Nanoscale crystal fabric of primary Ediacaran dolomite

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Abstract

Dolomite (CaMg(CO3)2) forms in minor quantities in few modern environments yet comprises most of the Precambrian carbonate rock record. Precambrian dolomites are often fine-grained and fabric-retentive and are interpreted to have precipitated as primary cements or formed as early diagenetic replacements of CaCO3. Primary dolomite precipitation from seawater in depositional environments has not yet been described. Here, we use synchrotron radiation to produce a nanoscale-resolution crystal orientation map of one exquisitely preserved ooid deposited at the onset of the Shuram carbon isotope excursion at 574 Ma. The crystal orientation map reveals small ($^{10} \mu m$) acicular, radially-oriented crystals grouped into bundles of similarlyoriented crystals with varying optical properties. We interpret this dolomite formed via primary, spherulitic precipitation during ooid growth in shallow marine waters. This result provides additional evidence that the physicochemical properties of late Precambrian oceans promoted dolomite precipitation and supports a primary origin for the Shuram excursion.

Nanoscale crystal fabric preserved in dolomite ooids at the onset of the Shuram Excursion

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7 Key Points:

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Fabric-preserving ooids at the onset of the Shuram carbon isotope excursion are comprised of micron-sized, stoichiometric dolomite crystals Dolomite crystals are acicular, radially-oriented, and arranged in plumose spherulitelike bundles

We interpret that this ooid formed as primary dolomite, with implications for seawater chemistry at the onset of the Shuram excursion

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14 Abstract

Dolomite $(CaMg(CO_3)_2)$ forms in minor quantities in modern environments yet comprises 15 most of the Precambrian carbonate rock record. Precambrian dolomites are often fine-16 grained and fabric-retentive and are interpreted to have precipitated as primary cements or 17 formed as early diagenetic replacements of CaCO₃. Detailed physical and chemical charac-18 terization of these dolomites could inform their origin and relevance for paleoenvironmental 19 reconstruction. Here, we use synchrotron radiation to produce a nanometer-resolution crys-20 tal orientation map of one exquisitely-preserved ooid deposited at the onset of the Shuram 21 carbon isotope excursion (\sim 574 Ma). The crystal orientation map reveals small (\sim 10µm) 22 acicular, radially-oriented crystals grouped into bundles of similarly-oriented crystals with 23 varying optical properties. We interpret that this dolomite formed via primary, spherulitic 24 precipitation during ooid growth in shallow marine waters. This result provides additional 25 evidence that the physicochemical properties of late Precambrian oceans promoted dolomite 26 precipitation and supports a primary origin for the Shuram excursion. 27

²⁸ Plain Language Summary

The mineral dolomite is a common constituent of ancient carbonate sedimentary rocks, 29 yet dolomite rarely precipitates from seawater today. For decades, this discrepancy has 30 caused researchers to wonder whether dolomite precipitated directly from seawater in the 31 deep past. If so, dolomitic rocks — like other carbonate sedimentary rocks — could pre-32 serve the physical and chemical properties of the water from which they formed and serve 33 as a record of ancient marine conditions. However, evidence for primary dolomite precipi-34 tation from seawater has not been described. Here, we apply a new method and study one 35 574 million-year-old dolomite at nanometer resolution using x-ray light, creating a three-36 dimensional map of crystals in this sample. We discover our sample is comprised of tiny, 37 needle-shaped dolomite crystals that are arranged in bundles of similarly-oriented crys-38 tals. After comparison to modern primary and lab-grown dolomites and to other ancient 39 dolomites, we interpret this crystal fabric to have formed via precipitation from seawater. 40 Our discovery of a new dolomite crystal fabric and our interpretation that it precipitated 41 from seawater shed new light on the ancient environment at the onset of Earth's largest 42 carbon cycle perturbation. 43

44 **1** Introduction

45 Carbonate rocks serve as the primary sink for carbon in the Earth system and preserve
 46 a record of the physical, chemical, and biological properties of marine settings throughout
 47 geologic time. The interpretation of the physical and chemical properties of carbonates

through Earth history elucidates past changes in climate and carbon cycling, and also provides insight into potential future changes to the Earth system. However, carbonates are susceptible to post-depositional, often cryptic, diagenetic alteration which can chemically or physically alter a carbonate mineral's composition and diminish a carbonate's usefulness as a paleoenvironmental proxy.

