1 **The effect of weathering on U-Th-Pb and oxygen isotope systems of ancient**
2 **zircons from the Jack Hills, Western Australia.**

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4 **By**

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16

17 **Abstract**

18

19 We report the result of a SIMS U-Th-Pb and O-OH study of 44 ancient zircons from
20 the Jack Hills in Western Australia with ages ranging from 4.3 Ga to 3.3 Ga. We have
21 investigated the behaviour of oxygen isotopes and water in the grains by determining
22 $\delta^{18}\text{O}$ and OH values at a number of locations on the polished surfaces of each grain.
23 We have divided the zircons into five groups on the basis of their U-Th-Pb and OH-
24 oxygen isotopic behaviour. The first group has concordant U-Th-Pb ages, minimal

25 common Pb, $\delta^{18}\text{O}$ values consistent with zircons derived from mantle source rocks and
26 no detectable OH content. U-Th-Pb systems in zircons from Groups 2, 3 and 4 vary
27 from concordant to extremely discordant where influenced by cracks. Discordia
28 intercepts with concordia at approximately zero Ma age are interpreted as disturbance
29 of the zircon U-Th-Pb systems by weathering solutions during the extensive, deep
30 weathering that has affected the Archean Yilgarn Craton of Western Australia since at
31 least the Permian. Weathering solutions entering cracks have resulted in an influx of
32 Th and U. $\delta^{18}\text{O}$ values of Group 2 grains fall approximately within the “mantle “ range
33 and OH is within background levels or slightly elevated. $\delta^{18}\text{O}$ values of Group 3 grains
34 are characterised by an initial trend of decreasing $\delta^{18}\text{O}$ with increasing OH content.
35 With further increase in OH this trend reverses and $\delta^{18}\text{O}$ becomes heavier with
36 increasing OH. Group 4 grains have a distinct trend of increasing $\delta^{18}\text{O}$ with increasing
37 OH. These trends are explained in terms of the reaction of percolating water with the
38 metamict zircon structure and appear to be independent of analytical overlap with
39 cracks. Group five zircons are characterised by U-Pb systems that appear to consist of
40 more than one age but show only minor U-Pb discordance. Nevertheless trends in $\delta^{18}\text{O}$
41 versus OH in this group of grains resemble trends seen in the other groups. The
42 observed trends of $\delta^{18}\text{O}$ with OH in the Jack Hills zircons are similar to those reported
43 in a previous study of zircons from an Archean granite from south-western Australia.

44

45 1. INTRODUCTION

46 The only surviving fragments of the Hadean period of Earth history are > 4Ga
47 detrital zircons found in ~ 3Ga quartzites and quartz pebble conglomerates from Mt
48 Narryer, The Maynard Hills and the Jack Hills in Western Australia (Froude et al.,
49 1983; Compston and Pidgeon, 1986; Nelson et al., 2000)(Fig.1). The > 4Ga zircons

50 have been subjected to numerous chemical and isotopic investigations including Hf
51 isotope studies (e.g. Amelin et al., 1999; Harrison et al., 2005, 2008; Kemp et al.,
52 2010), Ti thermometry (e.g. Harrison and Schmidt 2007), lithium (e.g. Ushikubo et al.,
53 2008), REE studies (e.g. Maas and McCulloch, 1991; Maas et al., 1992; Peck et al.,
54 2001) and oxygen isotope analyses (e.g. Mojzsis et al., 2001; Peck et al., 2001;
55 Cavosie et al., 2004, 2005; Trail et al., 2007; Harrison et al., 2008) in attempts to
56 identify their parent rocks and to investigate the Hadean history of the Earth.

57 These studies have generated a number of sometimes conflicting conclusions
58 on the nature of parent rocks of the >4Ga zircons and the evolution of the Hadean. The
59 oldest zircons in the Jack Hills conglomerate, with ages of about 4370Ma (Wilde et
60 al., 2001; Nemchin et al., 2006; Holden et al., 2009; Valley et al., 2014) represent the
61 earliest consolidation of the Earth's crust. From their Nd, U-Pb and geochemical
62 (including REE) results Maas et al. (1992) and Maas and McCulloch (1991) proposed
63 a granitic parent for the > 4Ga zircons indicating a differentiated continental source of
64 substantial thickness rather than a provenance of felsic differentiates within a
65 dominantly mantle ocean-type crust. Harrison et al (2005) reported Hf data that
66 supported formation of continental crust by 4.4 to 4.5 Ga. Kemp et al. (2010)
67 concluded, from the results of a concurrent Hf and Pb isotope study of Jack Hills
68 zircons, that Hadean history consisted of crustal reworking of an enriched mafic
69 magma extracted from primordial mantle at 4.4 – 4.6 Ga. From studies of oxygen
70 isotopes of Jack hills zircons Wilde et al. (2001), Mojzsis et al. (2001) Peck et al.
71 (2001) Cavosie et al. (2004) Trail et al. (2007) and Harrison et al. (2008) showed that
72 $\delta^{18}\text{O}$ values in some 4.4 to 3.9 Ga zircons are significantly heavier than expected for
73 zircons formed from mantle sources and proposed that they crystallised from evolved
74 granitic melts where “the protoliths of the magmas were altered by low temperature

75 interaction with liquid water near Earth's surface" (Cavosie et al. 2005). The model
76 was questioned by Hoskin (2005) who proposed that the high $\delta^{18}\text{O}$ signatures, and flat
77 REE patterns of Jack Hills zircons (Wilde et al., 2001; Peck et al., 2001) and other
78 Hadean Jack Hills zircons, could result from localized exchange with a light-REE-
79 bearing, heavy $\delta^{18}\text{O}$ (6–10‰ or higher) hydrothermal fluid at about 4.27 Ga. Cavosie
80 et al. (2006) discussed at length the evidence for a hydrothermal origin for flat LREE
81 patterns in some Jack hills zircons and concluded that this did not support the case for
82 external fluid interaction and that the role of fluids in the LREE enrichment process is
83 minor. The report by Harrison and Schmidt (2007) that "Ti contents associated with
84 very high apparent temperatures (Ti thermometry) were introduced into the crystal
85 along cracks and are thus unrelated to zircon formation" suggests external fluid
86 penetration into cracks depositing Ti. Valley et al. (1994) proposed that hydrothermal
87 fluids exchange oxygen with high magnetism (radiation damaged) zircons from
88 Adirondack gneisses lowered the $\delta^{18}\text{O}$ in some grains. The potential for low
89 temperature hydrothermal fluid interaction with radiation damaged zircon has been
90 shown experimentally by Geisler et al (2002). Nemchin et al (2006) reported that many
91 of the Jack Hills zircons had discordant U–Pb systems and excess common Pb (see
92 also Maas and McCulloch 1991) indicating a superimposed, relatively recent, reaction
93 between radiation damaged zircon and low temperature fluids. The effect of fluids on
94 Jack Hills zircons is therefore an important avenue of research and the purpose of this
95 contribution is to present the results of an investigation into the effects of low
96 temperature weathering fluids on the U-Th-Pb and the oxygen isotope systems of Jack
97 Hills zircons.

98

99 2. METHODS

100

101 **2.1 The zircon mounts**

102 An epoxy mount (Mount 1) of about 500 grains was prepared from the non
103 magnetic fraction (Frantz isodynamic separator) of zircons separated from a sample of
104 quartz conglomerate from sample site W74 in the Jack Hills originally studied by
105 Compston and Pidgeon (1986)(Fig.1). In a second procedure about 200 grains were
106 mounted on a SIMS mount (Mount A) and over 400 grains were mounted on a third
107 epoxy mount (Mount B) by handpicking grains from a magnetic (on the Frantz),
108 +100 μm , sieve fraction. These mounts were polished and cathodoluminescence (CL)
109 images of the zircons were made using the Swedish Museum of Natural History
110 electron microscope.

111

112 **2.2 U-Th-Pb analyses**

113 **Curtin University SHRIMP II**

114 Preliminary U-Th-Pb isotopic analyses were made on Mount 1 to identify > 4
115 Ga zircons using the sensitive high-resolution ion microprobe (SHRIMP II) at the John
116 de Laeter Centre of Mass Spectrometry, Curtin University, Perth, Western Australia.
117 The SHRIMP analytical procedure has been described by Compston et al. (1984) and
118 Kennedy and de Laeter (1994). The U-Pb data collection routine used consisted of one
119 scan through the mass stations. Every tenth analysis was made on the CZ3 standard
120 (Pidgeon et al., 1994). Data reduction was made using the SQUID and ISOPLOT
121 programs (Ludwig, 2001 a and b). The U-Pb systems of selected grains were analysed
122 in detail on the NordSIMS Cameca 1280 as described below.

123 **U-Pb analyses on the NordSIMS Cameca IMS1280 ion microprobe**

124 U-Th-Pb analytical methodology follows previously published analytical descriptions

(Whitehouse et al., 1999; Whitehouse and Kamber, 2005). A molecular oxygen beam (O_2^- at -13 kV) was imaged to give a ca. 6 nA current in an elliptical, ca. 20 μm spot on the polished surface of the grain. Secondary ions were extracted from the sample at +10 kV and admitted, via high-magnification transfer optics, to the mass spectrometer operating at a mass resolution ($M/\Delta M$) of 5400. Oxygen flooding of the sample chamber was used to enhance the Pb^+ yield. At the start of each analysis, a 70 second pre-sputter raster of 25 μm was used to remove the Au coating and minimise surface contamination. This was followed by automated centering of the beam in the field aperture, optimisation of the mass calibration using the matrix Zr_2O species and optimisation of secondary ion energy in the 45 eV energy window. Preliminary analyses of the zircon in mounts A and B were made to identify > 4Ga grains using one scan through the mass stations. For selected grains a second analytical session involved a peak-hopping data collection routine that consisted of 16 cycles through the mass stations, with signals measured on an ion counting electron multiplier with a 44 ns electronically gated dead time. Pb/U ratios were calibrated using an empirical correlation between Pb^+/U^+ and UO_2^+/U^+ normalised to the CZ3 standard (Pidgion et al. 1994).

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2.3 Oxygen and OH analyses on the NordSIMS Cameca IMS 1280 ion microprobe

Oxygen isotopes were measured on the CAMECA IMS1280 ion microprobe of the NordSIMS Facility, Swedish Museum of Natural History, using a method similar to that described by Nemchin et al. (2006b) with the exception that, for this study, besides measuring ^{16}O and ^{18}O concurrent measurements were also made of $^{16}\text{O}^1\text{H}$ (referred to in the paper as OH). Briefly, a 20 keV Cs^+ primary beam (+10 kV primary,

150 -10 kV secondary) of ca. 1.5 nA was used in critically focused (Gaussian) mode to
151 sputter a ca. 10 μm rastered sample area, with a normal incidence electron gun
152 providing charge compensation. Fully automated runs comprised a pre-sputter period
153 with a raster of 20 μm , field aperture and entrance slit centering, using the ^{16}O signal,
154 followed by 96s of data acquisition using two Faraday detectors in the multicollector
155 system operating at a common mass resolution of ca. 2500 to measure ^{16}O and ^{18}O and
156 an axial Faraday operating at a mass resolution of 6000 to separate $^{16}\text{O}^1\text{H}$ from ^{17}O .
157 During the analytical session the secondary magnetic field was locked at high precision
158 using an NMR sensor operating in regulation mode. Data from Jack Hills zircons are
159 presented in Table 2 with uncertainties reported at the 2σ level. Oxygen isotope data
160 were normalised to measurements of the CZ3 zircon standard and are reported with
161 reference to SMOW assuming a $\delta^{18}\text{O}$ value of $15.4 \pm 0.4 \text{ ‰}$ (2SD) for this standard
162 (Cavosie et al. 2011). We report measured $\delta^{18}\text{O}$ values with reference to SMOW and
163 OH as OH/O, determined as counts of $^{16}\text{O}^1\text{H}$ over counts of ^{16}O .

164

165 **2.4 Electron Probe analyses**

166 Analyses are reported for two traverses on the polished surfaces of grains 6
167 and 35 (Table 3, Fig. 9). The equipment used was the JEOL JXA8530F Hyperprobe
168 equipped with 5 tunable wavelength dispersive spectrometers at the Centre for
169 Microscopy and Analysis of the University of Western Australia. Analyses of crystal
170 PETJ was used for acquiring compositional information on U, Th and Zr. Further
171 details of analytical procedures are to be reported elsewhere. For the present traverses
172 detection limits were 60 ppm for U and Th and 140 ppm for Zr.

