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Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high $\delta^{18}\text{O}$ continental crust and oceans in the Early Archean

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Abstract—Ion microprobe analyses of oxygen isotope ratios in Early Archean (Hadean) zircons (4.0- to 4.4-Ga) reveal variable magmatic $\delta^{18}\text{O}$ values, including some that are high relative to the mantle, suggesting interaction between magmas and already-formed continental crust during the first 500 million yr of Earth's history. The high average $\delta^{18}\text{O}$ value of these zircons is confirmed by conventional analysis. A metaconglomerate from the Jack Hills in the Yilgarn Craton (Western Australia) contains detrital zircons with ages > 4.0 Ga (Compston and Pidgeon, 1986) and one crystal that is 4.40-Ga old (Wilde et al., 2001). The newly discovered 4.40-Ga grain is the oldest recognized terrestrial mineral. The Jack Hills metaconglomerate also contains a large 3.3- to 3.6-Ga-old zircon population with an average $\delta^{18}\text{O}$ value of $6.3 \pm 0.1\%$ (1 s.e., $n = 32$ spot analyses). Two 4.15-Ga zircons have an average $\delta^{18}\text{O}$ of $5.7 \pm 0.2\%$ ($n = 13$). In addition, a 4.13-Ga zircon has an average $\delta^{18}\text{O}$ of $7.2 \pm 0.3\%$ ($n = 8$) and another 4.01-Ga zircon has an average $\delta^{18}\text{O}$ of $6.8 \pm 0.4\%$ ($n = 10$). The oldest grain (4.40 Ga) is zoned with respect trace element composition (especially LREE), and intensity of cathodoluminescence, all of which correlate with oxygen isotope ratios (7.4‰ vs. 5.0‰). High LREE and high- $\delta^{18}\text{O}$ values from the 4.01- to 4.40-Ga grains are consistent with growth in evolved granitic magmas ($\delta^{18}\text{O}(\text{WR}) = 8.5$ to 9.5%) that had interacted with supracrustal materials. High $\delta^{18}\text{O}$ values show that low-temperature surficial processes (i.e., diagenesis, weathering, or low-temperature alteration) occurred before 4.0 Ga, and even before 4.40 Ga, shortly following the hypothesized date of core differentiation and impact of a Mars-sized body to form the Moon at ~ 4.45 Ga. This is the first evidence of continental crust as early as 4.40 Ga and suggests differentiation during the period of intense meteorite bombardment of the early Earth. The magnitude of water and rock interaction that would be necessary to cause the high $\delta^{18}\text{O}$ values suggests the presence of liquid water and thus the possibility of an ocean at 4.40 Ga. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

The history of the earliest 750 million yr of the Earth is constrained only by a handful of localities that preserve rocks older than 3.8 Ga. A key to the recognition of many of these rocks has been U-Pb dating of individual zircons by ion microprobe (e.g., Froude et al., 1983; Compston et al., 1985; Compston and Pidgeon, 1986; Bowring et al., 1989a; 1999; Bridgwater and Schiotte 1991; Collerson et al. 1991; Maas and McCulloch, 1991; Nutman et al., 1991; Maas et al., 1992; Mueller et al., 1992; Mojzsis et al., 2001; Wilde et al., 2001). Zircon in these rocks can preserve igneous age information despite polymetamorphic, high-grade events, in large part because of zircon's slow rate of cation diffusion (e.g., Cherniak et al., 1997; Cherniak and Watson, 2001). Recent work has shown that oxygen diffusion in zircon is also slow (Valley et al., 1994; Watson and Cherniak, 1997; Peck and Valley, 1998; Peck et al., 1999), and therefore, zircon is also extremely retentive of primary oxygen isotope ratios.

In this study we investigated early Archean detrital zircons found in metasediments from Western Australia, including the oldest known terrestrial mineral (Wilde et al., 2001). The

original igneous source rocks to these zircons are not known, and may not be preserved (Nutman et al., 1991). Thus, the earliest record of terrestrial crust is limited to the isotope geochemistry, crystal chemistry, morphology, mineral inclusions, and internal structures of these individual zircon crystals. These zircons have been the focus of numerous ion microprobe studies for U-Pb age (Froude et al., 1983; Compston et al., 1985; Compston and Pidgeon, 1986; Maas and McCulloch, 1991; Nutman et al., 1991; Maas et al., 1992; Mojzsis et al., 2001; Wilde et al., 2001), trace elements (Maas et al., 1992), Hf-isotopes (Kinny et al., 1991; Amelin et al., 1999), as well as conventional TIMS U-Pb determinations (Schärer and Allègre, 1985; Kober et al., 1989; Fanning and McCulloch, 1990).

Here, we present the first detailed results of the determination of oxygen isotope ratios from pre-3.5-Ga zircons, including the oldest dated mineral (Wilde et al., 2001). Pre-4.0-Ga zircons preserve igneous oxygen isotope variability between different populations of zircon with distinct U-Pb ages, and the values that we have measured provide a new perspective on surface and magmatic processes in the earliest continental crust.

2. BACKGROUND

2.1. Preservation of Igneous Oxygen Isotope Ratios in Crystalline Zircon

Oxygen isotopes are a sensitive, temperature-dependent tracer of fluid and solid interactions in the crust. Oxygen

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isotope ratios in igneous rocks are especially sensitive to contamination by materials that have undergone low-temperature interaction with the hydrosphere, sediments, and hydrothermally altered rocks (e.g., Taylor and Sheppard, 1986).

Many lines of evidence show that oxygen diffusion in crystalline zircon is extremely slow, resulting in retention of igneous oxygen isotope ratios in meta-igneous and meta-sedimentary rocks. Contaminated metagabbro in the granulite-facies Adirondack Highlands (Grenville Province, USA) contains zircon with igneous $\delta^{18}\text{O}$ values, preserving rock–zircon disequilibrium through $\sim 750^\circ\text{C}$ metamorphism (Valley et al., 1994). Detrital zircons in quartzite from the Adirondack Highlands and the nearby granulite-facies Frontenac terrane preserve disequilibrium with host quartz and show only partial exchange in the outermost few microns of individual zircons (Valley et al., 1994; Peck and Valley, 1998; Peck, 2000). Moreover, single zircons in one quartzite sample preserve grain-to-grain disequilibrium ($\delta^{18}\text{O}(\text{Zrc}) = 6$ to 9%), interpreted to record igneous $\delta^{18}\text{O}$ values inherited from their source-rocks (Peck, 2000). Zircons from slowly cooled orthogneisses of the Adirondack Highlands do not display a positive correlation of $\delta^{18}\text{O}$ and grain size, which would be predicted to develop by diffusion during slow cooling if oxygen diffusion in zircon was fast (Peck et al., 1999; Peck, 2000). All of these lines of evidence indicate slow oxygen diffusion and effective closure temperatures of oxygen diffusion in zircon of $\geq 700^\circ\text{C}$, which is consistent with anhydrous experiments (Watson and Cherniak, 1997). The oxygen isotope variability among Jack Hills zircons, which correlates with U–Pb age, further argues against metamorphic homogenization of detrital zircons during upper greenschist/lower amphibolite-facies metamorphism of the Jack Hills metaconglomerate.

2.1.1. Radiation damage

Radiation damage and metamictization are common in U-rich, Precambrian zircons (Speer, 1982), and can correlate with U–Pb discordance (Krogh, 1982), zones of microfractures (Murakami et al., 1991), and reset $\delta^{18}\text{O}$ values (Valley et al., 1994). For analysis of whole zircon crystals by laser fluorination, this problem is avoided by selecting nonmagnetic zircons (Valley et al., 1994) or zircons that are not etched by HF (King et al., 1998). Precautions were taken to avoid radiation-damaged zircons in this study. All zircons have high birefringence in grain mount. Key grains, including the 4.40-Ga crystal, were examined for microcracks by SEM, and all zircons were imaged by CL and BSE. Further evidence that samples analyzed for oxygen isotopes are not metamict comes from a comparison of $\delta^{18}\text{O}$ and U–Pb discordance. Ion microprobe spots yielding high $\delta^{18}\text{O}$ do not correlate with spots yielding discordant ages (see below).

2.1.2. Calculation of magmatic $\delta^{18}\text{O}$

Zircon does not fractionate oxygen isotopes relative to Ca-poor garnet at high temperatures (Valley et al., 1994), and this allows the use of published fractionation factors for garnet (e.g., Kohn and Valley, 1998) to calculate oxygen isotope ratios in parent magmas from $\delta^{18}\text{O}$ measurements of zircon (e.g., Valley et al., 1994; King et al., 1998). Thus, a monzonite

($\text{SiO}_2 = 60$ wt.%) is predicted to have $\Delta(\text{magma-zircon}) \approx 1.0\%$, while a granite ($\text{SiO}_2 = 75$ wt.%) has $\Delta(\text{magma-zircon}) \approx 1.5\%$ at magmatic temperatures.

2.2. Previous Work on Western Australian Detrital Zircons

Detrital zircons with igneous ages > 4.0 Ga are found in > 3 -Ga metasediments in the Narryer Gneiss Complex of the Yilgarn Craton, Western Australia (Myers, 1988). These metasediments are divided into the Mt. Narryer and Jack Hills Belts (see Maas and McCulloch, 1991). The Mt. Narryer metasediments consist of quartzites, conglomerates, and pelites, while these lithologies are accompanied by chemical sediments (chert and banded-iron formation) in the Jack Hills Belt. The Narryer Gneiss Complex is a package of Early Archean (3.3–3.7 Ga) gneisses, with younger (< 3.0 Ga) gneisses in its western half (Nutman et al., 1991). Mt. Narryer and Jack Hills metasediments are found intercalated with these Early Archean gneisses where they experienced folding and greenschist/amphibolite (in the Jack Hills) to granulite-facies (Mt. Narryer) metamorphism (Nutman et al., 1991) between 2.6 and 2.7 Ga.

