# The habitat of the nascent Chicxulub crater

T. J. Bralower<sup>1</sup>, J. Cosmidis<sup>1</sup>, M. S. Fantle<sup>1</sup>, C. M. Lowery<sup>2</sup>, B. H. Passey<sup>3</sup>, S. P. S. Gulick<sup>2</sup>, J. V. Morgan<sup>4</sup>, V. Vajda<sup>5</sup>, M. T. Whalen<sup>6</sup>, A. Wittmann<sup>7</sup>, N. Artemieva<sup>8</sup>, K. Farley<sup>9</sup>, S. Goderis<sup>10</sup>, E. Hajek<sup>1</sup>, P. J. Heaney<sup>1</sup>, D. A. Kring<sup>11</sup>, S. L. Lyons<sup>1</sup>, C. Rasmussen<sup>2</sup>, E. Sibert<sup>12</sup>, F. J. Rodríguez Tovar<sup>13</sup>, G. Turner-Walker<sup>14</sup>, J. C. Zachos<sup>15</sup>, J. Carte<sup>1</sup>, S. A. Chen<sup>1</sup>, C. Cockell<sup>16</sup>, M. Coolen<sup>17</sup>, K. H. Freeman<sup>1</sup>, J. Garber<sup>1</sup>, M. Gonzalez<sup>1</sup>, J. L. Gray<sup>18</sup>, K. Grice<sup>17</sup>, H. L. Jones<sup>1</sup>, B. Schaefer<sup>17</sup>, J. Smit<sup>19</sup>, S. M. Tikoo<sup>20</sup>

<sup>1</sup>Department of Geosciences, Pennsylvania State University, University Park, PA, 16802, USA

<sup>2</sup>Institute for Geophysics, Jackson School of Geosciences, University of Texas at Austin, Austin, TX 78758, USA

<sup>3</sup>Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109-1005, USA

<sup>4</sup>Department of Earth Science and Engineering, Imperial College London, UK

<sup>5</sup>Department of Palaeobiology, Swedish Museum of Natural History, Stockholm, Sweden

<sup>6</sup>Geophysical Institute, University of Alaska, Fairbanks, AK 99775, USA

<sup>7</sup>Eyring Materials Center, Arizona State University Tempe, AZ 85287-8301, USA

<sup>8</sup>Planetary Science Institute, Tucson, AZ, USA

<sup>9</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

<sup>10</sup>Department of Chemistry, Vrije Universiteit Brussel, BE-1050 Brussels, Belgium

<sup>11</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058-1113, USA

<sup>12</sup>Department of Earth and Planetary Sciences, Yale University, New Haven, CT, 06520, USA

<sup>13</sup>Departamento de Estratigrafía y Paleontología, Facultad de Ciencias, Universidad de Granada, Granada 18002, Spain

<sup>14</sup>Graduate School of Cultural Heritage Conservation, National Yunlin University of This is the author manuscript accepted for publication and has undergone full peer review but Science and Technology, 640 Yunlin, Taiwan has not been through the copyediting, typesetting, pagination and proofreading process, which may sead to difference by University of Californian Santa Cruz, Plasse pitght Sincet; cle as dSianta. Cruz/CX295064,0258A <sup>16</sup>School of Physics and Astronomy, University of Edinburgh, Edinburgh, EH9 3FD, UK

<sup>17</sup>Organic and Isotope Geochemistry Centre, The Institute for Geoscience Research, School of Earth and Planetary Science, Curtin University, Perth, WA, Australia

<sup>18</sup>Materials Research Institute, Pennsylvania State University, University Park, PA, 16802, USA

<sup>19</sup>Department of Geology and Geochemistry, VU University Amsterdam 1081HV Amsterdam, The Netherlands

<sup>20</sup>Department of Geophysics, Stanford University, Stanford, CA 94305, USA

Corresponding author: Timothy J. Bralower (bralower@psu.edu)

## **Key Points:**

- Sediments derived from decarbonation of the Chicxulub impact target were deposited by tsunami and seiche waves over months to years followed by a layer with atmospheric fallout
- Temperatures in the ocean above the hotter regions of the crater were in excess of 70 °C, with heat likely derived from the central impact melt pool
- Cooler regions within the crater basin became habitats soon after impact with diverse life ranging from microbes to marine arthropods, and possibly fish

1 Abstract

-

Author Manuscri

2 An expanded sedimentary section provides an opportunity to elucidate conditions in the 3 nascent Chicxulub crater during the hours to millennia after the Cretaceous-Paleogene (K-Pg) 4 boundary impact. The sediments were deposited by tsunami followed by seiche waves as 5 energy in the crater declined, culminating in a thin hemipelagic marlstone unit that contains 6 atmospheric fallout. Seiche deposits are predominantly composed of calcite formed by 7 decarbonation of the target limestone during impact followed by carbonation in the water 8 column. Temperatures recorded by clumped isotopes of these carbonates are in excess of 70 9 °C, with heat likely derived from the central impact melt pool. Yet, despite the turbidity and 10 heat, waters within the nascent crater basin soon became a viable habitat for a remarkably 11 diverse cross-section of the food chain. The earliest seiche layers deposited with days or weeks 12 of the impact contain earliest Danian nannoplankton and dinocyst survivors. The hemipelagic 13 marlstone representing the subsequent years to a few millennia contains a nearly monogeneric 14 calcareous dinoflagellate resting cyst assemblage suggesting deteriorating environmental 15 conditions, with one interpretation involving low light levels in the impact aftermath. At the 16 same horizon, microbial fossils indicate a thriving bacterial community and unique phosphatic 17 fossils including appendages of pelagic crustaceans, coprolites and bacteria-tunneled fish 18 bone, suggesting that this rapid recovery of the base of the food chain may have supported the 19 survival of larger, higher trophic-level organisms. The extraordinarily diverse fossil 20 assemblage indicates that the crater was a unique habitat in the immediate impact aftermath, 21 possibly as a result of heat and nutrients supplied by hydrothermal activity.

- 22
- 23

---Author Manuscrip

## 24 Plain Language Summary

The newly formed Chicxulub crater was rapidly filled by seawater then disturbed by tsunami 26 27 and seiche waves. Sedimentary layers deposited as wave energy declined provide a unique 28 window into the environment of the nascent crater in the months and years to millennia after 29 the impact. Geochemical data show temperatures in hotter regions of the crater in excess of 70 30 °C for the first few years with heat derived from the underlying melt sheet via hydrothermal 31 circulation. Cooler regions of the crater became habitats soon after impact with a suite of fossils 32 indicating diverse life on the seafloor and sea surface, ranging from microbes to marine 33 arthropods, and possibly fish. We suggest that this community was sustained by nutrients and 34 heat from the hydrothermal system. The rapid early recovery in the Chicxulub crater and ocean 35 above demonstrates the resiliency of life under extraordinarily harsh conditions, which has 36 important ramifications for early life on Earth and life on other planets.

37

25

38

## 39 **1. Introduction**

40 In one of the most rapid geomorphic events in Earth history, the 200 km diameter Chicxulub crater formed in minutes to hours<sup>1</sup> and caused major environmental upheaval that led to mass 41 42 extinction marked by the Cretaceous-Paleogene (K-Pg) boundary<sup>2,3 4</sup>. The shallow sea as well 43 as the carbonate and evaporite rocks at the location of impact (i.e., the target rocks), amplified 44 the environmental effects of the event. Prolonged impact winter, cessation of photosynthesis, and, perhaps acid rain resulting from release of  $SO_2$  from evaporite sulfates<sup>5-8 9-13</sup>, were likely 45 46 major killing mechanisms on land and in the oceans. These effects may have been enhanced by soot released by wildfires<sup>14,15</sup> and combusted target rock hydrocarbons <sup>16 17</sup>, and carbonate 47

dust<sup>18</sup>, though this latter material has not been identified in boundary deposits. The impact 48 occurred either between eruptive phases of the Deccan traps<sup>19</sup>, or largely before these phases<sup>20</sup>. 49  $CO_2$ -related warming from these eruptions was either over<sup>21</sup> or served as a minor mitigating 50 factor<sup>22</sup>. The effects of the impact are, however, directly tied to the mass extinction 51 event<sup>4,10,12,18</sup>. Once formed, impact craters such as Chicxulub can provide unique habitats for 52 life<sup>23,24</sup>, a function that may also have been in operation early in Earth history<sup>23</sup>. Hydrothermal 53 54 systems initiated by impact have the potential to release nutrients and energy for microbial activity<sup>25-28</sup>, and the presence of hydrothermal minerals within the crater's peak ring confirm 55 that hot fluids circulated in these rocks after crater formation<sup>29</sup>. These impact lithologies today 56 host diverse microbial communities shaped by the impact event<sup>30</sup>. However, to this point there 57 58 has been little exploration of the connection between hydrothermal activity and local marine life in the aftermath of an impact  $^{29,31}$ . 59

60

61 The geological record of the Chicxulub crater offers clues regarding the dynamic processes 62 that occurred in the immediate aftermath of the impact and affected the habitability of the 63 nascent crater. Immediately after impact, a ~200-km wide impact basin was formed with an internal 80- to 90-km-diameter topographic peak ring surrounding a central basin containing 64 a thick suevite (i.e., melt-bearing impact breccia) layer above an impact melt sheet<sup>25</sup>. 65 Heterogeneity in topography, structure and nature of the near-surface rocks led to considerable 66 67 variability in heat and fluid flow, which would have affected the chemistry of the initial waters 68 that entered the crater. While Chicxulub has been the target of extensive geophysical exploration in the past<sup>32 33</sup>, existing boreholes were either only spot cored or located on the 69 70 inner ring crater slope where accommodation space was limited and the boundary sequence is

condensed and incomplete<sup>34 35</sup>. The Yaxcopoil-1 (YAX-1) core, drilled adjacent to the inner ring of the crater contains evidence for hydrothermal circulation in impact breccias <sup>36 37 38</sup> and overlying Paleogene limestones that suggests that hydrothermal activity persisted for hundreds of thousands of years after the impact <sup>39</sup>. However, repeated mass wasting events at YAX-1 from the adjacent inner crater rim obscure the sedimentary record of the years after the impact <sup>40,41</sup>, limiting our ability to document the history of the recovery of life and of hydrothermal activity.

78

International Ocean Discovery Program-International Continental Scientific Drilling Program 79 (IODP-ICDP) Expedition 364 drilled into the Chicxulub peak ring at Site  $M0077^{42}$ . The site 80 81 was located in a depression on top of the peak ring, providing the accommodation space for 82 the accumulation of a remarkable boundary sequence. Site M0077 recovered 587 m of felsic basement rocks overlain by 130 m of suevite. The lowermost suevite was emplaced as the 83 84 central uplift collapsed to form the peak ring, and suevite deposition continued during ocean 85 resurge, seiche (internal to the crater) and tsunami waves<sup>12</sup>. Site M0077 granitoid rocks and suevites show mineralogical and paleomagnetic evidence of long-lasting hydrothermal 86 circulation<sup>29,42</sup>. The uppermost 8.5 m [617.33-625.85 meters below sea floor (mbsf)] of these 87 88 deposits, largely very fine-grained, layered suevite that was laid down by a succession of 89 seiches, are capped by a coarser grained, cross-bedded tsunami-deposited unit. The suevite (Unit 2A of Gulick et al., 2017<sup>43</sup>) grades into a 75 cm generally upward-fining, brown, fine-90 grained limestone termed the "transitional unit"<sup>44</sup> (Unit 1G of Gulick et al., 2017<sup>43</sup>; 617.33 to 91 616.58 mbsf), which was deposited by settling, tsunami, and seiches<sup>45</sup>. This unit is in turn 92 overlain by a 3-cm thick green marlstone<sup>43</sup>; 616.58 to 616.55 mbsf that grades into pelagic 93

111

white limestone (Unit 1F of Gulick et al., 2017<sup>43</sup>) (Figure 1). The lower 52 cm of the 94 95 transitional unit contains mm-scale laminations and graded beds, and the upper 19 cm also 96 contains cross beds and hummocky cross stratification which signify deposition by bottom currents associated with residual seiches within the crater<sup>45</sup>. The fine silt and clay grain size 97 98 of the transitional unit suggests that the majority of sediment was delivered by resuspension 99 and settling. A 20-cm interval of soft-sediment deformation occurs in the middle of the transitional unit, and the upper ~15 cm of the unit is burrowed<sup>44</sup>. The transitional unit contains 100 101 clay and pyrite, and is bounded by two intervals enriched in charcoal, which likely settled from the ocean surface transported by either wave energy or through the atmosphere<sup>12</sup>. The 102 103 occurrence of charcoal and evidence for high-energy transport suggests that the majority of 104 the transitional unit was deposited very rapidly within days to, at most, years after the impact. 105 This interpretation was originally based on Helium-3 measurements and Stokes Law calculations<sup>44</sup>, and is confirmed by enrichment of Ir in the uppermost transitional unit and 106 107 green marlstone (between 616.60 and 616.55 mbsf) that indicates settling of meteoritic 108 material, likely within a few years of the impact<sup>46</sup>. Site M0077 thus represents the most 109 expanded post-impact drill core record yet recovered of the immediate aftermath of the Chicxulub impact event<sup>12</sup>. 110

The transitional unit contains rare calcareous nannofossils and common planktic foraminifera, with survivor species of the latter group becoming more common upsection, indicating the appearance of pelagic life in the crater at least by the time burrows suggest a benthic infauna, less than a few years after impact<sup>44</sup>. The majority of the unit is composed of microcrystalline calcite, also known as micrite. Scanning electron microscopy (SEM) reveals rare microcrystals

that have been interpreted as microbial in origin<sup>47</sup>. The bulk of the micrite was likely derived 117 118 from CaO via thermal decarbonation (emission of CO<sub>2</sub>) of sedimentary target-rocks during 119 impact followed by carbonation (backreaction via addition of  $CO_2$ ) to  $CaCO_3$ , as suggested for select carbonate particles found at other K-Pg sites<sup>48</sup> 47,49. However, the mechanics of 120 121 carbonation are not well understood and it is unclear whether it took place in the late stages of 122 impact plume expansion, during the resurge of ocean waters back into the crater, in the water 123 column after crater flooding, or during burial in the months to years that the transitional unit 124 was formed.

125

Rapid deposition of the transitional unit offers the potential to determine the effects of reduced 126 127 photosynthesis, impact winter and hydrothermal activity on life at the dawn of the Cenozoic 128 era. Yet the proxy record can only be evaluated once the formation of micrite is constrained. 129 Moreover, interpretation of the fossil record is complicated by the high-energy depositional environment in which reworking of microscopic plankton tests is common<sup>44</sup>. Here we explore 130 131 the origin of the materials in the transitional unit and green marlstone on top of Chicxulub's 132 peak ring at Site M0077 and probe evidence for recovery of the food chain in the early crater 133 in the first months to thousands of years of the Cenozoic. We use optical microscopy, scanning 134 and transmission electron microscopy (SEM and TEM), clumped, strontium, and carbon and 135 oxygen stable isotopes (see Supplemental Materials for Methods), and current age models to 136 constrain conditions in the early crater, and compare them to the fossil evidence for the 137 recovery of life at ground zero. Our results illustrate that, despite harsh post-impact conditions, 138 the incipient crater became home to the most diverse post-impact marine assemblage

documented to date. This illustrates that craters can be viable habitats for life even in theimmediate aftermath of impact.

