1	Running Title: CALCITE & DOLOMITE DIAGENESIS IN BAKKEN SANDS USING SIMS O
2	ISOTOPE MICROANALYSIS
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4	OXYGEN ISOTOPE MICROANALYSIS BY SECONDARY ION MASS SPECTROMETRY SUGGESTS
5	CONTINUOUS 300-MILLION-YEAR HISTORY OF CALCITE CEMENTATION AND
6	DOLOMITIZATION IN THE DEVONIAN BAKKEN FORMATION
7	
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#### 22

# ABSTRACT

23 Calcite cementation and dolomitization are key diagenetic processes in many sedimentary systems. Unravelling detailed histories and timescales of cementation and replacement is, 24 however, often compromised by the limited spatial resolution of many analytical 25 26 techniques; in some cases multiple grains are co-analyzed so that diagenetic histories are 27 blurred and reaction periods are difficult to establish. In this study we have used 10micrometer-resolution, in situ secondary ion mass spectrometry to determine the oxygen 28 29 isotope composition of 197 individual, 10-50-micrometer-size crystals of dolomite and 30 calcite from six samples in a single core of Upper Devonian Middle Bakken Member siltstones and sandstones, the major tight oil formation of the Williston Basin, USA. This 31 32 amount of data places important constraints on the range of temperatures and times that carbonate cementation and replacement occurred. Petrographic data show that 33 microcrystalline calcite cement is an early phase, and combined with mineralogical data 34 35 suggest that much of the dolomite replaces calcite. Over spatial scales of less than a 36 centimeter, analyses of individual calcite crystals have a range of 5‰ for  $\delta^{18}$ O in the group 37 of crystals, and for the group of individual dolomite crystals, 10%. These sub-centimeter ranges are as great as those observed in previous studies of carbonate cements sampled 38 39 over many meters and remind us that previous low-resolution studies may have inadvertently analyzed mixed phases. There is no relationship between dolomite texture 40 and isotopic composition at this spatial scale; microscale backscattered electron imagery 41 42 and scanning electron microscopy cathodoluminescence zoning is seen, but cannot be 43 resolved with a 10 micrometer spot size. Assuming, since it is an early cement, that calcite

44	precipitated from seawater ( $\delta^{18}$ O = -1.5‰), it formed at <i>ca</i> . 15-40°C, mainly at the lower
45	temperatures. Present-day formation waters in Devonian rocks in this region have oxygen
46	isotope compositions of 7-8‰ VSMOW. Using these values as a likely dolomitizing fluid, we
47	suggest that dolomitization occurred continuously between 40 and 140°C over 150 – 200
48	million years, most likely in a fluid with a high Mg/Ca ratio resulting from gypsum formation
49	in local evaporites. We suggest that this exceptionally low rate of dolomitization was
50	controlled by the low rate of supply of Mg in a very sluggish flow regime; dolomitization is
51	incomplete because of a limited supply of Mg.

#### INTRODUCTION

54 Burial diagenesis transforms sediments into sedimentary rocks through a range of 55 mechanical and chemical processes driven by changes in effective stress and the 56 requirement that mineral assemblages attempt to achieve thermodynamic equilibrium as a 57 function of temperature, pressure, and fluid composition (e.g., Bjørlykke 2014). Although the chemical diagenetic reactions are wide-ranging, depending for example on initial 58 59 mineralogy and fluid chemistry, questions which are generic to all processes involve (a) the 60 rate of reactions, (b) the extent to which a pre-defined "system" (for example a sand body) is chemically open or closed, and (c) whether or not the reactions occurred continuously or 61 were punctuated (e.g., Giles 1997; Burley et al. 1989; Giles et al. 2000; Gluyas and Coleman 62 1992; Robinson and Gluyas 1992; Taylor et al. 2010; Bjørlykke and Jahren 2012; Bjørlykke 63 2014). 64

These fundamental questions continue to be asked, in part at least, because of limitations in 65 the analytical techniques available to answer them. Many studies have used some 66 67 combination of petrography, fluid inclusions, and stable isotopes to evaluate diagenetic 68 histories (e.g. Haszeldine et al. 1984; Land et al. 1987; Glasmann et al. 1989; Brint et al. 69 1991; Aplin and Warren 1994; Williams et al. 1997; Sullivan et al. 1997; Taylor et al. 2000; Girard et al. 2001; Goldstein 2001; Marchand et al. 2002; Schmid et al. 2004). However, 70 diagenetic silicate and carbonate minerals in sandstones commonly form grains or 71 72 overgrowths on scales less than 100 micrometers and may have grown over many millions 73 of years. Detailing growth histories of individual phases thus requires probes which can operate on a sub-10-micrometer scale. Conventional stable-isotope and fluid-inclusion 74 studies cannot unravel these histories because (a) the resolution of isotopic analyses is 75

insufficient and (b) fluid inclusions tend to occur in specific locations of diagenetic phases,
for example at grain-overgrowth boundaries or in healed microfractures (e.g., Osborne and
Haszeldine 1993).

79 Oxygen isotopes preserve important information about the temperature at which minerals 80 form and the nature of the fluids from which they precipitate. Earlier isotopic studies on diagenetic quartz and carbonate were made on whole overgrowths or areas sampled with 81 82 microdrills, and could not generate temporal data (Lee and Savin 1985; Land et al. 1987; 83 Brint et al. 1991; Hart et al. 1992; Macaulay et al. 1993; Aplin and Warren 1994; Taylor et al. 84 2000; McBride and Milliken 2006). In situ isotope studies on well-identified minerals can 85 overcome uncertainties of what is being analyzed, but neither the resolution (20–30  $\mu$ m) 86 nor the precision (± 2‰; 2SD) of earlier work using single-collector secondary ion mass spectrometers (SIMS) were sufficient to constrain growth histories (Graham et al. 1996; 87 88 Williams et al. 1997; Lyon et al. 2000; Girard et al. 2001; Marchand et al. 2002). Technical advances in SIMS now allow *in situ* analyses to be made on 2-10- $\mu$ m-diameter regions and 89 have revealed up to 10‰ ranges in  $\delta^{18}$ O in single quartz overgrowths and carbonate 90 91 cements (Pollington et al. 2011; Harwood et al. 2013; Śliwiński et al. 2016b).

Carbonates are common and often pervasive cements in marine sandstones (e.g. Bjørkum
and Walderhaug 1990, 1993; Macaulay et al. 1993; Klein et al. 1999; Taylor et al. 2000;
McBride and Milliken 2006). Although significant carbonate cement can be formed during
early burial (e.g., Bjørkum and Walderhaug 1990; 1993), oxygen and carbon isotope data
often show a wide range of values which imply a range of precipitation temperatures and/or
fluid compositions (e.g., Klein et al. 1999; Taylor et al. 2000). However, detailed
petrography, for example using backscattered electron microscopy, commonly reveals

99 chemically distinct carbonate phases on a sub-millimeter scale (e.g., Hart et al. 1992; Taylor 100 et al. 2000; Śliwiński et al. 2016b). This means that conventional isotope analyses, in which 101 areas of at least a few millimeters are sampled, are likely to result in the analysis of mixed 102 phases or of a single phase that has grown over a long period of time. Equally, studies which 103 have used selective leaching to isolate compositionally distinct carbonate phases rely on the 104 specificity of the leaching method (e.g., Macaulay et al. 1993; Klein et al. 1999). The nature 105 of these analytical tools means that diagenetic histories are inevitably blurred or uncertain.

106 Dolomite and calcite grains examined in this study of the Upper Devonian Middle Bakken 107 Member in North Dakota are often smaller than 100 micrometers. The use of high-108 resolution SIMS, an analytical tool which allows oxygen isotope data to be collected from areas 10 micrometers in diameter, is thus essential if the timing and evolution of fluids 109 responsible for the formation of these diagenetic phases are to be unravelled accurately. 110 111 The Bakken Formation has recently received much attention as a highly significant unconventional hydrocarbon accumulation, and the occurrence of both calcite and dolomite 112 113 is central to the quality of the petroleum reservoir (e.g., Li et al. 2015). Previous work on the 114 oxygen-isotope composition of carbonates in the Bakken has been limited to studies of calcite in fracture fills (Pitman et al. 2001), the bulk analysis of mixed carbonates (Karasinski 115 2006), and one grain-scale study (Staruiala et al. 2013). Here, we report oxygen isotope data 116 obtained by SIMS on calcite and dolomite grains and focus on four questions: (a) over what 117 temperature and period of time did the carbonate phases form; (b) was carbonate 118 119 diagenesis continuous or punctuated; (c) is the dolomite a primary cement or did it form 120 through dolomitization of earlier calcite (e.g., Warren 2000; Machel 2004); and (d) to what extent did diagenesis occur in a closed or open geochemical system? 121

123

# **GEOLOGICAL CONTEXT**

124 The Upper Devonian-Lower Mississippian Bakken Formation was deposited over wide areas 125 of the intracratonic Williston basin, which covers 770,000 km<sup>2</sup> of Montana, North Dakota, 126 and South Dakota in the USA and parts of Saskatchewan and Manitoba in Canada (Fig. 1). The basin is structurally simple with an almost complete stratigraphic section and only 127 gentle, low-wavelength folding (Webster 1984; Meissner 1991). The burial history, based on 128 129 a well which has a stratigraphy very similar to that of the core used in this study and in which the Bakken is buried to essentially the same depth, is one of continual subsidence 130 131 from deposition to ca. 50 Ma, followed by modest uplift and renewed subsidence from 35 132 Ma to the present day (Kuhn et al. 2012) (Fig. 1C). The present-day temperature for the samples of this study is around 125 °C with a modelled maximum temperature between 150 133 and 160 °C. 134

135 The Bakken is divided into three stratigraphic members (Fig. 2). The Upper and Lower members are both organic-rich shales whilst the Middle Bakken Member, the subject of this 136 137 study, comprises a variably but often highly carbonate-cemented series of very fine-grained 138 sandstones and siltstones deposited over large areas of a shallow, epicontinental sea 139 (Meissner 1978; Freisatz 1995; Egenhoff et al. 2011). At the depocenter of the Williston Basin the Middle Bakken reaches a maximum thickness of 46 m but varies in thickness 140 across the basin (Pitman et al. 2001). Most current work suggests that the Middle Bakken 141 142 was deposited in a variety of shallow-marine environments during a Late Devonian to Early 143 Mississippian regression (e.g., Li et al., 2015). Whilst the sedimentology of the Middle 144 Bakken has been extensively described (McCabe 1959; Meissner 1978; Webster 1984;

145	Holland et al. 1987; Smith and Bustin 1996; Pitman et al. 2001; Egenhoff et al. 2011;
146	Egenhoff 2017), diagenetic studies are more limited. Nevertheless, pervasive early calcite
147	cement has been recognized in several studies (Last and Edwards 1991; Pitman et al. 2001;
148	Ferdous 2001; Li et al. 2015), along with the interpretation of several phases of dolomite
149	(Ferdous 2001).
150	
151	EXPERIMENTAL METHODS
152	Samples
153	Samples for this study come from a single core drilled in McKenzie County, North Dakota,
154	USA (Fig. 1B). The core was described using the five facies associations defined by Simenson
155	(2010) in a study of the Middle Bakken from the Parshall Field, Mountrail County, North
156	Dakota. A total of 32 core plugs were taken over the full thickness of the Middle Bakken
157	section; 6 of the 32 samples were selected for this study, including samples from each of the
158	five different facies.
159	
160	Petrography
161	Thin sections were cut perpendicular to bedding from core plugs and carbonate textures
162	investigated using both transmitted-light and electron microscopy. Transmitted-light
163	microscopy was carried out using a Nikon Eclipse 50iPOL polarizing microscope. 300 points
164	per sample were counted using a Petroglight petrographic point counter. The thin sections
165	were then coated with a 30 nm layer of carbon before analysis by electron microscopy.

Electron microscopy was performed at Durham University's GJ Russell Electron Microscopy
Facility on a Hitachi SU 70 FEG SEM in secondary (SE) and backscatter (BSE) and
Cathodoluminescence (CL) modes. Images were acquired at 15 kV, 2-4 nA and a working
distance of 15-16 mm.

Dolomite crystal textures were classified using the scheme described by Sibley and Gregg
(1987). Whilst proposed principally for dolomite crystals in carbonate rocks, this scheme is
also appropriate for low-temperature, mixed clastic-carbonate systems like the Bakken
because it focuses on the grain-boundary and grain-size relationships of individual crystals,
which can be used to infer the genetic origin of each dolomite crystal class.
Scanning Electron Microscopy - Cathodoluminescence (SEM-CL) images were acquired on

carbon-coated thin sections and round resin plugs using the Hitachi SU 70 FEG SEM with a
Gatan Mono-CL detector operated in panchromatic mode. Images were obtained at an
accelerating voltage of 10 kV and a working distance of 17 mm. Spectral information was
obtained over a wavelength search range of 505 - 800 nm and a dwell time of approximately
3,200 µs per pixel for an image resolution of 2250 x 2250. Intensity values were corrected
using the system response curve.

Using SEM-WDS, the elemental compositions of 58 calcite crystals and 155 dolomite crystals
with different textures in 13 samples were determined, including the six samples on which
SIMS analyses were performed. Analyses were repeated three times per crystal, and the
results for each crystal are reported as the mean of the three analyses.

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Mineralogy

Bulk mineralogy was determined by KT Geoservices (Table 1). X-ray diffraction (XRD)
analysis was conducted using a Siemens D500 automated powder diffractometer equipped
with a copper X-ray source (40 kV, 30 mA) and a scintillation X-ray detector. Both bulk and
clay (< 4 µm) analyses were conducted. Quantitative data were obtained from the whole-</li>
rock pattern using whole pattern fitting (WPF) and Rietveld refinement methods.

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#### Bulk C and O Isotope Analysis

196 The carbon and oxygen stable-isotope composition of bulk calcite and dolomite were 197 analyzed at the Scottish Universities Environmental Research Centre (SUERC) on an 198 Analytical Precision AP2003 mass spectrometer equipped with a separate acid injector system (Table 1). We attempted to separate calcite and dolomite through the preferential 199 200 dissolution of calcite by reaction with 105%  $H_3PO_4$  under a helium atmosphere at 70 °C. As 201 shown later, our results in fact indicate that the fine-grained dolomite in these samples was also substantially dissolved with this method. Measured O isotope ratios are reported as per 202 mil deviations relative to Vienna standard mean ocean water (VSMOW) and C isotopes 203 204 relative to Vienna PeeDee Belemnite (VPDB) using conventional delta ( $\delta$ ) notation. Mean analytical reproducibility based on replicates of the SUERC laboratory standard MAB-2 205 206 (Carrara Marble) was around ± 0.2‰ for both carbon and oxygen. MAB-2 is an internal 207 SUERC laboratory standard extracted from the same Carrara Marble quarry as the IAEA-CO-208 1 international standard. It is calibrated against IAEA-CO-1 and NBS-19 and has exactly the 209 same C and O isotope values as IAEA-CO-1 (-2.5‰ and 2.4‰ VPDB respectively).

# 211

## Secondary Ion Mass Spectrometry

212 In-situ, sub-grain-scale oxygen stable-isotope data were obtained using secondary ion mass 213 spectrometry. Based on their mineralogy and petrographic characteristics, six 214 representative samples were selected, one from each facies. Soluble organic matter was removed using a standard, 96 hour soxhlet extraction procedure using a mixture of 215 dichloromethane and methanol. The samples were then mounted in epoxy resin in 1-inch 216 round plugs. Several crystals (2 or 3) of calcite standard UWC-3 ( $\delta^{18}O_{VSMOW}$  of UWC-3 is 217  $12.49\% \pm 0.03\% 1$  SD, n = 9; Kozdon et al. 2009) were mounted at the center of each 218 219 sample. The sample was then polished sequentially with 6  $\mu$ m, 3  $\mu$ m, and 1  $\mu$ m diamond 220 paste on a low-nap pad. The final polish was obtained using a 0.05 µm colloidal alumina solution on a vibrating pad for 30-200 seconds. The polished sample plugs were then gently 221 222 cleaned with deionized water and ethanol, and dried in a vacuum oven for 5 hours at 40°C. 223 To prevent charging during analysis, samples were coated with 60 nm gold. The flatness 224 across the samples was measured using a white-light profilometer across both the polished 225 rock, the mounted and polished calcite standard, and enclosing epoxy. The maximum 226 topography recorded was 3  $\mu$ m (sample) and 7  $\mu$ m (sample and standard). Analysis spots were not placed near localized areas with relief > 3  $\mu$ m. 227

In-situ oxygen isotope data were acquired using a CAMECA IMS 1280 large-radius multi collector ion microprobe at the WiscSIMS Laboratory at the University of Wisconsin Madison (Kita et al. 2009; Valley and Kita 2009). A <sup>133</sup>Cs<sup>+</sup> primary ion beam with a current of
 1.4 nA was focused at the analytical surface, resulting in ellipsoidal pits ca. 10 µm x 13 µm in

size. The typical secondary  ${}^{16}O^{-}$  ion intensity for the 300 analyses of this study was approximately 2.5 x  $10^{9}$  cps.

