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► **To cite this version:**

E. Dobrică, K.K. Ohtaki, C. Engrand. Dolomites in hydrated fine-grained Antarctic micrometeorites: Effective tools for analyzing secondary processes. *Geochimica et Cosmochimica Acta*, 2022, 317, pp.286-305. 10.1016/j.gca.2021.11.018 . hal-03572244

HAL Id: hal-03572244

<https://hal.science/hal-03572244>

Submitted on 17 Nov 2022

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Geochimica et Cosmochimica Acta

DOLOMITES IN HYDRATED FINE-GRAINED ANTARCTIC MICROMETEORITES: EFFECTIVE TOOLS FOR ANALYZING SECONDARY PROCESSES

--Manuscript Draft--

| | |
|------------------------------|---|
| Manuscript Number: | |
| Article Type: | Article |
| Keywords: | carbonates; micrometeorite; transmission electron microscope; shock metamorphism; asteroid |
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| Abstract: | <p>We report detailed transmission electron microscope (TEM) observations of carbonates from one hydrated fine-grained Antarctic micrometeorite (H-FgMM). These carbonates show the occurrence of complex chemical variations and microstructures that provide important evidence regarding the formation and evolution of rarely analyzed H-FgMMs. The chemical variations were identified at both micrometer and nanometer scales, indicating that these carbonates formed under localized fluid conditions that suggest a variable chemical microenvironment. Individual carbonates grew from isolated reservoirs of fluid. Moreover, these carbonates contain manganese amounts almost twice as high as those measured in CM chondrites but similar to those identified in CI chondrites. Their particular compositions indicate reducing and progressively evolving conditions in the fluid from which these carbonates precipitated, probably due to water consumption during phyllosilicates formation. In addition to the compositional variability, microstructural features are pervasive in these carbonates, similar to those described in heavily shocked meteorites indicating that these carbonates were probably modified during shock processes after their formation. Since carbonates are highly susceptible to shock metamorphism, we suggest that it is essential to investigate their structure in detail before interpreting the isotopic measurements related to the time of their formation. Additionally, associated with carbonates, ubiquitous phosphates were identified in the micrometeorite analyzed. Future studies of these mineral associations will provide us further insight into the formation and evolution of asteroids, especially since they were both identified in the surface materials of Ryugu and Bennu.</p> |
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1 **DOLOMITES IN HYDRATED FINE-GRAINED ANTARCTIC MICROMETEORITES:**
2 **EFFECTIVE TOOLS FOR ANALYZING SECONDARY PROCESSES**

3
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32 **Abstract** - We report detailed transmission electron microscope (TEM) observations of
33 carbonates from one hydrated fine-grained Antarctic micrometeorite (H-FgMM). These
34 carbonates show the occurrence of complex chemical variations and microstructures that provide
35 important evidence regarding the formation and evolution of rarely analyzed H-FgMMs. The
36 chemical variations were identified at both micrometer and nanometer scales, indicating that these
37 carbonates formed under localized fluid conditions that suggest a variable chemical
38 microenvironment. Individual carbonates grew from isolated reservoirs of fluid. Moreover, these
39 carbonates contain manganese amounts almost twice as high as those measured in CM chondrites
40 but similar to those identified in CI chondrites. Their particular compositions indicate reducing
41 and progressively evolving conditions in the fluid from which these carbonates precipitated,
42 probably due to water consumption during phyllosilicates formation. In addition to the
43 compositional variability, microstructural features are pervasive in these carbonates, similar to
44 those described in heavily shocked meteorites indicating that these carbonates were probably
45 modified during shock processes after their formation. Since carbonates are highly susceptible to
46 shock metamorphism, we suggest that it is essential to investigate their structure in detail before
47 interpreting the isotopic measurements related to the time of their formation. Additionally,
48 associated with carbonates, ubiquitous phosphates were identified in the micrometeorite analyzed.
49 Future studies of these mineral associations will provide us further insight into the formation and
50 evolution of asteroids, especially since they were both identified in the surface materials of Ryugu
51 and Bennu.

52

53 **1. Introduction**

54 Carbonates are excellent candidates to study secondary processes that modified the primitive
55 materials that formed in the Solar System (Brearley 2006; Tyra et al. 2013). They have the potential
56 to provide us with a high-fidelity record of environmental conditions and the timing of their
57 formation (Brearley 2006; Tyra et al. 2013; Alexander et al. 2015; Telus et al. 2019). Furthermore,
58 they have been commonly identified in carbonaceous chondrites (<2 vol%), though they are rare
59 in dust particles such as Antarctic micrometeorites (AMMs) and interplanetary dust particles
60 (IDPs, Sandford and Walker 1985; Tomeoka and Buseck 1986; Germani et al. 1990; Rietmeijer
61 1990; Bradley et al. 1992; Zolensky and Lindstrom 1992; Brearley 2006; Duprat et al. 2007; Aleon
62 et al. 2009; de Leuw et al. 2009; Dobrică et al. 2009; Tyra et al. 2012; Fujiya et al. 2013; Lee et

63 al. 2014; Alexander et al. 2015; Dobrică et al. 2019). Recently, centimeters-thick, roughly meter-
64 long veins of carbonates were identified in outcrops at the surface of the asteroid Bennu (Kaplan
65 et al. 2020), and curation analyses of asteroid Ryugu also suggest the presence of carbonates in the
66 samples (Yada et al. 2021). Therefore, in preparation for the analyses of returned asteroidal
67 samples, our study expands on earlier efforts to investigate the secondary processes and the
68 alteration conditions of H-FgMMs, with a focus on carbonate crystals (Dobrică et al. 2019). We
69 use site-specific extraction techniques to investigate the mineralogy, texture, chemical
70 compositions of several electron transparent sections extracted from one H-FgMMs described
71 previously using oxygen isotopic measurements (Dobrică et al. 2019). Our detailed TEM
72 observations of carbonates aim to understand a more detailed picture of carbonate formation and
73 evolution of rarely analyzed hydrated micrometeorites.

74

75 **2. Sample and methods**

76 One unmelted H-FgMMs (03-36-46) was analyzed in this study using extensive TEM
77 techniques. The sample was collected from the pristine Concordia snow during the 2002 campaign
78 (Duprat et al. 2007). The size of the particle analyzed in this study is 84 x 114 μm , which
79 corresponds to the whole particle collected from snow (Fig. 1). The polished and carbon-coated
80 petrographic section was first characterized by scanning electron microscopy (SEM) using
81 backscattered electron imaging on a Helios 660 dual-beam focused ion beam SEM (FIB-SEM)
82 instrument at the Advanced Electron Microscopy Center (AEMC) at the University of Hawai'i at
83 Mānoa. Four electron transparent sections were prepared by the conventional *in situ* FIB technique
84 (Fig. 1). A platinum protective layer was deposited on top of the region of interest, first by electron
85 beam deposition and then by ion beam deposition, to avoid gallium primary ion beam damage
86 during the FIB sample preparation. The section was transferred to Cu TEM half grids with a
87 micromanipulator. The final ion milling of the 2 μm thick section to electron transparency was
88 carried out with the sample attached to the TEM grid. The final thinning stages were performed at
89 2 kV with a current of 72 pA. Each FIB section was studied using a variety of TEM techniques,
90 including scanning transmission electron microscopy (STEM) imaging, nanodiffraction, and
91 energy-dispersive X-ray spectroscopy (EDS). All imaging and analysis were carried out at 300 kV
92 using the Titan G2 analytical (S)TEM at AEMC. Crystalline phases were identified by electron
93 nanodiffraction and EDS measurements. Nanodiffraction was carried out with an accelerating

94 voltage of 300 kV, a camera length of 295 mm, and a convergence angle of 0.1–0.3 mrad.
95 Additional EDS hyperspectral maps were performed at the Molecular Foundry, Lawrence
96 Berkeley National Laboratory using a 80–300 kV TitanX “ChemiSTEM” with four windowless
97 X-ray silicon drift detectors (~0.7 sr solid angle).

98 The elemental compositions of carbonates reported here were extracted from EDS mapping (at
99 the Molecular Foundry). The EDS maps were collected at 200 kV and displayed using the Esprit
100 1.9 software package (Bruker Corporation) as color-coded maps. Compositions were normalized
101 to 100%. Oxygen abundances should be viewed with caution because oxygen K X-rays are subject
102 to variable amounts of self-absorption by the sample.

103

104 **3. Results**

105 **3.1 SEM observations**

106 Figure 1 shows the compact fine-grained, unmelted external surface (Fig. 1a) and the polished
107 section (Fig. 1b) of the H-FgMMs (03-36-46) analyzed in this study. In the polished section,
108 several coarse-grained minerals (sulfides, Mg-rich carbonates, Ca-phosphates, and magnetites)
109 were observed embedded in a fine-grained material (Fig. 1b-f). Euhedral to subhedral sulfides (5
110 x 7 μm , Fig. 1d) and magnetites (3.5 x 7 μm , Fig. 1c) are the largest minerals found at the surface
111 of the polished section. Additionally, multiple anhedral to subhedral, micron-sized Mg-rich
112 carbonates (≤ 3 x 4.5 μm , Fig. 1c and 1f) and Ca-phosphates (≤ 2 x 3.5 μm , Fig. 1) are identified
113 by EDS in this micrometeorite. Carbonates represent ~1.4 vol% (~2 μm^2) of the entire surface of
114 the polished section (~150 μm^2) and phosphates cover ~0.6 vol.% (~0.9 μm^2). In this study, we
115 focus on two distinct regions containing carbonates found at ~20 μm distance (Fig. 1b). For
116 simplification purposes, we will call these regions A and B (see Fig. 1b). The carbonates from
117 region A are associated with magnetite (anhedral and framboidal magnetite). The oxygen isotopic
118 compositions of the magnetite-carbonate assemblage (13 x 15 μm in size) were described
119 previously by Dobrică et al. (2019). The largest carbonate crystal in this region is porous and
120 presents multiple fractures (3 x 4.5 μm , Fig. 1c). Additionally, in this region, Ogliore et al. (2019)
121 measured the ^{53}Mn - ^{53}Cr systematics in the largest carbonate crystal. Therefore, several crystals in
122 region A could potentially have been modified during the secondary ion mass spectrometry (SIMS,
123 O isotopic measurements, Dobrică et al. 2019) and NanoSIMS measurements (^{53}Mn - ^{53}Cr
124 measurements, Ogliore et al. 2019). The carbonate cluster in region B is ~4 x 7 μm in size and has

125 similar pores and fractures as those observed in the carbonates from region A (Fig. 1f). However,
126 these carbonates remained undamaged since no ion microprobe measurements were performed in
127 this region.

128

129 **3.2 TEM observations**

130 Four FIB sections were prepared in the H-FgMMs (03-36-46) analyzed in this study. Figure 1c
131 to 1f shows the location of these FIB sections extracted in this study (white rectangles). These
132 regions were selected based on the minerals identified in the polished section by SEM/EDS.
133 Additionally, we selected the regions that were the least damaged by the ion microprobe
134 measurements performed during previous studies (Dobrica et al. 2019, Ogliore et al. 2019). The
135 first FIB sections were extracted from carbonates in region A (UH-001, Fig. 1c) and region B (UH-
136 002, Fig. 1f). The other two FIB sections were extracted from the remaining fine-grained material
137 targeting regions containing micrometer-sized secondary phases such as Ca-phosphates (UH-003,
138 Fig. 1e) and magnetite (UH-006, Fig. 1d).