At \sim 574 Ma, as animal life was emerging (Rooney et al., 2020), carbonate rocks on 53 at least six paleocontinents preserve evidence for Earth's largest negative carbon isotope 54 anomaly, known as the Shuram excursion (Derry, 2010; Fike et al., 2006; Grotzinger et al., 55 2011; Husson et al., 2020). Understanding whether the anomaly and the $-12\% \delta^{13}C_{VPDB}$ 56 values recorded at its nadir (Grotzinger et al., 2011) reflect a primary environmental per-57 turbation or post-depositional processes is an ongoing geochemical and sedimentological 58 challenge. Conventionally, carbonate carbon isotopes (δ^{13} C) are understood as a global 59 steady-state balance between the isotopic composition of a carbon source (i.e., the man-60 tle) and carbon sinks (organic and carbonate carbon). Perturbations in δ^{13} C arise due to 61 changes in the amount or isotopic composition of sources and sinks. For the case of the Shu-62 ram excursion, a global carbon cycle perturbation mechanism may have involved oxidizing 63 a large pool of isotopically light organic (Rothman et al., 2003), or methane (Bjerrum & 64 Canfield, 2011) carbon – mechanisms with implications for atmospheric pO_2 during Shuram 65 time. Diagenetic or post-depositional hypotheses argue that such negative δ^{13} C values were 66 caused as a result of fluid-rock interactions during late burial diagenesis (Derry, 2010), dia-67 genetic meteoric waters depleted in δ^{13} C due to an active terrestrial biosphere (Knauth & 68 Kennedy, 2009), or the precipitation of authigenic carbonates from non-seawater-like fluids 69 (Schrag et al., 2013). In these scenarios, any primary environmental data would be over-70 printed by secondary alteration. Because the Shuram excursion is hosted in strata that also 71 host early Ediacaran (635-539 Ma) biota and precedes the evolution of metazoans by < 2072 Myr (Rooney et al., 2020), understanding the cause of the Shuram excursion and whether 73 it represents a primary perturbation to the global carbon cycle has implications for how we 74 understand the environments in which early animals evolved. 75

In this study, we approach the question of whether Shuram carbon isotope values are 76 hosted in diagenetically-altered carbonates by analyzing the physical and chemical charac-77 teristics of a distinctive dolomite ooid grainstone that appears exquisitely fabric-preserving 78 in this section (Figure 2) and records the onset of the Shuram excursion ($\delta^{13}C = -2.8\%$) in 79 the upper Khufai Formation, Huqf outcrop area, Sultanate of Oman (see Table 3, sample 80 MD6 258.6 in Bergmann et al. (2018)). Ooids are spherical carbonate grains that form a 81 cortex surrounding an inner nucleus via precipitation from seawater. Because they form 82 only in very shallow water high-energy settings, ooids serve as useful paleoenvironmental 83

indicators, and their tendency to preserve mineralogy-dependent crystal fabric makes them useful samples for petrographic analysis (Sandberg, 1975). The upper Khufai oolite is a stromatolite bioherm-bearing, 1-30m thick, cross-stratified ooid and intraclast grainstone that directly overlies mudstones containing evaporite pseudomorphs and is interpreted to have been deposited in a high-energy, shallow marine setting with elevated seawater sulfate concentrations (Figure 1, Osburn et al. (2014); Cui et al. (2021)).

Using x-ray diffraction (XRD), electron probe microanalysis (EPMA), and synchrotron-90 based nanoscale crystal orientation mapping, we reveal the mineralogy and crystal morphol-91 ogy (size, shape, arrangement) of the ca. 574 Ma upper Khufai oolite. We then interpret 92 these observations in the context of previously proposed dolomitization models, laboratory 93 experiments, and modern dolomite-forming environments. We assess whether this ooid 94 precipitated as a diagenetic replacement of primary $CaCO_3$ or directly from seawater and 95 discuss implications for the genesis of the Shuram excursion and properties of Precambrian 96 shallow marine environments. 97

98 2 Results

To assess the mineralogy and fabric of the upper Khufai oolite, we analyzed portions of one ~ 10 cm $\times 10$ cm oolite sample using electron probe microanalyis (EPMA), x-ray diffraction (XRD), thin section microscopy, and Polarization-dependent Imaging Contrast (PIC) mapping (see Materials and Methods).

