

1 *Technical Brief*

2 **A calcite reference material for LA-ICP-MS U-Pb geochronology**

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23
24 **Key Points:**

25 1) We present a calcite reference material (WC-1) for U-Pb LA-ICP-MS
26 geochronology

27 2) We provide Isotope Dilution reference values for WC-1

28 3) WC-1 can be used for normalisation of U-Pb LA-ICP-MS data

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33 **Abstract**

34 U-Pb dating of calcite is an emerging but rapidly growing field of application in
35 geochronology with great potential to inform problems in landscape, basin and
36 mountain belt evolution, through age determination of diagenetic cements, vein
37 mineralisation and geological formations difficult to date otherwise. In this brief, we
38 present isotope dilution U-Pb isotope measurements on a sample of calcite (WC-1)
39 that has and will continue to be used as a reference material for in-situ U-Pb Laser
40 Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) dating, and
41 which is suitable to be distributed to and used by the geochronological community.
42 We present in-situ measurements using LA-ICP-MS to demonstrate the suitability of
43 WC-1 for use as a U-Pb dating reference material, in spite of it not being isotopically
44 homogeneous. The WC-1 calcite sample is 254.4 ± 6.4 Ma old, and comprised of 85
45 to 98% radiogenic lead. It presents a suitable reference material that can facilitate
46 dating of calcite ranging in age from Precambrian to late Neogene age.

47

48 **Introduction**

49 Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has
50 greatly facilitated U-Pb accessory mineral dating because of its high spatial resolution
51 and rapid data acquisition, as compared to Isotope Dilution Isotope Ratio Mass
52 Spectrometry techniques (ID-IRMS; i.e. Thermal Ionisation Mass Spectrometry,
53 TIMS and/or multi-collector ICP-MS). Although LA-ICP-MS has lower measurement
54 precision ($\sim 1\%$ compared to $\sim 0.1\%$ on U-Pb ratio), this suits a wide variety of
55 applications using a very wide range of minerals and materials. The method has also
56 been applied successfully to minerals with lower U (sub-ppm) concentrations than are
57 generally feasible with in-situ SIMS (Secondary Ion Mass Spectrometry) methods ($<$
58 1ppm calcite, Coogan et al. 2016). Calcite and other carbonate materials (aragonite,
59 dolomite) have been dated by U-Pb via ID-IRMS (see Rasbury and Cole, 2009), but
60 so far have largely been focussed on dating speleothems (e.g. Woodhead et al., 2006;
61 2012; Pickering et al., 2010). This is because they generally have higher initial
62 $^{238}\text{U}/^{204}\text{Pb}$ (μ) contents than other sources of carbonate (i.e. hydrothermal or marine),
63 which is a requirement for precise U-Pb dating (Rasbury & Cole, 2009). Dating by

64 LA-ICP-MS will broaden the opportunities for calcite geochronology because it can
65 tackle calcite where high μ regions are found on a sub-mm scale (Coogan et al., 2016;
66 Roberts & Walker, 2016). The LA-ICP-MS method is also useful for materials (such
67 as calcite) which typically require initial evaluation in terms of suitability for dating to
68 find the best material, in order to optimize both the dating and the effort and expense
69 involved. The basic method, like that for zircon and other accessory minerals,
70 involves comparing isotope signal intensities of an unknown with that of a reference
71 material whose $^{206}\text{Pb}/^{238}\text{U}$ ratio is known, to determine the age of the sample material
72 of unknown age, a procedure that has been termed U-Pb ‘normalisation’. It is clear
73 that with either SIMS or LA-ICP-MS methods, the reference material must ideally be
74 of the same mineral (matrix-matched) as that of the unknown to ensure reliability of
75 any date and its precision. However, the lack of carbonate reference materials limits
76 progress in advancing and adoption of the LA-ICP-MS method. One reference
77 material, WC-1, is currently being used by several laboratories. In this communication
78 we present ID-IRMS measurements of WC-1 that underpin its use as a reference
79 material for geochronology, so that upon further distribution and use by additional
80 laboratories worldwide, carbonate dating can expand in its application by research
81 laboratories worldwide.