Detrital zircons from Mt. Narryer and Jack Hills metasediments can be grouped into four age populations: 3.05 to 3.10 Ga, 3.30 to 3.50 Ga, 3.60 to 3.75 Ga, and > 3.80 Ga. The proportions of each age population vary from rock to rock (see Nutman et al., 1991). The oldest zircon known before our study is the 4.28-Ga crystal dated by Compston and Pidgeon (1986). In this study we examined detrital zircons from Jack Hills sample W74, an amphibolite-facies metaconglomerate collected in 1984 by S. Wilde and R. Pidgeon and previously the focus of study using U–Pb geochronology by ion microprobe (Compston and Pidgeon, 1986; Wilde et al., 2001) and single-zircon U–Pb evaporation (Kober et al., 1989). Of previously dated zircons in this sample, $\sim 12\%$ belong to the oldest (4.1–4.3 Ga) population, and the rest of the dated zircons have predominately 3.35- to 3.55-Ga ages. Nutman et al. (1991) interpret the abundance of 3.35- to 3.55-Ga zircons in W74 as indicating derivation of the bulk of the zircon from exposed rock in the Narryer Gneiss Complex, but the provenance of the 4.1- to 4.3- and 4.40-Ga zircons is unknown.

Jack Hills and Mt. Narryer metasediments are characterized by variable Nd isotope ratios ($\epsilon_{\text{Nd}} = +5$ to -12 at 3 Ga) and are moderately LREE-enriched (Maas et al., 1992). Maas et al. (1992) interpret these isotope and geochemical signatures to reflect the contribution of $\geq 10\%$ pre-4.0-Ga sediment, higher than the amount of pre-4.0-Ga zircons found in all other samples but W74 (Maas and McCulloch, 1991). Compston and Pidgeon (1986) concluded that the general lack of visible zonation, the blunted prismatic form of some zircons, low Th and U contents (30 to 200 ppm Th; 20 to 150 ppm U; Th/U = 0.3 to 1.8), and the lack of inclusions in the zircons that they analyzed from W74 are a consequence of metamorphic zircon growth in mafic parent rocks. In contrast, Maas et al. (1992) present ion microprobe determinations of trace elements of 4.15- to 4.20-Ga zircons which show variable, fractionated REE patterns, positive Ce and negative Eu anomalies, low Sc contents, and Zr/Hf = 10 to 68, all broadly consistent with granitic source rocks. They also report quartz, K-feldspar, and monazite inclusions in three 4.15- to 4.20-Ga zircons (some

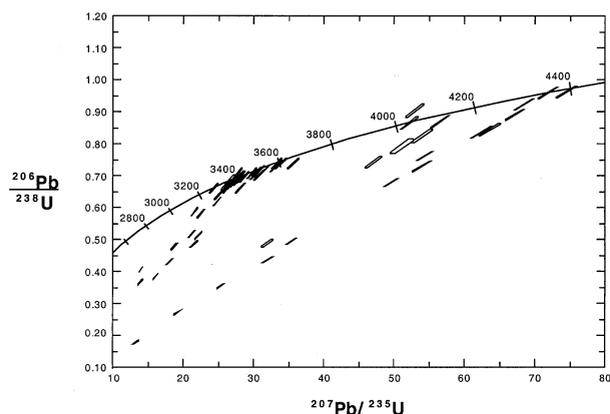


Fig. 1. Concordia diagram showing U-Pb ages (Ma) by SHRIMP II ion microprobe of detrital zircons from metaconglomerate sample W74, Jack Hills, Western Australia. ± 1 s.e. uncertainties are shown. The 14 analyses of the 4.40-Ga zircon are from Wilde et al. (2001).

with 3.93-Ga metamorphic (Th/U = 0.1–0.2) rims). These inclusions are consistent with the trace element arguments for a granitic source, while the metamorphic rims (which formed within the parent lithology) suggest crust thick enough to allow metamorphic zircon growth at 3.9 Ga and therefore, a continental rather than an ocean crust setting (see Maas et al., 1992).

3. ANALYTICAL METHODS

3.1. Ion Microprobe Analysis of Oxygen Isotopes and Trace Elements

Analyses of oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$) within individual zircon crystals (all dated by SHRIMP II) (Fig. 1; see Wilde et al., 2001) were made at the University of Edinburgh with a Cameca ims-4f ion microprobe (Slodzian, 1980) equipped with a Charles Evans and Associates control system. Details of the techniques used are described in Hervig et al. (1992), Graham et al. (1996), and Valley et al. (1998a). Before ion microprobe analysis, epoxy grain mounts of zircon were imaged with reflected light, and with backscattered electrons and cathodoluminescence using a Cameca SX-50 electron microprobe at the University of Wisconsin. Sputtering was achieved using a primary $^{133}\text{Cs}^+$ beam defocused to ~ 20 μm (producing pits ~ 3 μm deep) accelerated onto Au-coated, polished mounts with a net impact energy of 14.15 keV. Charge neutralization of the analyzed area was effected using the Cameca normal incidence electron flood gun (Migeon et al., 1990). Secondary $^{18}\text{O}^-$ and $^{16}\text{O}^-$ ions with an energy offset of 350 ± 20 eV were extracted and counted on an ETP electron multiplier and a Pulse Technology fast counting system with a total deadtime of 13 to 15 ns. Typical ^{18}O and ^{16}O peaks were flat topped within counting statistics over a peak width of 0.06 amu, using a mass resolution ($M/\Delta M$) of ~ 300 . Each point analysis of $^{18}\text{O}/^{16}\text{O}$ in zircon comprised 80 cycles of counting ^{16}O (1 s) and ^{18}O (8 s), employing magnetic peak switching. After an initial burn-in period of 2 to 3 min to remove the Au coating, typical analysis times were ~ 20 min. Primary beam currents were maintained close to 3 nA, giving count rates for ^{16}O of $\sim 1 \times 10^6$ cps. Total ^{18}O counts for each analysis were $> 1 \times 10^6$, yielding theoretical internal precisions close to $\pm 1.0\%$ (1 standard deviation, s.d.), based on Gaussian counting statistics (Valley and Graham 1991; Valley et al. 1998a), in good agreement with duplicate analyses of individual samples and of standards.

On some spots, a second analysis was made in the same sputter crater, increasing the depth of the pit by ~ 2 μm . These double analyses are noted in Table 1. Double analyses show no systematic difference in $^{18}\text{O}/^{16}\text{O}$ ratio between first and second analyses of standards or unknowns (Peck, 2000), and the precision of each pair of analyses is in

excellent agreement with theoretical precision based on counting statistics for 2×10^6 counts on ^{18}O (1 s.d. = 0.7‰).

Oxygen isotope data were collected from July 26 to August 2, 1999 (Table 1; Appendixes 1,2; Figs. 2,3,4). During this time, the instrument was tuned and optimized with respect to charge neutralization, electron multiplier gain, and alignment of the primary and secondary beam. The treatment of standard data and corrections for instrumental drift are as in previous studies (see Valley et al., 1998a) and are briefly given here. Drift in instrumental mass fractionation (IMF = $(^{18}\text{O}/^{16}\text{O}_{\text{measured}} - ^{18}\text{O}/^{16}\text{O}_{\text{actual}}) / ^{18}\text{O}/^{16}\text{O}_{\text{actual}} \times 1000$) is commonly observed during single analytical sessions and is generally linear with respect to time, as observed by successive analyses of standard material. We divide our data (Table 1; Appendix 1) into four sessions, corresponding to periods between major retuning of the instrument or changes in electron multiplier gain. Analyses of KIM-5 (a homogeneous zircon standard; $\delta^{18}\text{O} = 5.04\%$) exhibited linear drift throughout each session. KIM-5 is from a suite of large, well characterized zircon megacrysts from kimberlite at Kimberly, South Africa, which are homogeneous in $\delta^{18}\text{O}$ (Valley et al., 1998b). In each case, $^{18}\text{O}/^{16}\text{O}$ ratios of KIM-5 decrease over time (e.g., Fig. 2). The primary column of the instrument was aligned and the gain on the electron multiplier was increased at the beginning of sessions 1 and 2, resulting in a high initial $^{18}\text{O}/^{16}\text{O}$ ratio. The decrease of $^{18}\text{O}/^{16}\text{O}$ over time is attributed to a relative decrease in ^{18}O counts as the electron multiplier ages (Eiler et al., 1995). The first analysis of sessions 3 and 4 occurred, 22 and 44 analyses, respectively, after the last adjustment of the electron multiplier. Data are corrected for IMF using repeated analyses of KIM-5 zircon standard. A total of 74 standard analyses was made. The order of analyses and standard and sample data are given in Appendix 1 and Table 1.

Ion microprobe analyses of trace elements in the zircons were made at the University of Edinburgh using a 14.5 keV primary beam of O^- defocused to ~ 20 to 30 μm spot. Positive secondary ions were collected using an energy offset of 125 V. Analyses were standardized to SRM-610 glass. Energy filtering and strategies for isobaric interferences are after Hinton and Upton (1991), and results are given in Table 2 and Figures 5, 6, and 7 (normalized to chondrite; Anders and Grevesse, 1989).

3.2. Assessing Instrumental Mass Fractionations Due to Hf in Zircon

The measurement of oxygen isotope ratios by ion microprobe uses the $\delta^{18}\text{O}$ value of a standard (KIM-5) to calculate $\delta^{18}\text{O}$ from unknowns. This approach assumes that after drift correction, instrumental mass fractionation (IMF) is the same for all the zircons studied. IMF among different minerals and glasses is a strong function of matrix chemistry, especially the presence of heavy network-modifying cations (Eiler et al., 1997), and therefore, there is a potential of IMF differences between zircons of different cation composition. The most common substitution into zircon is Hf for Zr. Igneous zircons typically show small variations in HfO_2 content on the order of ~ 0.5 to 3.0 wt.%, but in some cases, contain up to 7 wt.% (Speer, 1982).

Hervig et al. (1992) and Eiler et al. (1997) found a general correlation between mean atomic mass of minerals and IMF, but also found that in detail, the correlation is not always linear within solid solution series. Figure 3 shows the extrapolation of the trend of the IMF vs. mean atomic mass of orthosilicates (garnets and olivines) analyzed by Eiler et al. (1997). By this extrapolation, the IMF is predicted to vary $\sim \pm 0.1\%$ for the range of HfO_2 in zircons we have analyzed (1.25 ± 0.12 wt.% HfO_2 ; Appendix 3).