173

174 **3. RESULTS**

3.1 Analyses and terminology

We present 147 SIMS U-Th-Pb and 189 OH/O - $\delta^{18}\text{O}$ analyses on 44 zircons from a sample of quartz conglomerates from the W74 site in the Jack Hills (Fig. 1) (Tables 1 and 2). In describing the data grains have been assigned to one of five groups based on the behaviour of their U-Pb and O-OH systems. Group 1, includes grains with closed U-Th-Pb and oxygen isotope systems. Group 2, includes grains that are complex in the sense that they have discordant and concordant U-Pb areas within the same grain but have an apparently closed oxygen isotope system with an OH content that is approximately background. Group 3 grains show an initial trend to lighter $\delta^{18}\text{O}$ values with increasing OH content. Group 4 grains show a trend of increasing $\delta^{18}\text{O}$ with increasing OH. Group 5, includes grains with complex U-Pb isotopic systems.

In the Discussion and on Fig.11 individual U-Th-Pb analyses have been assigned to three types on the basis of the discordance of their $^{208}\text{Pb}/^{232}\text{Th}$ ages. Type 1 analyses have $^{208}\text{Pb}/^{232}\text{Th}$ ages that are > 95% concordant with respect to the $^{207}\text{Pb}/^{206}\text{Pb}$ age. Type 2 analyses have $^{208}\text{Pb}/^{232}\text{Th}$ ages that are 95-65% concordant and Type 3 have $^{208}\text{Pb}/^{232}\text{Th}$ ages that are less than 65% concordant. In the Discussion we have also introduced the terms Stage 1 and Stage 2 to describe the behaviour of the OH-O results. Stage 1 is where $\delta^{18}\text{O}$ values show an initial trend to lighter values with increasing OH, which then reverses to a second, Stage 2 trend, where $\delta^{18}\text{O}$ values become heavier with a further increase in OH.

3.1 Background $^{16}\text{O}^1\text{H}$

200 A serious limitation for SIMS measurements of OH (water) in sample zircons is
 201 the OH background in the ionprobe source chamber. The OH background is largely
 202 dependent on the pressure in the source chamber and the instrument was pumped
 203 overnight for as long as was practical, given limits on machine time, to lower the
 204 source chamber pressure. The pressure was also improved using a liquid nitrogen trap.
 205 Chips of the CZ3 Zircon Standard were included in all mounts. This has a minimal
 206 water content, and OH counts on this standard were adopted as a measure of the
 207 background (see Pidgeon et al., 2013). However, OH and OH/O for the standard chips
 208 were different for each of the three analytical sessions. In the first analytical session on
 209 Mount 1 OH/O background for CZ3, was $0.045 \pm 0.003 (1\sigma) \times 10^{-2}$. The second
 210 analytical session on Mount A has a higher background OH/O of $0.115 \pm 0.004 \times 10^{-2}$
 211 and a value of $0.148 \pm 0.009 \times 10^{-2}$ was determined for CZ3 from the third
 212 analytical session on Mount B (Fig.2). The three background counts did not relate
 213 directly to small changes in the pressure of $\sim 7 \times 10^{-9}$ torr and are possibly a
 214 function of the mount surfaces. In addition we found that for the analytical session on
 215 Mount 1, OH/O measurements of concordant “closed system” Group 1 grains (Fig. 2,
 216 Fig.4) of 0.050 to 0.065 (OH/O, $\times 10^{-2}$) are systematically higher than the range of OH
 217 counts from zircon CZ3 (0.04 to 0.05×10^{-2}) although the spread in the OH/O values
 218 of the Group 1 grains (Fig.2) is similar to that of the CZ3 standard. Analyses of zircon
 219 standard 91500 are also significantly higher in OH/O than the CZ3 standard (Fig.2).
 220 The range of OH/O for Group 2 grain 122 in Mount A was close to the values of the
 221 standard in this run that in turn was lower than OH/O for the standard in the SIMS run
 222 on Mount B. Also, the OH/O values for Grains 91 and 123 (thought to have no water
 223 component) on Mount B were marginally higher than the measurements of the CZ3
 224 standard in the Mount B analytical session (Fig.2). The reason for these discrepancies

225 between samples and standard in the same SIMS analysis run has not been resolved. It
226 is possible conditions on the mounts affected background OH counts for individual
227 grains and that each grain has its own background. This needs to be kept in mind when
228 interpreting the background for individual grains.

229

230 **3.2 Water species in metamict zircon**

231

232 A number of analyses of grains from Groups 2, 3 4 and 5 have OH content
233 significantly above background demonstrating that water or OH is present in the
234 metamict zircon. The question of whether OH, H₂O or both species are present in the
235 metamict zircon has been investigated by a number of researchers. Aines and Rossman
236 (1986) and Woodhead et al. (1991) reported IR spectra of a metamict zircon that
237 exhibit a broad asymmetric isotropic OH band similar to H₂O bands but considered
238 that the absence of the H₂O bending-mode band indicated that OH is the dominant
239 water species. However these results were questioned by Nasdala et al. (2001) who
240 state that “ the fact that no distinct water bending modes are observed in the IR spectra
241 does not necessarily mean that these bands are non existent”. Instead, it seems that if
242 there are H-O-H bending vibrations, these IR bands are fully obscured by the much
243 stronger silicate combination modes in both crystalline and metamict zircon. Geisler et
244 al. (2002) reported the presence of OH but not H₂O in reaction rims of low temperature
245 hydrothermal experiments on metamict zircon and concluded that that water in the
246 rims occurs mainly as OH⁻. However, whereas SIMS measurements will detect OH⁻
247 molecular H₂O itself will not be recognised. As indicated by Pidgeon et al. (2013) any
248 water present in the amorphous zircon as H₂O would probably be ionized to OH⁻ under
249 the caesium ion beam and as a consequence present data cannot resolve the question of

whether OH, H₂O or both are present in the metamict zircon or the background.

3.3 Group 1 grains

For U-Pb analyses of concordant grains (Table 1) (Fig3) the f_{206} ($^{206}\text{Pb}_{\text{common}}/^{206}\text{Pb}_{\text{total}}$) is less than 0.12% and generally less than 0.04%, indicating that grains do not contain a significant amount of common Pb. The U contents vary from 40 ppm to 177 ppm (Table 1) and Th/U are consistent within each grain and range from 0.36 to 1.51. The lack of any indication of disturbance of the isotopic systems suggests that Th/U ratios are primary values.

Seven Group 1 grains from Mount 1 were analysed for O-OH (Table 2, Fig. 4). From Table 2 and Fig.4 it can be seen that $\delta^{18}\text{O}$ values fall within a range of 4.8 to 6.5 ‰ with a mean value of ~5.5 ‰. This range is similar within the uncertainty to the spread of $\delta^{18}\text{O}$ of 5.3 ± 0.6 ‰ (2 SD) proposed by Valley et al. (2005) as representing zircon formed at high temperature in equilibrium with the mantle. The restricted range of $\delta^{18}\text{O}$ for the seven concordant grains therefore represents primary, undisturbed zircon within the “mantle” range of values determined using laser fluorination measurements (e.g. Taylor, 1968) and provides a basis for comparison with $\delta^{18}\text{O}$ values determined on grains in the other mounts.

3.4 Group 2 grains

This group contains 8 grains from Mount 1 and 7 Grains from Mounts A and B (Tables 1 and 2). Group 2 grains are characterised by containing discordant and concordant parts (Fig.3), OH at or above background and relatively undisturbed “mantle” $\delta^{18}\text{O}$

values (Fig.5). From the representative concordia plots on Fig. 3 it can be seen that, for all grains, discordant data points define linear discordia that intersect concordia at approximately zero million years. The U-Pb complexity of the grains is illustrated from the results of Grains 35, 97, 66 and 81 (Table 1), which have one concordant spot (Fig. 5 A, B, C and D), whereas other analytical spots are discordant. Strongly discordant parts are correlated with elevated Th/U ratios, high U and Th contents and elevated common Pb (e.g. Table 1). A number of the high U and Th analyses were seen to overlap cracks. Most concordant analytical areas of grains from Mounts A and B reported in Table 1 have U contents less than 370 ppm (366ppm for Grain 142). However, the possibility that this concentration represents a limit, dividing concordant from discordant grains, is not universally true. For example, analysis 79-1 with 195 ppm U is discordant with a strongly disturbed $^{208}\text{Pb}/^{232}\text{Th}$ age (Table 1). Also analysis 97-3 has only 101 ppm U but is discordant and has 2.75% common ^{206}Pb , a Th/U ratio of 2.78 and a measured $^{208}\text{Pb}/^{232}\text{Th}$ age of only 164 Ma (Table 1). These analyses are clearly disturbed and at least one overlaps a crack, raising the possibility that the U concentrations are not the primary values.

Oxygen isotope and OH are shown on Fig.5 as separate plots for grains from Mounts 1 and Mounts A and B. In both plots grains with essentially background OH have $\delta^{18}\text{O}$ values that are generally within the “mantle” range ~5 to 6.5‰, although the same grains have discordant U-Pb analyses (Fig.3). For example whereas U-Pb analyses of grain 79 are discordant, some falling on cracks, the measured OH concentrations are within the background and $\delta^{18}\text{O}$ of 6.0 ‰ is well within the “mantle” range although some analytical spots also overlap cracks. Similarly, while U-Th-Pb analyses of grain Grain 66 (Fig.9) are discordant, OH is at background levels and $\delta^{18}\text{O}$ is within the “mantle” range. A feature of Group 2 grains is that U-Th-Pb

analyses located on cracks are strongly disturbed with a characteristic increases in U and Th. On the other hand O-OH analyses have background OH content and “ mantle “ $\delta^{18}\text{O}$ values despite also overlapping cracks.

3.5 Group 3 grains

This group consists of six grains from Mounts A and B and 3 grains from Mount 1. Group 3 grains have complex U-Pb systems (Table 1), some with concordant and discordant analyses (e.g. grain 128, Fig.3), while U-Pb analyses in others (e.g. grains 56 and 151, Fig. 3 C1 and C3) appear to be entirely discordant (Table 1). The presence of high U-Th and common Pb contents in some discordant analyses of grains 56, 65, 128 and 151 (Table 1) can probably be related to overlapping cracks. Analyses on Grain 11 are discordant but have unaltered U and Th (Table 1) suggesting that leaching of radiogenic Pb is the dominant discordance mechanism.

The most striking feature of Group 3 grains is the trend to light $\delta^{18}\text{O}$ values (Fig.6). $\delta^{18}\text{O}$ for analyses on grains 271, 32, and 11 decrease from “mantle” values to values as low as $\sim 1\text{‰}$ for grain 11. OH in these analyses is near background levels so any trend in OH is masked by the background. However, for analyses on Grain 282 (Fig 6A) (and grain 11 to some extent), OH is above background and $\delta^{18}\text{O}$ is seen to decrease with increasing OH. Analyses on all other grains (Fig.6A and B) show a similar initial trend of decreasing $\delta^{18}\text{O}$ with increasing OH but, at higher values of OH, this trend changes and $\delta^{18}\text{O}$ values are seen to increase with increasing OH. This trend in $\delta^{18}\text{O}$ with OH is also shown for Grain 65 in Fig.10A. Although the fine structure in the OH is obscured by the background for analyses 1 and 6, the trend in $\delta^{18}\text{O}$ with increasing OH is firstly to lighter $\delta^{18}\text{O}$, progressing from $\sim 5\text{‰}$ to $\sim 3.8\text{‰}$ and then,

325 with a further increase in OH, $\delta^{18}\text{O}$ becomes markedly heavier reaching a value of ~6.2
326 ‰ (Fig. 10A).

327

328 **3.6 Group 4 grains**

329

330 U-Pb data points for three of the Group 4 zircon grains (Fig 3), define a
331 discordia line that intersect concordia at close to zero million years. Two of the grains
332 (72 and 156) shown on Fig.3 have concordant analysis spots with low U contents
333 (Table 1), whereas analyses of grain 57 (Fig.3) are all discordant. The Th/U ratios of
334 concordant low U data points 6-4, 72-2, 113-1 of 0.33 to 0.56 (Table 1) are interpreted
335 as primary values. In discordant grains the degree of discordance is associated with an
336 increase in Th/U. For example in grain 56 the Th/U ratio increases from 0.46 in the
337 concordant spot to 2.4 in the most discordant analysis and in grain 113 the Th/U ratio
338 ranges from 0.56 in the concordant analysis to 3.9 in the highest U and most discordant
339 analysis. The high Th/U values are generally in analytical areas overlapping cracks.

340 The $\delta^{18}\text{O}$ and $^{16}\text{OH}/^{16}\text{O}$ ratios of multiple SIMS analyses of the five grains of
341 this group are presented in Table 2 and Fig. 7. The striking feature of these analyses is
342 their coherent systematic trend of increasing $\delta^{18}\text{O}$ with increasing OH. $\delta^{18}\text{O}$ values of
343 analyses on Fig.7 ranged from ~ 5‰ to ~ 8‰. An extreme value of ~15‰ with high
344 OH content determined on area 57-8 (Table 2) is not shown on Fig.7. The grouping of
345 points at the background level on Fig. 7 could mask a possible initial trend to lighter
346 $\delta^{18}\text{O}$ values, but this would be limited, as $\delta^{18}\text{O}$ of analyses with near background OH,
347 fall in the range of 5 to 6‰ (Fig.7), which is within the range expected for “mantle”
348 oxygen in zircon.