141

142

143

2. Results

#### 144 2.1 Character of micrite

145 Dramatic changes in the size and shape of micrite particles from the upper suevite through the 146 transitional unit into the green marlstone are observed via backscatter electron microscopy 147 (BSE) (Figure 1; Supplemental Materials Figure 1). Abundant micrite is found in the upper suevite (617.54 to 617.43 mbsf) where it is generally angular in shape. In the topmost suevite 148 149 (617.43 to 617.33 mbsf) and lowermost transitional unit (617.33 to 617.30 mbsf), micrite 150 particles are generally rounded to subrounded, flattened, and 10 to 150 µm in size, and samples 151 have a low porosity and a high clay content, as observed in BSE images (Figure 1; Pl. 7-11; 152 Supplemental Materials Figure 1; Pl. 6-10). The compacted nature of rounded micrite particles 153 in this interval (Figure 1; Pl. 8-10; Supplemental Materials Figure 1; Pl. 6-9) indicates 154 alteration by pressure solution during burial. In the remainder of the transitional unit, between 155 617.33 and 616.58 mbsf, micrite particles are generally highly irregular in size, and smaller, 156 between 0.5 and 20  $\mu$ m, more angular in shape, densely packed but rarely compressed, and 157 with a lower clay content (Figure 1; Pl. 3-6; Supplemental Materials Figure 1; Pl. 2-5). Calcite 158 in the green marlstone (616.58 to 616.55 mbsf) is composed of miniscule planktic foraminifera 159 (generally 20 to 40  $\mu$ m) and very fine micrite (<0.5 to 2  $\mu$ m; Figure 1; Pl. 1, 2; Supplemental Materials Figure 1; Pl. 1). Rare silicate melt particles are also observed (Figure 1; Pl. 1; 160 161 Supplemental Materials Figure 2; Pl. 1-5) and clay content increases in this interval. The fine

177

micrite resembles micrite in the transitional unit under cross-polarized light and is distinctfrom micrite in the overlying white limestone.

164

165 2.2 Character of charcoal and pyrite

166 Charcoal is generally rare throughout the transitional unit but is common in two intervals 167 (Figure 2): (1) at the base of the transitional unit and the underlying cross-bedded sand-sized 168 interval at the top of the uppermost suevite (617.34 to 617.27 mbsf); and (2) at the top of the transitional unit, and especially in the overlying green marlstone 616.605 to 616.545 mbsf; 169 170 Figure 3, Pl. 1,2). The lowermost transitional unit contains several distinct layers of pyrite (Figure 3; Pl. 6), while the green marlstone contains a diffuse pyritic interval between 616.56 171 and 616.545 mbsf (Figure 3, Pl. 1,2)<sup>12</sup> with two thin concentrated layers, as well as several 172 large (cm-sized) pyrite nodules<sup>46</sup>. A distinct band of pyrite also occurs at 617.24 to 617.25 173 174 mbsf. Two other intervals contain abundant pyrite without a corresponding peak in charcoal, 175 a band at 617.0 to 616.99 mbsf (Figure 3, Pl. 5) at the base of the interval of soft sediment 176 deformation, and two lenses at 617.22 to 617.24 mbsf.

178 Charcoal is high-grade and preserves original wood structure (Supplemental Materials Figure 179 3; Pl. 1-12); petrified wood composed of C, P, and Si as analyzed in Energy Dispersive X-ray 180 Spectrometry (EDS) is also found (Figures 4; Pl. 10-12; Supplemental Figure 4; Pl. 10-12). 181 Pyrite in all intervals is preserved as 5-100  $\mu$ m rhombic and hexagonal sheet-like crystals 182 (Supplemental Materials Figure 4; Pl. 1), and as 10-75  $\mu$ m long blades that look like shards at 183 the base of the green marlstone (Figure 4; Pl. 1, 2; Supplemental Materials Figure 4; Pl. 5; 184 Supplemental Materials Figure 5; Pl. 7-9). BSE images of hexagonal and blade-like pyrite

This article is protected by copyright. All rights reserved.

185 often show remnant woody structure including grainy texture and pits, even in the intervals 186 where charcoal is rare or absent (Figure 4; Pl. 4-6); images also illustrate grains that preserve 187 a transition between partially- and more fully-pyritized areas (Figure 4; Pl. 4, 5). BSE images 188 of pyrite grains from the base of the transitional unit show delicate needle clusters that we 189 interpret as pyritized conifer needles (Figure 4; Pl. 7, 8; Supplemental Materials Figure 4; Pl. 190 4). The organic matter of these needles is exposed when damaged by the electron beam 191 (Supplemental Materials Figure 4; Pl. 7-9). Both upper and lower transitions contain up to 400 192 µm unburned woody material, sometimes with delicate organic structures (Supplemental 193 Materials Figure 3; Pl. 10,11).

195 2.3 He isotopes

We have measured <sup>3</sup>He on two samples from the uppermost transitional unit and combine these data with values from Lowery et al. (2018<sup>44</sup>). Compared to deeper in the transitional unit, measurements at 616.605 and 616.57 mbsf show increasing <sup>3</sup>He contents which suggest slower sedimentation rates (Figure 2; see Supplemental Materials Table 2).

200

194

## 201 2.4 Stable O and C isotopes

Bulk carbonate  $\delta^{18}$ O values lie between -6.5 and -8.7 ‰ in the uppermost suevite and lowermost transitional unit (617.42 to 617.31 mbsf), then increase to -6.8 to -5.7 ‰ for most of the transitional unit 617.24 to 616.73 mbsf), then show a steady increase to -2.3 ‰ just above the green marlstone (616.54 mbsf) (Figure 5). Bulk carbonate  $\delta^{13}$ C values generally increase through the uppermost suevite and transitional unit (617.47 to 616.73 mbsf) from 0.48 ‰ to 1.45 ‰, although an interval of low values also occurs in the interval of soft-sediment

This article is protected by copyright. All rights reserved.

deformation, including samples at 616.93 to 616.84 mbsf (Figure 5). Values decrease at the top of the transitional unit and within the lower green marlstone (between 616.73 and 616.57 mbsf) from 1.45 to 0.75 ‰ then increase through the remainder of the green marlstone and the white limestone from 0.75 (616.5 mbsf) to 1.44 ‰ (616.25 mbsf).

213 2.5 Clumped isotopes

Clumped isotope-based temperatures are  $88 \pm 11$  °C (1 $\sigma$ ) for the uppermost suevite (617.47 to 617.34 mbsf), 73 ± 13 °C (1 $\sigma$ ) for most of the transitional unit (617.31 to 616.64 mbsf) (Figure 5), and decrease within the uppermost transitional unit and green marlstone to 27 ± 7°C in the overlying Danian foraminiferal limestone (616.54 to 616.25 mbsf).

218

212

219 2.6 Strontium isotopes and trace elements

220 Strontium isotopic compositions (<sup>87</sup>Sr/<sup>86</sup>Sr) of sample aliquots leached in 0.1 M ammonium 221 acetate-acetic acid buffer (pH 4.7) and 0.1 N HCl are similar suggesting that Sr is derived from 222 carbonate (see Supplemental Materials Figure 6c). There is likewise no correlation between Sr and lithogenic indicators such as Al that suggests an influence of clay dissolution on <sup>87</sup>Sr/<sup>86</sup>Sr. 223 The <sup>87</sup>Sr/<sup>86</sup>Sr ratios of weak HCl-soluble sediment systematically decrease in the lower 224 225 transitional unit to  $\sim 0.70763$  in the slump, and then increase to  $\sim 0.70771$  in the upper 226 transitional unit (Figure 5). More radiogenic values (0.70782-0.70789) are recorded in the 227 overlying green marlstone and Danian foraminiferal limestone, values that exceed 228 contemporaneous K-Pg boundary seawater ( $\leq 0.707828 \pm 0.000004^{50}$ ).

229

230 2.7 Micropaleontology

231 Samples from the lowermost and uppermost transitional unit and the green marlstone were 232 taken every 0.5 cm for nannoplankton and 2 cm for palynomorphs. Thin sections were also 233 observed in both intervals. Nannoplankton in the lowermost transitional unit include rare 234 specimens of Upper Cretaceous species along with rare specimens of the survivors 235 Braarudosphaera spp., Cyclagelosphaera reinhardtii, and Zeugrhabdotus sigmoides 236 (Supplemental Materials Figure 7; Pl. 1-4, 9, 10). A single specimen of the basal Danian 237 marker, *Biantholithus sparsus* is observed at 617.295 mbsf (Supplemental Materials Figure 7; 238 Pl. 5, 6). Dinoflagellates in the lower interval (at 617.3 mbsf) are rare but exclusively 239 represented by the cyst *Trithyrodinium evittii* (Supplemental Materials Figure 7; Pl. 11, 12). Nannoplankton in the green marlstone (616.58 to 616.545 mbsf) include abundant small 240 241 fragments of a primitive form of *Cervisiella* spp. (Supplemental Materials and Supplemental 242 Materials Figure 7; Pl. 7, 8), but lack the Cretaceous survivor taxa with only very rare reworked 243 specimens of long-ranging Cretaceous species. A single specimen of the earliest Danian genus 244 *Neobiscutum* is observed at 616.575 mbsf (Supplemental Materials Figure 8; Pl. 9). There are 245 no organic-walled dinoflagellates in the green marlstone but cyanobacterial fossils are common<sup>47</sup> (Supplemental Materials Figure 8; Pl. 1-8). The green marlstone also contains a 246 247 diverse and abundant assemblage of planktic and benthic foraminifera (the latter represented 248 by at least 63 species typical of the "Velasco Fauna"<sup>51</sup>). Earliest Danian planktic foraminifera 249 here include Parvularugoglobigerina, Woodringina, Praemurica, Eoglobigerina, and the 250 Cretaceous survivor, Guembelitria<sup>44</sup>.

A diverse array of microfossils composed of apatite are observed in thin section in the green marlstone between 616.58-616.56 mbsf: (1) 25-100 μm pellets consisting of micron-sized

254 clusters of ellipsoidal to spherical forms, often showing concentric layers (Figure 6; Pl. 1-3; 255 Supplemental Materials Figure 9; Pl. 1-4, 7-9); similar size and shaped objects often have 256 round, ellipsoidal and disk-shaped particles (Supplemental Materials Figure 9; Pl. 5, 10, 11, 257 13-16; (2) Large (~600 µm) pieces of apatite with irregular, cylindrical pores often containing 258 small apatite spheres (Figure 6; Pl. 5-7; Supplemental Materials Figure 9; Pl. 18-20); (3) 259 Arrangements of thin 1-5 ( $\mu$ m), elongated pieces of apatite in a skeletal-like structure (Figure 260 6; Pl. 13-16; Supplemental Materials Figure 10; Pl. 4, 6-8); and (4) More common 50 to 200 261  $\mu$ m, elongate, often wispy blades or lenses of apatite with a sub-horizontal orientation that are 262 commonly fractured, hooked, and rarely coiled (Figure 6; Pl. 9-12; Supplemental Materials Figure 10; Pl. 1-3, 5, 9-30). Although the blades are largely recrystallized, their internal texture 263 264 sometimes reveals discrete striations (200-800 nm in thickness) (Figure 6, Pl. 10; 265 Supplemental Materials Figure 10; Pl. 22, 23). These objects are also rare in the lowermost 266 transitional unit. The apatite blades appear to penetrate surrounding sediment (Supplemental 267 Materials Figure 10; Pl. 16, 17) indicating overgrowth or dissolution in the compacting 268 sediment column, while carbonate grains continued to coalesce around them (Figure 6; Pl. 9).

#### 270 **3. Discussion**

271

269

## 272 <u>3.1 Origin of micrite in the transitional unit and green marlstone</u>

273 Samples in the upper part of the suevite contain very rare Ca-rich spherules and accretionary 274 lapilli (Figure 1; Pl. 11) similar to those described in other K-Pg boundary sections<sup>49</sup>, areas of 275 silicate melt and clay lenses that appear to be altered silicate impact melt (Figure 1; Pl. 10), 276 and elliptical areas filled with mixed fine grained silicate and CaCO<sub>3</sub>, likely carbonate ash282

filled bubbles (Figure 1; Pl. 12; Supplemental Materials Figure 1; Pl. 11, 12 Supplemental Materials Figure 2; Pl. 7-12). The spherules and lapilli were part of the Chicxulub ejecta transported back to the crater by the tsunami. The highly angular shape and variable size of the majority of micrite in the transitional unit (Figure 1; Pl. 3-6) may be partially related to the lower energy of the seiche waves, but likely indicate a different origin.

283 Waters in the nascent Chicxulub crater would have been Ca-rich as a result of the interaction 284 with the products of degassed target limestone and anhydrite, thus it is possible that calcite 285 could have precipitated directly from early crater waters. Calcite (and aragonite) precipitated 286 from seawater in whitings or from fluids in hot springs shows regular prismatic or trigonal crystals<sup>52,53</sup>, very different from the irregular texture of micrite in the transitional unit. The 287 288 transitional unit texture strongly resembles that of calcite derived by thermal decarbonation along fault zones<sup>54 55</sup> (Figure 7; Pl. 9 compare with Pl. 10) and experimentally<sup>56</sup>. Moreover, 289 290 transmission electron microscope (TEM) images of a sample at 617.15 mbsf reveals regular 291  $\sim 100$  nm-spaced lineations that resemble features in experimental decarbonation of Iceland spar<sup>57</sup> (Figure 7; Pl. 1-6 compare with Pl. 11, 12). These properties suggest that production of 292 293 the angular micrite in the transitional unit involved decomposition of carbonate particles to 294 CaO during shock devolatization followed by entrainment in the low velocity ejecta at the final 295 stages of excavation, rather than from the hot vapor-rich cloud. Models indicate solid particles 296 will remain internal to the Chicxulub crater or be ejected just outside it in the final stages of 297 crater excavation when ejection velocities are relatively slow<sup>58</sup>. Externally ejected material 298 would have been delivered to the peak ring site by resurge most likely via the breach in the crater rim to the northeast<sup>59</sup>. Subsequent carbonation or backreaction of CaO to CaCO<sub>3</sub><sup>48</sup> likely 299

300 took place in the water column during suspension and settling; however, particles appear to 301 have grown around grains such as apatite (Figure 6; Pl. 9, 13; Supplemental Materials Figure 302 10; Pl. 4, 5, 12), suggesting continued precipitation during early burial. The green marlstone 303 also contains abundant micrite (Supplemental Materials Figure 11) along with clay and 304 calcareous microfossils<sup>44</sup>. This micrite commonly shows a Moiré fringe in TEM (Figure 7; Pl. 305 7, 8) suggesting fine overlapping crystals. More diagnostically, the micrite strongly resembles 306 micrite in the transitional unit showing low-order birefringence colors under cross-polarized light, likely as a result of the sheet-like nature of decarbonated calcite, and is distinct from 307 308 micrite in the white limestone whose high-order birefringence colors resemble diagenetic 309 calcite (Supplemental Materials Figure 11). This suggests that at least a fraction of the micrite 310 in the green marlstone was also derived via backreaction in the water column, or possibly in 311 the vapor plume (fine carbonate dust).