Three zircons of known $\delta^{18}\text{O}$ (determined by laser fluorination) and HfO_2 content (determined by electron microprobe, Appendix 3) were analyzed by ion microprobe in a fifth analytical session to determine if there is a significant change in IMF due to variation in HfO_2 content in zircon. These oxygen isotope analyses are reported in Appendix 2 and Appendix 4. Figure 3 shows IMF vs. HfO_2 content for these samples, and samples KIM-2 and Jwan from Eiler et al. (1997) are also plotted (normalized to the least-squares fit of samples Aber, Kim-5, and Mog). Sample Mog is zoned with respect to HfO_2 concentration (from 0.6–1.4 wt.%), and the HfO_2 analyses were performed in the vicinity of the ion microprobe analyses.

No strong dependence of IMF on HfO_2 concentration is observed (Fig. 3). HfO_2 concentration of the W74 zircons are, on average,

Table 1. Oxygen isotope analyses by ion microprobe of detrital zircons from metaconglomerate sample W74, Jack Hills, Western Australia.

Grain number	Spot number	Analysis number	Measured $^{18}\text{O}/^{16}\text{O}$	$\delta^{18}\text{O}$ VSMOW
4.40 Ga Zircon W74/2-36	m2-1	2 (15)	1.9378E-03	4.8
	m2-2d	2 (16)	1.9388E-03	5.3
				AV = 5.0 ± 0.3
	m2-3	2 (21)	1.9414E-03	6.8
	m2-4d	2 (22)	1.9436E-03	8.0
			AV = 7.4 ± 0.6	
4.15 Ga Zircon W74-10	m1-33	2 (9)	1.9396E-03	5.5
	m1-34	2 (10)	1.9398E-03	5.6
	m1-35	2 (11)	1.9399E-03	5.7
	m1-36	2 (12)	1.9393E-03	5.4
	m1-37	2 (13)	1.9404E-03	6.0
	m1-38	2 (14)	1.9401E-03	5.9
	m1-51	2 (6)	1.9378E-03	4.4
	m1-53	2 (8)	1.9414E-03	6.5
				AV = 5.6 ± 0.6 (1se = 0.2)
4.15 Ga Zircon W74-43	m1-39	2 (38)	1.9369E-03	5.1
	m1-40	2 (39)	1.9410E-03	7.3
	m1-41	2 (40)	1.9390E-03	6.3
	m1-42	2 (41)	1.9394E-03	6.5
	m1-43	2 (42)	1.9354E-03	4.5
			AV = 5.9 ± 1.1 (1se = 0.5)	
4.13 Ga Zircon W74/2-52	m2-5	2 (23)	1.9407E-03	6.6
	m2-6	2 (24)	1.9427E-03	7.6
	m2-7	2 (28)	1.9405E-03	6.6
	m2-8	2 (29)	1.9431E-03	8.0
	m2-9	2 (30)	1.9443E-03	8.6
	m2-10	2 (31)	1.9398E-03	6.4
	m2-11	2 (32)	1.9393E-03	6.1
	m2-12	2 (33)	1.9417E-03	7.4
			AV = 7.2 ± 0.9 (1se = 0.3)	
4.01 Ga Zircon W74-1	m1-7	1 (24)	1.9441E-03	6.8
	m1-8	1 (25)	1.9398E-03	4.6
	m1-9	1 (26)	1.9462E-03	7.9
	m1-10	1 (27)	1.9419E-03	5.7
	m1-11	1 (28)	1.9466E-03	8.1
	m1-12	1 (29)	1.9416E-03	5.6
	m1-50	4 (5)	1.9441E-03	7.5
	m1-52	4 (7)	1.9414E-03	6.4
	m1-54	4 (9)	1.9440E-03	7.9
	m1-55	4 (10)	1.9430E-03	7.5
				AV = 6.8 ± 1.2 (1se = 0.4)
3.3 to 3.6 Ga Zircons W74-2	m1-1	1 (12)	1.9430E-03	6.0
	m1-2	1 (13)	1.9434E-03	6.3
W74-8 W74-9	m1-3	1 (14)	1.9456E-03	6.1
	m1-4	1 (15)	1.9425E-03	7.4
	m1-5	1 (16)	1.9418E-03	5.8
W74-4 W74-17	m1-6	1 (17)	1.9444E-03	5.5
	m1-13	1 (34)	1.9428E-03	5.6
	m1-14	1 (35)	1.9437E-03	6.8
W74-19	m1-15	1 (36)	1.9447E-03	6.3
	m1-16	1 (37)	1.9431E-03	6.8
			7.3	
			6.5	
			6.9	

(Continued)

Table 1. Continued

Grain number	Spot number	Analysis number	Measured $^{18}\text{O}/^{16}\text{O}$	$\delta^{18}\text{O}$ VSMOW
W74-18	m1-17	1 (38)	1.9418E-03	5.9
	m1-18	1 (39)	1.9401E-03	5.0
	m1-19	1 (40)	1.9428E-03	6.4
				AV = 5.7 ± 0.7 (1se = 0.4)
W74-20	m1-20	1 (44)	1.9420E-03	6.0
	m1-21	1 (45)	1.9427E-03	6.4
				AV = 6.2 ± 0.2
W74-6	m1-22	1 (46)	1.9453E-03	7.8
	m1-23	1 (47)	1.9402E-03	5.1
				AV = 6.5 ± 1.4
W74-5	m1-24	1 (48)	1.9411E-03	5.6
	m1-25	1 (49)	1.9453E-03	7.8
				AV = 6.7 ± 1.1
W74-14	m1-26	1 (54)	1.9416E-03	6.0
	m1-27	1 (55)	1.9369E-03	3.6
	m1-28	1 (56)	1.9396E-03	5.0
	m1-29	1 (57)	1.9412E-03	5.8
	m1-30	1 (58)	1.9392E-03	4.8
				AV = 5.0 ± 1.0 (1se = 0.6)
W74-7	m1-31	1 (59)	1.9421E-03	6.3
	m1-32	1 (60)	1.9388E-03	4.6
				AV = 5.5 ± 0.9
W74-33	m1-44	3 (5)	1.9418E-03	6.7
W74-34	m1-45	3 (6)	1.9397E-03	5.7
	m1-46	3 (7)	1.9418E-03	6.9
				AV = 6.3 ± 0.6
W74-35	m1-47	3 (8)	1.9390E-03	5.6
	m1-48	3 (9)	1.9408E-03	6.7
				AV = 6.2 ± 0.6
W74-36	m1-49	3 (10)	1.9395E-03	6.2

Note: Spot numbers of sample analyses indicate the epoxy mount of zircons from W74 and the sequential number of each ion microprobe pit for that mount (example: m1-12 is mount #1, pit #12). Analysis numbers indicate the analytical session and the order of analysis (example: 1(29) indicates session 1, analysis 29). d indicates a double analysis. See text for discussion.

slightly higher than the analyzed control samples (Appendix 3). W74 zircons average 1.25 ± 0.12 wt.% (1 s.d.) and range from 1.06 to 1.52 wt.% HfO_2 (typical values from other Australian detrital zircons; Maas et al., 1992). All but two of the zircons from W74 analyzed in this study (and all of the > 4.0-Ga zircons) are within 0.2 wt.% HfO_2 of KIM-5, which correlates with differences in IMF of $< \pm 0.15\%$. This is much

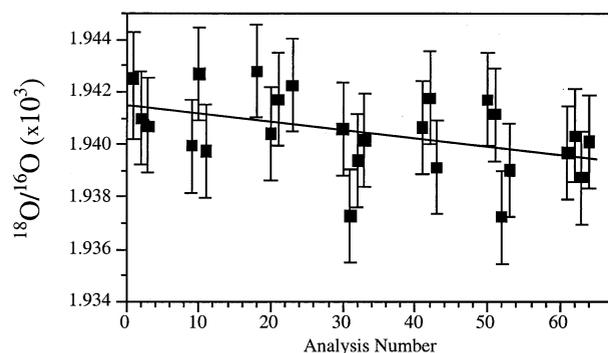


Fig. 2. Measurements of $^{18}\text{O}/^{16}\text{O}$, uncorrected, by ion microprobe in homogenous zircon standard KIM-5 over a 21 h period (analysis session #1). Error bars are ± 1 s.d. for each spot analysis. Drift in raw oxygen isotope ratio was 0.02% /20 min analysis. Thirty-nine sample analyses were bracketed by 25 standard analyses and are not shown for clarity (see Table 2). Least-squares regression is shown.

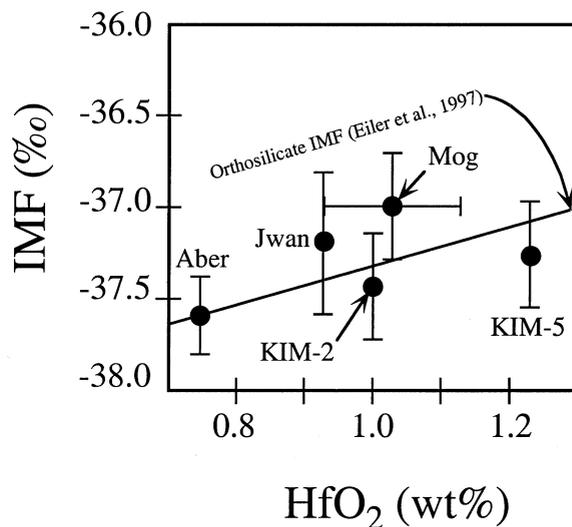


Fig. 3. Instrumental mass fractionation (IMF) for ion microprobe analysis of $\delta^{18}\text{O}$ in homogeneous zircon standards of known HfO_2 content. Zircons, KIM-2, and Jwan are from Eiler et al., (1997) and Valley et al. (1998b). Also plotted is the correlation of IMF and mean atomic mass measured by Eiler et al. (1997) for other orthosilicates normalized to zircon Aber. Note that there is not a strong dependence between IMF and HfO_2 for the range of compositions seen in samples (see Appendix 3). Error bars are ± 1 s.e.; $\text{IMF} = ((^{18}\text{O}/^{16}\text{O})_{\text{measured}} - ^{18}\text{O}/^{16}\text{O}_{\text{actual}}) / ^{18}\text{O}/^{16}\text{O}_{\text{actual}} \times 1000$.

