and have concentrations on the order of tens to thousands of ppm (Hoskin and Schaltegger, 2003). Kimberlitic zircons show much lower U and Th concentrations (e.g. 10.9 and 3.3 ppm, respectively) (Belousova et al., 1998) and zircons sourced from eclogites and hydrothermal units show intermediate concentrations (U ~100 ppm and Th ~100-400 ppm) (Rubatto and Hermann, 2003; Pelleter et al., 2007). Considerable ambiguity may be present when constraining detrital zircon formation environment based on U and Th concentrations alone, due to the heterogeneous intracrystalline distribution of these elements (Hoskin and Schaltegger, 2003).

This heterogeneity is less when considering zircon Th/U ratios which allow an igneous versus metamorphic provenance for detrital zircons to be discerned. Igneous zircons have average Th/U < 1 (ratios as high as 10,000 have been reported in highly Th enriched rocks such as pegmatites and carbonatites) (Belousova et al., 2002). Metamorphic zircon Th/U ratios are generally less than 0.1 due to the preferential expelling of Th cations during protolith recrystallisation (Hoskin and Schaltegger, 2003).

#### 4.6.6. Resolution of felsic and mafic igneous zircons using elemental ratios

Though not necessarily differentiable using REE profiles alone, detrital zircons sourced from a number of crustal affinity (as well as mantle affinity) sources, may be distinguished from one another using a number of elemental ratios.

U/Yb ratios and their relationship to Hf and Y, P and HREE may help distinguish zircons from different crustal affinity igneous sources. U and Yb have very similar mineral/melt partitioning coefficients and near equivalent compatibility in zircon (Grimes et al., 2007; Grimes et al., 2009). Given this, U/Yb ratios in zircon will exactly reflect the whole rock U/Yb ratio of the melt from which they formed. In magmatic systems, U and Yb exhibit variable behaviours; with increasing differentiation U becomes enriched whilst Yb becomes depleted. As zircon U/Yb ratios replicate those of the host material, this results in low U/Yb ratios for mafic igneous zircons (around 0.2), higher values of ~1 for continental igneous zircons, and the highest values for kimberlitic zircons (2.1). The exact replication of host U/Yb found in zircons means it is possible to resolve between groups of zircons from continental and oceanic crust when plotted against Hf, Y, P or HREE (Fig. 4.11) (as illustrated in Grimes et al., 2007; Grimes et al., 2009).



Figure 4.11: Elemental bivariate plots used to distinguish between crustal-affinity zircons. When plotted on bivariate plots, zircons from continental vs. mantel sources show inherently difference characteristics. This Study refers to the source paper of this image (source: Grimes at al., 2007).

# 4.7. Internal zonation of trace elements: Insights into zircon provenance

The relative insolubility of zircon in crustal melts and fluids, as well as their general resistance to physical and chemical weathering means several generations of geochemical information are often preserved in a single grain (Cherniak and Watson, 2003). Preserved zonation within a crystal is a record of thermal and geochemical

evolution which can be investigated using in situ geochemical analysis techniques. Zoning in zircons can form from slight fluctuations in source chemistry, erosion of zircon during transportation on the Earth's surface or the absorption of pre-existing zircon. Sharp compositional zones are prevalent in zircon crystals and are occasionally on an extremely fine scale ( $\mu$ m to sub- $\mu$ m) (Cherniak et al., 1997). Due to the slow diffusivity rates of trace elements in zircons, sharp compositional zones have been proven to be long lasting, (a 1  $\mu$ m zone will be destroyed over 100 Myr and lost over 1 Gyr if consistently at 800 °C) (Cherniak et al., 1997).

#### 4.7.1. Analysis of internal zonation

An electron probe micro-analyser (EPMA) can be used to investigate internal geochemical zonation with a zircon crystal by back scattered electron (BSE) and cathodoluminescence (CL) imaging. BSE images are created when X-rays emitted by the EPMA hit the sample and cause electrons to become dislodged. The brighter the BSE image returned, the higher the atomic mass of the crystal. Thus BSE analysis is a sound way to distinguish between zircons and other crystals with lower atomic masses. CL images are created when X-rays hit a crystal causing trace elements within it to emit visible light (CL), the brightness of which correlates positively with Hf, Y, P REE, U and Th concentrations (Siebel et al., 2009; Corfu et al., 2003; Cherniak et al., 1997). The most prominent known CL characteristics for zircon from variable formation environments and how these may be used to infer zircon genesis are outlined below.

#### 4.7.2. Igneous zircon cathodoluminescence characteristics

There are a number of zoning characteristics inherent to igneous zircons the most pervasive being oscillatory growth zones (Fig. 4.12). Oscillatory zones are created in response to episodic growth of the crystal and the amount of trace elements available in the host rock (Corfu et al., 2003). Sector zoning (Fig. 4.13) occasionally occurs in igneous zircons, although the cause of this is still debated (Corfu et al., 2003). Occasionally, igneous zircons display very weak, faint, broad zoning (Fig. 4.14) which may represent zonation on a finer scale than is resolvable using current imaging techniques. This lack of zoning if often observed in mantle affinity zircons, such as those from carbonatites and kimberlites, due to hig temperatures and subsequent diffusion and homogenisation of trace elements (Belousova et al., 1998; Corfu et al., 2003). In such samples, the absence of zonation may be caused by prolonged residence in the mantle. Mantle zircons often show other, more complex zoning features, such as mosaic textures. Xenocrystic cores are common in igneous zircons and their internal zoning is often corroded, truncated and overgrown by igneous rims (Fig. 4.15) (Corfu et al., 2003). If zirconium undersaturation has occurred within the growth environment, dissolution and reprecipitation textures may cut primary growth zones (Geisler et al., 2007).



Figure 4.12: Oscillatory zoning in a granitic zircon with local resorption (source: Corfu et al., 2003).



Figure 4.13: A zircon showing sector zoning, as indicated by the dashed lines (source: Corfu et al., 2003).



Figure 4.14: Broad weak oscillatory zoning characteristic of kimberlitic zircon (source: Belousova et al., 1998).



Figure 4.15: Igneous zircons with xenocrystic cores (source: Corfu et al., 2003).

#### 4.7.3. Metamorphic zircon cathodoluminescence characteristics

Zircons found in metamorphic rocks have highly variable, complex and chaotic internal zonation patterns that reflect the highly changeable parameters present during metamorphic zircon formation/recrystallisation. Variables that influence metamorphic zircon internal zonation include the physio-chemical conditions during crystallisation, the duration of each metamorphic event, the pre-existing structures in the protolith zircon, and the overgrowth of new zircon (Corfu et al., 2003). Internal zonation found in metamorphic zircons include: protolith cores that preserve original growth zoning (Fig. 4.16) (predominantly in low-grade metamorphic rocks), chaotic textures that combine growth patterns, flow structures and overgrowths (Fig. 4.17), variants of sector zoning that are caused by variances in growth rates and homogeneous zones (Fig. 4.18).



Figure 4.16: High grade metamorphic zircons with xenocrystic cores that have preserved original (oscillatory) growth zones (source: Corfu et al., 2003).



Figure 4.17: Zircons with irregular concentric zoning with overgrowths on zircons of a metamorphic origin (source: Corfu et al., 2003).



Figure 4.18: Homogenous zones of a metamorphic origin (source: Corfu et al., 2003).

#### 4.7.4. Hydrothermal zircon cathodoluminescence characteristics

Hydrothermal zircon may form by growth of new crystals (including overgrowths) or from fluid alteration of pre-existing zircons, which often occurs in close association with metamorphic and igneous environments. Similarly to the chemical characteristics of hydrothermal zircons, the internal growth zones of this group are highly heterogeneous, reflecting the numerous variables involved during hydrothermal zircon alteration and/or growth. Zircons formed or re-crystallised in association with fluids may display convolute zoning (Fig. 4.19) and zones of enrichment of high field strength elements, REE and non-radiogenic lead (Fig. 4.20). Other zoning characteristics potentially displayed by hydrothermal zircons include secondary domains cutting primary growth zones and open, spongy, inclusion-rich textures (hydrothermal environment primary zircon growth) (Fig. 4.21).



Figure 4.19: Convoluted zoning characteristic of hydrothermal overgrowths/recrystallisation (source: Corfu et al., 2003).



Figure 4.20: Trace element enriched zircon patchy texture showing metasomatic replacement of low U domains by high U domains (bright areas) (source: Corfu et al., 2003).


Figure 4.21: BSE image of a zircon with a spongy, inclusion rich texture characteristic of zircon growth in a hydrothermal environment (source: Geisler et al., 2007).

# Chapter 5: Geochronological and geochemical analytical techniques, data reduction and analysis

# 5.1. Introduction

The analytical work for this thesis was conducted using the Victoria University of Wellington Geochemical Laboratory. Facilities used include the EPMA and LA-ICP-MS. For ease of explanation, this chapter has been structured in the chronological order in which the methods were conducted.

# 5.2. Sample acquisition

Eighteen hand-sized sample were taken from the working half of the CIROS-1 drill core at intervals of  $\sim$ 50 m (Fig. 5.1; Table 5.1). Sand-sized lithologies were targeted as zircons big enough to allow in situ geochemical analysis most commonly occur in these lithologies. On two occasions, samples were taken within  $\sim$ 5 m of one another. This was done to allow comparison of zircon content from temporally proximal samples that were deposited by different processes during orbitally forced variations in depositional environments (e.g. sand from the matrix of a diamict and its overlying sand unit). Thus, any potential fine-scale variation in the lithologies contributing sediments to the core would not be missed.

Sample	Location		
name	(mbsf)	Depositional Age	Source unit
28-21	28	Early Miocene	Poorly sorted coarse/very coarse sandstone
78-18	78	Early Miocene	Fine sandstone/mudstone
91-17	91	Early Miocene-Late	Sandstone matrix of a diamict
		Oligocene?	
148-16	148	Late Oligocene	Medium/coarse sandstone
205-15	205	Late Oligocene	Medium sandstone
249-14	249	Late Oligocene	Sandstone matrix of a diamict
292-13	292	Late Oligocene	Fine sandstone/mudstone
295-12	295	Late Oligocene	Fine/medium sandstone
362-11	362	Late Oligocene	Coarse sandstone
403-10	403	Late Oligocene-Late Eocene?	Medium/coarse bedded sandstone
462-7	462	Late Oligocene-Late Eocene?	Medium/coarse sandstone
465-8	465	Late Oligocene-Late Eocene?	Medium/coarse sandstone
507-6	507	Late Eocene	Medium/coarse sandstone
560-5	560	Late Eocene	Medium sandstone
610-4	610	Late Eocene	Medium sandstone
652-3	652	Late Eocene	Medium sandstone
687-1	687	Late Eocene	Sandstone matrix of a conglomerate
693-2	693	Late Eocene	Sandstone matrix of a conglomerate

Table 5.1: The names, locations, depositional ages and source units of the samples analysed in this thesis.

# 5.3. Sample preparation

Approximately half of each sample was disaggregated and the mud fraction was removed using water-based density separation. This was repeated for particularly muddy or aggregated samples. Once dry, the samples were sieved into  $< 53 \mu m$ , 53-150  $\mu m$ , 150-250  $\mu m$ , 250-300  $\mu m$  and  $> 300 \mu m$  fractions. The  $< 53 \mu m$  and  $> 300 \mu m$  fractions were stored and not used. Although the most likely size fraction for zircons is  $\sim$ 53-150  $\mu m$ , the two larger fractions were also processed to ensure no analysable zircons were missed. Per sample, the three size fractions were magnetically separated using the VUW Franz and from each a magnetic and non-magnetic fraction was obtained. Each non-magnetic fraction was density separated using sodium polytungstate (specific gravity = 2.9 g / cm<sup>3</sup>).

Approximately 100 zircon grains were picked from the heavier portions of each sample. There was a ~99 % occurrence of zircons within the 53-150  $\mu$ m fraction, with an occurrence of < 10 individual 150-300  $\mu$ m zircons. Zircons were placed on double sided cellotape in groups according to their size. Once sufficient zircons were picked the proto-mount was photographed under a binocular microscope to enable later investigations of zircon morphology and colour (Fig. 5.2). Prior to mounting in epoxy ~three, 1 mm shards of NIST 610 (an internal standard) were added to the tape. Round epoxy mounts were made and hardened on a hot plate. Mounts were polished using polishing paper and grinding lap until the widest sections of the zircon crystals were exposed.



Figure 5.1: CIROS-1 core log, sampling locations and sample names. Sample names first state the depth of the sample. The second number represents when it was sampled in the sampling process.

# 5.4. Sample imaging

Imaging methods used are similar to those utilised by Kitajima et al. (2008). Each polished mount was photographed using a binocular microscope to aid navigation during sample analysis (Fig. 5.3). The VUW JEOL 733 Electron Microprobe was used to conduct BSE and CL imaging of the zircons. During all imaging a current of 120 nA and a voltage of 15 keV was maintained. BSE images (e.g. Fig. 5.4) were used to distinguish between zircons and other minerals with lower atomic masses. Zircon grains were individually imaged (occasionally in groups of ~5) for internal zonation by CL (e.g. Fig. 5.5).



Figure 5.2: Binocular microscope image of zircons from the 53-150  $\mu$ m fraction of sample 91-17 prior to the mount being made. This imaging was done to allow later investigations into zircon morphology and colour.



Figure 5.3: Binocular microscope image of 53-150 µm zircons in a polished mount (249-14) used for navigational purposes when conducting EPMA and LA-ICP-MS analysis. Additionally, such images aided in the picking of appropriate spot locations at which to conduct LA-ICP-MS analysis.



Figure 5.4: BSE image of 53-150  $\mu$ m zircons in sample 292-13. Bright grains are zircons whereas less bright or invisible grains are other minerals with lower atomic masses.



Figure 5.5: CL image of a zircon from sample 292-13 showing zones of variable trace element composition (CL zones). A 25  $\mu$ m diameter ablation pit is visible in the relatively homogeneous zone on the left of the zircon. Note the high-U (bright) zone on the right of the grain and the bright crack, both of which are avoided when conducting LA-ICP-MS analysis of zircons.

# 5.5. Geochronological and geochemical analysis of zircon crystals

Spot locations for analysis were picked based on binocular microscope, CL and BSE images. If a zircon was not deemed to be in a relatively pristing condition, it was not analysed. CL imaging was used to find well defined zones, such as cores and rims, which were targeted for analysis. Inclusion-rich areas, identified using the binocular microscope and BSE imaging, as well cracks were avoided. Zones of excessive U concentrations, identified as very bright zones in CL images, were avoided as these indicate a degree of open system behaviour in the zircon which might yield unreliable results. Analysis of zircon spots was conducted using the VUW Agilent 7500 cs ICP-MS coupled to a NewWave 193  $\mu$ m solid-state Nd-YAG laser. Samples were thoroughly washed in methanol and Milli-Q water and dried in a 40 °C oven for ~4 hr prior to being analysed or at any time after being handled to remove surficial contamination.

#### 5.5.1. U-Pb geochronology using LA-ICP-MS

In recent years, LA-ICP-MS has been established as an accurate, fast and relatively cheap way to obtain radiometric ages of zircons (and other minerals) (Chang et al., 2006; Cocherie and Robert, 2008). The manner in which this method was applied in this research is outlined below.

# 5.5.1.i. Samples analysed for detrital zircon U-Pb ages

Zircons from all 18 samples were analysed for their U-Pb compositions. Many zircons were analysed in multiple locations to allow detailed insights into their growth histories and therefore possible provenance. Other sampling strategies used will be discussed later in this section.

#### 5.5.1.ii. Operational parameters

The operational parameters to obtain U-Pb and Pb-Pb ages for CIROS-1 zircons were developed and tested using the S-97-19 granitic zircon standard. The TIMS age for this standard is 1089  $\pm$  1 Ma (1se) (James Connolly, pers. comm., 2007). S-97-19 zircons were also used as an external standard. One to two runs comprising 12 S-97-17 zircon analyses were conducted before and after analysis of each CIROS-1 sample. The average ratios and apparent ages obtained for this standard over the duration of this project are given in Table 5.2 (n = 263).

Table 5.2: Average ratios, 2se errors and apparent ages for the 263 S-97-19 zircons analysed during sample analysis and method development. The TIMS age for this standard zircon is  $1089 \pm 1$  Ma (1se) (J. Connolly, pers. comm., 2007).

				A	Verag	e rat	io					
<sup>207</sup> F	$^{2}b/^{2}$	$^{206}$ Pb	2se	<sup>238</sup> U/	/ <sup>206</sup> Pb	2	2se	235	$U/^{20}$	<sup>7</sup> Pb	2se	
0.0	)763	5	0.0014	5.	3950	0.	1300	0	).045	02	0.0568	3
			Av	erage	appai	ent a	age (M	a)				
$^{207}$ Pb/ $^{206}$ I	Pb	2se	$^{238}U/^{2}$	<sup>06</sup> Pb	2se	<sup>235</sup>	$U/^{207}P$	b	2se	Co	ncordia	2se
1103		35	109	07	24		1089		18		1083	82

The internal standard used during age analysis was the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 610 glass. This glass has concentrations of ~450 ppm for many elements;

including U concentrations of 461.5 ppm and Pb concentrations of 426 ppm (GeoReM preferred values).

Individual runs (of both CIROS-1 and S-97-19 zircons) were set up as: one internal standard (NIST 610) spot, six unknown zircon spots, one NIST 610 spot, six unknown zircon spots, one NIST 610. Many analyses included multiple spots on a single zircon (e.g. cores and rims or repeats of zones in different runs to examine reproducibility). For each sample, approximately 4-8 runs of 12 unknown zircons were conducted. On completion of a sample, 1-2 runs of S-97-19 zircons were conducted to validate the age being obtained for the sample zircons.

Spot locations were pre-ablated prior to analysis. Pre-ablation (20 pulses of the laser) parameters were: 50  $\mu$ m spot size, 75 % power, 10 Hz frequency. Pre-ablation served a number of purposes:

(1) Clean the surface of the zircons (e.g. clear away any residual anthropogenic lead);

(2) Confirm the quality of spot locations (e.g. there were no cracks and/or inclusions present that were not yet identified). If a zircon was not in a relatively pristince condition it was not analysed; and

(3) Confirm the grain being analysed was a zircon. This was done by running the ICP-MS during pre-ablation and monitoring the <sup>90</sup>Zr peak. If the peak was less that 100,000-1,000,000 cps the grain was assumed not to be a zircon and excluded from further analysis.

Prior to each analysis session, the laser was warmed up (fired for ~20 min with shutter closed, 100 % power, 100  $\mu$ m spot size, 10 Hz frequency). It was auto-tuned 1-3 times preceding every run and was operated with an irradiance of ~2-4 Gw / cm<sup>2</sup> and a fluence of ~5-7 J / cm<sup>2</sup>. Runs were conducted with a laser power of 75 % and a frequency of 5 Hz. Spot sizes for zircons were 25  $\mu$ m and 35  $\mu$ m for NIST 610 spots. Smaller spot sizes for the samples allowed multiple analyses on many zircon grains. During each analysis active focusing, involving progressive raising of the stage, was used to reduce U-Pb fractionation and increase counts (Cocherie and Robert, 2008; Hirata and Nesbit, 1995). Ablation times were set at 60 s with ~100-

120 s wash-out intervals between analyses (as outlined in Kösler and Sylvester, 2003).

Prior to each analytical session the ICP-MS was stabilised for ~30 min. Once stabilised and after every sample change, the ICP-MS was tuned using NIST 610 shards in the mounts. Tuning was conducted by monitoring signal intensity and stability of a range of isotopes on the ICP-MS and reducing their RSD errors to < 5 %. Parameters changed during tuning were predominantly carrier (Ar) and optional (He) gases. The carrier gas was usually set to between 0.80-0.90 L / min and the optional gas was usually about 80-91 % flow. Additionally parameters that were less commonly altered during tuning include: RF power (never set to less than 1000 W), RF matching, torch position and ion extract lenses.

Isotopes used for tuning include <sup>206</sup>Pb,<sup>207</sup>Pb,<sup>208</sup>Pb,<sup>232</sup>Th and <sup>238</sup>U, which were tuned to RSD's of < 5 %. Typically cps when the ICP-MS was optimally tuned included ~15,000 for <sup>206</sup>Pb, ~40,000 for <sup>232</sup>Th and ~55,000 for <sup>238</sup>U. During tuning, the <sup>248</sup>ThO<sup>+</sup>/<sup>232</sup>Th was reduced to < 2 %, mainly by reducing the flow of carrier gas. If this was not possible more time was needed to flush the chamber and tuning was delayed for ~10 min. Additionally, the <sup>232</sup>Th/<sup>238</sup>U was measured during tuning. As both these isotopes occur in roughly equivalent amounts in the NIST 610 glass, tuning was conducted so that this ratio was 1.0 ± 0.1. This was done to ensure no excessive fractionation between U and Th was occurring at the given settings to which the machine was tuned. During tuning, wash out times were evaluated and an appropriate washout delay was set (most commonly all isotopes washed out in ~45-60 s and wash out delays of ~100-120 s were set).

Runs of 12 unknown zircons and three NIST 610 shards usually took ~40 min. The isotopes measured during sample analysis and their dwell times are listed in Table 5.3. A 10 ms dwell time was chosen for the more abundant isotopes that occur in zircons whilst 30 ms was used for <sup>204</sup>Pb and <sup>207</sup>Pb, which occur in very small quantities in zircons. <sup>235</sup>U concentrations were calculated from <sup>238</sup>U cps and <sup>235</sup>U/<sup>238</sup>U = 1/137.88.

Isotope	Dwell time (ms)
<sup>204</sup> Pb	30
<sup>206</sup> Pb	10
<sup>207</sup> Pb	30
<sup>208</sup> Pb	10
<sup>232</sup> Th	10
<sup>238</sup> U	10

Table 5.3: Isotopes and dwell times used during LA-ICP-MS zircon U-Pb isotopic analysis.

# 5.5.1.iii. Data reduction

Raw ICP-MS data was produced as .csv files that contained cps data for the selected isotopes measured through the duration of the run (Table 5.3). These files were cut and pasted into a Microsoft Excel data reduction spreadsheet used to obtain background and internal standard corrected isotopic ratios. Firstly, all the data were background corrected by removing the average background counts for the ~20 s prior to the laser firing. Then outliers were removed using a time sequence graphical representation of the data. <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>238</sup>U/<sup>206</sup>Pb, <sup>235</sup>U/<sup>207</sup>Pb, <sup>232</sup>Th/<sup>208</sup>Pb ratios were calculated for both NIST and zircon spots. As U and Pb fractionation is known to increase with increased ablation time (e.g. Hirata and Nesbitt, 1995), only the first 30 s of data were used for U/Pb and U/Th ratios whereas ~60 s worth of data was used for <sup>207</sup>Pb/<sup>206</sup>Pb ratios (to reduce 2  $\sigma$  errors). Correction factors to correct instrument drift or bias were calculated using the ratios obtained for NIST 610 spots and their published values (Table 5.4).

Table 5.4: Reference values for U and Pb isotopes in NIST 610 glass.  $^{207}Pb/^{206}Pb$  isotopes were obtained using MC-ICP-MS.  $^{238}U/^{206}Pb$  reference value was obtained by TIMS.  $^{235}U/^{207}Pb$  reference value was calculated from the  $^{238}U/^{206}Pb$  value.

Ratio	Reference Value	Source
<sup>207</sup> Pb/ <sup>206</sup> Pb	$0.9099 \pm 0.003$	Baker et al. (2004)
<sup>238</sup> U/ <sup>206</sup> Pb	3.9984 ± 2.4 %	Bea et al. (2006)
<sup>235</sup> U/ <sup>207</sup> Pb	$0.0315 \pm 2.4 \%$	From <sup>238</sup> U/ <sup>206</sup> Pb

Correction values based on these known and the measured NIST ratios were applied to all sample ratios. Two  $\sigma$  errors were calculated for all ratios using the formula showed in Equation 5.1. U-Pb age calculations using LA-ICP-MS typically does not require large common lead corrections (Kŏsler and

Sylvester, 2003). As such, <sup>204</sup>Pb counts were observed and if the average background corrected <sup>204</sup>Pb counts were above ~100 cps, the analysis was discounted.

$$2\sigma = (2*sd)/(\sqrt{n})$$

Equation 5.1: Standard error calculations to a two  $\sigma$  level. sd is the standard deviation within the populations and n is the number in the population.

Ages were calculated in a separate spreadsheet from background and internal standard corrected ratios. U-Pb ages were calculated and Pb-Pb ages were iteratively obtained using decay constants from Jaffey et al. (1971). Concordia ages, errors and MSWD's were calculated from rho values, U-Pb ages and errors using Isoplot 3.7 (Ludwig, 2003). Two  $\sigma$  errors were first converted to percentage errors and there after to years.

Once the ages for the zircons were calculated, the most reliable age for each was assessed (for use in age probability diagrams etc).  $^{207}$ Pb/ $^{206}$ Pb ages are not reliable under an age of ~0.5-1 Ga (Hirata and Nesbit, 1995) as the percentage error in age increase significantly with decreasing age (Mattinson, 1987). As such, a cut off of 700 Ma was chosen below which U-Pb ages were only used. For zircons of age > 700 Ma Pb-Pb ages were used, as this system is the most reliable way to date older zircons. If a zircon of age < 700 Ma was discordant, it was discounted from age probability diagrams. This step may cause biasing of the ages as it may cause cutting out of zircons less that 750 Ma, formed by an event that caused discordant zircons. If it was concordant, the  $^{238}$ U/ $^{206}$ Pb age was used, as the isotopes that make up this ratio are the most abundant and therefore yield the most reliable and precise ages. No post-analysis CL imaging of spot locations was conducted to ensure zones were co-analysed.

#### 5.5.1. iv. Data analysis: Concordia plots and discordant zircons

In addition to calculating concordia ages and age probability diagrams, Isoplot 3.7 was used to construct concordia diagrams (Fedo et al., 2003). As discussed above, if zircons were concordant (and less than ~700 Ma in age) the age obtained was deemed reliable and used in construction of age probability diagrams. The age of concordant zircons is reflected by their location upon the concordia line on concordia diagrams (Fig. 5.6). Discordant zircons will not fall within error of the concordia line. Discordant zircons with ages < 700 Ma were not used in age probability diagrams as their age was deemed unreliable. Though not useful in age probability diagrams, discordant zircons can yield useful provenance information. Discordant zircons from the same suite within a sediment sample may fall on a straight line, their location there on reflecting their initial U content. If these discordant zircons fall on a straight line and are confirmed to be of the same suite, the upper intersect of this line will represent the timing of zircon crystallisation and the lower intersect will indicate the timing of the event that caused lead loss and subsequent discordance. Discordant zircons were plotted on concordia diagrams and any linear trends observed were used to discern whether they came from the same suite, their formation age and the age at which they underwent lead loss.



Figure 5.6: U-Pb concordia diagram. Note the differing decay schemes on the x and y-axes and the curved concordia line. Concordant samples will fall within error of the concordia line. Discordant samples (black dots) are those that are not within error of the concordia line (source: http://www.tulane.edu /~sanelson/images/discordiapbleakage.jpg).

#### 5.5.1.v. Data analysis: Age probability diagrams

Once the appropriate ages were selected for each zircon an age probability diagram was created for each sample (Fedo et al., 2003). If a zircon's core and rim had been analysed, the rim age was included in the age probability diagram (as this yields information on the latest event that formed the zircon, thus making it easier to constrain provenance). If a zone in a zircon had received multiple analyses that were within error of one another, an average age of the ages was used in the age probability diagram. Age probability diagrams were constructed using Isoplot 3.7 (e.g. Fig. 5.7).



Figure 5.7: An age probability diagram for sample 78-18, constructed from the most reliable ages obtained for zircons from this sample. The diagram was constructed from zircon age and 2 se error data using Isoplot 3.7. Note the red line which represents the age probability, which was calculated using both ages and errors. The blue bars represent the number of zircons whose age falls within a given age bin.

#### 5.5.1.vi. Data analysis: U and Th concentrations

U and Th concentrations for each zircon analysed were calculated. This was done using the known U (or Th) concentration ( $\mu$ g/g) in NIST 610 (461.5 ppm (GeoReM preferred value)) and the cps of U (or Th) measured in the NIST glass. By dividing NIST 610 counts per second by its known concentration, a 'conversion factor' was obtained. This was used to convert the U (or Th) cps in the zircon to U (or Th) concentration. The cps obtained for the zircon was divided by the cps obtained for the NIST glass. This value was multiplied by the 'conversion factor' giving the U (or Th) ppm concentration in the zircon.

U and Th concentrations were used to calculate the Th/U ratios of all zircons. This ratio is indicative of an igneous or metamorphic origin for zircons (Hoskin and Schaltegger, 2003), with a low Th/U ratio < 0.1

indicating a metamorphic origin and a high ratio of > 0.1 indicating an igneous origin (for more details refer to Chapter 4).

#### 5.5.1.vii. Validation of results

To validate the age probability diagrams and zircon numbers (n) obtained for each sample, two samples were completely re-analysed. This included obtaining a new aliquot of the sediment sample and conducting sample crushing, sieving and magnetic and density separations. From the zircon concentrate zircons were picked and mounted. The new mounts were imaged using EMPA and their ages determined by LA-ICP-MS.

The first sample for which the entire process of obtaining age data was repeated was sample 295-12. During initial processing this sample yielded high zircon numbers and thus a reliable age probability diagram. It was repeated to assess the repeatability of its age probability diagram and the degree to which the variable number of zircons analysed influences its shape. The results from this (Figs. 5.8 and 5.9) show a distinct overlap between the age probability diagram obtained from the original processing and those created from the reprocessed sample. For example, both show a wide 500 Ma peak and overlapping Palaeozoic peaks. The repeat of sample 295 has a smaller zircon number (due to time limitations involved with picking), which is reflected when the age probability diagrams are compared. For example, the repeated sample shows a reduced number of zircons with ages older than Palaeozoic. The reduced number of age peaks observed in the reprocessed sample (which had lower n) displays the expected correlation between the number of zircons analysed and the reduced numbers of age peaks.



Figure 5.8: Age probability diagram for initial 292-12 analysis. n = 45.



Figure 5.9: Age probability diagram constructed for the repeat of sample 292-12. n = 31.

The second repeated sample was 148-16. During initial processing relatively few zircons were obtained, thus it was re-processed to confirm it was indeed zircon poor or if the zircons had been lost during the initial processing. The similarly low number of zircons obtained during reprocessing proved that low (or high) zircon counts in given samples were inherent to the sample, and not a function of sample preparation.

#### 5.5.2. Trace element analysis by LA-ICP-MS

Trace element analysis allows insights into detrital zircon provenance. Thus, age and chemical data for a detrital zircon allows a two fold approach to investigating provenance as both age and zircon chemistry can be used to match the zircon to source lithologies. As such, geochemical investigations of zircons were conducted on a number of samples as outlined in the following section.

#### 5.5.2.i. Samples analysed for trace element content

Trace element analysis was conducted on zircons obtained from three samples, 205-15, 462-7 and 652-3, which were chosen for the following reasons:

(1) The sample depths (205, 462 and 652 mbsf) were evenly spaced throughout the core;

(2) Each sample contained a high number of zircons, meaning a large number of zircons would have matching age and chemistry data; and

(3) Most importantly, the combined age probability diagrams of these three samples covers the entire spectra of ages populations observed in the CIROS-1 core, thus chemistry data for all age populations in the core was obtained by analysing three samples (assuming all age populations in the core were sourced from the same lithology).

#### 5.5.2.ii. Operational parameters

This section will outline those methods used to conduct elemental analysis of zircons in samples 205-15, 462-7 and 652-3. Isotopes of elements selected for analysis needed to fit the following criteria:

(1) Concentrations in zircons must be high enough to yield signals above detection limits of LA-ICP-MS;

(2) Isotopes used must not have interferences from other elements; and

(3) Each element must give insights into the conditions present during zircon formation/alteration.

To test which isotopes yielded signals above background, a range of isotopes were initially tested using S-97-19 standard zircon. The results of this are given in Table 5.5. Of those isotopes that yielded signals detectable by LA-ICP-MS, only those that did not have interferences from other elements were

used. For example, <sup>181</sup>W may have an interference from <sup>165</sup>Ho and <sup>16</sup>O, whereas a false signal may be generated for <sup>137</sup>Ba due to a combination of <sup>90</sup>Zr and <sup>47</sup>Ti.

The measured isotopes and analytical dwell times are listed in Table 5.6. The following isotopes were selected for the reasons outlined below:

(1) Both <sup>88</sup>Sr and <sup>86</sup>Sr were analysed as although <sup>88</sup>Sr is the larger isotope (so would yield more reliable data) it has a number of potential interferences. Thus the smaller and interference-free <sup>86</sup>Sr was also measured as a control;

(2) <sup>91</sup>Zr was analysed as it is a minor Zr isotope (thus the detectors would not be swamped during zircon analysis); and

(3) <sup>7</sup>Li was analysed as recent research has shown interesting results in Li variation from zircon from variable sources (Cherniak and Watson, 2010; Ushikubo et al., 2008; Chapter 4), and Li concentrations within zircons was found to be well above the detection limit of the LA-ICP-MS.

Table 5.5: Elements analysed using LA-ICP-MS and S-97-19 standard zircon to ascertain which elements were detectable above background.

		Detectable			Detectable
Mass	Element	(Y/N)	Mass	Element	(Y/N)
7	Li	Υ	95	Mo	Υ
11	В	Ν	133	Cs	Υ
24	Mg	Ν	137	Ba	Y
27	Al	Ν	139	La	Υ
29	Si	Y	140	Ce	Y
31	Р	Y	141	Pr	Υ
34	S	Ν	146	Nd	Y
44	Ca	Ν	147	Sm	Υ
45	Sc	Y	153	Eu	Υ
47	Ti	Υ	157	Gd	Y
51	V	Ν	159	Tb	Y
52	Cr	Ν	163	Dy	Y
55	Mn	Ν	165	Но	Υ
59	Со	Ν	166	Er	Υ
60	Ν	Ν	169	Tm	Υ
63	Cu	Ν	172	Yb	Y
66	Zn	Ν	174	Lu	Y
69	Ga	Ν	175	Hf	Υ
72	Ge	Ν	181	Та	Υ
75	As	Ν	182	W	Ν
85	Rb	Ν	185	Re	Ν
86	Sr	Y	189	Os	Ν
88	Sr	Υ	205	Th	Υ
89	Υ	Y	209	Bi	Ν
93	Nb	Y			

Spot locations on zircons were within the same growth zones (identified using CL images) in which U-Pb age dating had been conducted. Runs were set up as: one NIST 612 spot, six zircons, one NIST 612, six zircons, one NIST 612. Spot sizes for NIST 612 was 35 µm and 25 µm for zircons.