82 **Sample Context – WC-1**

83 WC-1 is taken from a ~1 kg hand sample of marine calcite cement that filled a fault-
84 related discordant Neptunian dyke (Figure 1A) in the Permian (Capitanian) Reef
85 Complex, exposed in the Guadalupe Mountains on the western side of the Delaware
86 Basin of West Texas. Its locality is at BM3647 (1112m elevation) with coordinates
87 $32^{\circ} 10.62'\text{N}$ and $104^{\circ} 22.90'\text{W}$, about 0.5 km west of Whites City, New Mexico,
88 USA. According to the International Chronostratigraphic Chart of 2015 (Cohen et al.
89 2013, updated), the Capitanian stage ranges from about 265-260 Ma, and therefore,
90 the dyke must be younger than the Capitanian stratigraphy that it ‘intrudes’ which is
91 the Tansil-equivalent reef facies. The Castile Formation overlies the Tansil Fm, and
92 was dated by Becker et al. (2002) at 251.5 ± 2.8 Ma using ID-TIMS U-Pb carbonate
93 geochronology. This age was re-evaluated by Rasbury and Cole (2007) to 257 ± 3
94 Ma, using the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio as a monitor of alteration, and selecting only those
95 aliquots that showed lowest alteration for the isochron age. The Radar Ash underlies

96 the Tansil FM. and is dated at 262.6 ± 0.5 Ma (Nicklen, 2011) by U-Pb zircon
97 geochronology, providing a maximum age constraint for the Neptunian dyke.

98 The marine cements comprising the dyke were aragonite crystals that have been
99 neomorphosed to calcite. In hand specimen, the botryoidal forms and fibres that make
100 up the botryoids are easily visible. In thin section, the blocky calcite engulfs
101 inclusions that show the original fibres that make up the botryoids. A ca. 6 x 3 cm
102 slab of WC-1 material (Figure 1B) has been sub-sampled and characterised for its U-
103 Pb isotopic composition by ID-IRMS and LA-ICP-MS at the NERC Isotope
104 Geosciences Laboratory (NIGL, Nottingham). Additionally, a region of the slab has
105 been analysed for trace element distribution using LA-ICP-MS. Measurement of four
106 samples from the interior of the Neptunian dyke at the WC-1 locality have a mean
107 $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.706895 ± 0.000048 2σ (E.T. Rasbury, unpublished data).

108 **Analytical Methods**

109 *ID-IRMS*

110 The ultrasonically-cleaned sample pieces, weighing 0.005 to 0.010g, were fully
111 dissolved in ultrapure 4 N HNO₃ before being spiked with a mixed ^{205}Pb – ^{233}U – ^{235}U
112 tracer. Following sample-spike equilibration, organic matter in samples was destroyed
113 by addition and evaporation of a mixture of 0.5 ml of concentrated HNO₃ and 0.5 ml
114 H₂O₂. The precipitate was then re-dissolved in 1 ml 1 N HBr for anion exchange
115 chemistry. Eichrom® anion exchange resin (AG 1 - × 8) was used to separate and
116 purify Pb. Uranium was purified using Eichrom **UTEVA resin** in nitric acid. The
117 chemistry blanks were < 10 pg for U and < 20 pg for Pb. The $^{207}\text{Pb}/^{206}\text{Pb}$ composition
118 of the blank is based on repeat measurements and measured at 0.86 ± 0.08 (2σ).

119 The separated Pb fractions were loaded individually, with silica gel and H₃PO₄, onto
120 single outgassed rhenium filaments and analyzed using a Thermo Scientific Triton
121 mass spectrometer fitted with an axial MasCom secondary electron multiplier (SEM)
122 at the NERC Isotope Geosciences Laboratory (NIGL) British Geological Survey,
123 Keyworth, UK. Data were obtained in either dynamic single-collector mode (where
124 the ^{206}Pb signal was <1M cps), or in a multi-static routine where all isotopes except
125 ^{204}Pb were measured on a Faraday detector and the Faraday-SEM yield was
126 determined in real time using ^{205}Pb which was measured on both detectors. The U

127 separates were run in static Faraday mode using the Nu Instruments Nu Plasma multi-
128 collector ICP-MS, also at NIGL. Pb and U reference solutions SRM 981 and
129 REIMEP-18(B), were analysed to monitor mass spectrometer performance, ensuring
130 that the SEM linearity, accuracy and reproducibility were better than $\pm 0.1\%$. Mass
131 bias for Pb analysed by TIMS was corrected using SRM-981 (linear law), and U
132 analysed by MC-ICP-MS was corrected using REIMEP-18(B). Residual mass bias
133 (average 0.02% per amu at U) was corrected using a linear law using the $^{233}\text{U}/^{235}\text{U}$
134 ratio.