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2.1 Mineralogy

Magnesium-to-Calcium ratios from EPMA (Fig. 2b) and the presence of the (015) and 104 (021) ordering peaks (Kaczmarek et al., 2017) in the XRD spectrum (Fig. 2c) indicate 105 that ooids are comprised of stoichiometric, ordered dolomite: Ca and Mg are present in 106 equal parts within the carbonate lattice within coherent cation-specific planes. Elemental 107 maps (Supplemental Figure 1) and thin section images (Figure 2d-f) show the ooids are 108 loosely cemented by a dolomite cement bearing higher concentrations of Si than the ooids 109 (Supplemental Figure 1c-d), and show Mn-rich concentric banding in the cortices of many 110 ooids (Supplemental Figure 1b). 111

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2.2 Fabric

We leverage the nanoscale resolution of synchrotron-based Polarization-dependent Imaging Contrast (PIC) mapping to produce a high-resolution map of crystal orientations and geometries within one ooid grain from the upper Khufai oolite (Figure 3). Using soft x-rays with variable linear polarization angle, PIC mapping measures the c-axis orientations of nanocrystals and displays them in 3D, at 20nm resolution, using color: hue and brightness represent in- and out-of-plane angles, respectively (see Appendix A2 and Gilbert et al. (2011)). Since PIC mapping is based on x-ray linear dichroism — a physical effect that depends on bond angle orientation and crystal structure — its prior observation and use in aragonite, calcite, and vaterite (DeVol et al., 2014) suggests that it also works for dolomite, as demonstrated here for the first time.

PIC mapping reveals that this ooid's cortex is dominantly comprised of small, acicular 123 (needle-shaped) dolomite crystals; dolomite crystals in the nucleus are generally larger and 124 equant (Figure 3). We focus our analysis on the well-preserved fabric of the outer cortex, 125 in which individual dolomite crystals are small ($\sim 2\mu m$ by 15 μm), acicular, and radially 126 oriented. Some crystals are grouped into bundles of similarly-oriented crystals; within bun-127 dles, crystal orientations span a range of just $\sim 60^{\circ}$ (Fig. 3b, c, e). While crystals within 128 each bundle maintain similar orientations (Fig. 3), the optical characteristics of crystals 129 differ between bundles: some are length-fast, with the c-axes pointing along the same vector 130 as the bundle (e.g., purple bundle, Fig. 3c), while others are length-slow, with the c-axes 131 pointing perpendicular to the bundle orientation (e.g., green bundle, Fig. 3b). Each bundle 132 has a curved, plumose morphology that becomes more expansive towards the edge of the 133 ooid. This curvature is visible as a change in brightness, hue, or both across a given bundle 134 (Figure 3e). Finally, most plumose spherulitic bundles terminate at the preserved curved 135 outer edge of the ooid (labeled in Figure 3a). 136

¹³⁷ **3** Discussion

The small volumes of modern dolomite compared to the large volumes of geologic, 138 and especially Precambrian (> 541 Ma) dolomite (Given & Wilkinson, 1987; Cantine et 139 al., 2020) has inspired decades of work aimed at determining the conditions that promote 140 dolomite formation. The apparent abundance of dolomite in the late Precambrian that 141 preserves finely crystalline and mimetic crystal fabrics (Corsetti et al., 2006; Hood et al., 142 2011; Hood & Wallace, 2018; Tucker, 1982, 1983) has prompted efforts focused explicitly on 143 the question of how these fabric-retentive dolomites formed and why they abound in late 144 Precambrian strata. Since geologic dolomite is predominantly a replacement of precursor 145 $CaCO_3$, many dolomite-replacement studies have investigated the conditions under which 146 fabric-preserving or mimetic dolomitization can occur and the resultant petrographic and 147 geochemical qualities of these dolomitized calcium carbonates (e.g., Bullen & Sibley, 1984; 148 Zempolich & Baker, 1993). But dolomite can also form as a primary precipitate under 149

laboratory experiments and in modern environments. Below we explore which formation
 mechanism best explains our observations of the upper Khufai oolite.

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3.1 Mimetic dolomitization of primary CaCO₃

Mimetic dolomitization preserves the primary textures, or fabrics, of a precursor calcium carbonate. Most studies of mimetic dolomites invoke an "early diagenetic" or synsedimentary origin for the secondary dolomite (e.g., Hood & Wallace, 2018; Corsetti et al., 2006; Osburn et al., 2014; Zempolich & Baker, 1993), an interpretation derived from comparison to fabric-destructive (interpreted as late diagenetic) dolomites (e.g., Corsetti et al., 2006) and experimental results (Zempolich & Baker, 1993).