The laser ablation parameters used for trace element analysis were similar to those used for U-Pb isotopic analysis. The laser was warmed up by running it with the shutter closed for ~15 min (100 % power, 10 Hz, 100  $\mu$ m spot size). The laser was tuned 1-3 times prior to each run and was run with an irradiance of ~2-4 Gw / cm<sup>2</sup> and a fluence of ~5-7 J / cm<sup>2</sup>. Pre-ablation (four times five bursts at 50  $\mu$ m spot size, 75 % power, and 10 Hz frequency) was conducted at each spot location. Spots were run at a spot size of 35  $\mu$ m, 5 Hz and 75 % power. Analytical times were 80 s and washout delays varied between 80-120 s (dependent on the washout time measured during tuning).

Table 5.6: Isotopes measured and their dwell times during LA-ICP-MS trace element analysis.

Mass	Element	Dwell time (s)	Mass	Element	Dwell time (s)
7	Li	0.01	157	Gd	0.02
29	Si	0.01	159	Tb	0.02
31	Р	0.01	163	Dy	0.02
49	Ti	0.01	165	Но	0.02
86	Sr	0.01	166	Er	0.01
88	Sr	0.03	169	Tm	0.02
89	Υ	0.01	172	Yb	0.01
91	Zr	0.01	175	Lu	0.02
93	Nb	0.03	178	Hf	0.01
139	Ca	0.03	181	Та	0.03
140	Ce	0.02	183	W	0.02
141	Pr	0.03	184	W	0.02
146	Nd	0.03	232	Th	0.01
147	Sm	0.03	238	U	0.01
153	Eu	0.03			

The ICP-MS was stabilised for ~30 min after being turned on. At the start of every run the ICP-MS was tuned using NIST 610. Isotopes used for tuning covered the spectrum of masses measured during each run, including <sup>7</sup>Li, <sup>47</sup>Ti, <sup>93</sup>Zr, <sup>140</sup>Ce <sup>147</sup>Sm <sup>165</sup>Ho <sup>181</sup>Ta and <sup>238</sup>U. Additionally, <sup>248</sup>ThO<sup>+</sup>/<sup>232</sup>Th was monitored to assess the oxide in production. As tuning was conducted on such a range of masses, the ICP-MS was tuned to RSD's of < 10 %.

After tuning, washout delays to be used were assessed. The amount of time it took for all elements to wash out was usually ~45-75 s and washout delays of ~80-120 s were set. Prior to running sample zircons, pulse-analogue factors for those elements likely to have > 1,000,000 cps were assessed. This was done so that PA corrections could be applied to these elements. Pulse analogue factors were analysed by lasering a sample zircon that was not used for analysis. Pulse analogue corrections were applied to  $^{29}$ Si,  $^{91}$ Zr and  $^{178}$ Hf.

# 5.5.2.iii. Data reduction

Raw trace element data was in a .csv format containing cps data. For each zircon, the raw data was cut and pasted into an individual MS Excel spreadsheet. Data reductions methods followed those outlined by Allen et al. (2008). To obtain trace element compositions, a minor isotope of a major element in zircon was used. (<sup>29</sup>Si). Previous studies have shown Si concentrations in zircon to be ~30 wt% (300,000 ppm) and this known value was used for normalisation (Deer et al. 1997). NIST 612 was used as an internal standard with known concentrations of <sup>29</sup>Si (GeoReM preferred values). For each zircon, background corrections were applied based on the average background count of the element for the 45 s prior to the laser starting. Thereafter, all scans were normalised to mean Si values (average Si composition of ~30 %) (as outlined in Allen et al., 2008). Following this, outliers were identified using time resolved analysis and removed. These data were scrutinised using the methods outlined below.

#### 5.5.2.iv. Data presentation: Chondrite-normalised REE plots

Processes that occur in the Earth's crust and mantle cause a deviation from REE chondritic values. REE characteristics of a zircon will be influenced by the REE composition of their parental rock and the partitioning coefficients between the parental rock and the zircon (Belousova et al., 2002; Whitehouse, 2003). As such, by comparing a zircon's REE concentration to that of chondrites, insights into the processes that formed the zircon may be gained. This can be done using chondrite-normalised REE plots (Fig. 5.10; Chapter 4).



Group 1 representative REE profiles

Figure 5.10: Chondrite-normalised REE profile for a group of CIROS-1 zircons.

To construct chondrite-normalised REE plots using the REE concentrations obtained the following steps were taken:

- (1) Chondritic REE values were obtained from McDonough (2000);
- (2) Zircon/chondrite ratios were calculated for REE from each zircon; and
- (3) These ratios were plotted to form a chondrite-normalised plot (Fig. 5.10).

#### 5.5.2.v. Data analysis: Ti-in-zircon geothermometer

Ti-in-zircon saturation geothermometry allows Ti concentration-based formation temperatures to be calculated for zircons. When applied to detrital zircons, this formula will give a minimum formation temperature. This system and recent investigations as to the robustness of the Ti-in-zircon geothermometer (e.g. Fu et al., 2008) are outlined in Chapter 4. The equation used to calculate Ti-in-zircon temperatures is given below. Ti-in-zircon geothermometry was conducted for all zircons analysed for their trace (and minor) element composition.

 $Log (Ti_{zircon}) = (6.01 \pm 0.03) - ((5080 \pm 30) / (T(K)))$ 

Equation 5.2: Ti-in-zircon geothermometer (source: Watson et al., 2006).

#### 5.5.2.vi. Data analysis: Elemental concentrations and ratios

Elemental ratios are a key tool to gain insights into the conditions present during zircon formation and/or zircon provenance. Thus, ratios and concentrations that may yield useful information were calculated and used to help constrain the detrital zircons formation environment. Ratios and concentrations analysed include: Li concentration, Zr and Hf concentrations and the Zr/Hf ratio, U and Th concentrations and the U/Th ratio, U/Yb, Ce/Ce\*, Eu/Eu\*, Sm/Pr and U/Th (for more information refer to Chapter 4).

# Chapter 6: Geochronology and geochemistry of detrital zircons in the CIROS-1 core

# 6.1. Introduction

This chapter reviews the results of the LA-ICP-MS geochemical and geochronological investigations of CIROS-1 conducted in this study. The associated implications of these results for our understanding of the record of Antarctic climate change and tectonism contained in CIROS-1 are also reviewed.

This chapter reviews the following results:

(1) Zircon U-Pb age results for the 18 samples analysed and inter-sample variations therein;

(2) The cumulative age probability diagrams constructed using U-Pb ages of all of the analysed CIROS-1 zircons;

(3) The results of trace element analysis conducted to constrain the provenance of CIROS-1 zircons; and

(4) The geochemical characteristics of zircons within each age population in the cumulative age probability diagram.

The second half of this chapter reviews the implications of these results. This includes a discussion of the record of zircon growth events contained in CIROS-1, an overview of source lithologies for CIROS-1 zircons, and a review of potential causes for the temporal variations of zircon characteristics observed in the core.

# 6.2. Results

#### 6.2.1. Zircon numbers and U-Pb and Pb-Pb ages

In this research, 18 sand-sized samples from various stratigraphic levels of the 702 m long CIROS-1 core were taken. Sample nomenclature was based on stratigraphic depth and the order in which samples were taken (e.g. Sample 292-14 was the 14<sup>th</sup> sample taken and came from 292 mbsf). In total 854 zircons were analysed for U-Pb ages and 119 were analysed for trace element chemistry. The range of zircon numbers analysed per sample (n) was 18 to 77 with a per sample average of 46 zircons.

Zircon numbers per sample vary systematically down core; zircon numbers increases steadily down core from 28 mbsf to 148 mbsf (n = 55 and 19, respectively). Below this depth, zircon numbers increase to a depth of 292 mbsf (sample 292-13; n = 77) and decrease steadily to the lowermost sample at 693 mbsf (n =  $\sim$ 20) (Table 6.1; Fig. 6.1).

A cumulative probability diagram was created using the ages of all zircons analysed in addition to the construction of age probably diagrams for each sample. The number of age peaks (age populations) in each individual probability diagram was counted, the results of which are shown in Figure 6.2. Seventeen of the 18 samples analysed show a positive correlation between number of age populations ( $N_{age}$ ) and total zircon numbers ( $N_{zirc}$ ) (Fig. 6.2; Table 1).



Figure 6.1: Combined diagram of total zircon number per sample (n), percentage of 450-650 Ma 'Ross' age population and the occurrence of Devonian aged zircons. The blue line is a graphical trend line drawn through the data.

Sample 292-13 had the largest zircon population (n = 77) and the largest spread of ages (~19 individual age peaks) (Figs. 6.2 and 6.3; Table 1). The most prominent feature in this sample's age probability diagram is the large peak at ~450-700 Ma. Lesser but distinct age peaks also occur at 800-1000 Ma and 1000-1200 Ma (Fig. 6.3) and additional smaller peaks are present (e.g. ~210 Ma, 1200 Ma, 1350 Ma, ~1900 Ma, 3300 Ma). The smallest zircon population was found in sample 687-1 (687 mbsf; n = 18) which also had the smallest spread of ages, containing only six zircon age populations (Fig. 6.3). Similarly to sample 292-13, sample 687-1 had its most prominent age peak at 400-600 Ma with a smaller but distinct peak at 900-1200 Ma. Additional smaller age peaks occurred only between 2200-2800 Ma (Fig. 6.3).

Sample 28-21, the uppermost sample analysed (28 mbsf), did not show a trend of increasing  $N_{zire}$  = increasing  $N_{age}$  (Fig. 6.1; outlier on bottom right of graph). This sample has a relatively high total zircon number (n = 55) and an abnormally small spread of ages ( $N_{age}$  = 6) (Fig. 6.3). Forty nine of its 55 zircons have ages between 449-551 Ma with only six older grains. There is also a distinct lack of a peak at 900-1200 Ma, which occurs in all other samples (Fig. 6.3).



Figure 6.2: Graph displaying the number of zircons and the number of age populations in each sample. This shows a trend of increasing number of age populations per sample with increasing number of zircons analysed, as defined by the trend line.



Figure 6.3: Summary of age probability diagrams obtained for each of the 18 samples analysed for U-Pb. The column headed 'Cumulative age probability diagram' depicts the age probability diagram for all the zircons obtained for a single sample. The column named 'Age probability 120-700 Ma' shows the probability over 120-700 Ma. This has been included to allow detailed examination of the 450-650 Ma age peak, which is the dominant peak on all age probability diagrams. Note the sample names, depositional ages and relative climate during sedimentation, shown to the right of the core log.

# 6.2.2. Late Proterozoic-Early Palaeozoic (450-650 Ma) 'Ross' age population

The 450-650 Ma age population is dominant in all samples (Fig. 6.3). Due to the dominance of this age peak, zircons of this age are numerous enough to allow statistically sound investigations of any variances within this population (as discussed below). The majority of zircons in this population fall within the ages of the Ross Orogeny (Allibone et al., 1993a) and are referred to a 'Ross' aged zircons in much of this work.

The percentage of total zircon numbers (n) that comprises of 450-650 Ma 'Ross' aged grains is plotted per sample in Figure 6.1. This variable is defined by a bell-shaped curve with a general decrease in the percentage of 450-650 Ma grains between samples 28 and ~300 mbsf (from ~90-30 %). From ~300 mbsf to the base of the core, the percentage of 'Ross' aged zircons increases again from ~30 to ~80 % (Fig. 6.1).



Figure 6.4: Average, minimum and maximum ages of zircons 450-650 Ma 'Ross' age population zircons per sample. The error bars depict one standard deviation errors on the ages.

The average, minimum and maximum ages for zircons in the 450-650 Ma 'Ross' age population are plotted in Figure 6.4. The maximum ages of 'Ross' aged zircons in each sample (Fig. 6.4; red squares) define a bell shape down core; ages systematically increase between 28-295 mbsf (from ~550-660 Ma) and thereafter decrease to a minimum of ~535 Ma at 693 mbsf. The minimum ages of the 'Ross' age population show a different trend (Fig. 6.4; blue squares). These ages remain more or less constant for the entire length of the core (between ~440-490 Ma). The average age of the 'Ross' aged zircons in each sample is shown in green. The trends follow those

observed in the maximum ages, but are not as distinct due to a lack in relative variation. At the very top of the core the average age is very low  $\sim$ 500 Ma. This age increases to  $\sim$ 550 Ma between 100-480 mbsf and decreases again to  $\sim$ 510 Ma at the base of the core (Fig. 6.4).

Table 6.1: Zircon data per sample. Data includes total zircon numbers (n), the number of age populations in each age probability diagram and the proportion of 450-650 Ma grains in each sample. Also shown are the minimum, maximum and average ages for zircons in the 450-650 Ma 'Ross' age population per sample.

			%			Average
			(Total)	Youngest	Oldest	age
			450-	450-650	450-	450-650
	Ν	N age	650 Ma	Ma	650 Ma	Ma
Sample	zircons	populations	grains	grains	grains	grains
28-21	55	6	91	449	551	496
78-18	39	8	54	449	569	502
91-17	24	10	63	469	610	537
148-16	19	8	63	469	596	545
205-15	45	15	44	475	642	554
249-14	70	18	31	457	640	538
292-13	77	19	45	481	657	555
295-12	45	15	44	442	669	521
362-11	53	13	58	468	649	542
403-10	55	13	35	484	641	553
462-7	62	17	45	490	639	554
465-8	49	9	39	489	681	550
507-6	38	14	34	483	617	532
560-5	41	12	46	453	597	508
610-4	63	17	46	456	635	535
653-3	48	13	58	455	630	524
687-1	18	6	61	477	529	514
693-2	24	9	75	470	565	518

#### 6.2.3. CIROS-1 cumulative age probability diagram

The cumulative age probability diagram (Fig. 6.5) was constructed by combining the ages of all zircons analysed into a single age probability diagram (n = 854). The black line bars represent the number of zircon ages that fall within each 40 Myr age bin. The relative probability of a zircon sourced from CIROS-1 being of a certain age is shown as the red line. This has been calculated using the ages and associated (two standard error) errors for each zircon analysed. It must be noted that this diagram shows an artificial bias towards younger ages as the rims of many zircons were preferentially analysed. This was done as rim analyses yield insights into the most recent processes that influenced the zircons.



Figure 6.5: Cumulative age probability diagram for the entire suite of CIROS-1 zircons (n = 854). The histograms reflect the counts of zircon ages that fall within 40 Myr age bins. The red line reflects the probability of a CIROS-1 zircon being a certain age and was calculated from zircon counts, individual zircon ages and two sigma errors.

Peaks at 450-650 Ma, 900-1250 Ma and 1400-1650 Ma are clearly distinguishable on the diagram. Smaller, less discernable peaks occur at 200-250 Ma, 320-390 Ma, 810-870 Ma, 1800-2050 Ma (Fig. 6.5).

## 6.2.4. Trace element chemistry of CIROS-1 zircons

Trace element analysis was conducted on 119 zircons from three samples located at 205, 462 and 652 mbsf. Combined, these zircons fall in all of the age peaks in the cumulative age probability diagram (Fig. 6.5). Examination of zircon trace element data shows that four chemically distinct groups of zircons are present in CIROS-1. The geochemical characteristics that define these groups from one-another and potential provenance of these groups are discussed in this section and are summarised in Table 6.2 and Figures 6.8-6.11.

#### 6.2.4.i. Suggested provenance of Group 1 zircons

With 106 of the 119 zircons falling within this category, Group 1 zircons were by far the most common zircons analysed. The geochemical characteristics that define zircons in Group 1 are discussed below. Zircons of this Group showed the greatest spread of trace element concentrations with large ranges of Ce/Ce\*, Eu/Eu\*, HREE/LREE, HREE/MREE, Ti-in-zircon formation temperatures and Li concentrations (Table 6.2). All but three zircons within this population have Th/U ratios above 0.1. Although highly variable in absolute concentrations, the chondrite-normalised REE profiles obtained from these zircons share many common features including typically steep positive slopes (i.e. Nd/Yb average is 258 and Lu/Gd average is 2.74) and an enrichment in HREE (average Lu<sub>zircon</sub>/Lu<sub>chondrite</sub> in this population is 2240) (Fig. 6.8).

Zircons in this group have pervasive and large Ce anomalies, with a Ce/Ce\* of 2-2635 and an average Ce/Ce\* of 176. Negative Eu anomalies are also ubiquitous, with Eu/Eu\* ranging between 0.01-0.83 and averaging 0.21 (Fig. 6.8). The chemistry of Group 1 zircons suggests they are of a crustal-affinity igneous provenance given that:

(1) The high degree of chemical variability seen within the trace elements is similar to the high degree of chemical variability known to be present in igneous bodies within the crust and in zircons that form therein (Hoskin and Schaltegger, 2003);

(2) The Th/U ratio is generally > 0.1 is suggestive of an igneous origin (Hoskin and Schaltegger, 2003);

(3) The range of Zr/Hf ratios between 35-73 (all but three Group 1 zircons yielded Zr/Hf > 60 and the group yielded an average Zr/Hf of 46) are indicative of a crustal igneous origin where Zr/Hf ratios are know to vary between ~ 60 for mafic, early formed rocks such as gabbros and diorites and ~30-40 for granites (Gulson, 1969; Clairborne et al., 2006);

3. Average apparent minimum Ti-in-zircon formation temperatures between 545 °C and 1611 °C (with only three temperatures above 1000°C and an average formation temperature of 737 °C) are consistent with formation temperature of known zircons of a crustal origin (Watson et al., 2006);

(4) The features on chondrite-normalised REE profiles obtained from Group1 zircons are consistent with those obtained from zircons of known crustal

igneous origin (Fig. 6.8). The steep positive slopes on chondrite-normalised REE patterns, HREE enrichments and pervasive Ce and Eu anomalies are all features known to occur in crustal-affinity igneous zircon REE profiles (Whitehouse, 2003); and

(5) The oscillatory zonation patterns inherent to many Group 1 zircons (examples Fig. 6.6) are consistent with known CL patterns of igneous zircons (Corfu et al., 2003).



Figure 6.6: CL image showing the oscillatory zoning inherent to many Group 1 zircons (right picture shows zircons 16 and 17 from Sample 205-15 and left picture is zircon 49 from Sample 462-7).

#### 6.2.4.ii. Suggested provenance of Group 2 zircons

This group only comprises three zircons that have Th/U < 0.13, particularly large Ce and Eu anomalies (average Eu/Eu\* = 0.3 and average Ce/Ce\* = 19) and are relatively depleted in REE (average  $\Sigma REE = 190$  ppm). These zircons have steep positive slopes between the LREE and MREE on a chondrite-normalised REE profile (Fig. 6.9) (average Nd/Yb = 12.3) but are depleted in HREE with average Luzircon/Luchondrite of 90 and average Nd/Yb of 0.07. The average apparent minimum formation temperature for this group is 729 °C. The CL characteristics of Group 2 zircons are dominated by broad homogeneous zones (Fig. 6.7). The chemical characteristics of Group 2 zircons indicate a high-grade metamorphic provenance. Low Th/U (usually < 0.1) values are known to be inherent to zircons with a metamorphic petrogenesis and the characteristics seen on chondrite-normalised REE profiles for these zircons (Fig. 6.9), such as large Eu and Ce anomalies and are similar to those produced by zircons with known metamorphic origins (Hoskin and Schaltegger, 2003). The depletion of HREE relative to MREE is known to be a common feature in zircons that formed in high grade metamorphic environments (Rubatto and Herman, 2007). The homogeneous

zones seen in the CL images of these zircons (Fig. 6.7) are a feature inherent to zircons formed in metamorphic environments (Corfu et al., 2003).



Figure 6.7: CL images of Group 2 zircons. These include zircon 60, from sample 462-7 (right picture, left hand grain) and zircon 16, from sample 462-7 (left hand picture, grain on the right). Both show homogeneous and trace element depleted (dark) zones that are characteristic of metamorphic zircons (Corfu et al., 2003).

#### 6.2.4.iii. Suggested provenance of Group 3 zircons

The nine zircons within Group 3 which are characterised by:

(1) Very high total REE concentrations, with an average  $\Sigma$ REE of 1102 ppm (Table 6.2);

(2) Exceptionally high LREE and MREE concentrations. Group 3 zircons have an average  $Pr_{rcon}/Pr_{chondrite}$  of 18 (other groups all had values < 2.2) and average  $Sm_{rcon}/Sm_{chondrite}$  values of 147 (other groups all had values < 33);

(3) Very small Eu anomalies; average Eu/Eu\* in this Group is 0.59. Ce anomalies were moderate, averaging a Ce/Ce\* of 23;

(4) Mid-range concentrations of U and Th; zircons in this group had average

U and Th concentrations of 285 and 240 ppm, respectively;

(5) High Th/U ratios, with an average Th/U of 1.12 and relatively high Zr/Hf (average Zr/Hf = 52);

(6) Low Li concentrations that were  $\sim$ 1.3 ppm average; and

(7). Chondrite normalised REE profiles that show steep positive slopes and pervasive Ce and Eu anomalies (Fig. 6.10).



Figure 6.8: Representative REE profile for Group 1 zircons.



Figure 6.9: REE profile for Group 2 zircons.



Table 6.2: Trace element compositions and ratios of the four zircon populations identified in CIROS-1 using LA-ICP-MS.

TE group	p n Eu/Eu*		n Eu/Eu* Ce/Ce* Nb/Yd		Lu/Gd	Lu/Gd U/Th			Zr/Hf Ti-in-zircon (°C)			Li (ppm) ΣREE							
		Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
Group 1	105	0.01-0.83	0.21	2.63-26.35	175.92	12.25-2129.07	257.77	0.24-10.29	2.74	0.05-7.41	0.70	32.58-72.47	45.83	545-1611	737	0-37.02	4.95	2124-116	778.71
Group 2	3	0.01-0.04	0.03	3.62-47.66	18.68	2.14-22.9	12.28	0.05-0.09	0.07	0.05-0.13	0.09	25.04-34.43	30.84	713-756	729	1.28-12.44	7.50	52-375	190.37
Group 3	9	0.28-1.02	0.59	2.27-76.10	22.81	9.28-96.47	26.86	0.35-3.45	1.06	0.24-2.66	1.12	40.74-65.2	51.77	701-857	780	0-5.02	1.34	387-1801	1101.71
Group 4	2	0.28-0.46	0.37	161.94	161.94	56.25-228.72	142.49	2.10-6.23	4.17	0.34-0.58	0.46	46.44-59.8	53.12	528-726	627	0.88-1.19	1.03	223-240	231.61



Figure 6.12: Examples of CL zonation in Group 3 zircons. The dominant CL zoning within this group is oscillatory. Oscillatory zoned Group 3 zircons include zircon 41 (right hand image, middle zircon) from sample 462-7 and zircon 3 from sample 652-3 (right hand image, middle grain).

The high Th/U ratios suggest an igneous source (Hoskin and Schaltegger, 2003) and the high amount of total REE of zircons in this group suggests that they formed from an enriched source(Schluz et al., 2006). This igneous provenance is supported by oscillatory CL zonation patterns observed within these zircons (Fig. 6.12) and the shape of their chondrite normalised REE profiles (Fig. 6.10) which show characteristics similar to those produced by known igneous zircons (Hoskin and Schaltegger, 2003). The average apparent (minimum) formation temperatures for these zircons (~780 °C) as well as their chemical and zonation characteristics is suggestive of an enriched igneous environment such as a granite or a pegmatite.

# 6.2.4.iv. Suggested provenance of Group 4 zircons

Group 4 contains two zircons that are relatively depleted in REE (average  $\Sigma REE = 232$  ppm), and have comparatively steep REE slopes (Fig. 6.11) with an average Nd/Yb of 143 and an average Lu/Gd of 4.2 (Table 6.2). Group 4 zircons have low Th and U concentrations (average 126 ppm and 48 ppm respectively) and an average Th/U of 0.46. The average formation temperature for Group 4 zircons is a relatively low 627 °C. These zircons have the highest Zr/Hf of all the populations (averaging 53) and the lowest Li concentrations with an average of 1.0 ppm (Table 6.2).

Given the limited and ambiguous data available for these zircons it is difficult to constrain their provenance. From the total REE it is evident that their source(s) were depleted in trace elements (Belousova et al., 2002). The steep slope between LREE and HREE on chondrite-normalised REE profiles suggests that this source/these sources may have been igneous (Fig. 6.11) (Hoskin and Schaltegger, 2003). This hypothesis is supported by the oscillatory growth zones seen in the CL images (Fig. 6.13) (Corfu et al., 2003). A depleted igneous source would usually be a mafic one, such as a gabbro or basalt (Hoskin and Schaltegger, 2003). This provenance seems plausible considering the high average Zr/Hr, however, the low average formation temperature does not fit with a mafic igneous provenance as these units often form at high temperatures (~1000-1400 °C) (e.g. Wendlandt, 1982). Recent studies have outlined that the Ti-in-zircon geothermometer may yield formation temperatures for mafic zircons considerable lower than expected (Fu et al., 2008). Consequently, all that can be concluded about these zircons is that they formed in a trace element depleted, possibly mafic igneous, source such as a gabbro or potentially a kimberlite.



Figure 6.13: CL images of the two Group 4 zircons showing oscillatory growth zones. Zircon 4 is shown in the left hand image and zircon 12 is on the right. Both Group 4 zircons are sourced from sample 652-3.

#### 6.2.5. Possible provenance of CIROS-1 zircon age populations

This section reviews the possible provenance of zircons that fall within the age peaks on the cumulative age probability diagram (Fig. 6.5) in order to gain insights into the units contributing zircons to CIROS-1. This has been summarised in Table 6.3 and is discussed below.

The dominance of Group 1 igneous zircons implies the main contributing units of CIROS-1 zircons were relatively enriched and differentiated/crustal igneous units such as granites or rhyolites of a range of ages. The occurrence of Group 2, 3 and 4 zircons suggests both highly enriched and depleted (probably igneous) units and metamorphic units of various ages contributed sediments to the core.

The only zircon analysed for trace element compositions with an age in the 200-250 Ma age has a 'Group 1' igneous chemistry (Table 6.3). This suggests CIROS-1 zircons of this age were sourced from a granitic or rhyolitic unit. Both grains with

ages in the 320-390 Ma age range were of Group 1 igneous origin (Table 6.3), implying CIROS-1 zircons of this age were sourced from a relatively enriched (rhyolitic or granitic) igneous source.

Provenance of Zircons per Age Peak									
	Ν	Provenance							
Age Peak	Zircons	Group							
200-250 Ma	1	Group 1							
320-390 Ma	2	Group 1							
450-650 Ma	49	Group 1							
	1	Group 2							
	4	Group 3							
	2	Group 4							
810-870 Ma	2	Group 1							
	1	Group 3							
900-1250 Ma	25	Group 1							
	1	Group 2							
	2	Group 3							
1400-1650 Ma	11	Group 1							
~1750 Ma	2	Group 1							
~1814 Ma	1	Group 1							
~1950 Ma	1	Group 1							
	1	Group 2							
2460-3350 Ma	6	Group 1							
	1	Group 3							

Table 6.3: Overview of the provenance groups within each age peak visible on the cumulative age probability diagram (Fig. 6.5). This includes the amount of zircons per age peak that fall within a provenance group.

The 450-650 Ma age peak is dominant on the cumulative age probability diagram (Fig. 6.5) and 56 of the 119 zircons analysed for trace elements have ages within this range. Zircons in this population fall within all four geochemical groups. Group 1 zircons are dominant within this age population (49 zircons are Group 1). The only two Group 4 zircons are 440-460 Ma old, making them the youngest grains in this age population. Their characteristics indicates a ~440-460 Ma old, REE depleted, possibly igneous source contributed sediments to the core. Four, Group 3 REE enriched igneous zircons of various ages and one Group 2 metamorphic grain (age 624 Ma) fall within this age population. The dominance of Group 1 igneous zircons in the CIROS-1 core. The presence of zircons with Group 2, 3 and 4 chemistry in this age range indicates metamorphic units in addition to enriched and depleted igneous units also contributed a minor proportions zircons of this age to the CIROS-1 core.
Three grains occur within the relatively minor 810-870 Ma age population (Fig. 6.5). Two of these are Group 1 igneous whilst one is Group 3. This suggests that a unit or units of this age contributed sediments to the core and it/they were igneous in origin and enriched to very enriched in trace elements.

Twenty-eight analysed zircons fall within the 900-1250 Ma age population, which is the second most distinct on the cumulative age probability diagram (Fig. 6.5). All but three of these all within Group 1, with two Group 3 zircons and one Group 2 zircon. This implies that the units contributing zircons of this age to the core were predominantly enriched igneous units such as granites but also consisted of much enriched, possibly igneous units and metamorphic units.

Eleven analysed zircons fall within the 1400-1650 Ma age peak seen on the cumulative age probability diagram (Fig. 6.5). All of these are Group 1 igneous zircons, suggesting that a granitic/rhyolitic igneous source contributed Mid-Proterozoic aged zircons to CIROS-1.

It is challenging to discern any distinct age groups on the cumulative age probability diagram for older zircons (Fig. 6.5). Thus, the trace element characteristics of zircons older than ~1.7 Ga will be discussed for individual zircons or for zircons with ages that fall within error of one another (Table 6.3). Two zircons with ages ~1750 Ma have Group 1 chemical characteristics. This indicates that a ~1.7 Ga felsic igneous unit contributed zircons of this age to the core. One zircon of 1814 Ma was likewise Group 1, suggesting a granitic/rhyolitic unit contributed ~1.8 Ga old zircons to CIROS-1. Two zircons analysed for their trace element compositions had an age of ~1950 Ma. One had a chemical signature that fell within the Group 1 category and the other showed characteristics of a Group 2 zircon. This indicates that two units of similar age but different provenance (one granitic/rhyolitic, one metamorphic) contributed sediments of this age to the core.

The seven oldest zircons analysed for their trace-element compositions have ages that do not fall within error of one another (age range 2.46-3.35 Ga), signifying a range of units contributed the oldest zircons contained in CIROS-1. All but one of these zircons have chemistries that fall within Group 1 (the 2.73 Ga old zircon fell within Group 3) (Table 6.3). This indicated that the Late Proterozoic and Archaean units contribution zircons to the core were enriched to highly igneous units such as granites and pegmatites.

# 6.3. Discussion

### 6.3.1. Implication of age peaks in the cumulative age probability diagram

It is well established that peaks in global zircon ages broadly correlate to periods of supercontinent assembly and that during periods of supercontinent stasis and breakup, global zircon numbers of that age are low (Condie and Aster, 2010) (Fig. 6.14).



Figure 6.14: Age distribution of zircons sourced from orogenic granitoids and sedimentary samples from a range of globally-distributed locations. In the upper section, known periods of supercontinent assembly and breakup are given. Note the correlation of zircon age peaks and periods of supercontinent formation and zircon minima and supercontinent breakup and/or stasis (source: Condie and Aster, 2010).

The cumulative age probability diagram constructed for CIROS-1 (Fig. 6.15) contains peaks that correlate to periods of known supercontinent formation (Fig. 6.14) (Condie and Aster, 2010). These include the pronounced age peaks at  $\sim$ 600 Ma and 1000 Ma and to a lesser degree the age peaks at 1870 Ma and 3000 Ma. There is also limited correlation with zircon minima on the CIROS-1 cumulative age probability diagram and periods of known continental breakup or stasis. This includes minima at 650-750 Ma and < 200 Ma. This means that CIROS-1 zircons hold a partial record of global supercontinent history (Fig. 6.14).



Figure 6.15: Cumulative age probability diagram for the 854 zircon grains analysed in this study. Zircon numbers for each 40 Myr age bin are given in the bar graphs and the relative probability is shown as the red line. Orogenic episodes known to have occurred on the EAC are shown in the grey bars (sources: Tingey, 1991; Fitzsimons, 2000; Goodge et al., 2001).

More specific to Antarctic history, the age probability diagram shows a broad correlation between age peaks and orogenic episodes known to have occurred on the continent (Fig. 6.15). There is a strong correlation between the Ross/Pan-African Orogeny and the dominant 450-650 Ma age peak indicating that zircons formed during the Ross and Pan-African orogenies were a dominant source of zircons in CIROS-1 sediments. There is limited correlation between the distinct 0.8-1.3 Ga age population and the timing of the Grenville Orogeny, with the CIROS-1 age peak containing zircons that are overlapping and slightly younger than the age of this orogeny (Fig. 6.15). If CIROS-1 zircons in the 0.8-1.3 Ga age population were definitely sourced from Grenvillian units, the offset in the age peak and the timing of the Grenville Orogeny may indicate that: (1) Zircons of this age formed in the very latest stages of the Grenville Orogeny; or (2) The Grenville Orogeny in this sector occurred later. Alternatively, zircons in this age peak may have been sourced from granitic/metamorphic units that formed during an as yet unknown event. This would imply that an orogenic event younger than and partially coeval with the Grenville Orogeny occurred in the Ross Sea Sector of the EAC.

A lesser degree of correlation is present between the older orogenies that occurred in the EAC and CIROS-1 zircon age peaks (Fig. 6.15). This lack of correlation may be due a number of factors, including: (1) The orogenic episodes did not have a large impact on the Ross Sea Sector of the EAC; (2) Zircons formed during these events are not well preserved, perhaps due to overprinting of subsequent orogenic events (e.g. Goodge et al., 2001); or (3) An artificial bias on the cumulative diagram towards younger ages caused by the preferential use of rim over core analyses in zoned zircons.

### 6.3.2. Potential source units for CIROS-1 zircons

The youngest age peak on the cumulative probability diagram consists of zircons the few zircons of age between 200-250 Ma (Fig. 6.5). This age peak occurs in many detrital samples in the Ross Sea region (e.g. Palmer, 2008; Elliot and Fanning, 2008). From trace element evidence of this study it appears these zircons were, in part at least, sourced from a 200-250 Ma, intermediate-felsic igneous unit. The Victoria Group, the younger of the two members of the Beacon Supergroup, occurs in the upper reaches of the Ferrar Fiord (Barrett, 2010, per. comm.; Elliot and Fanning, 2008; Licht et al., 2005). In Queen Maud Land it is known to contain zircons of 200-250 Ma age, that are inferred to have an igneous provenance (Elliot and Fanning, 2008) (Fig. 6.16).

The Victoria Group also contains a silicic tuff that has zircons (Elliot and Fleming, 2008) and has an unconstrained Triassic or Jurassic age (Ross et al., 2008). This tuff outcrops between SVL (Coombs-Alan Hills area) and the Queen Alexander Range in the TAM (Elliot and Fleming, 2008; Ross et al., 2008). Thus, the 200-250 Ma age peak observed in the CIROS-1 zircon population may have been sourced from the erosion of the Victoria Group with the silicic tuff being a minor contributor due to its limited volume (Elliot and Fleming, 2008).



