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1 DETECTION OF INCIPIENT AQUEOUS ALTERATION IN  
2 CARBONACEOUS CHONDRITES

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23  
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25           **ABSTRACT**

26           We discuss if the detection of aqueous alteration depends on the techniques that are used.  
27           We apply different methods to estimate the extent of aqueous alteration on four ungrouped  
28           carbonaceous chondrites showing limited aqueous alteration and thermal metamorphism:  
29           Chwichiya 002, El Médano (EM) 200, Northwest Africa (NWA) 12957 and NWA 11750,  
30           classified as C3 or C3.00-ung. The aim is to propose a reliable methodology to identify the most  
31           primitive chondrites. Chwichiya 002, NWA 11750 and NWA 12957 display very primitive  
32           matrices and could be amongst the most primitive chondrites currently known, similar to the least  
33           altered lithologies of the CM chondrites Paris (CM2.9) and Asuka (A) 12085 (CM2.8), A 12236  
34           (CM2.9) and A 12169 (CM3.0). The structure of organic matter and Cr<sub>2</sub>O<sub>3</sub> in ferroan olivines  
35           show that the four meteorites have been less heated than the least metamorphosed  
36           standard/reference type 3 chondrite, Semarkona (LL3.00), with Chwichiya 002, NWA 12957 and  
37           NWA 11750 similar to the CO3.0s, Acfer 094 (C2-ung) and Paris meteorites. Chwichiya 002 and  
38           NWA 12957 show similar alteration phases and degree of alteration, with high abundances of  
39           amorphous material with embedded metal and sulfide, resembling Glass with Embedded Metal  
40           and Sulfide (GEMS)-like materials, and tochilinite-cronstedtite intergrowths (TCIs) as the major  
41           alteration phases. The matrix in NWA 11750 contains aggregates of nanoscale olivine crystals  
42           and abundant carbonates, observed as micrometer-sized carbonate veins surrounding chondrules,  
43           and as nanoscale carbonates mixed with the fine-grained materials. It also contains abundant  
44           grains of metal and a low abundance of phyllosilicates. El Medano 200 shows a high abundance  
45           of magnetite (~ 10 vol%), nanoscale phyllosilicates, troilite, and organic matter. The variability  
46           of the secondary alteration phases in the meteorites suggests different alteration mechanisms,  
47           likely depending on both the starting composition of the meteorites and the composition of the  
48           fluids of alteration.

49 Scanning and transmission electron microscopy (SEM and TEM) allow the identification  
50 of primitive phases, the composition and spatial distribution of the secondary phases. X-ray  
51 diffraction (XRD) can detect alteration products, including some amorphous phases, although  
52 this is limited by the small coherence domains of small TCIs and other phyllosilicates.  
53 Transmission infrared (IR) spectroscopy can detect phyllosilicate and carbonate, but is ineffective  
54 for the detection of amorphous phases, metal, or sulfide. Both matrix defocused electron  
55 microprobe analyses (EMPA) and thermogravimetric analysis (TGA) allow detection of hydrated  
56 minerals, such as phyllosilicates and carbonates, but are strongly influenced by the presence of  
57 organic matter and do not reflect the overall alteration state of a meteorite. We conclude that the  
58 assessment of the primitivity of a chondrite is highly technique dependent. We propose a  
59 combination of XRD and the  $\text{Cr}_2\text{O}_3$  in ferroan olivines or Raman spectroscopy for a rapid  
60 characterization of the alteration state of a chondrite, and the detection of the most primitive  
61 meteorites. Finally, the combination of XRD and TEM allows for the detection of all primary and  
62 secondary phases and represents an ideal methodology for the characterization and detailed study  
63 of primitive chondrites and the different types of incipient aqueous alteration.

## 64 **1 Introduction**

65 The knowledge of the spatial distribution and composition of small Solar System bodies  
66 provides insight into the formation and dynamical evolution of the Solar System. Chondrites  
67 represent an invaluable source of samples from these bodies, allowing us to assess the detailed  
68 composition of the materials that accreted in the early Solar System. However, most chondrites  
69 underwent secondary processes: aqueous alteration, and thermal and shock metamorphism, which  
70 modified their primary mineralogy, textures, and isotopic compositions (e.g., Brearley, 2006;  
71 Huss et al., 2006). Even though they blur the information about the building blocks of the Solar

72 System, these secondary features give precious information about the geologic activity of the  
73 chondrites' parent bodies.

74 Although chondrites are nearly all affected by secondary processes (e.g., Barber, 1981;  
75 Zolensky and McSween, 1988; Stöffler et al., 1988; Scott et al., 1992; Buseck and Hua, 1993;  
76 Brearley, 2006; Marrocchi et al., 2021), the search for the least processed samples has been a  
77 long-standing one in meteoritics, as such material would provide access to the physico-chemical  
78 conditions in the solar nebula. From this perspective, it is necessary to constrain secondary  
79 processes based on robust qualitative and quantitative parameters. Thermal metamorphism leads  
80 to known modifications in some carbonaceous chondrites, such as partial or complete  
81 dehydration of hydrous minerals (Nakamura, 2005), changes in composition and/or texture of Fe-  
82 Ni metal and sulfide phases (Kimura et al., 2008, 2011), and changes of the structure of organic  
83 matter (Bonal et al., 2016, 2020). Those modifications can be evidenced by using numerous  
84 proxies, such as petrographic characteristics (e.g., Rubin et al., 2007), chemical and isotopic  
85 compositions, as well as infrared (IR) and Raman signatures (Tonui et al., 2014; Bonal et al.,  
86 2016; Hanna et al., 2020). The latter indicates a temperature range of thermal metamorphism in  
87 some carbonaceous chondrites from  $< 250^{\circ}\text{C}$  to  $> 750^{\circ}\text{C}$  (Nakamura, 2005; Tonui et al., 2014).  
88 The source and timing of thermal metamorphism through decay of the short-lived radionuclide  
89  $^{26}\text{Al}$  and/or impact is hard to identify in carbonaceous chondrites (McSween et al., 1988; Grimm  
90 and Mcsween, 1989; Rubin, 2015; Huss et al., 2006; Tonui et al., 2014; Vacher et al., 2018).  
91 Besides long term thermal metamorphism through  $^{26}\text{Al}$  decay, some carbonaceous chondrites  
92 show evidence of shock metamorphism, which can be observed in deformation and/or  
93 transformation of minerals inside chondrites and creates localized melting, metal-troilite  
94 mixtures, and changes of abundances of rare gases and volatile trace elements (Bischoff and  
95 Stöffler, 1992).

96           In addition to thermal and shock metamorphism, assessing the extent and nature of  
97 aqueous alteration in carbonaceous chondrites is necessary to understand the secondary processes  
98 in primitive asteroids. Aqueous alteration of chondrites may have taken place before final  
99 accretion (Barshay and Lewis, 1976; Grossman and Larimer, 1974; Lewis, 1972; Prinn and  
100 Fegley, 1989; Metzler et al., 1992, Bischoff 1998; Ciesla et al., 2003; Toppani et al., 2005) on  
101 temporary protoplanetary bodies, subsequently broken by collisions, scattering the altered  
102 materials into the nebula and mixing them with unaltered, anhydrous materials; or after accretion  
103 on a parent body formed by unaltered nebular materials (Brown et al., 2000; Browning et al.,  
104 1996; Bunch and Chang, 1980; Hanowski and Brearley, 2000, 2001; McSween, 1979a; Tomeoka  
105 and Buseck, 1985; Trigo-Rodriguez et al., 2006; Zolensky et al., 1993). The temperature at which  
106 aqueous alteration took place is still debated and could range from -10°C to 250°C (Baker et al.,  
107 2002; Benedix et al., 2003; Clayton and Mayeda, 1984; Guo and Eiler, 2007; Verdier-Paoletti et  
108 et al., 2017; Vacher et al., 2019a; Zolensky et al., 1993). Moreover, different mechanisms, such  
109 as direct precipitation (Morse et al., 1997) or interface dissolution-precipitation (Morse et al.,  
110 1997, 2007; Putnis and Putnis, 2007; Ruiz-Agudo et al., 2014) could be at the origin of aqueous  
111 alteration products. These reactions can produce a variety of secondary products (Krot et al.,  
112 2021): carbonates (Horita, 2014; Morse et al., 1997, 2007), phyllosilicates, tochilinite-  
113 cronstedtite-intergrowths (TCIs), sulfides (and sulfates), magnetite (Pignatelli et al., 2016; Rubin  
114 et al., 2007), fayalite (Doyle et al., 2015) and kirschsteinite (MacPherson et al., 2017).

115           In addition, deciphering the composition of the fluids responsible for the aqueous  
116 alteration is not straight-forward. Indeed, temperature, oxygen fugacity ( $fO_2$ ), pH, water/rock  
117 ratio, as well as the chemical composition of the primary phases, can have an impact on the  
118 kinetics of the reactions and the secondary products. For example, formation of tochilinite in CM  
119 chondrites requires alkaline conditions, low  $fO_2$  and low temperature (Zolensky and McSween,  
120 1988; Vacher et al., 2019b). Indeed, localized variations in geochemical conditions, particularly

121 in pH, are present in CM chondrites, called “microchemical environments” (Brearley, 2006), as  
122 for example, the alteration fluids in the fine-grained rims and matrix of CM chondrites are  
123 thought to be more alkaline than those in the interior of chondrules (e.g., Chizmadia and  
124 Brearley, 2008, Brearley, 2006). Most CM chondrites are also considered to be complex breccias,  
125 comprising multiple lithologies that preserve differing hydration conditions (e.g., Lentfort et al.,  
126 2020), making classification of their alteration state challenging.

127         Efforts to quantify the degree of secondary processing in chondrites have resulted in the  
128 definition of a scale, called petrologic type. In 1967, Van Schmus and Wood proposed a  
129 secondary classification of chondrites based on mineral chemistry (olivine and pyroxene  
130 homogeneity, water and carbon content, Ni in sulfides), petrography (low-Ca pyroxenes  
131 crystallinity, feldspar modal abundance) as well as matrix and chondrule textures. This  
132 classification splits chondrites into 6 petrographic groups, scaling from 1 to 6, with type 3  
133 indicating the most primitive chondrites, based on their aqueous alteration and thermal  
134 metamorphism. This scale is independent of shock metamorphism, which is classified with its  
135 own scale (Stöffler et al., 1988, Scott et al., 1992). Types from 3 to 1 present increasing degrees  
136 of aqueous alteration. Types from >3 to 6 show increasing degree of thermal metamorphism. This  
137 single digit scale is the accepted classification framework for petrologic types used to date, as  
138 attribution of a type for meteorites requires necessary simplification. Nonetheless, this  
139 classification has the disadvantage of separating thermal metamorphism and aqueous alteration,  
140 whereas numerous studies prove they can both occur within a single chondrite (Buseck and Hua,  
141 1993; Kerridge and Bunch, 1979; Krot et al., 1998; Tomeoka and Buseck, 1985; Zolensky and  
142 McSween, 1988; Zolensky et al., 1997; Nakamura, 2005; Tonui et al., 2014). Other  
143 classifications based on various characteristics, such as petrography, textures and chemistry  
144 (Browning et al., 1996; Rubin et al., 2007), bulk element composition (H, C and N) (Alexander et

145 al., 2013), and/or phyllosilicate content (Howard et al., 2015) can also be used to classify  
146 chondrites, but are usually not established for all chondrite groups.

147 Subtypes of the type 3 chondrites have been defined by Sears et al. (1980) using  
148 thermoluminescence parameters. These subtypes can also be separated using the Cr<sub>2</sub>O<sub>3</sub> content of  
149 ferroan olivine (Grossman and Brearley, 2005), or Raman spectral properties of the fine-grained  
150 matrix (Bonal et al., 2006, 2016). Subtypes between 2 and 3 have also been established for CM  
151 chondrites based on petrologic criteria (Rubin et al., 2007; Rubin, 2015; Kimura et al., 2020).  
152 Meteorites with subtype 3.0 to  $\geq 3.7$  show evidence of both metamorphism and aqueous alteration  
153 (Sears and Dodd, 1988; Sears et al., 1995; Bonal et al., 2020). One ambiguity of the current  
154 classification is that chondrites considered to be the most primitive are found between types 2.9  
155 and 3.00 (Hewins et al., 2014; Kimura et al., 2020). Also, detecting aqueous alteration is the  
156 intrinsic properties of the meteorites (e.g., porosity, permeability) and may thus be found only in  
157 specific parts of a meteorite (Bland et al., 2009). In addition, the nature and composition of the  
158 fluid can vary (e.g., water, calcium rich fluids, partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) abundance,  
159 supercritical fluids), and thus induce a variety of alteration products, making the use of a trans-  
160 group aqueous alteration scale difficult. As it depends on the variety of effects of thermal  
161 metamorphism and/or aqueous alteration, identifying the most primitive chondrites turns out to  
162 be a challenge. In addition, many previously classified chondrites have not been studied in detail  
163 according to the most recent classification criteria, implying the existence of potential mis-  
164 classified meteorites (e.g., Marrocchi et al., 2020). The study of aqueous alteration in meteorites  
165 is also of interest in relation to the Hayabusa2 and Origins, Spectral Interpretation, Resource  
166 Identification, and Security-Regolith Explorer (OSIRIS-REx) spacecraft to asteroids (162173)  
167 Ryugu and (101955) Bennu, respectively. Both missions showed that surface materials from  
168 those asteroids were hydrated (Hamilton et al., 2019; Kitazato et al., 2019; Lauretta et al., 2019;  
169 Pilorget et al., 2021).