To characterize the nature of fabric-retentive Precambrian ooids, Zempolich and Baker 159 (1993) dolomitized modern aragonitic ooids over 180 hours at 200°C. In these experiments, 160 dolomitization begins at the outer surface of an ooid with the formation of a dolomite rind 161 and progresses inward via micro pore spaces, replacing $<\mu m$ primary CaCO₃ with euhe-162 dral, microrhombic (2-8µm) dolomite crystals (Zempolich & Baker, 1993). The precipitated 163 dolomite crystals faithfully preserve the ooids' primary tangential macrostructure and over-164 all shape (enveloped by a rind of euhedral dolomite crystals) but do not preserve their 165 primary optical characteristics (pseudo-uniaxial cross), and appear distinctly rhombohedral 166 in SEM images (Zempolich & Baker, 1993). In another mimetic dolomitization experiment, 167 Bullen and Sibley (1984) dolomitized a range of skeletal materials and produced fine, but 168 coarser than primary CaCO₃, crystal sizes in echinoids and preserved radial extinction in 169 forams, but found similar coarse dolomite rhombs as Zempolich and Baker (1993) on the 170 exterior of the fossils that protruded into pore space. 171

Our results highlight key differences with these dolomitization experiments (Zempolich 172 & Baker, 1993; Bullen & Sibley, 1984). We see no evidence for an outer rind of euhedral 173 dolomite crystals, which would be visible as a thin ring around the PIC mapped ooid (Figure 174 3a), nor do we observe replacement rhombs protruding into pore space. Dolomite crystals 175 within the cortex of Khufai ooids are predominately acicular, not euhedral or rhombic, 176 and are coherently organized into bundles of similarly-oriented crystals, preserving primary 177 optical characteristics. There is also no evidence that replacement occurred from the outer 178 edge of the ooid inwards. If dolomite did replace primary CaCO₃ in the Khufai, it did so via 179 a different, and possibly novel mechanism capable of precipitating non-euhedral dolomite 180 pseudomorphically, to preserve primary crystal orientations and thus optical properties. 181

3.2 Primary dolomite precipitation from seawater

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To understand whether paleoenvironmental conditions could have promoted primary 183 dolomite precipitation and the characteristics we observe in the upper Khufai Formation, 184 we turn to reports of modern dolomite-forming environments and laboratory studies that 185 successfully precipitate dolomite from solution. Dolomite can only be found forming as the 186 primary carbonate mineral on Earth's surface today in small quantities in unique hyper-187 saline, hydrothermal, lacustrine, or biologically-mediated environments. In the Coorong 188 lakes of South Australia, fine grained (<1 μ m - 20 μ m), spherulitic dolomite precipitates 189 during the hottest $(> 30^{\circ} C)$, most evaporitic portion of the year in high-salinity, high pH, 190 high $[Mg^{2+}]$ settings dominated by sulfate-reducing bacteria (Wacey et al., 2007). In Lagoa 191 Vermelha, Brazil, Ca-rich dolomite with depleted $\delta^{13}C$ (-7.49 to -8.98 %) forms in anoxic, 192 hypersaline conditions dominated by sulfate-reducing bacteria at the sediment-water inter-193 face (Vasconcelos & McKenzie, 1997; Vasconcelos et al., 2006). This primary precipitated 194 dolomite then "ages" in the anoxic sediment column (<1m depth) to a more stoichiometric, 195 ordered form (Vasconcelos & McKenzie, 1997; Vasconcelos et al., 2006). The presence of 196 sulfur-reducing bacteria is thought to be critical to dolomite formation in both of these 197 modern examples, and has been identified in laboratory studies as a potential mechanism 198 (through the production of dissolved sulfide and subsequent disruption of Mg²⁺-water com-199 plexes) for the precipitation of dolomite in the geologic record (Zhang et al., 2012; Fang, 200 Zhang, et al., 2021). 201