139

140 *Carbonates chemistry and microstructures*

141 Detailed TEM observations confirm the presence of multiple carbonate crystals in two different
142 FIB sections (Figs. 2, 4, and 5). They occur both as separate, anhedral, single crystals (Figs. 2a-b
143 and 4, region A) and as a polycrystalline cluster (Figs. 2c-e and 5, region B). The size of the cluster
144 (Fig. 2c-e) in the TEM section is $\sim 1.5 \times 3 \mu\text{m}$ and it has a heterogeneous chemical composition
145 compared to the carbonates identified in region A (Fig. 2a-b). Figure 2d-e shows the Mn and Fe
146 distribution in this large, polycrystalline carbonate cluster (FIB section UH-002). Three distinct
147 regions with variable Mn and Fe concentrations are identified in the EDS maps (2.9-8.1 wt.%
148 MnO, 2.5-6.0 wt.% FeO, Fig. 2c-e). Note that this chemical heterogeneity is not easy to notice in
149 the Z-contrast DF-STEM micrograph (Fig. 2c). These carbonates from region B are in average
150 more enriched in Mn and Fe (Fig. 3, region B - N = 19, 6.1 wt% MnO, S.D. 1.4; 3.1 wt% FeO,
151 S.D. 1.0) compared to those from region A (Fig. 3, region A - N = 8, 4.1 wt% MnO, S.D. 0.7; 2.6
152 wt% FeO, S.D. 0.4). Figure 3 shows a ternary diagram to compare the MgCO_3 , CaCO_3 , and
153 $(\text{Fe}+\text{Mn})\text{CO}_3$ components (mol%) of carbonates from both regions (region A - dark grey symbols,
154 region B - white and light grey symbols). The chemical compositions measured in the carbonates
155 from 03-36-46 sample indicate the presence of both dolomite and ankerite in this micrometeorite.

156 The term dolomite is here restricted to material with $\text{Mg/Fe} \geq 4:1$ (Deer et al. 1992). All carbonates
157 in region A are dolomite crystals (9.9-15.8 Mg/Fe ratio, avg. 10.5, Table 1). According to the
158 diffraction data, the carbonate cluster in region B is composed of two chemically zoned crystals of
159 dolomite, with one of the crystals having an ankeritic rim (Figs. 2 and 5). The Mg/Fe ratio of the
160 largest dolomite crystal in the cluster (left crystal, Fig. 5a) varies from 9.8 Mg/Fe ratio at the top
161 part (LT - left crystal, top part; Fig. 5a) to 9.2 Mg/Fe at the bottom part (LB - left crystal, bottom
162 part; Fig. 5a). The dolomite rim (LB) is Mn-rich (Fig. 2d, 10.21 mol% MnCO_3) compared to the
163 top part of the crystal (8.0 mol% MnCO_3). Several, Fe-rich inclusions (~20 nm in diameter) were
164 observed in this dolomite rim (LB, Fig. 5b, white arrows); however, the exact mineralogy of these
165 inclusions was not obtained due to the small size of the crystals and that their identification after
166 the regions were damaged during the acquisition of the EDS maps. The smaller crystal in the
167 cluster (right side, Fig. 5) is also chemically zoned, with a dolomite at the top part (RT - right
168 crystal, top part; 9.7 Mg/Fe ratio) and with an ankerite at the bottom part (RB - right crystal, bottom
169 part; 4 Mg/Fe ratio). The bottom part is Mn-poor and Fe-rich (4.7 mol% MnCO_3 , 8.8 mol% FeCO_3)
170 compared to the top part of the crystal (Fig. 5b-c, 8.5 mol% MnCO_3 , 3.8 mol% FeCO_3). Table 1
171 shows more details about the chemical compositions of the two chemically zoned crystals in the
172 cluster.

173 All dolomite crystals identified in this study (regions A and B) contain intragranular pores
174 (white arrows, Fig. 4). Additionally, a number of pores are observed at the crystal boundaries, in
175 association with C-rich amorphous material (details described in the next section). The largest
176 intergranular pore identified has ~90 nm in diameter (Fig. 4c). Note the surface of the dolomite
177 crystals (~450 nm in thickness) was damaged during the NanoSIMS measurements (white dashed
178 line, Fig. 4c; Ogliore et al. 2019).

179 Figures 4 and 5 show the occurrence of complex microstructures of the carbonates identified in
180 this micrometeorite. The most pervasive microstructural features are called modulations and they
181 were observed in carbonates from both A and B regions (Figs. 4b, 5d and 5i). These modulations
182 appear as near-parallel lamellae or domains alternating dark/light contrast when imaged with a
183 small convergence angle (0.1-0.3 mrad) in the STEM mode. The modulations affect the entire
184 crystal and show multiple orientations (Fig. 5d). Additionally, the EDS analysis indicates that these
185 modulations correspond to local compositional variations in manganese up to 2.0 wt% MnO at a
186 few nanometer scale. The black arrows show the location of the Mn-rich regions (Fig. 5, avg. 6.3

187 wt% MnO compared to the Mn-poor region avg. 7.5 wt% MnO). Figure 5e-f shows the modulation
188 and the Mn distribution in the largest dolomite crystal in the cluster.

189 Additionally, the interface between the two crystals in the cluster displays a moiré pattern
190 formed by the superimposition of two periodical structures (Figs. 5g-h and 5j). The diffraction
191 pattern obtained on the superposition of the two periodical structures exhibits peaks caused by
192 diffraction on each individual periodical structure (Fig. 5h). Extra peaks due the moiré structure
193 are apparent in the fast Fourier transform (FFT) diffraction pattern made at the boundary between
194 the two crystals (Fig. 5h). Furthermore, the two dolomite crystals show an orientation mismatch
195 of a relative rotation angle of $\sim 4^\circ$ between lattice fringes of the two carbonates in the cluster (Fig.
196 5j).

197

198 *Materials associated with carbonates*

199 All nanometer to micrometer-sized minerals identified in the H-FgAMM analyzed are
200 embedded in a coarse- and fine-grained phyllosilicate matrix (Fig. 6a, coarse-grained
201 phyllosilicates - C-g phyllo.; fine-grained phyllosilicates - F-g phyllo.). The chemical
202 compositions and basal spacing (~ 0.7 - 0.9 nm) of the fine-grained phyllosilicates are consistent
203 with serpentine (Fig. 6, Table 1). The coarse-grained phyllosilicates are FeO-rich (26.5 wt% FeO)
204 and SO₃-rich (5.3 wt% SO₃) compared to the fine-grained phyllosilicates (avg. 15 wt% FeO, 1.3
205 wt% SO₃). Additionally, we identified a subhedral region where phyllosilicates have a compact
206 texture (Fig. 6b, white dashed line). This compact region is composed of phyllosilicates enriched
207 in sulfur (7 wt% SO₃) with an intermediate composition of iron (20.9 wt% FeO) compared to the
208 coarse- and fine-grained phyllosilicates described previously. The chemical compositions of the
209 phyllosilicates are shown in Table 1.

210 Magnetite is common in this H-FgAMM and was identified in three out of the four FIB sections
211 analyzed in this study. It is present as individual grains embedded in phyllosilicates or as
212 aggregates of framboidal and radial magnetite (Fig. 6c). Framboidal magnetite is the most frequent
213 occurrence, though one with a radial texture was identified in the association with the framboidal
214 magnetite. The size of each framboid magnetite crystal varies from ~ 0.5 μm to 1.4 μm (Fig. 6).
215 The radial magnetite aggregate (~ 1.5 x 2.5 μm in size) is composed of fibrous, needle-like, or
216 acicular crystals with sizes up to ~ 40 nm in width and 1.2 μm in length. Additionally, the individual

217 crystals of magnetite embedded in fine-grained phyllosilicates range in size from ~0.8 μm to 1.8
218 μm .

219 Most sulfides in this micrometeorite are nanometers in size (Fig. 6a, white arrows). However,
220 several micrometers sized ($<3.8 \times 3.9 \mu\text{m}$, Fig. 6d) Ni-poor sulfides ($<1.9 \text{ at. } \text{S}$) were identified
221 in all the FIB sections analyzed. Most of these micrometer sulfides contain pores (up to 700 nm in
222 length and 100 nm wide) and have irregular surfaces, with embayments up to ~340 μm long (Fig.
223 6d).

224 Two Ca-phosphates [apatite - $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$] were identified in two different FIB
225 sections (Fig. 6e-f, Table 1). They contain irregular pores with sizes ranging from a few
226 nanometers up to 190 nm (Fig. 6e-f, white arrows).

227 Additionally, we observed one subhedral, polycrystalline aggregate identified using electron
228 nanodiffraction and EDS measurements as phosphide, more precisely barringerite $(\text{Fe},\text{Ni})_2\text{P}$ (Fig.
229 6b). The aggregate shows embayments (106 nm in length) that are ~3 times smaller than the entire
230 size of the polycrystalline aggregate (~330 x 375 nm).

231 A C-rich amorphous material was identified in contact with the carbonates from region A (Fig.
232 2a-b). This carbonaceous matter contains 80.6 wt% C, 15.8 wt% O, and other minor elements,
233 such as 0.9 wt% Mg, 0.3 wt% Si, 0.1 wt% S, 1.3 wt% Ca, 0.9 wt% Mn, and 0.1 wt% Fe. Figure
234 2b shows the elemental map (C, Mn, and Fe) of the carbonaceous matter (C-rich am.) associated
235 with the carbonates from region A. Most of this carbonaceous matter contains several large pores
236 (up to ~1 μm).

237

238 **4. Discussion**

239 Carbonates in micrometeorites have been studied previously (Duprat et al. 2007, 2010; Dobrică
240 et al. 2009, 2012). However, although SEM and electron microprobe studies have been performed,
241 they have not received such close examination by TEM as in the present work. The observations
242 presented here focus on the occurrence of complex microstructures and zonations in carbonates
243 (dolomite and ankerite) from one particular micrometeorite (03-36-46) that was previously
244 described by Dobrică et al. (2019) and Ogliore et al. (2019), which report a combined
245 mineralogical, oxygen isotopic measurements, ^{53}Mn - ^{53}Cr isotope systematics studies of the
246 magnetite-dolomite assemblage identified in region A (Fig. 1). In the following discussion, we
247 examine the occurrences and the formation processes of the carbonates in different types of

248 extraterrestrial materials from a perspective gained at the TEM scale. In addition, we examine the
249 implications for the presence of multiple complex microstructural features and their possible role
250 in the interpretation of shock-metamorphic events and the timing of their formation.

251

252 **4.1. Carbonates occurrence in micrometeorites: A comparison with other extraterrestrial** 253 **materials**

254 Micrometeorites represent the main source of extraterrestrial matter accreted by the Earth
255 nowadays; however, they are only rarely described as containing carbonates (Love and Brownlee
256 1993; Duprat et al. 2007; Dobrică et al. 2009; Duprat et al. 2010; Sakamoto et al. 2010; Dobrică
257 et al. 2012; 2019). So far only calcite (CaCO_3) and dolomite [$(\text{CaMg})\text{CO}_3$] were identified in the
258 AMMs collections and no systematic mineralogical study is currently available. These carbonates
259 are mostly found in fine-grained fluffy and ultracarbonaceous AMMs (Dobrică et al. 2009;
260 Sakamoto et al. 2010). The largest ($\sim 14 \mu\text{m}$ in diameter) euhedral, single-crystal carbonate was
261 identified in an ultracarbonaceous AMM (Duprat et al. 2007; Dobrică et al. 2009; Duprat et al.
262 2010; Dobrică et al. 2012). Additionally, Noguchi et al. (2002) suggest that phyllosilicate-rich
263 micrometeorites show evidence of the breakdown of carbonate grains when the AMMs entered the
264 Earth's atmosphere.