170 Beyond the limitations of classification scales, the definition of aqueous alteration in  
171 chondrites remains vague. There are no widely accepted unique criteria to estimate if a chondrite  
172 has suffered aqueous alteration or not. In this paper, we review different methods used to estimate  
173 the extent of aqueous alteration in chondrites and apply them to the study of four ungrouped  
174 carbonaceous chondrites showing very little aqueous alteration and thermal metamorphism:  
175 Chwichiya 002, El Medano (EM) 200, Northwest Africa (NWA) 12957 and NWA 11750. We  
176 discuss whether the detection of aqueous alteration in these chondrites depends on the technique  
177 used or the investigation scale. We then propose the most reliable methodology to identify  
178 chondrites with no trace of metamorphism and low degree of aqueous alteration. We also  
179 compare the chondrites of this study to the chondrites long considered as the least aqueously  
180 altered and metamorphosed and show that three of the four chondrites in this study could be part  
181 of the most primitive material in the current meteorite collection.

## 182 **2 Methodology**

### 183 **2.1 Samples**

184 In order to investigate the ambiguity of the subtype 3.0-2.9-2.8, we chose to study four  
185 ungrouped carbonaceous chondrites whose official classification indicates no effects of  
186 metamorphism nor aqueous alteration; El Medano 200 (C3), Chwichiya 002, NWA 11750 and  
187 NWA 12957 (all C3.00-ung) (Ruzicka et al., 2015; Gattacceca et al., 2020; 2021).

### 188 **2.2 Petrography**

189 Optical maps of the four meteorites were made with a Leica DM2500P petrographic  
190 microscope, using reflected light on thick polished sections. Backscattered Electron (BSE) images  
191 were taken with a scanning electron microscope (SEM) for all meteorites with a Hitachi S3000-N at  
192 the Centre Européen de Recherche et d'Enseignement en Géoscience de l'Environnement  
193 (CEREGE). Higher-resolution SEM images and element maps were made with a Field Emission Gun

194 (FEG) microscope Jeol JSM 7900F equipped with an EDS (Energy-dispersive X-ray spectroscopy)  
195 XFlash 6/60 detector at Centre Interdisciplinaire de Nanoscience de Marseille (CINaM) laboratory.  
196 Elemental maps were done using a probe current of 10 nA, an acceleration voltage of 5 kV and 20  
197 min counting time.

198 Focused Ion Beam (FIB) sections were extracted from Chwichiya 002 at IEMN,  
199 University of Lille, using a dual-beam Thermo-Fisher Strata DB235 workstation; and NWA  
200 11750 and EM 200 FIB sections were extracted at CP2M (Centre Pluridisciplinaire de  
201 Microscopie Électronique et de Microanalyse) Marseille using a dual-beam FIB (FEI Helios 600  
202 Nano Lab), with a Gallium ( $\text{Ga}^+$ ) ion beam, starting with 30 keV current. To limit the damage  
203 and amorphization of the slide faces under the ion beam, the current is reduced to 5 keV for  
204 thinning and then 1 keV for final cleaning. TEM observations of the FIB sections were made on a  
205 Thermo-Fisher Titan Themis S/TEM at the microscopy platform of the University of Lille for  
206 HAADF imaging and EDS mapping. Elemental maps were obtained using a four-quadrant,  
207 windowless, super-X SDD EDS detector with a probe current of 300 pA, an accelerating voltage  
208 of 300 keV, and a counting time of ~20 min. The uncertainties are of the order of 3% for major  
209 elements in silicates (O, Si, Mg and Fe-, and ~20% for the minor elements (Al, Ca, Mn, Cr).  
210 High-resolution TEM (HR-TEM), and selected area electron diffraction (SAED) patterns were  
211 made on a TEM Jeol JEM-2010 at CINaM laboratory.

### 212 **2.3 Modal abundances**

213 The modal abundances of chondrite components (chondrules, matrix, opaques) were evaluated  
214 by point counting on optical maps, with 95% confidence interval around the modal abundance  
215 computed after Howarth 1998. Chondrule sizes were measured by contouring chondrules' outlines on  
216 optical maps, followed by image analysis, using the *ImageJ* software. Modal abundances of minor  
217 and alteration phases were measured on both FEG-SEM and STEM-EDS composite elemental maps,  
218 using pixel counting with the *ImageJ* software.

## 219        **2.4 Mineral major and minor elements**

220            Electron defocused beam (10  $\mu\text{m}$ ) microprobe analyses of the matrix were done using an  
221 electron microprobe (EMP) Cameca SX100 at UPMC CAMPARIS facility. The operating conditions  
222 were 15 kV accelerating voltage with a current of 10 nA and a counting time of 30 s. Both natural and  
223 synthetic standards were used for calibration: albite for Na; anorthite for Al; apatite for P; diopside  
224 for Mg, Si, Ca; orthoclase for K; pyrite for S;  $\text{MnTiO}_3$  for Mn and Ti;  $\text{Cr}_2\text{O}_3$  for Cr;  $\text{Fe}_2\text{O}_3$  for Fe; and  
225 NiO for Ni. The detection limits are (in ppm): 445 for Na, 466 for Al, 714 for Mg, 669 for Si, 605 for  
226 Ca, 602 for K, 392 for S, 1044 for Mn, 419 for Ti, 496 for Cr, 1271 for Fe, and 1331 for Ni.  
227 Defocused EMP analytical totals in the matrix are reduced by the presence of elements such as H and  
228 C, from hydrated minerals such as phyllosilicates (interlayered  $\text{H}_2\text{O}$  and -OH groups), or hydration in  
229 the amorphous materials, as well as organic matter (C, H) and carbonates (C) not measured during  
230 matrix EMP analyses. Porosity does not lower the analytical total unless it is filled with epoxy resin  
231 (C-, H- and O-rich) (Prêt et al., 2010). The samples used in this study were not embedded in epoxy  
232 under vacuum, thus only a negligible part of the porosity is filled with epoxy resin and should not  
233 influence the EMPA totals. Major elements' composition of minerals and alteration phases were  
234 obtained by EDS microanalyses on the Thermo-Fisher Titan Themis S/TEM of the University of  
235 Lille.

## 236        **2.5 Bulk major and trace elemental analyses**

237            Around ~50 mg of powdered samples were divided in 3 fractions to evaluate the possible  
238 chemical heterogeneity of the samples. Each subfraction was mixed with ~0.3 g of a 4:1 ultrapure  
239 metaborate-tetraborate mixture. The mixture was heated in a graphite crucible at  $1000^\circ\text{C}$  for 10  
240 minutes. After cooling down, the bead was dissolved in 50 ml of 2N  $\text{HNO}_3$  with a stirring magnet for  
241 5 hours. Major element oxide concentrations were determined by measuring solutions on an  
242 ThermoScientific iCAP 7000 Series inductively coupled optical emission mass spectrometer (ICP-  
243 OES) at Laboratoire G-Time at ULB. Yttrium was used as internal standard and the calibration curves

244 were obtained on artificial multi-element standards. Natural standards from USGS (BHVO-2, RGM-  
245 2) were used for quality control. The external reproducibility expressed as relative standard deviation  
246 (RSD) for individual oxide, based on 5 replicates of BHVO-2 and RGM-2 was better than 2%, except  
247 for K<sub>2</sub>O (<10%) and P<sub>2</sub>O<sub>5</sub> (<13%).

248 Trace elements measurements were performed on an Agilent 7700 ICP-MS at Laboratoire G-  
249 Time at ULB. Indium was used as internal standard for trace elements analyses, and the calibration  
250 curves were also obtained on artificial multi-element standards. The USGS BHVO-2 natural standard  
251 was used for quality control. The RSD is better than 5% (based on 6 replicates of BHVO-2) for trace  
252 elements (except Rb and Lu, 7 and 10% respectively). It is better than 10% (based on 5 replicates of  
253 the BHVO-2), except Pb, better than 28%.

## 254 **2.6 Infrared (IR) spectroscopy**

255 IR reflectance spectroscopy was performed at the Institut de Planétologie et d'Astrophysique  
256 de Grenoble (IPAG), using the SHADOWS instrument (Potin et al., 2018). The instrument was used  
257 in normal standard mode as well as in a  $\mu$ -beam mode enabling measurements of IR reflectance  
258 spectra of areas of  $\sim 3$  mm<sup>2</sup>. Spectra were measured under nadir incidence and with an observation  
259 angle of 30°. Spectra were normalized to Infragold™ and Spectralon™. Each spectrum was measured  
260 from 0.3  $\mu$ m to 2.6  $\mu$ m, with a step of 20 nm.

261 Infrared transmitted spectra were obtained at IPAG at Grenoble France, using a Bruker  
262 Hyperion 3000 infrared microscope and a Vertex 70V Fourier transform infrared spectroscopy  
263 (FTIR) spectrometer. The infrared beam was focused through an 15x objective, creating a spot on the  
264 sample of 50x50  $\mu$ m<sup>2</sup>. Spectra were measured at 4 cm<sup>-1</sup> spectral resolution over a range of 4000-650  
265 cm<sup>-1</sup>. Matrix pieces were chosen under binocular microscope ( $\sim 50$   $\mu$ m) and transferred onto a 3x0.5  
266 mm type IIa synthetic diamond window. The pieces were then crushed by another diamond window.  
267 Spectra of the four chondrites were also acquired from powdered samples. The window containing  
268 the most crushed pieces with optical shapes was analyzed in an environmental cell enabling exposure

269 of the sample to a vacuum ( $10^{-6}$  mbars). Infrared transmission spectra were acquired under vacuum at  
270 20°C, at 100°C and 250°C or 300°C, in order to progressively remove the effect of adsorbed ambient  
271 water and study the meteorites under “dry conditions” (Beck et al., 2010).

## 272 **2.7 Raman spectroscopy**

273 Raman spectroscopy was performed at Laboratoire de Géologie de Lyon, Université Claude  
274 Bernard, Ecole Normale Supérieure de Lyon in France. Data were collected using a Labram HR800  
275 spectrometer equipped with an Nd ion laser providing 532 nm excitation. Spectra were recorded in  
276 the 490-2230  $\text{cm}^{-1}$  range.

## 277 **2.8 Magnetic analyses**

278 Petrophysical parameters (magnetic properties) were also used for a better characterization of  
279 the studied meteorites. Magnetic susceptibility was measured with a MFK1 or a KLY2 instrument,  
280 depending on the sample size. Saturation magnetization was determined from hysteresis loops  
281 measured with a Princeton model 2900 Micromag vibrating sample magnetometer (see Gattacceca et  
282 al., 2014 for a comprehensive description). All magnetic measurements were performed at CEREGE.

## 283 **2.9 X-ray Diffraction (XRD)**

284 XRD analyses were conducted on both a polished section and bulk powder for NWA 11750  
285 and NWA 12957, in order to see differences between the two sample preparation methods. For EM  
286 200, analyses were made on a polished section, and for Chwichiya 002 on a powdered sample.  
287 Classical XRD analyses were carried out with an X'Pert Pro MPD diffractometer (Panalytical)  
288 equipped with a cobalt tube ( $\lambda = 1.79 \text{ \AA}$ ) operating at 40 kV and 40 mA, with a  $\theta - 2\theta$  goniometer, at  
289 CEREGE. A rotation of the samples (powders and sections) in the horizontal plane at 15 rpm was  
290 used in order to improve the counting statistics. The powders were placed on Si supports (non-  
291 diffracting), using a few drops of ethanol, in order to obtain a thin and homogeneous layer of crystals,  
292 and the polished sections were fixed on circular supports. Analytical conditions were for powders,  
293 counting from  $5^\circ$  to  $75^\circ$  ( $2\theta$ ) in steps of  $0.033^\circ$ , for a total counting time of 4 hours; for the polished

294 sections, from  $4^\circ$  to  $75^\circ$  ( $2\theta$ ) in steps of  $0.033^\circ$ , and a total counting time of 5 hours. Mineral  
295 identification was done using the X'Pert Highscore Plus (Panalytical) software and the ICDD's PDF2  
296 database.