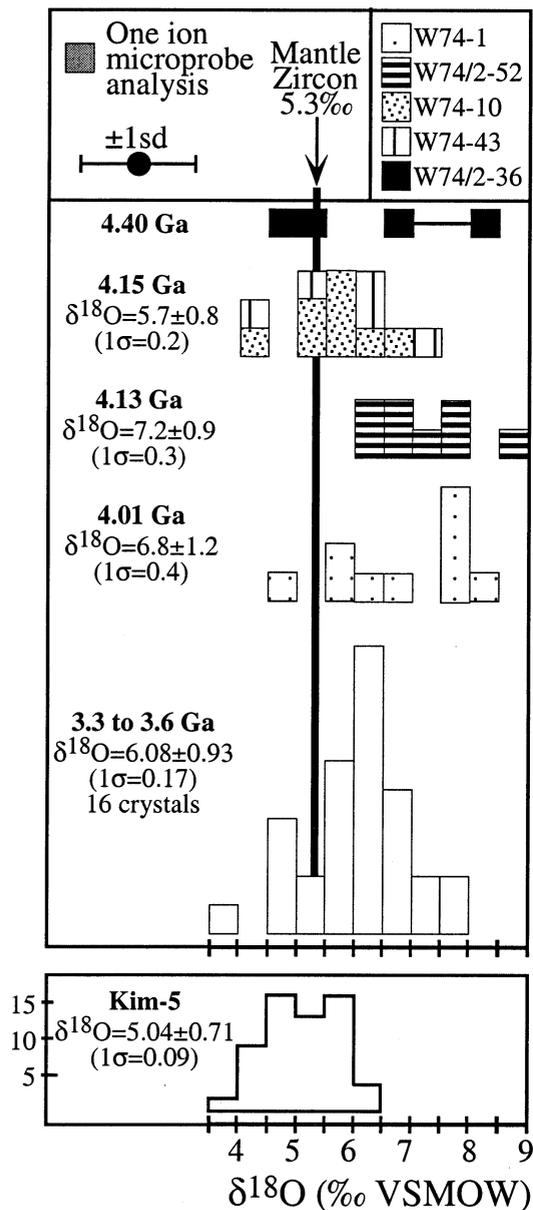


Fig. 4. Compilation of oxygen isotope analyses of detrital zircons from Jack Hills, Western Australia, sample W74, by ion microprobe. Each analysis is shown as a square, and the ± 1 s.d. error bar shows the statistical error (based on counting statistics). Uncertainty in the mean $\delta^{18}\text{O}$ of each crystal (1 s.e.) is given in Table 1 and on the figure as 1σ . Note that all age populations except the two 4.15-Ga grains are elevated in $\delta^{18}\text{O}$ relative to mantle values and relative to a homogeneous zircon standard (KIM-5) with approximately mantle $\delta^{18}\text{O} = 5.04\text{‰}$ (King et al., 1998; Valley et al., 1998b).

smaller than the precision of the ion microprobe, so no correction based on variable HfO_2 concentration is applied.

3.3. Analysis of Oxygen Isotope Ratios by Laser

Zircon standards were analyzed for oxygen isotope ratios by laser fluorination at the University of Wisconsin (Valley et al., 1995, 1998b). This method uses a CO_2 laser ($\lambda = 10.6 \mu\text{m}$) to liberate oxygen from 1 to 3 mg mineral separates by reaction with BrF_5 , with a precision and

accuracy typically better than $\pm 0.1\text{‰}$. The oxygen isotope ratio of four or more aliquots of garnet standard (UWG-2) were determined on each day of analysis to assess daily precision, accuracy, and day-to-day drift. Analyses on each day were adjusted up to 0.18‰ , the amount of the difference between the measured average $\delta^{18}\text{O}$ value of UWG-2 and its accepted value of 5.80‰ (based on a value of 9.59‰ for NBS-28; Valley et al., 1995). The $\delta^{18}\text{O}$ of KIM-5 is $5.04 \pm 0.03\text{‰}$ ($n = 5$).

4. RESULTS

4.1. 3.3- to 3.6-Ga Zircons

Analyses of oxygen isotope ratios by ion microprobe were made on 16 crystals from sample W74 with U-Pb ages of 3.3 to 3.6 Ga (Table 1, Fig. 4). Six of these grains were also analyzed for trace element chemistry by ion microprobe (Table 6, Fig. 5). U-Th-Pb data for all 16 grains are given in Appendix 5. Taken together, the average $\delta^{18}\text{O}$ of all the 3.3- to 3.6-Ga grains is $6.3 \pm 0.6\text{‰}$ (1 s.d.; uncertainty in the mean, s.e., = 0.1‰), statistically identical to the average of all 32 spot analyses of this population: $6.1 \pm 0.9\text{‰}$ (s.e. = 0.2‰). No correlation is seen between $\delta^{18}\text{O}$ and age in this suite, and there is no evidence for subpopulations based on oxygen isotope ratio. In terms of trace element chemistry, this suite is characterized by prominent positive Ce anomalies and negative Eu anomalies, enrichment of HREE relative to LREE, and LREE contents < 1 to $30 \times$ chondrite values (Fig. 5), similar to that determined for grains of the same age range by Maas et al. (1992). In general, the overall REE patterns are typical of igneous zircons as determined by ion microprobe (e.g., Hinton and Upton, 1991). Trace element evidence is consistent with an evolved source for zircons of this age (Maas et al., 1992), and oxygen isotopes are elevated by an average of $\sim 1.0\text{‰}$ relative to zircon values in equilibrium with the mantle ($5.3 \pm 0.3\text{‰}$; Valley et al., 1998b).

4.2. 4.0- to 4.15-Ga Zircons

Two zircon crystals with ages of 4.01 Ga (W74-1) and 4.13 Ga (W74/2-52) and two crystals with an age of 4.15 Ga (grains W74-10 and W74-43) were analyzed for oxygen isotope ratios (Fig. 4) and trace element compositions (Fig. 6). U-Th-Pb data for these grains are given in Appendix 5. Zircon W74/2-52 has $\delta^{18}\text{O} = 7.2 \pm 0.3\text{‰}$ ($n = 8$) and W74-1 has $\delta^{18}\text{O} = 6.8 \pm 0.4\text{‰}$ ($n = 10$). Both of these zircons are statistically distinct (98% confidence level by t -test) from the older 4.15-Ga grains which average $5.7 \pm 0.8\text{‰}$ (1 s.e. = 0.2‰ , $n = 13$). The spread in $\delta^{18}\text{O}$ data for some of these grains is slightly larger than that of KIM-5 (the homogeneous working standard), allowing the possibility that these grains may in fact be zoned with respect to oxygen isotope ratios (e.g., Bindeman and Valley, 2000). Trace element compositions of these grains are similar to the compositions of 3.3- to 3.6-Ga zircons from this study (Figs. 5 and 6) and to the zircon data of Maas et al. (1992).

4.3. 4.40-Ga Zircon

Four oxygen isotope analyses were performed on grain W74/2-36, which has a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4.40 Ga (Wilde et al., 2001). This crystal is a broken grain that is concentrically zoned in cathodoluminescence and BSE, with a distinct center of growth (Fig. 8). The grain also contains three inclusions

Table 2. Trace element analyses (ppm) by ion microprobe of detrital zircons from metaconglomerate sample W74, Jack Hills, Western Australia.

Grain Number	Spot Number	Sr	Y	Nb	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Yb	Lu	Th	U
W74/2-36	m2-13	10.7	2282	46.9	1.1	4.6	112	7.8	46.2	34.5	5.3	83.3	28.2	282	88.3	555	113	2064	586
	m2-14	11.4	3900	40.6	13	7.7	102	7.9	49.1	35.5	4.7	129	39.1	432	144	888	188	1542	664
	m2-17	11.4	2861	53.9	—	0.5	50.9	0.9	7.8	10.3	0.8	70.9	23.4	289	103	640	133	299	434
	m2-30	11.2	2494	27.4	2.2	11.3	188	18.2	99.2	65.3	10.6	142	40.6	353	99.2	560	108	3259	756
	m2-31	11.1	3346	60.3	—	0.3	57.4	0.5	7.7	15.3	1.2	90.0	30.2	365	124	731	152	625	440
W74-1	m1-1	18.1	563	3.9	0.6	0.7	9.0	0.5	3.2	3.4	0.5	11.7	4.2	51.3	19.1	209	54.7	107	297
	m1-2	17.3	631	9.5	0.8	1.9	31.0	2.6	13.5	8.4	1.3	19.1	6.0	60.4	20.4	215	54.6	269	347
W74-10	m1-3	19.7	850	9.9	11	2.4	34.4	1.8	8.9	8.0	1.2	26.0	8.4	85.8	27.9	245	57.8	521	346
	m1-4	20.0	707	11.1	0.1	—	16.3	0.1	0.8	1.3	0.1	10.1	4.4	57.3	22.8	242	61.8	174	339
W74-43	m1-5	14.8	743	8.7	0.2	0.1	4.8	0.1	1.0	2.8	0.3	12.7	5.1	72.7	28.3	232	54.2	28.1	72.6
W74/2-52	m2-15	15.5	606	6.1	0.2	0.1	5.7	0.1	0.8	1.3	0.2	11.1	3.8	50.9	22.2	198	48.7	41.3	77.3
	m2-16	15.5	1689	23	1.1	0.4	25.2	0.7	3.9	5.5	0.6	29.8	11.9	159	62.7	520	122	189	209
	m2-32	13.0	566	1.9	0.2	—	4.4	0.1	0.3	1.8	0.3	11.1	3.9	49.3	20.3	179	43.0	19.8	39.4
W74-34	m1-7	17.7	1209	6.3	0.3	—	11.8	0.1	1.1	3.4	0.2	21.1	8.0	108	42.8	359	86.7	103	216
W74-35	m1-8	15.9	236	7.3	1.5	5.1	25.4	2.3	11.2	4.9	0.8	8.8	2.2	22.6	7.7	103	32.5	144	170
W74-19	m1-9	15.9	620	3.6	1.2	0.4	30.4	0.9	4.9	4.1	0.7	16.0	5.4	60.1	21.7	183	43.9	609	245
W74-20	m1-10	15.1	651	11.4	3.1	2.0	33.8	2.4	12.8	7.8	1.6	19.7	6.3	67.2	22.3	182	43.0	640	233
W74-6	m1-11	16.0	1070	—	1.1	0.9	16.3	0.7	7.0	9.8	1.2	42.8	11.3	117	38.6	218	51.8	207	216
W74-7	m1-12	19.9	1180	6.7	0.2	0.4	33.8	0.6	3.8	4.2	0.3	27.4	8.9	103	39.1	314	73.4	130	141