Both before and after every set of 8-17 sample analyses, a sample-mounted calcite standard (UWC-3) was measured four times. As for conventional analyses, stable-isotope ratios are reported using the standard delta notation relative to VSMOW ( $\delta^{18}O$  ‰). The reproducibility of each set of unknown samples is reported as 2 SD of the bracketing standard analyses; the average 2 SD of bracketed analyses was 0.27‰ (refer also to the supplementary material). Detailed analytical protocols can be found in Kita et al. (2009).

240 Initial SEM-EDX observations indicated the presence of iron in some of the dolomite 241 crystals. Śliwiński et al. (2016a) show that the extent of isotopic fractionation occurring 242 during SIMS analysis of carbonates (matrix effect) is a function of the concentration of iron. Thus, instrument standards for the dolomite – ankerite series were analyzed during the 243 same SIMS session to ensure the accuracy and precision of analyses for the full range of 244 245 potential carbonate chemistries. In addition, the carbonate in each pit analysed by SIMS was identified in the SEM, and the iron composition of the crystal measured using SEM-WDS 246 247 (adjacent to the pit), using an INCA Wave 700 spectrometer WDS detector attached to a 248 Hitachi SU-70 FEG SEM. The SEM "spot size" (beam diameter) was between 1.7 and 5 nm with an interaction depth of up to 800 nm and width of around 3  $\mu$ m. To ensure that the 249 analyses were of specific crystals, only crystals with the shortest visible length of > 2  $\mu$ m 250 were analysed. Three sets of standards were used for SEM-WDS: (a) an elemental cobalt 251 252 instrument standard was used at the start of every session; (b) at the start and end of each analytical session, the calcite standard UWC-3 (see Kozdon et al. 2009) which was mounted 253 to the center of all of the analyzed samples was measured five times; (c) a series of 254

255	carbonate standards with known chemical compositions (calcite, ankerite, dolomite, and
256	siderite) were analyzed to measure accuracy and precision (see Supplementary Material 2).
257	Using the results of SEM-WDS analysis, we used the mass bias calibration method proposed
258	by Śliwiński et al. (2016a) to correct SIMS $\delta^{18}$ O measurements for the presence of iron in the
259	dolomite crystals (Supplementary Material). Only 8 analyses required correction for the
260	presence of iron, since iron contents were generally less than the detection limit of 0.1 wt.
261	% FeO. The residual of the dolomite-ankerite calibration curve, fitted through seven
262	standard materials measured during the same SIMS session, was 0.25‰.
263	
264	RESULTS
265	Sedimentology, Mineralogy and Petrography
266	The Middle Bakken is a sedimentologically heterogeneous fine sandstone - siltstone unit
267	that is pervasively but variably cemented by both calcite and dolomite. Using the framework
268	provided by Simonsen (2010) and the sedimentologic description of this core by Li et al.
269	(2015), five facies (B, C, D1, D2, and E) were defined from the base (3206 m) to the top
270	(3182 m) of the core, with a gradational facies between B and C. Facies B comprises strongly
271	
	bioturbated, argillaceous, calcareous sandstones and siltstones; facies C consists of very
272	bioturbated, argillaceous, calcareous sandstones and siltstones; facies C consists of very fine-grained sandstones and siltstones showing both planar and undulose lamination, with
272 273	bioturbated, argillaceous, calcareous sandstones and siltstones; facies C consists of very fine-grained sandstones and siltstones showing both planar and undulose lamination, with some thin mud-rich horizons; facies D1 is a fine-grained sandstone with common soft-
272 273 274	bioturbated, argillaceous, calcareous sandstones and siltstones; facies C consists of very fine-grained sandstones and siltstones showing both planar and undulose lamination, with some thin mud-rich horizons; facies D1 is a fine-grained sandstone with common soft- sediment deformation features; facies D2 consists of a light brown to light gray, parallel to

275 undulating-laminated, low-angle cross-laminated sandstone; facies E comprises a dark gray

siltstone interbedded with a light gray, thinly parallel-laminated, very fine-grainedsandstone.

278 Core photographs taken with both white and UV light (Fig. 3) suggest that in all facies, there 279 are multiple 2-30 cm-thick zones of layered or nodular diagenetic carbonate where porosity has been infilled to the extent that they do not contain fluorescing oil (i.e., calcite 280 281 cementation pre-dated oil migration; Li et al. 2015). Other areas, which do contain 282 fluorescing oil, are more lightly and/or more variably carbonate-cemented. Based both on the XRD analysis of 13 samples and point counting of 15 samples, calcite (both primary, 283 bioclastic calcite and diagenetic calcite) constitutes 3-56% of the rock volume and diagenetic 284 285 dolomite between 5 and 41% (Table 1). Total carbonate content (calcite plus dolomite, including bioclastic calcite) varies between 32 and 72%. The average minus-cement porosity 286 is 42% (range 36-46%), close to depositional porosity, and suggesting that cementation 287 288 started close to the sediment-water interface. The inverse correlation between the amounts of calcite and dolomite ( $r^2 = 0.62$ ) lends support to the idea that dolomite is replacing calcite 289 290 rather than being a primary cement.

At the core scale, calcite- and dolomite-cemented regions are present in approximately 70% of the core. In thin section, diagenetic calcite and dolomite cement occurs as bands. These bands vary in thickness from a couple of millimeters up to the size of the full section. Whilst in most instances the millimeter-scale bands form sharp contacts parallel to bedding, in some cases there is no clear lithological control on the morphology of the contact or the spatial distribution within the section.

Diagenetic calcite is observed in two textural types. By far the most volumetrically
 important texture (Type 1) is pervasive, poikilotopic cement in which detrital grains "float"

within the calcite (Figs. 4D and 5A). Similar, early, massive calcite cement is common in
shallow-marine sandstones (e.g., Bjørkum and Walderhaug 1993). Type 2 calcite comprises
individual crystals which (a) appear to cement small numbers of grains to form a globular
morphology (Fig. 5B), and (b) occur as individual, discrete grains which do not connect other
grains; visual estimates from SEM show that these phases form < 1% of calcite.</li>

Dolomite occurs as six different morphologies. Type 1 dolomites are nonplanar, anhedral, 304 305 crystals with rounded edges, 15-30 μm in size (Fig. 6A). Type 2 dolomites are euhedral 306 rhombs, 10-50 µm in size with micrometer-scale pores in their core (Fig. 6B). Type 3 307 dolomites are euhedral rhombs, 10-50 µm in size but without pores (Fig. 6C). Type 4 308 dolomites are subhedral, geometric, angular crystals which vary in size from 5 to 35 µm (Fig. 6D). Type 5 dolomites are 2-10-µm-thick ferroan rims which form around more 309 stoichiometric, iron-poor dolomite. This phase has been observed around all other dolomite 310 311 types (Fig. 6E). Type 6 dolomites are euhedral rhombs which are less than 5 μm in diameter (Fig. 6F). Under transmitted light, some dolomites show a "cloudy core" texture which has 312 313 been previously suggested to result from the dolomitization of a calcite precursor, resulting 314 in a close-to-stoichiometric dolomitic outer zone and a more calcium-rich and porous core (Murray and Lucia 1967; Sibley 1982). 315

In most cases, except in the relatively unusual cases of Fe enrichment towards the edge of
crystals, BSEM shows no evidence of significant changes in the chemical composition of
dolomite crystals from core to edge. Scanning electron microscopy - cathodoluminescence
(SEM-CL) does however reveal zoning within individual dolomite crystals. Zones of different
luminescence can reflect both subtle changes in crystal chemistry and/or variations in
growth mechanisms (e.g. Boggs and Krinsley 2006), and our data are insufficient to

322	determine the reasons for the zonation. In total, 48 crystals were viewed in 10 samples. The
323	CL character of individual dolomite types was consistent in all the samples and is reported in
324	Figure 7. All dolomite phases luminesce in the red part of the spectrum, including the "dull"
325	zones which simply have a lower - intensity luminescence (Fig. 7). Anhedral, Type 1
326	dolomites show incomplete concentric zones which have decreasing luminescence intensity
327	towards the edge of the crystals. Textural types 2-4 and 6 exhibit similar CL characteristics: a
328	single, concentric, low - intensity luminescence zone around a much more intensely
329	luminescing core. The rims are approximately 1-10 $\mu m$ in thickness (Fig. 6E). Type 5
330	dolomites are ferroan rims which form single homogeneous layers around other dolomite
331	crystals; they show low emission intensity in the red spectrum.
332	
333	Chemical Composition
334	Calcite cement has a very consistent chemistry, averaging 97.4 mol % Ca, 2.4 mol % Mg, and
335	0.2 mol % Fe (Fig. 8). Eighty percent of dolomite analyses have chemical compositions
336	between $Ca_{0.55}Mg_{0.45}CO_3$ and $Ca_{0.45}Mg_{0.55}CO_3$ , with a modal value close to that of
337	stoichiometric dolomite. There is no obvious relation between dolomite composition and
338	textural type (Fig. 8). Almost all dolomites have low iron contents, with 85% containing less
339	than 2 mol % Fe and only 2 % with more than 6 mol % Fe. Note however that because of
340	their spatial scale, Type 5 dolomites (ferroan dolomite rims) were not systematically
341	measured, although they quite commonly form either as discrete rims or more diffuse
342	alteration zones around all other textural types of dolomite; they also form small, individual

343 crystals with anhedral to euhedral habits.

Diagenetic dolomite containing more than 55 mol % Mg are uncommon in the literature;
however, in this study, 17% of the analyses are more Mg-rich than Ca<sub>0.45</sub>Mg<sub>0.55</sub>CO<sub>3</sub>. Most of
these analyses are from Samples 2 and 4, and the most common chemistry is around
Ca<sub>0.4</sub>Mg<sub>0.6</sub>CO<sub>3</sub>, i.e., between the composition of stoichiometric dolomite (Ca<sub>0.5</sub>Mg<sub>0.5</sub>CO<sub>3</sub>) and
huntite (Ca<sub>0.25</sub>Mg<sub>0.75</sub>CO<sub>3</sub>).

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#### Bulk C and O Isotope Composition

351 The results of bulk carbon and oxygen isotope analyses are reported in Table 1. The ranges for putative calcite and dolomite overlap substantially and are approximately -3 to +3% for 352 carbon and +20 to +30 ‰ for oxygen (putative dolomite) and +22 to +26‰ (putative 353 354 calcite). We use "putative" because with the benefit of the SIMS oxygen isotope analyses of 355 individual calcite and dolomite crystals (see below) it is clear that the selective leach 356 partially dissolved dolomite as well as calcite. This is readily understood, as, in practice, the 357 "calcite" fraction is that gas extracted from the bulk samples after three hours of acid digestion in a vacuum; the "dolomite" fraction is the gas then extracted after a further 24-358 359 hour acid digestion on the residue (both corrected back to original carbonate as true calcite 360 or dolomite). Whilst such "dolomite" analyses are likely to be free of calcite, the "calcite" is 361 susceptible to contamination, as is shown by this study. Retrospectively, the advice is to proceed with caution when interpreting previous studies, which have used similar selective 362 leaching techniques in an attempt to separate finely intergrown calcite and dolomite, 363 particularly with the "calcite" data. 364

The main result of the bulk isotope analyses is that most of the carbon in both dolomite and (probably) calcite is from marine carbonate, with only minor inputs from organic sources. Values between -3‰ and +3‰ suggest the addition of relatively small amounts of organic carbon from processes involving coupled methanogenesis and CO<sub>2</sub> reduction, which would result in more positive values, and from the oxidation of organic matter, which would result in more negative values (e.g., Curtis et al. 1986).

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#### SIMS: Grain-Scale Oxygen Isotope Data

Three hundred and eight sites were analyzed from the six samples selected for SIMS 373 374 analysis. After analysis, SEM was used to examine the shape of the pits formed by the ion 375 beam. Previous work (Cavosie et al. 2005; Linzmeier et al. 2016) has shown that data from 376 morphologically irregular pits are less reliable than those from regularly shaped pits. In this 377 study we took a very strict approach to ensure that only the most reliable data were 378 included. Some data were rejected due to the very fine nature of these samples, such that some mixed phases were measured. Most of the rejected data are in fact from crystals with 379 380 minor irregularities such as surface asperities. All rejected data are reported in the 381 Supplementary Material. Using these strict criteria, we accepted 197 analyses, i.e., between 382 16 and 46 analyses from six sample areas, each of which is approximately 5 mm in diameter. Values of  $\delta^{18}$ O for individual calcite grains are almost all between +28.9 and + 33.7‰ (-1.9 – 383 2.8 ‰ VPDB), with a similar range in samples from each facies (Fig. 9). For dolomite, the full 384 385 range is +22.5 – 32.2‰ (-8.1 – 1.3 ‰ VPDB), with a mean value of +26.8‰ and with 93% of values between +24 and +30‰ (Fig. 9). There is a similar range of  $\delta^{18}$ O values in each 386

morphological type of dolomite. There is no relation between  $\delta^{18}$ O and the Ca/Mg ratio of dolomite.

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## DISCUSSION

The oxygen isotope data in this study show as great a range on a sub-centimeter scale as 391 392 many studies have found on conventional studies of diagenetic carbonates in sandstones 393 sampled on scales of many meters (e.g., Bjørkum and Walderhaug 1993; Klein et al. 1999; Taylor et al. 2000). Given the sub-millimeter complexity observed in this study (Fig. 10), it is 394 395 clear that conventional sampling methods can easily homogenize complex mixtures and result in an enforced, simplistic picture of diagenetic histories. Equally, however, our results 396 397 show an overall commonality from sample to sample which show that carbonate diagenesis, although complex on a sample scale, proceeded in a similar way throughout fifteen meters 398 399 of the Middle Bakken. With SIMS, the large number of analyses of accurately identified mineral phases allows us to draw a temporal picture of diagenesis which is not possible with 400 conventional data. As we discuss below, our data suggest that carbonate diagenesis in the 401 Middle Bakken was not episodic but occurred continuously over an approximately 300-402 million-year period of burial. 403

High minus-cement porosities suggest that diagenetic calcite started to precipitate close to the sediment-water interface, as observed in many similar studies (e.g., Wilkinson 1991; Gluyas and Coleman 1992; Bjørkum and Walderhaug 1990; 1993; Taylor et al. 2000). Our isotopic data support the early formation of calcite. Using the isotope paleothermometer proposed by O'Neil et al. (1969) for calcite and assuming a  $\delta^{18}$ O of = -1.5‰ for Late

409 Devonian seawater (Hudson and Anderson 1989; van Geldern et al. 2006), the vast bulk of
410 calcite formed between 15 and 35 °C (Fig. 11).

411 The temperature histogram in Figure 11A suggests that the bulk of calcite cementation 412 occurred between 15 and 20 °C with steadily decreasing amounts at higher temperatures. Assuming a mean seawater temperature of 15 °C, a geothermal gradient of 25 °C/km, and 413 an unchanging  $\delta^{18}O_{H2O}$ , calcite cementation occurred at decreasing rates during burial to *ca*. 414 800 meters. Linking this to the burial history (Fig. 1), calcite cementation occurred over the 415 416 first ca. 10 million years of burial. Given the occurrence of bioclasts in the Middle Bakken and the carbon isotope signature of calcite (0 ± 3‰), this calcite most likely represents the 417 418 redistribution of biogenic calcite via local dissolution and precipitation.