297 Additional PSD-XRD analyses were conducted on powder samples for all four meteorites at  
298 the Natural History Museum, London. For each meteorite,  $\sim 50$  mg of powder was packed into an  
299 aluminum sample holder and analyzed using an Enraf-Nonius PDS120 X-ray diffractometer with an  
300 INEL curved  $120^\circ$  position-sensitive-detector (PSD-XRD). Cu- $K\alpha_1$  radiation was selected with a Ge  
301  $\langle 111 \rangle$  monochromator, and the size of the primary beam on the sample was restricted to  $0.24 \times 2.00$   
302 mm using a set of post-monochromator slits. Samples were rotated throughout the analyses and XRD  
303 patterns were collected from each meteorite for 16 hours, and from terrestrial mineral standards under  
304 the same analytical conditions for 30 minutes. Mineral abundances in the meteorite powders were  
305 determined using a profile-stripping method that has previously been described in detail (Bland et al.,  
306 2004; Howard et al., 2009; King et al., 2015). Briefly, the XRD pattern of a mineral standard was  
307 scaled to the same measurement time as the meteorite analysis (i.e.,  $\times 32$ ) and then reduced by a factor  
308 in order to match its intensity in the pattern of the meteorite. The standard XRD pattern was then  
309 subtracted, leaving a residual meteorite pattern. This process was repeated for all phases identified in  
310 the meteorite until there were zero counts remaining in the residual and the sum of the fit factors was  
311 one. Fit factors were corrected for relative differences in X-ray absorption to give a final volume  
312 fraction in the meteorite (Cressey and Schofield, 1996). Uncertainties in the mineral abundances are  
313 typically  $< 1\%$  (King et al., 2015).

## 314 **2.10 Thermogravimetric analysis (TGA-DSC)**

315 Thermogravimetric and Differential Calorimetry analysis (TGA-DSC) were performed using a  
316 Mettler-Toledo TGA-DSC3+ instrument at the Institute des Sciences de la Terre (ISTerre, Grenoble,  
317 France). 50 mg of each sample was manually crushed with an agate mortar in order to obtain a fine  
318 powder. 35mg of this powder was then measured in a  $70 \mu\text{L}$  alumina crucible under a  $50\text{mL}/\text{min}$  inert

319 N<sub>2</sub> atmosphere. The temperature was increased from 25°C to 1075°C at a heating rate of 10°C/min.  
320 FTIR spectra of the degassed species were measured every 23 s over a period of 120 min. From the  
321 resulting TGA mass loss curve, the first derivative (DTG) curve can be calculated, which allows for a  
322 better visualization of temperature regions associated with strong mass losses. This, coupled with the  
323 IR spectra measured of the degassed phases, provides information about the quantity and type of  
324 hydrated mineral in the sample. The IR spectra are interpreted by integrating over wavelength ranges  
325 of specific chemical compounds of interest and looking at the evolution of these peak areas over time.  
326 The wavelength ranges of interest used here are CO (2240-2040 cm<sup>-1</sup>), CO<sub>2</sub> (2450-2240 cm<sup>-1</sup>), CH  
327 (3000-2800 cm<sup>-1</sup>), H<sub>2</sub>O (4200-3000 cm<sup>-1</sup>) and SO<sub>2</sub>/SO<sub>3</sub> (1420-1330 cm<sup>-1</sup>). For correction of  
328 background noise, several measurements of empty crucibles were performed and later subtracted  
329 from the TGA curves of the samples. To get boundaries on the evolution of the chemical compound  
330 peak areas in the IR spectra, the same wavelength ranges as mentioned above are assessed for the  
331 empty crucible, and the average and standard deviation are determined for each compound. This is  
332 done for all empty crucible measurements, and an average standard deviation is determined. The  
333 boundaries are shown as green dotted lines in the plots (Fig. S4-7).

## 334 **2.11 X-ray computed tomography**

335 Two chips of NWA 11750 were imaged on a Zeiss Versa 620 XRM at 100 kV and 12 W at  
336 the University of Texas High Resolution X-ray CT (UTCT) facility. For the smaller chip, 3001 views  
337 were collected on the 0.4× objective with an acquisition time of 5s per view. A LE2 filter was used  
338 and a beam hardening correction of 0.3 was applied during reconstruction and the final voxel size was  
339 3.00 μm. The larger chip was imaged using the flat panel detector with 9001 views and a 0.05 s  
340 acquisition time per view. A LE3 filter was used and a beam hardening correction of 0.25 was applied  
341 during reconstruction with a final voxel size of 4.50 μm.

342

343 **2.12 Oxygen isotopes**

344 Carbonate oxygen isotopic compositions were analysed using a CAMECA IMS 1270 E7 at  
 345 the Centre de Recherches Pétrographiques et Géochimiques (CRPG) laboratory in Nancy, France. A  
 346 Cs<sup>+</sup> primary ion beam (~15×10 μm spot area) with a current of ~5 nA was used in order to collect  
 347 <sup>16</sup>O<sup>-</sup>, <sup>17</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> secondary ions in multi-collection mode using three Faraday cups (L'2, FC2 and  
 348 H1). Charge compensation was applied using a normal-incidence electron gun. Mass Resolving  
 349 Power (MRP = M/ΔM) was adjusted to ~7000 to resolve interference from <sup>16</sup>OH<sup>-</sup> on the <sup>17</sup>O<sup>-</sup> peak  
 350 and achieve maximum flatness on the top of the <sup>16</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> peaks (entrance and exit slits of FC2  
 351 were adjusted to ~70 μm and ~170 μm, respectively). <sup>16</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> secondary ions were collected on  
 352 L'2 and H1, respectively (slit 1, MRP ≈ 2500). Pre-sputter on a large area (~20×20 μm) was applied  
 353 before each measurement during 60 s, to remove carbon coating at the surface of the calcite grains.  
 354 Acquisition time was set to ~5s, and measurements were repeated over 30 cycles to achieve counting  
 355 statistics ~0.2‰ (1σ) for δ<sup>18</sup>O and ~0.3‰ for δ<sup>17</sup>O. Isotope ratios (<sup>17</sup>O/<sup>16</sup>O and <sup>18</sup>O/<sup>16</sup>O) are presented  
 356 in per mil (‰) relative to Standard Mean Ocean Water (SMOW):

357 
$$\delta^x O_{SMOW}(\text{‰}) = \left( \frac{xO/^{16}O_{sample}}{xO/^{16}O_{SMOW}} - 1 \right) \times 1000 \quad (1)$$

358 where  $x$  represents <sup>17</sup>O or <sup>18</sup>O and SMOW the ratios of the SMOW standard. We used three  
 359 terrestrial standard materials (San Carlos olivine, diopside and calcite) to define the instrumental mass  
 360 fractionation line for the three oxygen isotopes. Instrumental Mass Fractionation (IMF) for calcite  
 361 matrix was determined from our in-house Mexican calcite standard at the beginning and end of each  
 362 analytical session. IMF values for each sample analysis were then calculated by accounting for the  
 363 linear deviation over the time of the IMF values. Typical measurement errors (2σ), accounting for  
 364 errors on each measurement and the external reproducibility of the standard, were estimated to be  
 365 ~0.5‰ for δ<sup>18</sup>O, ~0.6‰ for δ<sup>17</sup>O, and ~0.7‰ for Δ<sup>17</sup>O (i.e., Δ<sup>17</sup>O = δ<sup>17</sup>O - 0.52 × δ<sup>18</sup>O), where Δ<sup>17</sup>O  
 366 represents the departure from the TFL.



## 367 **3 Results**

### 368 **3.1 Petrographic description**

369 The petrographic characteristics of the studied chondrites are reported in Table 1.  
370 Chwichiya 002, NWA 11750, and NWA 12957 show overall CM-like petrography (Fig. 1), with  
371 high matrix abundance (63.3-74.0 vol%), low chondrule abundance (12.9-26.0 vol%), and small  
372 chondrule apparent diameter (average in the range 240-480  $\mu\text{m}$ ) (Table 1), but differ from CM  
373 chondrites in their bulk oxygen isotopic compositions and lack of evidence for significant  
374 aqueous alteration (Gattacceca et al., 2020). No amoeboid olivine aggregate (AOA) or calcium-  
375 aluminum rich inclusions (CAIs) were observed in those meteorites. They were approved as type  
376 3.00, based on the absence of detectable phyllosilicates in XRD patterns and IR transmission  
377 spectra, as well as Raman spectroscopy of the fine-grained matrix polyaromatic carbonaceous  
378 matter reflecting a peak metamorphism temperature lower than that for Semarkona (LL3.00)  
379 (Bonal et al., 2016). They show a high FeO content in their matrices: 34.86 wt% for NWA  
380 12957, 34.30 wt% for NWA 11750 and 39.39 wt% for Chwichiya 002 (Table 1). A  
381 distinguishing feature of NWA 11750 is the presence of large carbonate veins cutting through the  
382 matrix and as cracks in the fine-grained rims all around chondrules (Fig. S1). The position of the  
383 carbonate veins around the chondrules suggests hexagonal shapes, resembling desiccation  
384 patterns, an observation confirmed by CT data (Fig. S2). Carbonates in NWA 11750 have  $\delta^{18}\text{O}$   
385 values of  $\sim 30\text{-}40\text{ ‰}$ , with slightly negative  $\Delta^{17}\text{O}$  (average  $-0.63\text{ ‰}$ ) (Fig. 2). Although the  
386 carbonate O-isotopic compositions plot within errors on the TFL, they show do not show  $\delta^{18}\text{O}$   
387 and  $\delta^{17}\text{O}$  values close to  $0\text{ ‰}$  as commonly observed for carbonates resulting from terrestrial  
388 weathering (Tyra et al., 2007). Due to the low permeability of CM chondrites (Bland et al.,  
389 2009), contamination by the terrestrial water occurs only in fractures, and can be associated with  
390 evaporite minerals. The veins in NWA 11750 contain only calcite, with no gypsum. The oxygen

391 isotopic composition of the calcite at the locations analyzed suggests that it is extraterrestrial in  
392 origin. EM 200 (C3 with affinities with CO3) (Ruzicka et al., 2015) has a smaller amount of  
393 matrix (44.1 vol%), a high proportion of magnetite (10.7 vol%) and a small chondrule size  
394 ( $130\pm 80$   $\mu\text{m}$ ) (Table 1). It is classified as a type 3 based on similar characteristics as Chwichiya  
395 002, NWA 11750 and NWA 12957 and shows a lower concentration of FeO in its matrix (23.79  
396 wt%) (Table 1). Because these four chondrites show a similar primitive petrologic type as the  
397 ungrouped chondrite Acfer 094, with limited secondary alteration, we followed the protocol in  
398 Abe et al. (2017) to look for cosmic-symplectites (COS). We used a polished section of Acfer  
399 094 to verify our method enabled us to identify COS using Fe-S-O EDS mapping. We were able  
400 to identify COS in Acfer 094, but no COS was observed in the four chondrites of this study.

### 401 **3.2 Metamorphic state**

402 The Raman parameters of the structural order of the polyaromatic matter in the matrices  
403 show that the studied chondrites appear to be less heated than the least heated type 3 ordinary  
404 chondrite Semarkona (LL3.00). Comparison of the Raman spectral parameters with the data from  
405 Quirico et al. (2018) show that the four studied meteorites do not show evidence for protracted  
406 metamorphic heating due to  $^{26}\text{Al}$  decay observed in type 3 chondrites, but are rather similar to  
407 type 2 meteorites such as Murchison with only minor short-term heating probably due to shock  
408 (Fig. 3). EM 200 shows a larger variability of heating compared to the other three meteorites,  
409 with potentially slightly more heated zones. The ferroan olivine show  $\text{Cr}_2\text{O}_3$  content of  $0.27 \pm$   
410  $0.12$  wt% (n=31) for NWA 11750,  $0.32 \pm 0.10$  wt% (n=16) for NWA 12957,  $0.36 \pm 0.10$  wt%  
411 (n=42) for Chwichiya 002 and  $0.36 \pm 0.24$  wt% (n= 30) for EM 200. The mean and standard  
412 deviations for Chwichiya 002 and NWA 12957 are close to the data for Acfer 094 (C2-ung)  
413 (Newton et al., 1994), while the data for NWA 11750 are close to the Y-81020 (CO 3.0), Colony  
414 (CO 3.0), and Paris (CM2) meteorites (Fig. 4) (Grossman and Brearley, 2005; Hewins et al.,

415 2014). EM 200 has a higher standard deviation for Cr<sub>2</sub>O<sub>3</sub> content of ferroan olivine, setting it  
416 apart from the carbonaceous chondrites trend, and close to type 3.1 ordinary chondrites (Fig. 4).

