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1 **Record of ancient Martian hydrosphere preserved in zircon from a Martian**
2 **meteorite**

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16

17 **Ancient Mars exhibits ample evidence of a surface hydrosphere, but oxygen isotope**
18 **compositions of carbonates in meteorite ALH 84001 and alteration products in nakhlites**
19 **(group of Martian meteorites) suggest this hydrosphere is not in isotopic equilibrium with the**
20 **lithosphere¹⁻⁴. The recent discovery of zircon grains in meteorite NWA 7533⁵ provides an**
21 **opportunity to use their chemical and isotopic characteristics to elucidate Mars' ancient**

22 **hydrosphere. We report the results of an oxygen isotope study of four zircon grains from NWA**
23 **7533 that reveal evidence of regolith assimilation by the Martian melts at ~4.43 Gyr and later**
24 **re-equilibration of metamict zircon domains with water near the Martian surface. One zircon**
25 **studied has the highest $\Delta^{17}\text{O}$ (+2‰) of any Martian sample yet analysed. Like previously**
26 **reported oxygen isotope compositions of Martian carbonates and sulphates, our observed**
27 **variation of $\Delta^{17}\text{O}$ in zircon demonstrates extensive and prolonged interaction between**
28 **Martian regolith and atmosphere.**

29 NWA 7533 is a siderophile element-rich, brecciated Martian meteorite, compositionally
30 representative of Martian highlands rocks⁶. It contains zircon associated with monzonitic clasts and
31 as crystal clasts⁵. U-Pb analyses of this zircon define a discordia line on the Concordia plot⁵ with
32 intercepts at 4428 ± 25 and 1712 ± 85 million years. The upper intercept dates zircon crystallization
33 while the lower intercept records a major heating event. The latter is slightly older than ages of
34 1441 ± 85 Myr (zircon) and 1345 ± 47 Myr (apatite) from closely related meteorite NWA 7034⁷,
35 suggesting the possibility of a complex and prolonged compaction history of these breccias.

36 A total of 42 oxygen isotope analyses were performed on four NWA 7533 zircon grains for which
37 U-Pb ages have been reported⁵. Analyses that intersected zircon boundaries, inclusions, or fractures,
38 have been excluded from further discussion (see supplementary materials). The remaining 29
39 analyses (Table S1) lie on a trend that deviates from the mass dependent Martian fractionation line
40 (Fig. 1a), roughly coinciding with the mixing line defined by plagioclase and pyroxene bulk mineral
41 separates in NWA 7034⁸. This mixing line was interpreted to result from addition of oxygen from an
42 isotopically distinct Martian reservoir, probably the hydrosphere, during near-surface, low-
43 temperature fluid alteration of the regolith. However, examination of multiple analyses obtained
44 from individual zircon grains suggests that internally they exhibit mass dependent fractionation, but
45 there is a difference in $\Delta^{17}\text{O}$ between grains (Fig. 1b). This apparent decoupling of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in
46 the zircon grains cannot be explained by simple two-component mixing of a lithospheric component

47 (e.g. shergottites) and a hydrosphere with $\Delta^{17}\text{O}$ of 0.8‰ (e.g. ALH 84001 carbonates²) or 1.45 ‰
48 (e.g. iddingsite from Lafayette¹¹) and most likely results from early regolith assimilation by the
49 parental melt during zircon crystallisation followed by later fluid alteration. Operation of a ~4.43
50 Gyr assimilation-fractional-crystallisation (AFC) process is consistent with elevated siderophile
51 element concentrations (Ni, Ir) in the monzonitic clasts, which indicates their formation by impact
52 melting of regolith. Later near-surface alteration was governed by the accumulation of radiation
53 damage in zircon. It is well-known from terrestrial zircon¹² that metamict zircon can exchange
54 oxygen isotopes with fluid, even at low temperature, and for the NWA 7533 zircon, this likely
55 occurred at 1.7-1.4 Gyr, by which time parts of the zircon would have been metamict and hence
56 susceptible to fluid penetration.

57 The relative contribution of AFC and surface alteration processes to the zircon oxygen isotope
58 systematics can be evaluated by detailed analysis of the relationship between oxygen isotope
59 composition and U-Pb discordance. Although this is unavoidably hindered by the oxygen and U-Pb
60 analyses representing slightly different volumes within the zircon (see Methods summary for
61 details). The problem can be significantly reduced using ion imaging of U, Th, Y and Pb isotopes
62 following the oxygen isotope analyses (Fig.2 and S1-4, Table S2). These ion images allow
63 determination of $^{207}\text{Pb}/^{206}\text{Pb}$ (a discordance proxy) and the average count rate (a concentration
64 proxy) of investigated elements to be determined at or near the spots where oxygen was analysed.