Petrographic observations of (a) cloudy cores (transmitted light) and (b) porosity which 419 420 likely results from the volume reduction associated with the replacement of calcite by 421 dolomite (Weyl, 1960), combined with (c) the inverse correlation between the amounts of 422 dolomite and calcite, suggest that dolomite is largely replacing calcite rather than occurring as a pore-filling cement. In the absence of reaction fronts in individual crystals, it appears 423 that dolomitization is a dissolution – precipitation reaction in which calcite is dissolved and 5 424 425 - 50-micrometer-size dolomite crystals are precipitated. The carbon isotope data for 426 dolomite and calcite-dolomite mixtures are similar and are thus also consistent with dolomitization of calcite. Using the oxygen isotope paleothermometer proposed for 427 dolomite by Vasconcelos et al. (2005) for dolomite-water and assuming, as a first estimate, 428 that dolomite formed in unmodified seawater ( $\delta^{18}O_{H2O}$ = -1.5‰), a temperature range of 13 429 - 66°C is calculated (Fig. 11B). Based on a correlation between  $\delta^{18}$ O and the Ca content of 430 diagenetic dolomites, Vahrenkamp et al. (1994) suggested that when estimating 431

precipitation temperatures for dolomite, a correction of +0.1 per mil may be needed per
mol % of Mg deficiency due to variations in mineral-water isotope fractionation factors. For
most of our data, this results in a correction of only < 0.3‰, with a maximum correction of</li>
1.5‰; the range of estimated precipitation temperatures remains unchanged.

436 Since dolomite is supersaturated in seawater, dolomitization in unmodified seawater is geochemically feasible, but unusual (e.g., Machel 2004). Dolomitization more commonly 437 438 occurs in fluids in which the Mg/Ca ratio has been modified as a result of evaporation and precipitation of gypsum (e.g., Budd 1997; Warren 2000; Machel 2004 for reviews). 439 440 Anhydrite-bearing evaporites occur both below (Devonian Prairie Evaporite and Three Forks 441 formations) and above (Mississippian Charles Salt Formation) the Bakken Formation, and pre-Mississippian waters in this part of the Williston Basin are commonly hypersaline and 442 are likely dolomitizing fluids (lampen and Rostron 2000). Values of  $\delta^{18}$ O for present-day 443 formation waters from the Devonian Duperow aquifer, which occurs below the Bakken in 444 this part of the Williston Basin, are around +7.5 ‰ (Figure 1A; Rostron and Holmden 2003). 445 If we assume a value of +7.5‰, the maximum calculated precipitation temperature is 157 446 447 °C, approximately that of the maximum burial temperature (Fig. 11D). If all dolomite formed from water with  $\delta^{18}$ O = +7.5‰, then precipitation temperatures range from 61 to 157 °C 448 (Fig. 11D). Slightly lower  $\delta^{18}$ O values, for example +7‰, would give a temperature range of 449 58 – 150 °C. The histogram of estimated precipitation temperatures shows that the rate of 450 dolomitization increases steadily from 60 to 130 °C and then decreases at higher 451 temperatures (Figure 11D). Given that dolomitization rates increase with temperature, the 452 limited reaction at the highest temperatures might reflect the generation of petroleum from 453 454 the organic-rich shales above and below the middle Bakken and its emplacement into the

middle Bakken. If we assume that dolomitization occurred in fluids that evolved steadily
from the original seawater (-1.5‰) to the present-day brine (+7.5‰), then dolomite would
have formed throughout almost the whole burial history of the Bakken (Figs. 1, 11). In either
case, dolomitization occurred continuously over approximately 150 – 250 million years.

459 The rate of dolomitization depends on a range of factors, including the Mg:Ca ratio in solution (Kaczmarek and Sibley 2007), the mineralogy of the reactant (Gaines 1974), and 460 reactant surface area (Sibley et al. 1987). Rate constants for dolomite precipitation have 461 been measured experimentally (Arvidson and Mackenzie 1999), and even at low diagenetic 462 temperatures the resulting kinetics show that pervasive dolomitization and dolomite 463 precipitation can occur on timescales of less than one million years (Whitaker and Xiao 464 2010; Al Helal et al. 2012); this is consistent with the occurrence of Holocene dolomites in 465 modern sabkhas and carbonate islands (Budd 1997). Dolomitization rates increase markedly 466 467 with increasing temperature (Arvidson and Mackenzie 1999) so that at the estimated temperatures of dolomitization in the Bakken (61 – 157 °C), rates are not controlled by 468 469 kinetics. Rather, we suggest that the rate of dolomitization must be limited by the rate at 470 which Mg is delivered to reaction sites and thus the fluid flow regime (Machel 2004; Whitaker et al. 2004). We have no way of evaluating the detailed flow history through the 471 Bakken in North Dakota, but the highly saline and isotopically evolved waters which occur in 472 the region today are likely to be part of an ancient, highly restricted and almost stagnant 473 474 flow system (Rostron and Holmden 2003). With no topographic recharge in the area, fluid flow would be driven almost entirely by sediment compaction, with very low water:rock 475 ratios. The lack of fluid flow and related supply of Mg is the most likely reason why 476

dolomitization, despite the length of time available for reaction, is partial rather thancomplete.

479	As in almost all diagenetic studies, the lack of constraint of paleo- $\delta^{18}O_{H2O}$ limits our ability to
480	generate highly constrained diagenetic time-temperature histories. In principle, clumped-
481	isotope studies will allow this because precipitation temperatures can be fixed without the
482	need to assume $\delta^{18} O_{H20}$ (Dale et al. 2014; Millán et al. 2016). However, the sample sizes
483	currently required for clumped-isotope work precludes the grain-scale analyses such as
484	those reported here. For the finely intergrown dolomites and calcites analyzed in this study,
485	clumped isotopes would have yielded a range of temperatures depending on the mixture of
486	calcite and dolomite grains drilled from each sample.

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# SUMMARY AND CONCLUSIONS

- 489 Shallow-marine fine-grained sandstones and siltstones from the Devonian Middle Bakken
- 490 Member are pervasively cemented with calcite and dolomite. Petrographic and
- 491 mineralogical data show that dolomite occurs as a result of dolomitization of calcite.
- The oxygen isotope composition of 57 individual calcite and 174 individual dolomite grains
- 493 from six samples were determined using SIMS. A similarly wide range of values occurs in all
- 494 six samples: 5‰ for calcite and 10‰ for dolomite. For dolomite, there is no relationship
- 495 between morphology, chemistry, and isotopic composition, so that in this case petrography
- 496 is not a good guide to diagenetic history.

497 Since all samples display the same range of oxygen isotope values, we conclude that whilst carbonate diagenesis in the Middle Bakken is heterogeneous on a millimetre scale, the same 498 set of diagenetic processes are occurring on the same timescales on a 20-meter scale. 499 Furthermore, the range of oxygen isotope compositions that occur on a millimeter scale are 500 501 similar to the total ranges determined in many conventional isotope studies of carbonatecemented sandstones sampled on scales greater than a meter. It is likely that either mixed 502 503 phases or isotopically diverse single phases have been analyzed in previous studies, resulting 504 in blurred or incorrect diagenetic histories.

A great benefit of SIMS is that through the generation of a large number of analyses of 505 506 known phases, a much more accurate diagenetic history can be elucidated compared to conventional studies in which either sample numbers are restricted or there is uncertainty 507 over what phases have been analyzed. In this study we can be confident that carbonate 508 509 diagenesis has been almost continuous from deposition to maximum burial: a period of 300 million years. Within the uncertainty of  $\delta^{18}O_{H2O}$ , calcite formed over the first *ca*. 10 Myr of 510 511 burial, with most forming close to the sediment water interface. Dolomitization occurred continuously from ca. 61 – 157 °C over 150 – 250 million years. The rate of dolomitization 512 513 was probably controlled by the rate of supply of Mg in a very sluggish flow regime; dolomitization is probably incomplete because of a lack of Mg and perhaps, in this case, by 514 515 the fact that petroleum was emplaced into the sandstone late in the burial history.

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REFERENCES

518	Al-Helal, A.B., Whitaker, F.F., and Xiao, Y., 2012, Reactive transport modeling of brine reflux:
519	dolomitization, anhydrite precipitation, and porosity evolution: Journal of Sedimentary
520	Research, v. 82, p. 196-215.
521	
522	Aplin, A.C., and Warren, E.A., 1994, Oxygen isotopic indications of the mechanisms of silica
523	transport and quartz cementation in deeply buried sandstones: Geology, v. 22, p. 847-850.
524	
525	Arvidson, R.S., and Mackenzie, F.T., 1999, The dolomite problem: control of precipitation
526	kinetics by temperature and saturation state: American Journal of Science, v. 299, p. 257-
527	288.
528	
529	Bjørkum, P.A., and Walderhaug, O., 1990, Geometrical arrangement of calcite cementation
530	within shallow marine sandstones: Earth-Science Reviews, v. 29, p. 145-161.
531	
532	Bjørkum, P.A., and Walderhaug, O., 1993, Isotopic composition of a calcite-cemented layer in
533	the Lower Jurassic Bridport Sands, southern England: implications for formation of laterally
534	extensive calcite-cemented layers: Journal of Sedimentary Research, v. 63, p. 678-682.
535	
536	Bjørlykke, K., 2014, Relationships between depositional environments, burial history and
537	rock properties: Some principal aspects of diagenetic process in sedimentary
538	basins. Sedimentary Geology, v. 301, p. 1-14.

540	Bjørlykke, K., and Jahren, J., 2012, Open or closed geochemical systems during diagenesis in
541	sedimentary basins: Constraints on mass transfer during diagenesis and the prediction of
542	porosity in sandstone and carbonate reservoirs: American Association of Petroleum
543	Geologists, Bulletin, v. 96, p. 2193-2214.
544	
545	Boggs, S., and Krinsley, D., 2006, Application of Cathodoluminescence Imaging to the Study of
546	Sedimentary Rocks: Cambridge, UK, Cambridge University Press, 146 p
547	
548	Brint, J.F., Hamilton, P.J., Haszeldine, R.S., Fallick, A.E., and Brown, S., 1991, Oxygen isotopic
549	analysis of diagenetic quartz overgrowths from the Brent sands: a comparison of two
550	preparation methods: Journal of Sedimentary Research, v. 61, p. 527-533.
551	
552 553	Budd, D.A., 1997, Cenozoic dolomites of carbonate islands: their attributes and origin: Earth-Science Reviews, v. 42, p. 1-47.
554	
555	Burley, S.D., Mullis, J.T., and Matter, A., 1989, Timing diagenesis in the Tartan Reservoir (UK
556	North Sea): constraints from combined cathodoluminescence microscopy and fluid inclusion
557	studies: Marine and Petroleum Geology, v. 6, p. 98-120.
558	

- - -

559	Cavosie, A.J., Valley, J.W., and Wilde, S.A., 2005, Magmatic $\delta^{18}\text{O}$ in 4400–3900 Ma detrital
560	zircons: a record of the alteration and recycling of crust in the Early Archean: Earth and
561	Planetary Science Letters, v. 235, p. 663-681.
562	
563	Curtis, C.D., Coleman, M.L., and Love, L.G., 1986, Pore water evolution during sediment
564	burial from isotopic and mineral chemistry of calcite, dolomite and siderite
565	concretions: Geochimica et Cosmochimica Acta, v. 50, p. 2321-2334.
566	
567	Dale, A., John, C.M., Mozley, P.S., Smalley, P.C., and Muggeridge, A.H., 2014, Time-capsule
568	concretions: unlocking burial diagenetic processes in the Mancos Shale using carbonate
569	clumped isotopes: Earth and Planetary Science Letters, v. 394, p. 30-37.
570	
571	Egenhoff, S.O., 2017, The lost Devonian sequence - Sequence stratigraphy of the middle
572	Bakken member, and the importance of clastic dykes in the lower Bakken member shale,
572 573	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293,
572 573 574	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293, doi.org/10.1016/j.marpetgeo.2017.01.015
572 573 574 575	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293, doi.org/10.1016/j.marpetgeo.2017.01.015
572 573 574 575 576	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293, doi.org/10.1016/j.marpetgeo.2017.01.015 Egenhoff, S.O., Van Dolah, A., Jaffri, A., and Maletz, J., 2011, Facies architecture and
572 573 574 575 576 577	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293, doi.org/10.1016/j.marpetgeo.2017.01.015 Egenhoff, S.O., Van Dolah, A., Jaffri, A., and Maletz, J., 2011, Facies architecture and sequence stratigraphy of the Middle Bakken Member, Williston Basin, North Dakota, <i>in</i>
572 573 574 575 576 577 578	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293, doi.org/10.1016/j.marpetgeo.2017.01.015 Egenhoff, S.O., Van Dolah, A., Jaffri, A., and Maletz, J., 2011, Facies architecture and sequence stratigraphy of the Middle Bakken Member, Williston Basin, North Dakota, <i>in</i> Robinson, L., LeFever, J., and Gaswirth, S., eds., Bakken–Three Forks Petroleum System in
572 573 574 575 576 577 578 579	Bakken member, and the importance of clastic dykes in the lower Bakken member shale, North Dakota, USA: Marine and Petroleum Geology, v. 81, p. 278-293, doi.org/10.1016/j.marpetgeo.2017.01.015 Egenhoff, S.O., Van Dolah, A., Jaffri, A., and Maletz, J., 2011, Facies architecture and sequence stratigraphy of the Middle Bakken Member, Williston Basin, North Dakota, <i>in</i> Robinson, L., LeFever, J., and Gaswirth, S., eds., Bakken–Three Forks Petroleum System in the Williston Basin: Rocky Mountain Association of Geologists, Guidebook, p. 27–47 (on CD).

581	Ferdous, H., 2001, Regional sedimentology and diagenesis of the Middle Bakken member:
582	Implications for reservoir rock distribution in southern Saskatchewan (Doctoral dissertation,
583	University of Saskatchewan), 467 p.
584	
585	Freisatz, W.B., 1995, Fracture-enhanced porosity and permeability trends in the Bakken
586	Formation, Williston Basin, western North Dakota: 7 <sup>th</sup> International Williston Basin
587	Symposium, p. 389 - 398.
588	
589	Gaines, A.M., 1974, Protodolomite synthesis at 100 C and atmospheric pressure: Science, v.
590	183, p. 518-520.
591	
592	Giles, M.R. ed., 1997, Diagenesis: A Quantitative Perspective: Implications for Basin
593	Modelling and Rock Property Prediction: Dordrecht, Kluwer Academic Publishers, 526p.
594	
595	Giles, M.R., Indrelid, S.L., Beynon, G.V., and Amthor, J., 2000, The origin of large-scale quartz
596	cementation: Evidence from large data sets and coupled heat-fluid mass transport
597	modelling, in Worden, R.H., and Morad, S., eds., Quartz Cementation in Sandstones,
598	International Association Sedimentologists, Special Publication, 29, p. 21-38.
599	

600	Girard, J.P., Munz, I.A., Johansen, H., Hill, S., and Canham, A., 2001, Conditions and timing of
601	quartz cementation in Brent reservoirs, Hild Field, North Sea: constraints from fluid
602	inclusions and SIMS oxygen isotope microanalysis: Chemical Geology, v. 176, p. 73-92.
603	
604	Goldstein, R.H., 2001, Fluid inclusions in sedimentary and diagenetic systems: Lithos, v. 55,
605	p. 159-193, doi.org/10.1016/S0024-4937(00)00044-X
606	
607	Glasmann, J.R., Lundergard, P.D., Clark, R.A., Penny, B.K., and Collins, I.D., 1989,
608	Geochemical evidence for the history of diagenesis and fluid migration; Brent Sandstone,
609	Heather Field, North Sea: Clay Minerals, v. 24, p. 255-284.
610	
611	Gluyas, J., and Coleman, M., 1992, Material flux and porosity changes during sediment
612	diagenesis: Nature, v. 356, p. 52-54.
613	
614	Graham, C.M., Valley, J.W., and Winter, B.L., 1996, Ion microprobe analysis of <sup>18</sup> O/ <sup>16</sup> O in
615	authigenic and detrital quartz in the St. Peter Sandstone, Michigan Basin and Wisconsin
616	Arch, USA: contrasting diagenetic histories: Geochimica et Cosmochimica Acta, v. 60, p.
617	5101-5116.