135 Data reduction and uncertainty propagation were carried out using customized data
136 reduction spreadsheets following standard parametric statistical methods (Schmitz and
137 Schoene, 2007). The decay constants and U isotope composition used were those
138 proposed by Jaffey et al. (1971) and Hiess et al. (2012), respectively.

139 *LA-ICP-MS U-Pb*

140 U-Pb analyses utilised a Nu Instruments single-collector Attom ICP-MS, coupled to a
141 New Wave Research (ESI) NWR193UC laser ablation system equipped with a TV2
142 ablation cell. The method is adapted from the standard zircon method described
143 previously in Spencer et al. (2014). Laser ablation parameters for carbonates are a 100
144 μm static spot, ablated for 30 s, at 10 Hz, with a fluence of 7-8 J/cm^2 . The depth of
145 the ablation pit using these settings is ca. 45 μm . Normalisation uses a standard-
146 sample bracketing protocol. Firstly, NIST614 is used for correction of Pb-Pb ratios,
147 which on the instrument at NIGL is ca. 0.7 % mass bias for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio.
148 Secondly, the WC-1 calcite is used for correction of U-Pb ratios (as described in Li et
149 al., 2014; Roberts & Walker, 2016; see Appendix). Data are reduced using the Time
150 Resolved Analysis (TRA) functionality in Nu Instruments' Attolab software, with
151 normalisation and uncertainty propagation calculated offline using an in-house excel
152 spreadsheet. Data reduction and propagation of uncertainties follow the
153 recommendations for zircon geochronology outlined in Horstwood et al. (2016).

154 The methodology is feasible with any LA-ICP-MS system (including Q-ICP-MS)
155 using a variety of laser instrumental conditions provided that signal background
156 values and their variation are small and that instrumental sensitivity is sufficiently
157 high (for example, $>20,000$ cps/ppm U). The use of an isotopically homogeneous

158 material such as NIST glass (e.g. NIST 614) in the normalisation routine in
159 conjunction with WC-1 as a reference material is essential, since the Pb isotope
160 composition of the WC-1 calcite is not uniform owing to the somewhat variable
161 admixture of radiogenic Pb (age of 254 Ma) and common Pb.

162 *LA-ICP-MS trace elements*

163 For trace element mapping, the analytical set-up is the same as for U-Pb analyses.
164 Mapping utilises a set of line rasters created with a 100 μm square, translated at 50
165 $\mu\text{m/s}$, and ablated at 10 Hz with a fluence of 7-8 J/cm^2 . Normalisation uses NIST614
166 (Jochum et al., 2011) analysed at the beginning and end of the sample map, using ^{44}Ca
167 as an internal standard. Data are reduced and the maps created using the software
168 Iolite v.2 (Paton et al., 2011). Additionally, a portion of the total mapped region
169 (18000 * 200 μm) was split into 280 x 100 μm pixels, with the concentrations for
170 each pixel being calculated using the standard Trace Element Data Reduction Scheme
171 in Iolite.

172 **Results**

173 *ID-IRMS U-Pb*

174 Ten aliquots of WC-1 were taken for measurement by ID-IRMS. These aliquots were
175 sampled across the visible heterogeneous texture and colour of the slab (see Figure.
176 1B), with the aim that the resulting reference ID-IRMS data will provide a reasonable
177 representation of any heterogeneity that exists in the material. The resulting data
178 produce a regression in Tera-Wasserburg space with a lower intercept age of $253.3 \pm$
179 6.9 Ma (2σ ; MSWD = 1203; not shown). The upper intercept ($^{207}\text{Pb}/^{206}\text{Pb} = 0.77 \pm 0.15$)
180 overlaps with the expected common-lead composition for this age (0.85) based on
181 Stacey & Kramers (1975), but is not well-constrained due to a lack of analyses
182 comprising large amounts of high common lead. Measurements of other hand
183 specimen(s) of this same dyke at Stony Brook University had a larger dispersion in
184 $^{207}\text{Pb}/^{206}\text{Pb}$, with a resultant upper intercept for initial common Pb of 0.85 ± 0.04 . Since
185 this overlaps with the Stacey & Kramers (1975) model common lead intercept, we
186 choose to anchor the WC-1 data to this value. Anchoring the upper intercept of the
187 NIGL data to 0.85 ± 0.04 gives a regression with a lower intercept age of 254.4 ± 6.4

188 Ma (2s, MSWD = 1069, n=10). This lower intercept age is taken as the reference 'age'
189 for WC-1 (Figure 2A; Table 1).