265 Similar to AMMs, only rare carbonate crystals were identified so far in interplanetary dust
266 particles (IDPs, Aleon et al. 2009; Tomeoka and Buseck 1986; Zolensky et al. 2008). They occur
267 both as separated euhedral single crystals and as anhedral aggregates with sizes ranging from
268 50 nm to $2 \mu\text{m}$ (Aleon et al. 2009; Tomeoka and Buseck 1986; Zolensky et al. 2008). They are
269 typically identified in hydrated IDPs and are associated with Fe-Ni sulfide rather than with
270 magnetite or tochilinite as observed in AMMs and chondritic meteorites (Tomeoka and Buseck
271 1986; Schramm et al. 1989; Zolensky et al. 2008; Dobrica et al. 2019).

272 Spectroscopically, carbonates have been detected in outcrops and materials ejected from the
273 surfaces of comets and asteroids, which are likely the main sources of AMMs and IDPs (Lisse et
274 al. 2006, 2007; Wada et al. 2018; Kaplan et al. 2020). The identification of carbonates in the
275 samples returned from the comet 81P/Wild 2 is still debated due to possible contamination issues
276 (Flynn et al. 2008a; Mikouchi et al. 2007; Tomeoka et al. 2008; Wirick et al. 2007). However,
277 imminent analysis of return samples from the asteroids 162173 Ryugu and 101955 Bennu will

278 improve our understanding of the origin and evolution of carbonates in the small Solar System
279 bodies (Wada et al. 2018; Kaplan et al. 2020).

280 Tens of different types of carbonates have been identified in meteorites, but calcite, aragonite
281 (CaCO_3), dolomite (Ca,MgCO_3), breunnerite (Mg,FeCO_3), and siderite (FeCO_3) are the principal
282 carbonate phases in chondritic meteorites (CI, CM, CR, CV, CB/CH-like, and OC) (Fredriksson
283 and Kerridge, 1988; Johnson and Prinz, 1993; Weisberg et al. 1993; Riciputi et al., 1994; Endreß
284 and Bishoff, 1996; Benedix et al. 2003; Brearley 2006; Bonal et al. 2010; Rubin and Ma, 2017).
285 Their abundance in chondrites vary up to <4.5 vol%, though they are rare in CV and OC meteorites,
286 and absent in CO chondrites (Zolensky et al. 1997; Brearley 2006; de Leuw et al. 2010; Lee et al.
287 2012; Tyra 2013; Lee et al. 2014; Alexander et al. 2015; Tyra et al. 2016). Carbonate occurs most
288 commonly as (1) isolated grains and aggregates up to ~150 μm in size distributed in the matrix
289 and chondrule rims of chondrites and (2) veins up to ~25 μm in thickness, crosscutting chondrules
290 and calcium–aluminium-rich inclusions (CAIs, Zolensky et al. 1993; Abreu and Brearley 2005; de
291 Leuw et al. 2010; Verdier-Paoletti et al. 2017; Jilly-Rehak et al. 2018; Vacher et al. 2019).
292 Additionally, Mg-Fe-Ca-bearing carbonates [magnesite - MgCO_3 , siderite, and ankerite] were
293 identified in all subgroups of Martian meteorites (Gooding 1993; Treiman 1995; Treiman et al.
294 2000). In Allan Hills (ALH) 84001, an orthopyroxenite and one of the most famous and studied
295 Martian meteorites, carbonates are globular-shaped and compositionally zoned (Mittlefehldt 1994;
296 Treiman 1995; Bridges et al. 2001). They constitute ~1 vol% of the meteorite (Treiman 1995).
297 These carbonates (<30 μm in size) are characterized by two distinct features (1) randomly oriented
298 magnetite crystals (<10 nm to 100 nm) and (2) nm-sized voids (<10 nm to 70 nm) (Bradley et al.
299 1998; Barber and Scott 2003; Brearley 2003). Most of these features are found to be associated
300 with each other (Brearley 2003). The partially faceted voids identified in carbonates from Allan
301 Hills (ALH) 84001 are generally subrounded similar to those identified the H-FgMMs analysed in
302 this study (see section 4.4).

303 Though carbonates are scarce components in AMMs compared to meteorite samples, this is
304 probably due to a lack of standardized detection of these phases in these small and difficult to
305 analyze dust particles. Additionally, two additional factors could have played an important factor
306 in the identification of carbonates in micrometeorites, such as (1) terrestrial weathering of AMMs
307 in the ice collections and (2) atmospheric entry heating (Duprat et al. 2007; Noguchi et al. 2012).
308 However, carbonates should be more abundant in H-FgMMs since we show here in this study that

309 they represent, together with phosphates, the main sink for Ca after being mobilized from glass
310 with embedded metal and sulfides (GEMS), rare chondrules, and CAIs (Dobrică et al. 2009; 2012).
311 It is therefore desirable to achieve in the future a systematic database of the occurrence of
312 carbonates in dust particles (AMMs and IDPs) using non-destructive *in situ* spectroscopic
313 techniques, while avoiding complex sample preparation.

314

315 **4.2 Carbonate formation processes**

316 Carbonates are generally believed to have formed by parent-body aqueous processing (Brearley
317 2006; Tyra et al. 2012; Fujiya et al. 2013; Alexander et al. 2015; Doyle et al. 2015). However, it
318 has been suggested that their formation does not necessarily require liquid water and that they
319 could form prior to the accretion of the parent body (Metzler et al. 1992; Kemper et al. 2002;
320 Toppani et al. 2005). Nevertheless, textural evidence (e.g. veins, rims around chondrules, and
321 mineral associations with other secondary, aqueous alteration phases) and complex compositional
322 zoning are supportive of an aqueous alteration scenario (e.g. Brearley 2006). Their formation is
323 consistent with precipitation from aqueous solutions, so their analysis has the potential to provide
324 useful information about the spatial, temporal, and chemical alteration conditions that were present
325 on the parent body of micrometeorites (Brearley and Hutcheon 2002; Brearley 2006; Tyra 2013;
326 Jilly-Rehak et al. 2018; Telus et al. 2019).

327 Previous studies show that isotopic and chemical variations are ubiquitous in carbonates,
328 regardless of the morphology and sample, indicating changes in fluid composition during their
329 formation (Barber and Scott 2003; Tyra 2013; Tyra et al. 2016). Several studies described the
330 isotopic variations of carbonates (Benedix et al. 2003; Tyra et al. 2016; Telus et al. 2019); however,
331 here we will focus on the compositional variability of carbonates. Generally, compositionally
332 zoned carbonates are commonly observed in chondritic and Martian meteorites with variations at
333 scale ranging from submicron to tens of micrometers (Brearley and Hutcheon, 2000; 2002; Barber
334 and Scott 2006; Bonal et al. 2010; Tyra 2013; Telus et al. 2019). It has been suggested that such
335 variations in composition would require that cation mobility was restricted; otherwise, the
336 compositional zoning pattern in adjacent dolomite grains would be similar. These variations reflect
337 on the local geochemical microenvironments within the parent body of meteorites, in which
338 individual carbonates grew from isolated reservoirs of fluid during aqueous alteration (Brearley et
339 al. 2001; Brearley and Hutcheon 2002; Lee and Ellen 2008; Tyra 2013; Tyra et al. 2016). In CM

340 chondrites, the compositional zoning in dolomite is heterogeneous with no consistent core-to-rim
341 relationships, suggesting that the crystallization probably started on a substrate with growth
342 occurring into a fluid-filled pore space with very limited communication between pores (Tyra
343 2013; Tyra et al. 2016). These pores became isolated as a result of serpentinization processes that
344 may have caused a reduction in porosity in the fine-grained materials (Tyra 2013). Therefore, this
345 decreased porosity could have generated localized dissolution reactions that would have controlled
346 the fluid chemistry, resulting in large variations in the dolomite compositions (Tyra 2013; Tyra et
347 al. 2016). Similarly, carbonates in this study exhibit significant localized, compositional variations
348 identified at both (1) micrometer-scale between regions A and B (Fig. 1) and (2) nanometer-scale
349 inside dolomite crystals (Fig. 4). Therefore, according to previous studies, this fine-scale zoning
350 shows that they were formed under localized fluid conditions, which suggests a variable chemical
351 microenvironment, in which individual carbonates grew from isolated reservoirs of fluid.

352 Furthermore, carbonates in region A deviate from the typical 1:1 Ca-Mg stoichiometry (1.2-1.6
353 Ca/Mg ratios), displaying excess Ca in the dolomite structure (Fig. 3). We report that the average
354 dolomite in region A has 51.4 mol% CaCO₃ and ankerite is 54.8 mol% CaCO₃, which shows that
355 their composition is non-stoichiometric. However, the carbonates from region B are stoichiometric
356 overall with CaCO₃ values ranging from 49.2 mol% CaCO₃ to 50.9 mol% CaCO₃ (Fig. 3).
357 Carbonates in CM have been also described as non-stoichiometric, displaying similar excesses in
358 Ca (Fouke and Reeder, 1992; Johnson and Prinz 1993), in addition to the stoichiometric dolomites
359 reported by Zolensky et al. (1997) and Tyra (2013). At the same time, CI chondrites, dolomites
360 display Ca deficiencies compared with the ideal stoichiometry (Johnson and Prinz 1993; Riciputi
361 et al. 1994; de Leuw et al. 2010). All these differences in chemistry between CM and CI dolomites
362 were suggested to result from differences in alteration temperatures of their parent bodies.
363 Nonetheless, Ca excesses was attributed to metastable growth of dolomite at low temperatures or
364 under briny conditions (Fig. 3, Goldsmith and Graf 1960; Fouke and Reeder, 1992; Johnson and
365 Prinz 1993; de Leuw et al. 2010; Tyra 2013). Therefore, here we argue that the chemical zonations
366 observed in the carbonates analyzed in this study indicate changes in fluid composition during low
367 temperature aqueous alteration.

368 Additionally, we observed that the carbonates in 03-36-46 contain manganese amounts almost
369 twice as high (avg. 10.0 mol% MnCO₃, S.D. 2.4, N = 25, range 5.4-13.5 mol% MnCO₃) as those
370 measured in CM chondrites (<6.9 mol% MnCO₃, de Leuw et al. 2009; Tyra 2016) and Martian

371 meteorites (<5.2 mole% MnCO₃, Mittlefehldt et al. 1994; Treiman 1995), though they are
372 comparable to those in CI chondrites (avg. 6.0 mol% MnCO₃, S.D. 4.5, N = 17, range 0.1-19.6
373 mol% MnCO₃; Johnson and Prinz 1993). The highest Mn values are in the carbonates identified
374 in region B (left crystal, rim – LB, 12.1 mol% MnCO₃). A substantial source of manganese for
375 these carbonates could be the aqueous alteration of Mg-rich silicates, more precisely, low-iron,
376 manganese-enriched (LIME) pyroxenes and olivines. Notably since LIME minerals were
377 previously identified in AMMs and no Mg-rich silicates were identified in this micrometeorite,
378 suggesting that these phases could have been the main source of Mn to the fluid for the formation
379 of carbonates (Dobrică et al. 2009). Similarly, the high Mg concentrations necessary for the
380 formation of dolomite could have been generated by the replacement of forsterite by serpentine
381 (Sleep et al., 2004; Oze and Sharma, 2007). This is consistent with previous observations
382 indicating that dolomite often forms from brines present once much of the water has been
383 consumed by serpentinization (Tucker and Write, 1990; Arvidson and Mackenzie, 1999).