Note: All trace element compositions are presented in parts per million (ppm), — indicates abundance below the detection limit. Spot numbers of sample analyses indicate the epoxy mount of zircons from W74 and the sequential number of each ion microprobe pit for that mount (example: m1-12 is mount #1, pit #12).

containing SiO₂ (Q), one adjacent to the core and two closer to the rim of the crystal (Fig. 8a). Trace element analyses from five spots on this zircon (Fig. 8b) show zoning from high to low LREE contents from core to rim (Fig. 7). This zoning correlates with Hf, Nb, Ba, Th, and U concentrations and zoning in cathodoluminescence (Fig. 8). Two analyses for oxygen isotope ratio were made in one spot on the high-LREE portion of the crystal (the core), and two were made in another spot on the

low-LREE portion of the crystal. The average $\delta^{18}\text{O}$ of the low-LREE spot is 5.0‰, while the high-LREE spot is 7.4‰ (Figs. 4, 8b).

The three inclusions of SiO₂ were examined closely by electron microprobe. The inclusion adjacent to the crystal core (Fig. 8a) measures 10 × 12 μm , is homogeneous in images by BSE and CL, and 17 spot analyses yield > 99.9 wt.% SiO₂. The other inclusions are smaller and comprise two or three

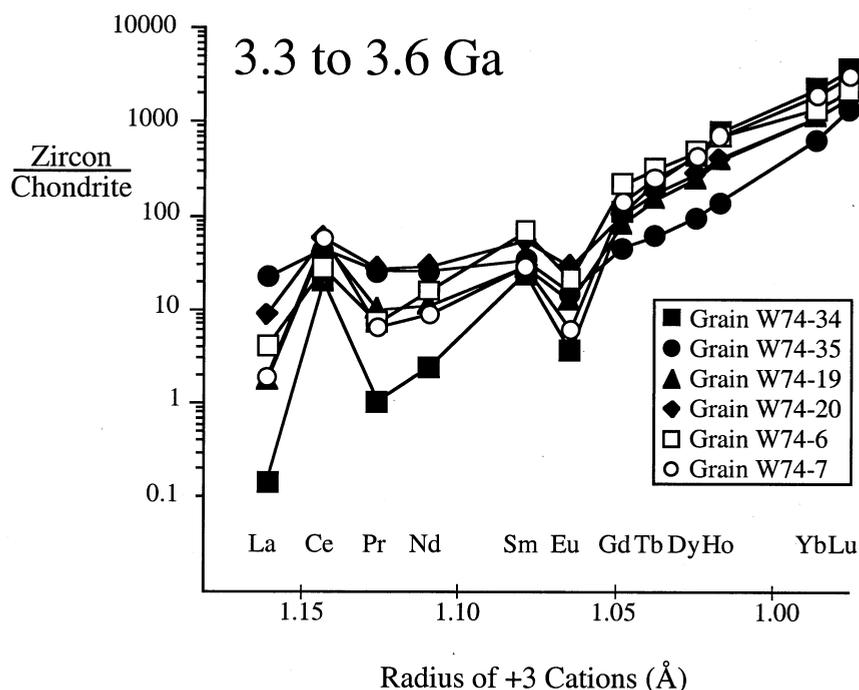


Fig. 5. REE compositions in 3.3- to 3.6-Ga zircons from Jack Hills metaconglomerate W74 measured by ion microprobe.

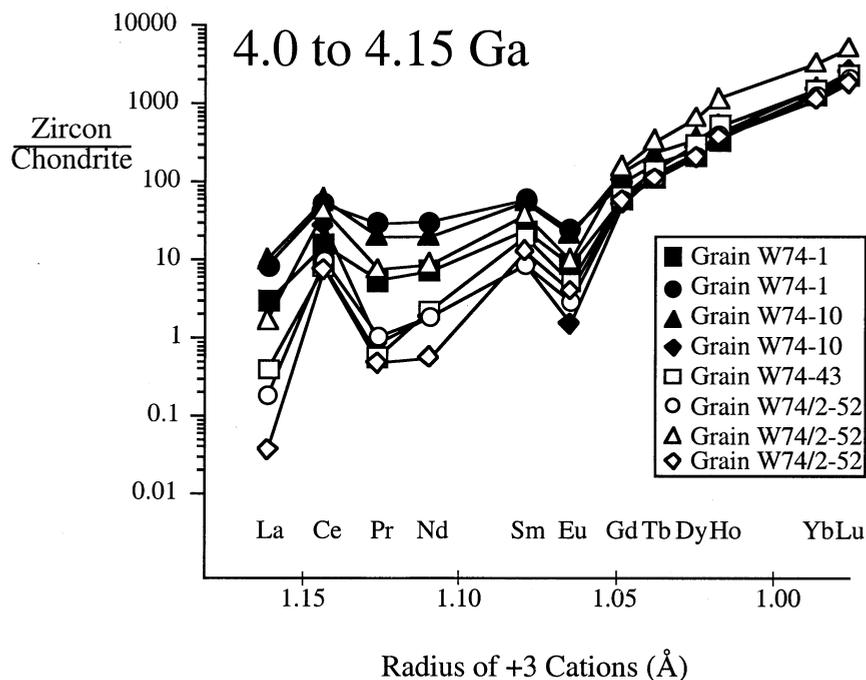


Fig. 6. REE compositions in 4.0- to 4.15-Ga zircons from Jack Hills metaconglomerate W74 measured by ion microprobe.

distinct phases by BSE. These inclusions measure 7×12 and $8 \times 14 \mu\text{m}$, but the internal phases are poorly polished and measure $< 2 \mu\text{m}$ in their shortest dimension and are not uniquely resolved by the $1 \mu\text{m}$ diameter electron beam, which can excite a $65 \mu\text{m}^3$ volume of sample (Reed, 1993). The small features will be investigated using other techniques and an improved polish. The most significant observation, at present, is that each inclusion contains a phase that appears to be SiO_2 and a second phase rich in K_2O (up to 4.3 wt.%) and Al_2O_3 (up to 13.8 wt.%), low in $\text{FeO} + \text{MgO}$ ($\Sigma < 1.2$ wt.%), and with no measurable CaO or Na_2O . These results are consistent with mixtures of K-feldspar + quartz \pm a third mineral, or with devitrified rhyolitic glass. Such “granitic” inclusions are similar to those reported in younger Hadean zircons from the Jack Hills (Maas et al., 1992).

The high- $\delta^{18}\text{O}$ spot overlapped a $\sim 500\text{nm}$ -thick crack, which is partly empty and contains secondary Fe- and Al-phosphates (imaged by SEM and analyzed by electron microprobe). However, these phosphates are thin coatings and could not have contributed more than a few percent of the oxygen analyzed by ion microprobe. Furthermore, the ion microprobe instrumental mass fractionation (IMF) for phosphate minerals is $\sim 20\%$ larger than the IMF for zircon (Eiler et al., 1997), which would cause us to underestimate the $\delta^{18}\text{O}$ of zircon (by up to 0.5‰). Therefore, the 7.4‰ value for the core of zircon W74/2-36 is not significantly affected by these cracks, although the actual $\delta^{18}\text{O}$ could be slightly higher.

The Hadean Earth was bombarded intensively from space and impact features might be expected to be common; however, the fracturing in these zircons is interpreted to postdate incorporation in Jack Hills metasediments at ~ 3.0 Ga for many reasons. Fractured zircons would be weak and would be de-

stroyed by sedimentary transport. Furthermore, none of the > 4 -Ga zircons in this study exhibit shock lamellae or other crystallographic features characteristic of shock metamorphism (e.g., Aaberg and Bollmark, 1985).

Zoning in elemental composition and oxygen isotopes correlates well with the observed zoning in cathodoluminescence (Figs. 8a vs. 8b), especially as revealed on surface #2, exposed after grinding and polishing for the second U-Th-Pb analytical session. Oscillatory cathodoluminescent bands wrap around a rectangular, cathodoluminescent-dark core zone, where the high-LREE and high- $\delta^{18}\text{O}$ values were measured. No major truncations or discontinuities in cathodoluminescence zoning are observed, which is consistent with zircon growth in an evolving, quartz-saturated (as shown by SiO_2 inclusions) magma chamber. Trace element values determined by ion microprobe decrease away from the core of the crystal, and the lower trace element concentrations correspond spatially with the lower $\delta^{18}\text{O}$ value (5.0‰). These low-LREE and $\delta^{18}\text{O}$ values appear to postdate texturally the high-LREE and $\delta^{18}\text{O}$ values, which are near (or in) the core of the crystal. X-ray maps of Y content (after Fournelle et al., 2000), determined by Cameca SX-50 electron microprobe, also correlate spatially with cathodoluminescence and trace elements determined by ion microprobe, with the highest Y contents (~ 0.5 wt.% Y_2O_3) in the core (Peck, 2000).