312

### 313 <u>3.2 The stratigraphic significance of charcoal layers</u>

314 The stratigraphic overlap of pyrite and charcoal, and the preservation of wood structures 315 (Figure 4; Pl. 1-8) suggest that the majority of pyrite replaced wood fragments transported into the crater from land or charcoalified during or after the impact process<sup>60</sup>, possibly through 316 317 bacterial sulfate reduction. One hypothesized origin of charcoal is ignition of vegetation 318 around the Gulf of Mexico by thermal radiation emitted by the impact plume or by wildfires ignited by ejecta heating the atmosphere  $^{12,60,62}$ . The 10-cm thick crossbedded unit at the top of 319 320 the suevite (Figure 2) was interpreted to be deposited by the reflected rim-wave tsunami, 321 supported by the presence of soil-derived biomarker perylene in this otherwise marine sequence<sup>12</sup>. The position of the lower charcoal layers directly above this suggests that the 322

charcoal and wood were also transported into the crater by the rim-wave tsunami and settled
 out more slowly than the sand fraction as energy declined<sup>12</sup>.

325

326 Pyritization can exaggerate the original charcoal abundance, and create artificial bedforms, as 327 in the case of the upper layers near the top of the green marlstone where the growth of large 328 pyrite crystals outline what appears to be a ripple (Figure 3; Pl. 1, 2). In fact, finely dispersed pyrite is more or less evenly distributed along the layers. Although it is hard to rule out wood 329 330 and charcoal derived from land, blades of pyrite (Figure 4; Pl. 1, 2; Supplemental Materials 331 Figure 4; Pl. 5; Supplemental Materials Figure 5; Pl. 7-9) in the thin uppermost (616.55 to 332 616.56 mbsf) layers (Figure 2) may be altered charcoal shards delivered by airfall, a hypothesis proposed by Gulick et al.  $(2019)^{12}$  given that tsunami deposits would not be expected years 333 334 after impact. This interpretation is supported by the overlap of the upper layers with the Ir anomaly which represents the atmospheric fallout of fine extraterrestrial material<sup>46</sup>, as does 335 clay in the marlstone. 336

337

#### 338 <u>3.3 Duration of the transitional unit and green marlstone</u>

Both chemical leaches show a significant decrease in micrite  ${}^{87}$ Sr/ ${}^{86}$ Sr in the lower part of the transitional unit, with values significantly lower than the  ${}^{87}$ Sr/ ${}^{86}$ Sr of contemporaneous global seawater at 66 Ma ${}^{63,64}$  (~0.707824 – 0.707832; Figure 5; Supplemental Materials Figure 6c). Hypotheses explaining the micrite  ${}^{87}$ Sr/ ${}^{86}$ Sr values include vaporization of the impactor or target limestone ${}^{65}$ . If micrite chemistry does indeed represent the local water column, as hypothesized above, then this suggests the impactor delivered enough Sr to the water column to alter its  ${}^{87}$ Sr/ ${}^{86}$ Sr, though this is likely limited to the local basin ${}^{63}$ . Assuming that (i) this shift

was instantaneous, (ii) the impactor had an <sup>87</sup>Sr/<sup>86</sup>Sr of ~0.703<sup>66</sup>, and (iii) seawater Sr 346 concentration is the same as modern (~90  $\mu$ M), the impactor delivered ~6.10<sup>5</sup> mol of Sr to the 347 348 local basin (this estimate would be higher if we accounted for active exchange with seawater and/or radiogenic hydrothermal inputs). If we assume an impactor volume of 525 km<sup>3</sup>, and a 349 350 density of 2 to 3 g/cm<sup>3</sup>, appropriate for carbonaceous chondrite, we estimate an impactor mass of 1 to  $1.6 \cdot 10^{15}$  kg<sup>67</sup>. If the impactor had bulk Sr concentrations of ~5 to 15 ppm<sup>68-70</sup>, then we 351 would estimate that only a very small fraction (<0.001%) of the impactor would have had to 352 solubilize. Alternatively, assuming  $\sim 200$  to 600 ppm Sr in the target rocks<sup>71,72</sup>, we estimate 353 that >4 $\cdot$ 10<sup>9</sup> kg of solubilized rock could explain micrite <sup>87</sup>Sr/<sup>86</sup>Sr; this estimate depends heavily 354 355 on the assumption of the target rock  ${}^{87}$ Sr/ ${}^{86}$ Sr, which could reasonably vary between ~0.70755 and 0.70765 (the latter of which is identical to the minimum micrite <sup>87</sup>Sr/<sup>86</sup>Sr<sup>65</sup>). Regardless of 356 source, <sup>87</sup>Sr/<sup>86</sup>Sr of the transitional unit suggests an age close to that of the impact, consistent 357 with <sup>3</sup>He isotope-based and biostratigraphic age controls<sup>44</sup>. 358

359

360 The <sup>3</sup>He technique assumes constant accumulation of cosmic-dust-derived <sup>3</sup>He in sediments and provides detailed interpretations of accumulation rate<sup>73</sup>. <sup>3</sup>He isotope data indicate 361 extremely rapid deposition for the majority of the transitional unit<sup>44</sup>, and, new measurements 362 363 (Supplemental Materials) suggest a significant slowdown in rates in the uppermost few cm (Figure 2). Although the likely duration of the transitional unit is below the resolution for the 364 365 technique, <sup>3</sup>He isotope data are consistent with the lower part of the transitional unit 366 representing months, and the entire unit representing an interval no more than years, a duration 367 that is consistent with the presence of the Ir anomaly beginning 2 cm from the top of the unit, 368 indicating deposition within, at most, a few years. The slow-down in sedimentation rates 369 continues in the green marlstone as the driver of deposition switched from waning impact370 energy and atmospheric fallout to hemipelagic sedimentation.

371

372 The age of the condensed green marlstone is more problematic as estimates derived from 373 impact-derived materials are in apparent conflict with those from traditional biostratigraphy and <sup>3</sup>He isotope data. Impact-related materials include the peak of the Ir anomaly between 374 616.55 and 616.60 mbsf, the upper charcoal layers between 616.55 and 616.56 mbsf, very 375 376 small (40-100 µm), altered, vesicular melt particles (Supplemental Figure 2; Pl. 1-5), and, as discussed, possibly fine calcite dust, immediately below the upper charcoal layers<sup>12</sup>. The Ir 377 anomaly generally signifies fallout within years of the impact<sup>74</sup>. These materials occur in a 378 379 condensed 5 cm interval which contains the first occurrence, and high abundance, of 380 Parvularugoglobigerina eugubina (whose appearance defines the boundary between Zones PO 381 and  $P\alpha$ ) and other common incoming Paleocene planktic foraminifera. Estimates of the base of P $\alpha$  range from ~30 kyr to as little as 3 kyr<sup>75</sup> above the K-Pg boundary with considerable 382 uncertainty (see Smit and Romein, 1985<sup>76</sup>), a range that is consistent with <sup>3</sup>He isotope data. 383

384

The green marlstone is bioturbated<sup>44</sup> and concentration of charcoal and wood in layers as well as the foraminiferal lags (Figure 3; Pl. 1) may be a result of minor winnowing, mixing materials from airfall, terrestrial and pelagic sources. Ichnofacies indicates only a few cm of mixing at most<sup>77</sup>. Moreover, the apparent age dichotomy may be explained by upward remobilization of Ir and other platinum group elements in reducing pore waters<sup>78</sup>. However, the distribution of impact-related materials in the green marlstone, especially the lightest charcoal and woody material near the top, is also consistent with settling through

392 the water column shortly after the impact. Particles in the green marlstone have a variety of sizes and would experience a range of settling rates<sup>79,80</sup>. Finer material including clay<sup>44</sup>, 393 394 abundant 1-2 µm-sized micrite (Supplemental Materials Figure 11; Pl. 4-6), and clay-sized 395 pieces of charcoal and wood (Figure 4; Pl. 7, 8) would take several years to settle to the 396 seafloor at 600 m water depth at 25°C and normal salinity. Large (>100 µm) pieces of 397 charcoal and wood (e.g., Supplemental Materials Figure 3; Pl. 1) would take a few days to 398 settle. Occurrence of larger charcoal particles near the top of the marlstone may have been 399 a result of delivery to the seafloor via density currents following gradual settling of the 400 underlying fines. Thus we conservatively interpret the marlstone to represent years to, at 401 most, millennia. We therefore interpret the appearance of the earliest Paleocene planktic 402 foraminifera in the crater in the immediate impact aftermath as part of a globally 403 asynchronous recovery with ecological implications that are explored in a later section.

404

#### 405 <u>3.4 Evidence for hydrothermal circulation in the early crater</u>

406 Heat and impact-induced rock fracturing and subsequent input of water at Chicxulub are 407 thought to have generated a hydrothermal system, driven by the elevated temperatures of the 408 melt sheet and uplifted lower crustal rocks in the crater center, that models suggest lasted for 409 over 1.5-2.5 Myr<sup>25</sup>. Indeed, evidence for hydrothermal alteration is observed in granites and suevites at Site  $M0077^{29,42}$ . Here we constrain the intensity of the hydrothermal system at the 410 411 seafloor, and its impact on the crater environment, by determining temperatures and fluid 412 chemistry during the deposition of the transitional unit and green marlstone using clumped, 413 strontium and stable carbon and oxygen isotopes.

415 The isotopic composition of micrite would have been first imprinted at the time and site of 416 carbonation, followed possibly by subsequent change during recrystallization to more stable 417 forms in the sediment column. Traditional oxygen isotope temperatures measured on calcium 418 carbonate ( $\delta^{18}O_{CaCO3}$ ) are limited by uncertainty in the isotopic composition of the water in which precipitation took place. Assuming a seawater  $\delta^{18}$ O value of -1.0 ‰, the traditional 419 oxygen isotope thermometer indicates largely invariant temperatures of  $41 \pm 4$  °C ( $\pm$  values 420 are 1 standard deviation of the pooled analyses) within the transitional unit, with higher 421 temperatures in the underlying uppermost suevite (54  $\pm$  2 °C), and a return to normal ocean 422 temperatures in the overlying pelagic limestone  $(22 \pm 2 \,^{\circ}\text{C})$  (Figure 5). The clumped isotope 423 424 paleothermometer, however, is independent of assumptions about the isotopic composition of the water<sup>81 82</sup> and thus is advantageous for determining the temperature of the early crater. 425 426 Very rapid precipitation could result in meta-stable carbonates susceptible to recrystallization 427 during early burial and, if so, the clumped isotope temperatures would reflect, at least in part, temperatures prevailing during recrystallization in the sediment column<sup>83</sup>. Clumped isotope-428 based temperatures are  $73 \pm 13$  °C (1 $\sigma$ ) with no clear trends for most of the transitional unit 429 (Figure 5) and decrease within the green marlstone to  $27 \pm 7^{\circ}$ C in the overlying Danian 430 foraminiferal limestone. 431

432

Together with  $\delta^{18}O_{CaCO3}$  values, the clumped isotope temperatures permit calculation of the apparent isotopic composition of water ( $\delta^{18}O_w$ ) in which carbonates formed. For the transitional unit, this approach yields a mean  $\delta^{18}O_w$  value of  $+4.3 \pm 1.9$  ‰ (Figure 8). This value is ~3 ‰ higher than any plausible open-ocean surface  $\delta^{18}O$  value for the latest Cretaceous. We offer two endmember scenarios that could result in such high apparent  $\delta^{18}O_w$ 

This article is protected by copyright. All rights reserved.

438 values. In the first scenario (Figure 8A), the high values represent actual water isotopic compositions, with the water being enriched in <sup>18</sup>O due to extensive evaporation of seawater 439 440 from heat generated by the impact event, or via high-temperature exchange with rock-derived O (which is enriched in <sup>18</sup>O relative to seawater) from the water circulating through the impact 441 442 melt rocks and suevite (or a combination of both). In this scenario, the ~70 °C clumped isotope 443 temperatures of the transitional unit reflect actual water temperatures during initial carbonate 444 mineralization in the water column or during early burial. This scenario is possibly supported 445 by the occurrence of evaporite minerals in the upper and lower transitions (Figure 9; Pl. 1-6, 446 8, 9; Supplemental Materials Figure 12; Pl. 1-3; see Supplemental Materials). These minerals 447 could be precipitates from local evaporation of seawater at the time of impact or trace residual 448 of the target rocks.

449

In a second scenario (Figure 8B), the carbonates initially formed in seawater of 'normal'  $\delta^{18}$ O 450 451  $(\sim -1\%)$  at temperatures indicated by the oxygen isotope thermometry (generally in excess of 452 30 °C but cooler than 60 °C). During early burial on the warmer seafloor, the carbonates 453 recrystallized under rock-buffered conditions (low water/rock ratio with respect to oxygen 454 atoms) such that the clumped isotope temperatures recorded by carbonates increased, but the  $\delta^{18}O_{CaCO3}$  value remained largely the same. This pattern is commonly seen in clumped isotope 455 studies of diagenetically-altered carbonate sediments<sup>84-86</sup>, and results in fictive  $\delta^{18}O_w$  values 456 457 that are higher than plausible seawater values. Under this scenario, the actual seafloor 458 temperatures were at least as high as the temperatures recorded by clumped isotopes (73  $\pm$  13 459  $^{\circ}$ C); if the carbonates were not completely recrystallized at this time (*i.e.*, if they retained some 460 of the isotopic signature attained prior to burial), then seafloor temperatures must have been

476

even higher. We disfavor this in situ high-temperature alteration scenario for three reasons. 461 462 First, as discussed in more detail below, heat flow models suggest that the >130m-thick mantle 463 of tsunami and suevite deposits overlying the impact melt rock on top of the peak ring and 464 even thicker deposits overlying the impact melt sheet in the central basin would have 465 functioned as a highly-effective thermal insulator, resulting in temperatures similar to 466 overlying seawater temperatures. Seawater temperatures, in turn, would largely reflect 'normal' Gulf water temperatures because the volume of distal Gulf water rushing back to the 467 impact site following the impact event would have been vastly larger than the volume of 468 469 (initially very hot) water in the immediate vicinity of the impact. Additionally, the presence of 470 clear indicators of pelagic and benthic life in the upper part of the transitional unit suggests 471 that water temperatures at the time these sediments were deposited were not too extreme for 472 life. Finally, and critically, the clear decrease in C-isotope values in the interval of soft 473 sediment deformation demonstrates that C-isotope values were acquired prior to burial, i.e. 474 represent water column values (Figure 5) and this interpretation is supported by the lack of 475 textural difference in micrite in this interval (Supplemental Materials Figure 1; Pl. 3).