65 All but two U-Pb analyses of grains Z14 and Z1 are concordant at the upper age intercept⁵. Oxygen
66 isotope compositions from these two zircons exhibit a similar $\delta^{18}\text{O}$ range of 3‰ (from 3.2 to
67 6.5‰), with Z14 having a $\Delta^{17}\text{O}$ ($+0.46\pm0.19$) identical within error to the Martian meteorite
68 fractionation line ($\Delta^{17}\text{O}=+0.3$), while the average $\Delta^{17}\text{O}$ of Z1 ($+0.92\pm0.19$) is similar to $\Delta^{17}\text{O}$ from
69 ALH 84001 carbonates², and higher than bulk NWA 7034^{6,8}. All U-Pb analyses of zircon grain Z2
70 are discordant and it has a larger range (4.0–9.8‰) in $\delta^{18}\text{O}$, with four analyses overlapping the
71 range observed in Z1 and Z14, while one analysis has $\delta^{18}\text{O} > +9\%$. The $\Delta^{17}\text{O}$ for Z2 ($+0.59\pm0.27$)

72 is similar to the bulk NWA 7034 value. Zircon Z19, also discordant⁵, exhibits the highest $\Delta^{17}\text{O}$
 73 ($+2.16 \pm 0.56$) yet reported from any Martian sample, with $\delta^{18}\text{O}$ of $+7\text{--}9\text{‰}$. Concordant zircon grains
 74 thus exhibit a large range of $\Delta^{17}\text{O}$ and variation of $\delta^{18}\text{O}$ in excess of that expected to form during
 75 fractional crystallisation from a magma¹². Metamict (discordant) zircon significantly extends the
 76 observed range of both $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ as also shown by a plot of $\delta^{18}\text{O}$ against $^{207}\text{Pb}/^{206}\text{Pb}$ ages
 77 obtained by ion imaging (Fig.2b). The negative correlation indicates that, to a first order, $\delta^{18}\text{O}$
 78 variability relates to the degree of accumulated radiation damage, although the data also indicate
 79 that concordant zircon has a scatter in $\delta^{18}\text{O}$ of about 3‰, which exceeds analytical errors (Fig.2b).

80 There are two possible models for the observed variation in oxygen isotope compositions of NWA
 81 7533 zircon. In the first model, an early (~ 4.43 Gyr) AFC process generated the range of $\Delta^{17}\text{O}$
 82 between the individual grains, followed by much later (~ 1.7 Gyr) exchange of oxygen in the
 83 metamict parts of the zircon grains with a low-temperature fluid producing the intra-grain range of
 84 $\delta^{18}\text{O}$ (Fig.3a). This model is supported by the significant variability of $\Delta^{17}\text{O}$ in crystalline grains,
 85 increasing variability of $\delta^{18}\text{O}$ and its general correlation with the extent of metamictization. The
 86 fluids that exchanged oxygen with the metamict zircon domains were possibly close in composition
 87 to that inferred for the water from NWA 7034⁶ (grouped with NWA 7533) while the $\sim 3\text{‰}$ scatter of
 88 $\delta^{18}\text{O}$ in the crystalline grains can result from difficulties relating analytical volumes used to obtain
 89 $\delta^{18}\text{O}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ as well as potential sub-micrometre scale variability of both. The second
 90 model attributes the $\sim 3\text{‰}$ scatter of $\delta^{18}\text{O}$ to the early AFC process, where the melt assimilated
 91 regolith enriched in ^{17}O and ^{18}O . The more extreme $\delta^{18}\text{O}$ values ($>+6\text{‰}$) and variability of $\Delta^{17}\text{O}$
 92 were introduced to metamict zircon domains during the later interaction with low-temperature fluids
 93 in the regolith (Fig.3b). The observed variability of oxygen compositions formed by this late
 94 process would then require a localised (perhaps of the order of the regolith grain size) isotopic
 95 inhomogeneity of the fluid exchanging oxygen with the individual zircon grains. Importantly, the
 96 AFC trend (Fig.3b), calculated on the basis of eight analyses corresponding to concordant U-Pb

97 ($^{207}\text{Pb}/^{206}\text{Pb}$) ages, coincides with that of oxygen isotopes in plagioclase and pyroxene fractions
 98 from NWA 7034⁸, which indicate mixing of melt with $\Delta^{17}\text{O} \sim +0.3$ (mantle composition) and
 99 regolith enriched in ^{17}O relative to this mantle composition. Therefore, regardless of the specific
 100 interpretation of oxygen isotope compositions observed in the studied zircon grains, these data
 101 indicate an early developed (≥ 4.43 Gyr) excess of ^{17}O in the Martian regolith.

102 Strong mass independent oxygen isotope fractionation between the Martian lithosphere and its
 103 volatiles is attributed either to photochemical processes taking place in the atmosphere¹³ or to
 104 accretion of volatiles from comets or asteroids¹⁴. Compared to Earth, the absence of plate tectonics
 105 on Mars prevents isotopic homogenization of hydrosphere and lithosphere³. Therefore, anomalous
 106 oxygen compositions in Martian samples are likely to reflect exchange of surface materials (soils,
 107 regolith) and atmosphere or hydrosphere during surface alteration. Once fixed in the regolith, $\Delta^{17}\text{O}$ -
 108 enriched materials can then be mixed into the upper crust for example by intense reworking of the
 109 crust by impacts.