4.4. Laser Fluorination of Jack Hills Zircons

Conventional analysis was performed to verify the high average $\delta^{18}\text{O}$ value obtained for W74 zircons by ion microprobe. A 10 mg aliquot of zircons was split from the same zircon concentrates that yielded samples for ion microprobe

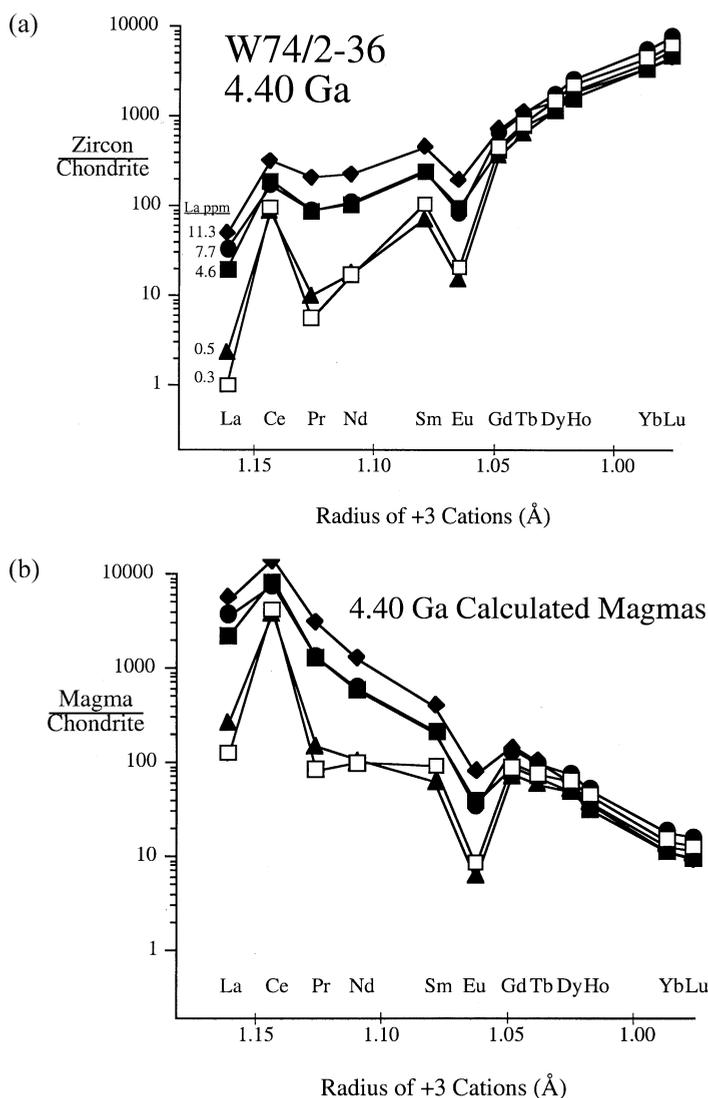


Fig. 7. (a) REE compositions measured by ion microprobe for zircon W74-2/36 (4.40 Ga) from Jack Hills metaconglomerate W74. Analysis spots are shown on Figure 8b. (b) Magmatic REE compositions calculated in equilibrium with zircon W74-2/36 (4.40 Ga) from Jack Hills metaconglomerate W74, using the distribution coefficients of Hinton and Upton (1991). Breaks in slope at Eu and Ce are due to the unknown oxidation state during zircon crystallization and probably do not reflect accurately the composition of the parent magma.

analysis (this study, Wilde et al., 2001). These zircons were separated by 105–135 μm sieves and were non-magnetic at a side tilt of 1° in a Frantz magnetic separator at Curtin University. The 10 mg aliquot was soaked in cold HF overnight and analyzed in bulk (2 mg) by laser fluorination/gas source mass spectrometry at the University of Wisconsin. Two analyses yield $\delta^{18}\text{O} = 6.05 \pm 0.03\%$ VSMOW.

Comparison of the bulk conventional value to spot analyses of individual zircons by ion microprobe is complicated by the heterogeneity of the W74 sample. Never the less, the average $\delta^{18}\text{O}$ of the 21 zircons analyzed by ion microprobe (Table 1) is $6.29 \pm 0.60\%$ VSMOW (1 s.e. = 0.13%) in excellent agreement with the conventional value of $6.05 \pm 0.03\%$. This agreement supports the conclusion that ion microprobe analyses of oxygen isotope ratio in the Edinburgh lab are accurate as well as precise at the stated uncertainties.

4.5. Other Measurements by Ion Microprobe of $\delta^{18}\text{O}$ in Archean Zircon

Mojzsis et al. (2001) report $\delta^{18}\text{O}$ from other Jack Hills detrital zircons (ages 3.91–4.28 Ga), determined using a Cameca ims 1270 ion microprobe under high mass resolution and low-energy offset conditions. Zircon cores measured range from $\delta^{18}\text{O} = 5.4$ to 9.0% , similar to our measurements, but they also report values of 10 and 15% from a zircon rim in their crystal #42. The high values are unique and deserve further comment. Zircons from over 120 Archean igneous rocks have been analyzed by laser fluorination from North America, Scotland, and Africa, and the highest value is 7.52% , consistent with the ion microprobe analyses reported here (King et al., 1998; Peck et al., 2000; Valley et al., 2000). A possible cause of anomalously high $\delta^{18}\text{O}$ values in crystal #42 is radiation

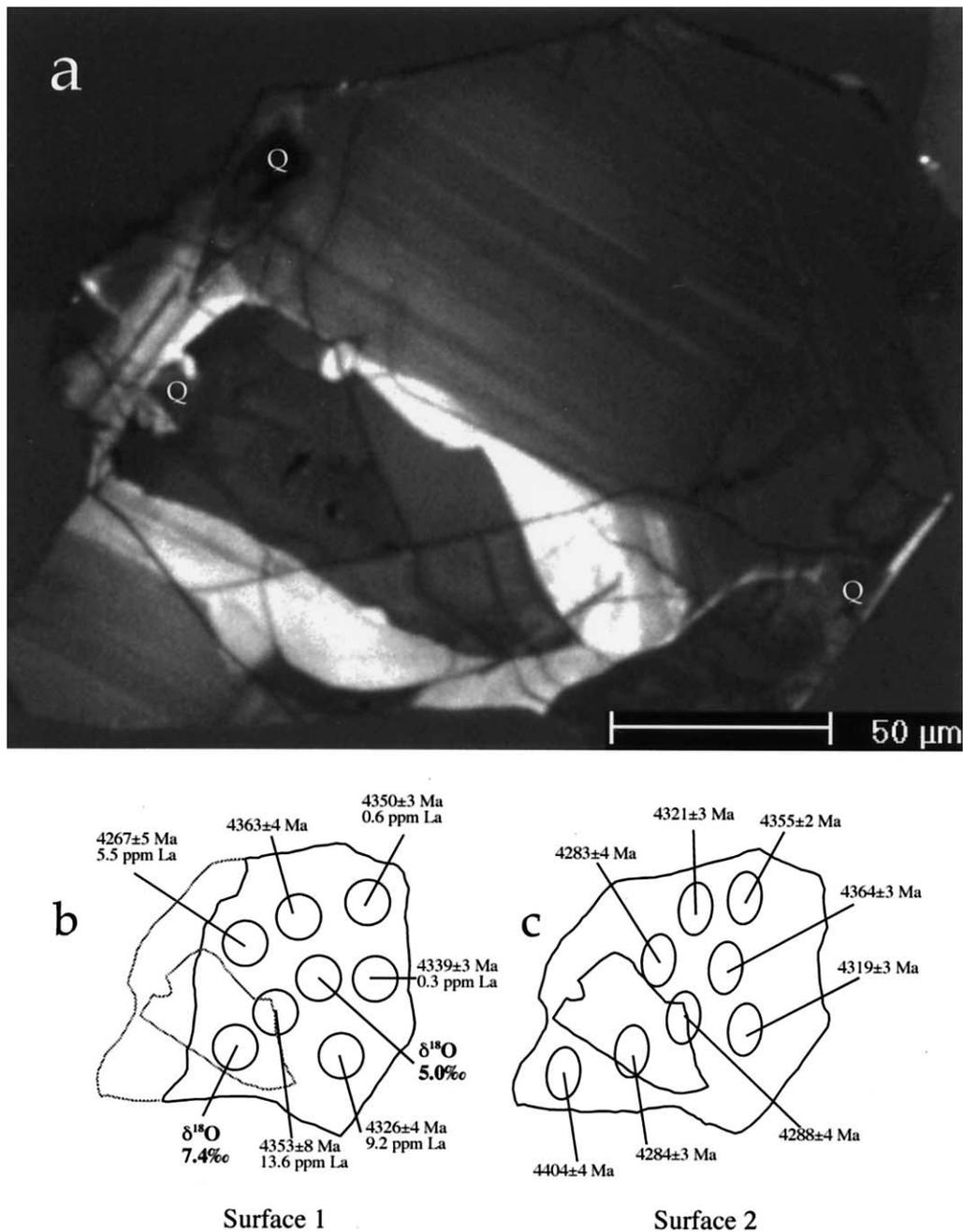


Fig. 8. (a) Cathodoluminescence image of the second U-Th-Pb analytical surface of the 4.40-Ga zircon (W74/2-36), showing banding around a visible dark core. The location of SiO_2 and granitic inclusions are indicated by Q. (b) A sketch of the crystal, showing the locations of ion microprobe pits for age, trace elements, and oxygen isotope analyses (surface 1). Data are shown for La (ppm), $\delta^{18}\text{O}$ (‰), and age (Ma). Note the correlation from core to rim in cathodoluminescence intensity, trace element composition, and oxygen isotope ratios. Shown for reference in gray outline is the projection from the edge of the crystal on surface 2 and the projection of the boundary of the dark core zone, both of which are $\sim 20 \mu\text{m}$ below surface 1. (c) A sketch of surface 2, showing the locations of additional U-Th-Pb analyses.

damage as suggested by its $^{206}\text{Pb}/^{238}\text{Pb}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 0.66, 2.08, and 4.11 Ga, respectively (Mojzsis et al., 2001). High magnetism, low-concordance zircon has been shown to be susceptible to late-stage hydrothermal alteration and exchange, altering igneous $\delta^{18}\text{O}$ values (Valley et al., 1994). It is possible that the high $\delta^{18}\text{O}$ values are from thin metamorphic or hydrothermal overgrowths, but we view it

unlikely that they represent igneous zircon. We cannot assess these data further without a more complete description of the samples and analytical technique.