Figure 6.16: Age probability diagrams obtained from outcrops of the Victoria Group in Marie Byrd Land. Note the presence of relatively young (Triassic-Devonian) ages, thought to be from zircons formed in an active magmatic arc during subduction of the Antarctic palaeo-Pacifc margin (source: Elliot and Fanning, 2008).

Zircons in the weak 320-390 Ma age peak in Figure 6.5 were partially or wholly sourced from an intermediate-felsic igneous unit. Elliot and Fanning (2008) found a Devonian age peak in the zircons from the Victoria Group in Queen Maud Land (Fig. 6.16). The source unit for these zircons was igneous and hypothesised to potentially be the Ford Granodiorite in Marie Byrd Land or 'an uncertain extension of that belt eastward toward the Antarctic Peninsula' (Elliot and Fanning, 2008). From this it appears the Devonian age population in CIROS-1 zircons (Fig. 6.5) may have been sourced from the erosion of the Victoria Group, located in the Upper Ferrar Fiord (Barrett, 2010, pers. comm.; Elliot and Fanning, 2008; Licht et al., 2005).



Figure 6.17: Age probability diagrams obtained for the Taylor Group at Sperm Bluff, South Victoria Land. The left hand image shows the age probability diagram for a granulite conglomerate, that is dominated by a  $\sim$ 500 Ma age peak. The right hand image shows the age probability diagram constructed from a granulitic conglomerate at a different locality on Sperm Bluff. As with the left hand image, this age probability diagram shows a dominant age peak at  $\sim$ 500 Ma with additional subordinate peaks at  $\sim$ 700-2200 Ma and  $\sim$ 3.3 Ga (source: Savage, 2005).

The 450-650 Ma age peak observed in the CIROS-1 zircons (Fig. 6.5) contains zircons of variable trace element chemistry. Zircons of this age were sourced from a number of temporally overlapping but distinctly different provenances. The most likely source for Group 1, 3 and 4 zircons within this age peak are the Granite Harbour units. These units occur throughout the TAM in SVL and are present in the Ferrar Fiord (Allibone et al., 1993a). The highly variable chemistries of these batholiths and the dykes (Allibone et al., 1993b) implies that Group 3 and 4 zircons of this age may have been sourced from chemically enriched and depleted enclaves within the Granite Harbour units. The youngest zircons in the 450-650 Ma age peak were possibly sourced from the youngest units of the Granite Harbour intrusives (post-tectonic Ross Granitoids which are of 460-510 Ma in age) (Allibone et al., 1993a) and older zircons from the syntectonic older batholiths (which are ~490-590 Ma in age) (Allibone et al., 1993a). The oldest zircons within this age group may have been sourced from the regional basement, which includes orthogneisses of the Skelton Group which have formation ages < 590 Ma (Allibone et al., 1993a). The Group 2 metamorphic grains that occur within this age peak (age 624 Ma) was likely sourced from the metamorphic Skelton Group. This group formed during the early stages of the Ross Orogeny and is the basement of the TAM and Ferrar Fiord (Allibone et al., 1993a; Rowell et al., 2001). Although direct deposition from erosion of the Granite Harbour Group seems most likely for zircon in this age group (due to the proximity of Granite Harbour batholiths to the CIROS-1 site and dominance of zircons source from these in CIROS-1), some contribution may have occurred from the Beacon Supergroup, which is known to contain a large amount of zircons sourced from the Granite Harbour Intrusives (Figs. 6.16 and 6.17).

CIROS-1 zircons with ages > 650 Ma can not be tied to any outcrops in the region. Rather they may have originated from one of the following:

(1) Recycled sources containing mature sediments. This may include the Beacon Supergroup which outcrops throughout the TAM and in the Ferrar Fiord (Elliot and Fanning, 2008), or unknown sedimentary units located under the ice;

(2) Direct but unknown sources located under the ice of under the current baseline of geologic exposure. This may include the cratonic components of the EAC or older units located under the ice in the TAM; and

(3) The inherited components in zircons sourced from the Granite Harbour Intrusives (e.g. Savage, 2005).

Due to considerable gaps in our knowledge of Antarctic geology, it is challenging to constrain sources of detrital zircons if there are no known outcrops (e.g. Elliot and Fanning, 2008; Goodge et al., 2002). Nonetheless, possible sources for > 650 Ma

zircons found in CIROS-1 have been investigated using the information obtained during this research, as outlined below.

Three 808-854 Ma old grains of felsic igneous provenance were found in CIROS-1. The source of these grains is likely an unknown igneous body located under the ice (perhaps a component of the EAS) which may be similar to the  $\sim$ 830 Ma igneous source identified for the zircon in the Byrd Group by Goodge et al. (2002). It is not possible to determine if these zircons were directly eroded from their source unit or from the Beacon Supergroup.

Zircons with ages 900-1200 Ma form a distinct peak on the age probability diagram (Fig. 6.5). Zircons of this age are very common in sediments of the region (e.g. Goodge et al., 2008; Palmer, 2008; Licht et al., 2005), however no known units of this age outcrop in the Ross Sea sector. Thus a likely source for these grains are units that formed during the Grenville Orogeny and are located under the ice and/or the current baseline of geologic exposure in the TAM. Direct erosion of these units may have resulted in the deposition of Grenvillian-aged zircons or they may have been sourced from the erosion of sedimentary units such as the Beacon Supergroup, that contain zircons of this age. The presence of a Grenvillian-aged metamorphic grain in the CIROS-1 core indicates both igneous and metamorphic units of this age are located under the ice and either directly or indirectly contributed sediment to the core.

The zircons of the 1400-1600 Ma age population appear to be wholly of an igneous origin. Sources for these zircons are most likely the cratonic components of the EAC located under the ice. One such unit may be the  $\sim$ 1.4 Ga granitic unit identified by Goodge et al. (2008) (Fig. 2.6). It is not possible to constrain whether sediments from these units were directly eroded from the EAC or if they were sourced from sedimentary units containing cratonic components, such as the Taylor Group (Fig. 6.17).

Zircons older than  $\sim$ 1.6 Ga are common in many sediments around the Ross Sea region (e.g. Palmer, 2009; Savage, 2005). It is likely such zircons are sourced from unknown igneous and to a lesser degree, metamorphic components of the EAC. It is not possible to constrain if they were directly eroded from these units or source from recycled units more proximal to the CIROS-1 site.

### 6.3.2.i. Summary of CIROS-1 detrital zircon provenance

Zircons found in CIROS-1 were likely sourced from:

(1) The regional basement, which includes the Skelton Group and the Skelton Metamorphic and Granite Harbour Intrusive units;

(2) The Beacon Supergroup (Victoria and Taylor Groups); and

(3) Direct erosion of unknown units located under the EAIS in the EAC and below the current levels of geologic exposure in the TAM.

George (1989) used sand mineralogy to constrain CIROS-1 sand provenance and found that sands in the core were sourced from four units: (1) The regional basement (including the Skelton and Granite Harbour Groups); (2). The MVG; (3) The Ferrar Dolerite; and (4) The Beacon Supergroup. The dominant sediment sources were found to be the basement units and the Beacon Supergroup and their relative contributions were estimated to be 3:1 (George, 1989; Roser and Pyne, 1989). The results of this research agrees with this previous work as the Beacon Supergroup and basement units were both identified to be major contributors for sediment provenance in each study.

The fact that zircons sourced from the MVG were not detected in this research indicates it is not a zircon producing lithology. The Ferrar Dolerite is known to produce zircons with ages  $\sim 183.6 \pm 1.8$  Ma (Encarnación et al., 1996). Zircons of this age were not observed in this study. It is challenging to speculate why zircons sourced from the Ferrar units were not observed in this research whilst it does appear the Ferrar is a contributor of CIROS-1 sands (George, 1989, Roser and Pyne, 1989). A cause may be that the Ferrar Dolerite does not contain many zircons, which seems likely given the general zirconium-undersaturated nature of many mafic rocks (Hoskin and Schaltegger, 2003).

When assessing CIROS-1 sand provenance, George (1989) and Roser and Pyne (1989), did not attribute any CIROS-1 sedimentation to direct erosion of the EAC. It may be impossible to constrain whether the > 650 Ma zircons found in this study were sourced directly by erosion of the EAC or recycled through erosion of the sedimentary lithologies such as the Beacon Supergroup.

### 6.3.3. Temporal trends in zircon characteristics

Temporal trends in zircon characteristic observed in CIROS-1 include:

(1) A bell shaped old-young-old trend in the maximum and average ages of the 450-650 Ma population down core (Fig. 6.4);

(2) A bell shape curve that defines the percentage (of total zircon number) of 450-650 Ma aged zircons (Fig. 6.2); and

(3) A bell shaped increasing trend of zircon number towards the midsection of the core followed by a progressive decrease in zircon numbers to the top of the drill core (Fig. 6.2).

The bell shaped curve in the maximum, and to a lesser degree average, ages of the 'Ross' aged zircons shows that from near the base of the core to  $\sim$ 250 mbsf, the oldest 'Ross' aged units being eroded increase in age from  $\sim$ 525 Ma to  $\sim$ 660 Ma. Above  $\sim$ 250 mbsf the age of the oldest 'Ross' aged zircon in each sample decreases from  $\sim$ 660 Ma to  $\sim$ 550 Ma (Fig. 6.4).

At the base of the core, 'Ross' aged zircons comprise  $\sim 70$  % of the total zircons per sample. This decreases to  $\sim 30$  % at  $\sim 250$  mbsf and increases again to the top of the core, where 'Ross' aged zircons consist of  $\sim 90$  % of total (Fig. 6.2). Figure 6.18 shows the same zircon trends in Figure 6.2, but plotted against sediment depositional age (between 40 and 20 Ma). Data gaps represent times of erosion and or non-deposition due to short-duration glacial processes and/or longer duration tectonic processes (see Fig. 3.9). The CIROS-1 core can be subdivided into three time zones/groups of strata representing quite different climatic regimes. In ascending stratigraphic order these zones are:

Zone 1: this is the red band on Figure 6.18 and 6.19 and consists of strata between  $\sim$ 700 and 366 mbsf, of late Late Eocene (37-34 Ma) age (Fig. 3.9; the sub-366 mbsf red-line chronology was used for this discussion). These units represent fluvio-deltaic deposition under generally warm temperate (Zachos et al., 2001a) ice free conditions with local alpine-style glaciers in the Trans-Antarctic Mountains. As discussed in Chapter 3, any or all of the  $\sim$ 9 Ma time interval missing in the CIROS-1 core may be distributed at the 342 mbsf unconformity, in additional to the unconformity located at 366 mbsf. However, for the purposes of the discussion in this thesis, the 366 mbsf datum has captured the 9 Ma unconformity.

Zone 2: Strata from 366 to 250 mbsf that were deposited during the Late Oligocene (~25 to 23.5 Ma) (green zone in Figs. 6.18 and 6.19). They are grounding line proximal glaciomarine sediments produced during cooler, sub-polar climate conditions. During this interval, an ephemeral EAIS regularly expanded onto the Ross Sea continental shelf (CIROS-1 drill site) via outlet glaciers through the TAM (including the Ferrar Fiord) during orbital-scale glaciations.

Zone 3: Comprises strata between ~250-20 mbsf deposited between ~23.5 to 22 Ma (Fig. 3.9 and blue zone on Figs. 6.18 and 6.19). These sediments represent regular oscillations in the grounding line of the Ferrar Glacier (interbedded diamictites and glaciomarine sands and muds) during progressively cooler climate conditions as the ice sheet progressively expanded during the cooling that culminated with the Mi-1 glaciation at ~23 Ma (Zachos et al., 2001a). A 600 kyr-long major erosional hiatus from 23.2 Ma is recorded in both CRP-2/2A and CIROS-1 (see Fig 3.9) and corresponds to widespread ice sheet expansion in western Ross Sea during the Mi-1 glaciation (Pekar et al., 2006; Naish et al., 2001a).





Figure 6.18: Average, minimum and maximum ages of zircons in the 'Ross' age population plotted against sample depositional age. The three zones discussed in the text are indicated by the coloured bands (red is Zone 1, green is Zone 2 and blue is Zone 3). The top and bottom depths of these zones are given. Note the trends of increasing maximum and average ages with decreasing depositional age in Zone 1 and the decreasing average and maximum ages observed up core in Zone 3. Zircons derived from Zone 2 show no distinct trends.



Figure 6.19: Percentage (of total) 'Ross' aged zircons present in each sample. The three zones noted in the text are indicated by the red (Zone 1), green (Zone 2) and blue (Zone 3) bands. The top and bottom depths of these zones are given. There is a correlation between decreasing depositional age and decreasing amounts of 'Ross' aged zircons in Zone 1 and the trend of increasing 'Ross' aged zircons with decreasing depositional age present in Zone 3. Zircons derived from Zone 2 show no distinct trend.

The Granite Harbour Intrusives in SVL were intruded in two stages: between 589-490 Ma (syntectonic) and 486-477 Ma (post-tectonic) (Allibone et al., 1993a; Cox et al., 2000). The older batholiths were emplaced synchronously with the Skelton Group in response to subduction of a palaeo-Pacifc cratonic margin. The younger granodiorite and granite plutons were emplaced at higher crustal levels. They formed in response to uplift and extension (Allibone et al., 1993a). All Granite Harbour plutons are known to contain high numbers of zircons. In Ferrar Fiord the oldest identified Granite Harbour pluton is the Bonney Pluton which is ~100 km long, 25 km wide and ~590 Ma old (Figs. 6.20 and 6.21). The smaller Catspaw Pluton, which at ~490-590 Ma is slightly younger than the Bonney, also outcrops in the Ferrar Fiord. These two plutons both belong to the lower-level, syntectonic group of plutons (Allibone et al., 1993a). Post-tectonic plutons in the Fiord include the Hedley, Rhone, Pearse and Mt. Falconer plutons which are ~490 Ma old (Smillie, 1992; Allibone et al., 1993a) (Figs. 6.20 and 6.21). The oldest identified igneous units in the Ferrar Fiord are orthogneiss units which occur below and around the Granite Harbour plutons and are > 590 Ma in age (Fig. 6.20; Allibone et al., 1993a).

It does not appear that the spatial chemical zonation within Ross Harbour granitoids has been investigated in detail. However, research into chemical zonation within granitic plutons shows that 'compositional zoning of granitic plutons is a common feature' (Hecht et al., 1997; Arniaud et al., 1984). This chemical zonation may be complex and involve younging of crystals both towards and away from the centre of the pluton. Thus erosion of granitic plutons may cause the exposure of zircons with systematically changing ages.



Figure 6.20: The geology of the Ferrar Fiord and Taylor Glacier region showing Granite Harbour plutons, regional basement and recent sediments (source: Smillie, 1992).



Figure 6.21: Timescale of Granite Harbour intrusive emplacement and formation and deformation of the basement (incl. Skelton Group) (source: Allibone et al., 1993a).

For ease of discussion the temporal distribution in zircon number and the characteristics of 450-650 Ma 'Ross' age peaks can be divided into two sections: below ~250 mbsf (Zones 1 and 2), and above ~250 mbsf (Zone 3).

# 6.3.3.i. Sub-250 mbsf section (Zones 1 and 2)

Original work on the provenance of sands in CIROS-1 found that a simple unroofing history of the TAM was not recorded in CIROS-1 (George, 1989; Roser and Pyne, 1989). The dominant provenance for sands was found to be the Granite Harbour Intrusive units which and sediments sources from these were intermixed with irregular influxes of Beacon Supergroup derived sands (George, 1989; Roser and Pyne, 1989). This study uses different techniques, which are able to detect more subtle changes in sediment provenance than the techniques available for previous work. In the zircon data presented in this thesis a degree of subtle unroofing may be recorded between ~366-700 mbsf. Sediments in this interval were deposited during the Late Eocene (Zone 1) (Figs. 6.18 and 6.19). Late Eocene erosion was primarily influenced by localised temperate alpine-style glaciation and fluvial outwash systems. The dominant ice flow direction was from the west, through the Ferrar Fiord (Fig. 22D). Thus we infer that in Zone 1, a gradual unroofing of the highly heterogeneous and differentiated units of the Granite Harbour and Skelton Groups in the Ferrar Fiord is recorded.

For the entire deposition of Zone 1 strata, the upper-level, post-tectonic Granite Harbour units (such as the Hedley Pluton) were being eroded, as evidenced by the continual presence of ~470 Ma zircons in the youngest age of the Ross population (Fig. 6.18). The age of the oldest 'Ross' aged zircons shows that first the oldest zircons in this population were sourced from the older, syntectonic Ross Granitoids (Bonney and/or Catspaw Plutons). At ~36 Ma (depositional age in CIROS-1) the oldest 'Ross' aged zircons become older than the ages of the Granite Harbour Plutons in the Fiord (Figs. 6.18 and 6.21). Thus, at this stage, the older orthogneisses located in the Ferrar Fiord were eroded (Figs. 6.20 and 6.21). It is not possible to constrain whether this change is due to the exposure of the older orthogneisses due to down cutting though Granite Harbour units, or if changes in ice dynamics caused erosion of pre-exposed but previously uneroded basement orthogneisses.

The termination of the unroofing history recorded in Zone 1 strata occurs at  $\sim$ 366 mbsf – the level of the unconformity that spans  $\sim$ 9 Myr at the Eocene-Oligocene boundary (Figs. 6.18 and 3.9). Though it is not possible to confirm with any certainty, the gradual but marked increases in the average and maximum ages of the zircons from the 'Ross' age population may be due to the erosion of chemically and temporally zoned granitic and orthogneiss units, a concept which requires further investigation.

Strata deposited in Zone 2 were eroded in a dynamic yet regionally-extensive glacial regime where ice sheets reached continental scale during glacial periods but may have retreated to 50 % of their present day size during interglacials. This style of glaciation was variably sub-polar to temperate and would have caused significant localised valley erosion in the TAM which were being uplifted isostatically as glaciers incised (Stern et al., 2005). Thus, it is inferred that during deposition of Zone 2 strata, the main direction of ice flow was from the west through the TAM/Ferrar Fiord (Fig. 6.22C). This interval (Zone 2) corresponds to a ~40-60 % proportion and relatively high age range for 'Ross' aged zircons (Figs. 6.19 and 6.20) and a high total amount of zircons per sample (Fig. 6.2), and may reflect the quite localised spatially-restricted erosion in steeply incised valley glaciers systems.

# 6.3.3.ii. Above 250 mbsf (Zone 3)

At approximately 250 mbsf in the core the trends in total zircon number and 450-650 Ma population change. The age of the oldest 450-650 Ma zircon in each age population starts decreasing (Fig. 6.19) and the percentage of 450-650 Ma zircons starts to increase (Fig. 6.20). As the age of the youngest zircon in the 450-650 Ma population remains more or less steady (Fig. 6.19), it appears that post-tectonic Ross granitoids were eroded during this entire interval. However, the decrease in the maximum (and average) ages for the 450-650 Ma population (from ~660 to 550 Ma) and increase in the percentage of 'Ross' aged zircons suggests that erosional, transportational and depositional dynamics changed.

# Paleoglaciological Reconstruction for McMurdo Sound Mi-1 Glaciation-~23Ma- Zone 3 Present day- LGM Skelton Gl Skelton GI. Byrd Gl. Mulock GI Mulock GI Bluff M Island B ~25-23.5 Ma- Zone 2 ~35-37 Ma- Zone 1 Skelton Gl. Mulock Gl. Byrd Gl. **Ross Sea**

CIROS D С

Figure 6.22: Ice flow lines for the western Ross Sea from ~34 Ma to present, partially reconstructed based clast lithologies in tills from the ANDRILL drill cores. The general climatic trend between ~34 Ma to present is one of cooling (Barrett, 2007). Between 37- 34 Ma (Fig. D), the WAIS was reduced or absent and ice flux from southern TAM outlet glaciers was reduced. The dominant ice flow direction to the CIROS-1 site would have been westwards through the Ferrar Fiord into the Ross Sea. It must be noted that during the Late Eocene the ice extent onland was considerably less than that is depicted in Fig. D. At ~25-23.5 Ma (Fig. C) the increased size of the EAIS meant that ice flowed from the south but the dominant ice flow direction to the CIROS-1 site was from the west, through the Ferrar Fiord. As the climate cooled, the flow of grounded ice in western Ross Embayment became from the south due to the confining influence of a large WAIS and increased flux from southern TAM outlet glaciers. Thus during this period the ice flow to the CIROS-1 site was from the south, was most probably from the Skelton and Mulock Glaciers (Fig. B), which is fairly similar to LGM configurations (Fig A) (modified from: McKay, 2008).

One possible interpretation is that the old orthogneisses in the Ferrar Fiord ceased contributing sediments and syntectonic aged batholiths became the oldest units contributing to the 450-650 Ma population. The uppermost sample analysed (28 mbsf) shows a marked dominance of 450-650 Ma aged zircons (Fig. 6.3), indicating that when CIROS-1 sedimentation ceased, a single (most probably syntectonic) Ross-aged granitoid was supplying the majority of zircons to the core.

In Zone 3, sediments between ~100-250 mbsf were deposited during the Latest Oligocene (~23.9-23 Ma) and sediments above ~100 mbsf were deposited in the Earliest Miocene. This stratigraphic interval spans a climatic cooling and ice sheet expansion leading into and spanning the Mi-1 glaciation (see Chapter 3 discussion and Fig. 3.9). The Mi-1 glaciation represents the largest ice volume on Antarctica since the initial glaciation (Oi-1) at the Eocene-Oligocene boundary. The ice volume of the EAIS may have been up to ~120 % of present (Naish et al., 2001; Pekar et al., 2006) causing the ice sheet to ground well out onto the Ross Sea continental shelf. Moreover, an ice sheet is inferred to have developed on West Antarctica (WAIS). This had major implications for regional glacial flow dynamics (Fig. 22 B).

Reconstructions for ice flow in western Ross Sea during the LGM provides a good analogue for the Mi-1 glaciation, and shows that the combined volume of WAIS and EAIS ice flow into Ross Sea results in grounded ice, sourced from the southern TAM outlet glaciers (e.g. the Mulock and Skelton glaciers), flowed south and west into McMurdo Sound (e.g. McKay, 2008; Licht et al., 2005) (Figs. 6.22A and B). Moreover, Naish et al. (2009) showed that such a glacial ice flow configuration has happened during numerous glacial periods over the last 14 Ma when the WAIS has been fully expanded confining the increased discharge of EAIS glaciers into western Ross Sea. Figure 6.22 shows a schematic paleo-glaciological evolution for the last 34 Ma. It is proposed here that the Mi-1 glaciation at 23 Ma would have had a glacial configuration similar to the LGM (Fig. 6.22B and A, respectively) and that during the latest Oligocene and earliest Miocene ice flow to the CIROS-1 site changed from west ward to the south. Thus, in this interval, zircons may have been sourced in tills from the Skelton and Mulock Glaciers rather than directly from the Ferrar Glacier catchment.

The Mt. Morning Volcanic Complex commenced eruption to the south of the CIROS-1 site around > 18.7 Ma (Martin, 2009). When conducting whole rock geochemical analysis of CIROS-1, Roser and Pyne (1989) noted an influx of MVG-type material above  $\sim$ 250 mbsf. As Mt. Morning is the

earliest known MVG volcano, Roser and Pyne (1989) indicated the observed influx may have been sourced from this volcano. The influx seen occurs at  $\sim$ 23.5 Ma, which is older than the oldest known outcrop of Mt Morning, suggesting that either Mt. Morning formed earlier than is currently known from radiometric dating of lavas, or that there was older now eroded volcano in a similar location. This line of evidence is supported by the occurrence of two pumiceous phonolitic tephra between 24 and 22 Ma in the CRP-2/2A core (Naish et al., 2001b; Wilson et al., 2002).

The change in zircon characteristics and the influx of MGV-type material noted by Roser and Pyne (1989) that occurs above ~250 mbsf may have been caused by cooling and ice sheet expansion associated with the Mi-1 glaciation. This caused a change in ice flow to the CIROS-1 site, due to the increased amount of ice entering western Ross embayment from WAIS and southern TAM outlet glaciers (Talarico et al., 2009; McKay, 2008). This means that rather than a localised source from the west for sediments (as seen beneath ~250 mbsf), the source for sediments above ~250 mbsf may have come from the south, from the Skelton and Mulock Glaciers (Fig. 6.22B) which flow though fiords that contain Skelton and Granite Harbour units (Cottle and Cooper, 2006; Cook and Craw, 2002). This would have resulted in the coincident influx of MVG/Mt. Morning material noted by Roser and Pyne (1989) which was brought from the Mt. Morning site to the north by the ice.



Figure 6.23: Summary of the conditions present above and below  $\sim$ 250 mbsf in the CIROS-1 core. This includes the relative climate and subsequent possible ice flow pathways (after McKay et al., 2008) and the timing/characteristics of volcanism. The zircon characteristics obtained for this research and the whole rock geochemical characteristics obtained by Roser and Pyne (1989) are outlined. Age model and sedimentology from Chapter 3.

# 6.4. Conclusions

LA-ICP-MS U-Pb and trace element studies of zircons in the CIROS-1 drill core have provided three key insights into the record of Antarctic tectonism and climate contained in the core:

(1) The cumulative age probability diagram of zircons in the CIROS-1 core reflects the orogenic episodes known to have occurred in the EAC. The relatively young ages for 'Grenvillian' aged zircons suggests that this orogeny occurred later in this sector or, alternatively, that these zircons were formed by a distinct event partially coeval with the Grenville Orogeny.

(2) The majority of ages and geochemical characteristics of zircons observed in the CIROS-1 drill core can be explained by a variable input of the basement (Skelton and Granite Harbour Groups), Beacon Supergroup (Taylor and Victoria Groups), and potentially the units located under the EAIS or current baseline of geologic exposure. More specifically, units that contributed zircons to the CIROS-1 drill core include granitic batholiths that formed post- and syn-tectonic to the Ross Orogeny (Granite Harbour Group), the metamorphic Skelton Group, the Victoria and Taylor Groups of the Beacon Supergroup and potentially currently unexposed EAC/TAM units. The latter may include early Pan-African units, a ~830 Ma igneous unit, ~1.0-1.3 Ga Grenvillian units, 1.4-1.6 Ga aged unknown cratonic components.

(3) Zircon characteristics, particularly within the 450-650 Ma age group, show systematic temporal variations throughout the core. Combined with knowledge from previous whole rock geochemistry and sand provenance work, these trends indicate a major shift in erosional, depositional and transportational mechanisms at ~250 mbsf (~23.5 Ma). This shift is reflected by progressive changes in zircon numbers and ages up core and by an influx of volcanogenic (possible early MVG-related) sediments at ~250 mbsf.

The sub-250 mbsf section of the core was deposited during the Late Eocene (Zone 1,  $\sim$ 37-34 Ma). During this relatively warm period, alpine-style glaciers flowed westward though the TAM and sediments were deposited at CIROS-1 via fluviomarine systems fed by land terminating glaciers in Ferrar Fiord. It is proposed that the sub-250 mbsf section of core contains a subtle unroofing history of the units in the Ferrar Fiord, with increasing ages of the 450-650 Ma 'Ross' population up core. This likely reflects an analytical advantage over the earlier studies of George (1989) and Roser and Pyne (1989), which were unable to distinguish a consistent temporal trend recorded in these sediments.

Above ~250 mbsf two distinct climatic periods are recorded (Zones 2 and 3). During the deposition of Zone 2 (~25-23.5 Ma) ice flow to the CIROS-1 site was from the west and CIROS-1 sediments were sourced from the Ferrar Fiord. The EAIS was ephemeral and oscillating on orbital timescales, and outlet glaciers were wet based and highly erosive. In this zone the proportion of 'Ross' aged zircons is highly variable and the total zircon number high.

The strata of Zone 3 were deposited between ~23.2-22 Ma, when the climate was rapidly cooling toward the Mi-1 glaciation, the ice volume of EAIS was increasing and the WAIS was establishing. During this period 'Ross' population ages decrease systematically up core and the proportion of 'Ross' aged grains increases significantly. Marked changes in CIROS-1 sediment provenance above ~250 mbsf were also noted by Roser and Pyne (1989), who reported a large increase of MVG-type material in the core from ~250 mbsf upwards. Additionally, MVG-type tephras were found at 24 and 22 Ma in CRP 2/2A (Naish et al., 2001; Wilson et al., 2002). These changes in sand and zircon provenance at ~23.5 Ma are proposed to result from a shift in ice flow direction from west to south, as a response to ice growth of the EAIS and WAIS in the lead up to the Mi-1 glaciation (McKay, 2008; Talarico et al., 2009).

# Chapter 7: Synthesis and suggestions for future work

# 7.1. Synthesis

The marine oxygen isotope record (e.g. Zachos et al., 2001a), provides a picture of the stepwise global cooling of the Cenozoic which has occurred since the climatic optimum in the Eocene. Antarctic margin sediment drill cores contain compelling proxy evidence for Antarctic climate during the Cenozoic and allow evaluation of Antarctica's response to global cooling events recorded in the global benthic oxygen isotope record. Drilled in 1986, the CIROS-1 drill core contains sediments deposited by Trans-Antarctic Mountain outlet glaciers (e.g. Ferrar, Mulock and Skelton glaciers) draining the EAIS during the Late Eocene-Early Miocene. Sediment deposition occurred during key global cooling climatic events associated with stepwise development of the Antarctic Ice Sheets between 20-40 Ma (including the Eocene-Oligocene boundary and the Mi-1 glaciation). Since the CIROS-1 core was recovered, new and advanced techniques for drill core and sediment analysis have been developed.

The primary aim of this thesis is to re-evaluate the record of Cenozoic Antarctic history contained in CIROS-1 using cutting-edge analytical techniques. New techniques utilised are based on revisions of sequence stratigraphic models (e.g. Dunbar et al., 2008) and facies schemes (e.g. Fielding et al., 2001) for sediments deposited on a glaciated continental margin. In Addition, new and re-evaluated chronological constraints on Antarctic sediment deposition (e.g. Naish et al., 2008b; Scherer et al., 2000) are used. CIROS-1 sediment provenance and broad scale temporal variances therein is investigated using advanced methods for geochemical analysis and detrital zircon dating (e.g. Veevers et al., 2008; DeGraaf-Surpless et al., 2003), not yet developed when the core was originally analysed.

In summary, two main research objectives of this thesis are to: (1) Re-evaluate CIROS-1 sedimentology, lithofacies, sequence stratigraphy and chronology using methods developed for the Cape Roberts and ANDRILL cores (e.g. Fielding et al., 1997; Fielding et al., 2001; Dunbar et al., 2008; Naish et al., 2008a); and (2) Re-assess the provenance of CIROS-1 sands and any temporal variances there-in using in situ LA-ICP-MS analysis techniques.

Key findings of this investigation include:

(1) CIROS-1 glaciomarine sequence stratigraphy shows that 14 sequences, occurring in two distinctive stratigraphic motifs, are present in CIROS-1 (Figs. 3.6 and 3.7). Four sequences, located beneath the 342 mbsf unconformity, are relatively complete in terms of systems tracts. They were deposited in shallow marine, fluvio-deltaic conditions with distal glaciers terminating on land and possibly calving into the ocean in adjacent valley glacier systems, as evidenced by occasional ice-rafted debris. Nine sequences are located above ~342 mbsf and have a fundamentally different architecture. They are incomplete (top-truncated), contain diamicts and were deposited under proximal glaciomarine conditions. Top truncation of these sequences represents overriding of the CIROS-1 site by the paleo-Ferrar Glacier during glacial phases (which occurred at least nine times during the Late Oligocene-Early Miocene).

(2) The new CIROS-1 chronology, developed using recently published improvements in the Geomagnetic Polarity Timescale (Gradstein et al., 2004), recent calibrations for Antarctic diatom zones (Naish et al, 2008a; Wilson et al., 2002) and the compilation of previous work (Roberts et al., 2003; Wilson et al., 1998; Hannah et al., 1997), shows CIROS-1 sediments were deposited ~37-22 Ma, between the Late Eocene-Early Miocene (Fig. 3.9). Sediments between 702-366/342 mbsf were deposited during the Late Eocene. The new age model provides equivocal ages to sediments between 366-342 mbsf, which may be between 31 to 22 Ma in age. Strata located between this depth interval and ~100 mbsf were deposited during the Latest Oligocene and those above ~100 mbsf are Early Miocene in age. Sediments above ~250 mbsf were deposited in an increasingly cool climate that culminated in the Mi-1 glaciation at Oligocene-Miocene boundary (~100 mbsf). In this new chronology, the 9 Myr hiatus historically thought to be exclusively located at an unconformity at 366 mbsf (e.g. Harwood et al., 1989; Roberts et al., 2003), may be wholly or partially distributed on this unconformity and another located at ~342 mbsf.

(3) The new CIROS-1 chronology allows direct comparison of Late Oligocene orbitally-paced sedimentary cycles in CIROS-1 with those in CRP-2/2A, and shows a fundamental orbital control on the dynamics of these EAIS outlet glaciers. Both glacier systems respond in-phase to longer period orbital components (e.g. Eccentricity, 100 kyr and 400 kyr cycles), but differ in their sensitivity to precession (20 kyr). Precession provides a first order influence on the long term intensity of

summer insolation and thus higher temperature (> 0°C) days when surface ablation can occur. Over a ~125 kyr period (in Chron 6n.3n) the paleo-Ferrar Glacier experienced five oscillations of glacial advance and retreat whilst the paleo-McKay Glacier experienced only one cycle of advance-retreat-readvance (Fig. 3.10). It appears that during the Late Oligocene, the Ferrar catchment responded to 20 kyr precession cycles, whilst the larger MacKay Glacier, which is more directly connected to the EAIS, responded to longer duration eccentricity (125 kyr) forcings. The Ferrar may have behaved more like a mid-latitude (New Zealand and Patagonian) glacier during past "warmer than present" climate. These respond directly to local seasonal insolation modulated by precession over longer timescales. In contrast the paleo-MacKay outlet glacier may have displayed a pattern of behaviour more related to the interior East Antarctic Ice Sheet, which is high, large, cold, more inert, and therefore may only have melted in response to thresholds in orbital geometry modulated by the longer-duration components.

(4) CIROS-1 zircons fall within four geochemical groups. Zircons formed in felsic igneous environments dominate the CIROS-1 population, with 89 % percent of zircons analysed showing geochemical characteristics inherent to granitic/rhyolitic zircons (Hoskin and Schaltegger, 2003). Approximately 7 % of CIROS-1 zircons have a highly trace element enriched igneous provenance and were most probably sourced from trace element enriched enclaves in granitic/rhyolitic units or from pegmatites. Approximately 3 % of CIROS-1 zircons have a metamorphic origin and  $\sim$ 1% formed in trace element depleted igneous environments.