384 This manganese enrichment, apart from cation concentration in the fluid, has important
385 information about potential redox reactions of the pore fluids, indicating reducing conditions in
386 the fluids from which the carbonates from 03-36-46 precipitated (Tucker and Wright, 1990;
387 Warren 2000). Furthermore, since Mn tends to increase during later episodes of recrystallisation
388 and considering that carbonates from CM chondrites have Mn-rich zones usually found at grain
389 peripheries, this suggests that the fluids from which these carbonates most likely formed
390 progressively evolved and became more saline with time, perhaps due to the consumption of water
391 during phyllosilicates formation (Brearley and Hutcheon, 2000; Tyra 2013; Tyra et al. 2016).
392 These observations are consistent with mineralogical and geochemical models of progressive
393 aqueous alteration in the CM chondrite parent body (Barnaby and Rimstidt, 1989; Schulte and
394 Shock, 2004; Alexander et al. 2015; Telus et al. 2019).

395

396 **4.3 Complex microstructures: Evidence of shock deformation**

397 Carbonates in the H-FgMM analyzed (03-36-46) show the presence of fine-scale complex
398 microstructures (modulations, moiré pattern, and pores) that are nevertheless related to several
399 compositional variations (iron-rich inclusions and zonations). These microstructures could be
400 associated either with (1) crystal growth or (2) lattice deformation mechanisms (Gunderson and
401 Wenk 1981; Miser et al 1987; Reeder 1992; Larsson and Christy 2008). Although their evaluation

402 is not without problems, their interpretation is extremely instructive in elucidating the formation
403 and evolution of carbonate-bearing samples.

404 Among the variety of microstructures (dislocations, twins, growth zoning, etc.) identified in
405 carbonates from terrestrial samples, modulations got most attention since they were first described
406 about forty years ago (Reeder and Wenk 1979). More precisely dolomite crystals typically exhibit
407 modulations in terrestrial rocks; however, no modulated microstructures were identified in
408 carbonates from extraterrestrial materials (Reksten 1990; Reeder 1992; Rodriguez-Navarro and
409 Ruiz-Agudo 2013). Despite numerous efforts to relate modulations to either compositional
410 variability or strain in the crystal lattice, their origin is still debated (Reksten 1990; Baronnet 1992;
411 Reeder 1992; Martinez et al. 1995; Rodriguez-Navarro and Ruiz-Agudo 2013). In this study,
412 manganese variations recall the modulation microstructures; however, these variations do not
413 perfectly overlay with the shape and orientation of modulations (Fig. 5d-f). This imperfection may
414 be due to the fact that the EDS maps and STEM micrographs were not taken at the same
415 crystallographic orientation. Therefore, looking solely at the nanometric variations of these
416 carbonates, it is unclear if these modulations are evidence of growth processes during a periodic
417 variation in fluid composition, lattice strain, or both.

418 An alternative way to understand the evolution of the parent body of this H-FgMM is to examine
419 the other microstructures and features identified in these carbonates (e.g., moiré patterns and
420 pores). In particular, the moiré patterns, which have been extensively used in the past for
421 measurement and analysis of strain (Theocharis 1969; Wang 1992; Sirohi and Chau 1999; Wang
422 et al. 2015). These features are generally described to appear whenever two periodical structures
423 are superimposed or stacked with a twist angle and/or lattice mismatch (Latychevskaia et al. 2019;
424 Reidy et al. 2021). They were previously identified in chondritic (CM, CV, CV) and Martian
425 meteorites, as well as in dust particles from comet 81P/Wild 2 captured by the NASA Stardust
426 spacecraft (Tomeoka and Buseck 1990; Barber and Scott 2006; Buseck and Hua 1993; Abreu et
427 al. 2017; De Gregorio et al. 2017). Different mineral phases, including carbonates, olivine,
428 phyllosilicates, and presolar hibonite and carbide grains were described as containing moiré
429 patterns (Tomeoka and Buseck 1990; Leitner et al. 2012; Abreu et al. 2017). Their presence was
430 constantly described as reminiscent of deformation (Tomeoka and Buseck 1990; Leitner et al.
431 2012; Abreu et al. 2017). Additionally, the occurrence of carbonates with moiré patterns showing
432 a local lattice mismatch were previously described in the heavily shocked Martian meteorite, Allan

433 Hills 84001 (shock pressures of ~35–40 GPa; Barber and Scott 2006). Although Barber and Scott
434 (2006) did not directly connect these patterns to shock, Brearley (2003) described the carbonates
435 from ALH 84001 as extensively strained as a result of multiple shock events. Therefore, we argue
436 that the occurrence of moiré patterns at the interface between the two dolomite crystals in the
437 carbonate cluster indicates that deformation processes produced during shock metamorphism were
438 active on the parent body of the micrometeorite analyzed. No other evidence of deformation,
439 indicating that the sample experienced shock-induced metamorphic effects, were identified.
440 However, the lack of minerals regularly used in the shock classification scheme of meteorites
441 (olivine, pyroxenes, and feldspars) precludes the evaluation of the degree of shock in this
442 micrometeorite (Stoffler et al. 1991; Scott et al. 1992; Rubin et al. 1997).

443 Additionally, the presence of pores associated with carbonates have important implications in
444 the investigation of shock metamorphism as well. For example, in the Fe-bearing carbonate from
445 ALH 84001, numerous pores are frequently associated with magnetite inclusions and were
446 interpreted as shock heating features (Brearley 2003). More precisely, their presence was
447 interpreted as the consequence of the loss of CO₂ resulting from the decomposition of the siderite
448 component in solid solution in the carbonate, via decarbonation reactions produced as a
449 consequence of the shock heating of ALH 84001 (Brearley 2003). Similar features are commonly
450 observed in the carbonates identified in this study and the adjacent phases (phosphates and C-rich
451 amorphous material, Figs. 2, 4, and 6). However, they are not associated with magnetite as
452 observed in ALH 84001 (Brearley 2003), though several nanometric Fe-rich inclusions were
453 identified in the dolomite grains (Fig. 5). The absence of clear evidence of magnetite inclusions in
454 the carbonates from the H-FgMM analyzed could be explained by a (1) reduced degree of shock-
455 induced metamorphism experienced by this micrometeorite and/or (2) lower Fe-rich carbonate
456 compositions than those described in ALH 84001 (Fig. 3).

457 Multiple studies of shock response of carbonate targets in nature, experiments, and numerical
458 models are reported in the literature (Osinski et al. 2008; Langenhorst and Deutsch 2012; Bell
459 2016; Hamann et al. 2018). However, despite the multitude of different approaches, the reaction
460 of carbonate-bearing targets to hypervelocity impact is not well understood and sometimes yields
461 contrasting results. Furthermore, detailed TEM studies of the shocked materials are scarce. A
462 recent TEM study shows that shocked calcite crystals to pressures varying from 9 GPa to ~61 GPa
463 display a systematic increase in the density of strain features (mottled contrast and twins) with

464 increasing shock pressure (Bell 2016). In calcite crystals recovered from shock experiments
465 produced at nominal pressure of 85 GPa, vesicles were reported by Langenhorst et al. (2000a,
466 2000b) and Langenhorst and Deutsch (2012). Therefore, we conclude that the carbonates in this
467 study display multiple evidence of shock. These are the first evidence of shock in carbonates from
468 micrometeorites, although impact-induced shock deformation features such as orientation of
469 dehydration cracks and fracture networks were first described in fine-grained micrometeorites by
470 Suttle et al. (2017).

471

472 **4.4 Implications of shock modified carbonates**

473 Carbonates have been extensively used to constrain the time scales of aqueous alteration of
474 meteorite parent bodies (Hutcheon et al. 1999; Petitat et al. 2011; Tyra et al. 2012; Lee et al. 2013).
475 However, they are highly susceptible to shock metamorphism because the bonding between Ca
476 cations and CO₃ groups is rather weak, allowing this structure to cleave and to deform easily
477 (Nicolas and Poirier 1976; Langenhorst 2002). Therefore, shock events could potentially disturb
478 the isotope chronometers measured in these phases. As a consequence, it is important to
479 characterize and understand the shock effect before interpreting the isotopic measurements related
480 to age dating as discussed by Fritz et al. (2017). Notably, this is important to be taken into account
481 since several studies suggest that young carbonate age measured in CM, CR, and CH/CB
482 chondrites could have resulted from discrete impact-related events on their parent bodies (Tyra et
483 al. 2012; Lee et al. 2013; Van Kooten et al. 2016; Jilly-Rehak et al. 2017).

484 Our TEM study shows evidence that carbonates in micrometeorites could have been modified
485 during shock processes after their formation. Therefore, we suggest that it is essential to investigate
486 in detail the structure of carbonates at the TEM scale before interpreting the isotopic measurements
487 related to time of their formation (Fritz et al. 2017). However, further studies are needed to be
488 carried out to fully assess if the wide range of alteration ages observed in chondrites is generated
489 by shock-driven isotopic disturbance (Jilly-Rehak et al. 2017).

490 Additionally, our study indicates that carbonates could possibly be important candidates in the
491 shock-metamorphism classification scheme, especially in hydrated clasts that lack minerals
492 regularly used in the shock classification scheme of meteorites (olivine, pyroxenes, and feldspars,
493 Stoffler et al. 1991; Scott et al. 1992; Rubin et al. 1997).

494

495 **4.5 Other minerals associated with carbonates: Clues to parent body evolution**

496 In this study, the carbonates are associated with a variety of (1) secondary phases (phosphates,
497 magnetite, and phyllosilicates) and (2) features (embayments, pores, and pseudomorphic
498 replacements of primary phases) indicating extensive aqueous alteration processes (Fig. 6; e.g.
499 Brearley 2006). No clear evidence of primary phases that have entirely escaped the alteration
500 event(s) were identified. Even the phosphide, barringerite, which is a high-temperature phase,
501 formed at very low fugacity values rather than the product of aqueous alteration contains
502 embayments indicating dissolution processes in the presence of aqueous fluids. Therefore, a
503 remarkable amount of lines of evidence indicates that water was widely available on the parent
504 body of this micrometeorite. Previous studies discuss the existence of these widespread aqueous
505 alteration processes in chondrites and micrometeorites (Kerridge et al. 1979; Schramm et al. 1989;
506 Rowe et al. 1994; Genge et al. 1997, 2008; Noguchi et al. 2002, 2017; Brearley 2006; Zolensky et
507 al. 2008; Blinova et al. 2014; Doyle et al. 2015; Jilly-Rehak et al. 2018; Dobrică and Brearley
508 2021). Thus, in this section, we focus on the phosphorus-rich phases, since (1) they can provide us
509 further clues relevant to the secondary processes that affected this micrometeorite and (2) they
510 have never been characterized in micrometeorites at such a fine scale.