### 417 **3.3 Bulk mineralogy**

#### 418 **3.3.1 Bulk compositions**

419 Table 2 shows the bulk chemical composition of the four studied meteorites. Chwichiya  
420 002, NWA 11750 and NWA 12957 show homogenous compositions throughout the three  
421 measured samples (RSD 0.86-1.31), whereas EM 200 shows more heterogeneous composition  
422 (RSD 5.91). Figure 5 shows the bulk chemical CI-normalized composition compared to CO and  
423 CM. The meteorites show trends similar to CM and CO chondrites, from refractory to volatile  
424 elements. Chwichiya 002, NWA 11750 and NWA 12957 show La and Sr enrichments, typical of  
425 hot desert weathering (Pourkhorsandi et al., 2017). EM 200 and NWA 11750 show a slight  
426 depletion of Na, and enrichment of K, which is not related to the metamorphic or weathering  
427 state and could come from element redistribution on the parent body (Braukmüller et al., 2018).  
428 The high Ca content of Chwichiya 002, NWA 11750 and NWA 12957 is linked to a bulk high  
429 abundance of carbonates.

#### 430 **3.3.2 Visible near infrared reflectance**

431 The visible-near-infrared (VIS-NIR) reflectance spectra show no strong absorption bands,  
432 with only very broad and shallow absorptions around 1 µm (Fig. 6). They do not display 2 µm  
433 absorption bands indicative of olivine and pyroxene and have a flat spectral VIS-NIR slope. They  
434 all show a reflectance maximum around 600 nm, with a slight positive slope from 1 µm to longer  
435 wavelengths. These dark and featureless spectra can be attributed to the high abundance of matrix  
436 (44.1, 63.0, 73.4 and 74.0 vol%) rich in phases producing no spectral features (carbonaceous  
437 matter, opaques) that can mask silicate absorption bands (Table 1). They are also consistent with  
438 the low abundance of chondrules (12.9 – 35.2 vol%), rich in silicates, that would produce deep  
439 absorption bands around 1 µm and 2 µm (Table 1). The absorption bands of phyllosilicates

440 (combination of the Fe<sup>2+</sup> and Fe<sup>3+</sup> absorptions at 0.7, 0.9, 1.1 μm, H<sub>2</sub>O absorption at 1.9 μm, and  
441 2.3 μm absorption of -OH) are absent from the IR reflectance spectra of the studied samples.  
442 Thus, no significant aqueous alteration products can be detected by VIS-NIR reflectance  
443 spectroscopy in those meteorites, agreeing with a type 3 classification for all meteorites.  
444 Although the absence of large absorption bands is also found in CM chondrite spectra, the overall  
445 spectra of the studied meteorites are very different from spectra of CM chondrites (Fig. 6).

### 446 **3.3.3 X-ray diffraction**

447 Semi-quantitative modal abundances were calculated from the XRD and PSD-XRD  
448 patterns (Table 3). Errors are around 5 vol% for XRD and 1 vol% for PSD-XRD, depending on  
449 the phase and crystallinity. Only modal abundances of crystalline phases could be extracted from  
450 XRD patterns and all abundances are normalized to a total of 100 wt%. However, even when  
451 amorphous phases could not be quantified in the modal abundances, some were clearly detected  
452 on the XRD patterns of Chwichiya 002 and NWA 12957, leading to overestimation of the  
453 abundances of crystalline phases. The PSD-XRD measurements enabled the estimation of  
454 amorphous phase modal abundances by using Cu K-α1 radiation. Iron-bearing components  
455 influence the fluorescent background, and thus after removing other crystalline phases from the  
456 XRD patterns, the contribution of any Fe-bearing amorphous phases can be approximated  
457 (Howard et al., 2015; King et al., 2015). For all of the meteorites, XRD patterns of polished  
458 sections and powdered samples showed similar minerals phases. Only the semi-quantitative  
459 abundances slightly vary, by no more than 5 vol%, depending on the sample preparation. This is  
460 within the error due to quantitative analysis of the patterns, as these abundances are only semi-  
461 quantitative. Primary phases such as olivine, pyroxene, and clinopyroxene are detected in all  
462 meteorites in variable abundance. Metal was not detected in EM 200 and Chwichiya 002, in  
463 contrary to NWA 11750 and NWA 12957 where small metal abundances were detected (Table  
464 1). NWA 12957 shows a high abundance of amorphous phases (23 vol%), phyllosilicates (Fe-

465 rich serpentine) (6 vol%), and minor carbonates (3 vol%), magnetite (2 vol%), pyrrhotite (2-5  
466 vol%) and troilite (1 vol%). Chwichiya 002 shows a high abundance of amorphous phases (12  
467 vol%), with phyllosilicates (Fe-serpentine) (2-5 vol%) and minor carbonates (1-7 vol%),  
468 magnetite (2 vol%), pyrrhotite (3 vol%) and troilite (3 vol%), resembling NWA 12957. The  
469 NWA 11750 XRD patterns indicate the presence of carbonate (2-6 vol%), pyrrhotite (2-6 vol%),  
470 troilite (1-5 vol%), metal (kamacite) (1-3 vol%), and phyllosilicates (serpentine) (2 vol% from  
471 the PSD-XRD pattern). EM 200 is composed of a high abundance of magnetite (16-20 vol%),  
472 troilite (6 vol%), and low abundances of pyrrhotite (1 vol%) and phyllosilicates (Fe-serpentine)  
473 (2 vol%). Pentlandite was not detected by XRD in any of the samples.

#### 474 **3.3.4 Thermogravimetric analysis**

475 Table 4 shows the mass loss in each meteorite for the different temperature ranges usually  
476 used in the literature for TGA analyses (Garenne et al., 2014). Those temperature ranges were  
477 chosen as carbonaceous chondrite alteration phases release volatiles at different temperatures  
478 (Garenne et al., 2014). Table 4 shows the associated IR signature of gasses lost during heating at  
479 the different temperature ranges. Indeed, IR signatures of the gas should allow the identification  
480 of the phases at the origin of the mass losses in TGA and permit the refining of the phases  
481 associated with the temperature ranges in Garenne et al. (2014) (Table 4).

482 Between 0-200°C, all meteorites show loss of adsorbed and loosely bound water that are  
483 commonly attributed to terrestrial contamination but could also originate from interlayer water in  
484 smectite. As XRD patterns did not detect any smectite in the studied meteorites, we believe this  
485 temperature range is only associated with terrestrial contamination. Surprisingly, no meteorites  
486 showed IR signature of H<sub>2</sub>O at <200°C, which will be discussed in section 4.1.1. The second part  
487 of the TGA between 200-400°C is supposedly due to release of H<sub>2</sub>O and OH from  
488 (oxy)hydroxide minerals, usually linked to terrestrial weathering, although organic matter in the  
489 matrix can also increase the mass loss in this temperature range (Gilmour et al., 2019). EM 200

490 shows a total mass loss of 13.43 wt%, with a signature of CH gases on the IR spectra, probably  
491 due to a high concentration of organic matter in the matrix. In this temperature range, NWA  
492 12957 shows a mass loss of 2.96 wt%, with an IR signature of CO<sub>2</sub>, which can also be attributed  
493 to organic matter. Chwichiya 002 and NWA 11750 show a mass loss of around 3.24 wt% and  
494 1.50 wt% respectively, with no signature on IR, probably due to loss of hydroxyl groups (-OH)  
495 from (oxy)hydroxides, according to their more weathered condition. The 400-770°C temperature  
496 range is directly correlated to abundance of phyllosilicates, due to the release of hydroxyl groups  
497 (-OH) (Garenne et al., 2014), but SO<sub>2</sub> from sulfides, as well as CO<sub>2</sub> and CH from organics in the  
498 matrix increase the mass loss. NWA 11750 shows a significant mass loss of 8.55 wt%, with a  
499 signature of CO<sub>2</sub>/CO and CH, from organics; EM 200 has a mass loss of 7.56 wt% with a  
500 signature of CO<sub>2</sub>/CO and SO<sub>2</sub>, due to sulfides and abundant organics; and Chwichiya 002 and  
501 NWA 12957 show a mass loss of 6.81 wt% and 4.85 wt% with an IR signature of CO<sub>2</sub>/CO from  
502 organics. Finally, the temperature range 770-900°C is assigned to the CO<sub>2</sub>/CO release from  
503 carbonates (Garenne et al., 2014). EM 200 shows a mass loss of 5.68 wt% at this temperature and  
504 the other three meteorites show minimal mass losses < 1.0 wt%.

### 505 **3.4 Matrix petrography**

#### 506 **3.4.1 Electron microscopy**

507 A combination of FEG-SEM, STEM, HR-TEM and SAED was used to identify phases, as  
508 well as to document textures and to determine modal abundances in the matrices of the four  
509 chondrites. SEM-EDS maps of the four meteorites have been acquired in order to document  
510 modal abundances in the matrix at a larger scale (crystals > 100 nm) (Fig. 7). A total of three  
511 SEM-EDS maps of ~225 μm<sup>2</sup> were studied for EM 200, Chwichiya 002 and NWA 12957, and  
512 five maps of ~225 μm<sup>2</sup> for NWA 11750. As all meteorites show heterogeneity in their matrices,  
513 we chose the most representative zone for each meteorite to extract the FIB sections used for  
514 TEM studies (Fig. S3). For Chwichiya 002, EM 200 and NWA 11750, one FIB section of ~60

515  $\mu\text{m}^2$  for each meteorite was extracted from the matrices in order to conduct High-angle annular  
516 dark-field imaging (HAADF) observations and STEM-EDS mapping. Modal abundance  
517 calculated from SEM-EDS and STEM-EDS maps are reported in Table 5.

518 On SEM-EDS images, Chwichiya 002 and NWA 12957 show broadly similar textures  
519 with micrometric forsterite and enstatite fragments, troilite, pentlandite, magnetite, and abundant  
520 micrometric TCIs aggregates, all set in a fine nanoscale grained matrix, named here “fine-grained  
521 mix” (Table 5, Fig. 7a and Fig. 7c). The difference in secondary phases between the two  
522 meteorites is the modal abundance of TCIs with 22.0 vol% and 5.3 vol% for Chwichiya 002 and  
523 NWA 12957; and sulfides with 4 vol% and 13.0 vol% for Chwichiya 002 and NWA 12957,  
524 respectively, with both Fe-Ni dominant sulfides. In addition, a minor abundance of metal, mostly  
525 kamacite, is observed in both meteorites. Chwichiya 002 shows a small amount of phosphates  
526 and brucite is observed in NWA 12957. Using STEM-EDS, the observation of the “fine-grained  
527 mix” in Chwichiya 002 allows the distinction of the different phases unresolved by SEM. It is  
528 composed of amorphous materials, TCIs, and a low abundance of forsterite, enstatite, metal, Fe-  
529 oxide, and pentlandite (Fig. 8a, Fig. 9a). Nanosized crystals of troilite are present in low  
530 abundance. The presence of amorphous material is confirmed using SAED that shows patterns  
531 typical of an amorphous material with characteristic diffuse rings (Fig. 10 A3). These amorphous  
532 phases contain abundant metal and sulfide inclusions (Fig. 10 A1, A2). The elemental  
533 composition of the amorphous component in Chwichiya 002 is on average O (63 at%), Si (16  
534 at%), Fe (9.2 at%), Mg (7.3 at%), Al (1.9 at%) and Ca (1.3 at%) (n=5). The assemblage of  
535 amorphous material with inclusions of metal and sulfide resembles Glass with Embedded Metal  
536 and Sulfide (GEMS)-like material. The modal abundances are similar to the ones found in SEM-  
537 EDS maps, except that the STEM-EDS maps show higher porosity in the matrix of Chwichiya  
538 002 (Table 5).