We also disfavor interpretations invoking kinetic fractionation as the primary explanation of the stable isotope data. The clumped isotope data do not record the extremely high-temperature processes within the initial vapor plume that would have prevailed during decarbonation and possibly during recarbonation in the plume. Mass independent triple oxygen isotope fractionation ( $^{17}O/^{16}O$  relative to  $^{18}O/^{16}O$ ) during decarbonation has been shown experimentally  $^{87}$ , with CO<sub>2</sub> anomalously-enriched in  $^{17}O$  and CaO anomalously depleted, with differences in  $\Delta^{17}O$  of ~400 per meg between the two phases. High-precision triple oxygen 484 isotope measurements of a sample from the transitional unit and a sample from the overlying 485 Danian foraminiferal limestone show no significant deviation from compositions expected for 486 equilibrium with seawater (Supplementary Materials Figure 12 and Supplementary Materials), 487 indicating that the carbonates do not contain O inherited from the precursor CaO or CO<sub>2</sub> 488 generated in the impact plume, unless the recombination was fortuitously stoichiometric, such that the negative and positive  $\Delta^{17}$ O anomalies precisely canceled. Carbon isotope compositions 489 490 show no evidence of kinetic fractionation and are within the range expected for latest 491 Maastrichtian and earliest Danian carbonates. Finally, timescales for oxygen exchange between DIC and water are extremely rapid at elevated temperatures; for example, at 50 °C, 492  $t_{1/2} = 420$  s for HCO<sub>3</sub><sup>-</sup> -dominated solutions, and  $t_{1/2} = 11.5$  h for CO<sub>3</sub><sup>2-</sup> -dominated solutions, 493 based on kinetic data from Beck et al. (2005)<sup>88</sup>. Therefore, carbonate formation would need to 494 495 be extremely rapid in order to incorporate DIC in isotopic disequilibrium with seawater. If the 496 carbonate growth were this rapid, the resulting carbonates would likely be metastable (poorly-497 ordered, high surface area) and hence susceptible to isotope exchange during recrystallization. 498 Collectively, these lines of evidence argue against a strong kinetic fractionation signal 499 preserved in isotopic compositions of the transitional unit carbonates.

500

The initial resurge flooded the > 1 km deep impact basin, covering the peak ring with ~ 600meters of relatively cool Gulf of Mexico waters<sup>44</sup>. The 130 meter-thick suevite section at Site M0077 would have thermally isolated the deep waters from the underlying granitoid rocks and impact melt during the deposition of the transitional unit as conduction would have been too slow to warm even the bottom of the ocean. The central melt sheet, which is over 10 km from the peak-ring site and covered by several hundred meters of suevite<sup>25</sup>, also cannot have

507 maintained warmer water temperatures within the entire impact basin during the formation of 508 the transitional unit. Thus we postulate that the carbonation took place nearer to the central 509 melt sheet where deep waters would have been heated by interactions with melt as well as via 510 ejection of hot fluids at hydrothermal vents. Precipitation of carbonate in such an 511 environment would have been promoted not only by the returning CaO flux, but also by the decreased solubility of carbonate in the high-temperature waters<sup>89-91</sup> and by increased rates of 512 513 backreaction in such waters<sup>92</sup>. Thus regardless of origin, seawater in proximity of the central 514 melt sheet may have precipitated voluminous micrite, a literal carbonate "factory" (Figure 515 10A). Yet CaO ejecta and subsequent backreaction would have been crater-wide and likely 516 greater, as resurge and later seiches transported these ejecta back into the crater. Thus it is 517 likely that transitional unit micrite was derived from a wide region but with a larger proportion 518 from waters near the central melt sheet. We thus view the clumped isotope values in the 519 transitional unit as representing some of the warmest, but possibly not the highest temperatures 520 in the nascent crater.

521

522 Hydrothermal venting near the central melt sheet would have been widespread and intensive <sup>25</sup>. Such venting would leave an imprint on the trace element chemistry of the waters in which 523 524 the transitional unit micrite formed. The abrupt increase in <sup>87</sup>Sr/<sup>86</sup>Sr above 616.65 mbsf (Figure 525 5) occurred over intervals of years to, at most, millennia, as argued above. This is more rapid than rates of evolution of seawater <sup>87</sup>Sr/<sup>86</sup>Sr which are much slower as reflected by the 526 527 residence time (5 million years) and cannot be a consequence of mass delivered by the impactor. Assuming an estimated mass of water of ~1.6·10<sup>11</sup> kg (180 km diameter, 1 km 528 529 average depth) in the local basin, a  $\sim 100$  year time frame and a moderate amount of exchange

530 with seawater (i.e., the water residence time in the crater is  $\sim 0.05$  to 1 yr) suggests a Sr mass flux of  $\sim 10^6$  to  $2 \cdot 10^7$  mol Sr/yr and a crater water column Sr concentration that increases by 531 532 7%. The rate of change at Site M0077 must therefore reflect local input of radiogenic Sr, 533 possibly from hydrothermal alteration of underlying crust, consistent with clumped isotope 534 temperatures. The impact melt sheet is thought to have an average (granitic) crustal composition<sup>93</sup>, suggesting that the micrite <sup>87</sup>Sr/<sup>86</sup>Sr reflects a water column that is influenced 535 536 by the hydrothermal alteration of granitic composition rocks near the central melt sheet. 537 Significantly from a stratigraphic viewpoint, the ordered progression of Sr isotope ratios 538 indicates a gradually evolving crater chemical system as well as a batch-like supply of micrite 539 to the peak ring site.

540

550

The acetic-soluble <sup>87</sup>Sr/<sup>86</sup>Sr trend is broadly comparable to those of Fe/Ca and Mn/Ca, 541 542 (Supplemental Materials Figure 6b) and both trace elements are enriched throughout most of 543 the transitional unit, consistent perhaps with higher temperatures. In addition, Mg/Ca values 544 are ~11 to 14 mmol/mol in the transitional unit (and only ~20 mmol/mol in the HCl-soluble 545 fraction), which are considerably higher than biogenic carbonates. Assuming recent constraints on the equilibrium partitioning behavior of Mg into calcite<sup>94</sup> are appropriate, and 546 547 that the measured Mg/Ca reflects inorganic CaCO<sub>3</sub> precipitation, pore fluid Mg/Ca would have 548 to be extremely low (<0.1) to explain these values. Such a low value is consistent with 549 hydrothermal input that is Mg-poor, such as might be expected in a granite-hosted system.

551 The transitional unit also contains the following mineralogical evidence of in situ 552 hydrothermal alteration: (1) Isolated grains of ZnS are observed in the upper pyrite layers 553 at the base of the green marlstone (616.56 to 616.55 mbsf) and in a thin chlorite vein in the 554 transitional unit at 616.96 to 616.91 mbsf (Figure 9; Pl. 10, 11; Supplemental Materials 555 Figure 5; Pl. 11, 12; Supplemental Materials Figure 12; Pl. 4-6), at 617.28 to 617.26 mbsf, 556 at 617.34 to 617.32 mbsf, and at 617.54 to 617.49 mbsf. (2) At the basal contact of the 557 transitional unit 617.33 to 617.3 mbsf), pyrite appears to occur in veins filled with chlorite and minor calcite that resemble fluid escape structures<sup>42</sup> (Figure 3; Pl. 7; Figure 9; Pl. 12; 558 559 Supplemental Materials Figure 12; Pl. 7-11). The occurrence of these sulfides in veins suggests that they precipitated directly from hydrothermal fluids, clearly a distinct origin 560 561 from the sub-horizontal charcoal-derived pyrite layers. This is consistent with sulfur isotope data which suggests high and low temperature generation of pyrite<sup>46</sup>. The 562 563 occurrence of chlorite suggests pore water temperatures in excess of 300 °C, which is consistent with independent temperature estimates<sup>29</sup>. (3) Wood petrified by 564 phosphatization and silicification (Figure 4; Pl. 10-12) also indicates alteration by fluids, 565 although this process can occur at low temperature<sup>95</sup>. (4) Small grains of apatite are also 566 567 observed within chlorite veins (Figure 9; Pl. 7). Apatite is a common phase in pegmatites as P and Ca are concentrated in late-stage magmatic fluids. Thus we suggest that these 568 569 apatite grains also precipitated from hydrothermal fluids.

570

The occurrence of pyrite in chlorite veins and ZnS within the transitional unit and at the base of the overlying green marlstone indicate thin fingers of higher temperature fluids penetrated the buried sediment column and that local hydrothermal activity persisted possibly a for long time after normal hemipelagic deposition resumed consistent with models showing a long-lived hydrothermal system at Chicxulub<sup>25</sup>. Clumped isotopes place 585

576 constraints on the integrated temporal duration of this hydrothermal fluid flow, because 577 internal clumping in carbonate minerals is susceptible to resetting via solid-state diffusion 578 at elevated temperatures. For sustained heating at 300 °C, kinetic models predict that clumped isotopes will inherit the 300 °C signature in  $10^1$  to  $10^7$  years (Brenner et al. 579 580  $(2018)^{96}$ , Table 5). At 275 °C, approximately  $10^2$  to  $10^8$  years would be required for inheritance of the 300 °C signature. The fact that clumped isotopes record far cooler 581 temperatures (88  $\pm$  11 °C and lower) indicates that the duration of transitional unit 582 583 hydrothermal activity was brief, a few years or less, or that fluid temperatures were cooler 584 than suggested by the presence of chlorite, or both.

586 Clumped isotope temperatures abruptly decline near the top of the transitional unit between 587 616.635 and 616.605 mbsf to assumed sea surface temperatures of  $27 \pm 7$  °C within the green 588 marlstone (Figure 5). This change is coincident with the switch from material transported from 589 warmer regions of the crater to hemipelagic deposition (Figure 10B) yielding temperatures 590 that can be interpreted as in situ surface water values from plankton and backreacted calcite. 591 In fact, we postulate that surface temperatures at the peak ring site remained within a few 592 degrees of this level during the deposition of the transitional unit, and that this location was 593 representative of surface water conditions for much of the crater given its limited size. In the 594 following we explore how the unique crater environment, involving hydrothermal activity, 595 allowed life to recover and flourish in the immediate post-impact environment.

596

597 <u>3.5 New evidence for life in the nascent crater</u>

Globally, data and models suggest that the first decades after the impact were characterized by low light and impact winter<sup>9,10 16 5,13,17</sup>. However, our results indicate that waters in the crater remained warm in the immediate post-impact interval, possibly as a result of hydrothermal activity, even with the possibility of low light levels as suggested by evidence for atmospheric fallout. Here we compare this environmental record with evidence for return of life to the crater<sup>44</sup>.

604

605 Site M0077 contains a remarkable fossil record that illustrates rapid colonization of the newly 606 -formed crater by organisms representing a range of trophic levels (Figure 11). Survivor 607 species of nannofossils and planktic foraminifera are generally rare throughout the transitional 608 unit (as might be expected with such rapid depositional rates), although they increase in relative abundance upsection<sup>44</sup>. Planktic foraminifera and nannofossil assemblages include 609 610 significantly older (late Campanian-early Maastrichtian) species, particularly near the base of 611 the transitional unit, indicating that at least part of the assemblage is reworked from older beds. Lowery et al. (2018)<sup>44</sup> interpreted the gradual increase in the abundance of planktic 612 613 foraminiferal and calcareous nannoplankton survivors at the top of the transitional unit as 614 evidence for the return of life to crater surface waters, and the presence of burrowing organisms 615 as an indication of a habitable sea bed. Here we focus on samples from the lowermost 616 transitional unit (617.24 to 617.3 mbsf) and the uppermost transitional unit and the green 617 marlstone (616.6 to 616.545 mbsf). These intervals represent lower-energy conditions as 618 tsunami and seiches waned (lowermost transitional unit) and suspended material settled out 619 and potentially less redeposition combined with a larger in situ component (uppermost +-Author Manuscri transitional unit and green marlstone). Both intervals might contain minor hiatuses, but thereis no evidence for a significant gap in deposition.

622

623 The lowermost transitional unit contains survivor nannoplankton *Braarudosphaera* spp., 624 Cyclagelosphaera reinhardtii, and Zeugrhabdotus sigmoides (Figure 11; Supplemental 625 Materials Figure 7), taxa that are generally rare in uppermost Maastrichtian samples but 626 become common to abundant immediately above the boundary. Specimens are rare but far 627 exceed typical Late Cretaceous sample abundance; thus their occurrence is interpreted as 628 significant. The occurrence of *Biantholithus sparsus* is surprising and also significant. This 629 species which is commonly used as a marker for the K-Pg boundary has been observed below the boundary only at one site likely as a result of bioturbation<sup>97</sup>. The dinoflagellate cyst 630 Trithyrodinium evittii also originates and is very rare in the latest Maastrichtian<sup>98 97</sup>, but 631 becomes a disaster taxon in the earliest Danian where it is highly abundant<sup>98</sup>. Nannoplankton 632 assemblages in the green marlstone are very different, dominated by a primitive form of 633 634 Cervisiella spp. (commonly known as Thoracosphaera; Supplemental Materials Figure 7; Pl. 7, 8), which is a cyst of a calcareous dinoflagellate<sup>99</sup> and this taxon continues to dominate 635 samples in the overlying white limestone<sup>100</sup>. There are no organic-walled dinoflagellates in the 636 637 green marlstone but calcite and apatite interpreted as fossils of cyanobacteria are common (Supplemental Materials Figure 8; Pl. 1-8), an interpretation supported by organic 638 biomarkers<sup>101</sup>. 639

640

Nannoplankton and palynomorphs are highly susceptible to reworking, especially by highenergy transport processes such as tsunami and seiches. Although the lowermost transitional

653

643 unit contains common reworked Cretaceous species, the abundance of typical early Danian 644 taxa including the survivors *Biantholithus sparsus* and the dinoflagellate *T. evittii* suggests that 645 at least part of the assemblage represents early recovery either in waters outside the crater and 646 subsequently transported in by tsunami or possibly within the crater as tsunami energy 647 subsided (Figure 11). Species in this interval are dominated by haptophytes that grew in the 648 photic zone, indicating sunlit surface oceans, and the dinocyst T. evittii is considered to be 649 heterotrophic<sup>102</sup>, which indicates food supply from primary producers, possibly nannoplankton 650 or cyanobacteria. The primary nannoplankton and dinoflagellate species in the lowermost 651 transitional unit are an unexpected discovery: direct survivors that thrived in or around the 652 nascent crater even as tsunami energy waned.