110 The variability of $\Delta^{17}\text{O}$ in the investigated zircon is similar to, or higher than, that reported for
 111 Martian water from Nakhla ($\Delta^{17}\text{O} = +0.9\text{‰}$ ³) or carbonates ($\Delta^{17}\text{O} = +1.0\text{‰}$ ¹) and sulphates ($\Delta^{17}\text{O} =$
 112 $+1.3\text{‰}$ ²) from ALH84001, Nakhla and Lafayette^{4,2} as well as iddingsite ($\Delta^{17}\text{O} = +1.45\text{‰}$) from
 113 Lafayette¹¹. In particular, $\Delta^{17}\text{O}$ in Z19 at $+2.2\text{‰}$ is higher than any $\Delta^{17}\text{O}$ reported for a mineral
 114 phase from a Martian sample. This has important consequences for the production of heavy $\Delta^{17}\text{O}$ on
 115 Mars. Importantly, the age of ALH84001 carbonates has been estimated as 3.9 Gyr¹⁵, while
 116 carbonates and secondary minerals in Nakhla and Lafayette must postdate their ~ 1.3 Gyr
 117 crystallisation ages¹⁶⁻¹⁹. Since the $\Delta^{17}\text{O}$ variations observed in zircon grains from NWA 7533 had to
 118 be formed before zircon crystallisation at about 4.43 Gyr, these data indicate that the conditions
 119 responsible for the formation of mass independent oxygen isotope trends in the Martian atmosphere
 120 and interaction of atmosphere with the surface had already been established by ~ 4.43 Gyr, placing
 121 significant constraints on the evolution and history of the Martian atmosphere. This conclusion is

122 similar to that drawn from the study of isotope compositions of H, C and O in Martian atmosphere
123 made by the Curiosity rover²⁰.

124 Significant depletion in light isotopes of noble gases in the Martian atmosphere²¹ and substantial
125 enrichment of Martian water in D relative to H²²⁻²³ have been interpreted to reflect profound loss of
126 the Martian atmosphere. While several processes such as impact erosion, atmospheric escape and
127 precipitation of secondary minerals can influence this loss at different times throughout Martian
128 history²⁴, precise modelling of their contribution to the overall loss is not yet possible. Nevertheless,
129 there is a general agreement that the early, primary atmosphere on Mars acquired during its
130 accretion was probably lost as a result of extreme ultraviolet (EUV) radiation flux from the young
131 Sun combined with relatively low gravity and early disappearance of a magnetic field²⁴. This early
132 atmosphere was probably replaced by a CO₂+H₂O-rich atmosphere formed by magma outgassing,
133 resulting in a relatively warm and wet early Martian climate^{24, 25}. Prior to this work, the timing of
134 the loss of the primary atmosphere was constrained from parameterisations of EUV radiation
135 indicating that EUV flux is saturated at about 100 times that of the present Sun for the first 100 Myr
136 of existence of the Solar System²⁶⁻²⁸ and after that decays as a power function of time²⁷. These
137 estimated EUV flux levels are high enough to effectively remove an atmosphere from Mars during
138 the first 100-150 Myr of the planet's history and perhaps contribute significantly to atmosphere loss
139 over a longer (few hundred Myr) period. Considering that the $\Delta^{17}\text{O}$ values recorded by zircon grains
140 in NWA 7533 imply continuous interaction between the Martian surface (regolith) and
141 hydrosphere/atmosphere since 4.43 Gyr it is highly likely that the primary atmosphere was lost
142 prior to 4.43 Gyr, i.e. within the first 120 Myr after planetary accretion.

143 The new oxygen isotope data also place some limits on how the secondary atmosphere might have
144 formed on Mars. It has been suggested that a magma ocean formed early in the history of the planet
145 should result in a massive outgassing of the Martian mantle²⁹, in turn producing a new atmosphere.
146 However, the presence of 4.43 Gyr zircon in NWA 7533 suggests that the crust was already formed

147 on Mars at this time and, therefore, any possible magma ocean had fully solidified. Consequently,
148 an atmosphere formed by the massive outgassing of this putative magma ocean would have been
149 subjected to the same high EUV flux responsible for annihilation of the primary atmosphere and
150 most likely lost, substantially depleting the overall inventory of gaseous species on the planet. If
151 that was the case, substantial amounts of volatiles would need to have been acquired during later
152 comet and meteorite flux, otherwise Mars would never have had enough volatiles to form the
153 relatively thick atmosphere predicted by observations of extensive fluvial activity, including the
154 presence of phyllosilicates that require a hydrous weathering regime in the early history of Mars³⁰.
155 Alternatively, if a magma ocean never existed on Mars, outgassing of the Martian mantle forming a
156 secondary atmosphere could have been more gradual and associated with extensive Noachian
157 volcanism and impact cratering that formed the Martian highlands⁵.

158

159 **Methods summary**

160 Oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) and ion images of Pb isotopes, Y, U and Th were
161 obtained using a Cameca IMS1280 ion microprobe at the Swedish Museum of Natural History
162 (Nordsims facility). A ca. 1 nA Cs^+ primary beam with impact energy of 20 kV was used in
163 critically focused (Gaussian) mode to sputter secondary oxygen ions from selected regions of
164 interest. The sample stage z-(height) focus was utilized in order to minimize centring both between
165 sample and standard mounts and within the sample section. Following a pre-sputter to remove the
166 gold coating, the secondary ion beam was centred in a 2000 μm field aperture (field of view $\approx 22 \times$
167 $22 \mu\text{m}$.). Data were acquired over 160 seconds (40 cycles) using static multi-collection in two
168 Faraday cups ($^{16}\text{O}^-$ and $^{18}\text{O}^-$) operating at low mass resolution ($M/\Delta M = 2460$) and the axial ion
169 counting electron multiplier ($^{17}\text{O}^-$) operating at a mass resolution sufficient to resolve $^{17}\text{O}^-$ from
170 $^{16}\text{O}^1\text{H}^-$ ($M/\Delta M = 7500$).

