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1 DETECTION OF INCIPIENT AQUEOUS ALTERATION IN
2 CARBONACEOUS CHONDRITES

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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 Cr₂O₃ 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 Cr_2O_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}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}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 Cr₂O₃ 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 ≥ 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 CO₂ (pCO₂) 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 (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 μm) 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; MnTiO_3 for Mn and Ti; Cr_2O_3 for Cr; Fe_2O_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 H_2O 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°C for 10
240 minutes. After cooling down, the bead was dissolved in 50 ml of 2N 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 K₂O (<10%) and P₂O₅ (<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 μ -beam mode enabling measurements of IR reflectance
258 spectra of areas of ~ 3 mm². 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 μ m to 2.6 μ 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 μ m². Spectra were measured at 4 cm⁻¹ spectral resolution over a range of 4000-650
265 cm⁻¹. Matrix pieces were chosen under binocular microscope (~ 50 μ 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 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° to 75° (2θ) in steps of 0.033° , for a total counting time of 4 hours; for the polished

294 sections, from 4° to 75° (2θ) in steps of 0.033° , 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, ~ 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° 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 0.24×2.00
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 N₂ 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⁻¹), CO₂ (2450-2240 cm⁻¹), CH
327 (3000-2800 cm⁻¹), H₂O (4200-3000 cm⁻¹) and SO₂/SO₃ (1420-1330 cm⁻¹). 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

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 μm) (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 ‰) (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 ‰ 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 ± 80 μm) (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}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 Cr_2O_3 content of $0.27 \pm$
410 0.12 wt% (n=31) for NWA 11750, 0.32 ± 0.10 wt% (n=16) for NWA 12957, 0.36 ± 0.10 wt%
411 (n=42) for Chwichiya 002 and 0.36 ± 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 Cr₂O₃ 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 Fe²⁺ and Fe³⁺ absorptions at 0.7, 0.9, 1.1 μm, H₂O 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 H₂O 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 H₂O 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 CO₂, 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 SO₂ from sulfides, as well as CO₂ 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 CO₂/CO and CH, from organics; EM 200 has a mass loss of 7.56 wt% with a
500 signature of CO₂/CO and SO₂, 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 CO₂/CO from
502 organics. Finally, the temperature range 770-900°C is assigned to the CO₂/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 μm² were studied for EM 200, Chwichiya 002 and NWA 12957, and
512 five maps of ~225 μm² 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 μm^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 μm 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, H_2O , 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⁻¹ absorbance is due to interlayer H₂O 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⁻¹ region,
598 making it difficult to make a clear mineral identification. The 1000 cm⁻¹ 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⁻¹ (Beck et al., 2014). At 250°C, NWA 11750 matrix
602 shows no hydration around the 3000 cm⁻¹ 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⁻¹ region. The presence of carbonates can be inferred from a band around 1440 cm⁻¹,
605 but mineral identification was not possible since the carbonate mode around 880 cm⁻¹, 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⁻¹ 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⁻¹ even at 250°C, and weak
610 signatures of phyllosilicates in addition to olivine and pyroxene in the 1000 cm⁻¹ region. Finally,
611 EM 200 spectra show low hydration around 3000 cm⁻¹ and low amounts of phyllosilicates in the
612 1000 cm⁻¹ 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 H₂O 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 μm ,
642 0.9 μm , 1.1 μm and 2.3 μm , 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 CO₂ 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 H₂O 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⁻¹ 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⁻¹ 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⁻¹. 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 (Fe_3O_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 (≤ 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 μm^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_2O_3 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_2O_3 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 μm 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 (≤ 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 CO₂-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 CO₂ 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 μm . 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 ± 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 μm , 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 H₂O-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 CO₂- 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 (Cr_2O_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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