Laboratory experiments support the observation that microbial mediation and disrup-202 tion of Mg²⁺-water complexes are important elements for dolomite precipitation. In experi-203 ments with anoxygenic photosynthetic microbes and Mn-enriched water, Daye et al. (2019) 204 successfully precipitated ordered, nano- to micro-crystalline, Mn-enriched dolomite within 205 biofilms. Recent abiotic experiments by Fang, Zhang, et al. (2021) and Fang and Xu (2022) 206 demonstrate that disrupting the Mg^{2+} -water "hydration barrier" to free Mg^{2+} in solution 207 is a critical step in precipitating primary dolomite from solution. In their experiments, dis-208 ordered micrometer-scale dolomite is precipitated from a water-ethanol or a $Si(OH)_4$ -rich 209 solution at room temperature (Fang, Zhang, et al., 2021; Fang & Xu, 2022). As a final exam-210 ple, at high temperatures (60-200°C) and high dolomite supersaturation, Rodriguez-Blanco 211 et al. (2015) precipitate protodolomite as nanocrystalline spherulites. These poorly ordered 212 precursors transform to ordered dolomite comprised of larger (>100 nm), planar crystals 213 over hours to days (Rodriguez-Blanco et al., 2015). Together, these studies demonstrate 214 that, with the correct combination of biological or chemical factors, primary, ordered, nano-215 to microscale dolomite – all qualities of the upper Khufai dolomitic ooids – can precipitate 216 as a primary carbonate mineralogy at Earth surface temperatures. 217

3.2.1 How do bundles of similarly-oriented crystals form?

Lastly, we seek an analogue or mechanism to explain the bundles of similarly-oriented 219 crystals we observe in the outer cortex of our PIC mapped ooid (Figure 3b, c, e). In some 220 ways, the PIC mapped bundles resemble the fascicular slow dolomite (FSD) cements de-221 scribed by Hood et al. (2011). These isopachous, length-slow dolomite crystals are arranged 222 in bundles that fan outward, and are interpreted to represent primary dolomite cements pre-223 cipitated in pore space in the early diagenetic environment of the ca. 650 Ma Balcanoona 224 Reef Complex (Hood et al., 2011; Hood & Wallace, 2012). However, FSD cements are char-225 acterized by their length-slow crystal orientation, while our PIC map reveals bundles that 226 are both length-fast and length-slow. 227

The bundles we observe, particularly the bundle shown in Figure 3b, nearly resemble 228 plumose spherulites – feather-shaped bundles of crystal fibers that grow radially outward and 229 have been observed and PIC mapped in aragonitic $(CaCO_3)$ coral skeletons (Sun et al., 2017, 230 2021). The co-orientation of crystals (within 60°) we observe in each bundle (Figure 3b, c) 231 are similar to the co-orientations Sun et al. (2017) observe in natural (coral) and synthetic 232 aragonitic spherulites. However, true spherulites have a length-fast optical character and 233 are space-filling. Our PIC mapped bundles are variably length-fast and length-slow, and 234 not individually space-filling, although the bundles we identify together create a space-filling 235 mosaic of acicular dolomite throughout the ooid's cortex. 236

The curvature across individual bundles, visible in the PIC map in Figure 3 as color gradients, shows that adjacent nanocrystals within each bundle are slightly misoriented with respect to one another, a characteristic of spherulites (Sun et al., 2017). Individual crystal orientations vary gradually, akin to the orientation of adjacent radii around a sphere. This observation of curvature, consistent across most bundles (Figure 3), indicates that these bundles of acicular, radially-oriented crystals had space to grow into as they formed (see, for example, Sun et al. (2017)).

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3.3 A model for the formation of primary dolomitic ooids in the Khufai Formation

Based on the PIC map and petrographic data presented and discussed above, we propose a primary dolomite mineralogy for the fabric-preserving ooids of the upper Khufai Formation. The geologic and geochemical context (Osburn, 2013; Osburn et al., 2014; Cui et al., 2021) suggests microbial processes that increased alkalinity or $[Mg^{2+}]$ (Rodriguez-Blanco et al., 2015; Daye et al., 2019; Wacey et al., 2007), the presence of chemical species that disrupted Mg^{2+} -water complexes (Fang, Zhang, et al., 2021; Zhang et al., 2012), elevated temperatures in shallow water environments (Bergmann et al., 2018), and hypersalinity (Wacey et al., 2007; Cui et al., 2021) could have individually or in tandem promoted
dolomite formation within the upper Khufai oolite.