171 Scanning ion images of zircon were acquired using a 2 μm diameter, ca. 100 pA O_2^- primary beam
172 with 23 kV impact energy rastered over a 70 x 70 μm area, the resulting secondary ion beam being
173 steered back onto the ion optical axis using a synchronised raster. The secondary ion species
174 $^{92}\text{Zr}_2^{16}\text{O}^+$ (matrix), $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$ and $^{208}\text{Pb}^+$ were measured simultaneously (12
175 seconds/cycle) at a mass resolution of 4860 in five ion-counting electron multipliers, with peak
176 hopping to measure the species $^{89}\text{Y}_2^{16}\text{O}_2^+$ (1 second), $^{232}\text{Th}^{16}\text{O}^+$ (2 seconds) and $^{238}\text{U}^{16}\text{O}^+$ (2
177 seconds), each analysis comprising 240 cycles. The CAMECA Winimage software was used to
178 generate images and isotope ratios from selected areas corresponding to the location of the oxygen
179 isotope analyses. Pb-isotope ratios were corrected for detector gains by analysis of the BCR-2G
180 basaltic glass.

181 An important issue inherited in the ion probe analytical procedure and relevant to the comparison of
182 U-Pb and oxygen isotope data discussed is the lack of ability to analyse different isotope systems in
183 the same volume of zircon. Even though the ion probe is rightly considered a microanalytical
184 technique, each analysis commonly uses a volume of material determined by the spot size (~5 to 20
185 micrometer diameter) and the depth of a few micrometers. Consequently a follow up analysis of the
186 same area on the exposed zircon surface has to use a different volume of material. In addition, when
187 oxygen analyses follow a U-Pb study it is customary to re-polish the surface to remove the U-Pb
188 spots, preventing O implantation from the oxygen primary beam affecting the oxygen isotope
189 analysis. Post-oxygen isotope analysis imaging is therefore the preferred method for the comparison
190 of the variation of oxygen isotope compositions with the degree of U-Pb discordance in the
191 investigated zircons, even though precise aligning of optical images used to identify oxygen spots
192 and ion probe images is complicated by the absence of sharp boundaries in the latter. In addition,
193 oxygen isotope analyses of Martian zircons was done during two sessions with the sample re-
194 polished between these sessions to avoid overlapping of analytical spots, which can be detrimental
195 to the quality of oxygen isotope analysis. Consequently, an error of ~2 micrometers is anticipated in
196 the alignment, which could generate an excess scatter when investigating the correlation between

197 oxygen isotope compositions and the degree of U-Pb discordance. As a result two possible
198 explanations of oxygen isotope variations observed in Martian zircons presented above are difficult
199 to distinguish.

200

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272 **Author contributions**

273 AN, MH, and MJW conceived the manuscript, directed the research and wrote the manuscript; RH,

274 JPL, MG and AK contributed to the interpretation of data and the revision of the manuscript; MJW

275 and AN performed oxygen isotope and U-Pb image analyses; BZ and CF prepared polished samples

276 for this study; RH and BZ performed petrological studies; SP, DD, JPL and BZ located and imaged

277 zircon by SEM

278

279 **Figure captions**

280 **Figure 1: Oxygen isotope compositions of Martian zircons.** (a) $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ diagram showing
281 results obtained for zircon grains from NWA 7533. Also shown are the terrestrial fractionation line
282 (TFL), the Martian fractionation line (MFL), the mixing line constrained from the analyses of rock
283 forming minerals from NWA 7034⁸, paired with the NWA 7533 (black circles)⁶ and whole rock
284 samples of SNC meteorites (blue circles)^{1,9,10}; (b) Variation and estimated average values of $\Delta^{17}\text{O}$ in
285 four zircon grains analysed for O isotopes, compared with $\Delta^{17}\text{O}$ of measured Martian sources

286 including the MFL^{2,9}, average NWA 7034⁶, carbonates from ALH 84001¹, and iddingsite from
287 Lafayette¹¹.

288 **Figure 2: Relationships between oxygen isotope compositions and $^{207}\text{Pb}/^{206}\text{Pb}$.** (a) $^{207}\text{Pb}/^{206}\text{Pb}$
289 maps of four analysed grains, showing location of oxygen spots (white circles). These circles were
290 drawn using optical images of spots (alignment of optical images of the oxygen analytical pits with
291 the ion images has a margin of error of a few microns; numbers correspond to those in Table S1;
292 $^{207}\text{Pb}/^{206}\text{Pb}$ ages calculated for the enclosed areas are shown in Table S2); (b) Relationship between
293 $\delta^{18}\text{O}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages; a scatter of about 3‰ superimposed on the correlation between $\delta^{18}\text{O}$ and
294 the degree of U-Pb discordance is evident.

295 **Figure 3: Schematic models of evolution of oxygen isotope compositions in Martian zircon.** (a)
296 Black ellipse - zircon that would crystallise from the melt unaffected by assimilation and/or
297 alteration; Blue arrows - $\Delta^{17}\text{O}$ formed as a result of mixing of this melt with the surface materials
298 enriched in ^{17}O (schematic, no specific end-member composition implied); Black arrows- $\delta^{18}\text{O}$
299 correlated with the degree of radiation damage in different sub-domains of the grains formed as a
300 result of exchange with the low-temperature hydrous fluids (converging to a single point where
301 zircon would be completely equilibrated with the water); (b) Thick error bars - the least radiation
302 damaged zircon (grey dashed line calculated using eight concordant analyses); Black arrows -
303 extreme $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ resulting from late equilibration of zircon sub-domains with a high degree
304 of radiation damage and the low-temperature solutions.