539 On SEM-EDS maps, NWA 11750 shows micrometric grains of silicates (Mg-rich olivine  
540 and enstatite), troilite, kamacite, and tetrataenite grains and micrometric diffuse patches of  
541 carbonates and serpentine (Fig. 7d, Fig. S3b). Some larger silicate grains, that may well represent  
542 chondrules fragments, can be found with sizes from 10  $\mu\text{m}$  to 1 mm. These grains are set in a  
543 large abundance of nanoscale fine-grained mix (Table 5). Pentlandite is found as traces in some  
544 matrix zones, although too small to be analyzed. STEM-EDS maps reveals that the “fine-grained  
545 mix” of NWA 11750 is composed of carbonates finely intermixed with abundant olivine, a few  
546 enstatite grains, Mg-rich serpentine, and subhedral to euhedral taenite metal grains (Fig. 8b, Fig.  
547 9b). The studied FIB section STEM-EDS map shows two types of olivine: small nanoscale  
548 olivines ( $\text{Fa}_{\sim 25}$ ) forming aggregates with an engrained texture (Fig. 10 B1, B3), and a porous  
549 aspect with nanometric sulfides inclusions; and larger micrometric to millimetric grains of olivine  
550 ( $\text{Fa}_{\sim 10}$ ) (bottom of the section Fig. 8b). Traces of troilite, sulfates and Ca-phosphates are also  
551 observed in STEM-EDS maps. A difference between SEM-EDS and STEM-EDS abundances in  
552 NWA 11750 is the modal abundance of carbonates. This phase is well intermixed with olivine  
553 and pyroxene, as observed on STEM-EDS maps (32.6 vol%). Therefore, on SEM-EDS maps,  
554 only the larger veins of carbonates are observed (3.66 vol%), while the small, intermixed  
555 carbonates are “lost” in the “fine-grained mix”.

556 SEM-EDS images of the matrix of EM 200 show micrometric silicates and magnetite,  
557 with submicrometric troilite, pentlandite, and metal (taenite) grains, all set in a nanosized “fine-  
558 grained mix”. No TCIs were found on FEG-SEM images (Fig. 7b, Fig. S3d). On STEM-EDS  
559 maps, the “fine-grained mix” is composed of olivine, pyroxene, metal, magnetite, troilite and  
560 pentlandite, embedded in a nanocrystalline phyllosilicates and organic matter assemblage (Fig.  
561 8c, Fig. 9c). We observed Mg-rich olivine ( $\text{Fe}_{\sim 10-35}$ ) as well as Ca-rich and Ca-poor pyroxene.  
562 Most of the FIB section shows recrystallization in fine lamellar nanoscale phyllosilicates and  
563 organic matter (Fig. 10 C1, C2), but silicate crystal borders do not show traces of alteration. EM



564 200 TEM maps also show thin and straight lamellae of TCIs, with dominant cronstedtite (Fig. 10  
565 C1, C2), and rare grains of phosphates and chromite. Rare amakinite  $\text{Fe}(\text{OH})_2$  is observed  
566 interlayered inside one exceptionally large TCI (Fig. S8). The large modal abundance of  
567 magnetite identified from the bulk analyses (Table 1) is not observed at the scale of the matrix  
568 FIB section. This shows that magnetite is distributed heterogeneously in micrometric crystals  
569 rather than in nanometric grains in the matrix. The modal abundances between SEM and TEM  
570 were not different within errors (Table 5), except for the porosity estimated abundance, higher on  
571 STEM, showing a nano-sized porosity.

### 572 **3.4.2 Electron microprobe (EMP) total in the matrix**

573 Figure 11 and Table 6 show the analytical total of the electron microprobe (EMP) analyses  
574 in the matrix of the four studied meteorites compared to the main carbonaceous chondrite groups.  
575 EMPA totals are lowered by the presence of volatiles (OH,  $\text{H}_2\text{O}$ , H) in the phyllosilicates or in  
576 the amorphous materials or by the carbon content (both in organic matter (OM) and carbonates),  
577 which were not measured during the EMPA. CV chondrites, known to have experienced  
578 metamorphism, have the highest totals in the matrix (highest frequency around 95-100 wt%). CM  
579 chondrites, most of them classified as CM2, have more aqueous alteration phases in their matrix  
580 and therefore lower EMPA totals in their matrix (highest frequency around 80-85 wt%). The  
581 most aqueously altered carbonaceous chondrites, the CI1 chondrites, show the lowest EMPA  
582 total in their matrices with a highest frequency around 75-80 wt%. The four chondrites show a  
583 large spread in their analytical EMPA totals. EM 200 shows the lowest total (72.34 wt%), at the  
584 bottom of the range of CI and CM. NWA 11750 has the highest total (96.45 wt%), close to CO  
585 and CV chondrites (Fig. 11, Table 6).

### 586 **3.4.3 Infrared Transmission Spectroscopy**

587 The analyses were performed on several fragments of matrix from each meteorite to be as  
588 representative as possible. In Figure 12, we show the most representative spectra for each

589 meteorite at 20°C, and 250°C (or 300°C for Chwichiya 002). Those two temperature steps were  
590 chosen to demonstrate the difference of hydration and reduce the effect of adsorbed terrestrial  
591 water. The 3000 cm<sup>-1</sup> absorbance is due to interlayer H<sub>2</sub>O and -OH groups in phyllosilicates  
592 (Tuddenham and Lyon, 1959; Oinuma and Hayashi, 1965; Bishop et al., 2002), or in the water  
593 from amorphous material. Indeed, recent studies showed that amorphous silicates in Acfer 094,  
594 Paris or CMs can contain considerable water (Le Guillou et al., 2018; Ohtaki et al., 2021;  
595 Villalon et al., 2021). The position and intensity of those absorptions vary with the structure and  
596 chemical composition of the phyllosilicates. The low abundance of phyllosilicates in the studied  
597 samples does not create a sharp spectral feature from phyllosilicates in the 3000 cm<sup>-1</sup> region,  
598 making it difficult to make a clear mineral identification. The 1000 cm<sup>-1</sup> spectral feature is due to  
599 the absorption by Si-O groups (stretching) and reflects the silicate compositions, including  
600 secondary phases such as phyllosilicates. Extraterrestrial phyllosilicates can be recognized by a  
601 broad symmetric band around 1000 cm<sup>-1</sup> (Beck et al., 2014). At 250°C, NWA 11750 matrix  
602 shows no hydration around the 3000 cm<sup>-1</sup> absorption band. It shows a mixture of olivine and  
603 pyroxene (with a dominance of olivine), with no clear signs of phyllosilicates on the spectra in  
604 the 1000 cm<sup>-1</sup> region. The presence of carbonates can be inferred from a band around 1440 cm<sup>-1</sup>,  
605 but mineral identification was not possible since the carbonate mode around 880 cm<sup>-1</sup>, most  
606 diagnostic of composition, could not be identified with enough accuracy. Chwichiya 002 shows a  
607 weakly hydrated matrix with a slight signature around 3000 cm<sup>-1</sup> at 300°C. Silicate bands show  
608 no sign of phyllosilicates absorptions. NWA 12957 has a slightly more hydrated matrix than  
609 NWA 11750 and Chwichiya 002, with a feature at around 3000 cm<sup>-1</sup> even at 250°C, and weak  
610 signatures of phyllosilicates in addition to olivine and pyroxene in the 1000 cm<sup>-1</sup> region. Finally,  
611 EM 200 spectra show low hydration around 3000 cm<sup>-1</sup> and low amounts of phyllosilicates in the  
612 1000 cm<sup>-1</sup> region, although higher than the other meteorites studied.

## 613 **4 Discussion**

### 614 **4.1 Techniques for evaluating the alteration extent**

615 Secondary phases can be generally found throughout meteorites. During the chondrite  
616 accretion process, water-ice grains are mainly accreted alongside the fine-grained matrix  
617 (Matsumoto et al., 2019), implying that the incipient aqueous alteration would first affect  
618 chondrite matrices. In addition, the fine-grained texture of the matrix is also prone to a faster  
619 alteration than larger silicates in chondrules. Therefore, most of the common alteration phases in  
620 chondrites are observed in the matrix, such as TCIs, carbonates, phyllosilicates, and sulfides (e.g.,  
621 Brearley, 2006).

622 Bulk studies (TGA, XRD in this study) have the benefit of being more representative of a  
623 whole meteorite compared to studies of matrices only, but the signal of the secondary phases is  
624 “diluted” by the presence of large silicates from the chondrules (Tables 2 and 6). Microanalyses  
625 of separated matrix pieces (transmitted IR, EMPA total in the matrix in this study) increases the  
626 ratio of the alteration phases compared to anhydrous silicates, facilitating their detection (Tables  
627 4 and 6). In addition, *in situ* analyses of the matrix (SEM, TEM) allow observation of the  
628 incipient aqueous alteration. Here we discuss the detection of secondary alteration phases in  
629 slightly altered chondrites. We conclude by proposing an ideal combination of methods to  
630 identify the most primitive chondrites through the characterization of the extent of aqueous  
631 alteration.

#### 632 **4.1.1 Bulk studies**

##### 633 *Vis-NIR reflectance spectroscopy*

634 Vis-NIR reflectance spectroscopy can be used to detect -OH, and H<sub>2</sub>O absorptions in  
635 meteorite samples, as well as on asteroid surfaces. In this work, we did not detect any hydration  
636 in the studied chondrites using Vis-NIR reflectance. The reflectance spectra are influenced by

637 many factors other than the hydration state of the meteorites. Indeed, temperature, texture, grain  
638 size, opaque minerals, organic phases and terrestrial weathering can change the slope of the  
639 spectra (Beck et al., 2010; Garenne et al., 2016; Johnson and Fanale, 1973; Singer and Roush,  
640 1985; Takir et al., 2019; Hapke, 2001; Cloutis et al., 2012). A high abundance of phyllosilicates  
641 can also influence the spectral slope, in addition to having weak absorption bands around 0.7  $\mu\text{m}$ ,  
642 0.9  $\mu\text{m}$ , 1.1  $\mu\text{m}$  and 2.3  $\mu\text{m}$ , such as those detected in CM chondrites (Fig. 6). For weakly altered  
643 samples, phyllosilicates are not present in large enough amounts (Table 3) to be detected by IR  
644 reflectance spectroscopy as observed in the four studied chondrites (Fig. 6). This method is useful  
645 to find potential parent bodies of altered chondrites, through a comparison of IR reflectance  
646 spectra of meteorites and asteroid surfaces (e.g., Krämer Ruggiu et al., 2021), but this technique  
647 is not efficient to detect minor degrees of aqueous alteration.

#### 648 **TGA**

649 In the literature, TGA data are interpreted using temperature ranges that are associated  
650 with different gases released from minerals phases (Garenne et al., 2014) (Table 4). However, in  
651 those temperature ranges, gases from other phases, such as organics or sulfides (including  
652 tochilinite from TCIs), can also be released (Table 4). The gases released at those temperature  
653 ranges show different signatures in the FTIR spectra than expected: CH and CO at 200-400°C;  
654 CH, CO, and CO<sub>2</sub> at 400-770°C (Table 4, Fig. S4-S7). Therefore, the mass loss abundances  
655 represent only a “maximum” of oxy-hydroxides from terrestrial alteration (200-400°C),  
656 phyllosilicates (400-770°C) and carbonate (770-900°C), all without taking into consideration the  
657 potential contribution of sulfides, TCIs, or organic matter (Table 4). Indeed, the high proportion  
658 of organic matter may explain the significant mass losses for EM 200 at 200-400°C (13.43 wt%)  
659 and at 700-900°C (5.68 wt%), as only small terrestrial alteration is observed, and no carbonates  
660 were detected with other instruments (Table 5, Table 7). In addition, the different temperature  
661 ranges do not allow for the distinction of different solid solutions of phyllosilicates, which are

662 important in the characterization of secondary alteration phases: TCIs (with Fe-serpentine  
663 cronstedtite) and Mg-serpentine from olivine alteration. Surprisingly, none of the studied samples  
664 showed an IR signature of H<sub>2</sub>O at <200°C, which we tentatively attribute to water abundances  
665 below the detection limit of the instrument. Also, Chwichiya 002, NWA 11750 and NWA 12957  
666 all show mass losses 1 wt% in the carbonate range (400-770°C), while showing bulk abundances  
667 of carbonates of 1-6 vol% on XRD (Table 3). Consequently, TGA associated with IR transmitted  
668 spectroscopy could represent a promising technique to measure the abundance of aqueous  
669 alteration phases, if some parameters (such as sulfides and organic matter content) are considered  
670 beforehand, and additional work on standards for the study of meteorites is made. Temperature  
671 ranges should be refined in order to precisely define the mass loss temperature for different  
672 phases. Furthermore, the organic matter content of each meteorite should be measured in order to  
673 calculate its influence in the mass loss.