654 By contrast, the abundance and unusual form of *Cervisiella* in the green marlstone, coinciding 655 with the lowest occurrence of a number of incoming planktic foraminifera, including P. *eugubina*<sup>44</sup>, is accompanied by near absence of Cretaceous taxa, suggesting that nannofossils 656 657 represent an in situ true recovery biota (Figure 11). Moreover, the distinct nature of nannofossil 658 assemblages from the lower and upper transitions suggests a primary environmental change 659 between these stages of the crater recovery. *Cervisiella* spp. is a dinoflagellate cyst, one of the 660 "disaster" taxa that was adapted to harsh environments and formed oceanwide blooms in the extinction aftermath<sup>100</sup>. The assemblage from the lowermost transitional unit disappeared, 661 662 suggesting that conditions had likely deteriorated to the point where surface oceans were 663 uninhabitable for almost all haptophyte nannoplankton and other dinoflagellates. The green 664 marlstone assemblage is unique; the lowermost samples at other proximal sites with expanded records contain a mixture of *Cervisiella* spp. and other survivors<sup>103</sup>, likely because they derive
 from a higher stratigraphic level or are mixed by bioturbation or winnowing.

667

668 The environmental significance of flora and fauna in the green marlstone depends on the 669 interpretation of impact-derived materials. At face value, the co-occurrence of the Ir anomaly, 670 charcoal, and impact spherules supports the conclusion that these impact derived materials and microfossils are in situ. In this case, we speculate that the nearly monogeneric Cervisiella 671 672 assemblages were a response to low light levels from dust and soot, a finding that would 673 represent a compelling link between one of the "kill mechanisms" and the plankton record. If 674 the planktic foraminifera in the green marlstone are also in situ, and not mixed relative to the 675 impact-derived materials, then it is possible that survivors and a dozen new taxa originated 676 within years of the impact which is unlikely, but not impossible. Even a few thousand year-677 long recovery, the maximum likely age for the green marlstone as discussed earlier, is far more rapid than has been observed at other continental margin and open marine sites<sup>104,105</sup>. Either 678 679 age interpretation would imply that conditions in crater waters were suitable for recovery 680 enabling a suite of planktic foraminiferal species to thrive before they were able to elsewhere. 681 How can this rapid recovery be explained?

682

The fossil record of the green marlstone, regardless of age interpretation, illustrates that as calcareous phytoplankton were experiencing harsh surface ocean conditions in the nascent crater, coexisting planktic foraminifera were recovering, even thriving<sup>44</sup>. Planktic foraminifera would have required an alternative food source given the decimation of the calcareous nannoplankton, their primary source in the Cretaceous. Possibilities include diatoms and

693

dinoflagellates which suffered lower extinction rates<sup>106</sup>, although neither group is found in the green marlstone. The occurrence of calcite and apatite microcrystals in the green marlstone are interpreted as precipitates induced or influenced by cyanobacteria<sup>47,101</sup>, and thus a burgeoning microbial community may also have served as food for the recovering planktic foraminiferal community and other zooplankton in the crater<sup>47</sup>.

694 Perhaps the most remarkable aspect of the crater fossil record is the discovery of a diverse 695 assemblage composed of apatite, predominantly at the base of the green marlstone but with 696 a few specimens at the base of the transitional unit (Figure 6; Supplemental Materials 697 Figures 9, 10). Identification of the small fragments of fossil apatite is difficult, especially 698 since specimens appear to have been heavily overgrown, but resemblance with modern and 699 other fossil materials provides some clues. (1) The clusters of ellipsoidal and spherical 700 forms strongly resemble fossil bacteria in coprolites in size and form (Figure 6; Pl. 1-3 701 compare with Pl. 4) and the pellet structures (Supplemental Figure 9; Pl. 5, 10, 11, 13-16) 702 resemble more modern fecal pellets from a terrestrial site (Supplemental Figure 9; Pl. 6,  $(12)^{107,108\ 109\ 110-112}$ . (2) The large pieces of apatite are more difficult to assign because they 703 704 are heavily altered. The random shape and orientation of cavities differ from known 705 biogenic materials such as bone or dentin. Their size and the occurrence of small apatite 706 spheres resemble highly altered bone fragments that have been tunneled by cyanobacteria<sup>113</sup> (Figure 6; Pl. 5-7 compare with Pl. 8; see also Supplemental Figure 9; Pl. 707 708  $(18-20)^{114-117}$ . (3) The apatite blades are also heavily overgrown and most of their original 709 structure has been erased. However, obvious striations in some of these blades do appear 710 to be primary structures (Figure 6; Pl. 9, 10; Supplemental Materials Figure 10; Pl. 9, 10,

711 14, 15), and blades are often clustered (Figure 6; Pl. 11; Supplemental Materials Figure 10; 712 Pl. 1, 2). The blades, including those in clusters, are generally hooked, with claw-like 713 protrusions on the ends, and resemble crustacean (e.g., copepod) appendages in size, 714 segmentation, and shape. Burial may have compressed the blades into the layered clusters. 715 Crustacean appendages are originally chitinous and have the potential to become phosphatized<sup>118</sup> and the underlying chitin structure can appear striated<sup>119</sup>, although 716 717 commonly occurring in spindles<sup>120</sup>. (4) The delicate layered structures (Figure 6; Pl. 13-718 16; Supplemental Materials Figure 10; Pl. 4, 6-8) also resemble fossil bone, which may 719 have come from small fish living in the crater. Fossilized bone is often recognized by 720 preservation of osteocyte lacunae, although numerous fish lineages bone can also be acellular<sup>121</sup>. As these structures are only 10-100 µm in size, they may represent juvenile or 721 722 small adult mesopelagic fish, rather than large predatory individuals. Selective survival and 723 rapid radiation of pelagic fishes, particularly small mesopelagic taxa is known to have occurred following the K-Pg<sup>122-124</sup>, so early recolonization by these taxa is quite possible. 724 725 Fish only experienced moderate levels of extinction at the K-Pg event and fish debris, including teeth <sup>125</sup>, are common in both marine and continental K-Pg boundary clays, 726 including the classic Stevns Klint Fish Clay K-Pg outcrop in Denmark<sup>126</sup> and the recently 727 described Hell Creek section in North Dakota<sup>127</sup>. We speculate that the coprolites, blades 728 and the piece of bone recovered from the sediments within the Chicxulub crater represent 729 730 the remains of pelagic metazoans, perhaps crustacean zooplankton (e.g. copepods) and 731 possibly fish that survived the extinction and were able to capitalize on the earliest Danian 732 phytoplankton food webs. The green marlstone may represent a unique preservational environment where the combination of pore-water euxinia and limited burrowing activityenabled the phosphogenesis of delicate specimens.

735

736 Smear slides from the lower transitional unit and the green marlstone contain clusters of 737 microglobular apatite that resemble spherulites grown in gels in the laboratory (Supplemental Materials Figure 14; Pl. 1, 7-9), and microbial Paleoproterozoic phosphorite<sup>128</sup>. A range of 738 739 other apatite forms are observed, which also could be of biological origin but whose affinity is 740 also unclear (Supplemental Material Figure 9; Pl. 17, 21, 22; Supplemental Material Figure 741 14; Pl. 2-6). Epifluorescence images also show the blades of apatite focused between 616.58-742 616.56 mbsf (Figure 3; Pl. 4) as well as occurring in elongated lenses between 616.6-616.57 743 mbsf. These lenses contain rare grains of apatite (Supplemental Materials Figure 12; Pl. 12), 744 and appear to be organic-rich based on their appearance in cross-polarized light (Figure 3; Pl. 745 3). We speculate that these grains originate from microbial mats that thrived during the time 746 interval represented by the boundary between the transitional unit and the green marlstone. 747 Such mats may have occupied the shallow water regions near the crater rim and these grains 748 may have been transported by the intense storms expected with the climatic changes across the K-Pg event<sup>129,130</sup>. 749

750

The occurrence of microbial mats at the time of the upper transitional unit and in the green marlstone has already been proposed based on elevated 3 $\beta$ -methylhopane indices in samples between 616.62 and 616.55 mbsf<sup>101</sup> which signify methanotrophic bacteria. Schaefer et al. (2020)<sup>101</sup> postulated that the microbial compounds were redeposited from shallower parts of the crater. Today phosphatized microbial mats accumulate in upwelling settings along

756 continental margins where the flux of organic carbon results in pore water supersaturation and 757 subsequent precipitation of apatite following bacterial phosphate remineralization<sup>131</sup>. 758 Phosphate is generally rare in sediments deposited in deeper ocean regions. Elevated P levels 759 may be a response to eutrophication that followed the decimation of planktic producers at the 760 K-Pg boundary<sup>132</sup>; indeed apatite fossils are also found in samples from the Fish Clay at Stevns 761 Klint (Supplemental Materials Figure 14; Pl. 10-12) that are thought to date to centuries and millennia after the impact. Resurge into the crater via the  $\sim 2$  km deep northeast ramp to the 762 Gulf of Mexico<sup>59</sup> (Figure 10) could have delivered nutrient-rich waters but microbial activity 763 764 would have readily depleted nutrient levels; thus there is likely another source of P. Occurrence 765 of apatite in chlorite veins lower in the transitional unit (Figure 9; Pl. 7) suggests a connection 766 between hydrothermal activity and P supply; indeed P is often enriched in late stage pegmatite 767 fluids<sup>133</sup>. Thus the nascent crater may have provided a productive refuge for survivors, 768 including the planktic foraminifera, explaining their earlier recovery.

769

Evidence for diverse life including morphological and molecular fossils<sup>44 47,101</sup> from Chicxulub 770 771 suggests that the crater became rapidly habitable in the immediate aftermath of the impact 772 (Figure 11), possibly earlier than in other parts of the ocean. This suggests that the unique 773 crater environment allowed life to flourish. We speculate that heat and nutrients from the 774 hydrothermal system were instrumental in sustaining a diverse community of primitive life, 775 and this community likely played a role in survival of higher orders of organisms, including pelagic crustaceans and fish<sup>125</sup>. The rapid appearance of life in the early Chicxulub crater, 776 777 including organisms at a range of trophic levels, demonstrates the resiliency of life under extraordinarily harsh conditions, which has important ramifications for early life on Earth and
life on other planets<sup>23</sup>.

781 **4. Conclusions** 

782 An expanded record from the peak ring of the Chicxulub crater illustrates the connection 783 between environment and recovery of life in the nascent Chicxulub crater. Water temperatures 784 in the were in excess of 70 °C immediately after the K-Pg impact with heat derived from the 785 central melt sheet. The cooler peak ring location was habitable within days to years of the 786 impact with survivor nannoplankton and monospecific, red-tide dinocyst assemblage arriving 787 in the aftermath of the tsunami waves. A monogeneric calcareous dinoflagellate resting cyst 788 assemblage is found at levels where charcoal and the Ir anomaly indicate atmospheric fallout, 789 and a possible interpretation is that the absence of photosynthetic plankton was a response to 790 low light levels. Microbial fossils are found throughout the sequence suggesting a thriving 791 bacterial community potentially supported by nutrients from hydrothermal activity. This 792 productivity likely supported the recovery of organisms representing a range of trophic levels 793 including planktic foraminifera, pelagic crustaceans and fishes over an interval of years to no 794 more than a few millennia.

795

## 796 <u>Acknowledgments</u>

797 This research used samples and data provided by IODP. Expedition 364 was jointly funded 798 by the European Consortium for Ocean Research Drilling (ECORD) and ICDP, with 799 contributions and logistical support from the Yucatán State Government and Universidad 800 Nacional Autónoma de México (UNAM). Research was funded by NSF-OCE OCE 801 1736951 (to TB and KHF), 1737351, 1737087, OCE 1736826, OCE 1737087, OCE 802 1737037, and OCE 1737199, and Post Expedition Awards from IODP to TB, NERC grant 803 NE/P005217/1 to JVM, and by the Swedish Research Council (VR) grant 2015-4264 to 804 VV. SG acknowledges the support by the Belgian Science Policy (BELSPO) and Research 805 Foundation - Flanders (FWO - Vlaanderen). We thank the Expedition 364 captain and

806 crew, drilling team and technical staff who participated in shipboard and shore based 807 activities, and the entire science party for their support. We acknowledge helpful 808 discussions with Cristiano Colletini, Maureen Feineman, Lee Kump, Ron Shahar and Andy 809 Smye. We thank Holger Kuhlmann, Chad Broyles, and Phil Rumford for help with 810 sampling, Julie Anderson and Wes Auker for assistance with the SEM, and Kat Crispin, 811 Mark Fairchilds and Tom Henderson with help with microscopy. We thank Drake Yarian, 812 Elise Pelletier, Natalie Packard, Sarah Katz, Emily Beverly, Dana Brenner, and Ian 813 Winkelstern for assistance with the clumped isotope and triple oxygen isotope analyses. 814 We are very grateful to Mark Leckie and two anonymous reviewers for extremely helpful 815 suggestions on an earlier version of the manuscript. This is UTIG Contribution #XXXX. 816

**Data Availability:** The data that support the findings of this study are available in the PANGAEA database (https://www.pangaea.de/).

## **References**

817 818

819

820 821 822

823 824

825

826

827

828

- Morgan, J. *et al.* The formation of peak rings in large impact craters. *Science* 354, 878-882 (2016).
   Hildebrand, A. R. *et al.* Chicxulub crater: a possible Cretaceous/Tertiary
- boundary impact crater on the Yucatan Peninsula, Mexico. *Geology* **19**, 867-871 (1991).
- Kring, D. A. & Boynton, W. V. Petrogenesis of an augite-bearing melt rock in the
  Chicxulub structure and its relationship to K/T impact spherules in Haiti. *Nature* **358**, 141 (1992).
- 8324Schulte, P. *et al.* The Chicxulub asteroid impact and mass extinction at the833Cretaceous-Paleogene boundary. *Science* **327**, 1214-1218,

834 doi:10.1126/science.1177265 (2010).

- Vellekoop, J. *et al.* Rapid short-term cooling following the Chicxulub impact at
  the Cretaceous–Paleogene boundary. *Proc Natl Acad Sci U S A* 111, 7537-7541
  (2014).
- Prinn, R. G. & Fegley Jr, B. Bolide impacts, acid rain, and biospheric traumas at
  the Cretaceous-Tertiary boundary. *Earth and Planetary Science Letters* 83, 1-15
  (1987).
- Alvarez, L. W., Alvarez, W., Asaro, F. & Michel, H. V. Extraterrestrial cause for
  the Cretaceous-Tertiary extinction. *Science* 208, 1095-1108 (1980).
- 843 8 Toon, O. B. *et al.* Evolution of an impact-generated dust cloud and its effects on
  844 the atmosphere. (1982).
- Brugger, J., Feulner, G. & Petri, S. Baby, it's cold outside: Climate model
  simulations of the effects of the asteroid impact at the end of the Cretaceous. *Geophysical Research Letters* 44, 419-427 (2017).
- Artemieva, N. & Morgan, J. Quantifying the Release of Climate-Active Gases by
  Large Meteorite Impacts With a Case Study of Chicxulub. *Geophysical Research Letters* 44, 10,180-110,188, doi:10.1002/2017gl074879 (2017).