305

306

Supplementary information

Analytical sequence

All analytical spots are shown in [figures S1, S3, S5 and S7](#). Initial U-Pb analyses were presented by Humayun and co-authors². All analytical spots have been removed prior to oxygen analysis at the Swedish Museum of Natural History in Stockholm to avoid possible implantation of oxygen during previous analytical work. Oxygen analyses have been done in two sessions. The initial gentle polishing to the depth of previous analytical pits made prior to the first session did not change the outline of the grains at the surface of the sample. Second deeper polishing of the sample was done prior to the second oxygen session changing the outline of the grains.

Oxygen isotope analyses

Oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) were determined in situ using a Cameca IMS1280 ion microprobe at the Swedish Museum of Natural History (Nordsims facility) with an analytical protocol modified from that presented by Nemchin and co-authors³¹. A ca. 1 nA Cs^+ primary beam with impact energy of 20 kV was used in critically focused (Gaussian) mode to sputter secondary oxygen ions from selected regions of interest. The 30 nm gold coating was first removed using a 15 μm raster for 50 seconds, with the analytical beam reduced to a 5 μm raster in order to homogenise the beam density and limit within-run drift. A normal incidence low energy electron gun was used to minimize sample charging during analysis. Following the pre-sputter, the secondary ion beam was centred in a 2000 μm field aperture (field of view $\approx 22 \times 22 \mu\text{m}$ using transfer magnification of 90x) by scanning the transfer deflectors; the sample stage z-(height) focus was utilized in order to minimize centring both between sample and standard mounts and within the sample section (cf. 32). Data were acquired over 160 seconds (40 cycles) using static multi-collection in two Faraday cups ($^{16}\text{O}^-$ and $^{18}\text{O}^-$) operating at low mass resolution ($M/\Delta M = 2460$) and the axial ion counting electron multiplier ($^{17}\text{O}^-$) operating at a mass resolution sufficient to resolve $^{17}\text{O}^-$ from $^{16}\text{O}^{1}\text{H}^-$ ($M/\Delta M = 7500$). The magnetic field was locked for each analytical session using an NMR field sensor in regulation mode, obviating the need for mass scanning for each analysis. Drift of the electron multiplier was monitored and corrected using the within-run

EM-drift adjustment routine in the Cameca CIPS software. Correction for instrumental mass bias and differences in detector efficiency was made using repeat analyses of the Geostandards 91500 reference zircon, which has a measured $\delta^{18}\text{O}$ value of +9.86 ‰³³ and an assumed $\delta^{17}\text{O}$ value of +5.20 ‰, both relative to Vienna SMOW. Since the sample of NWA7355 occupied almost the entire accessible sample mount area, measurements of the 91500 zircon were performed on a separate mount before and after a block (typically 5 to 8 analyses) of unknown analyses. The four analytical sessions used to generate data yielded reproducibility (1 standard deviation) on the 91500 reference zircon of between 0.17 ‰ and 0.25 ‰ for $\delta^{18}\text{O}$ and between 0.12 ‰ and 0.24 ‰ for $\delta^{17}\text{O}$. This reproducibility was propagated together with the within run repeatability (1 standard error of the mean of 40 cycles) to yield the overall uncertainty on each measurement reported in [Table S1](#). Detailed post-analytical imaging of the target zircons was used to identify analyses where cracks and/or inclusions might have perturbed the isotope ratios and in such cases, the data were discarded. Two analyses made in zircon Z14 ([Table S1](#)) show negative $\Delta^{17}\text{O}$ even though nothing out of ordinary has been found to explain this behaviour. There are no visible surface imperfections (like fractures) near the analytical spots and there are no unusual fluctuations in any analytical parameters associated with these two data points. However, these two analyses are sequential, which makes them a suspect. Additional spot analysis was done between these two spots in the following session, but did not confirm the previously observed low $\Delta^{17}\text{O}$ in this part of the grain. Taking into account that the negative $\Delta^{17}\text{O}$ values did not reproduce and can result from some residual O-implantation along fractures or crystal imperfections as a consequence of previous U-Pb, Ti and REE analyses, these two analyses have been excluded from further discussion. Although, including them with the rest of the analyses obtained for Z14, will not change average $\Delta^{17}\text{O}$ value for this grain. Finally, analyses where ^{16}O count rates were significantly lower than those in the standard ([Table S1](#)), were also excluded from further consideration.