#### 674 ***XRD***

675 The detection limits of our XRD analyses for quantitative modal abundances were ~ <5  
676 vol% for most phases (Table 3). The detection limits of XRD are largely related to the  
677 composition and the crystallinity of the phases. For example, as the XRD pattern of calcite has  
678 one very intense peak, making it easily detected even in low abundances (<1 vol%), it could  
679 easily be detected in all meteorites (~2 vol%) except for EM 200, which also showed no  
680 carbonates with all other instruments (Table 7). Metal was also detected by XRD in the matrix  
681 (~1 vol%) of NWA 12957 and NWA 11750. Low abundances of magnetite were also detected  
682 (down to 2 vol% for NWA 12957) (Table 3). Sulfide detection via XRD is more complicated and  
683 depends on chemistry. Indeed, Fe-sulfides are hardly differentiated from one another because  
684 troilite and pyrrhotite have the same crystalline structure, creating only a subtle shift in the  
685 position of the peaks in XRD patterns, and could consequently be mixed or inverted. Fe-Ni-  
686 sulfides (pentlandite) were not detected by XRD in the studied chondrites because of low

687 abundances and peak overlap with major silicate phases. XRD patterns showed small  
688 phyllosilicate (serpentine) peaks only in Chwichiya 002 (2 vol%). Phyllosilicates had been  
689 overlooked in the analyses performed for the registration of the meteorite by the Meteoritical  
690 Society (Gattacceca et al., 2019). PSD-XRD identified poorly crystalline phyllosilicates  
691 (serpentine) in all samples (2-6 vol%). XRD and PSD-XRD “phyllosilicate” detection include the  
692 detection of both Mg- and Fe-serpentine phases, also including cronstedtite in large TCIs (with a  
693 large enough coherence domain).

694 Poorly crystalline phases with low intensity peaks, such as small TCIs or phyllosilicates,  
695 are harder to detect than crystalline materials. The interstratified tochilinite and cronstedtite in  
696 TCIs results in small coherence domains, making detection by XRD challenging. PSD-XRD  
697 analysis found 2 vol% phyllosilicates in EM 200 (Table 3), although TEM analyses showed a  
698 high proportion of nanoscale phyllosilicate (54 vol% of the FIB section) (Fig. 10 C1, C2).  
699 Nanoscale phyllosilicates in EM 200 have too small coherence domains to be detected in XRD  
700 patterns. Abundances of amorphous material can be deduced from PSD-XRD patterns and are  
701 important to assess the potential presence of Glass with Embedded Metal and Sulfide (GEMS)-  
702 like amorphous material in primitive chondrites (Table 7). Although we suspect most amorphous  
703 phases are GEMS-like materials in Chwichiya 002 and NWA 12957, like those we observed in  
704 STEM in Chwichiya 002 (Fig. 9a), other phases such as extremely fine-grained phyllosilicates  
705 with small coherency domains also create broad and weak diffraction peaks, increasing the  
706 estimated amorphous phase abundance. Therefore, the amorphous abundances estimated from  
707 PSD-XRD provide an upper limit of GEMS-like phases and could also include other poorly  
708 crystallized alteration phases. In conclusion, XRD provides a useful bulk technique for detecting  
709 the diversity of primary and secondary phases in the studied chondrites. XRD can detect all  
710 primary phases, as well as secondary phases (phyllosilicates, carbonates, TCIs, secondary  
711 sulfides, magnetite).

## 4.1.2 Matrix analyses

### *IR transmitted spectroscopy*

Chwichiya 002, EM 200 and NWA 12957 show small absorptions around 3000 cm<sup>-1</sup> at high temperature (> 250°C) (Fig. 12), suggesting low abundances of phyllosilicates, including cronstedtite, in the TCIs. The hydration signal could also reflect the hydration of amorphous silicates, observed in Chwichiya 002 by HR-TEM. Weak phyllosilicate absorption bands in the 1000 cm<sup>-1</sup> region are also detected for EM 200, for which abundant nanoscale phyllosilicates were observed in the matrix by TEM-EDS (54 vol%) (Table 5). This demonstrates that IR transmission spectroscopy is sensitive to small bulk abundances (<2 vol%) of phyllosilicates, including the abundance of TCIs in the matrices of the meteorites. IR transmission analyses also allow the detection of carbonates around 1500-800 cm<sup>-1</sup>. NWA 11750 shows low IR absorption of carbonates (Fig. 12), while its matrix shows high abundances of carbonates up to 32.6 vol% using FEG-SEM/TEM (Table 5). IR transmitted spectroscopy is a useful tool to detect phyllosilicate as well as the cronstedtite in TCIs but is limited for the detection of carbonate. It is also unable to detect magnetite and sulfides (troilite, pentlandite, pyrrhotite), which are common products of aqueous alteration in carbonaceous chondrites.

### *Defocused EMP analyses in the matrix*

This technique allows for an initial characterization of the general alteration state and hydration of the meteorite groups, CV being the most metamorphosed, and CM/CI showing the highest abundance of secondary hydrated phases. With the four studied meteorites plotting close to CI (EM 200), CM and CO (Chwichiya 002 and NWA 12957), as well as CV chondrites (NWA 11750) (Fig. 11), this method is not adequate to directly characterize the aqueous alteration state of chondrites, because it is too highly influenced by other parameters. EMPA totals show deviations compared to bulk analytical methods due to the influence of the different densities of the various phases in the matrix on the quantification results (e.g., Zanda et al., 2018), and a

737 density correction should be added to improve the results (Zanetta et al., 2019). Defocused  
738 EMPA totals can be lowered by the content of magnetite ( $\text{Fe}_3\text{O}_4$ ) falsely reported as FeO, and the  
739 presence of organic matter (high in the studied chondrites, even if no quantification has been  
740 done on carbon). An additional complexity is the presence of metal counted as FeO, which will  
741 artificially increase the total. For Chwichiya 002, EM 200 and NWA 12957, this factor is  
742 negligible as they possess a low abundance of metal ( $\leq 1$  vol%) but it could increase NWA 11750  
743 EMPA totals. The totals can be corrected by using the approximative metal and magnetite  
744 compositions and abundances, although these methods do not seem adequate for the assessment  
745 of the aqueous alteration state of chondrites. In addition, sulfides (troilite, pyrrhotite, pentlandite)  
746 do not influence the EMPA totals but are very sensitive indicators of secondary alteration (e.g.,  
747 Rubin et al., 2007). In conclusion, the alteration stages defined by EMPA totals cannot reflect the  
748 overall alteration stage, as too many factors other than secondary alteration influence the totals,  
749 while major secondary products (sulfides) do not.

### 750 ***Electron microscopy***

751 SEM and TEM are the only instruments that enable observation of the relationships between  
752 the various phases and their locations *in situ*, and EDS mapping gives the chemical compositions  
753 of all different primary and secondary phases (Fig. 9). These techniques allow identification of  
754 metal grains, silicates, and amorphous GEMS-like material as well as incipient crystallization of  
755 known secondary phases, including TCIs, carbonates, secondary sulfides, and magnetite. The  
756 analyses using FEG-SEM and EDS are rapid and allow the study of multiple zones of the matrix.  
757 Nonetheless, the modal abundances obtained from SEM- and TEM-EDS maps are directly  
758 correlated to the spatial resolution of the techniques. The study of matrix using FEG-SEM is  
759 limited to the observation of ca.  $>100$  nm crystals (at 5 kV acceleration voltage). Thus, the nano-  
760 scale fine-grained matrix is not accessible through FEG-SEM mapping. FEG-SEM is used to  
761 determine the most representative area of the alteration state of the chondrite but cannot identify



762 the nano-scale secondary phases. Thus, the modal abundances obtained from FEG-SEM maps  
763 should be taken as the modal abundances of micron-sized and larger materials with an unresolved  
764 "fine-grained mix". The TEM resolution can go down to atomic resolution providing high-  
765 definition imaging that allows the identification of the nano-sized grains in the fine-grained  
766 matrix, with the additional application of EDS and SAED techniques. It can be used to refine the  
767 results of the larger-scale SEM EDS mapping, such as the "fine-grained mix" (Fig. S3). This  
768 "fine-grained mix" was identified as mainly GEMS-like material and TCIs, with smaller  
769 abundance of magnetite, pentlandite, pyroxene, olivine and metal in Chwichiya 002; mainly  
770 carbonates and olivine crystals, with smaller abundance of phyllosilicates, sulfides, magnetite,  
771 metal and pyroxene in NWA 11750; and as mainly nanophyllosilicates and organic matter, with  
772 smaller abundance of sulfides, magnetite, metal, pyroxene and olivine in EM 200.

773 The use of SAED in TEM is crucial as it is the only technique allowing the clear  
774 identification of GEMS-like material, whereas the detection of amorphous material by XRD can  
775 include weakly crystalline phases, and nanoscale intermixed crystals (small TCIs or  
776 phyllosilicates). HR-TEM can also be used to look for incipient alteration of the margins of the  
777 silicate grains as evidence of incipient aqueous alteration. The limitation of TEM studies for  
778 alteration in chondrites is the area of observation related to FIB preparation techniques: typical  
779 section prepared by FIB methods are ca. 60  $\mu\text{m}^2$  and are rarely representative of the matrix  
780 variability present in a meteorite. Careful selection of location of the FIB sections using SEM  
781 mapping can limit this bias. However, the zones of FIB section extraction are usually chosen  
782 away from large porosities to avoid breaking during the FIB section extraction, or away from  
783 large veins or crystals, or even away from zones with unusually monomineral-rich zones, which  
784 creates a sampling bias in the modal abundances estimated from TEM observations. Thus, other  
785 bulk analyses can identify some phases missing from TEM observation, due to an absence of  
786 those phases in the extracted region of the FIB section (e.g., large magnetite grains in EM 200;

787 large carbonates veins in NWA 11750; carbonates in NWA 12957 and Chwichiya 002) (Table 7).  
788 In conclusion, TEM allows the identification of all primary and secondary phases from incipient  
789 aqueous alteration, and thus the characterization of primitive chondrites, but should be used in  
790 combination with larger scale instruments such as SEM and/or XRD.

## 791 **4.2 The alteration state of the studied chondrites**

### 792 **4.2.1 Metamorphism**

793 Using Raman spectroscopy, Chwichiya 002, NWA 11750 and NWA 12957 show a  
794 petrologic type <3.00. Raman parameters are closer to those of type 2 chondrites having  
795 experienced short time heating, probably due to shock, equivalent to R1 (highly primitive with no  
796 structural modifications by heating) and R3 (slight structural modifications induced by a weak  
797 heating) from Quirico et al. (2018) (Fig. 3). Meteorites from R2 group (strongly heated  
798 chondrites) are described as potentially dehydrated, while R1 and R3 groups are generally not  
799 dehydrated. Thus, even if the studied meteorites have undergone short time heating, most likely  
800 triggered by shocks or impacts, their Raman spectra parameters do not show evidence of long-  
801 term metamorphism necessary to dehydrate CM chondrites.

802 The Cr<sub>2</sub>O<sub>3</sub> content in ferroan olivine of Chwichiya 002, NWA 11750 and NWA 12957  
803 are close to unmetamorphosed meteorites such as Acfer 094 (C2-ung), Y-81020 and Colony  
804 (both CO3.0 chondrites), and Paris (CM2.7-2.9) (Fig. 4). EM 200 shows higher standard  
805 deviation of the Cr<sub>2</sub>O<sub>3</sub> contents, which is consistent with its Raman spectra parameters that show  
806 a larger variability of short-time heating (Fig. 3). Ebert et al. (2019) show that a long-term peak  
807 temperature of 400-600°C is required to dehydrate CM chondrites.

808 In addition, heated CMs show no hydration absorption on infrared spectroscopy, but the  
809 IR spectra (transmission in matrix) of EM 200 shows a visible 3 μm band, Chwichiya 002 and  
810 NWA 12957 show a slight 3 μm band, but NWA 11750 shows no obvious 3 μm band from

811 hydration (Fig. 12). Finally, the 10  $\mu\text{m}$  absorption band does not reflect a high abundance of  
812 phyllosilicates, strengthening the non-dehydrated by heating hypothesis.