The large (> 1cm) size of some of the ooids in the upper Khufai oolite (Figure 2d, 255 e), the radially-oriented crystals in each ooid's cortex, and evident concentric banding in 256 many ooids (Figure 2b, e, f) fit the "bedform model" of ooid growth proposed by Anderson 257 et al. (2020). In this model, developed to explain giant ooids in the sedimentary record, 258 ooids grow while at rest in active bedforms and abrade during transport, forming concentric 259 bands (see Trower et al. (2017) for an alternative growth model). Invoking this "bedform 260 model," we suggest the upper Khufai ooids may have precipitated in pore spaces within the 261 sediment pile of periodically active bedforms from seawater that was kinetically favorable 262 for dolomite precipitation (Anderson et al., 2020). 263

Dolomite precipitation within each ooid's cortex may have proceeded spherulitically, either via non-crystallographic branching (Sun et al., 2017) or growth from randomly oriented "sprinkles" (possibly observed surrounding the ooid's nucleus in Figure 3a; Sun et al. (2021)). We cannot determine whether the dolomite precipitated as ordered dolomite (as in the experiments of (Daye et al., 2019)) or quickly "aged" to ordered dolomite (as observed by Vasconcelos et al. (1995) and Rodriguez-Blanco et al. (2015)).

The upper Khufai ooids were then partially cemented by Si-bearing dolomite cements 270 (Supplemental Figure 1). Other upper Khufai sections are more thoroughly silica cemented 271 and silicified (Osburn et al., 2014). Rapid silica cementation has been described in other 272 Ediacaran strata as a symptom of high Si saturation in Ediacaran oceans (Tarhan et al., 273 2016) and dissolved silica has also been shown to promote dolomite precipitation by dis-274 rupting the Mg²⁺-H₂O complexes in modern sediments and experiments (Fang, Hobbs, & 275 Xu, 2021; Fang & Xu, 2022), suggesting the presence of Si may have been important for 276 both precipitation and preservation of the upper Khufai Formation. The lack of pore-filling 277 cements in our analyzed onlite may be an indication that post-depositional diagenetic fluids 278 - which did produce fabric-destructive dolomitization in lower Khufai ooids elsewhere in 279 Oman (Wright et al., 1990; Bergmann et al., 2018) – did not come in contact with this 280 portion of the Khufai Formation. The fine-grained siliciclastic sediments of the overlying 281 Shuram Formation may also have protected the upper Khufai Formation from later fluid 282 alteration and cementation, and the ordered dolomite mineralogy of the ooids themselves 283 likely made them more recalcitrant to alteration than metastable phases like aragonite and 284 high Mg-calcite. 285

3.4 Implications for the Shuram excursion and Ediacaran environments

Our results support a primary origin for the Shuram excursion. We interpret the upper 287 Khufai dolomitic ooids to have formed as primary precipitates from seawater and do not 288 observe evidence for the precipitation of late diagenetic minerals, meaning most geochemi-289 cal signals hosted by these ooids should reflect the seawater from which they precipitated. 290 As has been discussed recently by carbonate sedimentologists working in modern and an-291 cient sediments (Geyman & Maloof, 2019; Ahm & Husson, 2021), this does not require 292 that seawater DIC at ~ 574 Ma was globally depleted in ¹³C. However, the occurrence of 293 similar, fabric-preserving dolomitic ooids with fine crystal sizes at the onset of the Shuram 294 excursion in the Johnnie oolite in southern California and Nevada, USA (Bergmann et al., 295 2011; Corsetti et al., 2006) suggests that perhaps the dolomite-precipitating conditions that 296 formed the upper Khufai oolite were present on shallow carbonate shelves elsewhere ca. 574 297 million years ago. Notably, the ooid fabrics in the Johnnie Formation are more variably 298 preserved likely due to the more significant burial and tectonic history of the Basin and 299 Range province(Bergmann et al., 2011; Corsetti et al., 2006). 300

This model suggests that the kinetics of dolomite precipitation were favorable during upper Khufai time: high [Si], sulfur reducing bacteria, hypersalinity, high temperatures, and high [Mn] may have played a role in the precipitation of the dolomitic ooids we describe. Whether the ooid fabric we present in Figure 3 represents a unique dolomitic ooid morphology remains an open question; we encourage the use of PIC mapping to reveal the nanometer-scale crystal orientations of other fabric-preserving dolomites throughout Earth history.