619	Hart, B.S., Longstaffe, F.J., and Plint, A.G., 1992, Evidence for relative sea level change from
620	isotopic and elemental composition of siderite in the Cardium Formation, Rocky Mountain
621	Foothills: Bulletin of Canadian Petroleum Geology, v. 40, p. 52-59.
622	
623	Harwood, J., Aplin, A.C., Fialips, C.I., Iliffe, J.E., Kozdon, R., Ushikubo, T., and Valley, J.W.,
624	2013, Quartz cementation history of sandstones revealed by high-resolution SIMS oxygen
625	isotope analysis: Journal of Sedimentary Research, v. 83, p. 522-530.
626	
627	Haszeldine R.S. Samson I.M. and Cornford C. 1984. Dating diagenesis in a netroleum
629	hasin a new fluid inclusion method. Nature y 207 n 254 257
028	basin, a new nulu inclusion method. Nature, V. 507, p. 554-557.
629	
630	Holland, F.D. Jr, Hayes, M.D., Thrasher, L.C., and Huber, T.P., 1987, Summary of the
631	biostratigraphy of the Bakken Formation (Devonian and Mississippian) in the Williston basin,
632	North Dakota: 5 <sup>th</sup> International Williston Basin Symposium, p. 68 – 76.
633	
634	Hudson, J.D., and Anderson, T.F., 1989, Ocean temperatures and isotopic compositions
635	through time: Royal Society of Edinburgh, Transactions, Earth Sciences, v. 80, p. 183-192.
636	
637	Iampen, H.T., and Rostron, B.J., 2000, Hydrogeochemistry of pre-Mississippian brines,
638	Williston Basin, Canada-USA: Journal of Geochemical Exploration, v. 69, p. 29-35.
639	

640	Kaczmarek, S.E., and Sibley, D.F., 2007, A comparison of nanometer-scale growth and
641	dissolution features on natural and synthetic dolomite crystals: implications for the origin of
642	dolomite: Journal of Sedimentary Research, v. 77, p. 424-432.
643	
644	Karasinki, D.R., 2006, Sedimentology and hydrocarbon potential of the Devonian Three
645	Forks and Mississippian Bakken Formations, Sinclair Area, southeast Saskatchewan-
646	southwest Manitoba: Master's Dissertation, University of Manitoba, 436 p.
647	
648	Kita, N.T., Ushikubo, T., Fu, B., and Valley, J.W., 2009, High precision SIMS oxygen isotope
649	analyses and the effect of sample topography: Chemical Geology, v. 264, p. 43-57.
650	
651	Klein, J.S., Mozley, P., Campbell, A., and Cole, R., 1999, Spatial distribution of carbon and
652	oxygen isotopes in laterally extensive carbonate-cemented layers: implications for mode of
653	growth and subsurface identification: Journal of Sedimentary Research, v. 69, p. 184-201.
654	
655	Kozdon, R., Ushikubo, T., Kita, N.T., Spicuzza, M., and Valley, J.W., 2009, Intratest oxygen
656	isotope variability in the planktonic foraminifer <i>N. pachyderma</i> : Real vs. apparent vital
657	effects by ion microprobe: Chemical Geology, v. 258, p. 327-337.

659	Kuhn, P.P., Di Primio, R., Hill, R., Lawrence, J.R., and Horsfield, B., 2012, Three-dimensional
660	modeling study of the low-permeability petroleum system of the Bakken
661	Formation: American Association of Petroleum Geologists, Bulletin, v. 96, p. 1867-1897.
662	
663	Land, L.S., Milliken, K.L., and Mcbride, E.F., 1987, Diagenetic evolution of Cenozoic
664	sandstones, Gulf of Mexico sedimentary basin: Sedimentary Geology, v. 50, p. 195-225.
665	
666	Last, W., and Edwards, W., 1991, Petrology of the Middle Bakken Member in the Daly Field,
667	southwestern Manitoba: 6 <sup>th</sup> International Williston Basin Symposium, p. 64-69.
668	
669	Lee, M., and Savin, S.M., 1985, Isolation of diagenetic overgrowths on quartz sand grains for
670	oxygen isotopic analysis: Geochimica et Cosmochimica Acta, v. 49, p. 497-501.
671	
672	Li, H., Hart, B., Dawson, M., and Radjef, E., 2015, Characterizing the Middle Bakken:
673	laboratory measurement and rock typing of the Middle Bakken Formation: URTeC 217485,
674	13 p.
675	
676	Linzmeier, B.J., Kozdon, R., Peters, S.E., and Valley J.W., 2016, Oxygen isotope variability
677	within growth bands suggests daily depth migration behavior is recorded in Nautilus shell
678	aragonite: PLOS One, p. 1-31. DOI:10.1371/journal.pone.0153890
679	

680	Lyon, I.C., Burley, S.D., Mckeever, P.J., Saxton, J.M., and Macaulay, C., 2000, Oxygen isotope
681	analysis of authigenic quartz in sandstones; a comparison of ion microprobe and
682	conventional analytical techniques, in Worden, R.H. and Morad, S., eds., Quartz
683	Cementation in Sandstones, International Association of Sedimentologists, Special
684	Publication, 29, p. 299-316.
685	
686	Macaulay, C.I., Haszeldine, R.S., and Fallick, A.E., 1993, Distribution, chemistry, isotopic
687	composition and origin of diagenetic carbonates: Magnus Sandstone, North Sea: Journal of
688	Sedimentary Petrology, v. 63, p. 33-43.
689	
690	Machel, H.G., 2004, Concepts and models of dolomitization: a critical reappraisal, in
691	Braithwaite, C. J. R., Rizzi, G. and Darke, G., eds., The Geometry and Petrogenesis of
692	Dolomite Hydrocarbon Reservoirs, Geological Society of, London, Special Publication, 235, p.
693	7-63.
694	
695	Marchand, A.M., Macaulay, C.I., Haszeldine, R.S., and Fallick, A.E., 2002, Pore water
696	evolution in oilfield sandstones: constraints from oxygen isotope microanalyses of quartz
697	cement: Chemical Geology, v. 191, p. 285-304.
698	
699	McBride, E.F., and Milliken, K.L., 2006, Giant calcite-cemented concretions, Dakota
700	Formation, central Kansas, USA: Sedimentology, v. 53, p. 1161-1179.

```
701
```

702	McCabe, H.R., 1959, Mississippian stratigraphy of Manitoba: Manitoba: Department of
703	Mines and Natural Resources Mines Branch, Publication 58, 99 p.
704	
705	Meissner, F., 1978, Petroleum geology of the Bakken Formation Williston basin, North
706	Dakota and Montana, in The Economic Geology of the Williston Basin: Montana Geological
707	Society 24th Annual Conference. Williston Basin Symposium, p. 207 - 227.
708	
709	Meissner, F.F., 1991, Petroleum Geology of the Bakken Formation Williston Basin, North
710	Dakota and Montana: Montana Geological Society. Guidebook to Geology and Horizontal
711	Drilling of the Bakken Formation, p. 19 – 42.
712	
713	Millán, M.I., Machel, H., and Bernasconi, S.M., 2016, Constraining temperatures of
714	formation and composition of dolomitizing fluids in the Upper Devonian Nisku Formation
715	(Alberta, Canada) with clumped isotopes: Journal of Sedimentary Research, v. 86, p. 107-
716	112.
717	
718	Murray, R.C., and Lucia, F.J., 1967, Cause and control of dolomite distribution by rock
719	selectivity: Geological Society of America Bulletin, v. 78, p. 21-36.
720	

721	O'Neil, J.R., Clayton, R.N., and Mayeda, T.K., 1969, Oxygen isotope fractionation in divalent
722	metal carbonates: Journal of Chemical Physics, v. 51, p. 5547-5558.
723	
724	Osborne, M., and Haszeldine, S., 1993, Evidence for resetting of fluid inclusion temperatures
725	from quartz cements in oilfields: Marine and Petroleum Geology, v. 10, p. 271-278.
726	
727	Pitman, J.K., Price, L.C., and Lefever, J.A., 2001, Diagenesis and fracture development in the
728	Bakken Formation, Williston Basin: Implications for reservoir quality in the Middle
729	member [No. 1653]. US Department of the Interior, United States Geological Survey [USGS]
730	Professional Paper 1653, USGS, Denver, [November 2001], p. 19.
731	
732	Pollington, A.D., Kozdon, R., and Valley, J.W., 2011, Evolution of quartz cementation during
733	burial of the Cambrian Mount Simon Sandstone, Illinois Basin: In situ microanalysis of
734	δ <sup>18</sup> O: Geology, v. 39, p. 1119-1122.
735	
736	Robinson, A., and Gluyas, J., 1992, Model calculations of loss of porosity in sandstones as a
737	result of compaction and quartz cementation: Marine and Petroleum Geology, v. 9, p. 319-

738 323.

740	Rostron, B.J., and Holmden, C., 2003, Regional variations in oxygen isotopic compositions in
741	the Yeoman and Duperow aquifers, Williston basin (Canada-USA): Journal of Geochemical
742	Exploration, v. 78, p. 337-341.
743	
744	Schmid, S., Worden, R.H., and Fisher, Q.J., 2004, Diagenesis and reservoir quality of the
745	Sherwood Sandstone (Triassic), Corrib field, Slyne basin, west of Ireland: Marine and
746	Petroleum Geology, v. 21, p. 299-315.
747	
748	Sibley, D.F., 1982, The origin of common dolomite fabrics: clues from the Pliocene: Journal
749	of Sedimentary Petrology, v. 52, p. 1087-1100.
750	
751	Sibley, D.F., and Gregg, J.M., 1987, Classification of dolomite rock textures: Journal of
752	Sedimentary Petrology, v. 57, p. 967-975.
753	
754	Sibley, D.F., Dedoes, R. E., and Bartlett, T. R., 1987, Kinetics of dolomitization: Geology, v. 15,
755	p. 1112-1114.
756	
757	Simenson, A., 2010, Depositional Facies and Petrophysical Analysis of the Bakken Formation,
758	Parshall Field, Mountrail County, North Dakota (Doctoral dissertation, Colorado School of
759	Mines), 190 p.
761	Śliwiński, M.G., Kitajima, K., Kozdon, R., Spicuzza, M.J., Fournelle, J.H., Denny, A., and Valley,
-----	---
762	J.W., 2016a, Secondary ion mass spectrometry bias on isotope ratios in dolomite-ankerite,
763	Part I: $\delta^{18}$ O matrix effects: Geostandards and Geoanalytical Research, v. 40, p. 157-172.
764	
765	Śliwiński, M.G., Kozdon, R., Kitajima, K., Denny, A., and Valley, J.W., 2016b, Microanalysis of
766	carbonate cement $\delta^{18}\text{O}$ in a CO_2-storage system seal: Insights into the diagenetic history of
767	the Eau Claire Formation (Upper Cambrian), Illinois Basin: American Association of
768	Petroleum Geologists, Bulletin, v. 100, p. 1003-1031.
769	
770	Smith, M. G., and Bustin, R. M., 1996, Production and preservation of organic matter during
771	deposition of the Bakken Formation (Late Devonian and Early Mississippian), Williston
772	Basin: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 142, p. 185-200.
773	
774	Staruiala, A., Qing, H., Chi, G., Stern, R., and Petts, D., 2013, Dolomite petrography and
775	stable isotope geochemistry of the Bakken Formation, southeastern Saskatchewan, in
776	Summary of Investigations 2013, Volume 1, Saskatchewan Geological Survey, Saskatchewan
777	Ministry of the Economy, Miscellaneous Report 2013-4.1, Paper A-8, 10 p.
778	
779	Sullivan, M.D., Macaulay, C.I., Fallick, A.E., and Haszeldine, R.S., 1997, Imported quartz
780	cement in aeolian sandstone grew from water of uniform composition but has complex
781	zonation: Terra Nova, v. 9, p. 237-241.

783	Taylor, K.G., Gawthorpe, R.L., Curtis, C.D., Marshall, J.D., and Awwiller, D.N., 2000,
784	Carbonate cementation in a sequence-stratigraphic framework: Upper Cretaceous
785	sandstones, Book Cliffs, Utah-Colorado: Journal of Sedimentary Research, v. 70, p. 360-372.
786	
787	Taylor, T.R., Giles, M.R., Hathon, L.A., Diggs, T.N., Braunsdorf, N.R., Birbiglia, G.V., Kittridge,
788	M.G., Macaulay, C.I., and Espejo, I.S., 2010, Sandstone diagenesis and reservoir quality
789	prediction: Models, myths, and reality: American Association of Petroleum Geologists,
790	Bulletin, v. 94, p. 1093-1132.
791	
792	Vahrenkamp, V.C., and Swart, P.K., 1994, Late Cenozoic dolomites of the Bahamas:
793	Metastable analogues for the genesis of ancient platform dolomites, in Purser, B., Tucker M.
794	and Zenger, D., eds., Dolomites: A Volume in Honour of Dolomieu, International Association
795	of Sedimentologists, Special Publication, 21, p.133-153.
796	
797	Valley, J.W., and Kita, N.T., 2009, In situ oxygen isotope geochemistry by ion microprobe, in
798	Fayek M., ed., Mineralogical Association of Canada Short Course: Secondary Ion Mass
799	Spectrometry in the Earth Sciences, v. 41, p. 19-63

801	Van Geldern, R., Joachimski, M.M., Day, J., Jansen, U., Alvarez, F., Yolkin, E.A., AND Ma, X.P.,
802	2006, Carbon, oxygen and strontium isotope records of Devonian brachiopod shell
803	calcite: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 240, p. 47-67.
804	
805	Vasconcelos, C., McKenzie, J.A., Warthmann, R., and Bernasconi, S.M., 2005, Calibration of
806	the $\delta^{18}$ O paleothermometer for dolomite precipitated in microbial cultures and natural
807	environments: Geology, v. 33, p. 317-320.
808	
809	Warren, J., 2000, Dolomite: occurrence, evolution and economically important
810	associations: Earth-Science Reviews, v. 52, p. 1-81.
811	
812	Webster, R.L., 1984, Petroleum source rocks and stratigraphy of the Bakken Formation in
813	North Dakota, in Woodward, J., Meissner, F.F., and Clayton, J.L., eds., Hydrocarbon Source
814	Rocks of the Greater Rocky Mountain Region, Rocky Mountain Association of Geologists
815	1984 Symposium, p. 57-81.

817 Weyl, P.K., 1960, Porosity through dolomitization: conservation of mass requirements:

S18 Journal of Sedimentary Petrology, v. 30, p. 85–90.

820	Whitaker, F.F., and Xaio, Y., 2010, Reactive transport modeling of early burial dolomitization
821	of carbonate platforms by geothermal convection: American Association of Petroleum
822	Geologists, Bulletin, v. 94, p. 889-917.
823	
824	Whitaker, F.F., Smart, P. L., and Jones, G.D., 2004, Dolomitization: from conceptual to
825	numerical models, in Braithwaite, C.J.R., Rizzi, G. and Darke, G., eds., The geometry and
826	petrogenesis of dolomite hydrocarbon reservoirs: Geological Society, London, Special
827	Publication, 235, p. 99-139.
828	
829	Wilkinson, M., 1991, The concretions of the Bearreraig Sandstone Formation: geometry and
830	geochemistry: Sedimentology, v. 38, p. 899-912.
831	
832	Williams, L.B., Hervig, R.L., AND Bjørlykke, K., 1997, New evidence for the origin of quartz
833	cements in hydrocarbon reservoirs revealed by oxygen isotope microanalyses: Geochimica
834	et Cosmochimica Acta, v. 61, p. 2529-2538.
835	
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873

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and fine nature.

894

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but are in most cases smaller than the data-point marker.

901

**Figure 10** - Secondary electron micrographs showing positions of SIMS analyses.  $\delta^{18}O_{SMOW}$ values are labelled for each analysis. A) Analysis pits ablated from dolomite (1 & 2) and calcite (3), sample 2, sites 2-004 (1), 2-013 (2) and 2-081 (3) [Excluded due to a boundary breach]. B) An analysis pit at the center of the dolomite crystal, sample 1, site 1-051. C) four analysis pits; 2-4 were taken in a transect across a crystal of dolomite, sample 1, sites 1-073

907	(1), 1-071 (2), 1-071a (3) and 1-071b (4) [Note that analysis 1 was excluded from the dataset
908	due to a boundary break]. D) Analysis pits from three crystals of dolomite (1) and calcite (2,
909	3 and 4), sample 3, sites 3-033 (1), 3-022 (2), 3-026 (3), 3-021 (4). [Note that analyses 1 and
910	2 were excluded from the data set due to a boundary breaches]. Refer to Table 1 and
911	Supplementary Information for further information on each sample and individual sites.
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914	A) Calcite, assuming $\delta^{18}O_{water}$ = -1.5‰; B) Dolomite, assuming $\delta^{18}O_{water}$ = -1.5‰; C)
915	Dolomite, assuming $\delta^{18}O_{water}$ = +3‰; D) Dolomite, assuming the $\delta^{18}O_{water}$ = +7.5‰.
916	

## 918 Figure 1.





























951 **Table 1** – Mineralogical and bulk stable carbon and oxygen isotope data for calcite and

952 dolomite obtained by sequential acid dissolution. Carbonate minerals calcite and dolomite

953 were separated using conventional phosphoric acid digestion and gas-source mass

954 spectrometric analyses on selected middle Bakken samples. Calcite is considered to be the

955 CO<sub>2</sub> extracted after 3 hours of acid digestion at 25°C in a vacuum and dolomite is considered

to be the CO<sub>2</sub> extracted after 24 hours at 100°C in a vacuum. Note that SIMS data from this

study indicate that calcite and dolomite were not separated by this procedure. SIMS sample

958 numbers are also shown.