349

3.7 Group 5 grains

This group consists of grains with U-Pb systems (Table 1, Fig 8) that do not fit the simple discordance pattern found in zircons in the previous three groups. O-OH data for this group are presented in Table 2 and shown on Fig. 8. The U-Pb data points for Grain 34 (Fig.8C) and 91 (not shown), fall near concordia at > 3580Ma and at ~ 3400Ma suggesting both grains experienced a later overgrowth at ~3400Ma. The grains have relatively low and uniform U and Th concentrations (Table 1) and show no indication that they have interacted with weathering solutions. This is in accord with oxygen isotopic data (Fig. 8D and Table 2) that show that grain 34 (and 91) have $\delta^{18}\text{O}$ values within the “mantle” range and OH at the level of the background or slightly elevated, similar to zircons from Groups 1 and 2.

U-Pb data points of grains 114 and 30 are dispersed along concordia (Fig. 8 A and E) suggesting that these grains either consist of a core and overgrowth or have experienced an early disturbance of their U-Pb systems. Three analyses on grain 114 are low in U, ranging from 84 to 115 ppm and have a consistent Th/U of ~ 0.35, whereas younger analysis 4 (Table 1)(Fig. 8A) also falls on concordia has a lower U and Th and a slightly lower Th/U ratio of 0.26. Except for the spread of data points along concordia this grain appears to have an undisturbed primary U-Pb system. However, as shown on Fig. 8B, grain 114 has high $\delta^{18}\text{O}$ values of 7.7 to 8.1‰. Analyses 1, 2 and 4 have approximately background OH while analysis 3 has OH significantly above background indicating the presence of water in this part of the zircon (Table 2). A further example is rounded Grain 30 which consists of a grey-CL curve-zoned termination surrounding a dark CL sector zoned core. U-Pb analyses of Grain 30 are low in U (< 300ppm)(Table 1) and the U-Pb system appears to be almost

375 undisturbed (Fig.8E). However, oxygen results on Fig. 8F show $\delta^{18}\text{O}$ values that
376 increase from ~ mantle values to ~ 9‰ with increasing OH, similar to the pattern
377 described for grains in Group 4. Grain 58 consists of a dark-grey, CL margin with
378 residual oscillatory zoning, surrounding a structureless, lighter CL centre. The U-Pb
379 system is concordant to reversely discordant (Fig.8G) and has a range of U (103 -
380 262ppm) and Th/U ~ 0.5 similar to grains 30 and 58 (Table 1) with no evidence of
381 interaction with weathering fluids. However, $\delta^{18}\text{O}$ values of grain 58 are light and
382 show a trend of decreasing $\delta^{18}\text{O}$ values from 4 to 3 ‰ with increasing OH, followed
383 by an increase in $\delta^{18}\text{O}$ values at higher OH (Fig. 8H), similar to the trend described for
384 grains in Group 3. It is noted that the relationship between the U-Pb and stable isotope
385 behaviour in this grain is uncertain as U-Pb analysis spots are concentrated along the
386 bright CL centre of one segment of this broken grain whereas oxygen analyses were
387 made in the dark-grey CL margin of the grain. It is likely that the lower CL intensity
388 grain margin has enhanced radiation damage compared to the centre and could have
389 been preferentially open to penetration by weathering solutions resulting in the
390 observed light $\delta^{18}\text{O}$ values which resemble those reported in zircon Group 3.

391

392 **3.8 Electron probe analyses**

393

394 To provide an independent measure of the U and Th concentrations of the
395 zircons we made electron probe traverses of U, Th and Zr across the polished surfaces
396 of grains A6 and B65 (Fig. 9 and Table 3). Grain A6 is oval shaped with rounded
397 terminations and consists of a light CL centre surrounded by a variably dark CL mantle
398 and an outer light CL rim. Grain 65 is subhedral and consists of a diffuse pattern of
399 oscillatory zones (Fig.9). Electron probe analyses were made every 10 μ along the

length of the grains and a number of analyses were seen, from a close examination of the images, to fall on cracks (as indicated on Table 3). Analyses that fall on or near cracks are low in Zr and exceptionally high in Th and U (Table 3). Examples are spot 18 in the traverse on Grain 6 which has low Zr , an exceptionally high Th of 39680 ppm and U of 2020 ppm and analysis spot 10 on Grain 65 which has low Zr, 22400ppm Th and 2436ppm U. These analyses are consistent with the Cameca 1280 U-Th measurements on Table 1 and confirm the importance of cracks as pathways for weathering solutions and locations for the precipitation of U and Th probably as oxides.

4. DISCUSSION

4.1 Zero age U-Pb discordance

Clarification of the event or process responsible for the ~zero age disturbance observed in U-Pb concordia plots (Figs 5, 8) of Group 2,3 and 4 zircons is basic to the interpretation of the present results. This zero age discordance pattern is not a new discovery as it has been known since the earliest studies of the ancient Jack Hills zircons. For instance Compston and Pidgeon (1986) remark that > 3.9 Ga Jack Hills zircons have undergone recent Pb loss, Amelin (1998) from a detailed TIMS study of Jack Hills zircons observes that “ lower intercepts of unforced discordia lines for the young group of grains are close to or within error of zero, indicting again the influence of recent lead loss.” Wilde et al. (2001), in describing old grain W74/2-36, comment that “large differences in the Pb/U ratios for similar $^{207}\text{Pb}/^{206}\text{Pb}$ ages indicates recent Pb loss”. Cavosie et al. (2004) state that “recent Pb loss has been

demonstrated to be the major cause of discordance in the Jack Hills zircons”. Nemchin et al. (2006a) in describing the results of a SIMS study of eight > 4.2Ga Jack Hills zircons commented that “The discordant trend in the present results confirm that fluid interaction has occurred relatively recently”. No igneous, metamorphic or hydrothermal events have affected the Yilgarn Craton at this time ruling these out as potential causes for a recent U-Pb disturbance. The only plausible explanation is that the observed discordance is the result of interaction of the zircons with ground water introduced during the pervasive deep weathering that has affected the Yilgarn Craton, including the Jack Hills, from at least the Permian (Anand and Paine, 2002; Anand and Butt, 2010; Chivas and Atlhopheng, 2010). The outcrop of the W74 sample in the Jack Hills is just beneath the overlying laterite profile seen in surrounding hills. Until exposed by relatively recent erosion the sample site was within the near surface weathering system. The quartz conglomerate host rock is fractured and porous and stained with iron oxides from the long-term penetration of weathering solutions.

The effect of weathering on the U-Pb system of zircons is not a new concept as reports on this date back to the 1960s. For example Catanzaro and Kulp (1964) proposed that that “necessary conditions for low-temperature loss of lead from zircons would appear to include a certain degree of metamictization and some event which chemically and/or physically activates ordinary ground water and enables it to leach lead from the metamict zircons”. Stern et al. (1966) described how “weathering has caused large losses of lead from zircon in residual clay derived from the Morton Gneiss of southwestern Minnesota, drastically reducing the $^{206}\text{Pb}/^{238}\text{U}$ and the $^{207}\text{Pb}/^{235}\text{U}$ ages”. These authors also suggest the possibility that U could also been leached from the zircons. In another report Black (1987) found that incipient

450 weathering was responsible for significant U-Pb discordance in zircon from 770 Ma
451 granite and pegmatite from the Rayner Complex in Antarctica. Kramers et al. (2009)
452 concluded that near-zero age discordia intersections were caused by weathering and
453 Pidgeon et al. (2013) reported the effects of weathering on zircons from a sample of
454 Archean granite in the South-Western Yilgarn Craton of Western Australia. They used
455 SIMS to measure the presence of OH in radiation damaged zircon and found
456 correlations between OH and increasing or decreasing $\delta^{18}\text{O}$, indicating complex
457 interaction between the grains and ground water.

458

459 **4.2 Interaction of ground water with the U-Th-Pb system**

460

461 The near-zero age discordance and the distribution of data points along
462 discordia of the Jack Hills zircons demonstrates that the U-Th-Pb isotopic systems
463 have been open to isotopic and possibly chemical leaching by ground waters during
464 long term weathering. In many grains this discordance behaviour is heterogeneous.
465 Some parts of a zircon grain remain closed U-Th-Pb systems whereas others have been
466 open to U-Pb disturbance. For example Th-U-Pb analyses 35-1 and 35-2 (Table 1) on
467 blurred oscillatory zoned, Group 2 grain 35 have essentially identical U and Th
468 contents and Th/U ratios (Fig.9). But analysis 35-1 is discordant with an elevated
469 common Pb while analysis 35-2 is concordant with no significant common Pb. We
470 interpret this as penetration of weathering solutions at location 35-2 resulting in loss of
471 radiogenic Pb and gain of common Pb whereas no fluid penetration or interaction
472 occurred at the location of analysis 35-1. The degree of radiation damage is considered
473 to be an important factor in permitting fluid access. For example analysis 66-1 (Fig. 3)
474 with 151 ppm U and 52 ppm Th (Table 1) and an α -dose of $0.66 \times 10^{15} \alpha/\text{mg}$

475 (assuming a radiation damage age of 1120 ± 130 Ma, Pidgeon 2014) is concordant,
476 whereas analysis 66-2 with 288 ppm U, 166 ppm Th, and an α -dose of 1.32×10^{15}
477 α/mg , is discordant and has elevated common Pb (Table 1, Fig. 3). We interpret these
478 results as indicating preferential penetration and interaction by weathering fluids into
479 the more radiation damaged zircon at location 66-2. The U-Th-Pb systems of analyses
480 (39-2, 43-3, 66-2, 97-2, 142-4) from grain Group 2 are similar and the discordance of
481 these analyses is interpreted as loss of radiogenic Pb (and addition of common Pb)
482 during interaction with weathering fluids without any change to the U and Th
483 concentration. These analyses, as far as we can ascertain, do not overlie fractures in the
484 grains. However, where analyses do overlie fractures the Th-U system is in general
485 severely affected. For example in grain 6 (Table 1, Fig. 9) all SIMS U-Th-Pb analyses
486 overlap a fracture and have high Th, U common Pb and measured Th/U ratios. For
487 oscillatory zoned grain 65 (Table 1, Fig. 9), analysis 65-4 on a crack-free part of the
488 grain has U and Th contents of 375 ppm and 164 ppm a concordant U-Th-Pb system,
489 minimal common Pb and measured and calculated Th/U ratio of 0.42 (see below for an
490 explanation of the terms measured and calculated Th/U). However, for analyses 65-2
491 and 65-3 which overlap fractures, U and Th and common Pb contents increase
492 markedly, particularly Th, the U-Th-Pb systems are strongly discordant and the
493 measured Th/U ratios are high (Table 1, Fig. 9). SEM traverses of U, Th and Zr on the
494 polished surfaces of grains 6 and 65 (Table 3, Fig. 9,) confirm the extremely high Th
495 and U concentrations determined by SIMS analyses on in these (and other) grains. A
496 decrease in Zr concentration is also characteristic of analyses that overly cracks (Table
497 3) as is the marked increase in the Th/U ratio. For example, the Th/U ratios of 19.6
498 (spot 6-18) and 9.2 (spot 65-10) are far in excess of general “magmatic” values of
499 about 0.5 suggested by Kirkland (2015). The secondary nature of the high Th/U is well

500 illustrated by comparing the measured Th/U with Th/U ratios calculated from the
501 radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$ and the zircon age. Assuming the evolving $^{208}\text{Pb}/^{206}\text{Pb}$ has not
502 been disturbed, the calculated Th/U ratio represents the long term undisturbed ratio
503 prior to the weathering disturbance. An indication of the degree of Th-U disturbance
504 can therefore be determined by the ratio of the measured (presently existing) over the
505 calculated (undisturbed) Th/U ratios $(\text{Th}/\text{U})_{\text{m/c}}$. This is shown on Figure 11 which
506 includes data for grains from Groups 2, 3 and 4. Where there has been no new addition
507 of Th and U the measured and calculated ratios plot as unity. $(\text{Th}/\text{U})_{\text{m/c}}$ increases with
508 increasing U concentration (Fig. 11) but is best correlated with increasing Th
509 demonstrating that during weathering the accumulation of Th in fractures in zircon is
510 favoured over U. This is also demonstrated on Figure 11 by the correlation between
511 increasing $(\text{Th}/\text{U})_{\text{m/c}}$ and increasing discordance of the $^{208}\text{Pb}/^{232}\text{Th}$ ages, from Type 1
512 analyses where the $^{208}\text{Pb}/^{232}\text{Th}$ ages are concordant and the $(\text{Th}/\text{U})_{\text{m/c}}$ values are near 1
513 to Type 3 analyses, where $^{208}\text{Pb}/^{232}\text{Th}$ ages are > 65% discordant and $(\text{Th}/\text{U})_{\text{m/c}}$ values
514 range from 2 to 300. This is attributed to the gradual accumulation in fractures of the
515 less soluble Th from the penetrating weathering fluids. In summary, it is evident from
516 the present results that U, Th, common Pb and probably other elements are being
517 transported during weathering into the zircon grains along cracks where they
518 precipitate probably as oxides.