511 Two different phosphorus-rich phases (phosphates - apatite and phosphides - barringerite) were
512 identified in the H-FgMM analyzed. However, apatite is the dominant phosphorus reservoir.
513 Recently, phosphates have been documented at the surface materials of the asteroid Ryugu by the
514 MicroOmega investigation onboard Hayabusa2 (Bibring et al. 2017). Phosphates have been
515 identified as a minor phase in many chondrites (CM, CV, CO, OC, etc.), though their presence in
516 ordinary chondrites (OCs) have received most of the attention (Ruzicka et al. 2005; Brearley and
517 Chizmadia 2005; Jilly and Huss 2012; Martin et al. 2013; Jones et al. 2014, 2016; Lewis and Jones
518 2016; Ward et al. 2017). Previous studies have shown that phosphates in OCs are secondary
519 minerals that form in response to thermal metamorphism (Jones et al. 2014, 2016; Lewis and Jones
520 2016). Their abundance in all three ordinary chondrite groups shows a small increase with the
521 increase of the petrologic type, particularly between type 4 (0.4 vol.%) and types 5, 6 (0.5 vol.%),
522 when averaged across phosphate abundances of individual H, L, and LL chondrites. The H-FgMM
523 analyzed in this study contains an important amount of phosphates (0.6 vol.%), which is similar to
524 the abundance in equilibrated ordinary chondrites (EOCs) (Lewis and Jones 2016). However, this
525 sample is chemically and texturally unequilibrated and experienced only a low intensity of thermal

526 metamorphism. According to Dobrică et al. (2019), the estimated temperatures (160-280°C)
527 inferred from the precipitation of magnetite and dolomite are similar to those of thermal
528 metamorphism in unequilibrated OCs. Therefore, the amount of phosphate in this micrometeorite
529 is higher compared to the values measured in EOCs, especially, knowing that this sample is not
530 metamorphosed; however, the amount of phosphate is within the limits of phosphates in
531 carbonaceous chondrites (<1 vol.%, Martin et al. 2013; Ward et al. 2017).

532 All phosphates identified in this micrometeorite contain a high amount of intragranular pores
533 (Fig. 6). These intragranular pores were previously observed in both phosphates from LL
534 chondrites and terrestrial analogs (Engvik et al., 2009; Jones et al. 2014). Though, secondary
535 porosity can form on the parent body during or after accretion and can be physical or chemical in
536 nature; the development of porosity in phosphates from chondrites was interpreted to result
537 typically during dissolution-reprecipitation mechanisms throughout multiple episodes of aqueous
538 alteration (Jones et al. 2014). Therefore, we suggest that the pores in the apatite crystals formed
539 during aqueous alteration processes, although their formation during shock metamorphism cannot
540 be excluded. Previous studies suggest that phosphates are among the first phases affected by
541 decomposition and vaporization, because they preferentially lose their volatile species, when
542 affected by shock-induced temperature increase (Krzysińska and Almeida 2019). However,
543 experimentally shocked phosphates do not indicate the formation of pores in phosphates (Adcock
544 et al. 2017; Krzysińska and Almeida 2019), though no detailed TEM studies were performed on
545 these shocked samples.

546 Barringerite, the other phosphorus-rich phase identified in 03-36-46, could provide a significant
547 constraint on the history of this sample. According to previous studies, barringerite is the low-
548 pressure phase of phosphide and allabogdanite is the high-pressure polymorph in the Fe–Ni–P
549 system (Britvin et al. 2019). The presence of barringerite-bearing phosphide in this micrometeorite
550 could indicate that this sample experienced maximum peak pressures of <8 GPa and temperatures
551 of <800°C (Britvin et al. 2019). However, recently, Litasov et al. (2020) have challenged this view
552 showing that both experimental and theoretical studies indicate that allabogdanite is not
553 necessarily associated with high pressure materials. Therefore, further research is needed to
554 understand if these phosphorus-rich accessory minerals can provide us with additional clues
555 related to the temperature and pressure limits experienced by the parent body of micrometeorites.

556

557 **5. Conclusions**

558 We report the first detailed TEM study of carbonates identified in the Antarctic micrometeorite
559 collections. The observations focus on the occurrence of complex chemical zonations and
560 microstructural features that provide us evidence of the carbonate formation and evolution of the
561 parent body of micrometeorites. Based on our electron microscopy study, we show that the
562 composition of fluids responsible for the alteration of this micrometeorite have varied locally
563 during the carbonate's growth, probably from isolated reservoirs of fluid enriched in manganese.
564 This enrichment, apart from cation concentration in the fluid, has important information about the
565 potential redox reactions of the pore fluids, indicating reducing conditions in the fluids that were
566 present on the parent body of this micrometeorite. Furthermore, we suggest that these carbonates
567 form from brines present once much of the water has been consumed by serpentinization. A
568 substantial source of manganese for these carbonates could be the aqueous alteration of Mg-rich
569 silicates, notably LIME minerals previously identified in AMMs.

570 Additionally, we show that carbonates in this micrometeorite record multiple evidence of shock.
571 These results are fundamental because they have implication in the interpretation of the isotopic
572 measurements related to time of their formation. Additionally, we suggest that carbonates should
573 be considered as important candidates in the shock-metamorphism classification scheme,
574 especially in samples that lack minerals regularly used in the shock classification scheme of
575 meteorites. Further studies of carbonates from meteorites that exhibit different shock
576 metamorphosis stages would allow us to constrain the temperature and pressure limits experienced
577 by the parent body of micrometeorites. Additionally, their association of phosphates, yet identified
578 at the surface of the asteroid Ryugu could provide us a record of interactions with parent body
579 fluids. Therefore, they may be useful recorders of the metamorphic environment and hence help
580 to interpret metamorphic conditions on asteroids.

581
582 **Acknowledgments:** The Antarctic Micrometeorite collection at Dome C benefits from the
583 logistical help from IPEV and PNRA. This work was supported by ANR (Project COMETOR 18-
584 CE31-0011), Region Ile de France (DIM-ACAV), PNP, CNES, IN2P3 and Labex P2IO in France.
585 We would also like to thank Dr. John Bradley for many helpful comments and discussions.
586 Electron microscopy was performed in the Advanced Electron Microscopy Center (AEMC) at the
587 University of Hawai'i at Mānoa and the Molecular Foundry. Work at the Molecular Foundry was

588 supported by the Office of Science, Basic Energy Sciences and U.S. Department of Energy. This
589 work was funded by NASA grant NNH16ZDA001N to E. Dobrica (PI).

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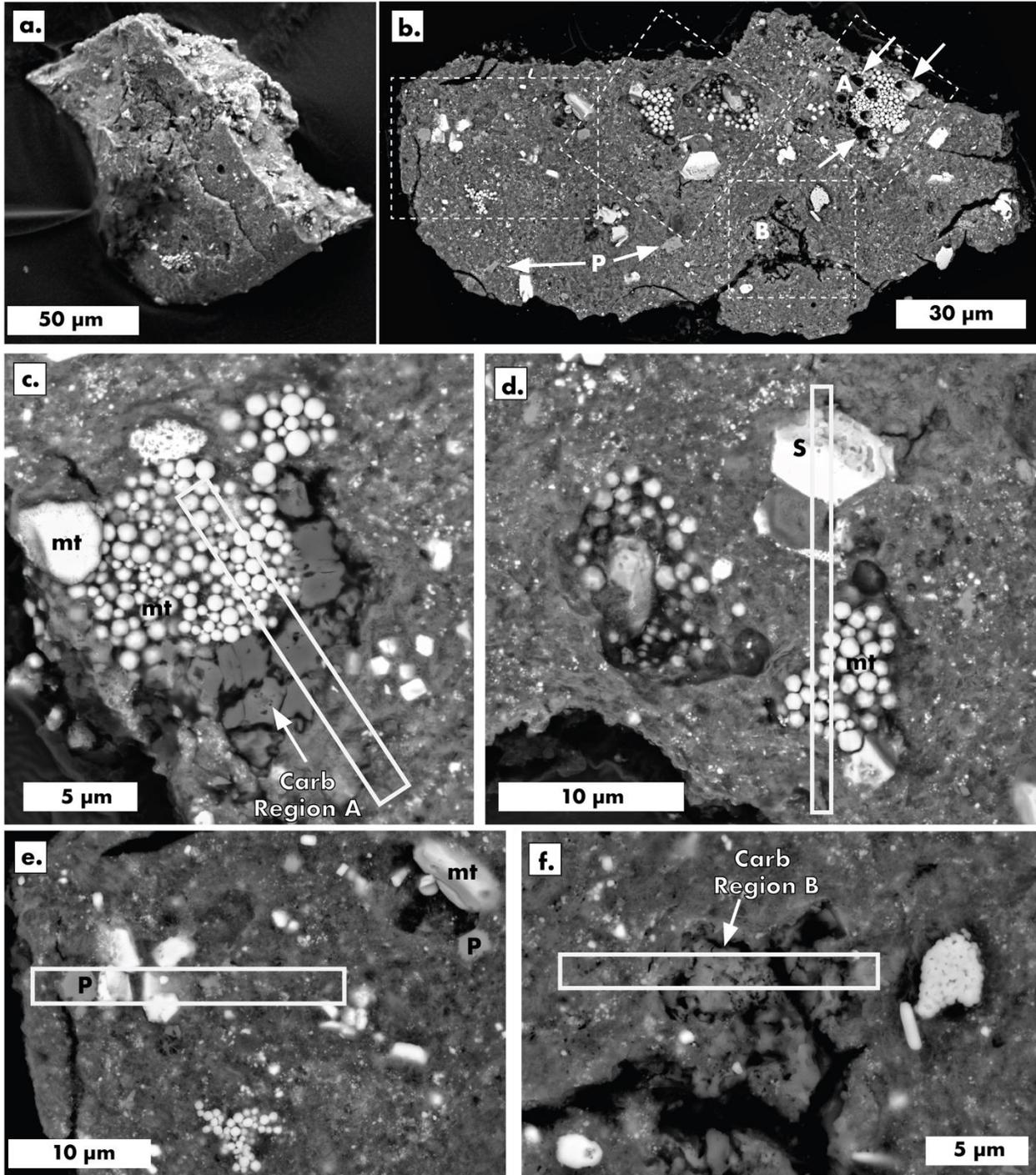
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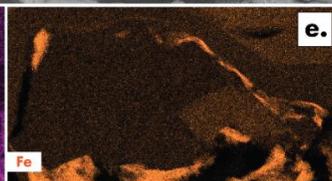
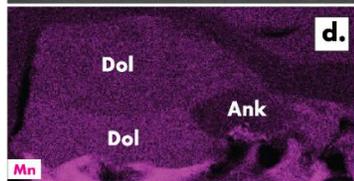
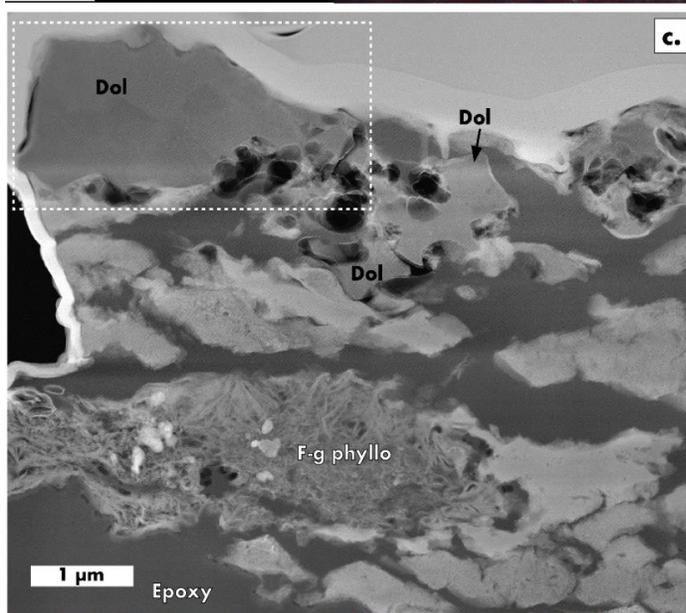
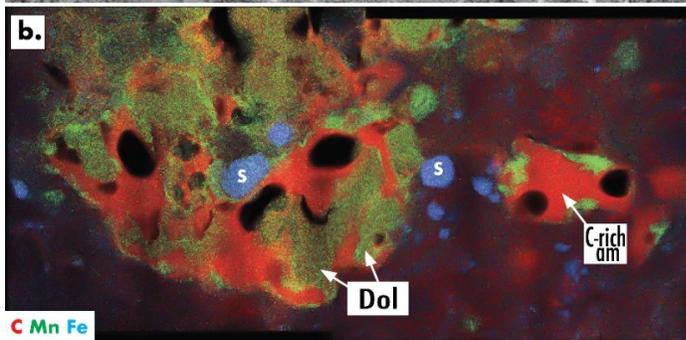
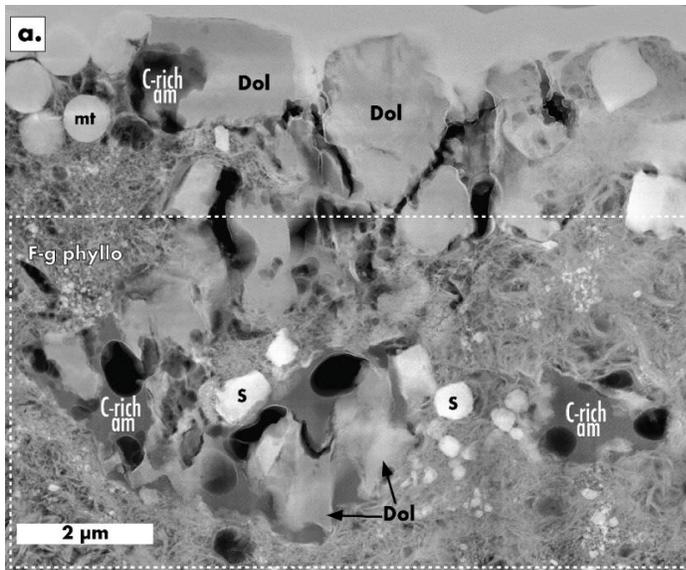
961 **FIGURE CAPTIONS**