(5) CIROS-1 zircons were sourced from: the local basement (Skelton and Granite Harbour Groups), the Beacon Supergroup and, potentially, lithologies of the East Antarctic Craton or Trans-Antarctic Mountains located under the ice or below the current baseline of geologic exposure.

(6) Large-scale, systematic temporal trends in zircon characteristics are present in CIROS-1. The core can be divided during three distinct climatic periods: Zone 1 (702-366 mbsf, Late Eocene), Zone 2 (366-250 mbsf, Late Oligocene) and Zone 3 (< 250 mbsf, Late Oligocene and Early Miocene). Zircons deposited during these periods exhibit distinct properties:

Zone 1: Antarctica experienced a relatively warm climate and alpine style glaciers flowed eastwards through the Trans-Antarctic Mountains. Zircons in this zone

record a subtle unroofing history of the units located in Ferrar Fiord, with the age of the 450-650 Ma age-range populations steadily increasing up core, coupled with a decrease in the abundance of this population. These trends may reflect the unroofing of geochemically zoned Granite Harbour and Skelton units (located in the Ferrar Fiord) by widespread glacial and fluvial erosion.

**Zone 2**: Glaciers flowing through the Trans-Antarctic Mountains drained the large and ephemeral East Antarctic Ice Sheet which oscillated on orbital time scales. Zircons in this interval show variable properties and high numbers, and were likely deposited as the paleo-Ferrar Glacier deeply incised the Ferrar Fiord. This downcutting caused dynamic topographic response, further localising valley glacier incision.

**Zone 3**: The Antarctic climate was cooling markedly, culminating in the Mi-1 glaciation at the Oligocene-Miocene boundary (~23 Ma) (Zachos et al., 2001a). At the base of Zone 3, previous workers noted a marked influx of McMurdo Volcanic Group-type detritus (Roser and Pyne, 1989; George, 1989), which was potentially sourced from the erosion of a paleo-Mt. Morning volcano, located to the south of the CIROS-1 site. This influx, together with systematic changes in zircon characteristics recorded in this zone (up core increase in the number of 450-650 Ma aged zircons and a coupled decrease of the average age of this population), indicates a change in ice flow to the site. During periods of cold climate, when a West Antarctic Ice Sheet is present (e.g. during the Last Glacial Maximum) ice flow to the CIROS-1 site is from the south from the Skelton and Mulock glaciers (McKay, 2008; Licht et al., 2005). During relatively warmer periods (such as the Late Eocene-Oligocene), ice flow is from the west through the Trans-Antarctic Mountains (Fig. 6.22). Thus Zone 3 zircons may record a change in ice flow direction to the CIROS-1 site from west to south due to climatic cooling.

# 7.2. Suggestions for future work

#### Analysis of temporal variations in CIROS-1 clasts

Talarico et al. (2009) petrographically analysed clasts in the ANDRILL-1B core and found that source units for the clasts changed during glacial and interglacial periods. In contrast, CIROS-1 zircons did not show intra-sequence variations in provenance, but do show broader scale shifts. Analysis of CIROS-1 clasts (particularly in the upper section of the core) would complement the data presented in this thesis by revealing short-scale variations in sediment source units not resolvable in zirconspecific work.

#### Investigate chemical zonation in Granite Harbour Intrusive Group batholiths

Granitic plutons commonly exhibit compositional zones (Hecht et al., 1997). This zonation may be reverse or normal and include temporal variances in the crystallisation times of constituent crystals. Naturally, erosion of these batholiths would create sedimentary deposits with systematically varying chemistries and/or ages following the pattern of unroofing. The spatio-chemical zonation of batholiths in the Trans-Antarctic Mountains has not yet been studied in detail, and would establish a more reliable framework for determining sediment provenance in the region.

### Conduct fission track analysis on CIROS-1 zircons

Fission track dating of zircons, apatites or titanites gives insight into the thermochronological history of the grains, with the potential to clarify exhumation processes and the cooling of metamorphic and igneous rocks (Kösler and Sylvester, 2003). Furthermore, dual fission track and U-Pb analysis of zircon can determine both the formation and cooling ages of grains, constraining depositional ages and the orogenic evolution of source terrains (Reiners et al., 2005). The benefits of conducting fission track analysis of the grains analysed for this thesis would be two-fold. First, it would allow easier identification of potential sources of detrital zircons. Secondly, it would shed light on the unroofing and thermal history of the Trans-Antarctic Mountains during the Late Eocene-Early Miocene.

### Conduct zircon analysis on temporally correlative sedimentary cores in the VLB

The analysis of zircon populations in sedimentary cores drilled in the Victoria Land Basin that were deposited during the same time intervals as CIROS-1 strata will allow the results of this research to be validated and compared. For example, if Oligocene-aged sediments found in CRP were analysed for zircon content, the systematic temporal trends observed in CRIOS-1 could be compared to those in CRP cores. Additionally, the sources for zircons in both cores could be compared and contrasted. This would allow a more robust and complete picture of zircon depositional dynamics in the McMurdo Sound area over the Eocene-Miocene to be constructed. This, in turn, would provide greater insights into the mechanisms responsible for sand deposition into the Victoria Land Basin, the response of the Antarctic cryosphere to climatic forcings and the tectonic state of the region over this time interval.

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# **Appendix 1: Sample descriptions**

#### Sample 28-21

Location: 28.3 mbsf. Depositional age: Early Miocene. Source unit: Poorly sorted coarse/very coarse sandstone. Sedimentology: coarse sandstone, yellow brown with grey to medium-dark brown grains, poorly sorted (medium to coarse sandstone), lithified and friable in places Clasts: <5 % clasts, poorly sorted (~1-7 mm), light-dark grey, rounded-angular, lithologies include granite. Sedimentary features: broad and irregular bedding of hard lithified sections and friable, coarse grained and better sorted sections. Fossils: no fossils visible.

#### Sample 78-18

Location: 78.9 mbsf. Depositional age: Early Miocene. Source unit: fine sandstone/mudstone. Sedimentology: fine sandstone, light yellow brown, poorly sorted (mud- medium sandstone, very hard and lithified, not friable. Clasts: <1 % clasts, well sorted (~5 mm), light to medium grey, angular, unknown lithology. Sedimentary features: massive sandstone, some vertical fractures present. Fossils: no fossils visible. Sample 91-17

Location: 91.8 mbsf. Depositional Age: Early Miocene.

Source unit: sandstone matrix of a diamict.

Sedimentology: medium sandstone, medium yellow brown, poorly sorted (mud-medium sandstone), hard and non friable.

Clasts: ~15 % clasts, very poorly sorted (~1-30 mm), variable colours include white, light and dark red browns and medium to dark greys, angular-subrounded, Lithologies include: granite, granodiorite.

Sedimentary features: massive.

Fossils: no fossils visible.

#### Sample 148-16

Location: 148.3 mbsf. Depositional age: Early Miocene. Source unit: medium/coarse sandstone. Sedimentology: medium-coarse sandstone, yellow brown, poorly sorted, hard, not friable. Clasts: <5% clasts, medium sorted (~2-5 mm), light-dark grey, angular-rounded, lithologies include granite. Sedimentary features: massive. Fossils: no fossils visible.

## Sample 205-15

Location: 205.8 mbsf.

Depositional age: late Oligocene.

Source unit: medium sandstone.

Sedimentology: medium-coarse sandstone, light brown grey, poorly sorted, hard and friable in paces.

Clasts: ~15 % clasts, very poorly sorted (~1-15 mm), light-dark grey, angular to rounded, light-dark grey, lithologies include, granite and a number of dark unknown lithologies. Sedimentary structures: vague and irregular bedding between friable, coarser units and diner grains hard massive units.

Fossils: no fossils visible.

## Sample 249-14

Location: 249.0 mbsf. Depositional age: Late Oligocene. Source unit: sandstone matrix of a diamict. Sedimentology: fine-medium sandstone, medium grey brown, poorly sorted, unlithified and very friable Clasts: <1 % clasts, medium sorted (~2-4 mm), white to dark grey, angular, unknown lithologies. Sedimentary structures: none seen. Fossils: no fossils visible.

## Sample 292-13

Location: 292.2 mbsf. Depositional age: Late Oligocene. Source unit: fine sandstone/mudstone. Sedimentology: fine sandstone/mudstone, medium grey, poorly sorted, lithified, hard and not friable. Clasts: <5 % clasts, poorly sorted (~1-8 mm), light-dark grey and medium brown, subrounded-angular, granite and unknown lithologies. Sedimentary structures: massive. Fossils: no fossils visible.

#### Sample 295-12

Location: 295.7 mbsf. Depositional age: Late Oligocene. Source unit: fine/medium sandstone. Sedimentology: coarse sandstone, medium-well sorted, light yellow grey, very friable both soft and hard. Clasts: ~5 % clasts, medium sorted (~2-6 mm), light-medium grey, subrounded-angular, unknown lithologies. Sedimentary structures: none seen. Fossils: no fossils visible.

## Sample 362-11

Location: 362.8 mbsf. Depositional age: Late Oligocene. Source unit: coarse sandstone. Sedimentology: coarse-very coarse sand stone, very poorly sorted, medium/light brown, hard and very friable. Clasts: ~20 % clasts, poorly sorted (~1-10 mm), dominantly dark grey; <1 % light grey, unknown lithology. Sedimentary features: none seen. Fossils: no fossils visible.

#### Sample 403-10

Location: 403.6 mbsf. Depositional age: Late Oligocene-Late Eocene? Source unit: medium/coarse bedded sandstone. Sedimentology: very fine sandstone/mudstone, light grey, hard and friable. Clasts: <1% clasts, well sorted (~1-2 mm), dark grey, unknown lithologies. Sedimentary features: massive. Fossils: no fossils visible.

#### Sample 462-7

Location: 462.8 mbsf. Depositional age: Late Oligocene-Late Eocene? Source unit: medium/coarse sandstone. Sedimentology: fine-medium sandstone, light brown (incl. white and dark pink, shiny grains ~0.5 mm, may be micas?), poorly sorted (incl. silt component), hard and friable. Clasts: ~5 % clasts, medium sorted (~1-5 mm), light-dark grey, angular, includes granite? and unidentified lithologies. Sedimentary structures: massive. Fossils: no fossils seen.

#### Sample 465-8

Location: 465.7 mbsf. Depositional age: Late Oligocene-Late Eocene? Source unit: medium/coarse sandstone. Sedimentology: fine sandstone/mudstone, light grey brown (incl. shiny white and black grains ~0.5 mm), poorly sorted, hard and not friable. Clasts: <1 % clasts, well sorted (~1-2 mm), light grey, angular-sub rounded, granite? Sedimentary structures: massive. Fossils: no fossils visible.

## Sample 507-6

Location: 507.4 mbsf. Depositional age: Late Oligocene-Late Eocene? Source unit: medium/coarse sandstone. Sedimentology: medium sandstone, medium yellow brown (incl. ~1-5 % white, shiny clasts), poorly sorted (incl. silt component), hard and moderately friable. Clasts: <5 % clasts, white-dark grey, poorly sorted (~1-6 mm), angular, unidentified lithologies. Sedimentary structures: none seen. Fossils: no fossils visible.

#### Sample 560-5

Location: 507.0 mbsf. Depositional age: Late Eocene. Source unit: medium sandstone. Sedimentology: medium to coarse sandstone, yellow brown, poorly sorted (incl. silt component), soft and very friable. Clasts: <1 % clasts, medium-dark grey, well sorted (~1-3 mm), subangular, unidentified lithologies. Sedimentary structures: none seen. Fossils: no fossils visible.

## Sample 610-4

Location: 610.4 mbsf. Depositional age: Late Eocene. Source unit: medium sandstone. Sedimentology: fine sandstone, medium grey brown (~5 % back, shiny clasts), moderately sorted (incl. ~10 % silt component), very hard and not friable. Clasts: no clasts visible. Sedimentary structures: vague fine scale bedding (~1-2 mm) between medium brown and medium grey sands, no grain size change. Fossils: 10-15 mm, curved, white shell fossils, bivalves?

## Sample 652-3

Location: 652.5 mbsf. Depositional age: Late Eocene. Source unit: medium sandstone. Sedimentology: fine-medium sandstone, medium brown grey (<5 % black shiny grains (biotite?), ~5 % white shiny clasts (incl. muscovite??)), hard and moderately friable.

Clasts:  $\sim$ 5-10 % clasts, white-dark grey, very poorly sorted ( $\sim$ 1-17 mm), angular-rounded, includes granite.

Sedimentary structures: none visible, massive.

Fossils: one white shell fragment, 3mm, unknown origin. One white, poorly preserved bivalve fossil, 22 mm long, >19 mm wide.

## Sample 687-1

Location: 687.0 mbsf. Depositional age: Late Eocene. Source unit: sandstone matrix of a conglomerate. Sedimentology: medium-coarse grained sandstone, light yellow brown (~5 % grains dark grey and ~1 % orange brown), medium sorting, soft and very friable. Clasts: < 1% clasts, medium grey, well sorted (~2 mm), subrounded, unknown origin. Sedimentary structures: none seen. Fossils: none present.

## Sample 693-2

Location: 693.4 mbsf.

Depositional age: Late Eocene.

Source unit: sandstone matrix of a conglomerate.

Sedimentology: very coarse sandstone, light grey brown (~15 % white shiny grains (muscovite?), ~50 % very light brown, not shiny grains with concoidal fractures (Quartz?), ~35 % medium-dark brown and grey grains), hard and not friable.

Clasts: none visible.

Sedimentary features: none visible.

Fossils: no fossils visible.

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			Isotopic ratios							Арра	rent ages	s (Ma)					
				<sup>207</sup> Pb		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
52	1965	702	2.8	0.059	0.001	11.437	0.198	1.370	0.026	576	24	541	9	557	8	549	130
50	282	125	2.3	0.061	0.002	11.366	0.296	1.495	0.068	627	56	544	13	520	18	535	150
49	191	100	1.9	0.060	0.002	12.393	0.411	1.675	0.101	612	67	500	15	476	22	492	13
48	814	224	3.6	0.057	0.001	12.376	0.351	1.590	0.056	510	35	501	13	496	13	498	10
47	281	152	1.9	0.058	0.002	11.831	0.372	1.618	0.074	529	60	523	15	489	17	508	220
46	5680	6927	0.8	0.057	0.001	8.858	0.224	1.130	0.024	503	22	690	16	644	10	discordant	
45	289	175	1.6	0.059	0.002	12.438	0.365	1.644	0.075	581	59	499	14	483	17	492	11
43	972	170	5.7	0.057	0.001	11.933	0.255	1.540	0.047	505	33	519	10	509	12	514	9
42	121	220	0.5	0.175	0.002	2.057	0.052	0.086	0.002	2608	22	2555	52	2575	22	2571	22
41	174	47	3.7	0.059	0.002	12.598	0.538	2.243	0.485	557	74	493	19	375	57	discordant	
40	714	336	2.1	0.058	0.001	12.109	0.265	1.559	0.046	549	40	512	11	504	12	508	1
39	1625	889	1.8	0.060	0.001	12.228	0.307	1.499	0.040	608	28	507	12	519	11	514	3
38	1257	201	6.3	0.060	0.001	11.968	0.293	1.464	0.041	601	29	518	12	529	11	523	9
37	188	88	2.1	0.059	0.002	12.579	0.509	1.772	0.130	584	79	493	18	455	25	480	250
36	1784	552	3.2	0.057	0.001	11.972	0.283	1.534	0.040	504	26	517	11	510	10	513	9
35	1793	285	6.3	0.058	0.001	12.024	0.274	1.523	0.037	545	26	515	11	513	9	514	9
34	300	135	2.2	0.058	0.002	12.469	0.539	1.631	0.087	545	60	497	20	486	20	491	15
33	3682	2061	1.8	0.057	0.001	13.558	0.408	1.709	0.049	503	27	459	13	468	10	465	10
32	173	132	1.3	0.060	0.002	12.790	0.763	1.793	0.170	617	86	485	26	450	32	471	22
31	1855	552	3.4	0.058	0.001	12.248	0.600	1.557	0.069	512	32	506	23	504	17	504	17
29 RIM	592	267	2.2	0.057	0.001	11.968	0.324	1.579	0.055	509	41	518	13	498	13	508	140
28	1161	744	1.6	0.059	0.001	11.215	0.436	1.385	0.051	583	30	551	20	552	15	552	14
26A CORE	446	256	1.7	0.058	0.001	12.061	0.587	1.562	0.074	535	53	514	23	503	18	506	16
26	1434	221	6.5	0.057	0.001	12.310	0.282	1.596	0.052	504	31	504	11	494	13	500	9
29 core	891	387	2.3	0.060	0.001	12.816	0.442	1.568	0.060	611	39	485	16	501	15	493	13
26A RIM	230	69	3.3	0.062	0.002	12.601	0.692	1.632	0.118	710	56	492	25	486	26	489	20
30	1078	502	2.1	0.061	0.001	12.316	0.450	1.494	0.053	644	41	503	17	521	14	514	13
25 CORE	3060	1158	2.6	0.064	0.003	12.014	0.877	1.479	0.104	741	103	516	34	525	27	521	26
25 RIM	1412	525	2.7	0.065	0.002	13.052	1.497	1.461	0.158	781	79	476	47	530	41	508	38

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				Isotopic ratios					Appa	rent ages	s (Ma)						
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
24 CORE	3641	4172	0.9	0.060	0.002	10.901	0.891	1.314	0.094	620	51	566	41	575	30	575	32
24 RIM	3040	844	3.6	0.061	0.002	13.487	1.336	1.581	0.135	646	64	461	40	498	31	484	27
23 CORE	962	325	3.0	0.064	0.002	13.009	1.400	1.439	0.138	758	61	478	45	536	37	521	730
23 RIM	1318	198	6.7	0.059	0.001	13.440	1.274	1.598	0.137	560	51	463	39	494	31	485	32
22 RIM	53	23	2.3	0.088	0.008	13.774	2.285	1.367	0.176	1375	168	452	62	558	50	519	770
21	240	146	1.6	0.060	0.002	12.630	0.987	1.635	0.142	607	69	491	34	485	31	487	28
12 rim	198	102	1.9	0.063	0.002	12.916	0.477	1.855	0.150	699	79	481	17	438	27	469	250
12 core	319	233	1.4	0.060	0.002	12.757	0.420	1.682	0.082	567	104	487	15	474	18	481	12
11	130	90	1.4	0.059	0.003	12.623	0.580	1.878	0.152	577	123	492	21	434	27	470	360
10 rim	174	75	2.3	0.061	0.002	13.088	0.515	1.831	0.153	657	82	475	17	443	28	466	15
10core	282	194	1.5	0.058	0.002	12.796	0.393	1.793	0.094	514	69	485	14	450	18	472	230
9core	586	483	1.2	0.057	0.001	12.608	0.457	1.660	0.072	510	56	492	17	479	16	485	14
9	271	179	1.5	0.059	0.002	12.848	0.502	1.775	0.130	552	61	483	18	454	25	474	15
8core	825	451	1.8	0.061	0.001	11.479	0.523	1.398	0.054	631	41	539	23	548	16	546	16
7core	764	473	1.6	0.061	0.002	13.305	1.040	1.600	0.107	647	73	467	33	493	25	488	25
7rim	712	365	1.9	0.060	0.002	13.369	0.973	1.628	0.099	607	60	465	31	487	23	481	23
6rim	164	118	1.4	0.061	0.003	12.984	0.997	1.831	0.156	623	94	478	33	443	29	457	25
6core	1213	367	3.3	0.058	0.001	12.368	0.251	1.574	0.038	535	20	501	10	500	9	500	7
5core	2588	1204	2.1	0.059	0.001	11.428	0.281	1.403	0.032	564	38	541	12	547	10	545	9
5coreish	1734	672	2.6	0.059	0.001	11.539	0.275	1.417	0.036	571	32	536	12	543	10	540	9
4core	231	113	2.0	0.060	0.002	12.662	0.421	1.688	0.092	603	79	490	15	473	20	484	13
4rim	190	89	2.1	0.059	0.002	13.084	0.483	1.855	0.146	550	89	475	16	438	26	465	210
3	867	565	1.5	0.058	0.001	11.462	0.241	1.429	0.036	542	32	539	11	539	10	539	8
2	808	236	3.4	0.060	0.001	11.322	0.231	1.410	0.041	594	36	546	10	545	12	545	8
1core	626	375	1.7	0.060	0.001	12.770	0.264	1.613	0.049	609	41	486	9	490	11	488	8
1rima	980	302	3.2	0.057	0.001	12.146	0.227	1.540	0.039	508	32	510	9	509	10	510	7
51core	1992	993	2.0	0.060	0.001	16.853	0.288	2.022	0.043	606	29	372	6	408	7	discordant	
51rim	404	101	4.0	0.058	0.001	12.220	0.282	1.563	0.058	543	50	507	11	502	14	505	9

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			Isotopic ratios						Appa	rent ages	s (Ma)						
				<sup>207</sup> Pb		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	- ±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1rimb	746	322	2.3	0.057	0.001	11.924	0.230	1.521	0.042	500	40	519	9	514	11	517	7
57	179	106	1.7	0.061	0.002	13.856	0.588	1.808	0.104	656	75	449	18	447	20	448	14
56	88	68	1.3	0.069	0.005	14.171	0.838	2.006	0.179	899	130	440	24	411	28	428	19
55	134	78	1.7	0.060	0.003	12.996	0.446	1.849	0.131	617	96	478	15	439	24	467	230
55ACORE	391	51	7.6	0.072	0.002	7.550	0.125	0.807	0.020	976	45	802	12	819	14	809	10
55ARIM	326	71	4.6	0.080	0.001	5.525	0.098	0.503	0.010	1204	30	1073	17	1112	13	discordant	
20	743	20	37.5	0.103	0.001	3.469	0.133	0.240	0.008	1677	22	1633	53	1667	26	1668	26
19	113	49	2.3	0.091	0.002	4.201	0.336	0.348	0.028	1440	50	1377	92	1376	58	1375	50
42(repeat)	107	241	0.4	0.175	0.003	2.142	0.055	0.088	0.002	2603	23	2470	52	2555	25	2542	480
18	193	82	2.4	0.059	0.002	13.164	1.026	1.822	0.163	566	89	472	33	444	30	456	29
17	194	75	2.6	0.057	0.002	12.952	0.529	1.868	0.148	499	72	480	18	436	26	465	260
16 c	211	105	2.0	0.058	0.002	13.401	0.896	1.920	0.164	527	82	464	28	426	28	444	290
16r	201	87	2.3	0.056	0.002	12.607	0.658	1.883	0.164	456	78	492	24	433	29	468	400
15a	195	125	1.6	0.059	0.002	12.562	0.406	1.775	0.122	559	78	494	15	454	24	483	230
15b	119	39	3.1	0.063	0.003	13.737	0.815	1.888	0.194	715	96	453	25	432	33	446	22
14 c	2331	729	3.2	0.057	0.001	12.095	0.206	1.526	0.030	508	25	512	8	512	8	512	6
14r	2436	888	2.7	0.057	0.001	12.658	0.196	1.596	0.026	487	18	490	7	494	6	492	5
13	127	72	1.8	0.058	0.003	12.884	0.541	1.930	0.157	539	95	482	19	424	26	discordant	
46 (repeat)	1049	771	1.4	0.057	0.001	12.068	0.215	1.539	0.039	490	29	513	9	509	10	511	7
45 (repeat)	90	42	2.1	0.059	0.002	13.556	0.717	2.098	0.217	591	38	459	22	396	31	437	386
17 (repeat)	1318	1314	1.0	0.062	0.002	13.911	0.707	1.693	0.087	689	78	448	21	472	19	462	240
18 (repeat)	84	96	0.9	0.061	0.003	14.480	0.975	2.053	0.224	646	94	431	26	403	33	420	22
20 (repeat)	2292	2872	0.8	0.107	0.002	14.601	0.262	1.780	0.041	1757	33	427	7	453	8	discordant	
21(repeat)	3970	9487	0.4	0.061	0.003	11.194	0.265	1.413	0.032	635	94	552	12	544	9	545	9
52 (repeat)	273	263	1.0	0.057	0.001	12.971	0.414	1.738	0.095	510	30	479	14	462	20	473	12
41 (repeat)	187	155	1.2	0.066	0.004	13.137	0.547	1.797	0.116	811	134	473	18	450	22	463	15
39 (repeat)	142	130	1.1	0.059	0.001	14.045	0.667	1.849	0.142	585	46	444	19	439	26	442	16
37 (repeat)	144	122	1.2	0.068	0.005	3.640	0.103	0.251	0.008	870	141	1565	38	1631	27	1609	440
32 (repeat)	121	179	0.7	0.059	0.001	13.086	0.557	1.863	0.146	560	28	475	19	437	26	462	230

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						Isotop	oic ratios	3			Appa	rent ages	s (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		$^{207}\mathrm{Pb}$		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
33c	645	588	1.1	0.059	0.002	13.886	1.276	1.742	0.141	586	79	448	37	461	28	458	29
34	1661	609	2.7	0.062	0.001	12.328	0.682	1.521	0.083	669	41	503	25	513	21	510	21
35	192	52	3.7	0.074	0.002	5.505	0.296	0.551	0.032	1046	48	1076	51	1051	36	1058	34
36	183	161	1.1	0.107	0.002	3.116	0.080	0.217	0.006	1743	30	1795	39	1753	24	1763	20
32c	170	63	2.7	0.064	0.003	13.235	1.114	1.857	0.270	750	86	470	35	438	46	459	33
38	1220	612	2.0	0.073	0.001	7.915	0.192	0.819	0.020	1020	41	767	17	811	13	discordant	
39	505	123	4.1	0.063	0.001	11.979	0.388	1.553	0.064	711	49	517	16	505	16	511	12
40	1345	647	2.1	0.060	0.003	12.427	0.456	1.584	0.054	608	99	499	17	497	13	498	12
41	547	172	3.2	0.059	0.001	12.609	0.556	1.553	0.069	578	47	492	20	505	17	500	15
41r	387	143	2.7	0.060	0.002	12.252	0.617	1.542	0.078	595	60	506	23	508	19	507	17
42	2389	380	6.3	0.065	0.001	28.476	0.950	3.192	0.110	777	36	223	7	277	8	discordant	
43	82	15	5.3	0.102	0.008	14.092	1.212	1.372	0.160	1659	144	442	34	556	46	discordant	
44	89	168	0.5	0.109	0.006	12.614	0.745	1.016	0.092	1780	98	492	26	696	43	discordant	
45	3092	1165	2.7	0.066	0.001	22.356	0.871	2.477	0.088	814	33	282	10	345	10	discordant	
46	95	27	3.5	0.073	0.004	8.415	0.517	0.986	0.085	1025	104	724	40	712	41	718	32
47c	230	118	2.0	0.059	0.002	12.508	0.846	1.664	0.124	575	75	496	30	478	27	485	22
47r	509	364	1.4	0.058	0.002	12.760	0.788	1.663	0.097	537	62	487	27	478	21	481	20
48	777	364	2.1	0.061	0.002	12.592	0.864	1.539	0.084	640	56	493	31	509	21	506	22
50r	2028	584	3.5	0.059	0.001	13.758	0.711	1.680	0.074	569	40	452	22	475	16	470	240
51c	385	110	3.5	0.061	0.002	12.919	1.106	1.645	0.123	626	77	481	37	482	27	482	28
49	1515	1442	1.1	0.072	0.002	15.979	1.187	1.722	0.110	992	52	391	26	465	23	discordant	
51r	122	72	1.7	0.063	0.007	12.685	1.425	1.755	0.237	700	209	489	48	458	45	472	39
1	254	106	2.4	0.056	0.002	11.345	0.755	1.544	0.136	450	80	545	33	507	33	526	29
2	1531	595	2.6	0.061	0.002	13.860	0.761	1.644	0.081	641	55	449	23	483	18	473	360
3	122	43	2.8	0.073	0.003	6.406	0.487	0.649	0.041	1016	74	935	62	947	38	945	38
4c	850	864	1.0	0.061	0.002	13.441	0.782	1.651	0.077	650	62	463	25	481	17	479	18
4r	1312	348	3.8	0.062	0.002	13.507	0.679	1.611	0.073	689	61	461	21	491	17	481	280
5	3914	4172	0.9	0.083	0.002	21.684	1.348	1.838	0.090	1270	40	291	17	441	17	discordant	

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				Isotopic ratios					Appa	rent ages	s (Ma)						
				<sup>207</sup> Pb		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	- ±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ma	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
6	2375	993	2.4	0.060	0.001	17.318	1.286	2.091	0.127	602	45	362	24	397	19	390	410
7	821	56	14.7	0.059	0.001	12.117	0.926	1.557	0.119	576	49	511	35	504	29	506	29
8	1289	404	3.2	0.078	0.002	12.150	0.760	1.113	0.059	1136	48	510	29	652	25	discordant	
9	1009	968	1.0	0.060	0.001	10.851	0.455	1.318	0.046	588	42	569	22	574	15	572	15
10	144	121	1.2	0.060	0.003	12.734	0.904	2.066	0.277	596	110	488	31	401	40	discordant	
11	1477	508	2.9	0.061	0.002	12.579	1.034	1.514	0.117	648	69	493	36	515	29	510	30
7(REPEAT)	721	512	1.4	0.060	0.001	11.996	0.495	1.479	0.058	615	40	516	20	525	16	522	15
8(REPEAT)	1743	760	2.3	0.099	0.002	13.632	0.402	1.278	0.040	1613	34	457	13	587	14	discordant	
9(REPEAT)	722	601	1.2	0.066	0.001	10.475	0.222	1.172	0.033	796	34	588	12	627	13	discordant	
10(REPEAT)	172	140	1.2	0.060	0.002	11.735	0.394	1.677	0.117	621	76	527	16	475	25	discordant	
11(REPEAT)	1207	603	2.0	0.059	0.001	11.949	0.198	1.481	0.033	583	29	518	8	524	9	521	6
12(REPEAT)	1808	289	6.2	0.058	0.001	10.662	0.191	1.386	0.032	533	26	578	10	552	10	discordant	
13c	1397	451	3.1	0.071	0.001	12.930	0.223	1.399	0.039	955	30	480	8	548	12	discordant	
13r	1353	390	3.5	0.065	0.001	13.690	0.260	1.600	0.037	792	16	455	8	493	9	discordant	
14	1197	544	2.2	0.059	0.001	11.405	0.232	1.486	0.042	558	27	542	10	523	11	533	140
15	1184	748	1.6	0.058	0.001	10.995	0.272	1.519	0.331	541	28	561	13	514	75	562	12
16	1002	333	3.0	0.064	0.001	15.350	0.531	1.711	0.054	754	43	407	13	468	12	discordant	
18	2505	873	2.9	0.059	0.001	14.996	0.488	1.878	0.055	575	24	416	13	434	10	429	180
19 <b>c</b>	2177	281	7.7	0.058	0.001	12.234	0.307	1.594	0.041	518	23	507	12	495	10	499	9
19r	1823	334	5.5	0.058	0.001	11.649	0.248	1.508	0.035	528	24	531	11	517	9	522	110
21c	1257	50	25.1	0.109	0.001	9.093	0.301	0.684	0.029	1777	22	673	21	915	25	discordant	
21r	711	96	7.4	0.162	0.002	4.317	0.118	0.192	0.005	2479	17	1344	32	1856	21	discordant	
22	278	191	1.5	0.057	0.002	11.234	0.276	1.551	0.071	498	64	550	13	506	18	discordant	
24	1186	645	1.8	0.057	0.001	11.024	0.161	1.454	0.034	505	25	560	8	532	10	discordant	
25c	998	575	1.7	0.057	0.001	11.163	0.161	1.506	0.034	509	28	553	8	517	9	discordant	
25r	1031	387	2.7	0.068	0.001	6.112	0.084	0.664	0.012	833	68	977	12	934	11	discordant	
26r	648	235	2.8	0.068	0.001	5.865	0.093	0.641	0.013	833	77	1015	15	955	12	discordant	
27	2583	1051	2.5	0.090	0.002	15.760	0.517	1.379	0.040	1434	41	397	12	554	12	discordant	

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					Isotopic ratios						Appa	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
28c	1665	905	1.8	0.079	0.001	17.352	0.362	1.885	0.044	1171	33	361	7	432	8	discordant	
28r	1774	540	3.3	0.066	0.001	15.876	0.240	1.836	0.037	817	32	394	6	442	7	discordant	
30c	170	107	1.6	0.091	0.001	3.940	0.082	0.331	0.009	1445	30	1458	27	1415	20	1428	300
30r	213	138	1.5	0.091	0.001	3.935	0.074	0.325	0.008	1452	28	1460	24	1429	18	1435	210
32r (repeat)	369	135	2.7	0.058	0.001	11.465	0.309	1.574	0.069	546	49	539	14	500	17	discordant	
36 (repeat)	243	210	1.2	0.105	0.001	3.050	0.050	0.221	0.004	1707	26	1829	26	1737	16	discordant	
41 (repeat)	502	193	2.6	0.057	0.001	12.332	0.259	1.680	0.056	483	50	503	10	475	12	discordant	
46 (repeat)	234	41	5.7	0.068	0.002	6.899	0.164	0.802	0.029	857	63	873	19	823	20	discordant	
48 (repeat)	894	379	2.4	0.058	0.001	11.888	0.229	1.553	0.042	531	37	521	9	505	11	514	100
51 (repeat)	395	91	4.3	0.060	0.002	11.204	0.216	1.483	0.044	595	65	551	10	524	12	discordant	

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					Isotop	oic ratios	3			Арра	rent ages	(Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
18c	596	268	2.2	0.058 0.001	12.580	0.308	1.633	0.062	528	40	493	11	485	14	490	10
18r	691	311	2.2	0.065 0.001	12.298	0.261	1.542	0.049	781	42	504	10	508	12	503	8
20	998	612	1.6	0.097 0.001	3.931	0.054	0.288	0.004	1561	13	1462	18	1522	11	discordant	
21	1698	632	2.7	0.081 0.001	12.770	0.166	1.157	0.019	1228	24	486	6	633	8	discordant	
22	3808	859	4.4	0.111 0.001	24.596	0.304	1.499	0.018	1823	11	257	3	519	5	discordant	
9	4292	926	4.6	0.059 0.000	11.478	0.154	1.421	0.020	566	17	539	7	541	6	540	5
8	4303	642	6.7	0.058 0.001	19.505	0.620	2.537	0.130	517	22	322	10	338	14	324	150
6r	1577	553	2.9	0.061 0.001	13.242	0.226	1.580	0.034	635	24	469	8	498	8	discordant	
6c	1185	316	3.7	0.061 0.001	12.364	0.209	1.420	0.030	642	28	502	8	542	9	discordant	
5	659	282	2.3	0.058 0.001	12.097	0.272	1.585	0.051	516	39	512	11	497	12	506	9
2c	1410	891	1.6	0.066 0.001	13.006	0.327	1.435	0.036	822	31	478	11	537	10	discordant	