519 The penetration and interaction of weathering fluids in the zircon matrix is
520 shown by U-Pb discordance in analyses away from cracks with no change in U and Th.
521 It is likely that a major control on the extent of fluid penetration and leaching of
522 radiogenic Pb is the degree of radiation damage. Hydrothermal experiments of Geisler
523 et al. (2002) showed that interaction of metamict zircon with low temperature (175°C)
524 solutions (AlCl_3 and HCl-CaCl_2) resulted in leaching of Si, U, Th and P as well as REE

525 from the altered sites, whereas Ca and Al as well as a water species infiltrated the
526 zircon structure to maintain charge balance. SIMS results showed that the altered areas
527 lost almost all their radiogenic Pb. Coincidental addition and removal of Pb from
528 metamict zircon was also shown in hydrothermal experiments by Pidgeon et al. (1973)
529 by observing the addition of spike Pb into a metamict zircon at the same time
530 radiogenic Pb was leached out. The penetration of fluids into metamict zircon under
531 experimental hydrothermal conditions at 175°C (Geisler et al. 2002) was seen to define
532 a reaction front marked by partial annealing of the zircon structure. However, under
533 weathering conditions, where the temperature is not expected to exceed 50°C,
534 penetration of fluids into the metamict zircon is not constrained by structural
535 annealing, permitting a range of leaching and exchange reactions which are poorly
536 known and are the subject of ongoing study.

537 One consequence of the open system behaviour of U and Th is that the relative
538 role of loss of radiogenic Pb compared to U-Th gain in controlling the discordance of
539 analysed areas of a zircon cannot be specified. Also, the late stage addition of U and
540 Th means that the measured U and Th contents do not represent the long term
541 concentrations of these elements in the zircons and cannot be used as a basis for
542 estimating α -doses.

543 The possibility needs to be kept in mind that some chemical and isotopic
544 changes present in the zircons are due to an early weathering event at about 3.0 Ga.
545 Many zircons, with ages extending back to ~4.35 Ga, would be sufficiently radiation-
546 damaged by 3.0 Ga to be susceptible to interaction with weathering solutions.
547 However, it is doubtful whether radiation fractured and weathered zircons would
548 survive mechanical transport and deposition. Nevertheless this could be considered
549 as a possible explanation for the spread of Archaean U-Pb ages along concordia and

low temperature water affected OH-O isotopic systems observed in some Group 5 grains.

In previous studies of Jack Hills zircons researchers have been conscious of the effect of cracks in disturbing isotope ratios and trace element contents (e.g. Cavosie et al, 2004, 2005, Bell and Harrison 2013). Cavosie et al. (2004) reported U-Pb results on complex grains from the Jack Hills with U-Pb concordant and discordant areas and attributed the most discordant analyses, and younger $^{207}\text{Pb}/^{206}\text{Pb}$ ages, to the location of these analyses on visible cracks. Also, Bell et al. (2015) report secondary xenotime, quartz and muscovite inclusions along cracks in Jack Hills zircons. They also report annealed cracks in some zircons and suggest these may represent a much earlier chemical and mechanical weathering history of the zircons followed by an annealing event. Cracks in zircons have long been proposed as pathways for rapid fluid penetration and alteration in zircons (e.g. Goldich and Mudrey 1972, Lee and Tromp 1995). Examples of botryoidally shaped alteration zones surrounding cracks in radiation damaged zircon were presented by Krogh and Davis (1974). Also, Harrison and Schmidt (2007 Fig.3) showed images of zircon grains with high Ti “alteration” areas situated around cracks.

The zircon OH- $\delta^{18}\text{O}$ system

In the present analyses Group 1 grains (Table 1) have remained closed Th-U-Pb systems and have a restricted spread of $\delta^{18}\text{O}$ of 4.8 to 6.4‰ broadly within the range of $\delta^{18}\text{O}$ of 5.3 ± 0.6 ‰ for zircons formed in equilibrium with the mantle (Valley et al., 2005) (Fig. 4). The scatter of OH values is within the range of the background, indicated by OH values of the CZ3 standard analyses (Fig. 2). However, the zero-age

575 U-Pb discordance of Group 2 grains indicates that the grains have interacted with
 576 weathering fluids, and many of the discordant analyses have high Th and U and
 577 overlap cracks confirming the importance of cracks as pathways for fluid access into
 578 these grains. A number of the O-OH measurements also overlap cracks. In Grain 66
 579 (Table 2), OH-O analyses 66-4 and 5 are on crack-free parts of the grain but analyses
 580 66-1 and 2 fall directly on cracks. However despite overlapping cracks all $\delta^{18}\text{O}$ values
 581 are within the mantle range within the uncertainties and OH values are within
 582 background. In another example the three Th-U-Pb analyses on grain 35 are on cracks
 583 and are discordant. However, O-OH $\square\square\square\square\square\square\square$ on grain 35 also overlap cracks
 584 but $\delta^{18}\text{O}$ values (Table 2) are in the mantle range within the uncertainties. These results
 585 indicate that cracks do not appear to have affected the oxygen isotopic systems of
 586 Group 2 grains. Analyses of our Groups 3 and 4 zircons also show evidence of ground
 587 water interaction with radiation damaged zircon (Figs 6, and 7). Six O-OH
 588 measurements were made on blurred (CL) oscillatory-zoned grain 65 (Fig.9). Analysis
 589 65-6, which overlaps the electron probe traverse analysis 8 (Table 3) with high Th and
 590 U, has background OH and a mantle $\delta^{18}\text{O}$ of 5.0‰. Analyses 65-1, 2 and 4 overlap
 591 zone boundary fractures and analyses 65-5 appear to be remote from fractures.
 592 However, $\delta^{18}\text{O}$ values appear to be controlled more by the position in the grain as
 593 Analyses 65-1, 4, and 5 in the southern part of the grain are significantly lighter with
 594 background OH, whereas analyses 65-2 and 3 in another part of the grain become
 595 progressively heavier with increasing OH (Figs 9,10). Oval shaped grain 6 is an
 596 example of a Group 4 grain. It consists of a complex centre of overlapping dark CL
 597 domains surrounded by a light CL rim (Fig.9). It is highly fractured and all analyses,
 598 including 6-1 in the light CL rim and, with the possible exception of analysis 6-2 in the
 599 grey CL central domain, overlap fractures. Of these analyses 6-1 has background OH

600 and “ mantle” $\delta^{18}\text{O}$ whereas analyses in the grey CL centre of the grain show
601 increasing $\delta^{18}\text{O}$ with increasing OH (Fig.12). Our conclusion from these results and
602 other analyses on Group 3 and 4 grains is that, unlike the U-Th-Pb system, the fracture
603 systems in zircon are not the main control of OH and $\delta^{18}\text{O}$, which instead are affected
604 by interaction with weathering solutions involving reaction between percolating water
605 and the radiation damaged zircon matrix. This is broadly in accord with conclusions of
606 Booth et al (2005) who relate observed light $\delta^{18}\text{O}$ values in zircons from a pegmatite
607 from Tibet to hydrothermal reaction with highly radiation damaged zircon domains
608 that have a range of discordant U-Pb ages defining a discordia line with an
609 approximately zero age intersection with concordia.

610 Oxygen isotope results from our zircon Group 1 (concordant U-Pb systems)
611 can be compared with previous oxygen isotope analyses of Jack Hills zircons. For
612 example Cavosie et al (2005) reported $\delta^{18}\text{O}$ values for 34 out of 42 Jack Hills zircons
613 that preserved REE compositions typical of igneous zircon from crustal rocks,
614 displayed a wide range of CL zoning patterns, and yielded concordant to nearly
615 concordant U/Pb ages from 4.4 Ga to 3.9 Ga. U-Pb concordance was considered by
616 Valley et al. (2005) as an index of radiation damage and minimizing radiation damage
617 and avoiding cracks has been a procedural objective by Valley et al. (2005) and other
618 researchers in oxygen isotope studies of Jack Hills zircons (Peck et al. 2001; Trail et al.
619 2007). Zircon $\delta^{18}\text{O}$ values from the Cavosie et al. (2005) study fall in the narrow range
620 4.7 ‰ to 7.3 ‰ that overlap or are slightly elevated relative to the oxygen isotope
621 composition of 5.3 ± 0.3 (1S.D.) ‰ for zircon from a mantle source (Cavosie et al
622 2005). $\delta^{18}\text{O}$ values in the range 6.5 to 7.5 ‰ are considered to be above the mantle-
623 derived plus igneous fractionation value (e.g. Valley et al. (2005) and are explained as
624 forming from parent magma with a history involving surface alteration of protolith by

625 liquid water at low temperatures to elevate $\delta^{18}\text{O}$, burial, melting to form high $\delta^{18}\text{O}$
626 felsic parent and crystallization of zircon with a heavy $\delta^{18}\text{O}$ (Peck et al. 2001; Mojzsis
627 et al. 2001; Valley 2003; Valley et al. 2005). Our Group 1 concordant grains (Fig. 4)
628 show a range of $\delta^{18}\text{O}$ values of 4.8 ‰ to 6.5 ‰. Within this group of data points (Fig.
629 4) grain 127 appears to be distinctly lighter than grains 104 and c115, suggesting small
630 but significant differences in the oxygen composition of the source rocks. However,
631 the spread of $\delta^{18}\text{O}$ values in Group 1 zircons (Fig. 4) does not extend into the 6.5 to 7.5
632 ‰ range suggesting that our Group 1 zircons have mantle-derived parent magmas.

633 Further insight into the processes of water-zircon reaction can be obtained from
634 the relationship between $\delta^{18}\text{O}$ and OH for Group 3 zircons on Fig. 6 (and including
635 grain 65 on Fig. 10) that we describe as defining two trends that we refer to as two
636 stages. In Stage 1, OH-O measurements on individual grains show an initial trend of
637 decreasing $\delta^{18}\text{O}$ with increasing OH (Figs 6, 10). $\delta^{18}\text{O}$ values as low as ~ 1 ‰ have
638 been recorded (e.g. grain 11). However, with further increase in OH this relationship
639 changes to a Stage 2 trend, where $\delta^{18}\text{O}$ values become heavier as OH continues to
640 increase as illustrated for grains 128 and 151 on figure 12. Grain 128 consists of a
641 broad, nebulously zoned rim around a uniform (CL) central segment. $\delta^{18}\text{O}$ values in
642 the rim show a clear Stage 1 trend with increasing OH progressing from a value of
643 4.7‰ to a $\delta^{18}\text{O}$ of 3.8‰. However the final analysis in the grain centre has the highest
644 OH, and a $\delta^{18}\text{O}$ value of 4.7 ‰ (Fig. 6b) indicating a change to a Stage 2 process.
645 Similarly for grain 65, $\delta^{18}\text{O}$ decreases initially with increasing OH but then the trend
646 reverses to Stage 2 trend where $\delta^{18}\text{O}$ becomes heavier with increasing OH (Fig. 10).
647 This Stage 2 trend is comparable with the behaviour of grains from Group 4 that show
648 a systematic increase in $\delta^{18}\text{O}$ with increasing OH (Fig. 7). Group 4 grains do not show

any indication of a trend to lighter $\delta^{18}\text{O}$ as analyses with background OH have $\delta^{18}\text{O}$ values in the “mantle range” between 5 and 6‰. The consistency of the observed trends in Group 3 and Group 4 grains suggests two consecutive processes are operating. Stage 1 records an influx of water into the zircon that is accompanied by a trend to lighter oxygen, whereas Stage 2 is characterised by a trend to heavier oxygen with a further increase in water content. Fractures may provide fast pathways for water influx but further explanations are needed to explain the two trends.