190 The scatter in the WC-1 ID-IRMS data cannot be attributed to the measurements, for
191 example the blank correction, since the $^{207}\text{Pb}/^{206}\text{Pb}$ composition of the blank ($0.86 \pm$
192 0.08) is very similar to the projected common lead composition of the samples, and
193 because the blank correction is no larger than $\sim 5\%$ of the total Pb in the measured
194 aliquots. Therefore, the scatter in the data implies some limited heterogeneity between
195 aliquots for the sample sizes used. This scatter may represent some limited isotopic
196 open-system behaviour within the calcite material of WC-1.

197 *LA-ICP-MS U-Pb*

198 To demonstrate the typical reproducibility of WC-1 using LA-ICP-MS, data from
199 eleven analytical sessions, individually normalised to the expected age of 254.4 Ma,
200 are pooled in Figure 2B and regress to an age and uncertainty of 254.4 ± 1.7 Ma (2σ ,
201 MSWD = 5.6, n = 214). The data are anchored to an upper intercept of 0.85 ± 0.04 .
202 Because these data are self-normalised using the reference age of 254.4 Ma determined
203 by ID-IRMS, the uncertainty of this age is a measure of the dispersion about the linear
204 mixing array between its age and the initial common Pb composition, as well as
205 providing a visual indication of the variability in the mixture of radiogenic to common
206 Pb within the material. The measure of over-dispersion of these data, calculated with
207 the weighted mean function in Isoplot (Ludwig, 2003), is 2.7% (2σ). This over-
208 dispersion is only slightly larger than the level of uncertainty in the ID-IRMS data
209 (2.5%), indicating that both datasets are probably a fair representation of the natural
210 heterogeneity of the material with respect to U-Pb. Figure 2, however, indicates that the
211 spatial resolution of the laser analyses have highlighted greater variation in the
212 proportion of radiogenic Pb in the material than the ID-IRMS sampling, which involves
213 the averaging of much larger volumes of material.

214 A set of LA-ICP-MS spot analyses measured from a traverse across the WC-1 slab are
215 shown in Figure 2C. The plots shows that the variability in the proportion of common
216 to radiogenic lead has some correlation with elemental zonation, for example the Th-
217 rich zone is high in common lead. However, the plots also show that the scatter about

218 the regression, i.e. scatter in U-Pb lower intercept ages, is not correlated with Pb, Th or
219 U zonation.

220 *Trace elements*

221 A region of the slab analysed for U-Pb was mapped for several trace elements (Fig. 1B,
222 3). In general, it is low-Mg calcite with a mean Mg concentration of ~700 ppm though
223 some fractures contain up to 1.47% by weight Mg. Even so, all regions analysed from
224 the slab have <4 mole% MgCO₃ and as such are characteristically low-Mg calcite. The
225 region (18 x 5 mm) was chosen as it has visible changes in texture and appearance. The
226 map shows that several trace elements show distinct variability, with darker areas of
227 calcite in hand specimen being higher in Mg and Mn, and paler areas lower in Sr. A
228 rare earth element (Tm) and the transition metals (V, Fe, Cu, Zn) are more uniform
229 across the material. A white alteration vein cross-cutting the mapped region is high in
230 both Th and the transition metals. Importantly for U-Pb geochronology, the U content
231 is fairly homogeneous across the mapped region, which is consistent with our
232 experience of measuring spot analyses from this material. The concentration data from
233 this mapped region are shown in Table 2. The average Pb, Th and U concentrations are
234 0.18, 0.014 and 3.7 ppm respectively.

235 **Discussion**

236 *Reference material requirements and usage*

237 For normalisation of LA-ICP-MS data, it is highly desirable to have an isotopically
238 homogeneous reference material. This allows for fewer analyses per session of the
239 reference material than the case of a reference material with isotopic heterogeneity, as
240 the latter will require more data to establish its intercept age with acceptable precision.
241 However, as described by Chew et al. (2014), normalisation can be achieved with a
242 material that is isotopically heterogeneous, as long as its composition falls along a
243 mixing line between initial common Pb and radiogenic components. The reason for the
244 preference of isotopic homogeneity, is that it allows for easier monitoring of drift during
245 an analytical session, identification of outliers, calculation of the session
246 reproducibility, and normalisation of both the Pb-Pb and U-Pb ratios.