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				Isotopic ratios							Appa	arent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ma	Concordia	±Ma
1c	138	50	2.8	0.154	0.005	9.696	0.346	0.468	0.024	2392	59	633	21	1162	34	discordant	
1 (repeat)	205	63	3.2	0.059	0.002	12.193	0.412	1.673	0.109	580	71	508	16	476	24	498	200
4	652	268	2.4	0.060	0.001	10.566	0.268	1.331	0.041	586	40	583	14	569	13	575	11
7	921	411	2.2	0.060	0.001	12.558	0.199	1.537	0.036	595	32	494	7	509	9	500	96
10	704	328	2.1	0.061	0.001	11.572	0.193	1.400	0.038	635	38	534	8	548	11	539	7
12r	726	245	3.0	0.059	0.001	12.384	0.205	1.542	0.041	577	36	501	8	508	10	503	6
12c	299	143	2.1	0.059	0.002	12.041	0.283	1.587	0.064	571	59	514	11	497	15	508	10
13	167	86	1.9	0.061	0.002	12.898	0.462	1.862	0.136	622	86	482	16	437	24	468	260
13(repeat)	194	82	2.4	0.060	0.002	12.593	0.369	1.760	0.125	619	75	493	14	457	25	485	190
14c	718	446	1.6	0.060	0.001	10.878	0.220	1.329	0.038	587	33	567	11	570	12	568	9
15c	273	52	5.2	0.071	0.001	6.717	0.178	0.692	0.024	963	39	895	22	908	20	902	17
15r	227	49	4.6	0.075	0.001	5.560	0.144	0.546	0.017	1074	36	1067	25	1057	20	1060	16
8	512	103	5.0	0.059	0.001	10.260	0.277	1.274	0.045	551	44	600	15	589	15	694	12
8(repeat)	978	223	4.4	0.059	0.001	10.244	0.253	1.299	0.038	560	34	601	14	580	13	589	170
6c	170	65	2.6	0.070	0.002	6.739	0.190	0.736	0.030	926	53	892	23	872	23	882	17
6r	208	84	2.5	0.070	0.002	7.179	0.247	0.772	0.038	927	51	841	26	844	27	842	21
7 <b>c</b>	380	253	1.5	0.059	0.001	10.115	0.301	1.292	0.048	582	47	608	17	582	16	594	190
7 <b>r</b>	484	384	1.3	0.063	0.001	10.039	0.306	1.233	0.045	703	43	612	17	603	16	607	13
9c	461	331	1.4	0.062	0.002	13.250	0.425	1.798	0.087	681	71	469	14	449	17	461	11
9r	366	260	1.4	0.060	0.001	12.353	0.377	1.427	0.090	614	50	502	14	540	25	510	210
1c	691	331	2.1	0.057	0.001	10.244	0.179	1.302	0.034	505	35	601	10	579	11	591	150
2	275	159	1.7	0.092	0.001	3.793	0.074	0.302	0.007	1467	25	1509	26	1486	18	1492	16
3	1004	726	1.4	0.097	0.001	12.533	0.245	0.970	0.031	1562	26	495	9	720	16	discordant	
4c	730	1125	0.6	0.161	0.003	15.721	0.234	0.727	0.018	2467	35	398	6	879	15	discordant	

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			Isotopic rat				3			Appa	irent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb $\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
 12	1671	417	4.0	0.058 0.001	11.071	0.194	1.401	0.030	537	35	558	9	548	9	552	7
11	127	58	2.2	0.067 0.004	13.269	0.744	1.861	0.177	835	114	469	24	437	31	457	21
9	393	179	2.2	0.067 0.001	7.747	0.156	0.860	0.025	837	35	783	15	784	16	783	11
8	288	124	2.3	0.057 0.002	11.152	0.344	1.575	0.104	479	60	554	16	499	25	discordant	
10	1109	740	1.5	0.058 0.001	11.559	0.179	1.472	0.036	511	29	535	8	527	10	532	6
13	254	95	2.7	0.059 0.002	10.985	0.260	1.531	0.091	551	79	562	12	511	23	discordant	
14	1412	282	5.0	0.059 0.001	10.947	0.142	1.327	0.025	561	25	564	7	571	8	566	5
15c	369	144	2.6	0.061 0.001	10.894	0.293	1.334	0.048	644	47	566	14	569	15	567	11
15r	920	188	4.9	0.058 0.001	10.828	0.245	1.355	0.033	541	32	570	12	562	10	565	8
17	191	171	1.1	0.159 0.002	2.811	0.072	0.129	0.003	2446	21	1963	43	2207	22	discordant	
16	446	55	8.2	0.071 0.002	5.886	0.163	0.615	0.021	959	47	1012	25	981	21	992	250
4	146	68	2.1	0.063 0.003	10.554	0.374	1.523	0.212	716	104	584	19	513	50	575	290
5	249	86	2.9	0.060 0.002	10.320	0.274	1.367	0.066	617	59	596	15	558	20	582	240
6	436	263	1.7	0.062 0.002	11.343	0.269	1.371	0.052	673	51	545	12	557	16	549	10
7	190	112	1.7	0.062 0.002	12.170	0.668	1.672	0.149	666	74	509	26	476	32	496	22
2a	253	145	1.7	0.085 0.003	12.752	0.363	1.176	0.045	1311	68	487	13	625	17	discordant	
4a	160	84	1.9	0.121 0.007	11.642	0.405	0.854	0.059	1978	96	531	17	788	36	discordant	
5a	155	292	0.5	0.127 0.005	13.057	0.537	0.748	0.040	2063	62	476	18	862	30	discordant	
6a	552	238	2.3	0.054 0.010	12.409	0.221	1.580	0.049	361	376	500	8	498	12	499	7
7a	135	530	0.3	0.104 0.005	12.646	0.512	1.001	0.073	1689	94	491	18	704	35	discordant	

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						Isotop	oic ratios	5			Appa	rent ages	s (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
56c	188	275	0.7	0.060	0.002	12.385	0.563	1.800	0.139	537	125	501	21	449	26	481	350
56r	38	94	0.4	0.068	0.005	13.505	0.983	1.876	0.217	870	153	461	30	434	37	450	26
55	84	88	1.0	0.085	0.006	13.791	0.878	1.554	0.164	1316	132	451	26	505	39	467	310
54c	33	78	0.4	0.069	0.005	12.034	1.124	1.787	0.206	913	152	515	42	451	38	479	400
54r	57	143	0.4	0.063	0.004	11.781	0.506	1.753	0.178	710	134	525	21	459	35	508	380
53	111	141	0.8	0.056	0.003	11.953	0.475	1.893	0.157	470	97	518	19	431	27	discordant	
52	184	318	0.6	0.061	0.002	10.915	0.336	1.387	0.069	633	53	565	16	552	20	560	13
51c	64	239	0.3	0.071	0.001	6.350	0.193	0.660	0.028	961	41	943	26	937	25	940	20
51r	58	316	0.2	0.069	0.001	6.175	0.167	0.646	0.020	901	32	968	24	951	19	956	16
50	38	60	0.6	0.116	0.008	12.068	0.742	0.998	0.111	1896	114	513	29	705	52	discordant	
48	52	167	0.3	0.057	0.002	11.156	0.415	1.639	0.134	509	92	554	19	484	30	discordant	
47a	156	1155	0.1	0.059	0.001	9.726	0.194	1.199	0.028	552	31	631	12	616	11	622	110
46	536	96	5.6	0.094	0.001	3.594	0.061	0.273	0.005	1505	24	1583	24	1565	14	1568	13
45	424	221	1.9	0.071	0.002	12.998	0.331	1.406	0.065	951	59	478	11	546	19	discordant	
44	557	204	2.7	0.063	0.001	9.558	0.199	1.156	0.035	712	44	642	12	633	14	638	10
43	225	68	3.3	0.079	0.002	4.787	0.098	0.453	0.013	1170	38	1223	22	1184	20	1200	260
42	128	136	0.9	0.098	0.003	3.440	0.084	0.265	0.010	1585	48	1646	35	1587	29	1609	380
41	1117	121	9.2	0.095	0.001	3.619	0.057	0.276	0.004	1526	13	1573	22	1555	12	1555	12
40	448	253	1.8	0.059	0.001	10.324	0.229	1.309	0.049	551	42	596	12	577	16	589	130
38c	386	186	2.1	0.058	0.001	10.102	0.235	1.317	0.052	548	44	609	13	574	17	595	230
38r	1033	1091	0.9	0.064	0.001	12.103	0.197	1.392	0.044	757	36	512	8	550	13	discordant	
37	168	78	2.2	0.111	0.002	3.206	0.078	0.219	0.006	1810	29	1751	36	1743	22	1744	20
36	362	126	2.9	0.145	0.002	3.712	0.063	0.187	0.003	2286	18	1538	23	1878	14	discordant	
35	531	215	2.5	0.071	0.001	6.461	0.103	0.655	0.015	960	21	928	14	942	14	934	10
34c	933	54	17.2	0.063	0.001	9.888	0.172	1.153	0.034	722	39	621	10	634	14	625	9
34r	634	585	1.1	0.076	0.001	5.130	0.076	0.486	0.009	1106	30	1149	15	1135	12	1140	10
32	287	313	0.9	0.058	0.002	12.653	0.309	1.795	0.113	511	82	491	11	450	22	482	210
33	333	151	2.2	0.081	0.003	5.009	0.131	0.454	0.016	1223	60	1174	27	1183	24	1178	19

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			Isotopic ratios								Appa	rent ages	s (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
31c	362	121	3.0	0.080	0.001	4.659	0.130	0.431	0.013	1190	29	1254	31	1220	21	1227	270
31r	255	90	2.8	0.059	0.002	10.707	0.466	1.412	0.086	573	56	576	23	544	24	561	18
30	220	119	1.8	0.160	0.002	2.407	0.088	0.108	0.003	2453	23	2241	67	2363	28	discordant	
29c	195	71	2.8	0.161	0.002	2.153	0.059	0.098	0.003	2469	21	2460	55	2457	27	2456	28
29r	556	84	6.7	0.077	0.001	5.048	0.167	0.482	0.015	1121	32	1166	34	1141	21	1142	21
28	743	208	3.6	0.059	0.001	9.875	0.277	1.205	0.037	583	33	622	16	614	14	617	11
27	254	130	2.0	0.091	0.001	3.571	0.073	0.289	0.007	1440	30	1592	28	1520	19	discordant	
25r	340	159	2.1	0.091	0.001	3.776	0.085	0.302	0.007	1449	23	1515	30	1484	17	1489	210
25c	673	371	1.8	0.055	0.001	16.197	0.399	2.227	0.089	409	53	386	9	377	12	383	8
24	96	41	2.4	0.070	0.003	7.632	0.319	0.919	0.077	927	81	794	30	748	42	778	25
23c	224	95	2.4	0.065	0.002	8.102	0.222	0.971	0.045	787	56	751	19	719	23	738	210
23r	82	43	1.9	0.087	0.004	5.884	0.234	0.576	0.051	1370	83	1012	36	1023	54	1015	32
22c	722	117	6.2	0.059	0.001	11.056	0.417	1.392	0.054	556	39	558	19	550	16	553	14
21	168	42	4.0	0.075	0.002	5.708	0.188	0.562	0.024	1058	47	1041	31	1038	27	1039	22
21(repeat)	407	123	3.3	0.109	0.001	2.986	0.088	0.202	0.006	1790	21	1863	46	1813	25	1812	410
18c	290	110	2.6	0.112	0.001	2.897	0.073	0.188	0.005	1838	22	1912	41	1873	21	1873	280
18r	166	33	5.0	0.060	0.003	11.609	0.451	1.641	0.125	612	89	533	19	484	28	517	300
17c	367	127	2.9	0.059	0.002	11.402	0.494	1.491	0.082	556	55	542	22	521	21	531	17
17 <b>r</b>	187	85	2.2	0.064	0.003	11.181	0.536	1.448	0.110	749	83	552	24	534	30	545	21
16	356	313	1.1	0.058	0.001	9.853	0.407	1.285	0.067	532	49	623	24	585	22	602	290
16(repeat)	431	243	1.8	0.063	0.001	9.782	0.328	1.180	0.052	693	50	628	19	624	20	625	15
14	338	134	2.5	0.072	0.002	6.785	0.188	0.715	0.025	990	37	887	22	889	20	887	16
13c	140	81	1.7	0.063	0.003	12.464	0.604	1.700	0.149	710	88	498	22	470	31	488	19
13r	264	201	1.3	0.060	0.002	12.327	0.395	1.590	0.081	614	79	503	15	496	19	500	12
12	170	110	1.6	0.063	0.002	11.414	0.353	1.452	0.106	711	69	542	16	532	29	539	14
10	52	46	1.1	0.076	0.004	5.908	0.309	0.762	0.084	1088	96	1008	47	852	59	discordant	
9	244	156	1.6	0.073	0.001	6.099	0.135	0.625	0.023	1012	37	979	20	971	23	975	15
8c	215	246	0.9	0.076	0.002	5.329	0.120	0.524	0.016	1103	41	1109	23	1085	20	1095	15

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						Isotop		Appa	rent ages	s (Ma)							
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm (2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
7c	119	61	2.0	0.066	0.003	13.054	0.601	1.836	0.198	777	115	476	20	442	36	468	19
7 <b>r</b>	96	47	2.1	0.068	0.004	13.105	0.622	1.864	0.197	857	114	474	21	436	35	464	19
6c	531	187	2.8	0.057	0.001	11.971	0.256	1.598	0.053	498	51	517	10	494	13	508	15
6r	632	214	2.9	0.055	0.001	12.735	0.252	1.743	0.065	427	43	487	9	461	13	discordant	
5c	227	141	1.6	0.214	0.002	1.711	0.028	0.058	0.001	2934	14	2968	39	2946	14	1946	13
4c	188	101	1.9	0.217	0.002	1.743	0.030	0.059	0.001	2963	9	2925	40	2937	16	2936	16
4r	191	28	6.8	0.076	0.002	5.478	0.152	0.548	0.021	1088	42	1081	27	1055	24	1065	22
3	268	191	1.4	0.077	0.002	5.654	0.139	0.554	0.018	1115	40	1050	23	1048	21	1048	16
2c	713	357	2.0	0.073	0.001	6.350	0.152	0.632	0.015	1010	27	943	20	964	14	957	13
2r	108	86	1.3	0.083	0.002	4.721	0.151	0.449	0.027	1261	49	1239	35	1191	40	1218	430
1c	482	80	6.0	0.076	0.001	6.954	0.190	0.676	0.021	1106	34	866	22	923	19	discordant	
1 <b>r</b>	745	34	22.1	0.097	0.001	3.756	0.088	0.282	0.006	1561	16	1522	31	1538	16	1535	16

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						Isotop		Арра	rent ages	s (Ma)							
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ma
70 <b>c</b>	614	223	2.7	0.074	0.001	6.967	0.120	0.709	0.017	1033	27	865	14	894	14	878	190
70 <b>r</b>	963	265	3.6	0.059	0.001	12.477	0.229	1.573	0.038	550	33	497	9	500	9	498	7
69	203	83	2.5	0.072	0.002	6.957	0.193	0.735	0.030	975	50	866	22	873	23	869	17
71	470	235	2.0	0.092	0.001	4.840	0.165	0.385	0.011	1463	26	1211	36	1301	20	discordant	
72	273	299	0.9	0.059	0.002	11.744	0.427	1.530	0.083	557	59	527	18	511	21	520	15
68	107	75	1.4	0.094	0.002	3.902	0.121	0.311	0.011	1503	38	1471	40	1462	28	1464	24
73	91	46	2.0	0.066	0.004	11.831	0.822	1.698	0.160	798	123	523	33	470	33	496	340
67(b)	475	78	6.1	0.146	0.001	2.437	0.055	0.120	0.002	2303	17	2218	41	2272	17	2274	320
75	104	54	1.9	0.282	0.003	1.556	0.043	0.040	0.001	3374	16	3201	69	3303	22	3304	440

	Isotopic ratios										Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
67	204	92	2.2	0.070	0.001	6.509	0.381	0.696	0.040	934	42	922	48	905	33	909	31
66	142	121	1.2	0.061	0.002	12.189	0.378	1.742	0.125	631	76	508	15	461	25	496	270
65	181	101	1.8	0.061	0.002	11.037	0.306	1.488	0.096	637	71	559	14	522	25	550	200
64	660	316	2.1	0.060	0.003	11.039	0.212	1.372	0.037	614	98	559	10	556	11	558	8
63	234	118	2.0	0.076	0.001	5.526	0.113	0.539	0.017	1084	33	1073	20	1066	20	1069	15
62	829	357	2.3	0.072	0.001	9.644	0.253	0.994	0.025	997	30	636	15	707	13	discordant	
61	441	272	1.6	0.073	0.001	6.371	0.189	0.637	0.018	1014	28	940	25	959	17	954	16
59	148	54	2.8	0.186	0.002	2.020	0.055	0.077	0.002	2707	17	2594	57	2686	21	discordant	
58	305	126	2.4	0.076	0.001	6.114	0.173	0.592	0.020	1096	39	977	25	1005	21	993	17
57	237	99	2.4	0.065	0.002	11.446	0.360	1.464	0.088	781	54	540	16	529	24	537	14
56	762	395	1.9	0.180	0.002	2.050	0.053	0.080	0.001	2648	16	2563	53	2650	17	discordant	
55	139	23	6.1	0.068	0.002	6.140	0.220	0.641	0.030	858	59	973	31	955	29	962	24
54	731	187	3.9	0.060	0.001	10.691	0.222	1.311	0.032	597	30	577	11	576	10	576	9
53	130	180	0.7	0.098	0.002	3.713	0.078	0.280	0.007	1589	31	1538	28	1544	21	1541	18
52	1461	419	3.5	0.059	0.001	11.425	0.204	1.432	0.030	552	27	541	9	538	9	539	7
51	335	201	1.7	0.071	0.001	6.851	0.167	0.725	0.021	944	37	879	20	880	17	879	14
50	241	1	162.5	0.062	0.002	9.590	0.243	1.221	0.060	682	58	640	15	608	22	629	190
49	267	131	2.0	0.092	0.001	4.303	0.077	0.347	0.008	1459	28	1348	21	1378	16	1367	200
48	191	115	1.7	0.059	0.002	11.475	0.350	1.567	0.097	584	67	539	15	502	23	527	220
47	276	45	6.1	0.060	0.002	11.498	0.289	1.560	0.075	599	63	538	13	503	18	526	210
46	139	107	1.3	0.063	0.002	12.926	0.539	1.701	0.114	706	76	481	19	470	24	476	15
45	212	108	2.0	0.060	0.002	11.810	0.329	1.550	0.077	612	77	524	14	506	19	518	11
42	99	166	0.6	0.159	0.002	2.191	0.048	0.099	0.002	2447	24	2424	43	2444	20	2440	20
41	370	218	1.7	0.225	0.002	1.859	0.042	0.059	0.001	3016	14	2776	50	2929	16	discordant	
40	328	193	1.7	0.102	0.001	3.731	0.078	0.270	0.006	1662	21	1531	28	1573	17	1565	330
39	515	271	1.9	0.059	0.001	11.939	0.233	1.517	0.050	555	47	519	10	514	13	517	8
38	747	281	2.7	0.060	0.001	12.096	0.240	1.480	0.036	595	35	512	10	525	10	518	7
37	307	119	2.6	0.111	0.001	3.145	0.057	0.209	0.004	1812	17	1780	28	1785	15	1783	15

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	Isotopic ratios									Appa	rent ages	s (Ma)					
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
36	237	153	1.5	0.061	0.002	10.997	0.288	1.398	0.067	625	56	561	14	548	19	557	12
35	72	39	1.9	0.066	0.004	11.586	0.505	1.815	0.194	793	116	534	21	446	35	discordant	
34	159	90	1.8	0.074	0.002	6.574	0.165	0.683	0.028	1037	46	913	21	916	24	914	16
33	35	27	1.3	0.103	0.005	4.036	0.164	0.341	0.022	1675	82	1427	50	1392	47	1407	36
32	69	58	1.2	0.094	0.002	3.937	0.118	0.331	0.013	1499	48	1460	38	1415	28	1429	23
31	192	181	1.1	0.180	0.002	2.280	0.042	0.091	0.002	2657	17	2346	36	2519	16	discordant	
30	264	160	1.6	0.120	0.002	3.062	0.074	0.186	0.005	1950	23	1822	38	1882	20	1847	430
29	396	109	3.6	0.124	0.001	3.571	0.064	0.212	0.003	2015	18	1592	25	1773	14	discordant	
28	131	103	1.3	0.093	0.002	3.998	0.095	0.322	0.011	1491	38	1440	30	1435	26	1436	20
27	249	109	2.3	0.124	0.001	2.742	0.048	0.161	0.003	2016	20	2005	30	2006	14	2004	14
26	85	59	1.4	0.112	0.004	3.085	0.090	0.207	0.007	1833	59	1811	45	1793	28	1797	25
25	95	68	1.4	0.080	0.002	5.114	0.136	0.514	0.024	1189	54	1152	27	1098	31	1127	340
24	754	120	6.3	0.059	0.001	10.496	0.171	1.316	0.031	567	31	587	9	574	10	581	7
23	793	201	3.9	0.060	0.001	10.547	0.170	1.308	0.030	601	29	584	9	577	10	581	7
22	1888	821	2.3	0.072	0.001	28.645	0.657	2.909	0.082	973	32	221	5	300	7	discordant	
21	214	79	2.7	0.095	0.001	4.011	0.071	0.313	0.007	1519	25	1435	22	1457	16	1449	14
20	215	136	1.6	0.071	0.001	6.419	0.149	0.683	0.023	948	42	934	20	916	20	924	14
19	40	109	0.4	0.066	0.003	12.339	0.441	1.668	0.157	819	94	503	17	477	33	497	16
18	247	281	0.9	0.081	0.001	4.892	0.128	0.445	0.014	1223	34	1199	28	1196	21	1196	18
17	806	814	1.0	0.070	0.003	20.551	1.232	2.084	0.126	838	175	306	17	398	19	discordant	
16	148	445	0.3	0.075	0.001	5.857	0.215	0.564	0.018	1072	36	1017	33	1036	20	1033	20
15	40	88	0.5	0.081	0.003	5.863	0.304	0.580	0.043	1233	59	1016	46	1018	45	1016	38
14	209	679	0.3	0.063	0.002	13.616	0.789	1.609	0.075	711	64	457	24	491	17	483	320
13	476	1155	0.4	0.064	0.001	14.363	0.361	1.589	0.043	731	26	434	10	496	10	discordant	
12	108	218	0.5	0.076	0.001	5.862	0.116	0.603	0.021	1089	34	1016	18	994	21	1006	15
11	139	324	0.4	0.059	0.001	11.437	0.253	1.529	0.064	574	53	541	11	511	16	531	170
10	324	1181	0.3	0.150	0.002	3.253	0.075	0.157	0.004	2348	21	1729	34	2029	19	discordant	
9	124	291	0.4	0.117	0.002	3.373	0.052	0.208	0.004	1906	33	1674	22	1788	15	discordant	

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						Isotop	oic ratio	s			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb		<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
8	100	206	0.5	0.059	0.002	11.889	0.422	1.790	0.139	584	87	521	17	451	27	discordant	
7	164	96	1.7	0.077	0.002	5.417	0.114	0.539	0.020	1119	41	1092	21	1066	24	1080	16
6	835	263	3.2	0.306	0.002	2.824	0.077	0.067	0.002	3500	10	1955	45	2810	25	discordant	
5	154	251	0.6	0.058	0.002	13.045	0.454	1.932	0.152	533	74	476	15	424	26	discordant	
4	173	96	1.8	0.091	0.002	4.194	0.091	0.341	0.009	1438	40	1379	27	1391	19	1387	17
3	236	177	1.3	0.094	0.001	3.783	0.063	0.291	0.006	1511	33	1513	22	1515	17	1513	14
2	1066	588	1.8	0.070	0.001	6.927	0.098	0.724	0.012	933	21	870	11	882	10	876	8
1	464	101	4.6	0.067	0.001	7.883	0.146	0.853	0.020	852	32	770	9	788	12	779	120

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					Isotop	pic ratios	\$			Appa	rent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ)	<sup>206</sup> Pb	$\pm(2\sigma)$	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
17c	264	82	3.2	0.073 0.001	6.112	0.148	0.625	0.021	1005	35	977	22	971	20	973	16
18r	633	368	1.7	0.132 0.001	2.487	0.040	0.138	0.002	2123	14	2179	29	2146	12	2144	200
16c	121	65	1.9	0.099 0.002	3.518	0.088	0.264	0.009	1597	37	1613	35	1592	27	1599	23
19r	148	49	3.0	0.068 0.002	7.578	0.230	0.872	0.045	865	62	799	22	777	27	790	18
20r	65	10	6.8	0.081 0.004	5.915	0.246	0.678	0.068	1224	101	1007	37	921	57	980	510
21	691	458	1.5	0.060 0.001	9.327	0.189	1.161	0.033	605	32	657	12	631	13	644	190
22	248	148	1.7	0.059 0.002	10.396	0.271	1.400	0.074	575	56	592	14	548	22	discordant	
23	106	76	1.4	0.270 0.003	1.984	0.044	0.054	0.001	3307	17	2632	47	3022	19	discordant	
24r	171	119	1.4	0.244 0.002	1.890	0.045	0.056	0.001	3149	15	2739	52	2991	20	discordant	
25c	1044	783	1.3	0.082 0.001	6.604	0.089	0.597	0.011	1257	23	909	11	1000	12	discordant	
26(a) c	1681	1163	1.4	0.068 0.001	18.060	0.550	1.910	0.061	873	25	348	10	428	11	discordant	
26r	736	271	2.7	0.059 0.001	11.551	0.227	1.487	0.043	579	40	535	10	522	12	530	8
27c	108	317	0.3	0.145 0.002	2.398	0.054	0.120	0.003	2282	24	2248	42	2269	20	2264	19
27(a)	61	242	0.3	0.120 0.008	13.892	1.088	0.999	0.086	1955	120	448	32	705	41	discordant	

	Isotopic ratios									Appa	rent ages	; (Ma)					
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		$^{207}$ Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
27(b)	186	30	6.1	0.099	0.003	12.666	0.456	0.972	0.048	1605	54	490	16	719	24	discordant	
28	115	87	1.3	0.134	0.002	2.665	0.065	0.144	0.004	2151	26	2055	42	2108	24	2095	320
29	515	85	6.1	0.072	0.001	5.690	0.100	0.568	0.012	988	29	1044	17	1032	14	1036	11
30	300	161	1.9	0.092	0.001	4.063	0.066	0.319	0.007	1462	25	1419	20	1443	17	1432	14
30(a)	105	63	1.7	0.060	0.003	12.654	0.708	1.879	0.205	612	92	491	25	434	35	471	340
30(b)	540	347	1.6	0.058	0.001	11.736	0.287	1.494	0.054	518	39	527	12	521	14	524	10
30(d)	168	26	6.4	0.138	0.004	11.314	0.337	0.684	0.027	2208	47	546	15	915	23	discordant	
31	1494	1129	1.3	0.082	0.001	12.719	0.172	1.128	0.022	1240	20	488	6	645	9	discordant	
34c	703	217	3.2	0.059	0.001	10.729	0.219	1.340	0.041	595	6	575	11	567	13	571	9
35	394	52	7.6	0.076	0.001	4.970	0.094	0.471	0.012	1108	30	1182	20	1157	17	1167	170
36	369	285	1.3	0.075	0.001	5.154	0.190	0.500	0.018	1062	33	1143	37	1116	24	1120	24
37	161	165	1.0	0.062	0.002	11.677	0.493	1.627	0.134	674	82	530	21	487	30	516	260
38	259	113	2.3	0.108	0.001	3.199	0.101	0.215	0.006	1758	24	1754	47	1760	23	1758	23
39	423	179	2.4	0.069	0.001	6.635	0.162	0.730	0.020	893	41	905	20	877	16	886	200
40	2201	913	2.4	0.070	0.001	17.386	0.477	1.791	0.044	929	26	361	9	451	9	discordant	
75	196	134	1.5	0.063	0.002	9.460	0.326	1.209	0.084	684	73	648	21	612	30	637	18
74(a)	103	55	1.9	0.075	0.002	6.677	0.240	0.725	0.050	1075	65	900	29	881	39	893	25
74(b)	71	560	0.1	0.175	0.007	11.287	0.686	0.468	0.051	2609	69	547	30	1162	70	discordant	
73	1405	474	3.0	0.061	0.001	12.993	0.320	1.565	0.044	637	28	478	11	502	11	discordant	
72c	183	71	2.6	0.236	0.002	1.588	0.035	0.047	0.001	3094	16	3150	54	3149	19	3147	19
71	314	97	3.2	0.061	0.002	10.699	0.329	1.338	0.055	649	53	576	16	567	17	572	13
69	436	135	3.2	0.058	0.001	10.314	0.241	1.337	0.054	533	48	597	13	567	17	586	200
68	648	433	1.5	0.057	0.001	11.950	0.280	1.574	0.058	506	37	518	11	500	14	511	140
67c	141	66	2.1	0.200	0.002	1.933	0.046	0.071	0.002	2822	17	2689	52	2760	22	2757	410
66	216	128	1.7	0.078	0.002	7.662	0.218	0.791	0.040	1139	58	791	21	830	28	804	250
64	151	104	1.5	0.118	0.002	2.976	0.073	0.184	0.005	1928	26	1868	39	1890	24	1883	22
65	658	252	2.6	0.061	0.001	9.837	0.189	1.185	0.035	635	37	624	11	622	13	623	9
63	806	354	2.3	0.059	0.001	10.797	0.237	1.348	0.035	555	34	571	12	564	11	567	9

						Isotop	pic ratios	3			Appa	rent ages	s (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
61r	702	194	3.6	0.060	0.001	11.263	0.220	1.389	0.039	597	38	549	10	551	12	549	8
60 <b>r</b>	361	206	1.8	0.060	0.001	11.950	0.291	1.510	0.059	591	46	518	12	516	15	517	10
62r	218	43	5.1	0.058	0.002	11.802	0.391	1.615	0.091	546	67	524	16	490	21	511	210
59	354	134	2.6	0.061	0.001	10.583	0.263	1.329	0.053	631	45	582	13	570	17	577	11
58	389	146	2.7	0.059	0.001	11.890	0.304	1.526	0.058	571	50	521	12	512	15	517	10
57	392	138	2.8	0.060	0.002	12.480	0.310	1.574	0.059	604	76	497	12	500	14	498	10
56	617	348	1.8	0.065	0.002	11.818	0.470	1.391	0.051	789	51	524	19	550	15	541	220
54	219	22	9.8	0.072	0.002	5.651	0.182	0.586	0.024	988	43	1051	30	1011	26	1026	300
53	77	116	0.7	0.068	0.004	13.105	0.828	2.126	0.265	866	115	474	27	392	37	discordant	
52	239	260	0.9	0.084	0.001	4.999	0.116	0.427	0.012	1301	33	1176	24	1226	20	1205	340
51	304	169	1.8	0.125	0.002	2.683	0.055	0.156	0.003	2034	43	2043	35	2038	16	2037	16
55	944	62	15.1	0.076	0.001	9.897	0.360	1.089	0.044	1084	34	621	21	662	19	discordant	
50	228	202	1.1	0.064	0.002	11.112	0.294	1.406	0.075	727	68	556	14	546	22	553	12
49	553	550	1.0	0.059	0.001	11.760	0.255	1.476	0.047	550	40	526	11	526	13	526	9
48	252	175	1.4	0.062	0.002	11.459	0.336	1.485	0.080	673	60	540	15	523	21	534	13
47	448	423	1.1	0.071	0.001	6.290	0.123	0.658	0.016	944	31	951	17	939	15	944	12
46	293	126	2.3	0.059	0.002	10.690	0.241	1.379	0.072	571	55	577	12	554	21	571	11
45	478	257	1.9	0.060	0.001	10.249	0.194	1.291	0.040	598	47	600	11	583	13	593	110
42	441	174	2.5	0.062	0.002	9.613	0.188	1.203	0.040	687	74	638	12	615	15	629	150
41	302	152	2.0	0.117	0.001	2.851	0.045	0.178	0.003	1914	19	1939	26	1921	14	1924	13
15	489	394	1.2	0.061	0.002	12.303	0.351	1.470	0.066	623	44	504	13	527	18	511	170
14	1033	166	6.2	0.076	0.001	5.278	0.067	0.509	0.008	1094	16	1119	13	1104	10	1109	8
13	546	76	7.2	0.061	0.002	10.999	0.314	1.359	0.057	623	77	561	15	560	18	561	13
12	377	173	2.2	0.069	0.001	6.937	0.136	0.758	0.022	885	33	868	16	855	16	861	12
11	402	288	1.4	0.059	0.001	11.384	0.251	1.482	0.059	569	47	543	11	524	16	537	120
10	407	293	1.4	0.156	0.001	2.616	0.046	0.123	0.002	2413	14	2088	31	2244	14	discordant	
9	586	397	1.5	0.060	0.001	11.905	0.271	1.467	0.053	607	35	520	11	528	14	522	11
8	164	60	2.7	0.065	0.002	12.360	0.438	1.630	0.120	777	74	502	17	486	27	498	15

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					Isoto	pic ratio	s			Арра	irent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2	2σ) <sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
44	406	205	2.0	0.060 0.0	01 10.944	0.244	1.389	0.047	594	44	564	12	551	14	558	9
43	362	105	3.4	0.060 0.0	01 10.094	0.242	1.277	0.049	614	47	609	14	588	17	601	150
7	385	340	1.1	0.059 0.0	02 28.278	1.400	3.850	0.227	570	83	224	10	235	12	229	9
6	96	37	2.6	0.069 0.0	03 8.926	0.446	1.088	0.097	894	75	685	31	663	41	679	26
5	511	132	3.9	0.059 0.0	01 10.526	0.338	1.324	0.047	580	49	585	17	572	15	577	12
4	1225	457	2.7	0.060 0.0	01 12.922	0.346	1.617	0.049	588	31	481	12	489	12	485	140
3	456	115	4.0	0.072 0.0	01 9.448	0.311	1.040	0.045	991	36	649	20	685	21	665	280
2	338	116	2.9	0.075 0.0	01 5.900	0.130	0.582	0.017	1061	31	1010	20	1016	18	1013	17
1	69	59	1.2	0.071 0.0	05 13.423	0.843	1.834	0.208	954	133	463	26	442	37	457	24