### 813 **4.2.2 Aqueous alteration**

814 The chondrites in this study are classified as type 3 for EM 200 and type 3.00 for the  
815 others, which all show a CO-CM-like petrography. The evolution of aqueous alteration in CM or  
816 CM-like chondrites has been studied extensively (e.g., Rubin, 2015; Suttle et al., 2021 and  
817 references therein). The composition of the alteration products is defined by the primary  
818 composition, but is also influenced by the fluid composition (Velbel et al., 2015). The four  
819 meteorites in this study show variation in both the degree of alteration and their alteration phases,  
820 suggesting different alteration conditions and/or fluid as well as primary compositions.

821 Chwichiya 002 and NWA 12957 show similar petrography as well as similar alteration,  
822 which strengthens their potential pairing. Their potential pairing is yet to be verified, however,  
823 because their oxygen isotopic compositions ( $\Delta^{17}\text{O}=-4.59$  for NWA 12957 and  $\Delta^{17}\text{O}=-3.88$  for  
824 Chwichiya 002) and Raman parameters show differences (Fig. 3). They show alteration with  
825 micron-sized aggregates of TCIs (Fig. 8a, Fig. 9a), and low abundances of carbonates, magnetite,  
826 and secondary sulfides (pyrrhotite, pentlandite) (Table 5). They show abundant amorphous  
827 material on PSD-XRD analyses, with GEMS-like materials identified using SAED in Chwichiya  
828 002, and extensive estimated porosity on TEM observations (Fig. 10, A1-A3). In addition, they  
829 have a low abundance of metal preserved from alteration ( $\leq 1$  vol%), probably dissolved or  
830 transformed into magnetite (Table 5). These meteorites suggest aqueous alteration by a fluid  
831 dissolving metal grains and troilite, while not completely altering amorphous materials to  
832 phyllosilicates, and crystalizing a low abundance of TCIs, carbonates, magnetite, and secondary  
833 sulfides (pentlandite, pyrrhotite). Small error bars of Raman parameters (Fig. 3) and small RSD  
834 of bulk major composition (Table 2) suggest homogenous alteration of the meteorites.

835 NWA 11750 shows abundant unaltered metal grains (3 vol% in the matrix) and primary  
836 troilite and pyrrhotite sulfides (~3 vol%), with a low abundance of phyllosilicates (serpentine),  
837 and no TCIs or magnetite (Table 5). NWA 11750 contains abundant carbonate in its matrix (Fig.  
838 2). It does not display GEMS-like materials (Table 5) and does not show a hydration signature in  
839 IR spectra (Fig. 12). All these characteristics attest to a minimally altered matrix, except for the  
840 absence of GEMS-like materials. Besides carbonates, NWA 11750 matrix is largely composed of  
841 nanocrystals of olivine (Fig. 10 B1, B3). NWA 11750 matrix composition can be interpreted as  
842 an alteration from CO<sub>2</sub>-rich aqueous fluid, dissolving any GEMS-like material that might have  
843 been present and/or converting it to phyllosilicates, while preserving metal and sulfides (troilite),  
844 and crystallizing abundant carbonates, similar to that observed in some CM chondrites  
845 (Tsuchiyama et al., 2021). NWA 11750 is an exceptional chondrite in view of its high amount of  
846 extraterrestrial carbonates in the matrix that contrasts with an overall very subtle aqueous  
847 alteration, making it a sample of choice to study CO<sub>2</sub> and Ca-rich aqueous fluid-assisted  
848 alteration, that could also give insight into the carbonate formation on CM-like asteroids such as  
849 Bennu (Kaplan et al., 2020). Both Raman parameters (Fig. 3) and bulk major composition (Table  
850 2) suggest homogenous alteration of NWA 11750.

851 EM 200 shows a different alteration style, with abundant preserved primary sulfides  
852 (troilite), and no amorphous phases, nor TCIs and carbonates. It shows a high abundance of  
853 magnetite, with 10.7 vol% by magnetic analyses (Table 1). TGA and defocused EMPA totals  
854 both indicate abundant organic matter in the matrix, which is also observed by TEM associated  
855 with abundant nanophyllosilicates (Fig. 10 C1, C2). EM 200 is the least primitive of the four  
856 studied meteorites, with a higher degree of metamorphism and aqueous alteration. Both Raman  
857 parameters (Fig. 3) and bulk compositions (Table 2) also suggest a more heterogeneous alteration  
858 compared to the other three meteorites. It was altered by a fluid dissolving any primary

859 amorphous phases that might have been present, while preserving primary troilite, and  
860 crystallizing abundant magnetite, with a low abundance of serpentine and carbonates.

### 861 **4.3 Aqueous alteration in CM-like chondrites**

#### 862 ***GEMS-like assemblage***

863 Glass with Embedded Metal and Sulfide (GEMS) are oxygen-rich amorphous materials,  
864 of ~50-500 nm diameter, found in interplanetary dust particles IDPs. They are dominated by a  
865 Mg-rich and Fe-poor amorphous silicate with nanoscale sulfides (pyrrhotite) and metal  
866 (kamacite) inclusions, typically ~a few to 10 nm diameter, with often admixed carbon (Bradley  
867 1994; Dobrică et al., 2012). So far, GEMS are identified in cometary-type (anhydrous chondritic  
868 porous) IDPs and ultracarbonaceous micrometeorites (UCAMMs) (Bradley 1994, 2013; Dobrică  
869 et al., 2012; Ishii et al., 2018). GEMS are thought to be radiation-processed presolar dust  
870 condensed prior to the presolar molecular cloud (Bradley 1994), and/or highly processed presolar  
871 interstellar dust condensed from the proto-solar nebula (Ishii et al., 2018), and/or condensed in  
872 the cold presolar molecular cloud and/or in the outer protoplanetary disk (Keller and Messenger  
873 2011).

874 Large abundance of amorphous silicates has been found in the matrices of primitive CR  
875 chondrites (Brearley 1993; Abreu and Brearley 2010; Le Guillou et al., 2015b; Le Guillou and  
876 Brearley 2014; Vollmer et al., 2020; Zanetta et al., 2022), as well as in several other  
877 carbonaceous chondrites (Brearley 1993; Vollmer et al., 2009; Nguyen et al., 2010; Nittler et al.,  
878 2013). Some of the least altered, most primitive carbonaceous chondrites show extremely fine-  
879 grained amorphous silicate with embedded metal and sulfides, resembling GEMS assemblages  
880 (Bradley 1994; Greshake 1997; Noguchi et al., 2017; Hopp and Vollmer 2018; Chizmadia and  
881 Brearley 2008), often referred to amorphous or GEMS-like materials (Barber 1981; Hewins et al.,  
882 2014; Marrocchi et al., 2014; Leroux et al., 2015; Rubin 2015; Vollmer et al., 2020; Zanetta et  
883 al., 2021; Ohtaki et al., 2021; Villalon et al., 2021). Those GEMS-like phases found in chondrites

884 are comparable to the GEMS assemblages found in IDPs, i.e. they consist of an amorphous  
885 silicate with embedded metal and sulfide inclusions. GEMS-like phases identified in Chwichiya  
886 002 are similar to GEMS-like phases found in the most primitive meteorites but differ in their  
887 higher Fe-content of the amorphous matrix, larger troilite and metal inclusions, and show larger  
888 sizes than IDPs GEMS phases.

889         Those GEMS-like materials could be the primary component of the chondritic matrix as  
890 they are observed in the most primitive micrometeorites, and in the most primitive CM, CR, CO  
891 and ungrouped chondrites such as Acfer 094 and ordinary chondrites. GEMS-like phases are  
892 thought to be the first phases to be dissolved by aqueous alteration, through leaching and  
893 oxidization, and are recrystallized in nanophase assemblages of hydrated phyllosilicates and  
894 secondary sulfides (e.g., Le Guillou et al., 2015; Noguchi et al., 2017; Vacher et al., 2019b).  
895 Their presence in Chwichiya 002 attests that the meteorite is relatively well preserved from  
896 aqueous alteration and thermal metamorphism. One of the least altered CM chondrites, Paris,  
897 contains a primitive lithology, classified as type 2.9 that contains abundant GEMS-like materials  
898 (Marrocchi et al., 2014; Hewins et al., 2014; Leroux et al., 2015; Rubin, 2015) (Table 8).  
899 Recently, Kimura et al. (2020) proposed three meteorites as the closest ones to theoretical  
900 CM3.00: Asuka (A) 12085 (CM2.8), A 12236 (CM2.9) and A 12169 (CM3.0). The Asuka  
901 meteorites contain abundant amorphous materials with sulfides and enstatite whisker inclusions  
902 in the matrix observed using TEM, suggesting a lower degree of alteration than the most  
903 preserved lithology of Paris (Noguchi et al., 2020). High abundances of amorphous phases are  
904 detected in Chwichiya 002 and NWA 12957 by PSD-XRD (12-23 vol%) (Table 3). GEMS-like  
905 materials are unambiguously identified in Chwichiya 002 and show amorphous structure on  
906 SAED (Fig. 10 A3), showing less recrystallization with aqueous alteration, as attested by more  
907 diffuse rings, than the most preserved lithology in Paris (Leroux et al., 2015), being similar to A  
908 12169 (Kimura et al., 2020). The high Ca content of the amorphous phases of Chwichiya 002 can

909 be created by terrestrial reactions, as those meteorites show a slight terrestrial weathering,  
910 potentially crystallizing small abundance of terrestrial carbonates.

### 911 ***Metal***

912 Most type 3.00 carbonaceous chondrites show abundant metal grains (>2 vol%) as  
913 observed in some C-ung meteorites (Davidson et al., 2019; Greshake, 1997; Kooten et al., 2018;  
914 Noguchi et al., 2017; Rubin, 2012, 2015; Rubin et al., 2007; Scott and Krot, 2005; Singerling and  
915 Brearley, 2018), A 12169 (> 2 vol%), A 12236 and A 12085 (1-2 vol%) (Kimura et al., 2020), or  
916 Paris (1.2-3 vol%) (Hewins et al., 2014; Rubin, 2015). In general, metal abundance decreases  
917 with aqueous alteration, and is thus thought to be a primary constituent of chondrites (Rubin et  
918 al., 2007), although tetrataenite or awaruite could be produced by secondary processes in CVs  
919 (Bonal et al., 2020). The meteorites in this study have variable metal abundances: NWA 11750  
920 shows 3 vol% by XRD, close to the most preserved lithology in the Paris meteorite, and higher  
921 than A 12169; Chwichiya 002 and NWA 12957 both contain 1 vol% by XRD, similar to the  
922 abundance of metal in A 12085 and the least preserved lithology in Paris; EM 200 contains <1  
923 vol% by XRD (Table 8). Point counting of metal is efficient for the estimation of the metal  
924 abundance as it is direct observations for grains <1  $\mu\text{m}$ . For the studied meteorites, point counting  
925 of the metal gave similar results as the XRD data (Table 1). The use of the metal content as an  
926 indicator of aqueous alteration could be questioned in view of the observations in the matrix of  
927 NWA 11750. The metal grains are subhedral to euhedral (Fig. 11b), with relatively large sizes  
928 (10-200 nm) compared to surrounding matrix crystals. These two characteristics point to  
929 secondary rather than primary constituents of the matrix, although those grains show mainly  
930 kamacite and tetrataenite composition.

### 931 ***Porosity of the matrices***

932 The high porosity observed in the highly primitive meteorite Acfer 094 suggests that  
933 primitive chondrites may have contained a lot of water-ice-filled pores during accretion

934 (Matsumoto et al., 2019). The matrices of the least altered chondrites consist mostly of GEMS-  
935 like or amorphous materials with high porosity (Leroux et al., 2015; Kimura et al., 2020; Suttle et  
936 al., 2021). During aqueous alteration, this porosity is filled with fine-grained to fibrous  
937 phyllosilicates or small TCIs (Leroux et al., 2015). Following Figure 15 in Leroux et al. (2015),  
938 describing the filling of the porosity around GEMS-like materials by TCIs or fine-grained  
939 phyllosilicates, Chwichiya 002 FIB section observations correspond to the second stage of  
940 incipient alteration, with fine grained TCIs forming in the porosity around the amorphous phases,  
941 with remaining porosity between the GEMS-like materials (Fig. 8a). Nevertheless, estimated  
942 porosity measurements using microscopy are highly scale dependent, which has to be taken into  
943 consideration when estimating porosity using SEM and STEM. The choice of the FIB sections  
944 for the TEM studies are usually made away from large porosity to avoid breaking during the FIB  
945 section extraction, which creates a sampling bias in the TEM porosity estimation.