247 The characteristics that would make an ideal calcite reference material include: 1) a
248 very high proportion of radiogenic Pb (>98%) to ensure virtual isotopic homogeneity;
249 2) U content that is not excessive (to match signal counts between the reference material
250 and unknowns); 3) and low common Pb (<<1 ppm). Calcite is typically low in U and
251 high in initial Pb, is susceptible to alteration or recrystallisation at low temperature in
252 the presence of fluids, and allows Pb diffusion above moderate temperatures (Cherniak,
253 1997). For these reasons, finding suitable reference materials is not straightforward.
254 The best characteristics are likely to be present in calcite with an age sufficiently old to
255 have allowed the radiogenic Pb to thoroughly dominate the Pb isotope composition,
256 and render the common Pb almost negligible. For example, if material as pristine as the
257 WC-1 sample had been allowed to decay for a further 2 Ga instead of being 254 Ma
258 old, nearly all analyses would return a radiogenic Pb content of >97%, and this would
259 lead to a very isotopically homogeneous material. This kind of material should be
260 sought for future reference materials, but has yet to be identified.

261 It is also desirable in LA-ICP-MS dating to have multiple matrix-matched reference
262 materials. This is required to provide robust validation of ages, especially where
263 textural and/or compositional variation leads to differences in ablation and U/Pb
264 fractionation. The most homogeneous materials should be used as primary reference
265 materials, and less perfect but still reliable materials can be secondary reference
266 materials, providing validation of accuracy including the method uncertainty limit.

267

268 *Suitability of WC-1 as a reference material*

269 WC-1 is not the perfect material because of its modest heterogeneity and lack of
270 concordance. The ID-IRMS and LA-ICP-MS data show that there is a level of
271 heterogeneity in the material, which thus far appears to be on the level of ca. 25% (95%
272 conf.) for $^{238}\text{U}/^{206}\text{Pb}$, ~110% (95% conf.) for $^{207}\text{Pb}/^{206}\text{Pb}$, and about 2-3% excess scatter
273 about the regression line, which is a direct measure of 'age dispersion' within the
274 material. Because the proportion of common Pb and hence the resulting measured U-
275 Pb ratio is variable, the mean value of multiple $^{238}\text{U}/^{206}\text{Pb}$ measurements within an
276 analytical session cannot be relied upon for normalisation. However, because the
277 isotope composition of WC-1 falls on a mixing line between initial and radiogenic lead,

278 it can be reliably used for normalisation of U-Pb data using a modified approach, and
279 with allowance for the 2.5% dispersion in its $^{238}\text{U}/^{206}\text{Pb}$ age. This approach (see
280 Appendix), as shown by Chew et al. (2014), allows for the use of reference materials
281 with variable common lead contents, such as WC-1, as long as they form coherent
282 arrays of data around a regression between common and radiogenic isotopic
283 compositions. A number of recent studies have demonstrated the validity of using this
284 approach with adoption of the WC-1 matrix-matched calcite material for determination
285 of U-Pb ages using LA-ICP-MS (Li et al., 2014; Harris et al., 2014; Coogan et al., 2016;
286 Methner et al., 2016; Ring & Gerdes, 2016; Roberts & Walker, 2016; Burisch et al.,
287 2017).

288 WC-1 calcite is from an abundant source that could be distributed widely. Given the
289 present lack of natural calcite reference materials with radiogenic U-Pb compositions,
290 or consistent and precise common-radiogenic mixing arrays, WC-1 will be a useful
291 primary reference material to generate LA-ICP-MS U-Pb dates of calcite over a very
292 wide range of age (Precambrian to late Neogene). Despite the limitations, due to its
293 documented age and isotope characteristics, we advocate use of WC-1 as the principle
294 reference material for U-Pb normalisation of calcite until a more ideal reference
295 material is available. **Acknowledgements**