5. DISCUSSION

Previous studies of early Archean rocks have shown characteristics such as pre-4.0-Ga crustal LREE enrichment relative to

the bulk Earth, highly radiogenic U/Pb ratios, and especially high ϵ_{Nd} values (e.g., Jacobson and Dymek, 1988; Bowring et al., 1989b; Bowring and Housh, 1995). Inferred ancient mantle depletions in incompatible elements have been questioned due to open-system behavior of some radiogenic isotope systems, especially for whole rocks (e.g., Vervoort et al., 1996) and the problem of correlating zircon ages with whole-rock isotope data (e.g., Moorbath et al., 1997). In situ analysis of well-characterized, dated zircons for oxygen isotope ratios by ion microprobe (as well as for Hf isotopes; e.g., Vervoort et al., 1996; Amelin et al., 1999) allows intracrystalline assessment of crystal chemistry, radiation damage, and growth history and so avoids many of the problems inherent in analysis of bulk mineral and whole-rock samples.

5.1. Preservation of Igneous Oxygen Isotope Ratios in Zircon

Sample W74 provides good internal evidence that zircon has preserved original oxygen isotope ratios. Zircons of each age population (especially the identical $\delta^{18}\text{O}$ in 4.15-Ga zircons) have distinct oxygen isotope ratios, preserving systematic crystal-to-crystal differences (Fig. 4) and demonstrating that oxygen diffusion in zircon was not fast enough to homogenize oxygen isotopes between individual zircons from W74. Furthermore, zircons in W74 are not in oxygen isotopic equilibrium with host quartz from W74 ($\delta^{18}\text{O} = 10.2\%$). For example, measured values of $\Delta(\text{Qtz-Zrc})$ for different zircons range from 3.2 to 4.5%. Zoning of $\delta^{18}\text{O}$ in W74-26/2-36 also argues against homogenization of oxygen isotope ratio by diffusion, because the high value of $\delta^{18}\text{O}$ is from the center of the crystal, while the normal mantle-like value comes from the rim, the opposite relation to that predicted if oxygen exchanged by diffusion inward from the grain boundary. Oxygen isotope analysis of zircon is thus more reliable for detecting supracrustal contribution in Early Archean magmas than whole-rock analyses of radiogenic or stable isotopes (also, cf. King et al., 1998).

5.2. 4.40-Ga Continental Crust

Zircon W74/2-36 (4.40 Ga) provides the earliest information available for understanding magmatism and crustal growth of the Earth. The trace element chemistry, oxygen isotope composition, inclusions, and internal zoning of W74/2-36 provide our only direct information on pre-4.3-Ga crust.

5.2.1. Trace element composition

The trace element composition of W74/2-36 (4.40 Ga) is similar to other > 4.0 Ga Australian zircons examined in this and other studies (e.g., Hf content, Zr/Hf ratio, positive Ce and negative Eu anomalies), but W74/2-36 has higher U concentration and high Th/U ratios. Compston and Pidgeon (1986) found low U (30–220 ppm), Th (20–330 ppm), and Th/U ratios (0.3–1.8 ppm) in slightly discordant old zircons from sample W74, similar in Th/U ratio (but somewhat less in U and Th content) to other zircons from Jack Hills and Mt. Narryer. In contrast, our eight ($\geq 86\%$ concordant) SHRIMP II analyses of W74/2-36 show 127 to 450 ppm U, 75 to 1224 ppm Th, and Th/U ratios of 0.6 to 2.7. These Th/U ratios contrast with those commonly reported from metamorphic zircons (Th/U < 0.1)

and further support magmatic growth of W74/2-36 (see Maas et al., 1992).

The REE concentration of W74/2-36 was determined by five spot analyses (Figs. 7 and 8b), which show zoning in LREE from high values in the center of the crystal (3 spots, $\sim 20\text{--}440 \times$ chondrite) to low values farther from the core (2 spots, $\sim 1\text{--}100 \times$ chondrite), variability not observed (or expected) in the heavy REEs. Partition coefficients from Hinton and Upton (1991), combined with the REE concentration in the core of the crystal, yields calculated magma compositions with pronounced LREE-enriched patterns ($\text{La/Lu}_n(\text{magma}) = 240\text{--}620$; LREE are $220\text{--}14,000 \times$ chondrite; Figure 7b). These calculated magmas show characteristics distinctive of evolved melts (e.g., LREE enrichment, prominent negative Eu anomalies) and are not consistent with the REE patterns of primitive mafic rocks. For example, La, Ce, Pr, and Nd compositions of the core of W74/2-36 are enriched up to $60 \times$ relative to a lunar zircon (Wopenka et al., 1996) and zircon from a basaltic diatreme (Hinton and Upton, 1991). The LREE contents in the core of the 4.40-Ga zircon are unusually high compared to REE concentrations of zircons determined by ion microprobe from other studies (e.g., Hinton and Upton, 1991; Paterson et al., 1992; Barbey et al., 1995) but are similar to LREE enrichment seen in the late zircons from $\sim 400\text{-Ma}$ aplitic rocks by Maas et al. (1992) (see their figure 9c). Growth of 4.40-Ga zircon in an evolved melt is also consistent with the observed granitic inclusions, indicating that the parent magma was quartz saturated during the growth of the core of W74/2-36 (Fig. 8). Although REE compositions of zircon are not necessarily useful for distinguishing between source lithologies in detail (e.g., Hoskin and Ireland, 2000), the high LREE content of the core W74/2-36 is inconsistent with mantle-like melts and suggests growth in an evolved magma.

5.2.2. Oxygen isotope ratios

Four analyses of oxygen isotope ratios from two spots on W74-2/36 gave average $\delta^{18}\text{O}$ values of 5.0 and 7.4‰ and with higher $\delta^{18}\text{O}$ value from the core of the crystal. As discussed in the “Methods” section, the predicted precision of these analyses from counting statistics is $\pm 0.7\%$ (1 s.d.), and the reproducibility of each of the two pairs of analyses is better: ± 0.3 and $\pm 0.6\%$, respectively. The lower $\delta^{18}\text{O}$ value of $5.0 \pm 0.7\%$ is indistinguishable from oxygen isotope ratios in equilibrium with the mantle ($5.3 \pm 0.3\%$), while the high $\delta^{18}\text{O}$ value of $7.4 \pm 0.7\%$ is elevated relative to oxygen in equilibrium with mantle-derived melts at magmatic temperatures.

We interpret zoning observed in trace elements and cathodoluminescence, which is coupled with the decrease in oxygen isotope ratio from core to rim, to be consistent with igneous processes. For example, this zoning could be caused by assimilation of primitive, lower-LREE normal $\delta^{18}\text{O}$ material (either country rock or another melt) by a high $\delta^{18}\text{O}$ parent magma. The decrease in $\delta^{18}\text{O}$ and trace element contents as the zircon grew could also have resulted from a more complicated growth history not resolvable with the U-Th-Pb data (Wilde et al., 2001). Zoning in oxygen isotope ratios in W74/2-36 may form from similar processes as zoned zircons from Yellowstone, which record assimilation of hydrothermally altered material by rhyolitic magma chambers (Bindeman and Valley, 2000).

It is clear that more oxygen isotope data from this grain (or others of the same age) are desirable; however, this would require grinding away existing ion microprobe pits and repolishing with the risk of using up all or much of the sample. We do not consider repolishing to be prudent given the unique nature of sample W74-2/36. In the absence of additional data, several important (if tentative) conclusions can be made. The analytical uncertainty based on two high- $\delta^{18}\text{O}$ analyses in the core of the grain means that the average $\delta^{18}\text{O}$ of 7.4‰ overlaps the mantle zircon value of 5.3‰ only at 3 s.d. Thus, the true $\delta^{18}\text{O}$ of the core of the grain is elevated with respect to mantle values at a confidence level of $\sim 99\%$. Based on this sampling, we conclude that growth of the core of this zircon was in a high- $\delta^{18}\text{O}$ (and high-LREE) environment, and that high $^{18}\text{O}/^{16}\text{O}$ ratios formed before 4.40 Ga due to low-temperature fluid–rock interaction on or near the Earth’s surface.

5.3. High- $\delta^{18}\text{O}$ Magmas From 4.01 to 4.40 Ga

A significant result of this study is the discovery of oxygen isotope ratios in 4.01-Ga, 4.13-Ga, and the 4.4-Ga zircon that are elevated compared with oxygen isotope ratios of zircon in equilibrium with the mantle. These values are similar to those reported in younger Archean zircons worldwide, which are interpreted to result from recycling of supracrustal material (e.g., King et al., 1998; Valley et al., 1998b, 2000, 2001; Peck et al., 2000). The relation of high- $\delta^{18}\text{O}$ magmas and S-type magmas is well established in younger rocks (Taylor and Sheppard, 1986). In this study, we recognize the $\delta^{18}\text{O}$ signature of these processes in the earliest samples of continental crust available.

There is good evidence that the $\delta^{18}\text{O}$ value of the mantle has remained essentially unchanged since its formation because of the restricted $\delta^{18}\text{O}$ values of mantle-derived rocks through time and the restricted $\delta^{18}\text{O}$ of lunar samples (e.g., Taylor and Sheppard, 1986). Oxygen isotope ratios from lunar samples are remarkably homogenous ($\delta^{18}\text{O}(\text{WR}) = 5.5\text{--}6.5\%$; Taylor and Epstein, 1970), the same as the Earth’s mantle and the bulk $\delta^{18}\text{O}$ of the Earth–Moon system (e.g., Clayton, 1993). Even highly differentiated lunar granites are only $\sim 0.5\%$ higher than lunar mafic rocks (zircon in magmatic equilibrium with these evolved rocks would have $\delta^{18}\text{O} \approx 5.0\text{--}5.5\%$, consistent with published zircon $\delta^{18}\text{O}$ values from Archean granitoids).

Zircons from geochemically primitive, mantle-like rocks also have similar low- $\delta^{18}\text{O}$ values, for example, Phanerozoic zircon megacrysts from South African kimberlites ($\delta^{18}\text{O} = 5.3 \pm 0.2\%$, $n = 28$; Valley et al. 1998b). Tonalite-trondhjemite-granite lithologies from the Superior Province ($\delta^{18}\text{O}(\text{zircon}) = 5.5 \pm 0.4\%$, $n = 39$) indicate little input ($< 14\%$) from high- $\delta^{18}\text{O}$ supracrustal material (King et al., 1998).