962 **Figure 1.** Backscattered electron (BSE) micrographs of the Antarctic micrometeorite (AMM, 03-
963 36-46) analyzed in this study showing the external surface (a) and the polished surface (b) of the
964 entire particle collected from the pristine Concordia snow. The white arrows (b) show the location
965 of the secondary ion mass spectrometer (SIMS) analyses that were carried out in the magnetite-
966 dolomite assemblage (Dobrică et al. 2019). c-f) Detailed BSE images of the regions of interest
967 highlighted by the white dashed line squares (b). Focused ion beam (FIB) sections prepared for
968 transmission electron microscopy (TEM) studies are shown as white solid line rectangles. The
969 carbonates (Carb) are located in two regions (c - region A, FIB section UH-001, and f - region B,
970 FIB section UH-002). Two other FIB sections (d - UH-003; e - UH-006) were prepared in the
971 remaining material. Phases identified in the secondary electron microscope (SEM) images using
972 energy-dispersive X-ray spectroscopy (EDS): carb - carbonates, mt - magnetite, P - phosphate, S
973 - sulfide.

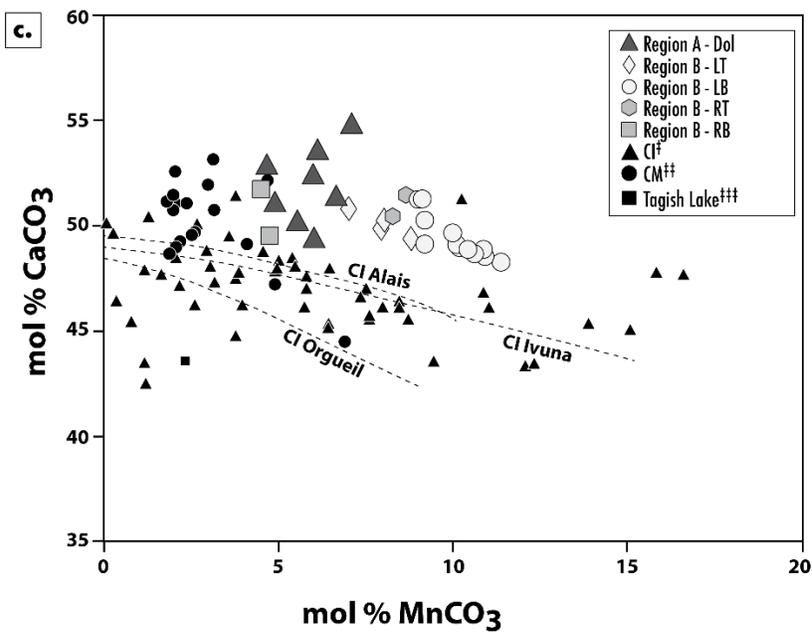
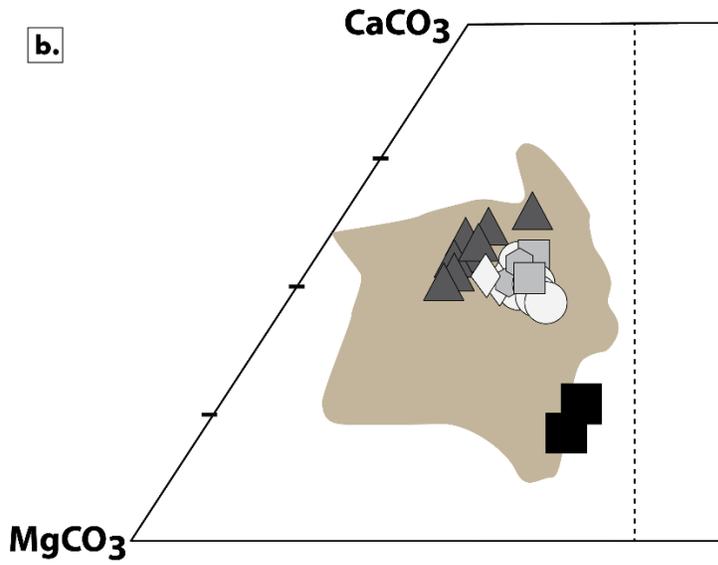
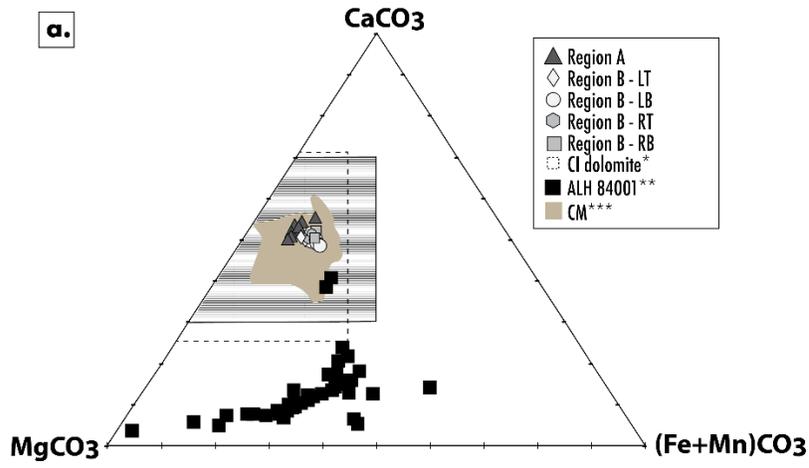


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976 **Figure 2.** Dark-field (a, c) micrographs and energy dispersive X-ray (EDS) maps (b, d-e) made by
977 scanning transmission electron microscopy (STEM) showing the texture and the chemical
978 composition of the carbonates identified in region A (a-b) and region B (c-e). The white rectangle
979 (a) shows the region where the EDS map of C, Mn, and Fe was made. This composite EDS map
980 shows the distribution of carbonates (Dol), C-rich amorphous material (C-rich am), and sulfides
981 (S). Additionally, we show the manganese (d) and iron (e) EDS maps of the carbonate cluster from
982 region B highlighted by the white, rectangle, dashed line shown in (c). Phases identified in the
983 TEM images using energy-dispersive X-ray spectroscopy (EDS): C-rich am - C-rich amorphous
984 material, dol - dolomite, Ank : ankerite, f-g phyllo - fine-grained phyllosilicates, mt - magnetite,
985 and S - sulfide.

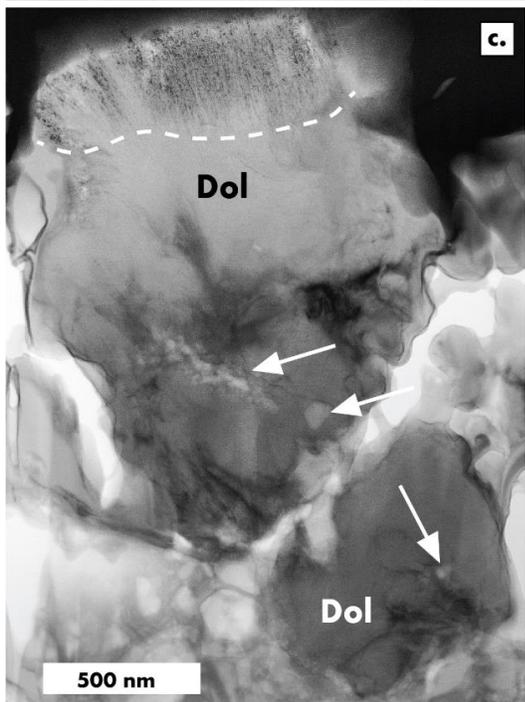
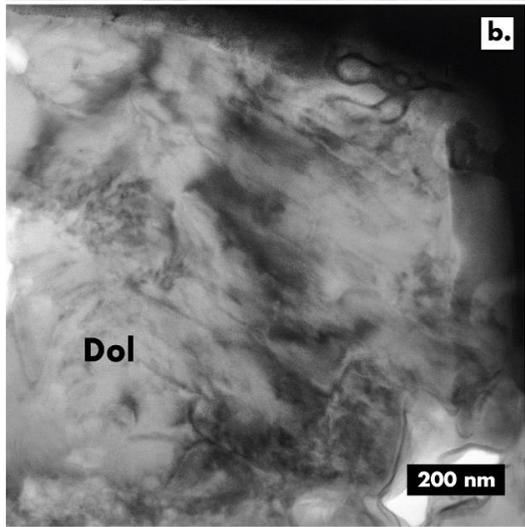
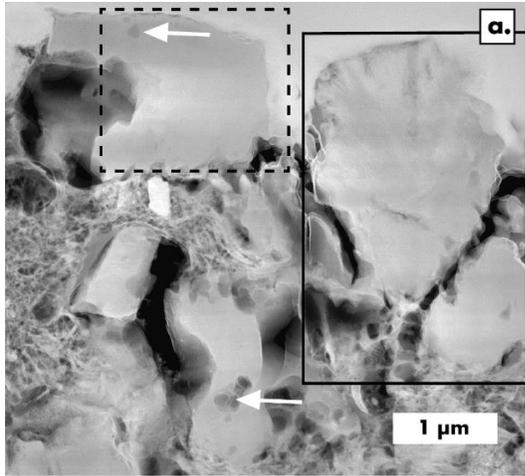


987 **Figure 3.** a-b) Ternary diagram [$\text{MgCO}_3\text{-CaCO}_3\text{-(Fe+Mn)CO}_3$, in mole%] and an enlarged region
988 of the ternary diagram indicated by the shaded area (a) showing the compositions of the carbonates
989 in region A (UH-001, dolomite - grey triangles) and region B (UH-002, dolomite - left crystal, top,
990 LT - white diamond; left crystal, bottom, LB - white circles; right crystal, top, RT - light grey
991 polygon; ankerite - right crystal, bottom, RB - light grey square, see Fig. 5 to locate these regions).
992 For comparison, we plotted the data for ALH 84001 (black squares, Mittlefehldt 1994; Brearley
993 2003), CM chondrites (brown area, Tyra 2013; Zolensky et al. 1997; Lee et al. 2012), and CI
994 chondrites (black dashed line, Petitat et al. 2011). c) MnCO_3 versus CaCO_3 (mol%) of dolomite
995 compositions measured in both regions A and B compared with CI chondrites ([‡], Endreß and
996 Bishoff 1996; Johnson and Prinz 1993), CM chondrites (^{‡‡}, Tyra et al. 2016), and Tagish Lake (^{‡‡‡},
997 C2-ung; Blinova 2013). Plotted are the Ca deficiencies in dolomites from CI chondrites (Alais,
998 Ivuna, and Orgueil from [‡]Endreß and Bishoff 1996) reflecting lower formation temperatures than
999 those described by Goldsmith and Graf (1960) in terrestrial dolomites.