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						Isotop	oic ratios	s			Appa	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1	370	156	2.4	0.060	0.001	11.185	0.323	1.516	0.071	615	47	552	15	515	18	discordant	
2	323	164	2.0	0.060	0.001	11.357	0.382	1.474	0.063	612	50	544	17	526	17	535	13
3	222	170	1.3	0.082	0.001	4.631	0.126	0.417	0.012	1240	34	1261	30	1243	21	1247	19
4c	695	45	15.5	0.191	0.002	2.751	0.065	0.105	0.002	2751	14	2000	40	2393	18	discordant	
5	145	195	0.7	0.084	0.002	4.534	0.148	0.415	0.015	1284	39	1285	37	1246	26	1257	23
7	402	274	1.5	0.059	0.001	10.833	0.335	1.421	0.059	585	48	569	16	541	17	555	210
6	453	305	1.5	0.057	0.001	11.632	0.323	1.573	0.056	504	43	532	14	500	14	discordant	
31	90	39	2.3	0.065	0.004	12.438	0.656	1.896	0.184	785	115	499	24	430	31	437	420
32	193	92	2.1	0.058	0.002	12.112	0.448	1.787	0.139	524	82	512	18	452	27	discordant	
33	373	80	4.7	0.218	0.002	1.566	0.041	0.047	0.001	2968	16	3184	64	3145	19	3139	19
34a	124	63	2.0	0.262	0.003	1.569	0.040	0.044	0.001	3256	22	3180	63	3228	20	3229	20
34	302	112	2.7	0.059	0.001	10.131	0.260	1.500	0.046	555	54	607	15	519	12	discordant	

Sample 295-12- Kound 1, Page	Samp	e 295-1	12- R	lound	1, I	Page	2
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						Isotop	oic ratios	3			Арра	rent ages	(Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
33	906	280	3.2	0.057	0.001	11.412	0.225	1.489	0.033	502	36	542	10	522	9	discordant	
35	99	43	2.3	0.095	0.002	3.611	0.081	0.296	0.012	1525	40	1576	31	1501	31	discordant	
36	326	38	8.6	0.075	0.001	5.415	0.094	0.543	0.011	1059	32	1093	17	1061	13	1071	250
37	253	166	1.5	0.095	0.001	3.604	0.061	0.283	0.005	1529	27	1579	23	1536	15	discordant	
38	453	167	2.7	0.070	0.001	6.621	0.111	0.709	0.014	923	32	907	14	894	11	898	10
40	1248	319	3.9	0.060	0.001	11.121	0.158	1.362	0.025	615	29	555	7	559	8	557	6
41	159	103	1.5	0.072	0.002	12.932	0.329	1.565	0.079	981	69	480	11	502	19	485	10
42	182	208	0.9	0.143	0.002	2.140	0.034	0.110	0.002	2262	21	2473	32	2345	15	discordant	
43	699	129	5.4	0.059	0.001	9.726	0.165	1.230	0.024	565	31	631	10	604	9	discordant	
44	245	270	0.9	0.061	0.002	9.707	0.203	1.265	0.039	633	57	632	12	592	13	discordant	
45c	209	145	1.4	0.062	0.003	13.692	0.966	1.778	0.140	684	87	455	29	453	27	454	24
45r	386	313	1.2	0.062	0.003	14.453	1.293	1.872	0.178	681	90	431	34	435	31	433	31
46	282	113	2.5	0.060	0.002	12.317	0.391	1.620	0.084	588	71	503	15	488	19	498	13
47	181	83	2.2	0.111	0.002	3.189	0.072	0.211	0.006	1815	27	1759	34	1774	23	1769	22
48	299	158	1.9	0.065	0.002	10.425	0.371	1.223	0.056	778	52	591	19	607	20	598	16
49	198	112	1.8	0.200	0.002	1.875	0.033	0.067	0.001	2829	20	2756	39	2808	15	2809	280
51	700	65	10.7	0.059	0.001	10.903	0.199	1.387	0.035	571	34	566	10	551	11	559	110
50	119	195	0.6	0.065	0.003	10.940	0.433	1.469	0.113	783	91	564	21	528	30	552	18
52	262	148	1.8	0.072	0.002	6.643	0.232	0.684	0.027	980	46	904	29	915	23	911	20
53	236	88	2.7	0.194	0.002	2.008	0.060	0.075	0.002	2778	16	2606	63	2702	23	discordant	
55	141	100	1.4	0.067	0.002	8.964	0.374	1.097	0.069	835	64	682	26	658	29	671	21
54	37	33	1.1	0.083	0.004	5.730	0.326	0.612	0.058	1263	82	1037	52	984	57	1013	41
30	156	80	1.9	0.182	0.002	3.485	0.069	0.146	0.003	2671	20	1627	28	2094	17	discordant	
29	417	241	1.7	0.058	0.001	11.377	0.238	1.500	0.059	533	48	543	11	519	16	536	160
28	627	281	2.2	0.060	0.001	13.053	0.441	1.625	0.063	612	47	476	15	487	14	482	12
27c	212	129	1.6	0.100	0.002	4.310	0.170	0.300	0.012	1623	40	1345	46	1490	30	discordant	
27r	197	134	1.5	0.098	0.003	4.298	0.188	0.322	0.013	1577	49	1349	51	1435	30	1417	570
26	1717	544	3.2	0.063	0.002	16.723	1.377	1.948	0.150	708	61	375	28	421	25	discordant	

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					Isotop	oic ratios	3			Appa	arent ages	(Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
25	1213	452	2.7	0.063 0.002	15.132	1.363	1.685	0.133	716	61	413	33	473	28	discordant	
24	59	42	1.4	0.101 0.005	5.297	0.705	0.412	0.062	1642	83	1115	121	1252	99	1203	1300
23	583	325	1.8	0.062 0.001	9.150	0.354	1.094	0.042	673	49	669	24	660	18	662	16
22	284	76	3.7	0.077 0.002	6.465	0.624	0.614	0.052	1112	55	927	77	982	50	971	52
21	984	197	5.0	0.084 0.002	9.835	0.942	0.826	0.068	1294	55	624	52	806	43	discordant	
20	232	127	1.8	0.074 0.002	6.786	0.395	0.680	0.036	1045	49	887	46	919	31	909	20
19	222	130	1.7	0.063 0.002	12.065	0.913	1.544	0.131	697	35	514	35	507	32	510	27
18	171	116	1.5	0.061 0.002	13.556	0.980	1.806	0.154	646	76	459	30	448	29	453	23
17	338	197	1.7	0.226 0.004	1.909	0.115	0.061	0.003	3021	27	2717	127	2909	44	discordant	
16	483	75	6.5	0.059 0.001	12.683	0.735	1.609	0.087	583	53	489	26	491	20	490	19
15	121	96	1.3	0.068 0.003	13.441	0.814	1.816	0.162	869	85	463	26	446	30	456	22
13	192	63	3.0	0.065 0.002	10.772	0.394	1.273	0.076	764	65	573	19	589	26	578	17
12	55	19	2.9	0.082 0.003	5.841	0.339	0.612	0.054	1256	77	1019	52	984	53	1001	43
11	81	178	0.5	0.082 0.003	5.331	0.353	0.508	0.035	1240	64	1109	64	1105	44	1105	41
10	320	284	1.1	0.063 0.002	10.456	0.372	1.281	0.060	694	57	589	19	586	20	587	16
9c	171	136	1.3	0.063 0.002	11.127	0.568	1.467	0.097	715	72	555	26	528	26	541	21
9r	132	93	1.4	0.062 0.003	11.278	0.662	1.512	0.125	669	88	548	29	516	31	533	24

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						Isotop	oic ratios	5			Appa	rent ages	; (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm (2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
1	370	156	2.4	0.097	0.009	4.391	0.135	0.375	0.018	1572	168	1323	36	1321	34	1321	26
2	323	164	2.0	0.071	0.002	7.933	0.147	0.838	0.019	960	52	766	13	798	13	discordant	
3	222	170	1.3	0.063	0.001	14.097	0.276	1.738	0.052	714	29	442	8	462	11	449	130
4	695	45	15.5	0.059	0.002	13.364	0.319	1.839	0.088	577	57	465	10	441	17	459	140
5	145	195	0.7	0.058	0.002	12.775	0.222	1.681	0.046	532	60	486	8	474	10	481	6
6	402	274	1.5	0.075	0.001	18.002	0.265	1.988	0.041	1081	31	349	5	414	7	discordant	
7	453	305	1.5	0.061	0.003	13.233	0.386	1.786	0.102	653	85	470	13	452	20	464	11
8	90	39	2.3	0.060	0.001	12.947	0.301	1.668	0.068	601	49	480	11	477	15	479	9
9	193	92	2.1	0.062	0.001	14.272	0.268	1.737	0.046	679	27	437	8	462	10	discordant	
10	373	80	4.7	0.052	0.009	15.267	0.635	2.165	0.145	283	368	409	16	386	20	400	13
11	124	63	2.0	0.059	0.001	14.524	0.250	1.831	0.045	558	28	429	7	443	9	438	83
12	302	112	2.7	0.066	0.001	15.890	0.221	1.822	0.035	805	31	394	5	445	7	discordant	
13	906	280	3.2	0.112	0.003	8.886	0.310	0.602	0.028	1825	47	688	22	994	29	discordant	
14	99	43	2.3	0.191	0.002	2.240	0.040	0.084	0.001	2752	15	2380	35	2598	14	discordant	
15	326	38	8.6	0.075	0.001	5.658	0.090	0.551	0.013	1077	37	1050	15	1051	16	1050	11
16	253	166	1.5	0.057	0.001	12.803	0.190	1.636	0.038	507	28	485	7	485	9	485	6
17	453	167	2.7	0.058	0.001	12.156	0.183	1.530	0.037	542	44	510	7	511	10	510	6
18	1248	319	3.9	0.091	0.001	4.077	0.065	0.321	0.006	1431	36	1414	20	1438	14	1430	170
19	159	103	1.5	0.069	0.002	7.166	0.236	0.755	0.041	910	60	842	25	857	30	848	21
20	182	208	0.9	0.098	0.001	3.672	0.066	0.269	0.005	1586	21	1553	25	1576	16	1570	15
21	699	129	5.4	0.058	0.001	12.467	0.179	1.531	0.031	547	24	498	7	511	8	503	87
22	245	270	0.9	0.071	0.002	6.575	0.158	0.704	0.027	952	42	913	20	898	22	906	15
23	209	145	1.4	0.059	0.002	11.302	0.221	1.427	0.043	554	57	547	10	540	12	544	8
24	386	313	1.2	0.067	0.001	8.033	0.306	0.903	0.040	833	44	757	26	757	23	757	20
25	282	113	2.5	0.073	0.002	6.843	0.218	0.769	0.050	1003	62	880	25	847	36	868	21
26	181	83	2.2	0.058	0.001	12.117	0.259	1.588	0.060	515	45	511	10	496	14	506	9
27	299	158	1.9	0.072	0.004	9.688	0.563	1.196	0.115	975	106	633	33	617	42	627	28
29	198	112	1.8	0.066	0.001	25.689	1.234	3.456	0.094	792	18	246	11	258	6	257	90

					Isoto	pic ratio	s			Арра	rent age	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2	2σ) <sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
30	700	65	10.7	0.067 0.0	01 8.212	0.161	0.910	0.030	833	35	741	13	753	17	745	11
31	119	195	0.6	0.064 0.0	13 12.201	0.357	1.663	0.105	748	389	508	14	478	23	501	180
32	262	148	1.8	0.063 0.0	06 12.127	0.417	2.358	1.436	720	194	511	16	359	122	514	17
33	236	88	2.7	0.086 0.0	03 5.593	0.227	0.593	0.050	1339	73	1061	38	1004	51	1040	33
34	141	100	1.4	0.059 0.0	01 12.563	0.217	1.612	0.046	559	43	494	8	490	11	492	7

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						Isotop	oic ratio	S			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm (2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1	127	66	1.9	0.078	0.002	5.720	0.185	0.545	0.022	1146	49	1039	30	1058	26	1050	22
2	59	59	1.0	0.099	0.003	4.052	0.164	0.317	0.016	1613	55	1422	50	1446	39	1437	34
3(a)	292	208	1.4	0.058	0.002	12.255	0.321	1.634	0.082	536	55	506	12	485	19	500	11
4	430	129	3.3	0.081	0.001	4.856	0.085	0.435	0.009	1215	25	1207	19	1213	15	1211	13
5	132	129	1.0	0.065	0.003	12.152	0.445	1.607	0.133	776	88	510	17	492	30	505	16
6	334	203	1.6	0.060	0.001	12.149	0.283	1.553	0.073	589	53	510	11	505	18	509	10
9	196	109	1.8	0.059	0.002	11.973	0.438	1.692	0.114	556	73	517	18	472	24	501	270
10	1192	49	24.2	0.061	0.001	10.467	0.181	1.264	0.029	655	30	588	10	592	10	599	8
11	138	334	0.4	0.059	0.002	10.902	0.417	1.469	0.093	583	79	566	20	528	25	551	250
12	295	106	2.8	0.061	0.001	10.594	0.261	1.312	0.056	641	49	582	13	576	18	579	11
13	553	356	1.6	0.058	0.001	12.605	0.254	1.611	0.052	511	40	492	9	491	12	491	8
13(a)	516	286	1.8	0.057	0.001	12.034	0.246	1.596	0.053	475	44	515	10	494	13	507	130
14	487	268	1.8	0.074	0.001	5.589	0.095	0.546	0.012	1041	27	1061	16	1058	14	1059	12
15	237	110	2.2	0.077	0.001	5.256	0.108	0.510	0.015	1118	36	1123	21	1103	20	1112	15
16	591	248	2.4	0.076	0.001	5.303	0.092	0.509	0.010	1091	24	1114	17	1104	13	1106	11
19	123	58	2.1	0.069	0.003	8.594	0.274	1.018	0.054	910	92	710	21	695	26	704	17

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						Isotop	oic ratios	5			Арра	rent ages	(Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		$^{207}$ Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
17	130	75	1.7	0.155	0.002	2.552	0.070	0.119	0.003	2405	22	2132	48	2279	23	discordant	
20	353	156	2.3	0.059	0.001	11.755	0.279	1.522	0.063	553	49	526	12	513	16	522	10
20(a)	678	33	20.4	0.061	0.001	10.384	0.263	1.257	0.038	638	36	593	14	595	13	593	10
21	71	35	2.0	0.067	0.004	13.275	0.794	2.143	0.252	843	116	468	26	389	35	discordant	
22	834	143	5.8	0.059	0.001	11.454	0.372	1.409	0.047	562	35	540	16	545	14	543	12
23	485	192	2.5	0.062	0.001	9.443	0.285	1.141	0.043	659	37	649	18	640	17	644	14
24	1536	764	2.0	0.059	0.001	10.813	0.293	1.320	0.033	557	30	570	14	573	11	572	10
25	408	222	1.8	0.057	0.001	12.261	0.299	1.588	0.058	497	53	506	12	496	14	502	9
26	230	258	0.9	0.056	0.002	12.061	0.442	1.733	0.097	465	67	514	17	463	20	discordant	
27	528	213	2.5	0.077	0.001	5.510	0.145	0.524	0.013	1120	26	1076	25	1085	17	1082	16
28	250	69	3.6	0.092	0.003	12.145	0.400	1.173	0.063	1464	55	510	16	627	24	discordant	
30	152	72	2.1	0.145	0.002	3.823	0.142	0.196	0.007	2286	29	1499	48	1839	31	discordant	
30(a)	255	228	1.1	0.060	0.002	11.183	0.468	1.464	0.086	619	58	552	21	529	23	541	17
31	234	138	1.7	0.100	0.001	3.528	0.118	0.257	0.008	1628	26	1609	46	1612	24	1610	24
30(b)	437	279	1.6	0.081	0.002	12.785	0.392	1.192	0.041	1218	54	486	14	619	15	discordant	
34	1140	165	6.9	0.059	0.001	11.035	0.326	1.362	0.043	584	30	559	15	560	13	559	12
37	101	82	1.2	0.069	0.005	13.157	0.639	1.981	0.190	898	138	472	21	415	30	545	350
36	3593	60	60.2	0.061	0.001	16.034	0.406	1.931	0.044	629	21	390	9	424	8	discordant	
38	253	72	3.5	0.062	0.002	11.965	0.429	1.584	0.095	681	61	518	17	497	22	510	15
39	521	79	6.6	0.057	0.001	11.937	0.311	1.518	0.054	509	44	519	13	514	14	517	10
40	102	78	1.3	0.089	0.002	3.931	0.104	0.336	0.013	1404	36	1462	34	1403	29	1425	400
41	153	54	2.8	0.098	0.002	4.166	0.113	0.308	0.009	1592	39	1388	33	1468	23	discordant	
42	1143	299	3.8	0.060	0.001	11.131	0.237	1.357	0.032	587	32	555	11	561	10	558	9
43	88	58	1.5	0.067	0.003	9.683	0.404	1.403	0.138	833	95	634	24	547	39	discordant	
44(a)	275	113	2.4	0.070	0.002	9.346	0.257	1.105	0.043	938	51	656	17	655	18	655	13
44	171	138	1.2	0.066	0.003	12.639	0.468	1.570	0.086	792	81	491	17	501	21	495	14
45	160	225	0.7	0.113	0.002	3.043	0.082	0.197	0.005	1846	26	1832	42	1833	23	1831	22
46	744	46	16.3	0.060	0.001	10.200	0.265	1.254	0.033	594	33	603	15	596	12	598	10

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						Isotop	oic ratios	S			Appa	arent ages					
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
47	306	96	3.2	0.136	0.002	3.888	0.093	0.202	0.004	2179	24	1476	31	1813	18	discordant	
48	118	67	1.8	0.062	0.002	13.001	0.603	1.847	0.165	690	79	478	20	440	30	466	230
49	571	468	1.2	0.059	0.001	10.707	0.276	1.322	0.042	595	33	576	14	572	14	574	11
50	1389	499	2.8	0.061	0.001	12.144	0.256	1.425	0.032	639	29	510	10	540	9	discordant	
51	357	203	1.8	0.093	0.001	3.969	0.088	0.310	0.007	1483	24	1449	28	1464	17	1460	17
52	484	303	1.6	0.058	0.001	12.126	0.290	1.605	0.058	540	44	511	11	492	14	503	130
52(repeat)	311	160	1.9	0.057	0.001	12.153	0.317	1.624	0.069	506	54	510	12	488	16	501	150
52(a)	213	160	1.3	0.075	0.001	6.035	0.147	0.610	0.020	1062	39	989	22	986	20	987	10
48(a)	223	68	3.3	0.062	0.002	10.254	0.281	1.349	0.075	676	57	600	15	564	23	589	220
53	68	54	1.3	0.072	0.004	10.641	0.584	1.498	0.185	980	102	579	29	520	46	562	340
53(a)	447	263	1.7	0.061	0.001	11.498	0.282	1.472	0.050	640	42	538	12	527	14	533	10
54	575	163	3.5	0.059	0.001	10.966	0.236	1.374	0.043	595	28	563	11	556	13	560	9
55	628	229	2.7	0.059	0.001	10.895	0.263	1.354	0.040	571	38	566	13	562	12	564	10

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						Isotop	oic ratio	S		Apparent ages (Ma)							
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb :	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
2	238	32	7.5	0.209	0.002	2.165	0.065	0.075	0.002	2897	15	2449	60	2711	25	discordant	
1	479	288	1.7	0.059	0.001	12.049	0.455	1.501	0.064	560	46	514	18	519	17	516	14
3	257	110	2.3	0.078	0.002	10.825	0.431	1.241	0.077	1167	31	570	21	600	27	580	18
4	574	234	2.5	0.066	0.001	12.193	0.350	1.392	0.045	794	44	508	14	550	13	discordant	
5	420	63	6.7	0.059	0.001	11.231	0.344	1.420	0.052	558	50	550	16	542	15	545	11
5(repeat)	133	84	1.6	0.061	0.003	11.729	0.496	1.752	0.194	643	88	528	21	459	38	512	370
6	502	226	2.2	0.122	0.001	2.887	0.072	0.170	0.004	1992	19	1918	40	1961	20	1957	280
11	537	268	2.0	0.121	0.001	3.335	0.073	0.199	0.004	1975	18	1691	32	1823	17	discordant	

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	Isotopic ratios								Apparent ages (Ma)								
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		$^{207}$ Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
12	376	86	4.4	0.102	0.001	3.516	0.085	0.249	0.005	1659	21	1614	34	1639	16	1636	16
13	513	167	3.1	0.084	0.001	4.485	0.109	0.390	0.009	1303	23	1298	28	1291	16	1291	16
14	498	69	7.2	0.067	0.001	11.826	0.325	1.286	0.044	824	39	523	13	585	15	discordant	
15	179	72	2.5	0.086	0.002	4.428	0.120	0.381	0.014	1344	35	1313	32	1308	26	1309	22
23	173	77	2.3	0.061	0.002	10.877	0.369	1.480	0.106	628	67	567	18	524	28	555	260
24	258	139	1.9	0.099	0.001	3.594	0.080	0.261	0.006	1610	28	1583	31	1601	19	1596	18
25	305	43	7.1	0.237	0.002	2.080	0.046	0.064	0.001	3099	16	2532	45	2858	16	discordant	
26	159	98	1.6	0.061	0.003	12.705	0.522	1.718	0.116	626	90	489	19	466	24	480	15
27	26	39	0.7	0.106	0.005	4.350	0.268	0.367	0.031	1727	86	1334	70	1337	60	1335	48
28	656	563	1.2	0.074	0.002	12.378	0.302	1.386	0.048	1051	42	501	11	552	14	discordant	
29c	273	79	3.5	0.205	0.003	4.342	0.107	0.167	0.004	2864	20	1337	29	1975	21	discordant	
31	134	141	0.9	0.059	0.002	11.994	0.457	1.690	0.135	582	81	516	18	472	28	504	260
39	155	63	2.4	0.059	0.003	12.823	0.655	1.881	0.155	567	91	484	23	433	27	463	350
32	183	76	2.4	0.058	0.002	11.144	0.379	1.569	0.100	514	71	554	18	501	24	discordant	
34	97	209	0.5	0.063	0.003	11.958	0.534	1.957	0.360	694	99	518	21	419	55	506	400
33	163	126	1.3	0.060	0.002	11.671	0.407	1.646	0.119	604	83	530	17	482	26	516	290
35	455	117	3.9	0.104	0.001	3.411	0.074	0.237	0.005	1690	22	1658	31	1680	19	1676	19
36	699	417	1.7	0.065	0.001	12.078	0.349	1.492	0.049	793	36	513	14	521	13	517	11
37	514	37	13.8	0.093	0.001	4.795	0.104	0.368	0.008	1490	29	1221	24	1333	16	discordant	
38	274	85	3.2	0.061	0.002	12.231	0.400	1.562	0.079	650	65	507	15	503	19	505	13
38(a)	179	161	1.1	0.087	0.003	12.586	0.548	1.111	0.060	1355	64	493	20	652	25	discordant	
22(a)	173	295	0.6	0.088	0.003	12.658	0.694	1.105	0.071	1390	72	490	25	655	29	discordant	
22	1376	545	2.5	0.067	0.001	13.820	0.426	1.401	0.039	832	33	451	13	547	11	discordant	
21	1352	771	1.8	0.072	0.002	16.357	0.659	1.501	0.047	989	43	383	14	519	12	discordant	
20	166	38	4.4	0.069	0.002	8.363	0.297	0.932	0.048	831	121	728	24	741	26	733	19
18	377	135	2.8	0.066	0.002	11.709	0.326	1.309	0.077	806	48	529	14	577	25	discordant	
17	703	15	46.4	0.058	0.001	11.200	0.380	1.461	0.056	545	42	552	17	530	15	538	180
16	384	232	1.7	0.060	0.002	11.451	0.401	1.533	0.088	605	54	540	18	510	22	528	190

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				Isotopic ratios							Apparent ages (Ma)							
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$				
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	- ±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма	
10	461	220	2.1	0.093	0.001	3.833	0.119	0.294	0.008	1498	25	1495	40	1506	21	1504	21	
9	769	297	2.6	0.073	0.001	6.190	0.164	0.617	0.016	1017	33	966	23	979	16	975	15	
8	340	93	3.7	0.060	0.002	11.529	0.432	1.486	0.071	590	56	536	19	523	19	529	14	
7	326	287	1.1	0.096	0.002	6.144	0.221	0.464	0.016	1549	34	972	31	1168	23	discordant		
17	129	59	2.2	0.077	0.002	4.267	0.139	0.425	0.021	1107	52	1358	39	1229	34	discordant		
16	502	156	3.2	0.076	0.002	4.856	0.301	0.461	0.026	1088	51	1207	65	1172	37	1177	37	
15	304	127	2.4	0.060	0.002	10.738	0.891	1.403	0.126	602	75	574	42	547	35	557	33	
14	852	5	159.2	0.154	0.005	2.105	0.207	0.096	0.009	2391	55	2506	189	2470	84	2465	87	
13	291	76	3.8	0.058	0.002	10.936	0.790	1.398	0.103	518	75	564	37	548	30	554	25	
12	85	84	1.0	0.079	0.005	7.175	0.637	0.823	0.085	1183	129	841	65	808	54	820	49	
11	56	59	1.0	0.090	0.003	3.631	0.210	0.340	0.044	1428	65	1569	77	1394	91	1491	1200	
10	384	246	1.6	0.058	0.001	10.001	0.259	1.348	0.064	539	52	615	15	564	20	discordant		
9	230	133	1.7	0.059	0.003	9.644	0.312	1.302	0.085	560	112	636	19	579	27	discordant		
8	507	177	2.9	0.056	0.001	9.584	0.223	1.254	0.048	471	45	640	14	596	17	discordant		
7	129	399	0.3	0.058	0.002	9.574	0.421	1.314	0.098	533	94	641	26	575	31	613	410	
6	440	16	28.1	0.073	0.001	4.534	0.121	0.446	0.013	1007	38	1285	30	1195	20	discordant		
5	171	75	2.3	0.061	0.002	11.346	0.363	1.556	0.111	641	68	545	16	504	27	534	230	
4	210	127	1.7	0.092	0.001	3.823	0.075	0.302	0.009	1476	28	1499	26	1484	22	1489	18	
3	301	109	2.7	0.096	0.002	11.236	0.302	0.857	0.027	1548	42	550	14	786	17	discordant		
2	52	91	0.6	0.070	0.005	11.161	0.649	2.136	0.586	917	143	553	29	390	72	discordant		
1	103	85	1.2	0.185	0.003	2.184	0.043	0.087	0.002	2699	23	2431	40	2566	20	discordant		
1(repeat)	97	100	1.0	0.186	0.003	1.931	0.037	0.076	0.001	2710	22	2692	41	2695	18	2693	18	

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	Isotopic ratios								Apparent ages (Ma)								
				<sup>207</sup> Pb	_	<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm (2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
5	134	114	1.2	0.236	0.002	1.543	0.034	0.047	0.001	3094	15	3223	55	3146	18	3146	320
6	200	249	0.8	0.098	0.001	3.575	0.078	0.266	0.006	1585	27	1591	30	1586	19	1586	17
7	68	29	2.3	0.068	0.005	10.685	0.637	1.457	0.137	854	133	577	31	531	36	557	25
8	176	82	2.1	0.194	0.002	1.859	0.034	0.070	0.001	2780	16	2776	41	2777	19	2775	18
9	68	69	1.0	0.245	0.003	1.609	0.049	0.048	0.001	3154	22	3117	73	3135	27	3131	26
10	177	299	0.6	0.054	0.002	10.877	0.412	1.583	0.109	359	81	567	20	498	26	discordant	
11	337	259	1.3	0.068	0.002	12.315	0.356	1.415	0.057	871	85	503	14	543	16	discordant	
12	469	92	5.1	0.063	0.001	9.970	0.210	1.169	0.036	711	37	616	12	628	14	621	10
13	164	96	1.7	0.076	0.003	11.234	0.431	1.024	0.056	1092	68	550	19	693	26	discordant	
14	302	141	2.1	0.067	0.002	12.416	0.426	1.443	0.068	846	75	500	16	535	19	514	220
15	143	50	2.9	0.066	0.002	7.568	0.219	0.911	0.045	808	63	800	21	753	25	780	320
16	271	17	15.7	0.072	0.001	6.571	0.136	0.673	0.020	994	38	913	17	925	18	919	13
17	1377	98	14.0	0.073	0.001	8.401	0.137	0.809	0.015	1020	24	725	11	818	10	discordant	
18c	307	405	0.8	0.080	0.001	5.341	0.138	0.473	0.015	1191	33	1107	26	1155	21	1135	330
18r	728	77	9.5	0.075	0.001	5.459	0.107	0.517	0.010	1080	24	1085	19	1094	13	1090	11
18(a)	50	174	0.3	0.154	0.011	14.530	1.257	0.822	0.093	2387	114	429	33	809	59	discordant	
19	62	108	0.6	0.065	0.004	12.017	0.996	1.912	0.243	770	135	515	38	428	40	473	550
23	349	89	3.9	0.069	0.001	7.890	0.243	0.830	0.034	889	43	770	22	803	22	785	240
24	506	211	2.4	0.063	0.002	11.417	0.401	1.393	0.103	723	51	541	18	550	30	543	16
25	334	197	1.7	0.076	0.001	5.136	0.124	0.493	0.015	1094	30	1147	25	1126	20	1133	17
26	131	126	1.0	0.091	0.002	3.904	0.123	0.315	0.013	1443	48	1470	40	1453	31	1458	27
27	279	132	2.1	0.060	0.002	10.546	0.243	1.304	0.046	618	55	584	13	578	15	582	10
20	905	229	4.0	0.061	0.001	10.304	0.170	1.211	0.023	628	28	597	9	612	9	605	110
28	133	298	0.4	0.059	0.002	10.438	0.358	1.343	0.077	579	79	590	19	566	24	580	15
29	282	346	0.8	0.092	0.001	3.790	0.108	0.296	0.008	1464	29	1510	38	1500	21	1501	20
30	348	697	0.5	0.060	0.002	10.647	0.330	1.421	0.102	588	57	579	17	541	28	569	210
33	256	101	2.5	0.062	0.002	11.123	0.482	1.333	0.063	672	68	555	22	569	20	562	16
34	152	186	0.8	0.063	0.003	10.623	0.502	1.383	0.085	723	83	580	25	553	25	566	19
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						Isotop	pic ratios	3			Appa	rent ages	; (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
35	497	440	1.1	0.085	0.002	4.625	0.151	0.388	0.011	1316	35	1262	36	1295	20	1292	20
36	666	173	3.8	0.119	0.002	2.941	0.077	0.175	0.004	1945	22	1888	42	1934	20	1931	300
37	222	238	0.9	0.058	0.002	11.966	0.506	1.625	0.086	546	73	518	20	487	20	502	220
38	165	66	2.5	0.074	0.002	6.392	0.188	0.625	0.026	1051	45	937	25	971	25	953	19
39	59	95	0.6	0.071	0.004	6.555	0.294	0.804	0.073	957	110	916	37	821	48	879	590
40	243	101	2.4	0.078	0.001	4.735	0.106	0.442	0.012	1154	36	1236	25	1201	19	1212	230
41	331	101	3.3	0.073	0.001	7.753	0.152	0.782	0.022	1017	41	782	14	837	16	discordant	
42	307	142	2.2	0.059	0.002	11.130	0.291	1.430	0.062	569	57	555	14	539	18	549	11
43	374	217	1.7	0.071	0.002	12.036	0.307	1.385	0.053	961	49	515	12	552	16	discordant	
44	530	204	2.6	0.059	0.001	10.526	0.243	1.327	0.044	559	47	585	13	571	14	579	10
45	170	83	2.1	0.065	0.003	11.507	0.657	1.431	0.105	760	88	537	28	538	29	538	22
46	330	149	2.2	0.059	0.002	11.942	0.528	1.575	0.103	557	63	519	21	500	25	510	17
47	928	188	4.9	0.063	0.001	9.603	0.232	1.150	0.041	696	33	639	14	636	16	637	12
49	132	48	2.7	0.073	0.004	13.299	0.870	1.799	0.214	1017	102	468	28	449	39	461	24
50	510	283	1.8	0.085	0.002	14.768	0.537	1.254	0.045	1324	41	423	14	596	16	discordant	
51	309	49	6.3	0.096	0.002	3.507	0.087	0.267	0.007	1543	32	1618	35	1583	22	1588	270
52	342	65	5.2	0.105	0.001	3.713	0.077	0.256	0.006	1722	23	1538	28	1617	19	discordant	
53	317	44	7.2	0.057	0.002	12.203	0.347	1.662	0.126	491	70	508	14	479	27	502	12
54	174	72	2.4	0.061	0.002	11.315	0.534	1.537	0.109	640	74	546	24	509	27	530	230
55	271	141	1.9	0.076	0.001	5.451	0.141	0.517	0.017	1099	33	1086	25	1094	21	1090	18
56	342	259	1.3	0.089	0.002	5.651	0.148	0.491	0.014	1401	28	1051	25	1129	20	discordant	
57	404	293	1.4	0.079	0.001	4.971	0.119	0.451	0.012	1177	25	1182	25	1187	18	1185	16
69	282	167	1.7	0.061	0.002	11.604	0.355	1.496	0.069	651	59	533	15	520	18	527	12
67	265	238	1.1	0.059	0.002	11.463	0.353	1.488	0.079	581	63	539	15	522	21	533	14
66	138	49	2.8	0.111	0.002	5.427	0.319	0.335	0.020	1820	40	1091	56	1406	44	discordant	
65	405	8	48.3	0.059	0.001	11.365	0.287	1.462	0.057	555	42	544	13	529	16	538	11
64	86	42	2.1	0.180	0.003	2.461	0.075	0.097	0.003	2651	26	2199	56	2466	30	discordant	
63	660	265	2.5	0.059	0.001	12.666	0.332	1.586	0.054	551	48	490	12	497	13	493	9

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						Isotop	oic ratios	5			Appa	rent age	s (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
62	587	243	2.4	0.071	0.001	6.472	0.147	0.650	0.018	901	77	927	19	946	17	937	14
61	449	255	1.8	0.062	0.001	10.166	0.234	1.259	0.045	683	39	605	13	594	16	600	11
60	515	66	7.7	0.120	0.001	3.049	0.060	0.184	0.004	1962	15	1829	31	1891	17	discordant	
59	74	22	3.3	0.075	0.003	5.768	0.189	0.628	0.043	1067	69	1031	30	967	41	1008	400
6(repeat)	361	325	1.1	0.059	0.001	11.126	0.239	1.393	0.053	559	48	555	11	550	16	553	10
4	259	238	1.1	0.097	0.001	3.602	0.068	0.275	0.007	1562	23	1580	26	1558	20	1565	16
3	228	78	2.9	0.061	0.002	11.214	0.288	1.388	0.066	649	75	551	13	551	19	551	11
2	237	201	1.2	0.061	0.002	12.617	0.374	1.660	0.087	625	62	492	14	479	19	487	11
1	211	97	2.2	0.064	0.002	11.241	0.569	1.469	0.097	728	69	550	25	527	26	538	20