Possible explanations include changes in the isotopic composition of oxygen in the ground water with time due to northern movement of the continent after breakup with Antarctica (Veevers, 1986). However, Chivas and Atlhopheng (2010) reported only a small variability in $\delta^{18}\text{O}$ of 18-20 ‰ in clays from weathering horizons in the Yilgarn Craton that corresponds to ground water $\delta^{18}\text{O}$ values of ~ 0 to -5 ‰ (using fractionation factors of Sheppard and Gilg, 1996). This is similar to $\delta^{18}\text{O}$ values of ~ -3.5 to -5.0 ‰ for the present ground water in the southern Perth Basin (Thorpe, 1992) and what appears to be a very limited change in $\delta^{18}\text{O}$ with time cannot by itself account for the extreme spread in $\delta^{18}\text{O}$ values observed in the present zircons, which range from -1 to + 15 ‰ (Table 2).

An alternative explanation for the observed trends in $\delta^{18}\text{O}$ with OH involves interaction between the penetrating ground waters and the radiation damaged zircon itself. It has been argued by Kober (1987) and Kramers et al. (2009) that recoil damaged areas are highly oxidizing and if we postulate that in Stage 1, percolating water forms weak bonds with positively charged ions with minimal fractionation of the oxygen isotopes such that $\delta^{18}\text{O}$ values fall on a mixing line between the mantle oxygen isotopic composition of the zircon and the ground water value of ~ -5‰. To explain the shift to a stage 2 trend, where in $\delta^{18}\text{O}$ is seen to increase with increasing OH, we

674 propose that coincident with the penetration of fluids into the oxidizing, radiation
 675 damaged domains, slower hydration and hydrolysis reactions occur, involving
 676 reduction of water, exchange of oxygen and release of H⁺ which enters the solutions as
 677 hydronium ions. In this reaction ¹⁸O is concentrated in preference to the lighter ¹⁶O and
 678 although the fractionation factor involved is not known this can be approximated by
 679 proposing an analogy between amorphous radiation damaged zircon and siliceous
 680 volcanic glass. In describing the long-term hydration of volcanic glass by seawater
 681 Garlick and Dymond (1970) estimated that “hydrated ashes would have $\delta^{18}\text{O}$
 682 lying between $+30$ and $+40$ ‰ if they were isotopically equilibrated with ocean
 683 water at deep sea temperatures”. Assuming that the fractionation factor for hydration
 684 of highly radiation damaged zircon is similar to glass, increasing hydration, measured
 685 as increasing OH, would be accompanied by an increase in $\delta^{18}\text{O}$ -values, along a
 686 mixing line trending to a $\delta^{18}\text{O}$ value of approximately 30‰. The maximum $\delta^{18}\text{O}$ value
 687 of ~ 15 ‰ for grain 57 suggests a possible 30% exchange between meteoric water and
 688 zircon oxygen. Garlick and Dymond (1970) proposed that isotopic exchange between
 689 silicate oxygen and the water of hydration is the rate-limiting step. This could explain
 690 the initial Stage 1 trend to light oxygen associated with the relatively rapid influx of
 691 water, followed by slower oxygen (water-SiO₄) exchange during hydrolysis as
 692 observed in Stage 2.

693 The occurrence of similar trends in the weathering of zircons from Archean
 694 granite W388 (Pidgeon et al., 2013) are shown Fig. 12B. These show a more extreme
 695 depletion of $\delta^{18}\text{O}$ values to less than 1 ‰ during Stage 1 influx of water followed by
 696 an increase in $\delta^{18}\text{O}$ values at the highest measured OH. The similar trends in $\delta^{18}\text{O}$ with
 697 increasing OH found in the two studies suggests they represent general processes that
 698 occur when radiation damaged zircon interacts with weathering solutions.

699 Many problems remain in our understanding of the movement and reaction of
700 low temperature weathering fluids in zircon. Experimental low temperature
701 hydrothermal studies such as those of Geisler et al. (2002) give some insights but
702 processes occurring at ambient temperatures without any annealing may not be the
703 same. Our results suggest that the disturbance of $\delta^{18}\text{O}$ values is not necessarily
704 affected by cracks as is the case for the U-Th-Pb system. But little is known about
705 actual mechanisms and the role of radiation damage in the admission of water and
706 reactions, such as hydrolysis, that lead to the exchange of oxygen isotopes between
707 water and the damaged zircon structure. For Group 5 grains the light $\delta^{18}\text{O}$ and high
708 OH values in grain 58, which appears to be low in radiation damage, are puzzling as
709 is the heavy oxygen in relatively low U grain 114. Nevertheless, the present results
710 provide a basis for a better understanding of $\delta^{18}\text{O}$ and U-Th-Pb behaviour of zircons
711 from weathered rocks. This is particularly relevant to studies of the Jack Hills zircons
712 themselves. For example the exceptionally heavy oxygen in Jack Hills zircons, with
713 $\delta^{18}\text{O}$ values up to 15 ‰, reported by Mojzsis et al (2001), could be the result of
714 interaction with weathering solutions. Weathering could also be considered as a
715 factor in explaining some of the light oxygen measurements in variably discordant
716 Jack Hills zircons reported by Trail et al. (2007). The zero age discordia intersection
717 for U-Pb analyses on the very old grain reported by Wilde et al (2001) indicates that
718 this grain has interacted with weathering solutions and the effect of weathering is also
719 a possible explanation for the increase in U, Th and Th/U in discordant Jack Hills
720 zircons reported by Cavosie et al. (2004). These issues together with important
721 questions on the mechanisms of interaction of weathering solutions with isotopic and
722 elemental systems of radiation damaged zircons need to be explored by further
723 research on zircons from weathered rocks.

5. CONCLUSIONS

Results of the present study demonstrate that ancient zircons from the Jack Hills have been isotopically and chemically disturbed by weathering processes that have affected the Yilgarn Craton since at least the Permian. Relatively low U zircons and parts of zircons have remained closed Th-U-Pb systems and retained primary oxygen isotopic compositions during the period of deep weathering. Other zircons have disturbed Th-U-Pb systems that define discordia lines intersecting concordia at approximately zero million years and are a result of weathering. Weathering solutions have penetrated into the zircons through surface cracks depositing U and Th, increasing the Th/U ratios and strongly reducing the $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages. Fluids disperse radially from cracks into the zircon matrix resulting in loss of radiogenic Pb, addition of common Pb, disturbance of the oxygen isotopic systems and addition of OH. In some U-Pb discordant zircons $\delta^{18}\text{O}$ systems are not altered even where analyses overlap cracks. In other weathering affected grains $\delta^{18}\text{O}$ becomes progressively lighter with increasing OH content and with further increase in OH this trend is seen to reverse and $\delta^{18}\text{O}$ becomes progressively heavier. The trends to lighter and then heavier oxygen are attributed to initial inflow of ground water into the metamict zircon without fractionation, followed by a slower hydrolysis exchange reaction between ground water and radiation damaged zircon that involves strong oxygen fractionation. The similarity of the trends in U-Pb systems and the $\delta^{18}\text{O}$ versus OH for zircons from a weathered Archean granite from south-western Australia to those observed in zircons from the Jack Hills, suggests that the trends in $\delta^{18}\text{O}$ with OH/O and the pattern of disturbance of the U-Th-Pb systems, represent general behaviour for radiation damaged zircons affected by weathering and that similar trends

will be recognised in zircons from samples of weathered rocks from other locations

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Figure Captions

- Figure 1 Map of the Yilgarn Craton in south-western Australia showing the major terrane subdivisions, greenstone belts (green) and the locations of the Jack Hills and Darling Range granite sample W388.
- Figure 2 Relationship between $\delta^{18}\text{O}$ and $^{16}\text{O}^1\text{H}/^{16}\text{O}$ and source pressure (Torr) for zircon standards and grains unaffected by weathering for the three analytical sessions.
- Figure 3 U-Pb Concordia plots for representative zircons from Groups 1, 2, 3 and 4.
- Figure 4 Plot of $\delta^{18}\text{O}$ versus $^{16}\text{O}^1\text{H}/^{16}\text{O}$ for U-Pb concordant Group 1 grains. Error bars in plots are $\pm 1\sigma$.
- Figure 5 Plot of $\delta^{18}\text{O}$ versus $^{16}\text{O}^1\text{H}/^{16}\text{O}$ for Group 2 zircons.
- Figure 6 Plot of $\delta^{18}\text{O}$ versus $^{16}\text{O}^1\text{H}/^{16}\text{O}$ for Group 3 zircons.
- Figure 7 Plot of $\delta^{18}\text{O}$ versus $^{16}\text{O}^1\text{H}/^{16}\text{O}$ for Group 4 zircons.
- Figure 8 U-Pb Concordia plots and plots of $\delta^{18}\text{O}$ versus $^{16}\text{O}^1\text{H}/^{16}\text{O}$ for Group 5 zircons.
- Figure 9 CL images of grains 66, 35, 6 and 65 showing O-OH and Th-U-Pb analytical spots and the location of the electron probe analytical spots along the traverses.
- Figure 10 Plot of $\delta^{18}\text{O}$ versus $^{16}\text{O}^1\text{H}/^{16}\text{O}$ for grains 6 and 65, showing an initial trend to lighter $\delta^{18}\text{O}$ values changing to heavier $\delta^{18}\text{O}$ values with increasing OH.
- Figure 11 Plot of $\ln \text{Th}/\text{U}$ (measured/calculated) versus $\ln \text{U}$ and $\ln \text{Th}$ for all analyses. Type 1 analyses have > 95% concordant $^{208}\text{Pb}/^{232}\text{Th}$ ages. Type 2 analyses have 95-65% Th age concordance and Type 3 analyses are those with Th-Pb ages < 65% concordant.
- Figure 12 Plot of $^{16}\text{O}^1\text{H}/^{16}\text{O}$ versus $\delta^{18}\text{O}_{\text{smow}}$ for (A) Group 3 zircons grains 128 and 151 and (B) zircons from Archean Darling Range granite sample W388 (grains 6 and 7) (Fig.1) showing the Stage 1 (to lighter $\delta^{18}\text{O}$) and Stage 2 trends (to heavier $\delta^{18}\text{O}$).

Table

Table 3 electron ptoebe traverse data											
Grain A6						Grain B65					
Analysis		Zr	Th ppm	U ppm	Th/U	Analysis		Zr	Th	U	Th/U
spot		Wgt %				spot		WT%	ppm	ppm	
1	c	46.4	2481	1454	1.71	1	c	40.6	9196	5669	1.62
2		47.7	123	472	0.26	2	c	45.3	973	551	1.77
3		47.6	65	343	0.19	3		48.0	80	226	0.35
4		46.8	8967	1135	7.90	4		47.7	3210	1075	2.99
5	c	45.0	14860	1287	11.55	5		48.1	1384	269	5.14
6		48.1	700	778	0.90	6		47.8	467	681	0.69
7	c	46.6	1216	709	1.71	7		47.8	147	359	0.41
8		48.2	17	468	0.04	8		47.9	509	205	2.49
9	c	44.1	767	1101	0.70	9		48.1	2418	312	7.75
10		47.8	120	112	1.07	10	c	39.9	22398	2436	9.20
11		47.8	27	62	0.43	11		47.5	2652	434	6.12
12		47.7	79	97	0.82	12		47.8	1472	342	4.30
13		47.5	153	278	0.55	13		47.7	668	141	4.73
14		47.9	22	91	0.24	14		48.1	55	10	5.46
15		48.0	137	136	1.01	15		47.9	114	206	0.55
16		48.0	206	105	1.96	16		47.9	62	120	0.52
17		47.8	60	160	0.37	17		47.9	130	242	0.54
18	c	42.4	39681	2020	19.64	18		46.6	6643	895	7.42
19		47.7	31	462	0.07	19		48.0	196	365	0.54
20		47.9	26	55	0.48	20		47.4	1621	408	3.97
						21		48.0	235	378	0.62
Note c- refers to overlap of observed crack											