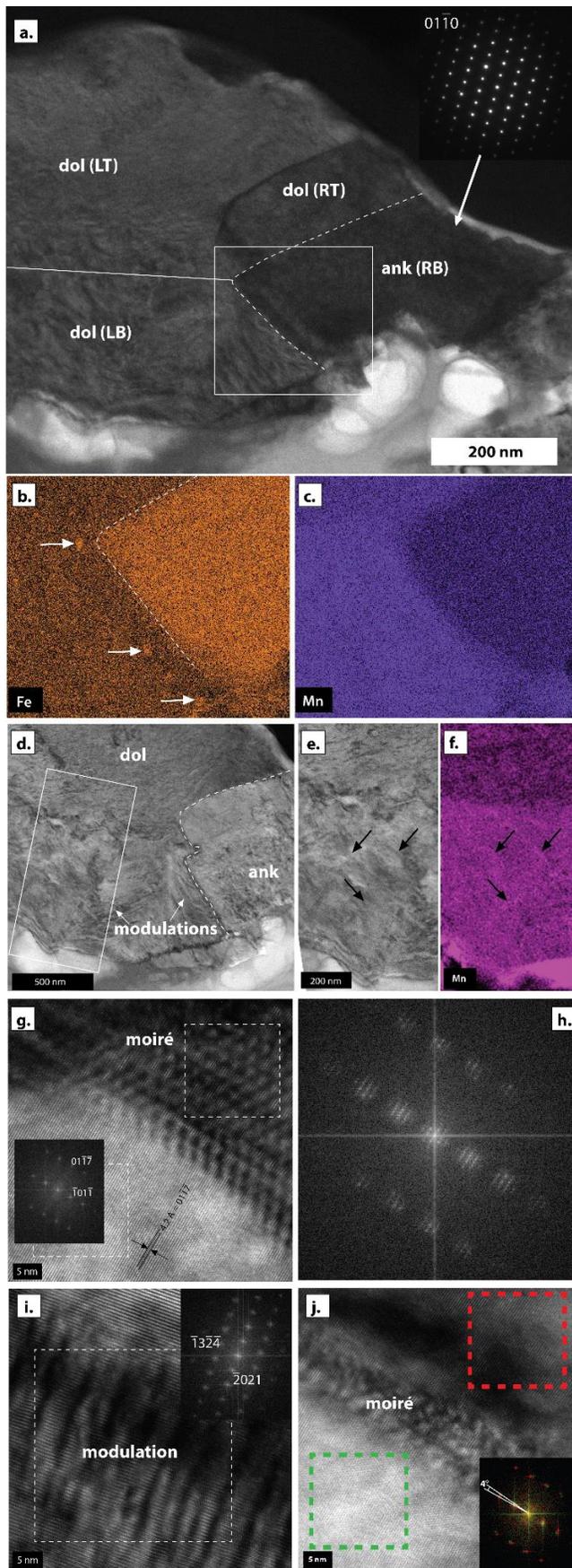


1001

1002 **Figure 4.** Dark- (a) and bright-field (b-c) scanning transmission electron microscopy (STEM)
1003 micrographs showing the texture of the dolomite (dol) crystals identified in region A. c-d) Detailed
1004 bright-field micrographs of the regions of interest highlighted by the black squares (b - dashed
1005 line; c - solid line) showing the presence molulations (b - parallel lamellae alternating dark/light
1006 contrast), pores (c - with arrows), and ion beam damaged top surface (~ 450 nm in thickness,
1007 white dashed line) produced during the NanoSIMS measurements (Ogliore et al. 2019). The pores
1008 have sizes up to ~90 nm in diameter.

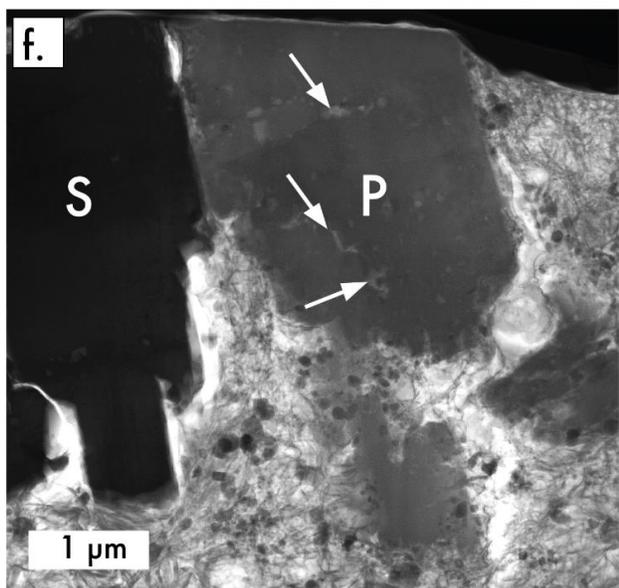
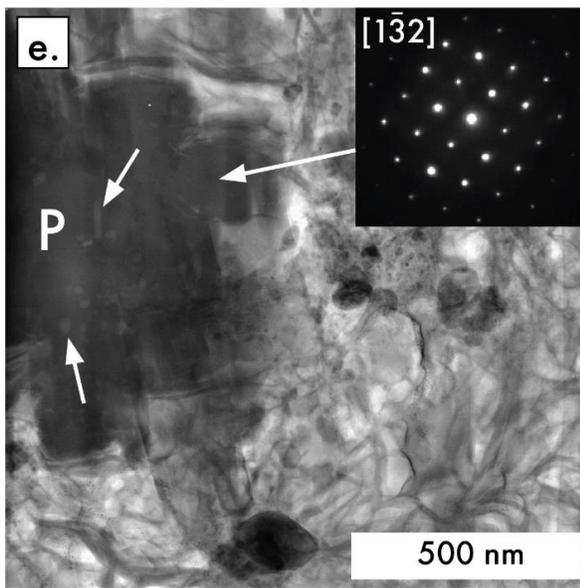
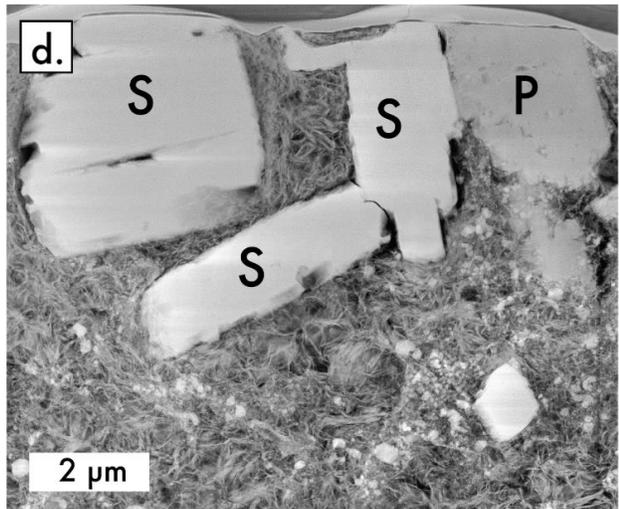
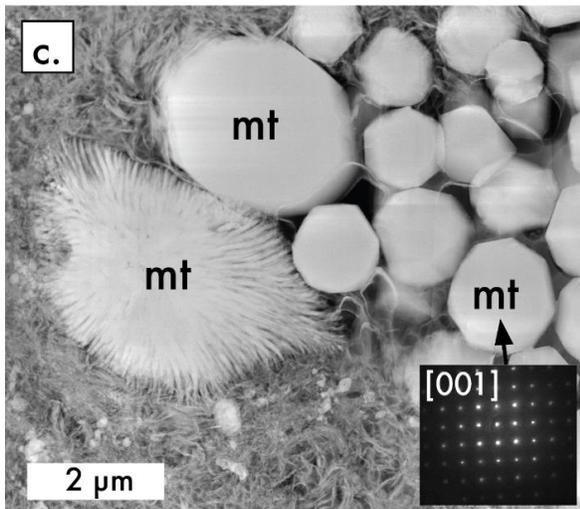
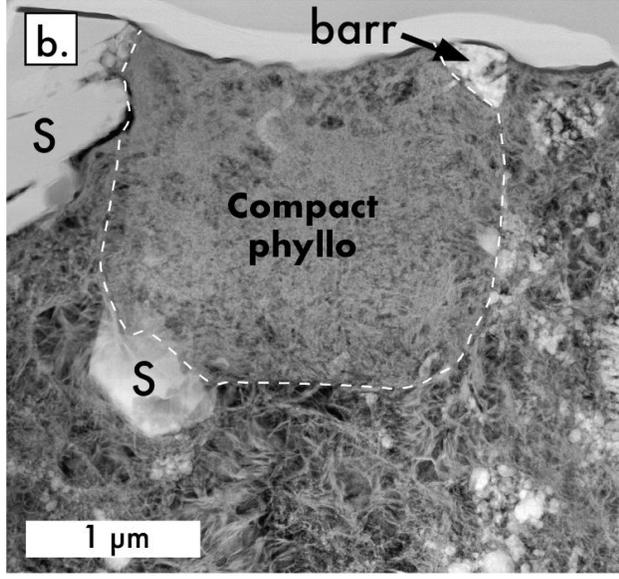
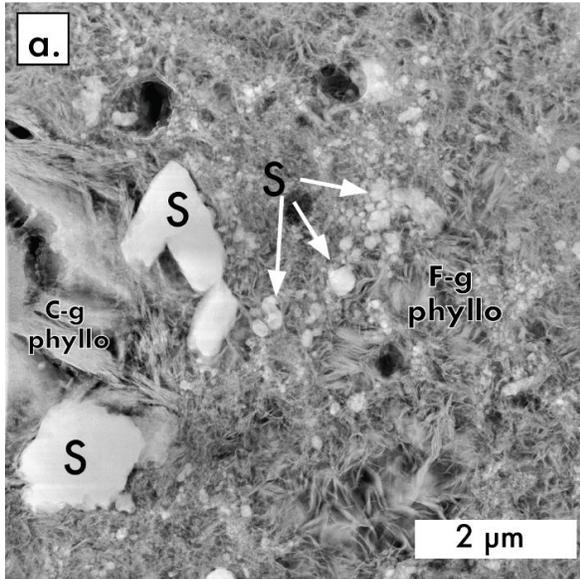