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						Isotop	oic ratio	s			Appa	rent age	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
13	379	264	1.4	0.059	0.001	10.991	0.210	1.410	0.048	566	47	562	10	545	14	556	110
11	221	149	1.5	0.082	0.001	4.405	0.084	0.402	0.010	1252	34	1319	22	1270	18	discordant	
10	242	142	1.7	0.060	0.002	12.526	0.339	1.633	0.087	608	69	495	13	485	20	492	11
9	156	73	2.1	0.081	0.002	4.793	0.112	0.448	0.016	1210	38	1222	25	1192	25	1206	18
8	325	115	2.8	0.073	0.001	5.882	0.106	0.589	0.014	1010	36	1013	17	1008	15	1010	11
7	67	19	3.5	0.063	0.003	11.648	0.621	1.561	0.132	700	111	531	26	503	32	520	21
3	305	158	1.9	0.061	0.001	10.511	0.247	1.292	0.059	632	53	586	13	583	20	585	11
4	409	209	2.0	0.061	0.001	12.020	0.322	1.535	0.084	652	45	515	13	510	21	514	12
6	461	348	1.3	0.061	0.001	11.738	0.247	1.394	0.040	646	43	527	10	549	12	536	140
5	261	75	3.5	0.110	0.002	2.966	0.052	0.195	0.004	1801	27	1874	28	1843	16	1849	14
2	306	248	1.2	0.078	0.001	5.166	0.111	0.485	0.012	1137	34	1141	22	1137	17	1138	14
1	211	113	1.9	0.059	0.002	11.230	0.320	1.571	0.119	564	67	550	15	500	28	539	260

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						Isotop	oic ratios	5			Appa	rent ages	(Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
12	300	119	2.5	0.077	0.001	5.641	0.108	0.514	0.013	1126	31	1053	18	1097	17	discordant	
1	601	124	4.8	0.070	0.001	11.583	0.210	1.229	0.039	941	34	534	9	605	14	discordant	
2	207	100	2.1	0.101	0.001	3.254	0.062	0.234	0.005	1635	26	1728	28	1689	17	1697	240
3	203	124	1.6	0.063	0.002	10.885	0.342	1.449	0.084	713	67	567	17	533	23	555	210
4	898	842	1.1	0.183	0.001	3.564	0.059	0.143	0.002	2683	14	1595	23	2114	12	discordant	
5	463	228	2.0	0.059	0.001	11.074	0.287	1.384	0.052	571	45	558	14	552	15	555	10
6a	222	119	1.9	0.059	0.002	12.687	0.403	1.796	0.143	574	72	489	15	450	27	481	210
6	411	211	1.9	0.060	0.001	11.200	0.235	1.423	0.055	613	48	552	11	541	16	548	9
7	137	74	1.9	0.061	0.004	11.216	0.320	1.609	0.097	634	145	551	15	491	22	discordant	
10	957	1107	0.9	0.106	0.002	14.916	0.247	0.928	0.025	1728	34	418	7	743	14	discordant	
11	435	189	2.3	0.059	0.002	10.948	0.226	1.391	0.054	575	56	564	11	550	16	559	9
12	122	63	1.9	0.173	0.002	2.099	0.040	0.087	0.002	2588	17	2513	39	2562	19	2560	350
13	193	65	3.0	0.078	0.003	11.248	0.282	1.019	0.038	1150	62	549	13	695	18	discordant	
15	436	291	1.5	0.060	0.001	11.881	0.287	1.534	0.064	591	46	521	12	510	16	517	10
17	179	60	3.0	0.113	0.003	3.480	0.295	0.217	0.016	1856	40	1629	113	1752	58	1764	960
18	85	62	1.4	0.101	0.004	5.428	0.675	0.364	0.038	1650	71	1090	112	1343	73	discordant	
19	88	65	1.3	0.067	0.004	13.162	1.285	1.759	0.218	834	124	472	41	457	41	465	34
20	365	94	3.9	0.073	0.001	6.525	0.227	0.662	0.026	1016	37	920	29	935	23	928	19
16	234	67	3.5	0.081	0.002	5.723	0.484	0.486	0.038	1227	46	1039	75	1136	51	1109	710
21	435	187	2.3	0.060	0.001	10.402	0.281	1.276	0.044	595	40	592	15	588	15	590	12
22	233	5	44.8	0.092	0.003	6.211	0.226	0.348	0.019	1475	65	963	31	1377	40	discordant	
23	349	190	1.8	0.071	0.002	11.029	0.235	1.113	0.055	960	61	560	11	651	23	discordant	
24	84	61	1.4	0.184	0.003	2.050	0.049	0.081	0.002	2691	31	2563	50	2637	20	2630	380
25	292	132	2.2	0.058	0.002	11.515	0.308	1.516	0.070	526	59	537	13	515	18	529	140
26	187	48	3.8	0.060	0.002	11.216	0.354	1.514	0.087	605	22	551	16	515	22	538	220
27	168	142	1.2	0.081	0.002	5.329	0.190	0.476	0.022	1224	43	1109	35	1150	31	1132	25
28	505	217	2.3	0.074	0.002	12.478	0.314	1.315	0.044	1046	45	497	12	575	14	discordant	
29	774	204	3.8	0.076	0.001	5.314	0.112	0.505	0.011	1084	32	1112	21	1110	14	1110	13

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						Isotop	oic ratios	s			Appa	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
30	136	83	1.6	0.076	0.002	5.590	0.174	0.551	0.024	1103	49	1061	30	1051	28	1055	22
31	163	149	1.1	0.077	0.002	5.496	0.154	0.534	0.021	1130	45	1078	27	1073	26	1075	19
32	504	188	2.7	0.067	0.002	11.071	0.277	1.445	0.066	837	50	558	13	534	18	550	140
33	155	48	3.2	0.060	0.002	11.475	0.407	1.680	0.155	603	78	539	18	475	32	discordant	
35	418	283	1.5	0.093	0.002	5.611	0.152	0.384	0.011	1486	34	1058	26	1302	21	d	0
34	391	49	8.0	0.062	0.001	8.975	0.841	1.091	0.099	685	44	681	56	661	41	667	38
36	346	65	5.3	0.059	0.002	11.501	0.387	1.500	0.081	576	68	538	17	519	21	530	14
37	232	44	5.3	0.069	0.002	7.362	0.210	0.802	0.033	894	48	821	21	823	22	822	16
38	277	189	1.5	0.062	0.002	11.184	0.320	1.394	0.052	691	70	552	15	549	15	551	11

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						Isotop	oic ratio	s			Appa	irent age	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	$\pm (2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1	603	125	0.2	0.071	0.002	6.230	0.160	0.651	0.026	962	45	960	22	946	24	953	17
3	898	1107	1.2	0.155	0.002	2.143	0.039	0.100	0.002	2402	16	2470	37	2441	17	2442	16
8	88	174	2.0	0.060	0.003	12.826	0.511	1.909	0.168	601	103	484	18	428	29	468	320
10	84	137	1.6	0.310	0.028	15.016	2.030	0.507	0.061	3522	132	416	48	1107	75	discordant	
9	85	180	2.1	0.116	0.001	3.297	0.063	0.206	0.004	1898	23	1708	28	1795	17	discordant	
12	436	842	1.9	0.071	0.002	7.494	0.204	0.812	0.038	965	46	808	20	815	25	810	17
15	203	156	0.8	0.093	0.004	12.016	0.580	1.077	0.087	1480	89	516	23	667	37	discordant	
16	349	83	0.2	0.070	0.001	6.087	0.117	0.640	0.017	926	33	981	17	957	16	967	180
17	137	65	0.5	0.065	0.002	12.225	0.395	1.452	0.072	775	60	507	15	532	20	516	170
18	222	61	0.3	0.197	0.014	12.004	0.781	0.573	0.041	2798	108	516	30	1026	44	discordant	
21	122	62	0.5	0.073	0.001	7.103	0.191	0.753	0.032	1013	38	849	21	859	24	853	16
25	411	291	0.7	0.077	0.002	5.540	0.212	0.566	0.030	1129	54	1070	36	1034	33	1049	26

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						Isotop	oic ratios	S			Appa	rent ages	s (Ma)				
				<sup>207</sup> Pb		<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ma
27	463	129	0.3	0.076	0.002	5.492	0.157	0.539	0.023	1102	40	1079	28	1066	28	1072	21
28	207	124	0.6	0.063	0.002	9.968	0.319	1.296	0.076	712	77	617	18	581	25	604	220
29	292	190	0.7	0.074	0.001	5.584	0.112	0.552	0.015	1037	31	1062	19	1051	17	1055	13
30	435	74	0.2	0.071	0.002	6.378	0.165	0.707	0.035	965	68	939	22	896	28	922	270
31	435	119	0.3	0.071	0.002	6.725	0.179	0.727	0.033	966	65	894	22	880	26	888	17
32	193	138	0.7	0.058	0.001	11.681	0.326	1.599	0.080	525	54	530	14	494	19	517	220
35	179	63	0.4	0.066	0.004	11.341	0.623	1.888	0.402	797	127	545	27	432	64	529	510
36	234	211	0.9	0.065	0.004	12.859	0.958	2.101	0.388	787	128	483	32	396	52	460	490
37	187	74	0.4	0.061	0.002	11.890	0.553	1.737	0.149	632	85	521	22	462	30	500	370
38	365	228	0.6	0.057	0.001	12.043	0.350	1.570	0.052	490	45	514	14	501	13	507	11
39	601	97	0.2	0.067	0.005	10.936	0.625	1.653	0.171	937	38	564	29	481	37	discordant	
40	233	100	0.4	0.097	0.004	3.780	0.166	0.316	0.018	1568	66	1514	57	1450	44	1471	37
46	258	60	0.2	0.060	0.002	10.784	0.298	1.389	0.063	619	57	572	15	551	19	564	13
48	93	132	1.4	0.070	0.001	9.969	0.206	1.016	0.021	919	23	616	12	696	10	discordant	
49	207	189	0.9	0.235	0.003	1.663	0.049	0.051	0.001	3085	22	3036	70	3066	22	3064	22
43	126	160	1.3	0.057	0.002	11.716	0.438	1.560	0.083	500	59	528	18	503	20	517	190
44	137	187	1.4	0.061	0.002	12.039	0.609	1.795	0.267	655	75	515	24	450	48	503	330
45	371	65	0.2	0.061	0.001	10.071	0.309	1.242	0.046	632	42	610	17	600	16	605	13
46	163	60	0.4	0.077	0.001	5.417	0.151	0.531	0.015	1110	32	1093	27	1075	18	1080	15
47	144	67	0.5	0.276	0.003	1.720	0.046	0.046	0.001	3338	19	2956	62	3182	21	discordant	
48	190	48	0.3	0.093	0.004	12.682	0.751	1.207	0.106	1491	88	489	26	613	38	discordant	
64	201	94	0.5	0.101	0.002	3.546	0.147	0.256	0.009	1649	28	1602	57	1616	27	1618	26
65	442	112	0.3	0.057	0.002	18.846	1.506	2.510	0.173	495	81	333	24	341	19	338	18
66	370	124	0.3	0.250	0.008	4.599	0.199	0.145	0.008	3185	18	1269	48	2102	46	discordant	
67	180	69	0.4	0.148	0.003	2.608	0.148	0.128	0.006	2328	38	2093	97	2208	42	2191	570
68	106	87	0.8	0.101	0.003	3.615	0.201	0.275	0.018	1644	50	1575	74	1558	50	1560	51

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						Isotop	oic ratios	5			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
55	425	476	0.9	0.069	0.001	13.167	0.315	1.490	0.066	885	42	472	11	522	17	discordant	
54	768	662	1.2	0.085	0.001	17.367	0.358	1.504	0.037	1315	31	361	7	518	10	discordant	
53	605	188	3.2	0.062	0.001	13.612	0.297	1.664	0.059	666	41	457	9	478	13	464	130
52	587	113	5.2	0.059	0.001	11.314	0.211	1.453	0.040	564	38	546	10	532	11	540	7
51	125	90	1.4	0.081	0.002	6.184	0.197	0.602	0.030	1210	49	967	28	995	30	979	21
50	321	245	1.3	0.059	0.002	12.073	0.308	1.557	0.074	575	57	513	12	504	18	510	10
49	41	82	0.5	0.142	0.009	13.381	0.952	0.953	0.134	2255	107	465	30	729	66	discordant	
47	59	27	2.2	0.080	0.003	5.955	0.266	0.666	0.069	1193	77	1001	40	931	59	978	34
46	416	288	1.4	0.063	0.001	12.568	0.314	1.548	0.066	695	35	494	12	506	16	498	10
45	258	138	1.9	0.075	0.002	6.927	0.161	0.686	0.022	1078	52	870	19	914	19	890	290
44	93	125	0.7	0.066	0.004	12.384	0.735	1.782	0.205	806	115	501	27	453	38	485	24
41	207	129	1.6	0.059	0.002	11.238	0.341	1.568	0.089	549	67	550	16	501	22	discordant	
42	126	60	2.1	0.059	0.003	12.722	0.523	1.742	0.143	559	97	488	19	461	29	480	16
29	137	137	1.0	0.065	0.003	13.729	0.645	1.869	0.192	760	86	453	20	435	34	449	18
39	371	69	5.4	0.098	0.001	3.637	0.061	0.270	0.005	1589	21	1567	23	1572	15	1570	14
38	163	174	0.9	0.074	0.002	10.904	0.704	1.233	0.093	1034	60	566	33	603	32	584	26
36	144	74	2.0	0.092	0.002	4.321	0.116	0.344	0.011	1468	36	1343	32	1386	24	1369	160
37	190	180	1.1	0.059	0.002	12.854	0.464	1.763	0.122	570	77	483	16	456	24	475	14
34	201	97	2.1	0.064	0.002	7.869	0.237	0.942	0.047	730	53	771	21	735	25	756	240
35	442	112	3.9	0.059	0.001	12.390	0.303	1.540	0.060	568	47	501	11	509	15	503	10
33	370	160	2.3	0.055	0.001	12.945	0.347	1.728	0.080	432	53	480	12	464	17	474	10
32	180	156	1.2	0.094	0.002	4.087	0.103	0.322	0.010	1501	41	1412	31	1435	23	1426	20
31	106	83	1.3	0.059	0.002	12.186	0.359	1.668	0.099	554	76	509	14	477	21	499	180
30	201	96	2.1	0.058	0.001	11.829	0.272	1.512	0.052	546	47	523	11	516	14	520	9
28	141	91	1.5	0.054	0.002	12.720	0.452	2.025	0.171	317	160	488	16	408	26	discordant	
24	162	113	1.4	0.059	0.002	12.085	0.428	1.614	0.090	566	71	513	17	490	21	504	14
23	147	63	2.3	0.063	0.003	13.088	0.474	1.952	0.177	703	83	475	16	420	29	462	290
9	78	41	1.9	0.095	0.003	4.169	0.150	0.349	0.019	1525	50	1386	43	1374	40	1379	31

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						Isotop	oic ratios	s			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
20	200	110	1.8	0.070	0.002	7.140	0.211	0.792	0.036	921	47	845	23	830	25	838	17
19	224	96	2.3	0.067	0.002	8.762	0.237	1.037	0.043	823	55	697	17	686	20	692	14
18	396	197	2.0	0.058	0.001	11.630	0.340	1.526	0.070	546	47	532	15	512	18	524	12
16	247	126	2.0	0.072	0.008	6.005	0.137	0.613	0.018	996	211	993	21	983	18	987	15
17	76	23	3.2	0.094	0.003	4.050	0.114	0.333	0.013	1507	50	1423	35	1410	30	1414	24
14	385	124	3.1	0.174	0.002	2.227	0.052	0.093	0.002	2596	20	2392	45	2508	16	discordant	
13	358	21	16.8	0.072	0.001	6.353	0.193	0.649	0.020	986	38	943	26	948	18	946	17
11	187	109	1.7	0.076	0.002	5.903	0.177	0.598	0.023	1082	41	1009	27	998	24	1002	19
8	147	59	2.5	0.074	0.002	5.934	0.145	0.608	0.025	1033	46	1004	22	988	25	997	18
7	667	194	3.4	0.060	0.001	10.756	0.248	1.326	0.038	618	23	573	12	571	12	572	10
6	71	34	2.1	0.065	0.004	12.862	0.745	1.704	0.152	784	132	483	26	469	31	477	21
5	594	107	5.6	0.059	0.001	11.787	0.274	1.490	0.046	585	42	525	11	522	12	523	9
4	141	70	2.0	0.064	0.003	12.185	0.504	1.676	0.151	736	82	509	19	475	32	500	17
3	314	220	1.4	0.061	0.002	10.305	0.315	1.267	0.046	648	54	597	17	591	16	594	12
1(a)	344	466	0.7	0.080	0.001	7.074	0.284	0.694	0.027	1199	32	853	31	907	23	890	460
1	1010	276	3.7	0.908	0.004	3.982	0.042	0.032	0.000	1442	9	1445	14	3539	8	discordant	

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					Isotop	oic ratio	s			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	$^{206}$ Pb $\pm(2\sigma)$	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1	981	259	3.8	0.060 0.001	11.496	0.177	1.363	0.029	616	27	538	8	559	9	discordant	
2	231	135	1.7	0.090 0.001	4.529	0.078	0.371	0.009	1418	29	1287	20	1328	18	1308	270
3	241	159	1.5	0.070 0.002	11.956	0.325	1.137	0.056	922	62	518	13	641	23	discordant	
4	837	331	2.5	0.087 0.001	4.413	0.072	0.354	0.006	1366	18	1317	19	1362	12	d	0
5	476	254	1.9	0.060 0.001	11.559	0.263	1.487	0.060	602	41	535	11	523	16	531	20

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						Isotop	oic ratios	3			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
6	213	330	0.6	0.060	0.002	11.915	0.345	1.559	0.084	602	68	520	14	504	20	514	12
7	668	231	2.9	0.113	0.001	3.002	0.045	0.190	0.003	1850	16	1854	24	1865	14	1862	14
8	753	321	2.3	0.098	0.003	15.695	1.275	1.145	0.078	1596	64	398	29	638	31	discordant	
9	235	114	2.1	0.135	0.004	2.797	0.153	0.154	0.007	2163	45	1971	88	2049	36	2060	470
10	109	48	2.3	0.081	0.002	5.734	0.189	0.548	0.034	1216	54	1037	31	1055	39	1043	26
11	270	157	1.7	0.055	0.002	12.776	0.366	1.879	0.115	411	78	486	13	434	21	discordant	
12	618	413	1.5	0.065	0.001	12.746	0.232	1.344	0.036	781	37	487	8	565	11	discordant	
13	436	227	1.9	0.057	0.001	11.860	0.243	1.542	0.055	501	49	522	10	508	14	517	8
14	244	128	1.9	0.059	0.002	11.460	0.303	1.619	0.099	561	66	540	13	489	23	discordant	
15	507	104	4.9	0.057	0.001	11.425	0.213	1.466	0.050	508	42	541	9	528	14	537	8
16	327	139	2.4	0.107	0.001	2.928	0.044	0.198	0.003	1753	18	1895	24	1830	14	discordant	
17	666	370	1.8	0.058	0.001	12.177	0.243	1.561	0.047	528	41	509	10	503	12	506	8
18	825	290	2.8	0.095	0.002	13.319	0.252	0.919	0.024	1523	38	467	8	748	13	discordant	
19	293	63	4.7	0.062	0.002	11.625	0.312	1.492	0.085	662	57	532	13	521	22	529	12
20	189	89	2.1	0.062	0.002	11.972	0.456	1.590	0.112	666	83	517	18	496	26	510	16
21	171	140	1.2	0.077	0.002	7.042	0.202	0.771	0.036	1122	51	856	22	845	26	851	18
22	994	647	1.5	0.060	0.001	10.129	0.376	1.259	0.049	608	41	607	21	594	17	598	15
24	139	114	1.2	0.059	0.003	12.644	0.659	1.738	0.113	581	89	491	23	462	23	476	18
25	173	84	2.1	0.078	0.001	5.206	0.124	0.485	0.014	1159	34	1133	24	1137	19	1135	17
26	195	104	1.9	0.074	0.002	6.418	0.170	0.653	0.025	1045	43	934	22	944	23	983	17
27	296	157	1.9	0.076	0.001	5.594	0.135	0.534	0.015	1096	34	1061	23	1072	18	1067	15
28	704	9	76.9	0.058	0.001	11.084	0.225	1.375	0.036	548	37	557	11	555	11	556	8
29	285	222	1.3	0.136	0.001	3.195	0.061	0.168	0.003	2175	17	1756	29	1968	17	discordant	
30	293	67	4.4	0.058	0.002	11.678	0.305	1.533	0.080	548	58	530	13	510	20	524	11
34	407	311	1.3	0.070	0.001	7.005	0.150	0.729	0.021	917	37	861	17	877	17	869	12
36	813	82	10.0	0.074	0.001	11.158	0.247	1.048	0.026	1028	33	554	12	681	12	discordant	
37	232	159	1.5	0.062	0.002	11.303	0.330	1.447	0.105	671	72	547	15	534	28	544	14
39	1079	104	10.4	0.060	0.001	9.664	0.171	1.154	0.024	608	27	635	11	634	9	634	8

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						Isotop	oic ratios	5			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	- ±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
40	122	159	0.8	0.080	0.002	4.901	0.141	0.460	0.018	1191	48	1198	31	1173	27	1183	21
41	193	69	2.8	0.063	0.002	11.214	0.304	1.432	0.094	710	82	551	14	538	26	548	13
42	347	125	2.8	0.093	0.001	4.319	0.083	0.336	0.007	1492	25	1343	23	1403	16	discordant	
43	1545	767	2.0	0.078	0.001	13.273	0.238	1.224	0.027	1151	26	468	8	607	10	discordant	
44	636	147	4.3	0.080	0.002	13.032	0.285	0.992	0.028	1198	44	477	10	709	14	discordant	
45	432	84	5.2	0.061	0.001	11.773	0.331	1.444	0.057	642	46	526	14	535	16	529	11
46	623	326	1.9	0.067	0.001	11.916	0.245	1.265	0.038	851	37	520	10	592	13	discordant	
47	1186	126	9.4	0.080	0.001	6.241	0.122	0.552	0.012	1195	24	958	17	1051	14	discordant	
48	273	108	2.5	0.060	0.002	12.108	0.431	1.598	0.091	598	65	512	17	494	21	505	14
49	734	171	4.3	0.070	0.001	13.089	0.392	1.391	0.042	942	39	475	13	550	13	discordant	
50	738	165	4.5	0.065	0.001	9.905	0.241	1.106	0.032	779	30	620	14	655	14	d	0
51	269	66	4.1	0.070	0.001	6.630	0.181	0.700	0.028	932	39	906	23	902	23	904	18
52	536	177	3.0	0.062	0.001	12.032	0.296	1.504	0.048	668	44	515	12	518	13	516	9
53	219	58	3.8	0.059	0.002	12.827	0.580	1.737	0.124	585	67	484	20	462	25	475	17
54	1603	511	3.1	0.075	0.001	13.242	0.378	1.285	0.038	1062	29	469	13	585	13	discordant	
55	262	193	1.4	0.077	0.002	6.206	0.238	0.594	0.025	1109	40	963	33	1004	26	989	320
56	353	220	1.6	0.060	0.002	12.433	0.613	1.572	0.093	598	56	499	23	500	22	499	18
57(a)	303	112	2.7	0.059	0.002	11.182	0.362	1.506	0.080	556	57	552	17	518	21	539	240
58	218	78	2.8	0.253	0.002	1.993	0.043	0.056	0.001	3204	15	2623	45	2986	18	discordant	
58(a)	642	492	1.3	0.124	0.001	3.855	0.074	0.221	0.004	2016	16	1487	25	1736	15	d	0
60	136	65	2.1	0.062	0.003	13.657	0.664	1.946	0.178	663	90	456	20	421	29	445	18
61	816	552	1.5	0.069	0.001	12.854	0.273	1.356	0.036	896	33	483	10	561	11	discordant	
62	155	66	2.3	0.059	0.002	12.042	0.532	1.745	0.139	561	78	514	21	460	28	494	330
64	366	169	2.2	0.060	0.001	11.643	0.293	1.468	0.056	592	50	531	13	528	15	530	10
65	218	148	1.5	0.062	0.002	12.266	0.358	1.497	0.079	681	72	505	14	520	21	509	12
66	936	207	4.5	0.059	0.001	12.074	0.458	1.477	0.051	559	45	513	18	525	14	521	12
67	457	159	2.9	0.066	0.002	11.836	0.522	1.416	0.070	791	58	523	21	543	20	533	17
68	195	106	1.8	0.172	0.003	2.393	0.036	0.099	0.001	2580	30	2252	28	2442	13	discordant	

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					Isotopic ratios					Appa	rent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
69	800	380	2.1	0.187 0.001	2.456	0.035	0.096	0.001	2714	9	2203	26	2476	13	discordant	
70	378	221	1.7	0.059 0.001	11.811	0.311	1.524	0.062	568	48	524	13	513	16	519	10
71	933	270	3.5	0.059 0.001	10.411	0.151	1.289	0.028	585	28	591	8	584	9	588	7
72	132	1	140.1	0.063 0.003	9.676	0.288	1.283	0.078	715	108	634	18	585	26	618	290
73	894	206	4.3	0.098 0.001	4.306	0.058	0.318	0.005	1578	17	1347	16	1445	12	discordant	
74	454	379	1.2	0.064 0.001	11.571	0.237	1.257	0.046	744	43	535	10	595	16	discordant	
75	702	357	2.0	0.097 0.001	5.729	0.083	0.432	0.007	1571	20	1037	14	1218	11	discordant	

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					Isotopic ratios						irent age	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb	_	<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2c	5) <sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1	169	52	3.3	0.096 0.00	4 7.202	0.726	0.707	0.065	1541	77	838	72	896	51	883	53
2	959	576	1.7	0.059 0.00	1 13.127	1.072	1.605	0.122	576	43	473	35	492	28	486	28
3	128	65	2.0	0.066 0.00	3 12.807	1.538	1.544	0.171	819	94	485	50	507	41	499	39
4	253	67	3.8	0.061 0.00	2 14.181	1.406	1.742	0.141	653	80	439	38	461	28	455	28
5	1041	211	4.9	0.076 0.00	2 14.338	1.770	1.355	0.144	1107	72	435	46	561	42	discordant	
6	238	215	1.1	0.069 0.00	3 10.622	1.282	1.124	0.122	900	83	580	60	647	48	625	610
7	2305	1402	1.6	0.137 0.00	6 7.311	0.949	0.373	0.045	2187	72	827	90	1325	83	discordant	
9	469	311	1.5	0.116 0.00	4 3.872	0.450	0.238	0.029	1895	62	1481	139	1674	94	1629	1700
8	182	116	1.6	0.065 0.00	3 13.695	2.030	1.709	0.325	782	90	454	57	468	62	460	54
10	260	260	1.0	0.063 0.00	2 12.781	1.117	1.585	0.178	699	76	486	38	497	40	490	34
11	166	110	1.5	0.108 0.00	3 3.716	0.170	0.249	0.010	1773	45	1537	60	1638	33	discordant	
12	403	100	4.1	0.148 0.00	3 2.640	0.204	0.126	0.009	2320	30	2072	129	2225	64	2233	1100
13	649	250	2.6	0.060 0.00	1 12.021	0.301	1.482	0.049	610	39	515	12	524	13	519	10
14	1023	200	5.1	0.061 0.00	1 9.751	0.226	1.170	0.030	638	28	630	14	628	12	628	10

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						Isotop	oic ratios	3			Appa	rent ages	; (Ma)				
				$^{207}\mathrm{Pb}$		<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb		$^{207}\mathrm{Pb}$			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
24	1562	380	4.1	0.060	0.001	11.620	0.549	1.371	0.058	618	34	532	23	557	18	552	270
15	268	205	1.3	0.058	0.002	12.431	0.473	1.619	0.092	539	63	499	18	489	21	495	15
17	773	181	4.3	0.099	0.001	4.057	0.140	0.293	0.009	1600	25	1421	43	1509	23	discordant	
19	190	61	3.1	0.060	0.002	12.368	0.715	1.677	0.160	586	85	501	26	475	34	492	23
16	1331	489	2.7	0.061	0.001	11.634	0.496	1.328	0.052	638	34	532	21	570	17	discordant	
18	420	216	1.9	0.062	0.002	12.120	0.584	1.442	0.067	677	57	511	23	535	19	526	17
20	129	116	1.1	0.098	0.003	4.340	0.263	0.335	0.018	1594	51	1337	69	1405	40	1400	550
21	1567	74	21.2	0.091	0.001	5.130	0.251	0.390	0.017	1454	29	1148	49	1292	32	discordant	
22	322	197	1.6	0.059	0.002	12.672	0.546	1.553	0.070	556	56	490	20	505	17	499	16
23	311	206	1.5	0.061	0.001	12.990	0.601	1.634	0.075	651	49	478	20	485	17	482	16
25	43	26	1.7	0.278	0.005	1.599	0.048	0.041	0.001	3350	27	3133	72	3279	23	discordant	
26	131	65	2.0	0.057	0.003	19.113	1.313	2.742	0.227	499	113	329	21	316	21	322	16
26a	70	101	0.7	0.157	0.008	13.917	0.963	0.719	0.078	2419	82	447	28	886	59	discordant	
4	142	59	2.4	0.064	0.003	11.496	0.421	1.604	0.215	755	80	538	18	492	47	532	18
5	793	106	7.5	0.147	0.001	2.721	0.037	0.135	0.002	2317	11	2018	23	2166	11	discordant	
6	195	115	1.7	0.074	0.002	6.620	0.191	0.680	0.027	1029	60	907	24	919	24	913	18
7	495	237	2.1	0.053	0.002	27.522	0.834	4.410	0.566	325	77	230	7	208	22	229	7
8	211	207	1.0	0.062	0.002	10.627	0.413	1.358	0.086	671	65	580	21	561	26	572	17
9	355	218	1.6	0.061	0.002	11.737	0.366	1.476	0.065	656	62	527	15	526	17	526	12
10	211	165	1.3	0.063	0.002	10.000	0.343	1.290	0.111	709	78	615	19	583	36	608	18
11	662	175	3.8	0.127	0.001	4.202	0.066	0.242	0.004	2057	18	1377	19	1663	12	discordant	
12	75	44	1.7	0.064	0.004	13.554	0.737	1.884	0.177	745	127	459	23	433	31	450	19
13	693	231	3.0	0.069	0.001	12.086	0.309	1.209	0.032	900	34	513	12	613	12	discordant	
14	170	96	1.8	0.077	0.002	5.350	0.133	0.523	0.019	1116	47	1105	25	1087	23	1094	18
15	220	63	3.5	0.075	0.002	5.583	0.162	0.558	0.019	1064	41	1063	28	1043	22	1050	18
18	179	60	3.0	0.061	0.002	11.223	0.399	1.513	0.099	637	70	550	18	516	25	538	210
19	984	80	12.3	0.061	0.001	9.848	0.217	1.190	0.029	634	30	624	13	620	11	621	9
20	374	256	1.5	0.064	0.002	11.989	0.329	1.446	0.064	752	73	517	13	534	18	523	11

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					Isotop	pic ratio	s			Арра	rent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
23	684	374	1.8	0.060 0.001	11.561	0.264	1.406	0.049	612	40	535	11	546	14	539	10
24	434	234	1.9	0.059 0.001	11.512	0.264	1.489	0.052	556	45	537	12	522	14	531	10
25	854	317	2.7	0.099 0.001	3.677	0.061	0.267	0.004	1607	17	1551	23	1583	13	1574	170
22	421	286	1.5	0.059 0.001	12.617	0.334	1.628	0.069	552	54	492	12	487	16	490	10
21	325	170	1.9	0.059 0.002	12.268	0.340	1.639	0.086	554	62	505	13	484	19	499	11
17	397	269	1.5	0.059 0.001	11.858	0.284	1.544	0.063	553	48	522	12	507	16	517	10
16	317	113	2.8	0.061 0.001	11.289	0.274	1.410	0.056	623	52	547	12	545	16	546	10

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				Isotopic ratios						Арра	arent age	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ	) <sup>206</sup> Pb	$\pm(2\sigma)$	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
1	328	205	1.6	0.058 0.002	2 11.966	0.315	1.562	0.070	517	57	518	13	503	17	512	11
2	311	100	3.1	0.076 0.002	5.551	0.186	0.525	0.020	1096	35	1068	32	1084	24	1078	23
3	1040	595	1.7	0.071 0.002	10.115	0.494	1.071	0.049	968	39	608	27	670	22	discordant	
4	1015	247	4.1	0.061 0.002	11.817	0.572	1.417	0.057	625	43	524	23	543	16	539	16
5	440	280	1.6	0.064 0.002	2 12.238	0.835	1.469	0.092	738	57	507	31	528	25	520	22
6	224	61	3.7	0.155 0.008	3 12.450	0.819	0.612	0.043	2396	87	498	30	985	42	discordant	
7	615	619	1.0	0.058 0.003	13.027	0.620	1.619	0.076	541	46	477	21	489	18	484	16
8	608	279	2.2	0.059 0.003	12.123	0.591	1.521	0.074	554	47	511	23	513	19	512	18
9	181	84	2.2	0.073 0.018	3 7.146	0.340	0.764	0.045	1005	430	845	36	851	33	848	29
10	687	214	3.2	0.059 0.002	12.011	0.628	1.483	0.075	559	46	516	25	524	20	521	19
11	488	280	1.7	0.073 0.002	2 12.963	0.660	1.471	0.071	1006	65	479	22	527	19	discordant	
12	330	168	2.0	0.061 0.002	2 11.694	0.570	1.476	0.080	640	61	529	24	526	21	527	18
13	779	365	2.1	0.059 0.003	11.919	0.457	1.497	0.059	583	45	520	18	520	16	519	14
14	967	714	1.4	0.063 0.003	<b>3</b> 11.778	0.707	1.344	0.070	730	76	526	29	565	22	553	350

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						Isotop	oic ratio	s			Арра	rent age	s (Ma)				
				<sup>207</sup> Pb	_	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb	±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
15	227	125	1.8	0.058	0.002	12.161	0.438	1.657	0.117	524	67	510	17	480	26	501	15
16	113	122	0.9	0.180	0.003	2.025	0.081	0.082	0.003	2649	29	2588	82	2621	30	2622	29
17	134	74	1.8	0.064	0.003	12.073	0.739	1.612	0.175	736	86	513	29	490	39	505	25
18	1601	100	16.0	0.141	0.003	6.600	0.427	0.312	0.017	2245	30	910	52	1459	40	discordant	