Depth (m)	Sample	SIMS	Facies	Oxygen		XRD Mineralogy (wt %)										
	NO.	Sample			Extr	action										
		NO.		Calcite	e @ 25°C	Dolomite										
				Carbon (δ <sup>13</sup> C <sub>VPDB</sub> )	Oxygen (δ <sup>18</sup> Ο <sub>VSMOW</sub> )	Carbon (δ <sup>13</sup> C <sub>VPDB</sub> )	Oxygen (δ <sup>18</sup> O <sub>VSMOW</sub> )	Quartz	Illite & Mica	Potassium Fspar	Plagioclase Fspar	Calcite	Dolomite	Pyrite	Halite	Chlorite
969.93	1-36B	7	E	-0.2	26.4	-0.5	25.7	42	13	4	5	3	29	2	2	0
970.02	1-37B	N/A	E	-0.8	26.1	-0.2	26.7	33	16	4	5	3	37	2	1	0
970.10	1-38B	N/A	E	-2.5	23.7	0.8	28.6	19	4	2	2	56	16	1	0	0
970.21	1-39B	N/A	E	-0.4	26.5	0.0	27.4	28	10	4	3	7	47	1	0	0
970.98	2_iiA	6	D2	3.1	25.8	1.5	28.7	46	3	4	2	31	14	1	0	0
971.00	4_iiA	5	D2	3.8	27.1	2.7	30.9	46	4	3	1	30	15	1	0	0
972.43	9_iiA	4	D1	3.3	26.0	3.6	30.8	38	5	6	3	36	12	0	0	0
	17_iiA	3	С	2.0	24.4	-0.3	26.1									
973.95								45	8	8	5	14	21	1	0	0
975.96	11_iiA	2	Grad	-0.5	25.3	-0.5	27.0	31	6	5	4	11	42	1	0	0
977.12	1-113B	N/A	В	-3.2	25.4	-3.3	26.5	18	11	4	3	21	41	1	1	1
977.17	1-114B	N/A	В	2.5	24.7	-2.1	19.8	29	12	4	3	37	12	2	0	1
977.27	1-115B	N/A	В	1.6	25.3	-0.3	26.1	23	10	3	3	53	5	3	0	1
977.36	1-116B	N/A	В	1.5	25.5	-0.3	27.1	30	13	4	3	36	9	3	0	1

960	- Supporting Online Material –
961	
962	Geochemistry of calcite and dolomite in the Middle Bakken Formation, USA.
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969	

## 971 Ion Microprobe Analysis of Carbonate Minerals

In situ oxygen isotope data were acquired in the WiscSIMS Laboratory at the University of Wisconsin–Madison by a CAMECA IMS 1280 large-972 radius multicollector ion microprobe (Kita et al., 2009, Valley and Kita 2009). Carbonate minerals calcite and dolomite were analyzed during 973 four analytical sessions in October 2016 (Error! Reference source not found.). During the analytical sessions the <sup>133</sup>Cs<sup>+</sup> primary ion beam had 974 an intensity of ~1.2 nA generating a beam diameter of ~13  $\mu$ m. The typical secondary <sup>16</sup>O<sup>-</sup> ion intensity was ~2.9x10<sup>9</sup> cps. Measurements were 975 performed in multi-collector Faraday Cup mode and with conditions similar to those reported by Kozdon et al. (2009). The secondary O<sup>-</sup> ions 976 (<sup>16</sup>O<sup>-</sup>, <sup>16</sup>O<sup>1</sup>H<sup>-</sup>, <sup>18</sup>O<sup>-</sup>) were detected by Faraday cup. Charging of the sample surface was compensated by Au-coating and an electron flood gun. 977 Grains of the University of Wisconsin calcite standard, UWC-3 [ $\delta^{18}$ O(VSMOW) of UWC-3 is 12.49‰ (±0.03‰ 1 SD, n= 9)] was mounted at the 978 centre of sample mounted in the polished block (Kozdon et al., 2009). Four consecutive measurements of UWC-3 calcite standard were 979 performed before and after every set of 8–17 sample analyses. The 2 SD of a set of bracketing standard analyses is assigned as the 980 reproducibility of the bracketed sample analyses. Detailed analytical protocols are described in Kita et al. (2009). 981

982

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984

**Table X** – Full details of SIMS & SEM-WDS analyses for individual crystals. Data not included in the plots and interpretation are also included to show the full bracketed analyses. External precision (reproducibility) is reported for each bracket. The 'Mineral/ Type/Comment' column gives details of the analysis including dolomite phase type as a number e.g. type 1 is '1', NF=Crystal was not found post-SIMS analysis, NC= Crystal was not composed of a carbonate mineral, Calcite = calcite crystal. What is "Er" type in that column? Can you annotate which Mass Biases were corrected using the calibration curve? Would it be possible/prudent to include the standard calibration measurements (up to you)?

No.	Sample ID	<sup>16</sup> O	δ <sup>18</sup> Ο	2SE	Mass	δ18Ο	2SD (ext.)	OH/O	Mineral / Type /	CaO	MgO	FeO
		(Gcps)	‰	(int.)	Bias	‰			Comment			
			measu			VSMO						
Com	nla Maurit Na. 2, 42 um has		red	Ostahar	C4h	W						
2015	pie mount No. 2. 15 µm bea	un, 1.2 na ir	itensity.	October	otn							
1	2 UWC3 G1	2.99	5.22	0.45								
2	2 UWC3 G1	3	5.04	0.45								
3	2 UWC3 G1	3.01	5.19	0.53								
4	2 UWC3 G2	2.97	5.2	0.5								
5	2-004	3.14	14.29	0.47	-12.28	26.9	0.21	0.003	2	51.93	51.44	0
6	2-005	3.07	15.38	0.45			0.21	0.005	NF			
7	2-006	3.01	13.75	0.46	-12.28	26.36	0.21	0.001	1	54.93	53.06	0.7
8	2-007	2.01	7.94	0.27	-5.41	13.41	0.21	0.001	NC			
9	2-008	2.91	13.95	0.53	-12.28	26.56	0.21	0.002	3			
10	2 UWC3 G1		5.34	0.54								
11	2 UWC3 G1		5.34	0.47								
12	2 UWC3 G1		5.15	0.54								
13	2 UWC3 G1		5.13	0.56								
		Average:	5.2	2SD:	0.21							
14	2-009	2.15	7.02	0.22	-5.41	12.5	0.25	0.002		39.95	61.79	0.0
15	2-009-2	2.04	8.14	0.3	-5.41	13.63	0.25	0.004	NC			
16	2-009-3	2.12	10.04	0.23	-5.41	15.54	0.25	0.005	NC			
17	2-011	3.09	13.41	0.39	-11.64	25.35	0.25	0.005	2	36.69	63.31	0.5
18	2-012	3.07	14.41	0.71	-12.3	27.05	0.25	0.006	1	39.16	62.72	0.0
19	2-013	3.05	14.15	0.45	-12.3	26.78	0.25	0.008	2			
20	2-017	2.89	17.4	0.45	-11.64	29.39	0.25	0.004	3	39.98	61.04	0.6
21	2-018	2.07	7.9	0.29	-5.41	13.38	0.25	0.006	NC			
22	2-061	2.08	10.35	0.52	-5.41	15.85	0.25	0.006	NC			
23	2-021	2.09	7.01	0.32	-5.41	12.49	0.25	0.005	NC			

24	2 UWC3 G1	2.85	5.13	0.47								
25	2 UWC3 G1	2.81	5.29	0.5								
26	2 UWC3 G1	2.9	5.01	0.48								
27	2 UWC3 G1	2.96	5.08	0.47								
		Average:	5.18	2SD:	0.25							
28	2-022	3.19	13.42	0.49			0.18	0.006	NF			
29	2-022a	3.17	12.32	0.43	-12.33	24.96	0.18	0.002	2	41.56	59.51	0.1
30	2-022b	3.03	16.59	0.49	-12.33	29.28	0.18	0.002	2			
31	2-024	3.06	12.81	0.43	-12.33	25.46	0.18	0.003	4	38.9	61.14	0.1
32	2-025	3.05	13.18	0.5	-12.33	25.83	0.18	0.004	3	37.46	62.69	0.1
33	2-026	3.11	12.2	0.45	-10.93	23.38	0.18	0.001	2	43.13	56.1	1.1
34	2-027	2.08	15.05	0.28	-5.45	20.61	0.18	0.010	NF			
35	2-028	3.2	15.79	0.53	-9.57	25.6	0.18	0.002	2	39.87	69.81	2.9
36	2-028a	2.09	6.97	0.22	-5.45	12.48	0.18	0.001	NC			
37	2-029	3.01	18.6	0.49	-10.93	29.86	0.18	0.004	1	38.61	60.56	1.0
38	2 UWC3 G1	2.84	5.12	0.5								
39	2 UWC3 G1	2.82	5.13	0.57								
40	2 UWC3 G1	2.9	5.26	0.45								
41	2 UWC3 G1	2.93	5.17	0.45								
		Average:	5.15	2SD:	0.18							
42	2-030	2.99	14.99	0.38			0.14	0.014	NF			
43	2-031	3.19	18.44	0.53			0.14	0.014	NF			
44	2-032	2.98	14.85	0.5			0.14	0.014	NF			
45	2-033	3.12	15.97	0.39	-12.28	28.6	0.14	0.006	4	41.41	59.02	0.1
46	2-034	2.86	17.24	0.58			0.14	0.003	NF			

47	2-035	3.07	13.65	0.53			0.14	0.007	NF			
48	2-036	2.94	15.39	0.49			0.14	0.004	NF			
49	2-036a	2.95	14.78	0.42	-12.28	27.39	0.14	0.004	4	42.72	57.84	1.7
50	2-038	3	12.82	0.57			0.14	0.005	NF			
51	2-039	3.02	12.82	0.52	-12.28	25.41	0.14	0.002	4	36.21	64.25	0.0
52	2 UWC3 G1	2.82	5.31	0.51								
53	2 UWC3 G1	2.8	5.27	0.58								
54	2 UWC3 G1	2.89	5.22	0.53								
55	2 UWC3 G1	2.94	5.16	0.49								
		Average:	5.2	2SD:								
56	2-040	3.12	14.48	0.52	-12.32	27.13	0.31	0.006	3	39.35	60.59	0.2
57	2-041	3.16	14.53	0.49			0.31	0.005	NF			
58	2-042	3.11	14.52	0.52	-12.32	27.18	0.31	0.002	3	36.17	63.79	0.3
59	2-043	3.04	15.06	0.49			0.31	0.004	NF			
60	2-043a	3.03	16.69	0.39	-12.32	29.37	0.31	0.004	2	36.92	63	0.1
61	2-044	3.12	12.89	0.58	-11.66	24.84	0.31	0.002	3	40.59	59.44	0.6
62	2-045	3.06	13.27	0.45			0.31	0.003	NF			
63	2-046	2.95	15.55	0.43	-12.32	28.22	0.31	0.005	3	36.21	63.65	0.0
64	2-047	3.03	13.84	0.42	-12.32	26.49	0.31	0.002	3	36.81	63.64	0.0
65	2-048	2.98	15.19	0.43	-2.21	17.44	0.31	0.006	2	38.17	60.2	0.0
66	2-049	3.03	14.03	0.58	-12.32	26.68	0.31	0.002	3	39.55	61.79	0.1
67	2-081	2.72	16.58	0.49	-12.32	29.26	0.31	0.002	2	39.07	61.38	0.0
68	2 UWC3 G1	2.83	4.82	0.5								
69	2 UWC3 G1	2.82	5.27	0.49								
70	2 UWC3 G1; Cs 127-128	2.92	5.13	0.52								
71	2 UWC3 G1	2.96	5.13	0.53								

		Average:	5.16	2SD:	0.31							
Sam	ple Mount No. 3. 13 um bea	am. 1.2 nA ir	ntensitv.	October	· 6th							
2015		,			•							
72	3 UWC3 G1	2.94	5.02	0.5								
73	3 UWC3 G1	2.94	5.1	0.5 2								
74	3 UWC3 G2	2.92	5.02	0.5								
75	3 UWC3 G2	2.89	5.31	0.4 9								
76	3-012	2.05	4.78	0.3	-5.4	10.23	0.33	0.001	NC			
77	3-015	2.94	14.77	0.7	-11.63	26.72	0.33	0.004	2	52.64	47.32	0.2
78	3-016	3.03	13.9	0.5	-11.63	25.83	0.33	0.001	1	51.65	48.27	0.4
79	3-017	3	16.62	0.4 9	-11.63	28.59	0.33	0.003	3	50.81	48.94	0.0
80	3 UWC3 G1	2.84	5.3	0.5 2								
81	3 UWC3 G1	2.83	5.49	0.5 6								
82	3 UWC3 G1	2.94	5.13	0.5 2								
83	3 UWC3 G1	2.95	5.18	0.4 9								
		Average:	5.19	2S D:	0.33							
84	3-018	3.19	16.43	0.4 1	-12.19	28.97	0.29	0.001	2	50.64	49.55	0.1
85	3-021	2.98	15.19	0.4 4	-12.19	27.71	0.29	0.003	4	53.39	46.96	0.1

86	3-022	2.98	12.54	0.4 3	-11.53	24.35	0.29	0.003	3	50.75	48.8	0.4
87	3-023	2.94	13.38	0.5 3	-12.19	25.88	0.29	0.005	2	50.85	49.03	0.0
88	3-024	2.87	14.03	0.3 9	-12.19	26.54	0.29	0.004	1	52.43	48.64	0.0
89	3-025	3.07	17.98	0.4 5	-8.83	27.04	0.29	0.002	4	53.58	44.76	0.0
90	3-026	2.65	16.98	0.5 4	-12.19	29.53	0.29	0.002	3	98.6	1.33	0.2
91	3-026a	2.83	14.72	0.4 5	-11.53	26.55	0.29	0.003	3	51.79	49.36	0.6
92	3-027	2.72	17.22	0.4 2	-12.19	29.77	0.29	0.005	2	54.28	44.19	1.5
93	3 UWC3 G1	2.68	5.34	0.5								
0.4	21114/02/04	0.00	<b>F F A</b>	4								
94	3 UVVC3 GT	2.08	5.51	0.5								
95	3 UWC3 G1	2.77	5.26	0.4 8								
96	3 UWC3 G1	2.91	5.18	0.5								
		Average:	5.3	2S D:	0.29							
97	3-028	3.06	13.29	0.5 4	-12.21	25.82	0.23	0.004	2	52.72	47.71	0.0
98	3-029	2.13	10.36	0.3	-5.32	15.77	0.23	0.008	NC			
99	3-030	2.02	11.45	0.2 8	-5.32	16.86	0.23	0.009	NC			
100	3-031	2.13	7.74	0.2	-5.32	13.14	0.23	0.001	NC			
101	3-032	3.23	14.37	0.5 3	-12.21	26.91	0.23	0.004	4	50.16	49.34	0.5
102	3-033	2.79	17.41	0.5 1			0.23	0.004	NF			
103	3-034	2.91	12.47	0.5 1			0.23	0.004	NF			

104	3-035	1.94	15.02	0.3	-5.32	20.45	0.23	0.001	NC			
105	3-036	2.94	12.58	0.4 3			0.23	0.004	NF			
106	3-037	3.08	15.2	0.5 2			0.23	0.005	NF			
107	3 UWC3 G1	2.88	5.19	0.5 3								
108	3 UWC3 G1	2.87	5.3	0.5								
109	3 UWC3 G1	2.87	5.16	0.4 3								
110	3 UWC3 G1	2.87	5.22	0.5 7								
		Average:	5.27	2S D:	0.23							
111	3-038	2.72	16.68	0.5			0.27	0.005	NF			
112	3-039	2.93	17.25	0.4 3			0.27	0.006	NF			
113	3-040	2.93	15.55	0.4 5			0.27	0.005	NF			
114	3-041	2.79	14.54	0.4 6			0.27	0.006	NF			
115	3-092	2.09	12.91	0.2 5	-5.31	18.32	0.27	0.001	NC			
116	3-093	3	15.58	0.4 8	-12.2	28.13	0.27	0.004	3	52.56	46.99	0.9
117	3-096	2.6	17.09	0.5 1	-12.2	29.66	0.27	0	2	98.55	1.16	0.2
118	3-097	2.87	15.09	0.5 5	-12.2	27.63	0.27	0.003	2	53.57	46.54	3.5
		0.55										
119	3 UWC3 G1	2.72	5.42	0.5 3								
120	3 UWC3 G1	2.69	5.55	0.5								