1010 **Figure 5.** Detailed transmission electron microscopy (TEM, a, d, e, g, i, j) micrographs, energy
1011 dispersive (EDS) X-ray maps (b, c, f), and fast Fourier transform (FFT) diffraction pattern (h)
1012 showing the complex microstructure and chemical composition (Fe and Mn) of a cluster of
1013 dolomite (dol, LT - left crystal, top part; LB - left crystal, bottom part; RT - right crystal, top part)
1014 and ankerite (ank, RB - right crystal, bottom part) crystals from the hydrated fine-grained Antarctic
1015 micrometeorite (H-FgMMs, 03-36-46) that was analyzed in this study. Different TEM modes were
1016 used to obtain these micrographs such as bright-field (BF, a) and high-resolution (HR, g, i, j)
1017 TEM mode and nanodiffraction (d-e, convergence angle of 0.1–0.3 mrad) in scanning transmission
1018 electron microscopy (STEM) mode. For diffraction, we used both selected area electron diffraction
1019 (SAED, d) and FFT of HRTEM images (g-j). The carbonate cluster is composed of two zoned
1020 crystals (a) of dolomite and ankerite with different crystallographic orientations. The Fe and Mn
1021 maps of the white box outlined in (a) are shown in (b-c). These EDS maps show the Fe and Mn
1022 zonation of the ankerite (see white dashed line separating the Fe-poor top of the ankerite crystal
1023 from the bottom Fe-rich. Note Fe-rich inclusions in the left dolomite crystals (b - white arrows).
1024 The dolomite crystal is also zoned (d-f). Bright-field (BF) STEM and EDS map (d-f) of manganese
1025 showing the Mn variation in the dolomite. We observe heterogeneity in the distribution of
1026 manganese in the bottom area of the crystal. The heterogeneities (f, black arrows) could correspond
1027 to the modulations shown in (d). These modulations appear as parallel lamellae alternating
1028 dark/light contrast. High-resolution TEM images of (g, i, j) moiré fringes (g, j) at the grain
1029 boundary between ankerite and dolomite and the modulation (i) in the center of the dolomite
1030 crystal. Fast Fourier Transform (FFT) patterns of the HR images are shown (g, h, i, j). The FFTs
1031 show the pattern resulting from the moiré structure (h) and the ankerite crystal close to the interface
1032 (g - bottom), and the modulation structure (i). Note streaking in the $T32\bar{4}$ direction (i), which
1033 generally appear in carbonates showing modulated structures. This moiré FFT pattern (h) exhibits
1034 peaks originating from the two lattices and the moiré peaks. Two FFTs stacks (red - top and green
1035 - bottom) of the ankerite and dolomite identified on each side of the boundary contain the moiré
1036 structure. The two crystals show an orientation mismatch (j) of a relative rotation angle of $\sim 4^\circ$
1037 between lattice fringes.



1039

1040 **Figure 6.** Detailed dark-field (a-d) and bright-field (e-f) scanning transmission electron
1041 microscopy (DF- and BF-STEM) micrographs showing the minerals associated with carbonates in
1042 the analyzed hydrated fine-grained Antarctic micrometeorite (03-36-46). Several minerals were
1043 identified such as coarse- and fine-grained phyllosilicates (a-f), magnetite (c), sulfide (a-b, d, f),
1044 barringerite (b), and Ca-phosphate (e-f). Additionally, a S-rich (7 wt% SO₃) region of compact
1045 phyllosilicates (b, white dashed line) was identified in contact with micrometer-sized, Ni-poor
1046 sulfides. Most of these micrometer-sized sulfides show irregular edges with embayments (b, d) up
1047 to ~340 μm long. Furthermore, nanometer-sized, Ni-poor sulfides (a, white arrows) are found
1048 embedded in the fine-grained phyllosilicate matrix. Magnetite with two different morphologies
1049 (framboidal and radial) are shown in (c). Detailed BF-STEM images showing the presence of Ca-
1050 phosphates (e-f) containing irregular pores (white arrows). Two selected area electron diffraction
1051 (SAED) patterns were indexed as [001] (c) and [132] (e) zone axis of magnetite and apatite,
1052 respectively. Phases identified in the STEM micrographs using energy-dispersive X-ray
1053 spectroscopy (EDS) and SAED: barr - barringerite, C-g phyllo - coarse-grained phyllosilicates, f-
1054 g phyllo - fine-grained phyllosilicates, mt - magnetite, P - Ca-phosphate (apatite), S - sulfide.



1056 **Table 1.** Major and minor element compositions (in atom % and wt% oxide) determined by energy-dispersive X-ray spectroscopy of
 1057 carbonates from region A and B, Ca-phosphate and coarse-grained and fine-grained phyllosilicates. The location of the carbonates is
 1058 indicated in Figure 5 (LT - left crystal, top; LB - left crystal, bottom; RT - right crystal, top; RB - right crystal, bottom).

| | Carbonates | | | | | | | | | | Ca-phosphates | | Phyllosilicates | | | | | | |
|--------------------------------|-------------------|------|-------------------|------|------|------|------|------|------|------|---------------|--------|-----------------|------|------------|------|------------|----------------|------------|
| | Region A (UH-001) | | Region B (UH-002) | | | | | | | | UH-001 | UH-003 | UH-001 F-g | | UH-003 C-g | | UH-003 F-g | UH-006 compact | UH-006 F-g |
| | | | LT | | LB | | RT | | RB | | | | | | | | | | |
| N | 8 | S.D. | 4 | S.D. | 11 | S.D. | 2 | S.D. | 2 | S.D. | 1 | 1 | 6 | S.D. | 2 | S.D. | 1 | 1 | 1 |
| wt% | | | | | | | | | | | | | | | | | | | |
| SiO ₂ | | | | | | | | | | | | | 53.6 | 3.3 | 39.9 | 1.0 | 52.2 | 43.6 | 50.2 |
| Al ₂ O ₃ | | | | | | | | | | | | | 2.2 | 2.5 | 3.7 | 0.0 | 4.6 | 5.5 | 5.9 |
| Cr ₂ O ₃ | | | | | | | | | | | | | 0.9 | 0.6 | 2.7 | 0.0 | 0.0 | 2.2 | 0.5 |
| FeO | 2.6 | 0.4 | 2.8 | 0.2 | 2.8 | 0.2 | 2.6 | 0.0 | 5.8 | 0.3 | 3.7 | 1.2 | 15.6 | 4.0 | 26.5 | 0.4 | 16.0 | 20.9 | 12.0 |
| MnO | 4.1 | 0.7 | 5.6 | 0.5 | 7.0 | 0.6 | 5.7 | 0.3 | 3.0 | 0.2 | | | 1.2 | 1.5 | 0.4 | 0.1 | 0.6 | 1.0 | 0.6 |
| MgO | 15.2 | 1.1 | 15.1 | 0.5 | 14.2 | 0.4 | 14.0 | 0.1 | 13.2 | 0.6 | | | 25.7 | 3.7 | 21.4 | 0.6 | 25.1 | 18.0 | 27.8 |
| CaO | 28.6 | 2.2 | 27.5 | 0.7 | 26.5 | 0.9 | 27.0 | 0.7 | 25.8 | 0.3 | 50.6 | 55.3 | 0.6 | 0.6 | 0.2 | 0.3 | 1.6 | 1.7 | 1.1 |
| SO ₃ | | | | | | | | | | | | | 0.0 | 0.0 | 5.3 | 0.4 | 0.0 | 7.0 | 1.8 |
| P ₂ O ₅ | | | | | | | | | | | 45.6 | 43.5 | | | | | | | |
| CO ₂ | 49.5 | 3.4 | 49.1 | 1.1 | 49.6 | 1.5 | 50.7 | 0.8 | 52.3 | 0.8 | | | | | | | | | |

| | | | | | | | | | | | | | | | | | | | |
|----------------------------|------|-----|------|-----|------|-----|------|-----|------|-----|------|------|------|-----|------|-----|------|------|------|
| Total | | | | | | | | | | | 100 | 100 | 100 | | 100 | | 100 | 100 | 100 |
| Mg/Fe | 10.5 | | 9.8 | | 9.2 | | 9.7 | | 4.0 | | | | | | | | | | |
| at% | | | | | | | | | | | | | | | | | | | |
| Si | | | | | | | | | | | | | 15.1 | 0.9 | 11.6 | 0.3 | 14.9 | 12.7 | 14.2 |
| Al | | | | | | | | | | | | | 0.8 | 0.8 | 1.3 | 0.0 | 1.5 | 1.9 | 2.0 |
| Cr | | | | | | | | | | | | | 0.2 | 0.1 | 0.6 | 0.0 | 0.0 | 0.5 | 0.1 |
| Fe | 0.7 | 0.1 | 0.7 | 0.0 | 0.7 | 0.0 | 0.7 | 0.0 | 1.5 | 0.1 | 1.6 | 0.6 | 3.7 | 0.9 | 6.4 | 0.1 | 3.8 | 5.1 | 2.9 |
| Mn | 1.1 | 0.2 | 1.5 | 0.1 | 1.9 | 0.2 | 1.5 | 0.1 | 0.8 | 0.0 | | | 0.3 | 0.4 | 0.1 | 0.0 | 0.1 | 0.2 | 0.1 |
| Mg | 7.1 | 0.6 | 7.0 | 0.3 | 6.6 | 0.2 | 6.5 | 0.0 | 6.1 | 0.3 | | | 10.8 | 1.6 | 9.2 | 0.2 | 10.7 | 7.8 | 11.8 |
| Ca | 9.6 | 0.9 | 9.2 | 0.3 | 8.9 | 0.3 | 9.0 | 0.3 | 8.5 | 0.1 | 28.3 | 34.3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.5 | 0.5 | 0.3 |
| S | | | | | | | | | | | | | 0.3 | 0.5 | 1.2 | 0.1 | 0.0 | 1.5 | 0.4 |
| P | | | | | | | | | | | 20.1 | 21.3 | | | | | | | |
| O | 60.5 | | 60.5 | 0.2 | 60.6 | 0.2 | 60.8 | 0.1 | 61.0 | 0.1 | 50.0 | 43.8 | 68.7 | 0.6 | 69.6 | 0.0 | 68.5 | 69.8 | 68.2 |
| C | 21.0 | 1.0 | 21.0 | 0.4 | 21.3 | 0.4 | 21.5 | 0.2 | 22.1 | 0.3 | | | | | | | | | |
| Structural formulae | | | | | | | | | | | | | | | | | | | |
| Si | | | | | | | | | | | | | 2.0 | 0.1 | 1.5 | 0.0 | 2.0 | 1.6 | 1.9 |
| Al | | | | | | | | | | | | | 0.1 | 0.1 | 0.2 | 0.0 | 0.2 | 0.2 | 0.3 |
| Cr | | | | | | | | | | | | | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 |
| Fe | 0.1 | | 0.1 | | 0.1 | | 0.1 | | 0.1 | | 0.5 | 0.2 | 0.5 | 0.1 | 0.8 | 0.0 | 0.5 | 0.7 | 0.4 |
| Mn | 0.1 | | 0.1 | | 0.2 | | 0.1 | | 0.1 | | | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Mg | 0.7 | | 0.7 | | 0.7 | | 0.6 | | 0.6 | | | | 1.4 | 0.2 | 1.2 | 0.0 | 1.4 | 1.0 | 1.6 |
| Ca | 0.9 | | 0.9 | | 0.9 | | 0.9 | | 0.8 | | 9.2 | 9.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.0 |
| S | | | | | | | | | | | | | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.2 | 0.1 |

| | | | | | | | | | | | | | | | | | | | |
|----------|-----|--|-----|--|-----|--|-----|--|-----|--|-----|-----|--|--|--|--|--|--|--|
| P | | | | | | | | | | | 6.5 | 6.1 | | | | | | | |
| C | 2.1 | | 2.1 | | 2.1 | | 2.1 | | 2.2 | | | | | | | | | | |

1059

*Number of ions on the basis of 9 O for phyllosilicates, 26 for phosphates, 6 for carbonates.

1060

S.D. - standard deviation.