#### 946 *TCIs*

947         Depending on the environment and the fluid composition, the dissolution of GEMS-like  
948 materials associated with the alteration of metal grains can be expected to form sulfides  
949 (tochilinite), phyllosilicates (cronstedtite) and/or magnetite (Palmer and Lauretta, 2011; Pignatelli  
950 et al., 2016, 2017). Those phyllosilicates and sulfides form finely intermixed materials (TCIs)  
951 that replaced most of the primary matrix (Rubin et al., 2007; Vacher et al., 2019b; Zolensky et al.,  
952 1993; Suttle et al., 2021). TCIs are used as proxies for the determination of CM chondrite  
953 subtypes (Rubin, 2015). The Paris type 2.9 lithology, A 12169 and A 12236 do not show TCIs,  
954 while A 12085 has minor TCIs, as is also observed in NWA 11750 and EM 200. Chwichiya 002  
955 and NWA 12957 show abundant TCIs (5.3-22 vol%), resembling the Paris least preserved  
956 lithology type 2.7 ( $12 \pm 3$  vol%) (Table 8).

#### 957 *Sulfides*



958           Whether the origin of the different sulfides in carbonaceous chondrites is primary or  
959 secondary is still uncertain. Indeed, pyrrhotite and pentlandite in CM can represent primary high-  
960 temperature phases (Schrader et al., 2016; Singerling and Brearley, 2018). In addition, GEMS, by  
961 definition, contain sulfides, present only as pyrrhotite. Conversely, the ratio of troilite compared  
962 to pentlandite and pyrrhotite is a criterion for defining the alteration subtype of chondrites, with  
963 major troilite for the least altered chondrites, and secondary euhedral pyrrhotite grains  
964 characteristic of secondary processes (McSween, 1979b; Rubin et al., 2007). The A 12169, A  
965 12236 and A 12085 chondrites contain troilite, but Paris contains mainly pyrrhotite and  
966 pentlandite (Table 8). Thus, in this study, when possible, we distinguished troilite as a primary  
967 phase and pentlandite/pyrrhotite as secondary phases, but this separation remains disputable. For  
968 techniques that did not allow distinction between sulfides (troilite, pyrrhotite, pentlandite), we  
969 postulate that sulfides count as secondary phases, as used as a proxy of secondary alteration  
970 (Rubin et al., 2007). EM 200 contains troilite, with no trace of pentlandite nor pyrrhotite, and  
971 abundances similar to A 12236 and A 12085; NWA 11750 has a similar abundance of troilite and  
972 pyrrhotite, but no pentlandite; and Chwichiya 002 and NWA 12957 contain rare troilite with  
973 dominant pentlandite, with abundance closer to the Paris meteorite (Table 8).

#### 974 ***Phyllosilicates***

975           With increasing aqueous alteration, TCIs are recrystallized into larger phyllosilicate  
976 aggregates of 20-60  $\mu\text{m}$ , associated with larger secondary euhedral pyrrhotite grains (McSween,  
977 1979b; Rubin et al., 2007). Afterward, pseudomorphic phyllosilicate crystals start to replace the  
978 anhydrous silicates (pyroxene and olivine). Ferroan olivines are altered faster than magnesian  
979 olivine (Wogelius and Walther, 1992; Hanowski and Brearley, 2001; Zolensky et al., 1993;  
980 Pignatelli et al., 2016), as ferroan olivines are altered from margin inwards, in contrast to  
981 magnesian olivine which suffer meshwork replacement, forming Fe to Mg-rich serpentine

982 (Velbel, 1993; Velbel et al., 2015; Wicks et al., 1977). Therefore, phyllosilicates are a major  
983 proxy for identification of chondrite subtypes (Rubin et al., 2015).

984 In the Asuka chondrites discussed above, only A 12085 (type 2.8) shows small serpentine  
985 detection with XRD, and in the Paris meteorite, the type 2.7 lithology shows abundant serpentine  
986 (Table 8). The four studied chondrite meteorites show minor serpentine detected by XRD (Table  
987 3), Chwichiya 002 and NWA 12957 having 2-6 vol% of phyllosilicates; and NWA 11750 and  
988 EM 200 2 vol% (Table 8), closer to A 12169, A 12236, and A 12085. Even if TCIs are counted  
989 separately in modal abundances, the abundance of serpentine by XRD comprises both serpentine  
990 from olivine alteration and cronstedtite from the TCIs, explaining the high phyllosilicate  
991 abundances for Chwichiya 002 and NWA 12957. Although no detection of phyllosilicates is  
992 made in A 12169 (3.0) by XRD, TEM observations show small phyllosilicates in the matrix  
993 (Noguchi et al., 2021). Finer grained phyllosilicates (serpentine and cronstedtite) might not be  
994 detected by XRD, but are visible by TEM, even in type 3.0 meteorites, as seen for A 12169 and  
995 the four meteorites of this study.

#### 996 ***Carbonates***

997 Carbonates crystallize during the earliest stages of alteration, generally in the form of calcite  
998 (e.g., Lee et al., 2014; Howard et al., 2015). First generation carbonates fill void spaces in the  
999 meteorite, whereas later carbonates replace primary anhydrous silicates and grow on already  
1000 existing secondary phases. Carbonates are found in altered subtypes <2.7 chondrites (Rubin,  
1001 2015). A 12169, A 12236 and A 12085 and the most primitive Paris lithology contain rare to no  
1002 carbonate, while the more altered Paris lithology contains 1-3 vol% carbonate (Table 8). EM 200  
1003 shows no traces of carbonates, similar to the referenced Asuka meteorites and the Paris primitive  
1004 lithology (Table 8). NWA 12957 and Chwichiya 002 contain 1-3 vol% carbonates (estimated by  
1005 XRD), comparable with the most altered Paris lithology. TEM observations of NWA 11750  
1006 contain extremely abundant fine-grained carbonates filling the porosity in between olivine along

1007 with fine grained phyllosilicates (Fig. 8b, Fig. 9b, Fig. 10 B2). Of course, carbonates can be  
1008 produced by terrestrial fluid circulation, and as shown by Tyra et al. (2007), the O-isotopic  
1009 composition of carbonates precipitated from terrestrial fluids plot along the mass-dependent  
1010 terrestrial fractionation line (slope 0.52) with  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values close to 0‰. Large carbonates  
1011 veins in NWA 11750 show  $\delta^{18}\text{O}$  around 30-40 ‰, with slightly negative  $\Delta^{17}\text{O}$  (average -0.63 ‰)  
1012 (Fig. 2), thus isotopic analysis of the carbonates in NWA 11750 showed that their origin is  
1013 extraterrestrial (Fig. 2). We are therefore confident that the majority of the carbonates in NWA  
1014 11750 were not formed by terrestrial alteration. Although, small terrestrial weathering observed  
1015 in NWA 11760 could have produced small abundance of terrestrial carbonates.

#### 1016 *Other primordial and secondary phases*

1017 A hypothetical CM3.00 would contain submicrometric primary silicates such as forsterite  
1018 and enstatite crystals. We observed nanometric to submicrometric crystals of forsterite and  
1019 enstatite in the four meteorites of this study (Fig. 7 and Fig. 8). Hypothetical CM3.00 matrices  
1020 would contain micron scale Ca-Al-rich inclusions (CAIs) and abundant presolar grains (Bland et  
1021 al., 2007), although those phases were not studied here. Iron-rich olivine, fayalite (Fa>90), could  
1022 result from aqueous alteration at low temperature (<300°C), as observed in CV and CO  
1023 chondrites (Krot et al., 1998). Even though, NWA 11750 shows abundant olivine in the matrix,  
1024 their Fa content is <30, suggesting no relation to fluid-assisted alteration, or a different fluid from  
1025 CV alteration. The abundant NWA 11750 olivine could be a primary nebular phase, but its  
1026 occurrence as polycrystalline, engrained aggregates could also suggest crystallization during a  
1027 secondary process, whose origin and nature remains undetermined.

1028 In this study, we investigate the most representative matrix of each of the four studied  
1029 meteorites. Of course, chondrites are also considered to be complex breccias, implying multiple  
1030 lithologies with different alteration conditions and degrees (e.g., Lentfort et al., 2020). Therefore,  
1031 a detailed investigation of potential different lithologies and the determination of presolar grain

1032 abundances in the matrices of Chwichiya 002, NWA 12957, NWA 11750 and EM 200 should be  
1033 performed in order to compare all possible lithologies to the several lithologies of Paris, A 12169,  
1034 A 12236 and A 12085, to confirm of their comparison.

## 1035 **5 Conclusion**

1036 We report on four ungrouped carbonaceous chondrites, Chwichiya 002, NWA 12957, NWA  
1037 11750, and EM 200, that show variations in both the degree and products of alteration,  
1038 illustrating different alteration conditions and/or primary constituents. We find that Chwichiya  
1039 002 and NWA 12957 are among the least altered chondrites, with abundant amorphous phases,  
1040 observed as GEMS-like assemblages in Chwichiya 002, and TCIs and sulfides as secondary  
1041 alteration phases. They could represent primitive CM-like chondrites, similar to the A 12169, A  
1042 12269, A 12085 meteorites (CM2.8-3.0), with only incipient H<sub>2</sub>O-rich fluid alteration. NWA  
1043 11750 contains a high abundance of extraterrestrial carbonates in the matrix and is an exceptional  
1044 meteorite to study incipient CO<sub>2</sub>- and Ca-rich aqueous fluid assisted alteration in the early Solar  
1045 System. Its matrix contains no amorphous material, but abundant preserved nanocrystals of  
1046 olivine and metal, with low abundance of magnetite, phyllosilicates and no TCIs, and we would  
1047 suggest a classification as a 2.9 subtype rather than the 3.00 subtype currently used in the  
1048 Meteoritical Bulletin database. EM 200 has a more altered matrix with a high abundance of  
1049 magnetite and nanoscale phyllosilicates, although primary troilite is preserved. Its matrix shows  
1050 no carbonate, no TCIs, and would thus suggest a classification as a 2.8 subtype rather than the  
1051 3.00 subtype currently used in the Meteoritical Bulletin database. The variety of alteration styles  
1052 among the studied samples reflect the variety of primary constituents of chondrites, aqueous  
1053 alteration conditions, and alteration fluid compositions.

1054 In addition, we demonstrate that the characterization of the alteration state of chondrites is  
1055 highly technique dependent. Indeed, some phases that are key to study the incipient aqueous  
1056 alteration of chondrites, such as small TCIs, nanoscale phyllosilicates (serpentine), or amorphous

1057 materials, are challenging to characterize with a number of techniques (e.g., FEG-SEM, IR  
1058 spectroscopy, EMPA or TGA). We show that the search for most primitive chondrites should  
1059 utilize multiple complementary techniques, in order to identify the widest variety of preserved  
1060 primary phases and secondary products, independently of the style of alteration. Our analyses  
1061 indicate that, as a first step, the combination of EMPA ( $\text{Cr}_2\text{O}_3$  content in ferroan olivine) or  
1062 Raman spectroscopy with XRD, is an efficient approach to identify the least altered chondrites  
1063 and characterize their alteration state. Although TEM remains a complex technique, it is the only  
1064 technique allowing nano-scale observation of fine-grained matrices, and a precise localization of  
1065 the start of aqueous alteration (GEMS-like material dissolution and recrystallization into TCIs,  
1066 fine phyllosilicate crystallization, silicate alteration). TEM, being limited by the small-scale of  
1067 FIB sections, should be used in combination with larger scale techniques, such as XRD or SEM,  
1068 to draw conclusions about the bulk meteorite. XRD, and especially PSD-XRD, allows the  
1069 detection of all primordial phases, as well as all various secondary alteration phases with low  
1070 detection limits. We propose that a combined PSD-XRD and TEM approach represents the ideal  
1071 methodology to study the incipient aqueous alteration in primitive chondrites at both the bulk and  
1072 nanometer scale, independently of the large variety of aqueous alteration conditions.

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## 1084 **7 Supplementary materials**

1085 Figure S1: RX tomography mapping of carbonates veins around a chondrule of NWA 11750.  
1086 Blue is the chondrule and yellow represents the carbonates. The hexagonal shapes of the  
1087 carbonates, resembling desiccation patterns, can be observed.

1088 Figure S2: NWA 12957 TGA analyses

1089 Figure S3: NWA 11750 TGA analyses

1090 Figure S4: Chwichiya 002 TGA analyses

1091 Figure S5: EM 200 TGA analyses

1092 Figure S6: HR-TEM image (left) and EDS-TEM (right) images of tochilinite-cronstedtite  
1093 intergrowths with amakinite  $\text{Fe}(\text{OH})_2$  interlayered in EM 200's matrix.

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