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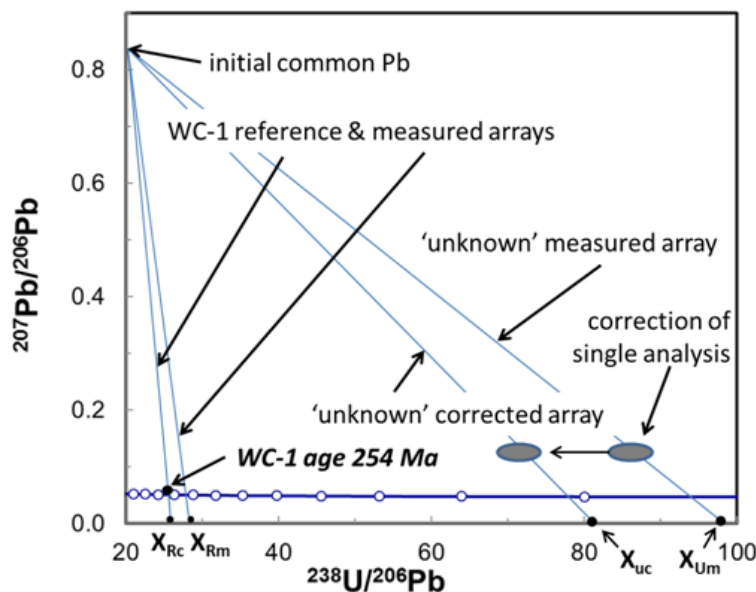
301 **Appendix**

302 *Normalisation procedure*

303 First, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of the WC-1 reference material and the unknowns are
304 corrected using the measured/accepted ratio of NIST glass (NIST614 is ideal), run
305 during the same analytical session as a bracketing reference material. This will correct
306 for multiplier gains if using a multi-collector instrument, alternatively these could be
307 corrected first. After correction for Pb-Pb, the data are corrected for U-Pb. Figure A1

308 shows hypothetical arrays of measured (m) data using a Tera-Wasserburg plot for both
 309 the WC-1 reference (R) material and a sample of unknown (U) age, prior to any U-Pb
 310 normalisation, but following normalisation for Pb-Pb. The X-intercepts of these arrays
 311 can be easily calculated using Isoplot (Ludwig, 2003) as X_{Rm} and X_{Um} as shown. The
 312 Pb-Pb corrected ratio of the WC-1 reference is shown, and a line anchored to the initial
 313 common Pb projected through the correct age will have an X-intercept of X_{Rc} . To
 314 obtain the correct $^{238}\text{U}/^{206}\text{Pb}$ value of any unknown, the $^{238}\text{U}/^{206}\text{Pb}$ of each measurement
 315 of unknowns is simply multiplied by the value given by X_{Rc}/X_{Rm} . Some laboratories
 316 adopt a NIST glass or zircon standard as the primary reference material for both
 317 $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$ normalisation, but this will likely result in a residual offset
 318 of the WC-1 calcite array from its correct value, as the ablation behaviour of calcite,
 319 glass and zircon is different (i.e. a matrix-related offset). Both correction procedures
 320 are equivalent but using a matrix-matched material will be more accurate over a greater
 321 range of instruments and run conditions.

322 Figure A1. Procedure for normalisation of sample $^{238}\text{U}/^{206}\text{Pb}$ using the measured array
 323 of WC-1 calcite as a reference.