851 852	11	Kring, D. A. The Chicxulub impact event and its environmental consequences at the Cretaceous–Tertiary boundary. <i>Palaeogeography, Palaeoclimatology,</i>
852		Palaeoecology 255, 4-21, doi:10.1016/j.palaeo.2007.02.037 (2007).
855	12	Gulick, S., Bralower, T.J., Ormö, J., Hall, B., Grice, K., Schaefer, B., Lyons, S.,
855	12	Freeman, K., Morgan, J., Artemieva, N., Kaskes, P. de Graaff, S., Whalen, M.,
856		Goto, K., Smit, J. and others. The first day of the Cenozoic. <i>PNAS</i> <b>113</b> , 19342-
857		19351 (2019).
858	13	Tabor, C. R., Bardeen, C. G., Otto - Bliesner, B. L., Garcia, R. R. & Toon, O. B.
859	15	
		Causes and Climatic Consequences of the Impact Winter at the Cretaceous -
860 861	14	Paleogene Boundary. <i>Geophysical Research Letters</i> <b>47</b> , e60121 (2020).
861	14	Wolbach, W. S., Gilmour, I. & Anders, E. Major wildfires at the
862 863		Cretaceous/Tertiary boundary. <i>Geological Society of America Special Paper</i> <b>247</b> , 391-400 (1990).
803 864	15	Tschudy, R., Pillmore, C., Orth, C., Gilmore, J. & Knight, J. Disruption of the
865	15	terrestrial plant ecosystem at the Cretaceous-Tertiary boundary, Western Interior.
865		Science 225, 1030-1032 (1984).
860 867	16	Kaiho, K. <i>et al.</i> Global climate change driven by soot at the K-Pg boundary as the
868	10	cause of the mass extinction. <i>Scientific Reports</i> <b>6</b> , 28427 (2016).
869	17	Lyons, S. L., Karp, A.T., Bralower, T.J., Grice, K., Schaefer, B., Gulick, S.P.S.,
870		gan, J., Freeman, K.H., 2020. Organic matter from the Chicxulub crater exacerbated
871	More	the K–Pg impact winter. PNAS, doi/10.1073/pnas.2004596117.
872	18	Artemieva, N. & Morgan, J. Global K - Pg layer deposited from a dust cloud.
873	10	Geophysical Research Letters, e2019GL086562 (2020).
874	19	Schoene, B. <i>et al.</i> U-Pb constraints on pulsed eruption of the Deccan Traps across
875	17	the end-Cretaceous mass extinction. <i>Science</i> <b>363</b> , 862-866 (2019).
876	20	Sprain, C. J. <i>et al.</i> The eruptive tempo of Deccan volcanism in relation to the
877	-	Cretaceous-Paleogene boundary. Science 363, 866-870 (2019).
878	21	Hull, P. M. et al. On impact and volcanism across the Cretaceous-Paleogene
879		boundary. Science <b>367</b> , 266-272 (2020).
880	22	Chiarenza, A. A., Farnsworth, A., Mannion, P.D., Lunt, D.J., Valdez, P.J.,
881		Morgan, J.V., Allison, P.A. Asteroid impact, not volcanism, caused the end-
882		Cretaceous dinosaur extinction. Proc Natl Acad Sci U S A, doi:202006087; DOI:
883		10.1073/pnas.2006087117 (2020).
884	23	Russell, M. J. & Hall, A. J. The onset and early evolution of life. Memoirs-
885		Geological Society of America <b>198</b> , 1 (2006).
886	24	Cockell, C. S., Osinski, G. R. & Lee, P. The impact crater as a habitat: effects of
887		impact processing of target materials. Astrobiology 3, 181-191 (2003).
888	25	Abramov, O. & Kring, D. A. Numerical modeling of impact - induced
889		hydrothermal activity at the Chicxulub crater. <i>Meteoritics Planetary Science</i> 42,
890		93-112 (2007).
891	26	Osinski, G. R. et al. Impact-generated hydrothermal systems on Earth and Mars.
892		<i>Icarus</i> <b>224</b> , 347-363 (2013).
893	27	Newsom, H. E., Hagerty, J. J. & Thorsos, I. E. Location and sampling of aqueous
894		and hydrothermal deposits in Martian impact craters. Astrobiology 1, 71-88
895		(2001).

896	28	Rathbun, J. A. & Squyres, S. W. Hydrothermal systems associated with Martian
897	20	impact craters. <i>Icarus</i> <b>157</b> , 362-372 (2002).
898	29	Kring, D. A., Tikoo, S.M., and others. Probing the hydrothermal system of the
899	20	Chicxulub Crater Science Advances 6 (2020).
900	30	Cockell, C.S., Coolen, M.J., Grice, K. and Schaefer, B., 2019. Microbial
901		communities and impact enhanced habitats in the Chicxulub impact crater.
902	01	Astrobiology Science Conference. AGU.
903	31	O'Sullivan, E. M., Goodhue, R., Ames, D. E. & Kamber, B. S.
904		Chemostratigraphy of the Sudbury impact basin fill: Volatile metal loss and post-
905		impact evolution of a submarine impact basin. <i>Geochimica et Cosmochimica Acta</i>
906	22	<b>183</b> , 198-233 (2016).
907	32	Morgan, J. V. & Warner, M. Chicxulub: The third dimension of a multi-ring
908	22	impact basin. <i>Geology</i> <b>27</b> , 407-410 (1999).
909	33	Gulick, S. <i>et al.</i> Geophysical characterization of the Chicxulub impact crater.
910		<i>Reviews of Geophysics</i> <b>51</b> , 31-52 (2013).
911	34	Arz, J. A., Alegret, L. & Arenillas, I. Foraminiferal biostratigraphy and
912		paleoenvironmental reconstruction at the Yaxcopoil - 1 drill hole, Chicxulub
913		crater, Yucatán Peninsula. Meteoritics & Planetary Science 39, 1099-1111
914		(2004).
915	35	Goto, K. et al. Evidence for ocean water invasion into the Chicxulub crater at the
916		Cretaceous/Tertiary boundary. Meteoritics & Planetary Science 39, 1233-1247
917		(2004).
918	36	Lüders, V. & Rickers, K. Fluid inclusion evidence for impact - related
919		hydrothermal fluid and hydrocarbon migration in Creataceous sediments of the
920		ICDP - Chicxulub drill core Yax - 1. Meteoritics Planetary Science 39, 1187-
921		1197 (2004).
922	37	Zürcher, L. & Kring, D. A. Hydrothermal alteration in the core of the
923		Yaxcopoil - 1 borehole, Chicxulub impact structure, Mexico. Meteoritics
924		<i>Planetary Science</i> <b>39</b> , 1199-1221 (2004).
925	38	Hecht, L., Wittmann, A., R T., S. & Stöffler, D. Composition of impact melt
926		particles and the effects of post - impact alteration in suevitic rocks at the
927		Yaxcopoil - 1 drill core, Chicxulub crater, Mexico. <i>Meteoritics Planetary Science</i>
928		<b>39</b> , 1169-1186 (2004).
929	39	Rowe, A., Wilkinson, J., Coles, B. & Morgan, J. Chicxulub: Testing for post -
930	57	impact hydrothermal input into the Tertiary ocean. Journal Planetary Science
931		Meteoritics <b>39</b> , 1223-1231 (2004).
932	40	Wang, YY., Yao, QZ., Zhou, GT. & Fu, SQ. Formation of elongated calcite
932 933	40	mesocrystals and implication for biomineralization. <i>Chemical Geology</i> <b>360</b> , 126-
933 934		133 (2013).
934 935	41	Whalen, M. T., Gulick, S., Pearson, Z. F. & Norris, R. D. Annealing the
936	71	Chicxulub impact: Paleogene Yucatán carbonate slope development in the
937		Chicxulub impact basin, Mexico. <i>Special Publication-SEPM</i> <b>105</b> , 282-304
937 938		(2013).
939 939	42	Morgan, J. & Gulick, S. Drilling the K-Pg Impact Crater: IODP-ICDP Expedition
940	- <i>74</i>	364 Results. <i>LPI Contributions</i> <b>2067</b> (2018).
740		50 TRESURS. LI I COMHDMIONS <b>200</b> 7 (2010).

This article is protected by copyright. All rights reserved.

941 43 Gulick, S. et al. Expedition 364 preliminary report: Chicxulub: drilling the K-Pg 942 impact crater. (2017). 943 Lowery, C. M. et al. Rapid recovery of life at ground zero of the end-Cretaceous 44 944 mass extinction. Nature 558, 288-291, doi:10.1038/s41586-018-0163-6 (2018). 945 Whalen, M.T., Gulick, S.P.S., Lowery, C., Bralower, T.J., Morgan, J.V., Grice, 45 946 K., Schaefer, B., Coolen, M., Vajada, V., Smit, J., and the IODP-ICDP Expedition 947 Science Party, 2018. Winding down the Chicxulub impact: the transition between 948 impactites and normal marine sedimentation, American Geophysical Union Fall 949 Meeting Abstracts, PP53B-08. 950 46 Goderis, S., H., S., Ferrière, L. & others, a. The final settling of meteoritic matter 951 on the peak-ring of the Chicxulub impact structure ar Site M0077A of IODP-952 ICDP expedition 364. . Large Meteorite Impacts and Planetary Evolution VI 953 (2019).954 47 Bralower, T. J., Cosmidis, J., Heaney, P., Kump, L.R. Morgan, J., Harper, D. 955 Lyons, S.L., Freeman, K.H., Grice, K., Wendler, J., Zachos, J.C., Artemieva, N., 956 Gulick, S., House, C., Jones, H.L., Lowery, C.L., Nims, C., Schaefer, B., Si, A., 957 Thomas, E., Vajda, V., 2020. Origin of a global carbonate layer deposited in the 958 aftermath of the Cretaceous-Paleogene boundary impact. Earth and Planetary 959 Science Letters, v. 548, 116476. 960 48 Schulte, P. et al. A dual-layer Chicxulub ejecta sequence with shocked carbonates 961 from the Cretaceous–Paleogene (K–Pg) boundary, Demerara Rise, western 962 Atlantic. Geochimica et Cosmochimica Acta 73, 1180-1204, 963 doi:10.1016/j.gca.2008.11.011 (2009). 49 964 Yancey, T. E. & Guillemette, R. N. Carbonate accretionary lapilli in distal 965 deposits of the Chicxulub impact event. Geological Society of America Bulletin 966 120, 1105-1118 (2008). 967 McArthur, J. & Howarth, R. 50 (Cambridge University Press: Cambridge, UK, 968 2004). 969 51 Alegret, L. & Thomas, E. Upper Cretaceous and lower Paleogene benthic 970 foraminifera from northeastern Mexico. *Micropaleontology*, 269-316 (2001). 971 Jones, B. Review of aragonite and calcite crystal morphogenesis in thermal spring 52 972 systems. Sedimentary Geology 354, 9-23 (2017). 973 53 Thompson, J. B. in *Microbial Sediments* 250-260 (Springer, 2000). 974 54 Collettini, C., Viti, C., Tesei, T. & Mollo, S. Thermal decomposition along natural 975 carbonate faults during earthquakes. Geology 41, 927-930 (2013). 976 55 Novellino, R. et al. Dynamic weakening along incipient low-angle normal faults 977 in pelagic limestones (Southern Apennines, Italy). Journal of the Geological 978 Society 172, 283-286 (2015). 979 Hamann, C. et al. The reaction of carbonates in contact with laser - generated, 56 980 superheated silicate melts: Constraining impact metamorphism of carbonate -981 bearing target rocks. Meteoritics & Planetary Science 53, 1644-1686 (2018). 982 57 Rodriguez-Navarro, C., Ruiz-Agudo, E., Luque, A., Rodriguez-Navarro, A. B. & 983 Ortega-Huertas, M. Thermal decomposition of calcite: Mechanisms of formation 984 and textural evolution of CaO nanocrystals. American Mineralogist 94, 578-593 985 (2009).

Author Manuscrip

39

	987	58	Kring, D. A. Hypervelocity collisions into continental crust composed of sediments and an underlying crystalline basement: Comparing the Ries ( $\sim 24$ km)
	988		and Chicxulub (~ 180 km) impact craters. <i>Chemie der Erde-Geochemistry</i> <b>65</b> , 1-
	989 990	59	46 (2005). Gulick, S. P. <i>et al.</i> Importance of pre-impact crustal structure for the asymmetry
	990 991	39	of the Chicxulub impact crater. <i>Nature Geoscience</i> <b>1</b> , 131-135 (2008).
		60	Kruge, M. A., Stankiewicz, B. A., Crelling, J. C., Montanari, A. & Bensley, D. F.
	993	00	Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic
	994		firestorm and megawave. <i>Geochimica et Cosmochimica Acta</i> <b>58</b> , 1393-1397
	995		(1994).
		61	Jones, T. P. & Lim, B. Extraterrestrial impacts and wildfires. <i>Palaeogeography</i> ,
	997	01	Palaeoclimatology, Palaeoecology <b>164</b> , 57-66 (2000).
		62	Melosh, H. J., Schneider, N., Zahnle, K. J. & Latham, D. Ignition of global
	999	° <b>-</b>	wildfires at the Cretaceous/Tertiary boundary. <i>Nature</i> <b>343</b> , 251 (1990).
		63	MacLeod, K. G., Huber, B. T. & Fullagar, P. D. Evidence for a small (~ 0.000
	001		030) but resolvable increase in seawater 87Sr/86Sr ratios across the Cretaceous-
	002		Tertiary boundary. <i>Geology</i> <b>29</b> , 303-306 (2001).
		64	Martin, E. & Macdougall, J. Seawater Sr isotopes at the Cretaceous/Tertiary
	004		boundary. Earth and Planetary Science Letters 104, 166-180 (1991).
		65	Belza, J., Goderis, S., Keppens, E., Vanhaecke, F. & Claeys, P. An emplacement
	006		mechanism for the mega - block zone within the Chicxulub crater, (Yucatán,
	007		Mexico) based on chemostratigraphy. <i>Meteoritics &amp; Planetary Science</i> 47, 400-
	008		413 (2012).
		66	Dickin, A. P. Radiogenic isotope geology. (Cambridge University Press, 2018).
		67	Durand-Manterola, H. J. & Cordero-Tercero, G. Assessments of the energy, mass
1	011		and size of the Chicxulub Impactor. arXiv preprint arXiv:1403.6391 (2014).
1	012	68	Wasserburg, G., Papanastassiou, D. & Sanz, H. Initial strontium for a chondrite
1	013		and the determination of a metamorphism or formation interval. Earth and
1	014		Planetary Science Letters 7, 33-43 (1969).
1	015	69	Faure, G. & Powell, J. L. in <i>Strontium isotope Geology</i> 78-91 (Springer, 1972).
$\bigcap 1$	016	70	Charlier, B., Tissot, F., Dauphas, N. & Wilson, C. Nucleosynthetic, radiogenic
$\bigcup$ 1	017		and stable strontium isotopic variations in fine-and coarse-grained refractory
	018		inclusions from Allende. Geochimica et Cosmochimica Acta 265, 413-430 (2019).
1	019	71	Schmitt, R. T., Wittmann, A. & Stöffler, D. Geochemistry of drill core samples
1	.020		from Yaxcopoil - 1, Chicxulub impact crater, Mexico. Meteoritics & Planetary
1	021		Science <b>39</b> , 979-1001 (2004).
$\overline{}$ 1	022	72	Tuchscherer, M. G. The petrology and geochemistry of the impactite sequence
	.023		and selected target rocks from the Yaxcopoil-1 borehole, Chicxulub Impact
	024		Structure, Yucatan Peninsula, Mexico, (2008).
		73	Farley, K. & Eltgroth, S. An alternative age model for the Paleocene–Eocene
	026		thermal maximum using extraterrestrial 3He. Earth and Planetary Science Letters
	027		<b>208</b> , 135-148 (2003).
		74	Artemieva, N. & Morgan, J. Modeling the formation of the K–Pg boundary layer.
1	.029		<i>Icarus</i> <b>201</b> , 768-780 (2009).