Ion imaging

Scanning ion images (SII) of zircon were acquired using the same CAMECA IMS1280 ion microprobe following a method modified from³⁴. Selected grain areas were analysed using a 2 µm diameter (aperture illuminated), ca. 100 pA O_2^- primary beam with 23 kV impact energy rastered over a 70 x 70 µm area, the resulting secondary ion beam being steered back onto the ion optical

axis using the synchronised raster of the CAMECA Dynamic Transfer Optical System (DTOS). The DTOS system retains the high mass resolution capability of the instrument despite ions being emitted from a large sample area. The secondary ion species $^{92}\text{Zr}_2^{16}\text{O}^+$ (matrix), $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$ and $^{208}\text{Pb}^+$ were measured simultaneously (12 seconds/cycle) at a mass resolution ($M/\Delta M$) of 4860 in five ion-counting electron multipliers, with peak hopping to measure the species $^{89}\text{Y}_2^{16}\text{O}_2^+$ (1 second), $^{232}\text{Th}^{16}\text{O}^+$ (2 seconds) and $^{238}\text{U}^{16}\text{O}^+$ (2 seconds); each analysis comprised 240 cycles. Oxygen flooding was employed in the sample chamber (pressure ca. 2×10^5 mbar) in order to enhance the yield of secondary Pb ions from the analysed zircon. Following data acquisition, the CAMECA Winimage software was used to generate images accumulated over the entire SII analysis, together with isotope ratios from selected areas corresponding to the location of the oxygen isotope analyses. Pb-isotope ratios were corrected for detector gains by analysis of the BCR-2G basaltic glass³⁵.

Table S1: Oxygen isotope compositions of analysed zircon grains

Sample	^{16}O cps ($\times 10^9$)	$^{16}\text{O}_{\text{samp}}$ av.std	$^{18}\text{O}/^{16}\text{O}$ drift corrected	$^{17}\text{O}/^{16}\text{O}$ drift corrected	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	Field aperture x y	
z1_1	0.87	1.03	0.0020041 $\pm$ 5	0.00038761 $\pm$ 6	5.20 $\pm$ 0.35	3.29 $\pm$ 0.22	0.54 $\pm$ 0.29	-19	-14
z1_2	0.89	1.05	0.0020006 $\pm$ 4	0.00038746 $\pm$ 5	3.48 $\pm$ 0.29	2.90 $\pm$ 0.21	1.06 $\pm$ 0.26	-20	-14
z1_3	0.86	1.02	0.0020012 $\pm$ 6	0.00038744 $\pm$ 6	3.78 $\pm$ 0.36	2.84 $\pm$ 0.21	0.84 $\pm$ 0.29	-20	-14
z1_9	0.74	1.00	0.0020023 $\pm$ 4	0.00038893 $\pm$ 6	4.42 $\pm$ 0.31	3.50 $\pm$ 0.20	1.16 $\pm$ 0.26	-33	-1
z1_10	0.69	0.93	0.0020047 $\pm$ 7	0.00038904 $\pm$ 8	5.65 $\pm$ 0.41	3.78 $\pm$ 0.24	0.79 $\pm$ 0.32	-37	0
z1_11	0.76	1.02	0.0020000 $\pm$ 6	0.00038835 $\pm$ 9	3.27 $\pm$ 0.39	1.99 $\pm$ 0.26	0.26 $\pm$ 0.33	-31	1
z1_12	0.67	1.10	0.0020035 $\pm$ 5	0.00038895 $\pm$ 6	5.41 $\pm$ 0.36	3.98 $\pm$ 0.28	1.12 $\pm$ 0.34	12	52
z1_13	0.66	1.07	0.0020009 $\pm$ 7	0.00038859 $\pm$ 7	4.13 $\pm$ 0.42	3.03 $\pm$ 0.29	0.85 $\pm$ 0.37	10	51
z1_14	0.60	0.98	0.0020026 $\pm$ 6	0.00038888 $\pm$ 7	4.96 $\pm$ 0.37	3.79 $\pm$ 0.30	1.17 $\pm$ 0.36	10	50
z1_15	0.65	1.06	0.0020055 $\pm$ 5	0.00038924 $\pm$ 6	6.44 $\pm$ 0.33	4.73 $\pm$ 0.29	1.33 $\pm$ 0.34	8	49
z2_1	0.87	1.03	0.0020133 $\pm$ 6	0.00038852 $\pm$ 6	9.83 $\pm$ 0.36	5.64 $\pm$ 0.22	0.46 $\pm$ 0.29	-8	132
z2_2	0.89	1.06	0.0020027 $\pm$ 5	0.00038757 $\pm$ 6	4.53 $\pm$ 0.32	3.18 $\pm$ 0.21	0.79 $\pm$ 0.27	-12	132
z2_3	0.90	1.07	0.0020074 $\pm$ 5	0.00038785 $\pm$ 5	6.85 $\pm$ 0.34	3.92 $\pm$ 0.21	0.30 $\pm$ 0.27	-10	132
z2_14	0.60	0.98	0.0020035 $\pm$ 5	0.00038883 $\pm$ 8	5.43 $\pm$ 0.35	3.65 $\pm$ 0.31	0.79 $\pm$ 0.36	5	-15
z2_15	0.57	0.93	0.0020008 $\pm$ 8	0.00038852 $\pm$ 7	4.04 $\pm$ 0.47	2.87 $\pm$ 0.29	0.73 $\pm$ 0.38	2	-16
z14_1	0.78	0.92	0.0020004 $\pm$ 4	0.00038718 $\pm$ 6	3.35 $\pm$ 0.30	2.18 $\pm$ 0.22	0.41 $\pm$ 0.27	14	-13
z14_2	0.78	0.92	0.0020007 $\pm$ 3	0.00038724 $\pm$ 6	3.51 $\pm$ 0.27	2.33 $\pm$ 0.21	0.48 $\pm$ 0.26	14	-12
z14_3	0.78	0.92	0.0020011 $\pm$ 3	0.00038723 $\pm$ 6	3.74 $\pm$ 0.26	2.32 $\pm$ 0.21	0.34 $\pm$ 0.25	13	-13
z14_8	0.74	1.00	0.0020005 $\pm$ 4	0.00038804 $\pm$ 6	3.55 $\pm$ 0.33	1.19 $\pm$ 0.19	-0.68 $\pm$ 0.26	10	-30
z14_9	0.72	0.97	0.0020015 $\pm$ 6	0.00038819 $\pm$ 7	4.05 $\pm$ 0.37	1.58 $\pm$ 0.21	-0.56 $\pm$ 0.29	11	-30
z14_10	0.73	0.98	0.0020039 $\pm$ 5	0.00038867 $\pm$ 6	5.26 $\pm$ 0.35	2.84 $\pm$ 0.19	0.06 $\pm$ 0.27	-8	-33
z14_11	0.72	0.97	0.0020034 $\pm$ 5	0.00038875 $\pm$ 6	4.99 $\pm$ 0.34	3.04 $\pm$ 0.19	0.40 $\pm$ 0.26	-7	-32
z14_12	0.71	0.97	0.0020035 $\pm$ 4	0.00038878 $\pm$ 7	5.02 $\pm$ 0.32	3.10 $\pm$ 0.22	0.45 $\pm$ 0.27	-4	-33
z14_13	0.71	0.96	0.0020042 $\pm$ 5	0.00038877 $\pm$ 6	5.37 $\pm$ 0.35	3.10 $\pm$ 0.19	0.26 $\pm$ 0.27	-8	-33
z14_14	0.61	1.00	0.0020057 $\pm$ 5	0.00038891 $\pm$ 7	6.52 $\pm$ 0.33	3.88 $\pm$ 0.29	0.44 $\pm$ 0.34	36	-24
z14_15	0.61	1.00	0.0020037 $\pm$ 5	0.00038885 $\pm$ 7	5.51 $\pm$ 0.35	3.72 $\pm$ 0.30	0.81 $\pm$ 0.35	35	-25
z14_16	0.59	0.97	0.0020021 $\pm$ 5	0.00038873 $\pm$ 6	4.71 $\pm$ 0.36	3.41 $\pm$ 0.29	0.93 $\pm$ 0.35	34	-26
z19_1	0.63	1.03	0.0020088 $\pm$ 8	0.00038989 $\pm$ 11	8.06 $\pm$ 0.46	6.40 $\pm$ 0.37	2.15 $\pm$ 0.45	-17	-48
z19_2	0.65	1.05	0.0020071 $\pm$ 6	0.00038973 $\pm$ 7	7.21 $\pm$ 0.39	5.98 $\pm$ 0.30	2.17 $\pm$ 0.37	-17	-46