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					Isoto	pic ratios	5			Appa	rent age	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U		<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(	2σ) <sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ma	<sup>235</sup> U	±Ма	Concordia	±Ма
27	100	37	2.7	0.063 0.0	003 12.302	0.549	1.743	0.262	714	93	504	21	461	50	450	17
26	289	137	2.1	0.059 0.0	002 11.517	0.318	1.539	0.122	561	55	537	14	509	30	483	11
25	358	210	1.7	0.060 0.0	004 11.520	0.265	1.536	0.074	591	123	537	12	509	18	475	280
24	244	72	3.4	0.124 0.0	001 2.636	0.041	0.152	0.003	2021	20	2074	27	2060	15	discordant	
23	810	222	3.6	0.062 0.0	001 14.193	0.285	1.652	0.049	662	39	439	8	481	11	discordant	
22	400	132	3.0	0.056 0.0	002 10.310	0.309	1.400	0.072	464	92	597	17	548	21	discordant	
21	359	54	6.6	0.060 0.0	002 11.795	0.383	1.672	0.106	586	77	525	16	476	23	discordant	
20	244	163	1.5	0.050 0.0	002 11.267	0.317	1.463	0.082	196	91	548	14	529	22	493	12
19	800	550	1.5	0.075 0.0	8.809	0.260	0.908	0.033	1054	47	693	19	755	19	discordant	
18	601	425	1.4	0.060 0.0	001 11.458	0.222	1.399	0.043	589	39	540	10	548	13	490	110
17	256	118	2.2	0.068 0.0	002 7.883	0.183	0.881	0.032	863	51	770	17	771	19	701	12
16	142	66	2.2	0.060 0.0	002 11.763	0.462	1.705	0.170	604	85	526	19	469	35	467	300
15	250	196	1.3	0.059 0.0	002 13.205	0.379	1.736	0.082	584	64	471	13	462	17	423	9
14	159	140	1.1	0.081 0.0	002 5.176	0.140	0.483	0.017	1212	44	1139	28	1141	23	1049	16
13	526	124	4.2	0.075 0.0	001 5.553	0.134	0.532	0.013	1067	28	1068	23	1075	15	990	210
12	646	203	3.2	0.055 0.0	001 17.265	0.376	2.348	0.091	398	46	363	8	361	11	327	5
11	244	105	2.3	0.059 0.0	002 12.828	0.365	1.675	0.082	567	75	484	13	476	18	435	9

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				Isotopic ratios						Appa	irent ages	s (Ma)				
				<sup>207</sup> Pb	<sup>238</sup> U	_	<sup>235</sup> U		<sup>207</sup> Pb		<sup>206</sup> Pb	_	<sup>207</sup> Pb			
Zircon	U (ppm)	Th (ppm)	U/Th	<sup>206</sup> Pb ±(2σ)	<sup>206</sup> Pb	±(2σ)	<sup>207</sup> Pb	±(2σ)	<sup>206</sup> Pb	±Ма	<sup>238</sup> U	±Ма	<sup>235</sup> U	±Ма	Concordia	±Ма
10	350	244	1.4	0.060 0.001	10.919	0.337	1.370	0.059	610	52	565	16	557	18	509	10
9	1191	73	16.3	$0.072 \ 0.001$	9.703	0.220	0.907	0.024	979	28	633	13	755	14	discordant	
8	265	125	2.1	0.059 0.002	12.718	0.372	1.793	0.128	561	60	488	13	450	25	434	170
7	754	202	3.7	0.061 0.001	12.583	0.251	1.531	0.048	638	35	493	9	511	12	452	130
6	366	163	2.2	0.060 0.001	11.666	0.335	1.469	0.057	602	49	530	14	528	16	480	9
5	325	22	15.1	0.058 0.001	11.779	0.397	1.492	0.059	542	46	525	16	521	16	475	11
4	479	164	2.9	0.058 0.001	12.583	0.517	1.585	0.063	515	38	493	19	497	15	450	12
3	217	90	2.4	0.060 0.002	11.503	0.608	1.436	0.072	600	55	538	26	537	20	488	16
2	165	96	1.7	0.065 0.002	11.908	1.047	1.371	0.106	766	68	520	41	557	31	498	410
1	386	237	1.6	0.054 0.002	31.068	2.745	4.597	0.427	350	78	204	16	200	16	181	12

Trace	Elemen	nt Data	i Sorte	d by Z	ircon Ag	ge Page 1	1																							
Sample	Zircon	Age	Error	TE	Eu/Eu*	Ce/Ce*	Nd/Yb	Lu/Gd	U	Th	Th/U	Zr/Hf	Ti	Ti temp	Li	$\Sigma$ REE	La	Се	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
		(Ma)	(2 <b>o</b> )	Group	<u>,</u>				(ppm)	(ppm)			(ppm)	(°C)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
652	7	230	7	1	0.01	44	115	1.87	394	265	0.67	40	3.95	665	0.13	518	0.09	24.3	0.03	0.54	1.78	0.43	10.4	3.73	48.5	19.5	99.6	23.3	235	50.9
652	z26	329	21	1	0.18	171	236	2.51	102	54	0.52	46	14.2	773	0.39	437	0.03	3.08	0.01	0.77	2.65	0.35	13.5	4.95	60.3	22.0	95.0	19.5	180	33.9
205	24	386	9	1	0.12	57	561	3.06	673	371	0.55	52	4.63	677	1.46	1313	0.02	6.19	0.04	1.09	3.55	0.40	29.6	12.0	157.74	62.4	275	62.5	613	90.4
652	z4	439	38	4	0.46	154	229	6.23	211	72	0.34	46	0.47	528	1.19	240	0.00	1.62	0.03	0.51	1.46	0.39	4.56	1.64	20.5	8.71	44.0	11.0	117	28.4
652	z8	454	57	1	0.13	191	31	0.64	415	202	0.49	39	12.9	764	2.89	116	0.01	3.78	0.06	1.03	2.00	0.19	9.54	2.45	23.4	6.71	25.2	4.03	31.77	6.08
652	12	459	23	4	0.28	162	56	2.10	41	24	0.58	60	8.39	726	0.88	223	0.01	3.79	0.07	1.56	2.01	0.39	9.34	2.66	30.1	10.6	45.8	9.38	87.84	19.7
652	z2	473	35	1	0.62	577	324	6.54	362	220	0.61	41	0.63	545	0.72	470	0.04	29.3	0.07	0.70	1.47	0.70	8.10	2.96	35.0	14.9	77.3	19.2	227	53.0
205	16	475	14	1	0.14	450	105	1.63	107	54	0.50	44	13.5	768	0.18	319	0.00	5.81	0.08	1.29	2.76	0.26	12.0	3.78	44.7	15.1	63.3	13.9	137	19.5
652	z23	478	20	1	0.30	240	307	4.31	311	206	0.66	43	8.05	722	0.38	1198	0.05	17.1	0.10	1.81	3.98	0.99	24.7	9.41	125	51.9	244	55.3	557	106
652	z22	490	20	1	0.21	403	274	4.08	374	223	0.60	40	5.27	687	2.59	692	0.05	17.1	0.03	1.16	2.63	0.43	15.3	5.59	69.1	28.8	139	31.9	318	62
462	63	490	12	1	0.21	85	193	2.50	301	121	0.40	41	5.15	686	2.64	453	0.02	12.3	0.05	0.99	2.22	0.39	13.8	4.72	56.2	20.9	93.7	20.3	192	34.4
205	33	491	11	1	0.12	4	132	1.59	287	313	1.09	38	7.68	718	4.34	680	0.23	3.36	0.22	2.14	4.21	0.40	26.4	10.38	112	34.3	134	28.9	283	42.0
652	22	492	12	1	0.16	31	75	2.47	324	229	0.71	42	6.83	708	0.02	857	0.87	22.0	0.59	4.59	6.17	0.67	26.8	9.61	113	41.7	184	37.7	342	66.3
205	9	498	22	1	0.15	103	136	1.96	140	81	0.58	59	3.98	666	0.03	612	0.07	7.76	0.09	2.03	4.90	0.49	20.5	6.97	79.9	28.2	119	26.5	275	40.2
652	z15	499	18	1	0.63	330	79	4.06	195	160	0.82	43	2.30	626	0.70	316	0.00	7.31	0.19	1.84	2.79	0.98	8.25	2.67	31.1	11.6	57.5	13.5	145	33.5
652	z19	501	26	1	0.12	39	270	3.13	91	48	0.53	47	33.9	861	3.54	347	0.07	2.45	0.06	0.56	1.65	0.15	9.37	3.42	41.2	16.6	75.9	16.3	150	29.3
652	21	505	13	1	0.17	52	180	2.66	287	208	0.73	40	2.19	623	0.30	856	0.45	16.5	0.23	1.98	3.61	0.53	23.7	8.97	112	41.7	187	38.4	357	63.1
462	53	508	14	1	0.24	45	483	2.94	352	134	0.38	45	2.10	620	0.20	690	0.00	12.2	0.02	0.63	2.33	0.51	17.6	6.70	82.3	32.9	145	32.7	305	51.8
652	z18	511	23	3	0.76	12	31	1.67	620	352	0.57	42	32.8	857	2.07	1801	1.87	27.2	2.84	22.8	25.5	11.0	76.2	22.9	249	86.9	375	77.8	694	127
462	37	518	20	1	0.09	164	88	1.21	170	187	1.10	49	10.3	743	0.29	404	0.01	19.1	0.10	1.85	3.60	0.24	17.6	5.29	59.3	19.4	77.0	16.8	162	21.4
462	46	519	21	1	0.07	35	279	3.21	462	212	0.46	51	27.1	837	2.05	877	0.15	17.0	0.09	1.42	3.11	0.18	20.0	7.96	102	40.4	183	41.8	396	64.1
205	54	520	22	1	0.17	96	179	2.02	45	110	2.46	45	289	1158	0.96	478	0.00	10.5	0.12	1.14	2.71	0.35	15.7	5.45	65.9	22.8	96.0	21.4	205	31.6
652	17	522	12	3	0.57	40	9	0.35	295	324	1.10	65	9.31	735	2.40	1588	0.32	35.2	2.54	39.3	51.7	17.9	178	41.9	341	91.6	317	44.9	364	62.6
652	9	527	15	1	0.21	33	113	2.68	109	66	0.61	47	4.32	672	1.27	502	0.31	9.30	0.26	1.81	2.67	0.43	14.7	5.41	64.1	25.1	111	23.1	204	39.3
652	z24	532	23	1	0.32	27	13	0.57	112	72	0.65	46	11.1	750	0.75	289	0.30	10.1	0.49	6.35	8.63	1.49	23.8	6.22	56.1	15.8	53.8	9.89	82	13.5
205	5c	533	19	1	0.83	16	147	5.29	166	33	0.20	72	3.94	665	0.00	293	0.02	3.33	0.11	1.04	1.46	0.75	5.18	2.14	25.2	10.2	50.9	13.0	152	27.4
462	69	533	15	1	0.08	18	113	1.78	357	266	0.75	43	9.01	732	8.97	1245	0.00	6.59	0.25	4.45	8.69	0.55	47.5	15.3	181	65.3	270	56.9	503	84.6
652	23	535	11	1	0.09	15	51	2.50	406	319	0.79	44	4.80	680	3.80	1149	3.69	34.0	1.37	9.02	8.06	0.51	34.3	12.3	146	55.0	245	51.3	462	86.0
652	24	537	12	1	0.05	61	590	5.19	387	98	0.25	33	6.64	706	25.1	2124	0.03	3.16	0.11	1.64	5.27	0.21	34.9	17.3	230	99.0	476	110	965	181
462	45	537	28	1	0.19	75	48	0.97	167	100	0.60	56	14.5	775	2.19	198	0.01	11.8	0.11	1.48	2.94	0.34	11.0	3.01	30.1	9.46	37.7	7.61	71.5	10.7
652	4	538	18	1	0.10	249	211	2.49	95	59	0.62	52	7.11	712	0.21	572	0.00	3.61	0.06	1.11	2.97	0.25	18.7	6.08	74.5	29.1	128	25.9	235	46.6
462	67	539	15	1	0.26	58	40	1.28	245	266	1.09	41	9.92	740	0.59	468	0.08	33.0	0.24	4.25	6.12	0.99	22.8	6.35	65.0	21.9	89.0	19.2	170	29.1
205	12	542	16	1	0.23	71	132	1.94	170	110	0.65	36	5.45	690	0.56	557	0.00	6.99	0.00	1.89	3.48	0.61	18.4	5.86	73.7	26.4	111	24.2	249	35.6
462	65	544	13	1	0.60	13	45	1.12	1209	371	0.31	46	4.66	678	16.9	750	0.13	12.5	0.40	6.13	10.0	4.08	43.7	11.9	118	37.5	149	29.7	277	49.0
205	6	547	16	1	0.11	17	340	2.49	277	106	0.38	47	7.36	715	0.58	660	0.00	6.02	0.00	0.89	2.53	0.23	17.4	6.09	82.6	30.7	140	31.3	301	43.3
652	18	550	18	1	0.24	238	2129	4.50	88	39	0.44	44	3.03	646	0.91	230	0.00	7.41	0.04	0.05	0.45	0.12	4.91	2.05	24.4	9.56	44.9	10.6	103	22.1
462	42	555	14	1	0.25	12	209	3.37	279	190	0.68	57	3.21	650	11.3	1310	0.15	8.48	0.20	2.76	5.45	1.12	33.4	12.2	153	61.2	281	62.6	575	113
462	6r	555	11	1	0.06	34	186	2.59	172	148	0.86	38	12.3	760	0.37	651	0.00	10.2	0.10	1.46	3.39	0.16	18.3	6.97	87.2	32.9	142	30.2	271	47.4
462	33	555	22	1	0.13	3	74	2.74	181	79	0.44	51	5.33	688	0.32	597	0.84	7.03	0.51	3.81	2.98	0.28	14.8	5.43	69.2	26.4	116	27.5	281	40.6

Trace Element	Data Sorte	d by Zircon	Age Page 2	
Trace Diemeine	Data Solite	a by Zheon	inge i age 2	

Sample	Zircon	Age	Error	TE	Eu/Eu*	Ce/Ce*	Nd/Yb	Lu/Gd	U	Th	Th/U	Zr/Hf	Ti	Ti temp	Li	$\Sigma$ REE	La	Ce	Pr	Nd	Sm	Eu	Gd	ТЪ	Dy	Но	Er	Tm	Yb	Lu
		(Ma)	(2 <b>o</b> )	Group	)				(ppm)	(ppm)			(ppm)	(°C)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
205	3	558	19	1	0.18	3	70	3.93	722	117	0.16	48	5.98	698	10.6	568	0.51	7.15	0.52	4.30	4.02	0.42	12.2	3.54	45.0	18.2	93.9	28.7	302	47.8
205	52	565	16	1	0.19	74	59	0.94	184	318	1.72	44	65.0	937	1.82	352	0.03	16.6	0.11	2.15	4.46	0.57	20.0	5.67	56.1	17.7	67.8	14.1	128	18.7
205	30	576	23	1	0.16	3	49	2.24	255	90	0.36	50	8.91	731	9.83	872	0.88	12.0	0.92	8.21	8.88	0.83	26.9	8.98	102	37.7	162	39.8	402	60.3
462	30	579	17	3	0.79	37	10	0.45	323	429	1.33	48	16.3	785	0.57	927	0.24	99.0	1.82	26.1	30.3	12.0	72.6	16.6	148	40.6	144	29.9	274	32.7
652	8	580	21	1	0.12	134	20	0.80	136	188	1.38	48	14.3	774	1.64	384	0.02	11.1	0.38	6.13	9.79	0.63	27.2	7.13	67.8	20.2	77.0	14.1	121	21.8
462	34	580.2	25	3	0.47	7	10.58	0.55	133	354	2.66	58	21.1	811	0.08	658	5.75	92.9	2.10	18.5	17.0	4.23	45.4	10.4	94.0	27.3	99.3	20.9	195	25.0
462	44	585.3	13	1	0.27	861	970.3	4.28	546	204	0.37	47	2.26	625	19.7	1242	0.02	49.0	0.01	0.61	2.56	0.65	21.3	8.97	127	50.9	239	58.3	592	91.1
462	28	590	19	1	0.50	70	12	0.48	128	282	2.20	54	26.8	836	0.56	235	0.15	64.2	0.33	4.70	5.96	1.58	15.7	3.56	28.6	8.14	30.3	6.08	57.6	7.59
205	38	602	9	1	0.03	87	185	1.83	417	219	0.53	42	6.66	706	0.47	1110	0.00	14.3	0.09	2.58	7.71	0.17	38.7	13.3	152	54.5	226	50.4	479	70.7
462	61	605	13	1	0.05	393	16	0.24	577	208	0.36	38	3.10	647	13.9	130	0.00	11.3	0.10	1.69	3.93	0.13	15.2	4.02	30.93	7.33	21.65	3.53	26.23	3.69
652	10	615	19	1	0.04	276	103	1.38	326	95	0.29	38	3.59	658	4.70	322	0.00	3.16	0.03	1.12	3.18	0.10	16.3	5.47	54.5	17.2	69.9	13.2	116	22.4
462	12	616	12	1	0.11	43	286	1.91	291	94	0.32	40	13.2	766	1.49	551	0.08	13.0	0.07	0.83	1.94	0.22	18.9	6.83	75.5	25.1	109	25.0	238	36.2
205	34R	621	10	1	0.17	60	308	2.24	933	54	0.06	42	7.83	720	0.45	604	0.03	9.69	0.05	0.87	2.50	0.37	17.3	6.35	78.1	29.1	126	28.2	267	38.7
205	27	622	16	1	0.14	39	163	1.86	743	208	0.28	45	6.88	709	1.58	358	0.03	7.39	0.08	0.97	1.95	0.22	12.0	3.95	46.5	16.9	72.3	15.9	158	22.2
652	19	624	13	2	0.01	48	23	0.06	969	95	0.10	25	7.71	718	8.78	375	0.02	1.65	0.05	1.32	7.44	0.10	69.7	20.4	159	23.0	53.1	4.89	30.3	4.32
205	7	626	15	3	0.47	23	22	0.77	394	278	0.71	58	14.3	773	0.00	881	2.53	41.5	1.38	13.9	16.8	4.81	57.9	14.6	142	42.6	161	34.4	304	44.3
652	z14	630	14	1	0.08	40	108	1.47	623	160	0.26	45	4.32	672	5.56	975	0.14	5.62	0.15	3.29	5.81	0.41	44.2	14.5	163	54.9	219	43.6	356	64.8
205	46	631	12	1	0.12	30	110	1.17	156	1155	7.41	43	6.05	699	1.54	341	0.02	4.48	0.07	1.22	2.93	0.29	17.0	6.01	57.9	17.5	65.7	14.3	134	20.0
462	47	639	14	1	0.18	105	313	2.83	145	69	0.48	52	18.7	799	1.21	357	0.02	10.72	0.03	0.50	1.53	0.23	9.31	3.49	42.3	16.7	72.5	16.7	156	26.4
205	43	642	12	1	0.11	4	100	1.72	557	204	0.37	55	21.5	813	1.47	887	0.21	4.36	0.32	3.83	6.87	0.55	34.2	10.8	123	43.2	179	40.6	381	58.8
205	1r	751	19	1	0.10	45	200	2.43	224	95	0.42	60	5.62	693	0.52	418	0.00	4.44	0.05	1.00	2.16	0.16	11.3	4.17	51.7	18.5	77.6	19.5	200	27.3
462	15	808	63	1	0.01	42	442	2.71	213	88	0.41	41	15.3	780	0.21	927	0.00	3.64	0.04	0.93	3.59	0.03	24.4	9.15	116	44.2	203	43.9	413	66.0
652	z3	819	94	3	0.46	76	17	0.75	107	81	0.75	55	19.4	802	0.62	387	0.06	12.7	0.45	6.91	8.00	2.34	29.5	7.56	68.1	20.8	76.1	14.2	118	22.0
462	7	854	133	1	0.20	33	48	0.94	137	85	0.62	43	14.2	772	0.00	559	0.03	12.1	0.24	4.06	8.25	1.11	33.7	9.67	98.5	30.5	114	22.6	194	31.6
652	z6	900	83	1	0.08	29	30.66	1.14	158	174	1.10	55	24.4	826	0.44	1303	0.18	12.1	0.99	14.8	19.4	0.98	71.8	21.8	219	74.2	278	54.3	454	81.6
462	62	901	77	1	0.33	48	186.2	3.06	339	139	0.41	45	4.68	678	3.14	540	0.06	14.1	0.08	1.33	2.68	0.68	14.7	4.93	58.5	22.3	104	24.3	247	45.1
205	51	931	26	1	0.01	16	721.82	4.27	61	278	4.52	37	23.4	822	4.71	1005	0.02	1.26	0.02	0.67	2.15	0.02	16.7	7.95	113	45.5	214	50.3	482	71.4
462	39	957	110	3	0.28	6	28.11	1.01	67	155	2.30	52	12.0	757	1.29	1114	1.95	42.2	1.72	15.2	15.2	2.62	55.8	15.7	169	54.4	210	45.3	428	56.4
462	43	961	49	1	0.43	107	807.2	6.72	416	173	0.42	44	5.44	690	2.10	295	0.02	11.0	0.03	0.19	0.87	0.28	4.48	1.65	22.4	8.74	48.9	13.5	152	30.1
205	8c	990	37	1	0.19	16	101.9	2.65	338	134	0.40	44	6.63	706	22.4	857	0.42	6.92	0.43	3.85	4.79	0.66	22.4	8.38	105	39.1	172	40.0	393	59.3
462	16	994	38	2	0.04	5	11.8	0.09	336	17	0.05	34	7.21	713	12.4	145	0.03	0.93	0.07	1.08	2.34	0.08	19.2	7.57	75.3	7.07	14.8	1.62	12.8	1.72
205	22c	1010	27	1	0.50	/2	217.9	3.35	713	357	0.50	63	9.14	733	16.7	739	0.11	7.47	0.10	1.70	2.85	1.18	18.0	5.71	73.3	28.4	135	33.4	371	60.1
462	41	1017	41	3	0.49	2	96.47	3.45	431	101	0.24	4/	18.4	/9/	5.02	1452	1.54	12.5	1.1/	7.39	6.//	2.22	28.8	12.0	156	60.3	282	68.9	/13	99.4
462	49	101/	102		0.04	3 70	83.35	2.55	341	101	0.4/	55	4.25	6/1	1.12	6/4 250	1.55	10.4	0.50	5.49 1.05	3.68	0.12	18.6	0.00	85.5	32.3	142	31.1	291	4/.3
462	1/	1020	24	1	0.4/	/8 146	/6.11	2.32	92	85 102	0.90	4/	5.98	666 708	2.25	350 715	0.00	24.5 12.0	0.13	1.95	3.05 7 E 4	0.95	12.7	5.50	36.6 100	13.3	60.8 150	14.5	148	29.6 40 5
052 205	0	1029	47		0.17	140	24.4 247.1	1.51	205 149	192	0.72	49 42	0./0	708	0.5/	/15	0.03	12.8 1.75	0.30	4.81 1.95	/.54	0.8/	32.7 32.0	9.98 11 1	109	5/.8	158	30.5 49.2	262 457	49.5 64 5
205	15	1050	4/	1	0.01	12	247.1	2.01	148	101	0.68	42	12.4	700	3.04	1036	0.00	1./3	0.08	1.85	4.80	0.06	32.0	11.1	139	20.8	224	48.3	437	04.5

Trace Element Data Sorted by Zircon Age Page 3																														
Sample	Zircon	Age	Error	TE	Eu/Eu*	Ce/Ce*	Nd/Yb	Lu/Gd	U	Th	Th/U	Zr/Hf	Ti	Ti temp	Li	$\Sigma$ REE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
		(Ma)	(2 <b>o</b> )	Group	- )				(ppm)	(ppm)			(ppm)	(°C)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
205	2r	1058	47	1	0.19	17	90.14	1.32	168	42	0.25	66	5.23	687	2.58	629	0.02	3.52	0.15	3.00	6.12	0.82	27.6	8.88	93.6	30.8	121	27.2	270	36.3
652	15	1064	41	1	0.01	76	366.3	3.53	192	88	0.46	35	11.3	752	7.83	1705	0.00	2.03	0.12	2.00	5.88	0.05	39.1	16.0	208	84.8	396	81.1	732	138
462	59	1067	69	1	0.38	87	1205	5.36	48	17	0.36	43	4.78	680	0.48	513	0.00	5.13	0.01	0.20	1.21	0.41	9.02	3.60	50.0	21.3	103	24.6	247	48.4
462	13	1092	68	1	0.23	3	64.88	2.42	342	281	0.82	44	7.88	720	0.91	1576	4.04	30.0	1.46	10.7	9.57	1.55	46.2	16.2	190	71.9	317	71.7	694	112
462	55	1099	33	1	0.07	22	49.25	1.04	391	232	0.59	45	2.93	643	0.32	1169	0.05	14.7	0.51	8.39	14.6	0.73	64.9	19.1	198	65.5	252	49.5	413	67.3
205	21	1102	29	1	0.03	54	573.4	2.93	230	109	0.48	42	35.2	865	3.03	1144	0.00	0.65	0.04	0.93	3.34	0.08	25.9	10.6	138	54.3	244	54.5	536	75.8
205	14	1103	41	1	0.39	99	85.53	2.32	215	246	1.14	46	10.2	743	0.06	940	0.20	25.4	0.34	4.79	6.88	1.81	29.3	9.68	112	42.0	188	41.7	410	68.1
205	32	1106	30	1	0.05	10	608.3	3.93	634	585	0.92	37	4.04	667	1.00	1678	0.02	1.45	0.08	1.32	4.23	0.18	31.9	13.4	188	76.0	349	82.2	805	125
205	23r	1106	34	1	0.39	15	95.16	2.89	482	80	0.17	41	5.32	688	1.72	273	0.21	3.00	0.20	1.35	1.76	0.44	6.63	2.74	34.2	12.2	50.5	12.9	128	19.1
652	14	1116	47	1	0.27	1066	148.9	2.57	128	71	0.56	52	10.1	742	1.12	388	0.00	9.85	0.05	1.10	2.26	0.47	12.8	4.07	48.5	18.2	75.7	17.8	164	33.0
205	28	1121	32	1	0.07	4	202	1.90	556	84	0.15	49	2060	1611	33.1	1751	0.26	4.43	0.31	3.70	8.42	0.53	56.2	21.2	257	91.2	373	81.0	747	107
462	40	1154	36	1	0.14	67	245.7	2.36	92	54	0.59	48	12.1	758	0.80	400	0.01	6.92	0.04	0.77	1.99	0.21	10.9	3.92	47.8	17.9	75.6	18.2	190	25.7
205	42	1170	38	1	0.10	64	336.7	2.67	225	68	0.30	48	9.01	732	21.9	1008	0.06	5.21	0.07	1.41	4.15	0.34	26.2	9.58	120	46.2	203	48.5	474	69.9
462	57	1177	25	1	0.05	145	239.9	3.63	396	304	0.77	36	17.1	790	20.1	393	0.01	10.8	0.04	0.74	1.80	0.07	8.76	3.46	44.3	16.6	77.5	18.8	178	31.8
205	31	1207	31	1	0.02	7	340.6	2.16	348	136	0.39	52	5.35	689	0.00	557	0.00	8.78	0.00	0.73	2.51	0.00	16.0	5.70	73.9	26.8	115	25.2	249	34.7
462	35	1316	35	1	0.43	5	95.064	1.35	427	385	0.90	60	11.0	749	1.71	2013	0.35	10.9	0.68	8.78	15.6	5.07	83.0	26.9	300	104	422	88.7	834	112
462	56	1401	28	1	0.36	41	171.29	3.27	209	156	0.74	37	3.91	665	1.33	690	0.04	12.3	0.15	1.85	3.05	0.87	17.9	5.90	74.91	28.93	137	32.3	317	58.7
205	25	1445	19	1	0.13	53	462.3	2.54	297	145	0.49	59	6.83	708	0.12	518	0.00	7.22	0.03	0.53	1.45	0.19	14.6	4.95	59.3	22.6	101	24.2	245	37.0
462	29	1464	29	1	0.62	44	71.02	1.64	311	414	1.33	46	89.2	978	8.12	1064	0.10	42.5	0.57	6.67	10.12	4.07	39.8	12.2	134	44.4	187	44.1	474	65.2
205	45	1505	24	1	0.05	10	608.3	3.93	536	96	0.18	37	4 04	667	1.00	1678	0.02	1 45	0.08	1 32	4 23	0.18	31.9	13.4	188	76.0	349	82.2	805	125
205	40	1526	13	1	0.03	3	<b>3</b> 70 1	4 91	1117	121	0.10	42	32.8	857	37.0	1890	0.31	3 27	0.24	2.58	4.88	0.51	29.3	13.1	189	77.6	377	92.9	955	144
652	70 71	1541	77	1	0.15	21	77 78	1.37	206	155	0.75	46	2.67	637	0.30	1212	0.00	8 46	0.29	5.60	11.00	1 23	57.5	17.9	192	69.6	281	53.0	436	78.8
462	51	1543	32	1	0.67	3	114 5	1.88	501	97	0.19	46	14 7	776	5.75	1394	0.94	8.10	0.6	5.00	10.5	5 39	58.1	17.5	185	57.9	251	60.5	624	109
205	47a	1561	16	1	0.10	5	153.6	4 41	745	34	0.05	37	11.7	751	0.59	1607	0.27	8.68	0.62	5.16	5 72	0.40	27.2	11.1	170	67.2	318	78.9	793	120
205	41	1585	48	1	0.10	240	374	5 23	128	136	1.06	60	7 51	716	8.52	2053	0.06	92.9	0.14	2.64	5.27	1 40	33.2	12.6	175	78.2	394	97.0	987	173
652	720	1505	51	1	0.29	1711	196.7	3.01	88	85	0.96	45	17.4	792	22.6	681	0.01	27.8	0.05	1 48	3.01	0.70	18.3	6.52	81.5	31.0	134	30.4	291	54.9
652	25	1607	17	1	0.10	17	86.62	3.01	163	90	0.55	36	5 70	694	0.37	534	1.04	10.8	0.39	2.69	2 30	0.18	13.7	4.85	59.7	26.0	114	24.7	233	41.2
462	52	1722	23	1	0.16	40	757.8	7 51	233	77	0.33	46	121	1020	1.75	1544	0.08	12.0	0.07	1.05	2.66	0.60	18.9	8 51	132	58 3	299	76.8	793	142
652	711	1773	45	1	0.20	2636	221.7	3 79	137	52	0.38	41	8.07	722	5 31	428	0.00	15.0	0.09	0.86	1.63	0.50	9 71	3 4 9	46.9	18.6	84.9	19.2	190	36.8
205	4	1814	48	1	0.14	2050	1653	10.29	349	117	0.33	45	5.70	694	34.9	761	0.00	3.08	0.01	0.28	0.76	0.11	7 34	2.80	45.3	20.3	114	35.7	457	75.5
462	36	1945	22	1	0.03	19	734.1	3.47	721	110	0.15	40	7 25	713	13.2	1426	0.02	2 31	0.05	0.20	3.68	0.11	26.8	12.00	171	66.3	201	68.8	689	93.1
462	60	1962	15	2	0.03	4	2 1 37	0.05	505	65	0.13	33	11.9	756	1 28	52	0.13	1.81	0.03	2.03	5 34	0.11	15.8	2 55	12.2	1.80	3.90	0.61	4 33	0.79
652	11	2057	18	1	0.35	40	87.65	2 21	449	212	0.15	30	5.82	695	25.8	1114	0.17	8 77	0.12	5.18	8.96	2 21	13.0	12.55	1/18	55.1	236	18.8	454	017
205	35	2037	18	1	0.05	8	138.3	1 70	362	126	0.35	45	11 1	750	10.0	668	0.17	2 37	0.50	2.16	4 34	0.10	23.1	7.67	80.8	32.6	135	30.7	700 200	/1.7
652	5	2317	10	1	0.00	708	333.3	3 33	243	84	0.35	44	10.0	800	10.7	782	0.04	3.81	0.15	1.01	3.00	0.12	19.6	7.07	94.5	37.4	175	36.7	338	65.2
652	712	2320	30	1	0.03	10	53.87	1 30	375	81	0.33	36	15.0	676	1.14	556	0.00	2.07	0.04	3.81	5.00	0.12	27.3	8.40	01 8	20.0	110	22.0	205	38.0
205	20	2461	16	1	0.17	152	190.1	2.15	207	05	0.46	69	т. <i>31</i> 6.60	706	0.09	480	0.20	7.16	0.03	1 22	2.72	0.70	120	4.41	51.0	10.2	20.1	22.7	205	27.0
462	29 64	2401	26	1	0.43	133	76 11	2.15	207	95	0.40	47	2.00	666	2.25	460 350	0.00	24.5	0.04	1.23	2.75	0.01	12.0	4.41 2.50	36.6	12.3	60.9	145	149	20.6
402	04	2031	20	1	1.02	12	17.29	2.32	92 105	00	0.90	47	5.96	701	2.23	1107	0.00	24.J	1.(1	1.95	21.0	10.95	12.7	25.50	211	13.3	202	14.J	224	29.0 50.1
40Z 20E	0	2/00	0	) 1	0.11	4 10	17.28 52.25	2.05	208	07 101	0.40	41	0.23	661	2.01	560	1.72	1/.8	1.01	10.//	2 22	19.0	104	20.0 5.60	211 70.7	30./ 26.4	205	20.3 25.9	324 242	52.1 27.1
462	10 5	2004 2004	0 15		0.11	420	52.25 07.10	2.05	200	121 275	1.20	41	5.75	607	5.01	702	1./3	10.0 62.9	0.07	4.02	5.54	1.40	10.1 26.0	0.09 0.17	02.2	20.4 22.0	113	23.0 22.0	24Z	5/.1
402	5	2154	10		0.37	420	106.0	2.17	02	010 01	1.00	44	5.95	602	1.20	192 572	0.01	19.6	0.20	5.25 1.21	3.01 2.5F	1.40	20.9 20.1	0.14 6.56	93.3 74 5	55.9 27 F	131	33.Z	014 020	JO.Z
462	9	2250	22	1	0.28	100	190.9	2.02	92	02 17	0.88	40	5.50	692	1.00	2/3	0.01	10.0	0.00	1.21	3.33	0.70	20.1	0.50	/4.3 20.1	27.5 14.6	110	23.0 14.0	238 146	40.8
652	ZZC	3350	21	1	0.55	1254	141.1	3.05	5/	1/	0.50	4/	5.07	693	0.13	334	0.00	/.44	0.06	1.03	2.23	0.82	9.94	3.43	38.1	14.0	00.2	14.9	140	30.3