This article is protected by copyright. All rights reserved.

	030	75	Berggren, W. A., Kent, D. V., Swisher III, C. C. & Aubry, MP. A revised
	031		Cenozoic geochronology and chronostratigraphy. Geochronology, Time Scales
	.032		and Global Stratigraphic Correlation, SEPM Special Publication No. 54 (1995).
	.033	76	Smit, J. & Romein, A. A sequence of events across the Cretaceous-Tertiary
	034		boundary. Earth and Planetary Science Letters 74, 155-170 (1985).
	.035	77	Rodríguez-Tovar, F. J., Lowery, C., Bralower, T.J., Gulick, S., and Jones, H.,
	036		2020. Rapid macrobenthic diversification and stabilization after the end-
	.037		Cretaceous mass extinction event. Geology, https://doi.org/10.1130/G47589.1.
	038	78	Colodner, D. C., Boyle, E. A., Edmond, J. M. & Thomson, J. Post-depositional
	039		mobility of platinum, iridium and rhenium in marine sediments. <i>Nature</i> <b>358</b> , 402
	040		(1992).
	041	79	Stokes, G. G. On the effect of the internal friction of fluids on the motion of
	.042		pendulums. Transactions of the Cambridge Philosophical Society IX, reprinted in
	.043		Mathematical and Physical Papers 3, 1–86, doi:
	044		https://doi.org/10.1017/CBO9780511702266 (1850).
	045	80	Maggi, F. The settling velocity of mineral, biomineral, and biological particles
	046		and aggregates in water. Journal of Geophysical Research: Oceans 118, 2118-
	.047		2132 (2013).
	048	81	Ghosh, P. et al. 13C-18O bonds in carbonate minerals: a new kind of
	049		paleothermometer. <i>Geochimica et Cosmochimica Acta</i> <b>70</b> , 1439-1456 (2006).
	050	82	Eiler, J. M. Clumped-isotope geochemistry—The study of naturally-occurring,
	051		multiply-substituted isotopologues. Earth Planetary Science Letters 262, 309-327
	052		(2007).
	.053	83	Gabitov, R. I., Watson, E. B. & Sadekov, A. Oxygen isotope fractionation
	054		between calcite and fluid as a function of growth rate and temperature: An in situ
	055		study. <i>Chemical Geology</i> <b>306</b> , 92-102 (2012).
	056	84	Ferry, J. M., Passey, B. H., Vasconcelos, C. & Eiler, J. M. Formation of dolomite
	.057		at 40–80° C in the Latemar carbonate buildup, Dolomites, Italy, from clumped
	058	~ ~	isotope thermometry. <i>Geology</i> <b>39</b> , 571-574 (2011).
	059	85	Henkes, G. A. et al. Temperature limits for preservation of primary calcite
	.060		clumped isotope paleotemperatures. <i>Geochimica et Cosmochimica Acta</i> <b>139</b> , 362-
	.061	0.5	382 (2014).
	.062	86	Shenton, B. J. <i>et al.</i> Clumped isotope thermometry in deeply buried sedimentary
	.063		carbonates: The effects of bond reordering and recrystallization. <i>GSA Bulletin</i>
	064	07	<b>127</b> , 1036-1051 (2015).
	.065	87	Miller, M. F. <i>et al.</i> Mass-independent fractionation of oxygen isotopes during
	066		thermal decomposition of carbonates. <i>Proceedings of the National Academy of</i>
	.067	00	Sciences <b>99</b> , 10988-10993 (2002).
	068	88	Beck, W. C., Grossman, E. L. & Morse, J. W. Experimental studies of oxygen
	069		isotope fractionation in the carbonic acid system at 15, 25, and 40 C. <i>Geochimica</i>
	070	20	et Cosmochimica Acta <b>69</b> , 3493-3503 (2005).
	071	89	Plummer, L. N. & Busenberg, E. The solubilities of calcite, aragonite and vaterite
	072		in CO2-H2O solutions between 0 and 90 C, and an evaluation of the aqueous
	073		model for the system CaCO3-CO2-H2O. <i>Geochimica et cosmochimica acta</i> <b>46</b> , 1011–1040 (1082)
1	074		1011-1040 (1982).

	1075	90	Mucci, A. The solubility of calcite and aragonite in seawater at various salinities,
	1076		temperatures, and one atmosphere total pressure. American Journal of Science
	1077		<b>283</b> , 780-799 (1983).
	1078	91	He, S. & Morse, J. W. The carbonic acid system and calcite solubility in aqueous
	1079		Na-K-Ca-Mg-Cl-SO4 solutions from 0 to 90 C. Geochimica et Cosmochimica
	1080		<i>Acta</i> <b>57</b> , 3533-3554 (1993).
_	1081	92	Agrinier, P., Deutsch, A., Schärer, U. & Martinez, I. Fast back-reactions of shock-
$\frown$	1082		released CO2 from carbonates: An experimental approach. Geochimica et
	1083		<i>Cosmochimica Acta</i> <b>65</b> , 2615-2632 (2001).
_	1084	93	Kring, D. A. The dimensions of the Chicxulub impact crater and impact melt
	1085		sheet. Journal of Geophysical Research: Planets 100, 16979-16986 (1995).
	1086	94	Lammers, L. N. & Mitnick, E. H. Magnesian calcite solid solution
1	1087		thermodynamics inferred from authigenic deep-sea carbonate. Geochimica et
$\smile$	1088		<i>Cosmochimica Acta</i> <b>248</b> , 343-355 (2019).
5	1089	95	Akahane, H., Furuno, T., Miyajima, H., Yoshikawa, T. & Yamamoto, S. Rapid
JJ	1090		wood silicification in hot spring water: an explanation of silicification of wood
	1091		during the Earth's history. Sedimentary Geology 169, 219-228 (2004).
	1092	96	Brenner, D. C., Passey, B. H. & Stolper, D. A. Influence of water on clumped-
	1093		isotope bond reordering kinetics in calcite. Geochimica et Cosmochimica Acta
	1094		<b>224</b> , 42-63 (2018).
_	1095	97	Pospichal, J. J. & Wise Jr, S. W. Calcareous nannofossils across the K/T
-	1096		boundary, ODP hole 690C, Maud Rise, Weddell Sea. Proceedings of the Ocean
U.	1097		Drilling Program, Scientific Results 113, 515-532 (1990).
	1098	98	Vellekoop, J. et al. Shelf hypoxia in response to global warming after the
	1099		Cretaceous-Paleogene boundary impact. Geology 46, 683-686 (2018).
>	1100	99	Brinkhuis, H., Zachariasse, W. J. & Dinoflagellate cysts, sea level changes and
	1101		planktonic foraminifers across the Cretaceous-Tertiary boundary at El Haria,
	1102		northwest Tunisia. Marine Micropaleontology 13, 153-191 (1988).
	1103	100	Jones, H. L., Lowery, C. M. & Bralower, T. J. Calcareous nannoplankton "boom-
	1104		bust" successions in the Cretaceous-Paleogene (K-Pg) impact crater suggests
	1105		ecological experimentation at "ground zero" Geology 47, 753-756 (2019).
$\mathcal{I}$	1106	101	Schaefer, B. et al. Microbial life in the nascent Chicxulub crater. Geology,
_	1107		doi: <u>https://doi.org/10.1130/G46799.1</u> (2020).
	1108	102	Brinkhuis, H., Bujak, J., Smit, J., Versteegh, G. & Visscher, H. Dinoflagellate-
	1109		based sea surface temperature reconstructions across the Cretaceous-Tertiary
_	1110		boundary. Palaeogeography, Palaeoclimatology, Palaeoecology 141, 67-83
_	1111		(1998).
	1112	103	Jiang, S., Bralower, T. J., Patzkowsky, M. E., Kump, L. R. & Schueth, J. D.
	1113		Geographic controls on nannoplankton extinction across the
T	1114		Cretaceous/Palaeogene boundary. Nature Geoscience 3, 280-285,
-	1115		doi:10.1038/ngeo775 (2010).
	1116	104	Birch, H. S., Coxall, H. K. & Pearson, P. N. Evolutionary ecology of Early
	1117		Paleocene planktonic foraminifera: size, depth habitat and symbiosis.
	1118		Paleobiology <b>38</b> , 374-390 (2012).

-

ŝ

5

ļ

<

1119	105	Coxall, H. K., D'Hondt, S. & Zachos, J. C. Pelagic evolution and environmental
1120		recovery after the Cretaceous-Paleogene mass extinction. <i>Geology</i> <b>34</b> ,
1121		doi:10.1130/g21702.1 (2006).
1122	106	Hull, P. M., Norris, R. D., Bralower, T. J. & Schueth, J. D. A role for chance in
1123		marine recovery from the end-Cretaceous extinction. <i>Nature Geoscience</i> <b>4</b> , 856-
1124		860, doi:10.1038/ngeo1302 (2011).
1125	107	Cosmidis, J. et al. Nanometer - scale characterization of exceptionally preserved
1126		bacterial fossils in P aleocene phosphorites from Ouled A bdoun (Morocco).
1127		<i>Geobiology</i> <b>11</b> , 139-153 (2013).
1128	108	Pesquero, M. D., Souza-Egipsy, V., Alcalá, L., Ascaso, C. & Fernández-Jalvo, Y.
1129		Calcium phosphate preservation of faecal bacterial negative moulds in hyaena
1130		coprolites. Acta Palaeontologica Polonica 59, 997-1006 (2013).
1131	109	Cosmidis, J., Benzerara, K., Menguy, N. & Arning, E. Microscopy evidence of
1132		bacterial microfossils in phosphorite crusts of the Peruvian shelf: Implications for
1133		phosphogenesis mechanisms. Chemical Geology 359, 10-22 (2013).
1134	110	Zatoń, M. et al. Coprolites of Late Triassic carnivorous vertebrates from Poland:
1135		an integrative approach. Palaeogeography, Palaeoclimatology, Palaeoecology
1136		<b>430</b> , 21-46 (2015).
1137	111	Pineda, A. et al. Characterizing hyena coprolites from two latrines of the Iberian
1138		Peninsula during the Early Pleistocene: Gran Dolina (Sierra de Atapuerca,
1139		Burgos) and la Mina (Barranc de la Boella, Tarragona). Palaeogeography,
1140		Palaeoclimatology, Palaeoecology 480, 1-17 (2017).
1141	112	Al-Bassam, K. & Halodová, P. in Annales Societatis Geologorum Poloniae. 257-
1142		272, doi: 210.14241/asgp. 12018.14009.
1143	113	Ramírez-Reinat, E. & Garcia-Pichel, F. Prevalence of Ca2+-ATPase-mediated
1144		carbonate dissolution among cyanobacterial euendoliths. Appl. Environ.
1145		<i>Microbiol.</i> <b>78</b> , 7-13 (2012).
1146	114	Emslie, S. D. et al. Chronic mercury exposure in Late Neolithic/Chalcolithic
1147		populations in Portugal from the cultural use of cinnabar. Scientific reports 5,
1148		14679 (2015).
1149	115	Atkins, A. et al. Remodeling in bone without osteocytes: billfish challenge bone
1150		structure-function paradigms. Proceedings of the National Academy of Sciences
1151		<b>111</b> , 16047-16052 (2014).
1152	116	Cohen, L. et al. Comparison of structural, architectural and mechanical aspects of
1153		cellular and acellular bone in two teleost fish. Journal of Experimental Biology
1154		<b>215</b> , 1983-1993 (2012).
1155	117	Seidel, R. et al. Ultrastructural and developmental features of the tessellated
1156		endoskeleton of elasmobranchs (sharks and rays). Journal of anatomy 229, 681-
1157		702 (2016).
1158	118	Xiao, S. & Schiffbauer, J. D. in From Fossils to Astrobiology 89-117 (Springer,
1159		2009).
1160	119	Astrop, T. I., Sahni, V., Blackledge, T. A. & Stark, A. Y. Mechanical properties
1161	-	of the chitin-calcium-phosphate "clam shrimp" carapace (Branchiopoda:
1162		Spinicaudata): implications for taphonomy and fossilization. <i>Journal of</i>
1163		<i>Crustacean Biology</i> <b>35</b> , 123-131 (2015).