Sample	^{16}O cps (x 10^9)	$^{16}\text{O}_{\text{samp}}$ av.std	$^{18}\text{O}/^{16}\text{O}$ drift corrected	$^{17}\text{O}/^{16}\text{O}$ drift corrected	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	Field apperture x y	
analyses where spot has a partial overlap with the grain margin or inclusion									
z1_8	0.52	0.70	0.0020265±6	0.00039078±7	16.57±0.38	8.28±0.22	-0.45±0.29	-19	-5
z2_4	0.85	1.01	0.0020078±4	0.00038785±5	7.05±0.29	3.91±0.21	0.18±0.26	-7	133
z2_5	0.63	0.83	0.0020126±6	0.00038857±7	9.80±0.33	6.00±0.26	0.83±0.32	-10	42
z2_6	0.59	0.78	0.0020258±5	0.00038978±6	16.42±0.31	9.14±0.25	0.49±0.30	-9	40
z2_9	0.55	0.72	0.0020132±7	0.00038903±7	10.10±0.40	7.21±0.25	1.88±0.33	-8	38
z2_11	0.54	0.89	0.0020018±6	0.00038841±7	4.55±0.37	2.58±0.29	0.18±0.35	5	-15
z2_13	0.54	0.88	0.0020098±4	0.00038929±9	8.57±0.31	4.86±0.33	0.33±0.37	6	-15
z2_16	0.56	0.91	0.0020027±6	0.00038875±7	5.00±0.37	3.46±0.29	0.82±0.35	2	-16
analyses with low $^{16}\text{O}_{\text{samp}}/\text{av.std}$									
z2_7	0.59	0.77	0.0020256±8	0.00039035±14	16.29±0.46	10.62±0.40	2.04±0.47	-10	41
z2_8	0.64	0.83	0.0020155±7	0.00038878±7	11.22±0.37	6.57±0.26	0.64±0.33	-10	41
z2_10	0.68	0.89	0.0020086±8	0.00038808±8	7.75±0.42	4.74±0.28	0.64±0.36	-11	40
z2_12	0.53	0.86	0.0020012±5	0.00038823±7	4.29±0.35	2.12±0.29	-0.14±0.35	4	-15
z3_1	0.60	0.78	0.0020196±6	0.00038929±10	13.27±0.35	7.87±0.32	0.87±0.37	-38	-5

Figure S1: Oxygen analytical spots in the grain Z1. (A) Cathodoluminescence (CL) image of the grain showing concentric zoning pattern compatible with magmatic origin of the grain; (B) Backscattered electron (BSE) image of the grain showing traces of oscillatory zoning in addition to the thicker concentric zones visible in CL; (C-E) Reflected light optical images of the grain, showing sequential analytical spots. Change of the grain outline between C and D is produced by repolishing of the sample between two oxygen sessions

Figure S2: Ion probe images of the grain Z1. In the last four images intensities of isotopes have been normalized to $^{92}\text{Zr}_2^{16}\text{O}$ intensity.