121	3 UWC3 G1; Cs 131-132	2.78	5.23	0.5 1								
122	3 UWC3 G1; Cs 132-133	2.94	5.18	0.4 1								
		Average:	5.28	2S D:	0.27							
126	3-098	3.29	16.62	0.4 7	-12.19	29.16	0.26	0.002	1	53.61	41.58	4.5
127	3-099	3.23	14.44	0.5 4	-12.19	26.95	0.26	0.020	1	50.64	47.75	1.7
128	3-091	2.82	17.36	0.5 4	-12.19	29.91	0.26	0.005	Calcite	97.25	2.54	0.1
129	3-090	3.19	15.1	0.4 4	-12.19	27.62	0.26	0.002	6	51.26	48.1	1.1
130	3-089	3.04	13.65	0.4 5	-12.19	26.15	0.26	0.005	2	65.33	36.39	0.2
131	3-088	3.06	15.73	0.5 7	-12.19	28.26	0.26	0.005	2	54.21	43.54	3.0
132	3-087	2.72	17.08	0.6 1	-12.19	29.63	0.26	0.003	Calcite	98.77	1.32	0.4
133	3-086	3.19	17.19	0.5 4	-12.19	29.74	0.26	0.002	6			
134	3-085	1.94	11.54	0.2 6	-5.3	16.93	0.26	0.001	NC			
135	3-084	2.02	9.39	0.2	-5.3	14.77	0.26	0.001	NC			
136	3-084a	2.09	3.61	0.2 9	-5.3	8.95	0.26	0.000	NC			
137	3-084b	3.03	13.8	0.4 6	-12.09	26.2	0.26	0.002	2	52.39	47.48	0.5
138	3-083	2.92	16.61	0.4 5	-12.19	29.15	0.26	0.003	2	51.34	49.07	0.6
139	3-081	2.97	15.22	0.5 1			0.26	0.004	3	49.49	50.29	0.0
140	3-080	2.98	15.04	0.5 7	-12.19	27.57	0.26	0.005	3	51.46	49.14	0.0
141	3-080a	2.85	14.38	0.5	-12.19	26.89	0.26	0.004	3	54.12	45.84	0.1

142	3-080b	3.03	18.67	0.3 9	-12.19	31.23	0.26	0.004	2	53.89	44.37	2.8
143	3 UWC3 G1	2.76	5.18	0.4 7								
144	3 UWC3 G1	2.73	5.3	0.5 1								
145	3 UWC3 G1	2.72	5.27	0.3 8								
146	3 UWC3 G1	2.71	5.25	0.5 6								
		Average:	5.3	2S D:	0.26							
Sam 2015	ple Mount No. 4. 13 µm bea	ım, 1.2 nA in	itensity.	Octob	ber 7th							
147	4 UWC3 G1	2.84	5.03	0.5								
148	4 UWC3 G2	2.87	5.37	0.5 5								
149	4 UWC3 G2	2.86	5.34	0.5 2								
150	4 UWC3 G2	2.87	5.19	0.5 1								
151	4-004	2.87	16.2 9	0.5 4	-12.3	28.94	0.26	0.002	Calcite	99.41	0.59	0.0
152	4-005	2.97	14.1 1	0.5 6	-12.3	26.74	0.26	0.006	3	29.56	70.59	0.1
153	4-006	2.72	19.1	0.5 6	-12.3	31.79	0.26	0.003	2	96.84	3.53	0.0
154	4-007	3.12	14.5 2	0.3 3	-11.64	26.47	0.26	0.001	4	43.54	56.22	0.3
155	4-008	2.11	5.18	0.2 1	-5.41	10.65	0.26	0.000	NC			

156	4-009	2.94	13.4 9	0.5 8	-12.3	26.11	0.26	0.002	4	42.06	57.74	0.0
157	4-010	3.03	14.6 1	0.6	-12.3	27.25	0.26	0.003	4	40.07	59.27	0.6
158	4-011	2.54	19.2 6	0.4 2				0.004	Er	95.32	3.47	
159	4 UWC3 G2	2.83	5.1	0.5								
160	4 UWC3 G2	2.85	5.12	0.4								
161	4 UWC3 G2	2.86	5.27	0.5 2								
162	4 UWC3 G2	2.89	5.04	0.5 3								
		Average:	5.19	2S D:	0.19							
163	4-012	3.11	12.6	0.4	-11.75	24.71	0.22	0.008	3	40.07	59.27	0.6
			7	4								
164	4-013	2.9	16.7 2	0.4 5	-12.41	29.5	0.22	0.002	Calcite	96.74	0.9	1.1
165	4-014	2.81	17.5 6	0.5 3	-12.41	30.35	0.22	0.003	Calcite	97.44	1.78	0.3
166	4-015	3.12	15	0.4 4	-12.41	27.76	0.22	0.003	2	42.26	57.67	0.2
167	4-016	3.32	16.5 7	0.5 7	-12.41	29.34	0.22	0.003	3	42.62	57.56	0.3
168	4-017	2.84	17.7 7	0.7 1	-12.41	30.56	0.22	0.010	Calcite	96.72	3.11	0.6
169	4-018	2.94	17.8 1	0.5 4	-12.41	30.6	0.22	0.003	Calcite	94.79	2.96	1.0
170	4-018a	3	18.7 4	0.5 9	-12.41	31.54	0.22	0.003	Calcite	95.49	4.4	0.0
171	4 UWC3 G2	3.19	4.98	0.5 9								

172	4 UWC3 G2	3.2	5.14	0.4 5								
173	4 UWC3 G2	3.15	4.97	0.4 9								
174	4 UWC3 G2	3.12	4.95	0.4 8								
		Average:	5.07	2S D:	0.22							
175	4-019	3.04	19.7 1	0.5	-12.46	32.58	0.15	0.002	Calcite	96.63	3.63	0.1
176	4-020	2.98	19.1 6	0.5 3	-12.46	32.03	0.15	0.002	Calcite	98.56	3.27	0.0
177	4-021	2.95	19.7 1	0.5 1	-12.46	32.58	0.15	0.002	Calcite	98.64	3.09	0.0
178	4-022	2.8	18.2	0.5 7	-12.46	31.05	0.15	0.003	Calcite	97.4	3.76	0.4
179	4-023	3.09	18	0.4 6	-12.46	30.85	0.15	0.002	Calcite	97.83	2.69	0.0
180	4-024	3.05	20	0.4 8	-11.81	32.18	0.15	0.001	3	53.01	46.48	0.6
181	4-025	3.08	18.2 9	0.5 8	-12.46	31.14	0.15	0.004	Calcite	95.31	4.3	0.0
182	4-026	3.14	17.7 1	0.4 6	-12.46	30.56	0.15	0.002	Calcite	95.67	4.53	0.0
183	4 UWC3 G2	3.26	5.05	0.5 1								
184	4 UWC3 G2	3.28	4.91	0.4 7								
185	4 UWC3 G2	3.16	5.04	0.5 1								
186	4 UWC3 G2	3.14	5.08	0.4 4								
		Average:	5.01	2S D:	0.15							

187	4-027	2.96	19.6 1	0.5 1	-12.45	32.46	0.18	0.000	Calcite	96.81	3.25	0.0
188	4-066	2.92	18.5 2	0.4 8	-5.8	24.46	0.18	0.002	2			
189	4-074	2.95	17.4 3	0.4 5	-12.45	30.25	0.18	0.004	Calcite	92.15	7.51	0.0
190	4-074a	3.44	15.4 1	0.3 5	-12.45	28.21	0.18	0.001	3	29.05	72.06	0.0
191	4-074b	3.07	19.7 7	0.4 6	-12.45	32.62	0.18	0.003	Calcite	94.64	5.6	0.0
192	4-028	3.13	19.4 1	0.4 9	-12.45	32.26	0.18	0.001	Calcite	98.12	1.63	0.1
197	4 UWC3 G2	3.24	4.93	0.5 4								
198	4 UWC3 G2	3.25	5.01	0.5 4								
199	4 UWC3 G2	3.14	5.08	0.5 1								
200	4 UWC3 G2	3.01	5.19	0.5								
		Average:	5.03	2S D:	0.18							
201	4-029	2.89	17.3 5	0.5 6	-12.33	30.05	0.3	0.000	Calcite	97.09	2.66	0.2
202	4-030	2.81	20.1 1	0.4 4	-12.33	32.85	0.3	0.002	Calcite	95.89	4.69	0.0
203	4-031	3.03	15.3 7	0.4 2	-12.33	28.05	0.3	0.004	2	43.23	57.03	0.0
204	4-032	2.7	19.1	0.5 4	-12.33	31.83	0.3	0.004	Calcite	96.96	4.33	0.0
205	4-033	2.82	18.5 3	0.4 7	-12.33	31.25	0.3	0.003	Calcite	98.43	2.05	0.3
206	4-034	3.08	15.3	0.4	-12.33	28.07	0.3	0.003	3	43.63	56.02	0.0
			9	0								

208	4-035a	2.73	18.8 9	0.5 3	-12.33	31.61	0.3	0.004	Calcite	99.73	2.26	0.0
209	4-036	2.86	18.1 1	0.5 1	-12.33	30.82	0.3	0.001	Calcite	99.77	0	0.0
210	4 UWC3 G2	3.02	5.33	0.5 5								
211	4 UWC3 G2	3.05	5.18	0.4 5								
212	4 UWC3 G2	3.04	5.35	0.5 2								
213	4 UWC3 G2	3.06	5.11	0.4 7								
		Average:	5.15	2S D:	0.3							
Sam 2015	ple Mount No. 4. 13 µm bea *	ım, 1.2 nA iı	ntensity.	Octob	per 7th							
214	4 UWC3 G2	3.09	5.3	0.4 6								
215	4 UWC3 G2	2.99	5.17	0.5 5								
216	4 UWC3 G2	2.95	5.16	0.5 3								
217	4 UWC3 G2	2.97	5.24	0.5 1								
218	4-038	2.16	4.78	0.2 3	-5.34	10.18	0.21	0.001	NC			
219	4-039	2.89	19.25	0.5 3	-6.37	25.78	0.21	0.001	6	95.97	3.56	0.0
220	4-048	2.89	17.3	0.4 6	-12.23	29.9	0.21	0.002	Calcite	99.15	0.89	0.5
221	4-051	2.74	18.27	0.4 8	-12.23	30.88	0.21	0.005	Calcite	98.53	1.41	0.5
222	4-056	2.38	21.05	0.5 4	-12.23	33.7	0.21	0.000	Calcite	95.62	3.99	0.2

223	4 UWC3 G2	2.69	5.49	0.5 1								
224	4 UWC3 G2	2.91	5.25	0.5 2								
225	4 UWC3 G2	3	5.19	0.4 7								
226	4 UWC3 G2	3.06	5.22	0.4								
		Averag e:	5.25	2S D:	0.21							
227	4-057	2 98	19 57	0.5	-12 32	32 29	0.38	0.000	Calcite	96 53	3 34	0.0
221	- 007	2.00	10.07	3	12.02	02.20	0.00	0.000	Odicite	50.55	0.04	0.0
228	4-058	3.23	12.41	0.4 1	-12.32	25.04	0.38	0.008	2	41.6	59.03	0.0
229	4-059	2.98	19.76	0.5 8	-12.32	32.48	0.38	0.000	Calcite	96.4	2.72	0.4
230	4-061	3.22	12.15	0.4 3	-11.66	24.1	0.38	0.002	2	38.76	60.38	0.6
231	4-069	2.27	12.13	0.2 3	-5.43	17.66	0.38	0.000	NC			
232	4-069a	3.23	12.25	0.4 6	-12.32	24.88	0.38	0.001	2	38.39	62.63	0.4
233	4-070	3.02	19.52	0.5 2	-10.92	30.77	0.38	0.001	3	97.11	3.82	0.1
234	4-072	3.02	18.12	0.5 5	-12.32	30.82	0.38	0.000	Calcite	95.66	2.9	1.3
235	4-078	3.28	14.99	0.5	-12.32	27.65	0.38	0.003	3	40.19	60.06	0.0
236	4-086	2.29	13.86	0.2 8	-5.43	19.4	0.38	0.003	NC			
237	4 UWC3 G2	3.09	5	0.4								
238	4 UWC3 G2	3.07	5.21	0.5								
239	4 UWC3 G2	3.11	5.08	0.5								
240	4 UWC3 G2	3.14	4.86	0.4 8								
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		Averag e:	5.16	2S D:	0.38							
251	4-092	3.11	18.29	0.4 7	-12.33	31	0.32	0.002	Calcite	97.07	3.63	0.0
252	4-097	3.17	17.24	0.5 3	-12.33	29.94	0.32	0.002	Calcite	98.76	1.45	0.2
253	4-097a	3.11	19.27	0.5 2	-12.33	31.99	0.32	0.002	Calcite	97.3	3.08	0.2
254	4-089	3.53	13.63	0.4 9	-11.67	25.6	0.32	0.016	2	40.25	58.72	0.4
255	4-042; Cs 141-139	3.27	12.17	0.5 9	-12.33	24.81	0.32	0.003	2	41.28	58.44	0.3
256	4-043	2.93	17.82	0.5 9	-12.33	30.53	0.32	0.003		94.62	4.76	0.0
257	4-100	2.19	14.22	0.3 4	-5.44	19.77	0.32	0.009	NC			
258	4-082	3.31	12.92	0.5 8	-11.67	24.88	0.32	0.001	2	39.81	60.54	0.3
259	4-082a	3.26	13.87	0.5 7	-12.33	26.52	0.32	0.002	2	39.03	60.9	0.0
260	4 UWC3 G2	3.09	5.35	0.4 8								
261	4 UWC3 G2	3.09	5.28	0.5								
262	4 UWC3 G2	3.1	5.21	0.5 5								
263	4 UWC3 G2	3.12	5.23	0.5 7								
		Averag e:	5.15	2S D:	0.32							
Sam 2015	ple Mount No. 5. 13 µm	beam, 1.2 nA i	ntensity.	Octob	er 8th							

264	5 UWC3 G1	2.86	4.86	0.4 q								
265	5 UWC3 G2	2.89	4.96	0.5								
266	5 UWC3 G2	2.98	4.62	0.5 4								
267	5 UWC3 G2	2.99	4.82	0.4 6								
268	5-015	3.04	16.74	0.2 1	-12.57	29.69	0.39	0.004	6	52.16	46.54	1.2
269	5-015a	3.2	15	0.4 5	-12.57	27.92	0.39	0.004	6	50.99	48.25	1.0
270	5-015b	3.12	15.54	0.3 7	-12.57	28.46	0.39	0.004	6	50.41	48.45	1.0
271	5-015c	3.18	15.26	0.4 6	-12.57	28.19	0.39	0.005	6	51.26	47.73	1.1
272	5-089	2.12	9.08	0.3 2	-5.68	14.84	0.39	0.002	NC			
273	5-015d	3.16	13.94	0.6 2	-12.57	26.84	0.39	0.005	6	44.91	58.97	1.7
274	5-100	3.05	13.6	0.5 1	-12.57	26.51	0.39	0.009	3	52.34	47.53	0.0
275	5-100a	2.95	14.52	0.4 1	-12.57	27.43	0.39	0.007	1	50.27	48.1	1.3
276	5 UWC3 G1	2.8	5.27	0.4 8								
277	5 UWC3 G1	2.82	5.04	0.4 8								
278	5 UWC3 G1	2.98	4.92	0.4 8								
279	5 UWC3 G1	3.04	4.78	0.4 9								
		Averag e:	4.91	2S D:	0.39							