1	164	120	Chandran, R., Williams, L., Hung, A., Nowlin, K. & LaJeunesse, D. SEM
1	165		characterization of anatomical variation in chitin organization in insect and
1	166		arthropod cuticles. <i>Micron</i> 82, 74-85 (2016).
1	167	121	Horton, J. M. & Summers, A. P. The material properties of acellular bone in a
1	168		teleost fish. Journal of Experimental Biology 212, 1413-1420 (2009).
1	169	122	Sibert, E. C. & Norris, R. D. New Age of Fishes initiated by the Cretaceous-
1	170		Paleogene mass extinction. Proceedings of the National Academy of Sciences 112,
	171		8537-8542 (2015).
	172	123	Alfaro, M. E. et al. Explosive diversification of marine fishes at the Cretaceous-
	173		Palaeogene boundary. Nature Ecology & Evolution 2, 688 (2018).
	174	124	Friedman, M. Ecomorphological selectivity among marine teleost fishes during
	175		the end-Cretaceous extinction. Proceedings of the National Academy of Sciences
	176		<b>106</b> , 5218-5223 (2009).
	177	125	Sibert, E. C., Hull, P. M. & Norris, R. D. Resilience of Pacific pelagic fish across
	178		the Cretaceous/Palaeogene mass extinction. <i>Nature Geoscience</i> 7, 667 (2014).
	179	126	Forchhammer, G. Om de geognostiske forhold i en deel af Sjelland og naboøerne.
	180		(1825).
	181	127	DePalma, R. A. et al. A seismically induced onshore surge deposit at the KPg
1	182		boundary, North Dakota. Proceedings of the National Academy of Sciences 116,
1	183		8190-8199 (2019).
1	184	128	Hiatt, E. E., Pufahl, P. K. & Edwards, C. T. Sedimentary phosphate and
	185		associated fossil bacteria in a Paleoproterozoic tidal flat in the 1.85 Ga
	186		Michigamme Formation, Michigan, USA. Sedimentary Geology <b>319</b> , 24-39
1	187		(2015).
1	188	129	Emanuel, K. A., Speer, K., Rotunno, R., Srivastava, R. & Molina, M. Hypercanes:
1	189		A possible link in global extinction scenarios. Journal of Geophysical Research:
1	190		Atmospheres 100, 13755-13765 (1995).
1	191	130	Covey, C., Thompson, S. L., Weissman, P. R. & MacCracken, M. C. Global
1	192		climatic effects of atmospheric dust from an asteroid or comet impact on Earth.
1	193		Global and Planetary Change 9, 263-273 (1994).
1	194	131	Crosby, C. H. & Bailey, J. The role of microbes in the formation of modern and
1	195		ancient phosphatic mineral deposits. Frontiers in Microbiology 3, 241 (2012).
1	196	132	Zachos, J. C., Arthur, M. A. & Dean, W. E. Geochemical evidence for
1	197		suppression of pelagic marine productivity at the Cretaceous/Tertiary boundary.
1	198		<i>Nature</i> <b>337</b> , 61 (1989).
1	199	133	Bucher, K. & Stober, I. Fluids in the upper continental crust. <i>Geofluids</i> 10, 241-
1	200		253 (2010).
1	201	134	Kim, ST. & O'Neil, J. R. Equilibrium and nonequilibrium oxygen isotope effects
1	202		in synthetic carbonates. Geochimica et Cosmochimica Acta 61, 3461-3475 (1997).
1	203	135	Petersen, S. et al. Effects of Improved 17O Correction on Inter - Laboratory
1	204		Agreement in Clumped Isotope Calibrations, Estimates of Mineral - Specific
1	205		Offsets, and Temperature Dependence of Acid Digestion Fractionation.
	206		Geochemistry, Geophysics, Geosystems (2019).
	207	136	Hollund, H. I., Blank, M. & Sjögren, KG. Dead and buried? Variation in post-
	208		mortem histories revealed through histotaphonomic characterisation of human
	209		bone from megalithic graves in Sweden. <i>PloS One</i> <b>13</b> , e0204662 (2018).

)t	1211 1212 1213 1214 1215 1216 1217	138	carbonates. <i>Geochimica et Cosmochimica Acta</i> <b>141</b> , 1-25 ( Luz, B. & Barkan, E. Variations of 17O/16O and 18O/16O <i>Geochimica et Cosmochimica Acta</i> <b>74</b> , 6276-6286 (2010).
$\bigcirc$	1217		
$\bigcirc$			
ပ			
-			
$\geq$			
H			
7 C			
$\leq$			

## Passey, B. H. et al. Triple oxygen isotopes in biogenic and sedimentary 1210 137

*mica Acta* **141**, 1-25 (2014). 70/160 and 180/160 in meteoric waters.

## 1218 Figure Captions

Figure 1. Photograph of the uppermost suevite (Unit 2A), transitional unit (Unit 1G) and green marlstone and Danian pelagic limestone (Unit 1F) (units after Gulick et al., 2017<sup>43</sup>) in Core 40R-1, and backscatter (BSE) images showing origin of micrite (core photo shows the location of samples). Depositional environment after Gulick et al. (2019)<sup>12</sup> and Whalen et al. (2018)<sup>45</sup>. Pl. 1, 2. Foraminiferal calcite (white arrow) with a small amount of silicate melt (black arrows), 32-34 cm (616.56-616.58 mbsf); Pl. 3-7 Micrite derived from decarbonation-carbonation (more angular grains); black arrows in Pl. 7 are clay; Pl. 3. 50-55 cm (616.74–616.79 mbsf), Pl. 4. 84-89 cm (617.08–617.13 mbsf), Pl. 5. 100-104 cm (617.24–617.28 mbsf), Pl. 6. 104-105 cm (617.28–617.29 mbsf); Pl. 8-12. Micrite largely derived from melt (rounded grain shown with white arrow in Pl. 11) along with silicate melt (white arrows in Pl. 9, 10), altered silicate melt (black arrow in Pl. 10), and mixed carbonate-silicate ash (white arrow in Pl. 12); Pl. 7-11. 108-110 cm (617.32-617.34 mbsf), Pl. 12. 110-118 cm (617.34–617.42 mbsf). Scale bars 50 µm.

Figure 2. Stratigraphy of uppermost suevite (Unit 2A), transitional unit (Unit 1G), and green marlstone and Danian pelagic limestone (Unit 1F) (units after Gulick et al., 2017<sup>43</sup>) in Core 40R-1. Planktic foraminiferal Zones after Lowery et al. (2018)<sup>44</sup>; He-isotopes after Lowery et al. (2018)<sup>44</sup> and data herein; counts of charcoal grains after Gulick et al. (2019)<sup>12</sup>. Small grey drops indicate occurrence of melt droplets.

Figure 3. Thin section views of important features in the uppermost suevite, transitional unit and green marlstone. Pl. 1, 2. Upper pyritized charocal layers in green marlstone. Pl. 1. Cross polarized light (white arrows show apparent bedforms; blue arrows show foraminiferal lags, see Discussion); Pl. 2. Reflected light (white arrows show apparent bedforms; see Discussion). Pl. 3, 4. Boundary between transitional unit and green marlstone showing clay seams and possible algal mats (as shown by green epiflourescence (shown by arrows in Pl. 4, see Discussion)); Pl. 3. Cross-polarized light-Epiflourescence; Pl. 4. Epiflourescence. Pl. 5, 6. Pyrite layers in lower transitional unit cross-polarized light. Pl. 7. Fluid escape structure in lowermost transitional unit with vein (shown with arrow), cross-polarized light. Pl. 8 Alternating interval of melt rich (base and top) and carbonate rich (middle) suevite, cross-polarized light. Samples all in Core 40R-1: Pl. 1, 2. 31-32 cm (616.54–616.56 mbsf); Pl. 3, 4. 33.5-34.5 cm (616.575–616.585 mbsf); Pl. 5. 100-104 cm (617.24–617.28 mbsf); Pl. 8. 108-110 cm (617.32–617.34 mbsf). Scale bars represent 2 mm.

Figure 4. Backscattered electron (BSE) and secondary electron images of pyrite and petrified wood from the lower transitional unit and green marlstone. Pl. 1, 2. Pyrite shards preserving wood structure (arrows); Pl. 3. Pyrite showing wood structure (arrow). Pl. 4, 5. Pyrite showing more (left) and less (right) pyritized areas with wood structure (right); Pl. 5 is close up view of the boundary between the two areas in Pl. 4. Pl. 6. Area of pyrite showing organic structure. Pl. 7, 8. Pyrite containing dark carbon needles (possible conifer needles). Pl. 9. Dolomite (shown by arrow as identified in EDS) underlying pyrite grain. Pl. 10-12. Petrified wood. Samples all in Core 40R-1: Pl. 1, 2. 31-32 cm (616.55–616.56 

mbsf); Pl. 3. 100-104 cm (617.24–617.28 mbsf); Pl. 4-6. 32-34 cm (616.56–616.58 mbsf);
Pl. 7, 8. 100-104 cm (617.24–617.28 mbsf); Pl. 9. 32-34 cm (616.56–616.58 mbsf); Pl. 10-12.
12. 31cm (616.55 mbsf). Pl. 1-9. BSE images of thin sections; Pl. 10-12. secondary electron images of strewn slides. Scale bars represent 5 μm.

Figure 5. Strontium, carbon, oxygen and clumped isotope data from the uppermost suevite (unit 2A), transitional unit (1G), the green marlstone and pelagic limestone (1F). Interval of soft-sediment deformation is shown by the horizontal gray shaded area as is interval of highest Ir enrichment after Goderis et al.  $(2019)^{46}$ . Sr isotope values are from HCl leaches. The  $\delta^{18}$ O temperatures are calculated from  $\delta^{18}$ Occ values using the relation of Kim & O'Neil (1997)<sup>134</sup>, assuming a seawater  $\delta^{18}$ O value of -1‰. Clumped isotope temperatures are calculated from  $\Delta_{47}$  values following Petersen et al.  $(2019)^{135}$ . Error bars for clumped isotopes are 95% confidence intervals, and smaller symbols denote samples that were not analyzed in replicate. Gray vertical bars indicate mean temperature values (± 1 $\sigma$ ) for the pelagic limestone (1F), the transitional unit (excluding the interval marked tr.), and the uppermost suevite (2A). Range of Sr isotope values for K-Pg sections<sup>64</sup> is shown. Occurrences of hydrothermal ZnS, pyrite, apatite and evaporite are indicated.

Figure 6. Backscattered electron (BSE) of apatite from the green marlstone including ancient and modern forms used for comparison. Pl. 1, 2, 3. Clusters of spherical fossil bacteria that resembles coprolites, Pl. 2 is close up of Pl. 1. Pl. 5-7. Piece of bone tunneled by cyanobacteria; Pl. 5. Whole object; Pl. 6, 7. Close up views of Pl. 5. Note apatite growing in pores in Pl. 7 (examples shown by arrow). Pl. 9-12. Layered and hooked specimens of possible marine arthropods. Pl. 13-16. Possible small fish fossils. Samples all in Core 40R-1, 32-34cm. Pl. 1-7, 9-12. BSE images of thin sections. Pl. 4. Encrusted bacterial cells in hyaena coprolite from Pesquero et al. 2017<sup>108</sup> (Figure 4C) (image available via a Creative Commons Attribution License (CC BY). Pl. 8. Brightfield reflected light image of section of an altered human bone tunneled by cyanobacteria from Hollund et al. 2018<sup>136</sup> (Figure 6C) (image available via a Creative Commons Attribution License (CC BY). Scale bars on individual images.

Figure 7. Transmission Electron Microscope (TEM) and secondary electron images showing ultrastructure of calcite in the transitional unit and comparison with calcite produced by thermal decarbonation; both classes of calcite shows planar features. Pl. 1-6 are of TEM micrographs of calcite in Sample 40R-1, 91cm (617.13 mbsf). Pl. 7, 8 are of TEM micrographs of calcite in Sample 40R-1, 33cm (616.57 mbsf) with Moiré fringe areas shown with insets. Pl. 9 is SEM of calcite in fault zone produced by thermal decarbonation (from Cristiano Colletini pers. comm.). Pl. 10 is backscattered electron (BSE) of 40R-1, 72-76 cm (616.94–616.98 mbsf). Scale bars in individual images. Pl. 11, 12 are SEMs of calcite produced by experimental thermal decarbonation from Rodriquez Navarro et al. (2009)<sup>57</sup>. Images used with permission from the Mineralogical Society of America.

Figure 8. (A) Apparent seawater  $\delta^{18}$ O versus clumped isotope temperature, contoured for constant  $\delta$ 18Occ (thin gray lines). The apparent seawater  $\delta^{18}$ O values are calculated using the oxygen isotope thermometer of Kim and O'Neil (1997)<sup>134</sup>, with temperatures based on clumped isotopes. The color scale indicates the traditional oxygen isotope-based 1310 temperatures under the assumption that  $\delta^{18}\text{Ow} = -1\%$ . (B) Illustration of the scenario where 1311 the initial carbonate forms in cooler (but still extremely warm) seawater with  $\delta^{18}\text{O} = -1\%$ 1312 (white symbols), and subsequently recrystallizes on the higher-temperature seafloor under 1313 rock-buffered ( $\delta^{18}\text{O}$ -preserving) conditions (black arrows). Such recrystallization results 1314 in increased clumped isotope temperatures but little or no change in  $\delta^{18}\text{Occ}$ , which results 1315 in apparent seawater  $\delta^{18}\text{O}$  values that are erroneously high.

Figure 9. Backscattered electron (BSE) and secondary electron images of anydrite, halite, apatite, ZnS and pyrite from the transitional unit and green marlstone. Pl. 1, 4, 6. Halite.
Pl. 2, 3, 5. Anhydrite. Pl. 7. Apatite (arrow) in chlorite vein. Pl. 8, 9. Apatite (arrows) surrounded by halite. Pl. 10-11. ZnS (light grey) with calcite (dark grey shown by arrow) crystals inside. Pl. 12. Pyrite crystals (upper arrow) in chlorite (lower arrow) vein. Samples all in Core 40R-1: Pl. 1, 4, 6. 31 cm (616.55 mbsf); Pl. 2, 3, 5. 108 cm (617.32 mbsf); Pl. 7, 12. 106-108 cm (617.30–617.32 mbsf). Pl. 8, 9. 110 cm (617.34 mbsf); Pl. 10, 11. 67-72cm (616.91–616.96 mbsf); Pl. 7, 10-12. BSE images of thin sections; Pl. 1-6, 8, 9. Secondary electron images of strewn slides. Scale bars on individual images.

Figure 10. Cartoon showing proposed origin of the transitional unit and green marlstone. Panel A Upper row -- deposition of transitional unit showing cross section (left) and birdseye view (right). Red arrows in section indicate convection from central melt sheet; thick black arrows show direction of seiche wave transport and depositon of CaCO<sub>3</sub> in transitional unit at Site M0077; location of Site M0077 indicated by green arrow. Birdseye view shows whole crater with opening to the Gulf of Mexico to the northeast and morphological features including the peak ring; seiche waves indicated by double ended arrows; tsunami waves by single arrows. Location of M0077 and YAX-1 indicated by red symbols; green line indicates section in Panel A. Site water depth after Lowery et al. (2018)<sup>44</sup>. Panel B Lower row – deposition of green marlstone at Site M0077 showing atmospheric fallout combined with eutrophic conditions.

Figure 11. Recovery of life and its relationship with environment in the nascent crater. At left is sediment core showing lowermost and uppermost transitional unit and green marlstone and its environmental interpretation. At right are fossil occurrences at various trophic levels and timing of the recovery. Higher orders include apatite remains of small fish and pelagic crustaceans. Planktonic protistans are represented by planktic foraminifera, calcareous nannoplankton and dinoflagellates. Microcystals that appear to be made by cyanobacteria<sup>47</sup>. Scale bars by individual images (bars by *Z. sigmoides* pertains to four nannofossil images).