Table

Table 1 U-Th-Pb results																
Sample/ Spot #	²⁰⁶ Pb/ measured	f _{inc} %	U ppm	Th ppm	Th/U calc	Th/U meas	²⁰⁷ Pb/ meas	±1σ	²⁰⁷ Pb/ ²³⁵ U	±1σ	²⁰⁶ Pb/ ±1σ	±1σ	²⁰⁶ Pb/ ±1σ	±1σ	²⁰⁶ Pb/ ±1σ	±1σ
			Age Ma													
			Age Ma				Age Ma				Age Ma					
Group 1 Grains																
Group 1 Grains from Mount 1																
Group 5																
#5-1	48453	0.04	68	25	0.36	0.36	0.3905	0.73	43.79	1.54	0.8134	1.36	0.2118	7.6	3873	11
#5-2	48857	0.02	76	26	0.35	0.34	0.3871	0.41	44.49	1.39	0.8337	1.33	0.2236	7.7	3860	6
Group 104																
#104-1	312807	0.01	61	43	0.68	0.71	0.4301	0.55	52.58	1.56	0.8865	1.46	0.2155	7.6	4018	8
#104-2	64097	0.03	61	43	0.69	0.70	0.4295	0.57	51.13	1.52	0.8634	1.40	0.2157	7.6	4016	9
Group 127																
#127-1	52523	0.04	95	53	0.53	0.55	0.4574	0.61	56.05	1.54	0.8887	1.41	0.2154	7.6	4109	9
#127-2	92573	0.02	95	63	0.65	0.67	0.4555	0.57	56.28	1.45	0.8962	1.33	0.2196	7.6	4103	8
#127-3	65277	0.03	104	58	0.54	0.56	0.4600	0.29	56.54	1.36	0.8914	1.33	0.2210	7.6	4118	4
Group 142																
#142-1	50059	0.04	40	23	0.56	0.57	0.4345	0.74	52.68	1.61	0.8794	1.43	0.2198	7.7	4033	11
#142-2	52669	0.04	46	25	0.54	0.54	0.4384	0.61	52.38	1.53	0.8665	1.41	0.2197	7.8	4046	9
Group C26																
C26-1	483452	0.00	117	134	1.15	1.15	0.4278	0.24	51.57	1.38	0.8743	1.35	0.2231	7.6	4010	4
C26-2	452413	0.00	97	218	1.21	1.23	0.4289	0.19	51.29	1.37	0.8674	1.33	0.2179	7.5	4013	5
C26-3	108658	0.02	93	92	0.96	0.98	0.4272	0.33	52.18	1.35	0.8859	1.33	0.2196	7.6	4008	3
Group C108																
c108-1	14970	0.12	57	81	1.38	1.43	0.2861	0.42	27.23	1.47	0.6905	1.41	0.1770	7.6	3396	7
c108-2	171325	0.01	64	97	1.48	1.51	0.2881	0.40	27.63	1.45	0.6957	1.40	0.1802	7.6	3407	6
Group C115																
c115-1	>1e6	0.00	59	47	0.77	0.81	0.4314	0.37	51.93	1.43	0.8729	1.38	0.2198	7.6	4022	6
c115-2	221609	0.01	127	82	0.63	0.65	0.4338	0.22	52.64	1.34	0.8802	1.33	0.2198	7.6	4030	3
Group 1 Grain from Mount A																
Group 122																
122-1	313266	0.01	49	27	0.56	0.56	0.3696	0.43	40.22	0.87	0.7893	0.75	0.2037	3.80	3790	7
122-2	174327	0.01	78	37	0.49	0.48	0.3687	0.48	40.15	0.89	0.7898	0.75	0.2074	3.59	3786	7
122-3	>1e6	0.01	59	28	0.49	0.48	0.3552	0.56	37.41	0.92	0.7637	0.73	0.2019	3.62	3730	8
GROUP 2 GRAINS																
Group 2 Grains from Mount 1																
Group 39																
#39-1	1256	2.49	168	369	1.04	2.20	0.4136	0.77	18.28	9.26	0.3207	9.23	0.0426	12.3	3959	11
#39-2	1774	1.05	149	143	1.19	0.96	0.4097	0.67	29.19	1.48	0.5167	1.32	0.1737	7.7	3945	10
#39-3	114858	0.02	74	100	1.30	1.36	0.4308	0.36	51.75	1.41	0.8712	1.37	0.2123	7.6	4020	5
#39-4	120992	0.02	74	72	0.94	0.97	0.4314	0.57	52.96	1.44	0.8904	1.33	0.2187	7.6	4022	8
Group 49																
#49-1	80116	0.02	87	42	0.45	0.49	0.4548	0.54	58.39	1.43	0.9311	1.33	0.2193	8.3	4101	8
#49-2	41716	0.04	75	49	0.63	0.66	0.4541	0.38	56.75	1.42	0.9063	1.37	0.2208	7.6	4099	6
#49-3	72607	0.03	114	71	0.61	0.63	0.4548	0.29	56.89	1.40	0.9072	1.37	0.2226	7.6	4101	4
#49-4	115905	0.02	75	27	0.36	0.37	0.4480	0.59	55.22	1.54	0.8939	1.42	0.2335	7.7	4078	9
#49-5	844	2.22	280	213	0.38	0.76	0.4210	0.48	9.37	3.98	0.1615	3.96	0.0297	9.0	3986	7
Group 63																
#63-1	19452	0.10	37	22	0.56	0.58	0.3680	1.55	40.42	2.08	0.7966	1.37	0.1995	7.7	3783	23
#63-1	102	18.37	1084	4150	0.75	3.83	0.4140	1.27	83.21	2.35	0.1455	1.97	0.0203	8.1	3961	19
Group 191																
#191-1	321	5.83	1165	6321	0.47	5.42	0.4027	0.75	1.33	1.55	0.0239	1.36	0.0100	8.0	3919	11
#191-2	>1e6	0.00	6	2	0.33	0.32	0.4329	1.11	53.28	1.40	0.8928	1.23	0.2350	8.8	4027	16
#191-3	2402	0.78	285	571	0.30	2.01	0.3708	0.29	10.28	2.88	0.2010	1.86	0.0094	8.7	3794	4
Group 208																
#208-1	2146	0.87	364	261	0.37	0.72	0.4508	0.69	34.78	2.35	0.5596	2.25	0.0867	8.6	4088	10
#208-2	551819	0.00	231	87	0.36	0.38	0.4793	0.52	60.92	1.43	0.9219	1.33	0.2216	7.6	4179	8
#208-3	1804	1.04	607	1220	0.36	2.01	0.4441	2.58	20.99	3.17	0.3428	1.85	0.0191	8.3	4066	38
Group C43																
c43-1	366671	0.01	477	152	0.32	0.32	0.3857	0.17	44.49	1.33	0.8367	1.32	0.2189	7.6	3854	3
c43-2	>1e6	0.00	440	108	0.25	0.25	0.3783	0.25	43.03	1.36	0.8251	1.34	0.2125	7.6	3825	4
c43-3	4891	0.28	742	401	0.41	0.54	0.3354	0.14	27.54	1.36	0.5955	1.35	0.2260	7.6	3642	2
Group C71																
c71-1	12262	0.15	139	229	1.53	1.64	0.2883	0.26	24.25	1.35	0.6101	1.32	0.1506	7.6	3408	4
c71-2	49469	0.04	204	372	1.75	1.82	0.2857	0.21	28.04	1.38	0.7117	1.36	0.1812	7.5	3395	3
Group C104																
c104-1	301404	0.01	66	52	0.79	0.79	0.4648	0.45	57.96	1.42	0.9043	1.35	0.2294	7.6	4133	7
c104-2	1985	0.94	375	473	0.22	1.26	0.4029	0.58	29.37	1.46	0.5288	1.34	0.0321	7.8	3920	9
Group 2 Grains from Mount A																
Group 46																
46-1	20429	0.09	411	159	0.08	0.39	0.3235	0.21	32.37	0.75	0.7266	0.72	0.0388	8.57	3584	3
46-2	38984	0.05	351	81	0.22	0.23	0.3866	0.25	42.71	0.77	0.8017	0.72	0.2003	3.54	3857	4
46-3	179	10.45	3743	7718	0.36	2.06	0.3470	1.54	3.54	3.29	0.0886	1.44	0.0041	34.48	3417	45
Group 79																
															547	8

79-1	9964	0.19	195	16	0.14	0.86	0.4308	0.26	39.58	7.99	0.6676	0.74	0.0278	3.83	4017	4	3297	19	546	21
79-2	6699	0.28	207	23	0.10	0.81	0.4346	0.39	44.78	1.09	0.7493	1.01	0.1724	7.51	4029	6	3605	28	3188	220
79-3	297095	0.01	182	127	0.70	0.70	0.4880	0.33	61.50	0.79	0.9142	0.72	0.2325	3.81	4205	5	4186	22	4226	145
Group 2 Grains from Mount B																				
Grain 35																				
35-1	2066	0.91	260	144	0.64	0.55	0.4246	0.35	28.60	1.13	0.4886	1.08	0.1433	4.06	3998	5	2564	23	2708	103
35-2	31146	0.06	264	179	0.67	0.68	0.4672	0.16	58.07	0.89	0.9015	0.87	0.2234	3.03	4141	2	4143	27	4075	112
35-3	847	2.21	1081	1979	0.59	1.83	0.3438	0.76	17.33	1.95	0.3656	1.79	0.2106	1.70	3680	12	2009	31	605	64
Grain 66																				
66-1	71150	0.03	151	52	0.34	0.35	0.4412	0.53	52.93	1.02	0.8072	0.87	0.2386	2.67	4056	8	4036	26	3996	96
66-2	1735	1088	288	166	0.62	0.58	0.4762	0.27	35.63	0.70	0.6210	0.65	0.1768	2.71	3969	4	3114	16	3184	80
66-3	404	4.63	1010	5193	0.45	1.54	0.3878	0.89	64.2	2.29	1.201	2.11	0.0027	6.11	3862	13	3714	15	54	3
66-4	1870	1	531	708	0.61	1.33	0.4347	0.52	28.44	1.13	0.4745	1.00	0.0567	3.99	4034	8	2503	21	1076	42
Grain 81																				
81-1	591	3.16	356	1153	0.26	3.24	0.3574	0.80	16.15	1.15	0.3277	0.72	0.0067	18.08	3739	14	1827	12	134	24
81-2	1149	1.63	323	807	0.36	2.50	0.3832	0.57	21.89	0.94	0.6216	1.74	0.0231	3.44	3644	9	3117	16	461	16
81-3	55834	0.03	149	32	0.21	0.21	0.4085	0.34	47.76	0.97	0.8480	0.91	0.2101	2.73	3941	5	3959	27	3855	95
81-4	14035	0.13	240	379	0.31	1.58	0.3969	0.84	42.50	1.07	0.7766	0.65	0.0396	3.99	3897	13	3705	18	785	31
81-5	4125	0.45	170	299	0.26	1.76	0.3804	0.55	34.73	0.86	0.6211	0.66	0.0252	5.25	3834	8	3275	17	504	26
81-6	309892	0.01	415	32	0.08	0.08	0.2901	0.20	28.97	0.72	0.7244	0.69	0.1943	2.83	3418	3	3512	19	3589	93
Grain 91																				
91-1	364652	0.01	332	105	0.32	0.32	0.3977	0.18	46.98	0.79	0.8458	0.77	0.2183	2.54	3901	3	3951	23	3991	92
91-2	2545	0.73	1203	1307	0.41	1.09	0.3873	0.13	17.98	1.19	0.3368	1.19	0.0329	3.92	3860	2	1871	19	654	25
91-3	24250	0.08	6252	272	0.42	0.42	0.3809	0.41	39.00	0.83	0.7427	0.72	0.1943	2.51	3835	6	3580	20	3588	82
91-4	829	2.26	1538	2827	0.20	1.84	0.3860	0.20	99.89	1.59	0.1859	1.58	0.0051	6.26	3855	3	1099	16	103	6
91-5	102899	0.02	254	60	0.24	0.24	0.3904	0.25	44.57	0.89	0.8279	0.85	0.2118	2.62	3873	4	3888	25	3884	92
Grain 97																				
97-1	4250	0.44	422	336	0.70	0.80	0.4220	0.20	44.93	0.77	0.7721	0.75	0.1738	2.54	3988	3	3688	21	3238	76
97-2	48827	0.04	307	207	0.67	0.67	0.4381	0.16	53.93	0.83	0.9005	0.92	0.2254	2.66	4045	2	4105	28	4108	98
97-3	680	2.75	101	280	0.25	2.78	0.4305	0.57	21.39	1.36	0.3603	1.23	0.0082	5.76	4019	9	1984	21	164	9
Grain 123																				
123-1	2984	0.63	711	558	0.45	0.78	0.4281	0.17	21.26	1.72	0.3601	1.71	0.0527	5.20	4011	3	1983	29	1037	63
123-2	2734	0.68	547	639	0.42	1.17	0.4277	0.26	22.79	3.93	0.3864	3.92	0.0354	14.65	4010	4	2106	71	703	101
123-3	39053	0.05	323	100	0.31	0.31	0.3732	0.60	39.39	0.99	0.7655	0.78	0.1965	2.60	3884	9	3664	22	3625	86
Grain 142																				
142-1	1690	1.11	905	2914	0.51	3.22	0.2671	0.21	9.45	2.47	0.2656	2.46	0.0108	38.89	3288	3	1472	32	217	8
142-2	51854	0.04	366	209	0.53	0.57	0.2712	0.19	25.31	0.93	0.5759	0.91	0.1666	2.58	3313	3	3332	24	3114	74
142-3	2598	0.72	371	2145	0.73	5.78	0.2795	0.31	16.60	1.43	0.5188	1.39	0.1737	17.21	3338	5	2681	31	347	59
142-4	8484	0.22	369	211	0.50	0.57	0.2707	0.19	24.10	0.86	0.8455	0.84	0.1507	2.80	3310	3	3211	21	2838	74
142-5	4447	0.42	730	448	0.76	0.61	0.2254	0.99	15.33	1.29	0.4933	0.85	0.1648	4.46	3020	16	2585	18	3083	156
GROUP 3 GRAINS																				
Group 3 Grains from Mount 1																				
Grain 271																				
#271-1	21946	0.09	51	35	0.65	0.68	0.4278	0.34	52.10	1.58	0.8833	1.54	0.2154	7.7	4010	5	4081	47	3943	273
#271-2	1697	1.10	70	44	0.61	0.62	0.4025	0.37	40.11	1.59	0.7228	1.55	0.2049	8.0	3918	6	3507	42	3767	274
Grain 282																				
#282-1	4858	0.38	137	430	0.73	3.14	0.5028	0.33	55.81	1.36	0.8050	1.32	0.0490	7.7	4250	5	3807	38	967	72
#282-2	23158	0.08	132	207	0.72	1.56	0.5123	0.20	66.07	1.34	0.9553	1.32	0.1083	9.8	4277	3	4256	41	2078	193
Grain 55																				
#55-1	665	2.82	1124	5685	0.47	5.06	0.4113	0.30	6.91	1.38	0.1218	1.35	0.0047	9.1	3951	4	741	9	84	8
#55-2	8597	0.21	127	77	0.44	0.61	0.4344	0.56	50.26	1.44	0.8392	1.33	0.1619	7.8	4033	8	3928	39	3034	219
#55-3	6931	0.27	357	804	0.31	2.25	0.4355	0.47	26.39	1.92	0.4379	1.87	0.0165	9.4	4037	7	2341	37	330	31
#55-4	954	1.96	800	2872	0.30	3.59	0.4090	0.28	10.83	1.44	0.1920	1.41	0.0062	8.9	3943	4	1132	15	126	11
Group 3 Grains from Mount A																				
Grain 11																				
11-1	271069	0.01	50	25	0.52	0.51	0.4313	0.98	51.44	1.22	0.8651	0.72	0.2221	3.69	4022	15	4018	21	4055	135
11-2	1036	1.81	298	94	0.31	0.32	0.3755	0.32	31.44	0.84	0.6213	0.74	0.1575	4.94	3779	6	3115	18	2957	190
11-3	110625	0.01	99	43	0.43	0.44	0.4281	0.30	51.47	0.80	0.8721	0.74	0.2163	3.90	4011	4	4042	22	3958	140
11-4	3359	0.56	188	110	0.60	0.59	0.3909	0.31	37.68	0.81	0.7036	0.75	0.1846	3.73	3865	5	3434	20	3425	117
11-5	1601	1.17	169	72	0.52	0.43	0.3937	0.23	33.48	2.19	0.6250	2.17	0.1939	4.29	3865	4	3130	54	3582	140
11-6	21999	0.09	106	67	0.61	0.63	0.4295	0.20	50.72	0.74	0.8571	0.72	0.2123	3.56	4015	3	3990	21	3890	126
Grain 32																				
32-1	3217	0.58	337	455	0.60	1.35	0.5315	0.20	31.09	0.94	0.4257	0.92	0.0473	3.62	4326	3	2286	18	934	33
32-2	144659	0.01	144	87	0.61	0.60	0.5444	0.27	73.23	0.77	0.9756	0.72	0.2462	3.53	4366	4	4389	23	4448	140
32-3	76656	0.02	125	108	0.62	0.86	0.5097	0.25	65.18	0.76	0.9276	0.72	0.1675	3.68	4269	4	4231	22	3129	106
Group 3 Grains from Mount B																				
Grain 56																				
56-1	414	4.52	1509	1342	0.53	0.89	0.3629	0.41	41.24	1.44	0.0839	1.38	0.0130	3.47	3762	6	519	7	261	9
56-2	158	11.85	1114	1673	0.63	1.50	0.3685	0.51	42.31	7.95	0.2227	5.74	0.0243	52.99	3785	81	1296	68	444	252
56-3	104	18.01	7327	25236	0.38	3.44	0.2196	0.19	11.7	1.47	0.0385	0.99	0.0012	7.87	2978	17	244	2	23	2
56-4	182	10.26	1603	3924	0.70	2.45	0.3593	0.86	5.09	1.90	0.1027	1.69	0.0004	7.12	3477	13	600	10	169	12
Grain 65																				
65-1	7883	0.24	371	349	0.64	0.94	0.2834	0.26	26.80	0.88	0.6859	0.84	0.1229	4.27	3382	4	3367	22	2343	94
65-2	6459	0.29	305	912	0.70	2.99	0.3014	0.20	25.69	0.91	0.6182	0.89	0.0491	3.08	3477	3	3103	22	969	29
65-3	1447	1.29	621	2336	0.62	3.76	0.2896	0.20	14.82	0.94	0.3711	0.91	0.0162	2.91	3415	3	2035	16	325	9
65-4	54560	0.03	375	164	0.42	0.44	0.3039	0.23	30.11	0.92	0.7184	0.89	0.1828	2.62	3490	4	3490	24	3393	82
Grain 128																				
128-1	1996	0.94	158	601	0.23	3.80	0.4310	0.52	13.12	1.75	0.2208	1.67	0.0033	4.55	4021	8	1286	20	67	3
128-2	83566	0.02	116	43	0.37	0.37	0.4708	0.34	58.26	1.23	0.8975	1.28	0.2037	2.84	4152	5	4129	39	4080	105