Figure S3: Analytical spots in the grain Z2. (A) Cathodoluminescence (CL) image of the hopper-shaped zircon grain; (B) Backscattered electron (BSE) image of the grain showing traces of oscillatory zoning compatible with magmatic origin of the grain in addition to an irregular combination of bright and dark patches visible in CL; (C-E) Reflected light optical images of the grain, showing sequential analytical spots.

Figure S4: Ion probe images of the grain Z2. In the last four images intensities of isotopes have been normalized to $^{92}\text{Zr}_2 ^{16}\text{O}$ intensity.

Figure S5: Analytical spots in the grain Z14. (A) Cathodoluminescence (CL) image of the grain showing concentric and oscillatory zoning pattern compatible with magmatic origin of the grain; (B) Backscattered electron (BSE) image of the grain showing similar internal features; (C-E) Reflected light optical images of the grain, showing sequential analytical spots. Change of the grain outline between C and D is produced by repolishing of the sample between two oxygen sessions.

Figure S6: Ion probe images of the grain Z14. In the last four images intensities of isotopes have been normalized to $^{92}\text{Zr}_2 ^{16}\text{O}$ intensity.

Figure S7: Analytical spots in the grain Z19. (A) Cathodoluminescence (CL) image of the grain showing concentric zoning pattern compatible with magmatic origin of the grain; (B) Reflected light optical image of the grain, showing oxygen analytical spots.

Figure S8: Ion probe images of the grain Z19. In the last four images intensities of isotopes have been normalized to $^{92}\text{Zr}_2^{16}\text{O}$ intensity.

Table S2: Isotopic ratios determined from areas in the zircon images corresponding to O analytical spots
(errors are 1 sigma per cent)

Spot	$^{204}\text{Pb}/^{206}\text{Pb}$	err %	$^{207}\text{Pb}/^{206}\text{Pb}$	err %	$^{208}\text{Pb}/^{206}\text{Pb}$	err %	$^{230}\text{ThO}/\text{Zr}$	err %	$^{238}\text{UO}/\text{Zr}$	err %	$^{207}\text{Pb}/^{206}\text{Pb}$ Age (Myr) (errors 2 sigma)
Z1											
1	0.0022	41	0.311	4	0.249	4	1.909	4	3.647	3	3439±151
2	0.0034	32	0.486	3	0.334	4	1.528	4	2.417	3	4136±112
3	0.0026	100	0.531	9	0.255	11	0.650	9	1.024	8	4289±280
9	0.0026	29	0.421	3	0.329	3	2.279	3	3.418	3	3923±96
10	0.0037	35	0.256	5	0.271	5	1.481	4	3.332	3	3020±245
11	0.0011	71	0.391	4	0.335	5	3.237	4	3.481	4	3843±146
12	0.0037	50	0.260	7	0.243	7	1.892	5	4.460	4	3048±337
13	0.0022	33	0.244	4	0.404	6	5.395	2	5.366	2	3027±152
14	0.0056	28	0.446	4	0.433	4	2.314	3	2.613	3	3942±155
15	0.0070	32	0.163	7	0.237	6	1.760	3	4.231	2	1516±1127
Z2											
1	0.0086	16	0.162	4	0.546	3	19.612	1	3.928	2	1196±834
2	0.0041	26	0.610	3	0.302	3	49.979	2	1.825	3	4484±89
3	0.0073	21	0.171	5	0.548	3	27.007	1	4.337	2	1683±660
14	0.0041	21	0.364	3	0.352	3	19.169	1	3.731	2	3638±111
15	0.0110	14	0.641	2	0.486	3	27.941	2	1.333	3	4475±100
Z14											
1	0.0040	41	0.617	4	0.179	7	0.350	6	0.781	4	4502±137
2	0.0102	29	0.628	5	0.217	7	0.265	8	0.589	5	4449±195
3	0.0044	50	0.638	5	0.182	8	0.200	9	0.440	6	4550±176
10	0.0090	32	0.588	5	0.169	8	0.223	8	0.559	5	4354±203
11	0.0187	30	0.603	7	0.263	9	0.428	11	0.738	8	4226±438
12	0.0013	100	0.590	6	0.202	9	0.369	12	1.054	8	4468±179
13	0.0279	36	0.638	9	0.219	14	0.220	20	0.642	12	4151±993
14	0.0030	71	0.428	7	0.304	8	1.873	6	2.521	5	3939±253
15	0.0185	45	0.589	10	0.285	13	0.689	13	0.820	12	4178±673
16	0.0038	71	0.590	7	0.207	11	0.419	9	0.848	7	4436±238
Z19											
1	0.0022	9	0.131	1	1.204	1	18.367	1	15.170	1	2682±67
2	0.0031	9	0.210	1	0.816	1	12.271	1	13.809	1	1810±81

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Figure 3

Figure 2

a

b

Figure 1

Error bars are 2σ Error bars are 2σ