280	5-099	3.19	11.31	0.5 3	-12.47	24.08	0.39	0.002	2	51.59	48.66	0.0
281	5-098	3.12	14.4	0.5	-12.47	27.21	0.39	0.005	4	54.05	46.27	0.0
282	5-028	2.18	22.62	0.2 5	-5.58	28.36	0.39	0.002	NC			
283	5-028a	2.2	22.45	0.2 7	-5.58	28.19	0.39	0.002	NC			
284	5-028b	2.2	22.1	0.3 1	-5.58	27.84	0.39	0.002	NC			
285	5-023	3.12	14.29	0.3 5	-12.47	27.09	0.39	0.007	2	51.27	49.06	0.0
286	5-004	3.31	13.24	0.5 7	-12.47	26.03	0.39	0.009	5	50.91	47.78	1.8
287	5-005	2.18	8.78	0.3	-5.58	14.44	0.39	0.001	NC			
288	5-078	2.9	12.4	0.5 6	-12.47	25.18	0.39	0.004	2	51.05	48.85	0.2
289	5 UWC3 G1	2.59	4.94	0.5 1								
290	5 UWC3 G1	2.67	5.01	0.4 6								
291	<del>5 UWC3 G1</del>	<del>2.89</del>	4	<del>10.</del> <del>72</del>								
292	5 UWC3 G1	2.82	5.32	0.4 4								
293	5 UWC3 G1	2.87	4.81	0.5 4								
		Averag e:	5.01	2S D:	0.39							
294	5-080	2.93	15.67	0.4	-12.43	28.45	0.37	0.005	2	50.92	48.96	0.3
295	5-081	3	12.69	0.4	-12.43	25.43	0.37	0.002	4	51.83	47.53	0.5
296	5-082	2.1	11.3	0.2 5	-5.54	16.93	0.37	0.001	NC			

297	5-084	2.97	17.5	0.5 4			0.37	0.009	Er			
298	5-053	1.86	10.58	0.2 7	-5.54	16.21	0.37	0.002	NC			
299	5 UWC3 G1	2.67	5.01	0.4 6								
300	5 UWC3 G1	2.75	5.07	0.5 1								
301	5 UWC3 G1	2.82	5.34	0.5 4								
302	5 UWC3 G1	2.87	4.94	0.4 6								
		Averag e:	5.05	2S D:	0.37							
Sam 2015	ple Mount No. 1. 13 µm beai	m, 1.2 nA	intensity.	Octob	per 8th							
303	1 UWC3 G1	2.87	5.12	0.4								
304	1 UWC3 G1	2.9	5.01	0.4								
305	1 UWC3 G1	2.93	5.24	0.5								
306	1 UWC3 G1	2.93	4.87	0.4 7								
307	1-079	3	14.05	0.3 3	-12.56	26.95	0.39	0.006	3	49.35	48.35	1.6
308	1-073	3.11	11.75	0.5 2	-11.16	23.17	0.39	0.002	4	47.48	51.42	0.0
309	1-072	3.07	14.41	0.5	-12.56	27.32	0.39	0.002	2	49.43	50.23	0.7
310	1-071	3.14	12.58	0.4	-12.56	25.46	0.39	0.005	3	49.92	50.55	0.0
311	1-071a	3.1	16.18	0.4	-11.9	28.42	0.39	0.005	2	46.15	53.38	0.3

312	1-071b	3.17	15.02	0.3 4	-12.56	27.93	0.39	0.004	2	48.36	51.38	0.7
313	1-074	3.24	13.91	0.5 1	-12.56	26.81	0.39	0.007	4	48.99	50.59	0.8
314	1-075	3.31	13.71	0.5 1	-11.9	25.93	0.39	0.004	4	45.64	54.67	0.0
315	1 UWC3 G1	3.17	4.91	0.5								
316	1 UWC3 G1	3.11	4.74	0.4 9								
317	1 UWC3 G1	2.98	4.74	0.4 6								
318	1 UWC3 G1	2.98	4.69	0.4 6								
		Averag e:	4.92	2S D:	0.39							
319	1-051	3.06	13.79	0.5 5	-11.96	26.06	0.28	0.004	2	47.21	52.91	0.5
320	1-051a	3.08	13.7	0.4	-10.5	24.46	0.28	0.006	2	46.63	53.15	1.9
321	1-051b	3.1	13.03	0.4 7	-12.61	25.98	0.28	0.007	2	47.02	53.07	0.0
322	1-052	3.13	13.37	0.5 5			0.28	0.008	Er			
323	1-053	3.15	11.64	0.4 7	-12.61	24.56	0.28	0.006	2	47.41	52.78	0.2
324	1-054	3.28	13.09	0.4 1	-12.61	26.03	0.28	0.002	2			
325	1-054a	3.23	13.23	0.5	-12.61	26.18	0.28	0.008	2	49.23	50.94	0.6
326	1-054b	3.2	12.84	0.4 4	-12.61	25.78	0.28	0.004	2	41.88	58.18	0.3
327	1-054c	3.16	12.66	0.4 6	-12.61	25.6	0.28	0.001	2	72.54	26.83	1.4
328	1-054d	3.11	13.95	0.4 6	-12.61	26.91	0.28	0.001	2	63.55	36	0.7

329	1 UWC3 G1	2.97	4.96	0.5 4								
330	1 UWC3 G1	3.03	4.8	0.5 6								
331	1 UWC3 G1	3.09	5	0.5 3								
332	1 UWC3 G1	3.14	5.07	0.5 2								
		Averag e:	4.86	2S D:	0.28							
333	1-067	3.33	13.28	0.5	-12.52	26.13	0.28	0.004	2	47.59	52.22	0.9
334	1-067a	2.87	16.88	12. 49	-12.52	29.78	0.28	0.006	2	49.33	50.53	0.2
335	1-067b	3.09	13.57	0.6 6	-12.52	26.42	0.28	0.001	2	47.32	52.88	0.4
336	1-067c	3.09	11.43	0.5 1	-12.52	24.25	0.28	0.008	2	48.78	52.04	0.0
337	1-067d	3.07	14.91	0.4 5	-11.86	27.1	0.28	0.004	2	47.31	53.36	0.7
338	1-067e	3.09	13.76	0.4 5	-12.52	26.61	0.28	0.007	2	48.51	52.41	1.9
339	1-067f	3.07	12.72	0.4 9	-12.52	25.56	0.28	0.007	2	49.24	50.82	0.3
340	1-067g	3.12	12.27	0.5	-12.52	25.11	0.28	0.002	2			
341	1 UWC3 G1	2.85	4.99	0.4 7								
342	1 UWC3 G1	2.83	5.18	0.5 4								
343	1 UWC3 G1	2.83	4.76	0.4 7								
344	1 UWC3 G1	2.8	4.9	0.5 6								

		Averag e:	4.96	2S D:	0.28							
Sam 2015	ple Mount No. 7. 13 µm bea	am, 1.2 nA i	ntensity.	Octob	per 8th							
345	7 UWC3 G1	2.86	5.08	0.5 5								
346	7 UWC3 G1	2.88	5.12	0.5 1								
347	7 UWC3 G1	2.85	5.06	0.4 9								
348	7 UWC3 G1	2.8	5.09	0.5 3								
349	7 UWC3 G1	2.87	5.24	0.4 6								
350	7-004	3.25	12.67	0.4 5	-11.79	24.75	0.25	0.009	1	50.03	49.95	0.3
351	7-005	3.21	11.58	0.4 6	-11.79	23.65	0.25	0.010	4	51.22	48.5	0.6
352	7-006	2.25	7.01	0.3	-5.56	12.63	0.25	0.001	NC			
353	7-020	2.36	10.81	0.2 3	-5.56	16.46	0.25	0.001	NC			
354	7-021	2.11	7.22	0.3	-5.56	12.85	0.25	0.002	NC			
355	7-023	2.33	8.82	0.2 7	-5.56	14.45	0.25	0.001	NC			
356	7-024	2.33	12.7	0.3 2	-5.56	18.35	0.25	0.002	NC			
357	7-060	2.36	12.84	0.2 8	-5.56	18.5	0.25	0.001	NC			
358	7 UWC3 G1	3.23	4.79	0.5 1								
359	7 UWC3 G1	3.15	4.94	0.5 3								

360	7 UWC3 G1	3.03	4.97	0.3 9								
361	7 UWC3 G1	2.91	5.02	0.4								
		Averag e:	5.04	2S D:	0.25							
362	7-048	3.15	14.95	0.5	-12.43	27.72	0.33	0.007	3	52.67	45.85	0.0
363	7-047	3.1	13.24	5 0.4 8	-12.43	25.99	0.33	0.007	4	51.45	48.36	0.2
364	7-041	2.99	13.77	0.4 4	-12.43	26.53	0.33	0.007	3	51.87	48.16	0.1
365	7-041a	1.96	5.55	0.2 6	-5.54	11.15	0.33	0.002	NC			
366	7-040	2.09	13.5	0.3 7	-5.54	19.15	0.33	0.002	NC			
367	7-100	2.94	13.59	0.4 4	-12.43	26.34	0.33	0.008	2	51.3	49.63	0.0
368	7-099	3.03	11.6	0.5 7	-12.43	24.33	0.33	0.010	3	52.11	48.4	0.0
369	7-098	2.13	7.3	0.2 5	-5.54	12.91	0.33	0.003	NC			
370	7 UWC3 G1	2.86	5.18	0.4 5								
371	7 UWC3 G1	2.85	5.05	0.5 1								
372	7 UWC3 G1	2.87	5.34	0.5 3								
373	7 UWC3 G1	2.91	5.11	0.4 8								
		Averag e:	5.05	2S D:	0.33							
37/	7-051	3 08	12 17	0.5	-12 21	24.68	03		<b>)</b>	51 / 8	17 05	0.0
5/4		5.00	12.11	2	- 12.21	24.00	0.5	0.006	2	51.40	-1.35	0.0

375	7-052	3.12	12.95	0.4	-11.56	24.79	0.3		3	52.16	47.27	0.3
070	7 050	1.00	0.04	9	5.00	45.04	0.0	0.008	NO			
3/0	7-053	1.99	9.01	0.2	-5.32	15.21	0.3	0.001	INC.			
377	7-054	2.79	14.44	0.5	-7.84	22.46	0.3	0.008	2	55.27	42.11	3.1
378	7-054a	1.85	15.6	0.4	-10.81	26.7	0.3	01000	3	51.3	48.99	0.8
				3				0.009				
379	7-054b	2.74	13.13	0.3	-12.21	25.65	0.3		3	50.63	49.74	0.0
			10 -0	9	10.01	~ ~ ~ ~		0.013			=0.04	
380	7-055	2.85	12.52	0.4 8	-12.21	25.03	0.3	0.007	4	50.19	50.04	0.0
381	7-070	2 76	15 81	0.5	-12 21	28 37	0.3	0.007	2	50.96	50.03	0.6
		2.1.0	10101	5		20.01	0.0	0.008	-	00100	00100	0.0
382	7 UWC3 G1	2.62	5.43	0.5								
				3								
383	7 UWC3 G1	2.62	5.4	0.5								
384	7 UWC3 G1	2.71	5.43	0.5								
				6								
385	7 UWC3 G1	2.8	5.23	0.4 9								
		Averag	5.27	2S	0.3							
		e:		D:	0.0							
386	7-073	3.14	13.47	0.3	-12.25	26.04	0.38		2	47.49	49.76	0.9
				5				0.007				
387	7-074	3.09	14.61	0.5	-12.25	27.18	0.38	0.007	2	50.75	48.8	0.1
200	7.075	2.00	14 56	3	1 00	16.41	0.20	0.007	2	10.46	<b>5</b> 2 <b>5</b> 2	0.0
300	7-075	3.09	14.50	0.4	-1.02	10.41	0.30	0.008	3	40.40	00.00	0.0
389	7-079	2.8	15.72	0.4	-2.2	17.96	0.38	0.000	Calcite	95.53	3.75	0.2
			-	4				0.005				_
390	7-080	3.07	13.25	0.4	-12.25	25.82	0.38		3	52.44	47.75	0.3
				5				0.008				
391	7-081	3.01	13.53	0.5	-10.84	24.64	0.38	0.040	2	50.13	49.45	0.2
				1				0.010				

392	7-081a	3.08	14.5	0.4 0	-12.25	27.08	0.38	0.007	2	53.33	47.05	0.0
393	7-081b	2.15	8.3	0.3	-5.36	13.73	0.38	0.006	NC			
394	7-082	2.15	8.3	0.3 2	-5.36	13.73	0.38	0.004	NC			
395	7 UWC3 G1;	2.89	5.04	0.5 3								
396	7 UWC3 G1;	2.98	5.35	0.4 3								
397	7 UWC3 G1;	3.01	5.01	0.5 4								
398	7 UWC3 G1;	2.99	5.03	0.4 7								
		Averag e:	5.24	2S D:	0.38							
399	7-029	2.23	8.28	0.2	-5.61	13.97	0.36	0.001		52.97	46.78	0.0
400	7-030	3.14	12.81	0.4 5	-12.5	25.63	0.36	0.009	2	52.12	47.92	0.1
401	7-037	3.23	12.34	0.4 7	-12.5	25.15	0.36	0.006	2	50.16	49.93	0.2
402	7-037a	3.29	15.37	0.4	-11.84	27.54	0.36	0.007	2	53.05	46.55	0.4
403	7-038	3.24	12.51	0.6 3	-12.5	25.33	0.36	0.006	2	50.6	49.28	0.1
404	7-038a	3.33	14.59	0.5 1	-12.5	27.44	0.36	0.010	2	53.44	46.08	0.2
405	7-043	0.02	32.95	26. 24	NA	NA	NA	0.277	NC			
406	7-044	2.18	17.09	0.2 1	-5.61	22.83	0.36	0.002	NC			
407	7 UWC3 G1	3	4.73	0.4 8								

408	7 UWC3 G1	3.04	4.89	0.4 9								
409	7 UWC3 G1	3.04	4.89	0.5 7								
410	7 UWC3 G1	3.1	4.9	0.4 8								
		Averag e:	4.98	2S D:	0.36							
Sam 2015	ple Mount No. 6. 13 µm be	eam, 1.2 nA i	intensity.	Octol	ber 9th							
411	6 UWC3 G1	2.75	5.16	0.4 4								
412	6 UWC3 G1	2.83	5.16	0.5 4								
413	6 UWC3 G1	2.87	5.13	0.4 8								
414	6 UWC3 G1	2.88	4.96	0.5								
415	6-004	2.12	8.21	0.2 6	-5.49	13.78	0.16	0.001	NC			
416	6-005	2.76	19.24	0.6 3	-12.38	32.02	0.16	0.005	Calcite	97.35	2.28	0.5
417	6-005a	3.05	16.42	0.4 1	-12.38	29.16	0.16	0.005	2	46.14	54.16	0.3
418	6-006	3.16	16.05	0.4 6	-12.38	28.78	0.16	0.005	2			
419	6-007	2.74	18.85	0.5 3	-12.38	31.62	0.16	0.002	4	44.92	51.46	3.5
420	6-009	2.83	19.19	0.5 5	-12.38	31.97	0.16	0.004	Calcite	97.41	2.32	0.4
421	6-010	2.83	19.19	0.5 5	-12.38	31.97	0.16	0.001	Calcite	96.3	3.06	0.3
422	6-027	0.01	-35.46	38. 45	NA	NA	NA	0.213	Er			

423	6 UWC3 G1	2.83	5.01	0.5 2								
424	6 UWC3 G1	2.79	5.1	0.5 3								
425	6 UWC3 G1	2.79	5.2	0.5 8								
426	6 UWC3 G1	2.78	5.09	0.5 1								
407	0.007-	0.07	4.40	0.4		NIA			<b></b>			
427	6-027a	0.07	-1.13	8.4 9	INA	NA	NA	0.074	Er			
428	6-027b	2.33	19.17	0.5 4	NA	NA	NA	0.006	Er			
429	6-027c	0.03	-3.65	20. 26	NA	NA	NA	0.136	Er			
430	6-028	2.94	12.21	0.4 6			0.25	0.007	NF			
431	6-029	2.62	18.95	0.5 3	-12.42	31.77	0.25	0.007	Calcite			
432	6-030	2.67	19.48	0.5 5	-12.42	32.3	0.25	0.004	Calcite	97.3	2.61	0.4
433	6-031	2.59	19.49	0.6 4	-12.42	32.31	0.25	0.006	Calcite	98.08	1.73	0.0
434	6 UWC3 G1	2.72	5.16	0.5 4								
435	6 UWC3 G1	2.8	5.15	0.4 1								
436	6 UWC3 G1	2.96	4.81	0.4 7								
437	6 UWC3 G1	2.99	4.97	0.5 2								
		Averag e:	5.1	2S D:	0.16							