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Appendix A Materials and methods

A1 Sample preparation

All of the analyses described here were conducted on different parts of one hand sample 310 (ca. 10 by 10 cm) of oolite collected by K. Bergmann from the upper Khufai Formation, 311 Sultanate of Oman (MD6 258.6, see Bergmann et al. (2018); Osburn et al. (2014)). To 312 prepare for PIC mapping, the sample was cut down to a 4mm³ cube, polished and coated 313 with 1nm of Pt following Sun et al. (2017). A second cut of the sample was thin sectioned, 314 finished with a microprobe-quality polish to 0.25µm and carbon coated for electron probe 315 spot analysis (Fig. 2b). For X-ray diffraction (Fig. 2c), a third section of the onlite sample 316 was powdered using a drill press (Bergmann et al., 2018). 317



Figure 1. Khufai and Shuram Formations, Huqf outcrop area, Sultanate of Oman. a: Khufai Formation and overlying red silts of the Shuram Formation, as exposed in Mukhaibah Dome (see (Bergmann et al., 2018; Osburn et al., 2014)). Arrow points to stratigraphic up, 's' denote stromatolitic bioherms within the upper Khufai oolite, which is also labeled. b: Hand sample of the upper Khufai oolite showing cross-stratification within the ooid grainstone. K.D. Bergmann photos. c: Upper Khufai δ^{13} C curve from section MD6 in Osburn (2013). Data (three overlapping points) measured from the same oolite horizon we discuss herein are shown in the labeled orange circle. Red shading denotes the onset of the Shuram carbon isotope excursion.



Figure 2. Petrographic images and mineralogy of the Khufai Formation oolite. a: Reflected light image. Yellow boxed region was PIC-mapped at 20µm resolution (shown in Figure 3a). b: Locations of electron probe micro analysis in a representative ooid within the upper Khufai oolite. Ca/Mg percent molar mass ratios in spots 1-4 are 21.8/13.2, 21.9/13.1, 22.3/12.7, and 21.8/13.0, respectively. c: XRD spectrum of the same oolite. Orange lines indicate dolomite ordering peaks (Kaczmarek et al., 2017). d: Reflected light image from the same hand sample as a. e, f: Thin section images of other ooids from the same bed in the upper Khufai Fm. Ooids in d, e, f all show the same novel dolomite crystal structure we observe and describe in detail for the ooid in a and Figure 3. Concentric banding, possibly due to intermittent abrasion during ooid formation (Anderson et al., 2020) is labeled. Scale bars are 500µm unless otherwise noted.



Figure 3. Crystal orientation maps of one fabric-preserving dolomitic ooid from the upper Khufai oolite. a: Polarization-dependent Imaging Contrast (PIC) map of the upper left quadrant of the ooid shown in Fig. 2a. Each region with one color corresponds to one crystal with a single crystal orientation. Colors and brightness represent in-plane and out-of-plane crystal c-axis orientations, respectively, as depicted by the dolomite rhombs and color bar (labeled "key"). The curved outer edge of the ooid is preserved; the black region in the upper left corner of this figure is void space filled with epoxy and with scattered, equant dolomite cements. b, c: Two bundles of similarly-oriented crystals extracted from the PIC map in \mathbf{a}, \mathbf{e} (labeled (1), (2)). Histograms of pixel colors within each bundle show that all crystals within each bundle are similarly oriented (within 60° , see Sun et al. (2017)). In each case, bundle elongation (dashed lines) and crystal length (solid arrows) are cooriented. Mode crystal orientation for each bundle is depicted by the sketched dolomite rhombs ((i), colored accordingly). The purple bundle, (2), is length-fast; the green bundle, (1), is lengthslow. Bundles are curved, as shown by the gradient of color across each bundle. d: A modeled spherulitic form (Hendler et al., 2015) resembles the PIC map in A, including plumose bundles, abrupt misorientations, and bundles that terminate at the edge of the form. e: Highlighted view of some of the plumose, quasi-spherulitic bundles of similarly-oriented crystals observed in a.

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A2 Polarization-dependent Imaging Contrast (PIC) Mapping