128-3		1031	1.81	811	4177	0.64	5.15	0.4631	0.23	7.79	0.75	0.1220	0.71	0.0038	2.70	4128	3	742	5	77	2
128-4		571	3.28	858	4532	0.28	5.29	0.4079	0.44	3.00	1.81	0.0533	1.76	0.0007	5.12	3938	7	335	6	14	1
128-5		2784	0.67	130	446	0.22	3.43	0.4381	0.57	20.35	0.93	0.3369	0.74	0.0056	5.65	4045	8	1872	12	112	6
Grain 151																					
151-1		190	9.83	2485	10723	0.43	4.31	0.4319	0.64	1.92	1.70	0.0359	1.42	0.0009	10.9	3863	14	227	3	19	2
151-2		160	11.68	1706	8402	0.56	4.93	0.4046	0.90	3.78	5.85	0.0789	5.54	0.0023	19.5	3696	28	489	26	47	9
151-3		1832	1.02	441	385	0.57	0.87	0.4108	0.31	31.72	1.13	0.5660	1.08	0.0936	3.02	3933	5	2891	25	1808	52
151-4		136	13.73	1251	6470	0.60	5.17	0.4644	1.10	9.32	3.82	0.1668	3.01	0.0050	31	3929	35	995	28	100	31
GROUP 4 GRAINS																					
Group 4 Grains from Mount A																					
Grain 6																					
6-1		1088	1.72	895	1210	0.18	1.35	0.3891	0.76	14.03	6.37	0.2668	6.32	0.0092	15.00	3837	12	1525	86	185	28
6-2		861	2.17	862	7189	0.30	8.34	0.3874	0.23	19.28	1.71	0.3705	1.69	0.0014	17.24	3822	5	2032	29	29	5
6-3		659	2.84	1535	8275	0.24	5.39	0.2847	2.01	8.96	3.03	0.2420	1.96	0.0029	18.37	3298	36	1397	25	58	11
6-4		1033	1.81	2089	829	0.09	0.30	0.3969	0.53	9.54	1.02	0.1779	0.86	0.0141	9.74	3866	8	1056	8	282	27
Grain 113																					
113-1		19430	0.10	267	148	0.52	0.55	0.2651	0.17	23.01	0.74	0.6307	0.72	0.1571	3.53	3274	3	3152	18	2950	97
113-2		38337	0.05	255	215	0.60	0.84	0.2688	0.18	23.94	0.74	0.6468	0.72	0.1228	3.59	3297	3	3216	18	2340	79
113-3		816	2.29	772	556	0.53	0.72	0.2750	0.24	8.70	1.01	0.2408	0.95	0.0472	6.14	3258	5	1391	12	933	56
113-4		1483	1.26	444	1731	0.62	3.90	0.2727	0.18	10.88	0.75	0.2972	0.72	0.0125	3.81	3280	3	1677	11	251	10
Group 4 Grains from Mount B																					
Grain 57																					
57-1		32	59.17	6053	48330	no data	7.98	0.2714	21.03	3.16	26.04	0.0845	15.35	no data	no data	3314	296	523	78	no data	no data
57-2		347	5.38	932	1311	0.75	1.41	0.4974	0.25	12.36	1.47	0.1802	1.45	0.0242	4.39	4234	4	1068	14	483	21
57-3		781	2.39	529	750	0.82	1.42	0.5196	0.27	21.88	0.94	0.3053	0.90	0.0441	2.73	4298	4	1718	14	872	23
57-4		343	5.45	419	841	0.58	2.01	0.5173	0.46	19.95	0.80	0.2797	0.65	0.0202	5.76	4291	7	1590	9	404	23
Grain 72																					
72-1		144	13.02	694	232	0.31	0.33	0.3429	0.93	4.65	1.29	0.0984	0.88	0.0237	7.99	3676	14	605	5	474	37
72-2		77340	0.02	120	39	0.32	0.33	0.4700	0.31	58.21	1.16	0.8981	1.12	0.2215	2.82	4150	5	4131	34	4044	103
72-3		707	2.65	937	1027	0.38	1.10	0.4778	0.40	11.97	0.85	0.1817	0.75	0.0159	3.64	4174	6	1078	7	318	11
Grain 156																					
156-1		53478	0.03	237	108	0.46	0.46	0.3883	0.87	42.65	1.09	0.7967	0.65	0.2048	2.94	3864	13	3777	19	3765	101
156-2		1201	1.56	404	573	0.39	1.42	0.4099	0.37	19.57	0.79	0.3462	0.70	0.0245	2.99	3946	6	1916	12	490	14
156-3		1479	1.26	327	784	0.42	2.40	0.4065	0.47	13.87	3.18	0.2474	3.15	0.0110	6.33	3933	7	1425	40	222	14
GROUP 5 GRAINS																					
Group 5 Grains from Mount A																					
Grain 91																					
91-1		247992	0.01	141	73	0.52	0.52	0.2868	0.22	26.88	0.98	0.6799	0.96	0.1775	3.62	3400	3	3344	25	3303	110
91-2		339132	0.01	146	23	0.16	0.16	0.3509	0.63	36.68	0.96	0.7582	0.73	0.1902	4.79	3711	10	3637	20	3519	154
91-3		310564	0.01	115	70	0.62	0.60	0.2855	0.26	27.82	0.76	0.7088	0.72	0.1874	3.68	3393	4	3446	19	3472	117
91-4		117675	0.02	170	53	0.31	0.31	0.2860	0.24	27.52	0.76	0.6981	0.72	0.1830	3.56	3396	4	3413	19	3397	111
Grain 114																					
114-1		335813	0.01	84	26	0.31	0.31	0.4700	0.52	58.38	0.89	0.9009	0.72	0.2289	3.60	4150	8	4141	22	4166	135
114-2		255446	0.01	99	36	0.37	0.37	0.4785	0.69	60.13	1.00	0.9153	0.72	0.2323	3.56	4170	10	4189	22	4222	135
114-3		407737	0.00	115	41	0.36	0.36	0.4700	0.36	58.50	0.81	0.9028	0.72	0.2288	3.57	4150	5	4147	22	4165	134
114-4		117687	0.02	41	10	0.27	0.26	0.4490	0.59	54.49	0.93	0.8803	0.72	0.2312	3.83	4082	9	4070	22	4204	145
Group 5 Grains from Mount B																					
Grain 30																					
30-1		16530	0.11	290	51	0.18	0.18	0.4549	0.59	53.09	0.99	0.8464	0.80	0.2245	2.97	4101	9	3953	24	4094	110
30-2		87229	0.02	99	54	0.54	0.55	0.4403	1.41	51.98	1.60	0.8561	0.77	0.2134	2.67	4053	21	3987	23	3910	95
30-3		79923	0.02	59	36	0.61	0.61	0.4470	1.11	54.39	1.64	0.8825	1.20	0.2208	3.08	4075	16	4078	36	4032	112
30-4		403743	0.00	56	30	0.53	0.54	0.4772	0.76	61.14	1.45	0.9292	1.24	0.2318	3.46	4172	11	4236	39	4214	131
Grain 34																					
34-1		101419	0.02	167	31	0.19	0.19	0.2856	0.26	27.44	1.28	0.6967	1.25	0.1927	3.03	3394	4	3408	33	3562	99
34-2		220070	0.01	229	88	0.38	0.38	0.3238	0.32	33.16	0.92	0.7428	0.86	0.1923	2.59	3588	5	3581	24	3555	84
34-3		>1e6	0.00	235	101	0.43	0.43	0.3228	0.28	33.11	0.86	0.7438	0.82	0.1943	2.61	3583	4	3585	22	3589	86
34-4		126364	0.01	216	85	0.39	0.39	0.3236	0.22	33.70	0.87	0.7554	0.85	0.1954	2.61	3587	3	3627	23	3607	86
Grain 58																					
58-1		12173	0.15	262	128	0.54	0.49	0.4438	0.48	58.55	0.85	0.9568	0.70	0.2873	2.83	4065	7	4328	22	4788	120
58-2		62152	0.03	103	56	0.53	0.54	0.4444	0.26	53.81	1.04	0.8781	1.01	0.2169	2.72	4067	4	4063	31	3968	98
58-3		89953	0.02	140	40	0.27	0.29	0.4504	0.32	55.79	0.95	0.8983	0.90	0.2147	2.71	4087	5	4132	28	3931	97