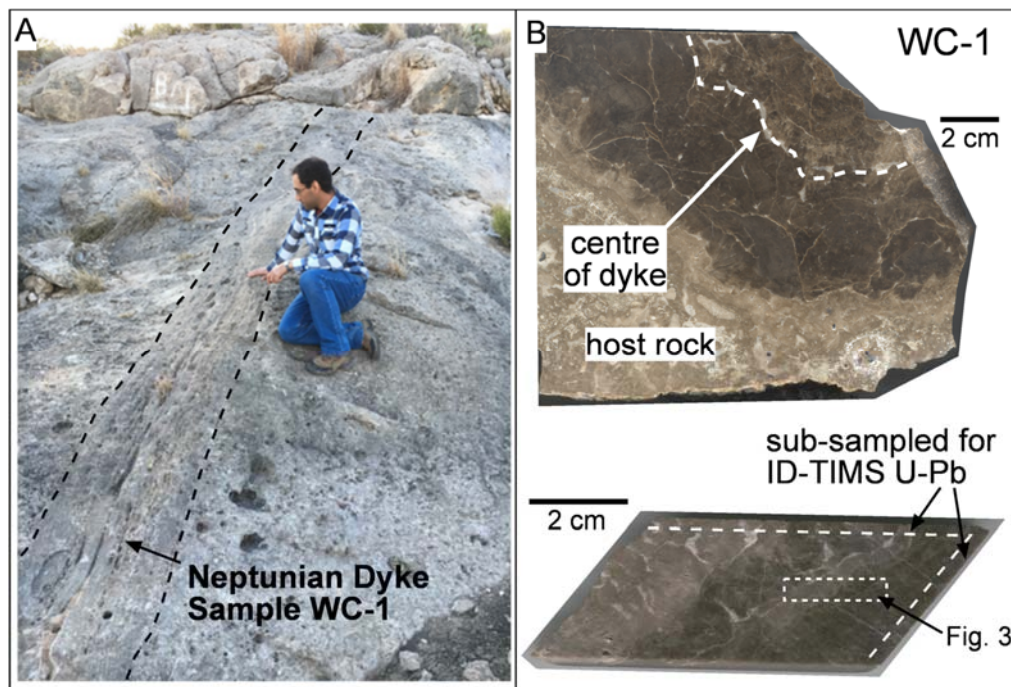


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326 **Figures**

327 Figure 1. A). Field photograph of the Neptunian Dyke from Walnut Canyon, with
328 person for scale. These dykes occupy fractures that are roughly parallel with a set of
329 faults that offset the Capitan reef complex of age at least as young as the Tansil
330 Formation. The boundaries of the discordant dyke are shown by dotted lines with the
331 crudely bedded Capitan reef facies. Nearby, the reef facies and dykes at this locality are
332 overlain by the Castile Formation which has organic-rich calcite that gives a U-Pb age
333 of 251.5 ± 2.8 Ma old (Bekker et al., 2002). B) Top: Photograph of the WC-1 hand
334 specimen; bottom: photograph of the sub-sampled slab analysed for U-Pb and trace
335 elements.