We collected the data displayed in the PIC map in Fig. 3 on beamline 11.0.1.1 at the 319 Advanced Light Source, Lawrence Berkeley National Laboratory, using X-ray PhotoEmis-320 sion Electron spectroMicroscopy (X-PEEM). The polished sample was mounted such that 321 incident X-ray beams hit the sample at a 60° incident angle. Working at a fixed photon 322 energy of 534 eV (π^* peak in carbonate oxygen K-edge spectra), the linear polarization was 323 rotated at the undulator source from 0° to 90° in 5° increments. The resulting 19 images 324 were stacked and analyzed using GG Macros (see Sun et al. (2017)). In each pixel of the 325 stack, the intensity (I) vs. polarization angle (χ) curve was fit using a cosine-squared func-326 tion: $I = a + bcos^2(\chi - c')$ (Malus's law) with three fit parameters -a, b and c' – where 327 c' is the in-plane and b/a the out-of-plane angle of the crystal c-axis orientation, displayed, 328 respectively, by by hue and brightness as shown by the color legend in Fig. 3 (Gilbert et 329 al., 2011; DeVol et al., 2014). This process was repeated for a series of 56 by 56 µm areas, 330 with 56nm pixels, partly overlapping to cover the entire quadrant of the ooid outlined in 331 Fig. 2a. The ~ 50 images were then stitched together using Adobe Photoshop CC 2017 to 332 produce the PIC map shown in Fig. 3a. Together, the hue and brightness of each pixel in a 333 PIC map completely describe the three-dimensional orientation of a crystal's c-axis at the 334 same coordinates as the pixel. 335

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A3 X-ray diffraction (XRD)

³³⁷ Oolite powder was analyzed on the PANalytical X'Pert Pro in the Material Science ³³⁸ Department at the California Institute of Technology by Bergmann et al. (2018). Scans were ³³⁹ run from 5-70° 2θ with a step size of 0.008 and a scan step time of 10.16 s. A Cu anode was ³⁴⁰ used at 45 kV and 40 mA. A zero-background silicon plate was used for all measurements. ³⁴¹ Mineralogical phases were identified using the X'Pert Highscore IDMin function in Jade.

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A4 Electron probe microanalysis (EPMA)

Electron probe spot analyses, shown in Fig. 2b, were taken using a JEOL JXA-8200 Electron Microprobe at the California Institute of Technology with an accelerating voltage of 15 kV, beam current of 20nA, and beam size of 1 µm. Non-quantitative elemental mapping was also conducted on the ooids to assess trace metal variability (Supplemental Figure 1). Calcite, dolomite and rhodochrosite standards were used to calibrate the Ca, Mg, and Mn measurements, respectively. Average detection limits for Ca, Mg and Mn were 177 ppm, 283 ppm, and 300 ppm respectively. The CITZAF method was used for matrix correction.

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Supporting Information for "Nanoscale crystal fabric preserved in dolomite ooids at the onset of the Shuram Excursion"

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Contents of this file

1. Figure S1 and S2

Additional Supporting Information (Files uploaded separately)

1. Table S1 $\,$

Introduction

Included in this file are (1) additional crystal orientation maps and histograms of the PIC mapped ooid displayed in Figure 3 of the main text (Figure S2), and (2) additional elec-

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tron probe microanalysis elemental maps and spot analysis measurements to accompany Figure 2b in the main text (Figure S1 and Table S1). Table S1 can be downloaded as a separate spreadsheet. Crystal orientatons were measured by J. Wilcots, K.D. Bergmann, and P.U.P.A. Gilbert over the course of two beamtime sessions in April and November 2018 on beamline 11.0.1.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory, using X-ray PhotoEmission Electron spectroMicroscopy (X-PEEM). Bundles were selected manually in Adobe Photoshop, after the ooid PIC map (Figure 3a) was produced. The color (orientation) of each pixel within each bundle are plotted in histograms. EPMA results were collected by K.D. Bergmann in November 2011 at the California Institute of Technology. All figures and data are stored in a Zenodo repository (DOI:10.5281/zenodo.5259649; Wilcots, Gilbert, and Bergmann (2021)). Wilcots, J., Gilbert, P. U., & Bergmann, K. D. (2021, August). juliawilcots/synchrotronpaper-data: Release for submission. Zenodo. Retrieved from https://doi.org/ 10.5281/zenodo.5259650 doi: 10.5281/zenodo.5259650



Figure S1. Elemental maps of two thin sections of the upper Khufai oolite. **a** and **d** show Mg and Si in sample MD6 258.6 B3 (see Table S1), respectively. **b** and **c** show Mn and Si in sample MD6 258.6 e1 (Table S1).

Table S1.Electron probe microanalyses (EPMA) collected by K.D. Bergmann on Nov. 162011.Methods are described in the main text and the data file is available as a separate file.

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Figure S2. Histograms of crystal orientations within three bundles highlighted in Figure 3e of the main text. Like the two bundles displayed in Figure 3b,c of the main text, crystals within these bundles are co-oriented within $\sim 60^{\circ}$ within in bundle. Each bundle is plotted in its original orientation.