Table

Table 2 O-OH results											
Sample	^{16}O cps	$\delta^{18}\text{O}_{\text{SMOW}}$	$\pm 1\sigma$	$^{16}\text{O}^1\text{H}/^{16}\text{O}$	$\pm 1\sigma$	Sample	^{16}O cps	$\delta^{18}\text{O}_{\text{SMOW}}$	$\pm 1\sigma$	$^{16}\text{O}^1\text{H}/^{16}\text{O}$	$\pm 1\sigma$
ID	(x 109)	‰		(x10-3)	%	ID	(x 109)	‰		(x10-3)	%
GROUP 1 GRAINS						GROUP 3 GRAINS					
Group 1 Grains from Mount 1						Group 3 Grains From Mount 1					
Grain 5						Grain 55					
5--1	0.900	5.57	0.31	0.533	0.16	55-1	1.020	5.25	0.34	0.659	0.16
Grain 104						55-2					
104-1	0.914	6.30	0.35	0.557	0.20	55-3	1.016	4.96	0.36	0.497	0.30
104-2	0.922	5.89	0.34	0.556	0.27	55-4	1.035	4.99	0.31	1.608	1.56
104-3	0.921	5.98	0.32	0.534	0.13	55-5	1.030	4.42	0.32	0.919	0.22
Grain 127						Grain 271					
127-1	0.887	4.88	0.34	0.572	0.08	271-1	0.882	3.96	0.34	0.569	0.16
127-2	0.910	4.93	0.33	0.541	0.21	271-2	0.830	4.91	0.32	0.549	0.20
127-3	0.913	5.24	0.32	0.557	0.23	271-3	0.858	4.39	0.38	0.608	0.17
127-4	0.892	5.21	0.33	0.613	0.26	Grain 282					
Grain 142						282-1					
142-1	0.881	5.57	0.32	0.522	0.20	282-2	0.944	3.36	0.35	0.894	0.49
142-2	0.892	5.26	0.31	0.509	0.25	282-3	0.939	4.22	0.34	0.585	0.20
Grain C26						282-4					
C26-1	0.882	5.92	0.33	0.608	0.14	Group 3 Grains from Mount A					
C26-2	0.883	5.67	0.33	0.589	0.16	Grain 11					
C26-3	0.918	5.44	0.34	0.617	0.17	11-1					
Grain C108						11-2					
C108-1	0.870	5.80	0.35	0.552	0.21	11-3					
C108-2	0.885	5.72	0.34	0.560	0.23	11-4					
Grain C115						11-5					
C115-1	0.881	6.06	0.34	0.528	0.19	11-6					
C115-2	0.877	6.55	0.32	0.537	0.29	11-7					
Group 1 Grains from Mount A						Grain 32					
Grain 122						32-1					
122-1	0.861	5.80	0.39	1.130	0.35	32-2					
122-2	0.854	5.51	0.38	1.190	0.36	32-3					
122-3	0.853	5.62	0.38	1.170	0.35	32-4					
						Group 3 Grains from Mount B					
GROUP 2 GRAINS						Grain 56					
Group 2 Grains From Mount 1						56-1					
Grain 39						56-2					
39-1	1.018	6.73	0.31	0.478	0.22	56-3					
39-2	1.019	6.44	0.33	0.566	0.12	56-4					
39-3	1.033	6.13	0.32	0.670	0.28	Grain 65					
39-4	1.034	6.16	0.33	0.530	0.39	65-1					
39-5	1.016	6.96	0.33	0.488	0.47	65-2					
Grain 49						65-3					
49-1	0.934	5.13	0.32	0.497	0.20	65-4					
49-2	0.952	5.51	0.34	0.501	0.26	65-5					
49-3	0.928	5.44	0.33	0.563	0.26	65-6					
49-4	0.943	5.34	0.31	0.485	0.36	Grain 128					
49-5	0.952	5.11	0.33	0.495	0.35	128-1					
Grain 63						128-2					
63-1	0.935	5.14	0.32	0.523	0.14	128-3					
63-2	0.918	5.70	0.34	0.515	0.31	128-4					
Grain 191						128-5					
191-1	1.018	5.38	0.32	0.811	0.41	128-6					
191-2	0.996	5.51	0.33	0.435	0.37	Grain 151					

191-3	0.965	4.87	0.33	0.422	0.39	151-1	0.935	4.02	0.33	1.630	0.14
191-4	0.982	5.38	0.33	0.472	0.38	151-2	0.948	3.59	0.36	3.280	1.49
Grain 208						151-3	0.945	3.97	0.34	1.650	0.27
208-1	0.939	5.62	0.32	0.586	0.16	151-4	0.946	4.64	0.35	4.550	4.24
208-2	0.949	5.25	0.32	0.609	0.23	151-5	0.951	3.94	0.34	2.800	0.82
208-3	0.932	5.20	0.33	0.578	0.27						
208-4	0.942	5.60	0.33	0.611	0.25	GROUP 4 GRAINS					
Grain C43						Group 4 Grains from Mount A					
C43-1	0.940	5.81	0.32	0.598	0.16	Grain 6					
C43-2	0.930	5.91	0.30	0.613	0.24	6-1	0.898	6.14	0.38	1.120	0.24
C43-3	0.940	5.73	0.34	0.833	0.24	6-2	0.897	5.26	0.37	1.320	0.08
C43-4	0.920	6.33	0.33	0.644	0.25	6-3	0.911	7.45	0.39	6.090	2.19
C43-5	0.940	5.47	0.32	1.070	0.33	6-4	0.894	7.24	0.36	4.650	1.26
Grain C71						Grain 113					
C71-1	0.856	6.54	0.37	0.568	0.13	113-1	0.845	5.60	0.38	1.350	0.17
C71-2	0.912	4.77	0.31	0.614	0.37	113-2	0.856	6.37	0.38	4.330	0.74
Grain C104						113-3	0.838	5.56	0.39	1.370	0.19
C104-1	0.921	6.30	0.35	0.557	0.49	113-4	0.841	6.45	0.39	6.780	0.96
C104-2	0.933	5.89	0.34	0.556	0.17	Group 4 Grains from Mount B					
C104-3	0.931	5.98	0.32	0.534	0.31	Grain 57					
Group 2 Grains from Mount A						57-1	0.987	7.77	0.34	4.720	0.36
Grain 79						57-2	0.977	5.70	0.33	1.790	0.29
79-1	0.872	5.77	0.36	1.280	0.20	57-3	0.983	5.77	0.35	3.520	1.42
79-2	0.875	5.90	0.40	1.760	0.29	57-4	0.971	5.58	0.34	2.020	0.29
79-3	0.857	6.01	0.39	1.630	0.25	57-5	0.980	5.75	0.34	1.790	0.36
Grain 46						57-6	0.983	5.72	0.34	1.840	0.22
46-1	0.877	5.72	0.38	1.660	0.13	57-7	0.977	6.95	0.36	4.580	0.85
46-2	0.885	5.49	0.37	1.550	0.35	57-8	0.970	14.48	0.35	13.230	1.56
46-3	0.874	5.35	0.39	1.720	0.16	Grain 72					
Group 2 Grains from Mount B						72-1	0.976	6.67	0.35	2.560	0.64
Grain 35						72-2	0.962	7.97	0.33	7.300	2.81
35-1	0.997	6.69	0.35	2.087	0.14	72-3	0.987	5.84	0.34	1.730	0.30
35-2	0.984	6.05	0.33	6.699	1.08	72-4	0.988	5.40	0.35	1.860	0.52
35-3	0.995	5.54	0.34	1.942	0.20	72-5	0.983	5.98	0.33	1.740	0.38
Grain 66						Grain 156					
66-1	0.923	5.72	0.34	2.218	0.09	156-1	0.958	5.37	0.33	1.850	0.77
66-2	0.907	5.80	0.33	2.389	0.19	156-1	0.937	5.12	0.34	1.700	0.23
66-3	0.909	5.93	0.35	1.553	0.26	156-3	0.930	5.53	0.34	2.350	1.22
66-4	0.915	5.79	0.33	1.762	0.09	156-4	0.924	6.21	0.36	3.140	2.89
66-5	0.916	6.66	0.39	2.424	0.69						
Grain 81						GROUP 5 GRAINS					
81-1	0.980	6.47	0.33	3.126	0.91	Group 5 Grains from Mount A					
81-2	0.972	6.38	0.35	1.673	0.35	Grain 91					
81-3	0.956	6.15	0.34	1.713	0.21	91-1	0.846	5.82	0.38	1.260	0.27
81-4	0.956	5.68	0.34	2.013	0.34	91-2	0.844	6.19	0.39	1.480	0.37
81-5	0.950	5.75	0.35	1.948	0.47	91-3	0.850	6.07	0.40	1.660	0.35
81-6	0.950	6.51	0.38	1.737	0.33	91-4	0.850	5.97	0.36	1.290	0.42
81-7	0.951	6.28	0.35	1.709	0.35	91-5	0.847	5.92	0.36	1.290	0.28
81-8	0.954	6.29	0.34	1.850	0.48	Grain 114					
Grain 91						114-1	0.862	7.74	0.37	1.180	0.18
91-1	0.929	6.10	0.35	1.640	0.22	114-2	0.856	7.71	0.38	1.200	0.31
91-2	0.935	6.40	0.33	1.592	0.26	114-3	0.860	7.73	0.40	1.310	0.42
91-3	0.931	6.13	0.33	1.749	0.46	114-4	0.858	8.14	0.40	1.220	0.31
91-4	0.937	6.23	0.36	1.778	0.22	Group 5 Grains from Mount B					
91-5	0.924	5.86	0.35	1.673	0.24	Grain 30					
91-6	0.914	6.27	0.33	1.999	0.28	30-1	0.998	6.22	0.32	1.810	0.20
91-7	0.910	5.63	0.37	1.636	0.30	30-2	0.991	6.25	0.34	1.760	0.04
Grain 97						30-3	0.988	6.57	0.33	1.710	0.37

97-1	0.944	5.22	0.34	1.622	0.18	30-4	0.988	8.93	0.34	5.770	2.17
97-2	0.936	5.76	0.37	1.877	0.18	30-5	0.987	8.06	0.36	2.260	0.72
97-3	0.912	5.79	0.38	3.647	1.09	Grain 34					
97-4	0.915	5.30	0.34	1.855	0.13	34-1	1.078	6.74	0.37	1.400	0.83
97-5	0.921	4.78	0.35	1.604	0.31	34-2	0.999	6.30	0.33	1.730	0.19
97-6	0.925	5.28	0.34	5.382	1.03	34-3	0.999	6.21	0.36	1.790	0.27
Grain 123						34-4	0.998	6.36	0.35	1.870	1.03
123-1	0.932	5.75	0.33	1.735	0.11	34-5	1.004	6.48	0.33	3.680	1.19
123-2	0.931	5.81	0.37	1.712	0.17	Grain 58					
123-3	0.944	6.18	0.35	1.765	0.14	58-1	0.988	5.82	0.34	1.940	0.13
123-4	0.943	6.50	0.35	1.688	0.62	58-2	0.985	3.49	0.35	1.950	0.07
123-5	0.939	6.09	0.36	2.177	0.62	58-3	0.992	3.86	0.33	1.650	0.39
Grain 142						58-4	0.999	5.23	0.33	1.890	0.20
142-1	0.972	5.06	0.32	3.339	0.82	58-5	1.006	3.87	0.34	1.630	0.36
142-2	0.983	5.68	0.33	3.254	0.33	58-6	1.010	3.62	0.35	1.760	0.33
142-3	0.970	5.35	0.34	2.109	0.27	58-7	1.001	3.13	0.39	1.730	0.37
142-4	0.976	5.29	0.35	1.824	0.33	58-8	0.997	3.24	0.38	1.660	0.27
142-5	0.958	5.08	0.34	1.938	0.21						
142-6	0.955	4.94	0.36	2.194	0.22

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12