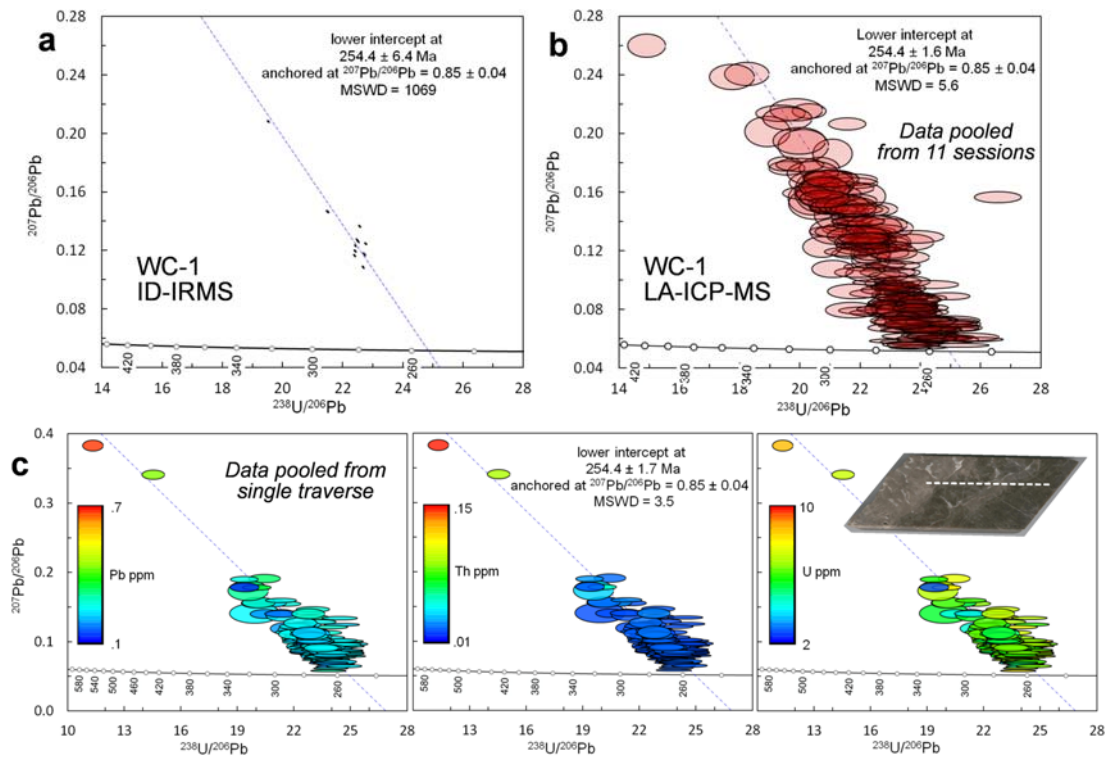


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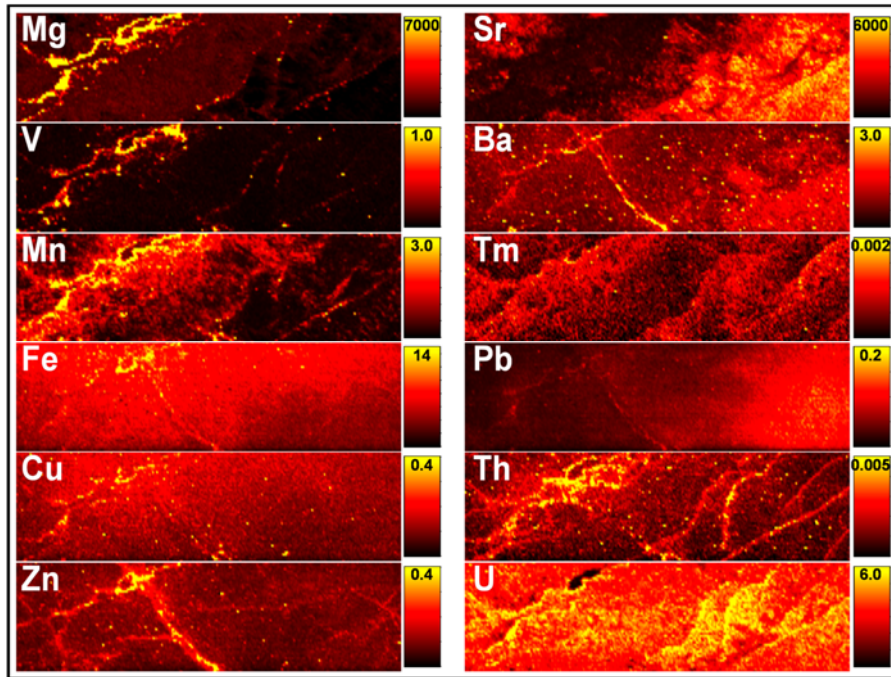
339 Figure 2. a) ID-IRMS U-Pb data for WC-1 (n=10) anchored at 0.85 ± 0.04 for initial
 340 common Pb; b) pooled LA-ICP-MS U-Pb data for WC-1 from eleven analytical
 341 sessions (n=226) from the NIGL laboratory; c) pooled LA-ICP-MS U-Pb data for a
 342 traverse of the WC-1 sample (n=151) crossing clear textural variation, colour-scaled to
 343 Pb, Th and U contents. Uncertainties and ellipses are 2σ .



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346 Figure 3. Trace element maps from the sub-sampled slab of WC-1. The concentrations
 347 in each scale bar are ppm.



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351 Table 1. Summary of ID-IRMS-derived reference values; lower intercepts refer to
 352 intercepts with the concordia curve, not the X-axis; all uncertainties quoted at 2σ .

353

Material	Upper intercept ($^{207}\text{Pb}/^{206}\text{Pb}$)	Lower intercept with concordia ($^{238}\text{U}/^{206}\text{Pb}$)	Lower intercept with concordia (Ma)
WC-1	0.85 ± 0.04	24.84 ± 0.62	254.4 ± 6.4

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357 Table 2. Concentrations (in ppm) from a portion of the mapped region of WC-1 based
 358 on a $280 \times 100 \mu\text{m}$ sampling size ($n=100$). The integer in brackets refers to the isotope
 359 measured. StDev = Standard deviation of the mean.

360

Element	Mean	2 StDev	Min	Max
Mg (24)	663	770	158	14700

V (51)	0.054	0.060	0.021	0.610
Mn (55)	0.65	0.78	0.12	2.55
Fe (57)	5.1	2.0	3.1	8.7
Cu (63)	0.070	0.036	0.043	0.183
Zn (66)	0.122	0.030	0.084	0.174
Sr (88)	1500	1900	445	5420
Ba (138)	0.56	0.25	0.36	1.80
Tm (169)	0.0043	0.0037	0.0000	0.0110
Pb (208)	0.18	0.017	0.07	0.40
Th (232)	0.014	0.011	0.005	0.042
U (238)	3.7	1.0	2.14	5.60

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