438	6-032	2.77	18.05	0.4 6	-12.53	30.97	0.3	0 004	Calcite	96.66	2.66	0.2
439	6-033	2.94	18.35	0.4	-12.53	31.27	0.3	0.004	Calcite	97.25	2.63	0.3
440	6-034	2.86	19.34	0.5 5	-12.53	32.27	0.3	0.007	Calcite	98.25	2.45	0.1
441	6-035	2.91	18.89	0.5 7	-12.53	31.81	0.3	0.004	Calcite	97.96	2.7	0.0
442	6-036	3.36	15.93	0.4 8	-9.76	25.94	0.3	0.002	3	42.99	54.48	2.1
443	6-037	3.27	12.93	0.4 8	-9.76	22.91	0.3	0.003	1	45.89	53.17	2.1
444	6-038	2.87	17.93	0.5 4	-12.53	30.84	0.3	0.004	Calcite	97.27	2.84	0.0
445	6-039	2.88	19.21	0.4 9	-12.53	32.14	0.3	0.005	Calcite	99.17	1.35	0.1
446	6 UWC3 G1	2.97	4.87	0.5								
447	6 UWC3 G1	2.96	4.88	0.4 8								
448	6 UWC3 G1	2.93	4.81	0.5 3								
		Averag e:	4.95	2S D:								
449	6-040	2.87	19.61	0.4 8	-12.42	32.44	0.43	0.002	Calcite	97.73	1.73	0.4
450	6-040a	3.27	15.7	0.4 4	-9.06	24.99	0.43	0.002	1	46.2	54.03	0.4
451	6-059	2.83	20.08	0.4 8	-12.42	32.91	0.43	0.002	Calcite	97.93	2.05	0.1
452	6-059a	2.82	19.4	0.6	-12.42	32.22	0.43	0.004	Calcite	99.09	1.33	0.0
453	6-059b	2.76	19.83	0.5 3	-12.42	32.66	0.43	0.005	Calcite	99.13	0.73	0.3
454	6-062	2.81	18.8	0.4 8	-12.42	31.62	0.43	0.005	Calcite	97.93	2.06	0.1

455	6-063	2.8	19.29	0.5 3	-12.42	32.11	0.43	0.007	Calcite	98.45	1.99	0.0
456	6-064	2.83	18.69	0.5 2	-12.42	31.51	0.43	0.002	Calcite	99.27	0.9	0.0
457	6 UWC3 G1	2.84	5.4	0.5 4								
458	6 UWC3 G1	2.85	5.08	0.5 2								
459	6 UWC3 G1	2.84	5.11	0.5 9								
460	6 UWC3 G1	2.85	5.24	0.4 9								
		Averag e:	5.06	2S D:	0.43							
461	6-074	2.75	19.25	0.5 7	-12.25	31.89	0.22	0.003	Calcite	97.51	2.48	0.0
462	6-075	2.75	19.47	0.5 5	-5.6	25.21	0.22	0.004	4	43.6	54.03	0.4
463	6-075	2.75	19.47	0.5 5	-5.6	25.21	0.22	0.004	Cal rep site number	97.05	2.19	0.0
464	6-077	2	15.64	0.3	-5.36	21.12	0.22	0.001	NC			
465	6-077a	1.99	15.96	0.3	-5.36	21.44	0.22	0.001	NC			
466	6-077b	2.07	8.37	0.2 7	-5.36	13.81	0.22	0.001	NC			
467	6-077c	2.06	8.66	0.3	-5.36	14.1	0.22	0.001	NC			
468	6-070	2.71	19.5	0.5			0.22	0.004	Er			
469	6-071	3.18	16.61	0.3 7	-12.25	29.22	0.22	0.002	Calcite	97.3	2.46	0.2
470	6-068	2.85	15.57	0.3 4	-12.25	28.17	0.22	0.006		42	58.55	0.0
471	6 UWC3 G1	2.78	5.23	0.4 9								

472	6 UWC3 G1	2.77	5.35	0.4 9								
473	6 UWC3 G1	2.76	5.17	0.5 4								
474	6 UWC3 G1	2.75	5.28	0.4 9								
		Averag e:	5.23	2S D:	0.22							
Sam 2015	ple Mount No. 1. 13 µm be	am, 1.2 nA i	ntensity.	Octob	per 9th							
475	1 UWC3 G1	2.98	5.29	0.5 3								
476	1 UWC3 G1	2.84	5.27	0.4 7								
477	1 UWC3 G1	2.78	5.19	0.5								
478	1 UWC3 G1	2.72	5.05	0.5 6								
479	1-084	2.8	13.06	0.6	-12.35	25.72	0.2	0.007	2	49.57	51.37	0.0
480	1-084a	2.88	14.37	0.6 4	-11.69	26.37	0.2	0.008	2	49.45	50.75	0.0
481	1-085	2.84	12.7	0.5 2	-12.35	25.35	0.2	0.008	2	50.05	49.94	0.0
482	1-101	2.76	13.95	0.5 8	-12.35	26.62	0.2	0.009	4	49.45	50.75	0.7
483	1-102	2.76	12.63	0.4 2	-12.35	25.29	0.2	0.005	4	47.69	56.15	1.4
484	1-103	2.81	13.7	0.5	-12.35	26.37	0.2	0.008	4	50.69	50.53	0.2
485	1-104	2.78	14.16	0.4 9			0.2	0.007	Er			
486	1-105	2.99	14.47	0.4	-12.39	27.2	0.16	0.005	4	48.66	52.15	0.0
487	1-106	2.96	13.04	0.4 4	-12.39	25.74	0.16	0.008	4	48.85	50.37	1.0
488	1-107	2.95	12.36	0.5 7	-12.39	25.06	0.16	0.006	4	47.98	52.14	0.2

489	1-108	2.93	13.37	0.4	-12.39	26.08	0.16		2	49.88	54.21	0.2
100	4 400		40.07	4	40.00	05.00	0.40	0.007		45.04	54.00	
490	1-109	2.93	12.97	0.4	-12.39	25.68	0.16	0.011	2	45.84	54.92	1.3
491	1-110	2 89	13.61	04	-12 39	26 32	0.16	0.011	3	47 54	52 23	0.0
401	1 110	2.00	10.01	8	12.00	20.02	0.10	0.008	5	+1.04	52.25	0.0
492	1-111	2.01	14.2	0.2	-5.5	19.81	0.16		NC			
				1				0.001				
493	1-112	2.88	12.22	0.4			0.16		Er			
				8				0.006				
494	1-113	2.84	13.6	0.3	-12.39	26.31	0.16	0.005	2	48.17	52	0.0
				8				0.005				
495	1 UWC3 G1	2.73	5.2	0.5								
106		2.66	5 1 2	07								
490	10000301	2.00	0.12	0.7								
497	1 UWC3 G1	2.7	5.19	0.4								
			00	6								
498	1 UWC3 G1	2.9	4.94	0.4								
				8								
		Averag	5.16	2S	0.23							
		e:		D:								
			10.01									
499	1-114	3.19	12.61	0.4			0.41	0.000	Er			
500	1 115	2 10	11 02	0			0.41	0.006				
500	1-115	5.10	11.05	0.0			0.41	0.016	C1			
501	1-116	3.15	14.19	0.4			0.41	0.010	Er			
				4			••••	0.007				
502	1-117	3.09	14.58	0.2			0.41		Er			
				5				0.013				
503	1-118	3.22	11.11	0.6			0.41		Er			
				6				0.021				
504	1-119	3.13	12.53	0.4			0.41	0.007	Er			
				5				0.007				

505	1-120	3.17	11.81	0.5			0.41	0.008	Er			
506	1 101	2.1	11 20	0.5			0.41	0.000				
500	1-121	3.1	14.30	0.5			0.41	0.007	EI.			
507	1-122	3.13	13.47	0.5			0.41	0.006	Er			
508	1 UWC3 G1	3.02	4.73	0.4 9								
509	1 UWC3 G1	2.99	4.97	0.5								
510	1 UWC3 G1	2.99	4.64	0.5								
511	1 UWC3 G1	2.96	4.97	0.5								
		Averag	4.97	2S	0.41							
		e:		D:								
Sample Mount No. 5. 13 µm beam, 1.2 nA intensity. October 9th 2015					per 9th							
512	5 UWC3 G2	3.04	4.92	0.5								
513	5 UWC3 G2	3.01	5.11	0.5								
514	5 UWC3 G2	3	4.94	0.5								
515	5 UWC3 G2	2.97	5.08	0.5 2								
516	5-072	3.21	15.35	0.3 7	-12.49	28.19	0.16	0.003	2	49.75	50.2	0.0
517	5-101	2.09	10.6	0.3 8	-5.6	16.3	0.16	0.001	NC			
518	5-102	2.99	11.28	0.5 3	-11.98	23.55	0.16	0.008	2	52.3	47.7	0.0
519	5-103	3.06	13.83	0.4 5	-12.13	26.28	0.16	0.006	3	50.1	49.9	0.0
520	5-104	2.14	5.23	0.2 8	-5.6	10.89	0.16	0.001	NC			

521	5-105	2.08	3.69	0.2 8	-5.6	9.35	0.16	0.008	NC			
522	5-106	2.13	5.87	0.2 5	-5.6	11.54	0.16	0.001	NC			
523	5-107	2.94	14.7	0.5 4	-12.49	27.54	0.16	0.003	4	50.85	49.1	0.3
524	5 UWC3 G2	2.91	4.9	0.4 9								
525	5 UWC3 G2	2.91	4.99	0.4 7								
526	5 UWC3 G2	2.88	4.93	0.4 5								
527	5 UWC3 G2	2.89	5.03	0.4 3								
		Averag e:	4.99	2S D:	0.16							
528	5-108	2.86	14.6	0.3 5	-12.29	27.22	0.14	0.004	6	51.51	48.03	0.3
529	5-109	3.15	17.58	0.4	-12.48	30.44	0.14	0.001	6	50.8	46.54	6.9
530	5-110	2.08	5.64	0.2 3	-5.63	11.34	0.14	0.001	NC			
531	5-111	2.08	5.56	0.2 5	-5.63	11.26	0.14	0.001	NC			
532	5-112	2.08	5.8	0.2 7	-5.63	11.5	0.14	0.001	NC			
533	5-113	3.05	15.47	0.4 7	-12.52	28.35	0.14	0.002	2	52.16	44.41	3.2
534	5-114	3.01	18.42	0.3 7	-12.52	31.34	0.14	0.005	3	50.43	50.01	0.3
535	5-115	2.97	14.19	0.4 2	-12.52	27.05	0.14	0.002	4	52.3	47.98	0.1
536	5 UWC3 G2	2.82	5.01	0.4 5								

537	5 UWC3 G2	2.82	4.82	0.5 3								
538	5 UWC3 G2	2.82	4.97	0.5 8								
539	5 UWC3 G2	2.81	5.02	0.4 1								
		Averag e:	4.96	2S D:	0.14							
540	5-116	2.04	6.99	0.2 6	-5.63	12.7	0.14	0.001	NC			
541	5-117	2.96	13.78	0.5 5	-12.52	26.63	0.14	0.001	4	51.29	48.6	0.1
542	5-118	2.92	12.88	0.4 1	-12.52	25.73	0.14	0.003	4	51.06	49.43	0.5
543	5-119	1.96	8.79	0.2	-5.63	14.5	0.14	0.001	NC			
544	5-120	1.94	9.77	0.2 6	-5.63	15.49	0.14	0.001	NC			
545	5-121	1.93	9.88	0.2 7	-5.63	15.6	0.14	0.001	NC			
546	5-122	2.83	12.4	0.3 9	-12.52	25.23	0.14	0.003	2	50.52	49.59	0.4

## **Pit Analysis**

999 After ion microprobe analysis a combination of Scanning Electron (SE), Back Scattered (BSE) microscopy and Wavelength Dispersive 1000 Spectroscopy (SEM-WDS) was used to relocate and characterise each individual pit. Pits with an irregular morphology were excluded. In this 1001 study 'pit irregularity' is defined as and includes pits which are positioned on cracks, spots which break into crystals and/or inclusions other 1002 than the target mineral and spots which overlap pores and vugs. Analyses which were not of calcite or dolomite were also excluded. Analyses 1003 were also excluded where the pit could not be found or the pit identity confirmed. An explanation each excluded analysis is given in Table X. In 1004 total 111 measurements were excluded from a total of 308 analyses



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1006 Figure X - Examples of SIMS pits a) Regular pit, positioned in the centre of a calcite crystal in sample 2-55B; note the ellipsoidal shape and size.

1007 Note, the pit is shown rotated 90° to the orientation it was created in; b) Irregular pit positioned at the edge of calcite cement, breaking into a 1008 second mineral (mineral 2), contaminating the ablated sample, in sample 2-55B.

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**Table X** – Details of pits excluded from further interpretations. Not found = where the pit couldn't be located for integrity checking. Other Mineral = analyses of minerals
other than calcite or dolomite and were commonly feldspar or quartz. Error = Refers to low count rates obtained by the detector.

Analysis ID	Explanation	Analysis ID	Explanation		Analysis ID	Explanation	]	Analysis ID	Explanation
1-051b	Irregularity	2-032	Not Found	1	3-084	Other Mineral	1	6-075	Not Found
1-052	Error	2-034	Not Found		3-084a	Other Mineral		6-077	Other Mineral
1-054	Not Found	2-035	Not Found		3-085	Other Mineral		3-086	Not Found
1-067g	Not Found	2-036	Not Found		4-008	Other Mineral	1	3-092	Other Mineral
1-073	Irregularity	2-038	Not Found		4-011	Irregularity	1	6-077a	Other Mineral
1-075	Irregularity	2-041	Not Found		4-038	Other Mineral		6-077b	Other Mineral
1-084a	Not Found	2-043	Not Found		4-043	Irregularity		6-077c	Other Mineral
1-104	Error	2-045	Not Found		4-066	Not Found		7-006	Other Mineral
1-111	Other Mineral	2-048	Irregularity		4-069	Other Mineral	1	7-020	Other Mineral
1-112	Error	2-061	Other Mineral		4-086	Other Mineral		7-021	Other Mineral
1-114	Error	3-006	Other Mineral		4-100	Other Mineral		7-023	Other Mineral
1-115	Error	3-011	Other Mineral		5-005	Other Mineral		7-024	Other Mineral
1-116	Error	3-012	Other Mineral		5-028	Other Mineral		7-029	Irregularity
2-005	Not Found	3-017	Irregularity		5-028a	Other Mineral	1	7-040	Other Mineral
2-007	Other Mineral	3-025	Irregularity		5-028b	Other Mineral	1	7-041a	Other Mineral
2-008	Not Found	3-029	Other Mineral		5-053	Other Mineral	1	7-043	Other Mineral
2-009	Irregularity	3-030	Other Mineral		5-082	Other Mineral	1	7-044	Other Mineral
2-009-2	Other Mineral	3-031	Other Mineral		5-084	Error	1	7-048	Irregularity
2-009-3	Other Mineral	3-033	Not Found		5-089	Other Mineral	1	7-051	Irregularity
2-013	Not Found	3-034	Not Found		6-004	Other Mineral	1	7-053	Other Mineral
2-018	Other Mineral	3-035	Other Mineral		6-006	Not Found	1	7-060	Other Mineral
2-021	Other Mineral	3-036	Not Found		6-027	Error	1	7-075	Irregularity
2-022	Not Found	3-037	Not Found		6-027a	Error		7-079	Not Found
2-022b	Not Found	3-038	Not Found		6-027b	Error		7-081b	Other Mineral
2-027	Not Found	3-039	Not Found		6-027c	Error		7-082	Other Mineral
2-028a	Other Mineral	3-040	Not Found	1	6-028	NC	1	7-098	Other Mineral
2-030	Not Found	3-041	Irregularity	1	6-068	Irregularity	1	7-098	Other Mineral
2-031	Not Found	3-081	Error	1	6-070	Error	1		•
								•	

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## **Iron Correction**

- 1019 (a) Plot relating the SIMS  $\delta^{18}$ O bias (‰) to the cation composition of the dolomite–ankerite solid solution series [Fe# = Fe/(Mg+Fe)] for a
- 1020 typical calibration using a 10µm diameter spot size. The sample matrix effect can be accurately estimated using the Hill equation, which is
- 1021 commonly employed to describe relations of 'concentration' versus 'measured effect' type, especially in systems that behave non-linearly and
- 1022 reach saturation. (b) Plot of the calibration residual. For most reference materials in the suite, the averaged measured value of  $\delta^{18}$ O
- 1023 bias\*(RMUW6220) differs by < 0.3‰ from the value predicted by the calibration (depicted by solid lines). Modified from Sliwinski et al., (2015).
- 1024 Figure from Orland et al., pers. com. (2015).



M.Brodie Session 2015.Oct.5 (10 µm spot-size)