In the Superior Province slightly higher $\delta^{18}\text{O}$ values are seen in syn- to post-tectonic LREE and Mg-enriched plutons called sanukitoids ($\delta^{18}\text{O}(\text{zircon}) = 6.4 \pm 0.2\%$, $n = 15$), indicating some high- $\delta^{18}\text{O}$ input from subducted ocean crust or oceanic sediments (King et al., 1998). The high- $\delta^{18}\text{O}$ values for the 4.01- and 4.13-Ga grains from Jack Hills are also consistent with magmatic assimilation or melting of supracrustal material, while the $\delta^{18}\text{O}$ values of the two 4.15-Ga zircons are indistinguishable from pristine mantle values (Fig. 4). The $\delta^{18}\text{O}$ values of the 4.15-Ga population are statistically indistinguishable

($> 98\%$ confidence) from mantle-derived juvenile rocks of the Superior Province (King et al., 1997, 1998, 2000). Conversely, 4.01- and 4.13-Ga zircons have higher $\delta^{18}\text{O}$ than mantle-like Superior Province and Barberton zircons and the mantle-derived Phanerozoic zircons from southern African kimberlites.

Maas et al. (1992) present several lines of evidence supporting a magmatic (rather than metamorphic or hydrothermal) origin for 4.0- to 4.3-Ga detrital zircons from Western Australia: euhedral growth zoning, evolved trace element chemistry (e.g., Th/U = 0.3 to 1.1), and granitic mineral inclusions (quartz, K-feldspar, and monazite). The samples examined in this study also show these characteristics and have REE compositions consistent with growth in evolved, quartz-saturated magmas.

Fractionation of oxygen isotope ratios to values significantly higher than the mantle are generally the result of low-temperature interaction with water, where large fractionations between solids and fluids (enriching minerals by up to 10‰ or more) result in high- $\delta^{18}\text{O}$ values in hydrothermally altered rocks, in sediments, and in soils (e.g., Hoefs, 1997). Closed-system fractional crystallization alone has a much more limited effect on oxygen isotope ratios, typically $< 1\%$.

Most meteorites have $\delta^{18}\text{O}$ values similar to the Earth’s mantle and to the Moon, or lower. Higher values are restricted to some chondrites and ureilites (Clayton, 1993), but these meteorites are not possible parental material for the high- $\delta^{18}\text{O}$ zircons, given the extreme LREE enrichment (up to 14,000 \times relative to chondrite) in the calculated parent magmas for W74/2-36 and the other > 4.0 -Ga zircons (Figs. 5, 6, 7). Furthermore, the identification of dozens of zircon crystals older than 4.0 Ga with distinct grouping of ages from different locations in Western Australia is strong evidence that the pre-4.0-Ga suite is not derived from meteorites.

Neodymium isotope studies of the Acasta Gneiss have suggested that an incompatible element-enriched reservoir (such as continental crust) existed even before 4.3 Ga (e.g., Bowring and Housh, 1995). If true, then the REE-enriched melts from which W74/2-36 crystallized at 4.40 Ga represents a portion of early crust with the appropriate geochemical characteristics to be the unrecognized enriched reservoir.

Amelin et al. (1999) reported hafnium isotope values for Jack Hills detrital zircons up to 4.14 Ga. New calibration of the ^{176}Lu decay constant reported by Scherer et al. (2001) suggest that the Hf data reported by Amelin et al. (1999) is unradiogenic relative to bulk Earth. This would indicate the existence of an enriched reservoir (such as continental crust) at least as old as 4.3 Ga, consistent with the age and chemistry of the 4.40 Ga zircon W74/2-36.

5.4. Liquid Water From 4.0 to 4.4 Ga

The earliest direct evidence for surface temperatures $< \sim 100^\circ\text{C}$ and a terrestrial hydrosphere is ≥ 3.85 -Ga meta-sediment from southwest Greenland, including banded iron formations that are of undoubted aqueous origin (Nutman et al., 1997). One constraint on the presence of a stable hydrosphere on the Earth is the extensive meteorite bombardment experienced in the Early Archean as deduced from the lunar record (Baldwin, 1974). Sleep et al. (1989) present limits on early meteorite bombardment in the context of kinetic energy im-

parted to the Earth and constrain the last ocean-vaporizing impact(s) to between ~ 4.4 and 3.8 Ga, and recent work has documented a strong peak in impact intensity at ~ 3.9 Ga (Cohen et al., 2000). However, a long-lasting hydrosphere is not necessary for water–rock interaction and granite production at 4.0 or 4.4 Ga. It is possible that the water–rock interaction and production of high- $\delta^{18}\text{O}$ lithologies could have occurred during intense meteorite bombardment but between cataclysmic events. The Earth's hydrosphere at this time may have alternated between water periods, when average surface temperatures were low and liquid water dominated, and steam periods, when temperatures were above the boiling point and oceans were completely or partially vaporized. The temperature of this transition is uncertain, because atmospheric pressure was considerably higher during steam periods and the mass of the Hadean hydrosphere is uncertain.

The production of felsic crust in the Early Archean requires the wet melting of mafic material, most probably hydrated oceanic crust. Campbell and Taylor, (1983) suggest that to have extensive hydration of primitive crust, large bodies of liquid water must be present to submerge midocean ridges. Steam would be an inefficient mechanism to hydrothermally alter large amounts of ocean crust, because it is unlikely to convect through rocks due to its low density; thus, magmatic water would pass at most once through hydrothermal systems and be lost to the atmosphere. Therefore, the high- $\delta^{18}\text{O}$ values measured in 4.01- and 4.13-Ga zircons strengthen the arguments of Campbell and Taylor (1983) and extend the evidence for the oceans at 4.0 to 4.4 Ga to the parent rocks of the Jack Hills zircons.

5.5. Implications for the First 150 Million Yr of the Earth

The discovery of a 4.40-Ga zircon with elevated LREE and $\delta^{18}\text{O}$ values allows new, first-order constraints on the first 150 million yr of Earth history. Hf-W isotope systematics of the Earth and published ages of lunar rocks are commonly interpreted to indicate that differentiation of the Earth's core, collision of the Earth with a Mars-sized meteor, and formation of the Moon all occurred within a period of < 80 million yr at 4.47 ± 0.04 Ga (see Halliday et al. 1996). These data are consistent with the 4.45 ± 0.02 Ga age of core formation calculated from I-Xe modeling (e.g., Zhang, 1998), as well as other published estimates of the age of core formation (e.g., Staudacher and Allègre, 1982; Jacobson and Harper, 1996), indicating resetting of terrestrial isotopic clocks and the possibility of a magma ocean at ~ 4.45 Ga, and that accretion was essentially finished by this time (Halliday et al. 1996; Meisel et al., 1996; Zhang, 1998).

Since the chemistry of zircon crystal W74-2/36 suggests the formation of continental crust as well as low-temperature alteration with water before 4.40 Ga, any magma ocean present at 4.47 ± 0.04 Ga must have cooled to low temperatures within $< \sim 70$ million yr of the hypothesized Mars-sized meteorite collision. This result is consistent with thermal modeling of the Earth, which predicts terrestrial thermal equilibration 1 to 10 million yr after a giant impact, even after an impact large enough to produce 50% melting of the Earth (Spohn and Schubert, 1991). However, this is contrary to the expectation of

a hot young earth caused by heat of planetary accretion, short-lived radionuclides, and possible collision with a Mars-sized impactor (Pollack, 1997). If the early Earth was hot, our new data for liquid water at 4.40 Ga constrains the length of time available for cooling and thus the amount of insulation by the early atmosphere. Our data are also consistent with alternate, nonimpact models for the genesis of the Moon. For instance, Jones and Palme (2000) suggest that mixing and differentiation in a terrestrial magma ocean could not preserve the primitive Re-Os (and some other trace element) systematics that are observed in fertile mantle xenoliths.

Following any initial rapid cooling, cooling of the early Earth's mantle is estimated to be on the order of ~ 30 to $90^\circ\text{C}/\text{billion yr}$. (see Galer and Mezger, 1998). Any continental crust and the hydrosphere present at 4.40 Ga would then be subjected to subsequent meteorite bombardment possibly capable of vaporizing the Earth's oceans (Sleep et al., 1989), and igneous and hydrothermal processes could occur between catastrophic impacts.

6. CONCLUSIONS

Detrital zircons from Jack Hills sample W74 have age populations of 3.3 to 3.6 Ga and 4.15 Ga, and single grains with ages of 4.10, 4.13, and 4.40 Ga. The 4.40-Ga zircon is the oldest terrestrial mineral known. Values of $\delta^{18}\text{O}$ of the 3.3- to 3.6-Ga population are, on average, 6.3‰, $\sim 1\%$ higher than mantle values and are similar to other Archean zircons (King et al., 1998; Peck et al., 2000; Valley et al., 2000, 2001). The $\delta^{18}\text{O}$ of the 4.01-Ga grain is 6.8‰ and the 4.13-Ga grain is 7.2‰, while the two grains at 4.15 Ga average 5.7‰. The 4.40-Ga grain is zoned with respect to trace element composition and oxygen isotope ratio, from 7.4 to 5.0‰. This zoning suggests igneous processes involving supracrustal materials as early as 4.40 Ga.

Oxygen isotope ratios higher than mantle values in these zircons indicate magmatic assimilation or melting of high- $\delta^{18}\text{O}$ materials, and there is no known primitive mantle reservoir of such values. These high- $\delta^{18}\text{O}$ materials could be sediments or hydrothermally altered rocks that underwent low-temperature interaction with water, even as the pre-4.0-Ga Earth was undergoing meteorite bombardment. These data provide a perspective on the early Archean when high- $\delta^{18}\text{O}$ rocks and granitic magmas interacted in a continental setting. The possible presence of a pre-4.40-Ga hydrosphere suggests that the surface of the Earth had cooled to temperatures that allowed liquid water within < 100 million yr of the formation of the Moon and the Earth's core.

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