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DETECTION OF INCIPIENT AQUEOUS ALTERATION IN CARBONACEOUS CHONDRITES

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ABSTRACT

We discuss if the detection of aqueous alteration depends on the techniques that are used. We apply different methods to estimate the extent of aqueous alteration on four ungrouped carbonaceous chondrites showing limited aqueous alteration and thermal metamorphism: Chwichiya 002, El Médano (EM) 200, Northwest Africa (NWA) 12957 and NWA 11750, classified as C3 or C3.00-ung. The aim is to propose a reliable methodology to identify the most primitive chondrites. Chwichiya 002, NWA 11750 and NWA 12957 display very primitive matrices and could be amongst the most primitive chondrites currently known, similar to the least altered lithologies of the CM chondrites Paris (CM2.9) and Asuka (A) 12085 (CM2.8), A 12236 (CM2.9) and A 12169 (CM3.0). The structure of organic matter and Cr$_2$O$_3$ in ferroan olivines show that the four meteorites have been less heated than the least metamorphosed standard/reference type 3 chondrite, Semarkona (LL3.00), with Chwichiya 002, NWA 12957 and NWA 11750 similar to the CO3.0s, Acfer 094 (C2-ung) and Paris meteorites. Chwichiya 002 and NWA 12957 show similar alteration phases and degree of alteration, with high abundances of amorphous material with embedded metal and sulfide, resembling Glass with Embedded Metal and Sulfide (GEMS)-like materials, and tochilinite-cronstedtite intergrowths (TCIs) as the major alteration phases. The matrix in NWA 11750 contains aggregates of nanoscale olivine crystals and abundant carbonates, observed as micrometer-sized carbonate veins surrounding chondrules, and as nanoscale carbonates mixed with the fine-grained materials. It also contains abundant grains of metal and a low abundance of phyllosilicates. El Medano 200 shows a high abundance of magnetite (~ 10 vol%), nanoscale phyllosilicates, troilite, and organic matter. The variability of the secondary alteration phases in the meteorites suggests different alteration mechanisms, likely depending on both the starting composition of the meteorites and the composition of the fluids of alteration.
Scanning and transmission electron microscopy (SEM and TEM) allow the identification of primitive phases, the composition and spatial distribution of the secondary phases. X-ray diffraction (XRD) can detect alteration products, including some amorphous phases, although this is limited by the small coherence domains of small TCIs and other phyllosilicates. Transmission infrared (IR) spectroscopy can detect phyllosilicate and carbonate, but is ineffective for the detection of amorphous phases, metal, or sulfide. Both matrix defocused electron microprobe analyses (EMPA) and thermogravimetric analysis (TGA) allow detection of hydrated minerals, such as phyllosilicates and carbonates, but are strongly influenced by the presence of organic matter and do not reflect the overall alteration state of a meteorite. We conclude that the assessment of the primitivity of a chondrite is highly technique dependent. We propose a combination of XRD and the Cr$_2$O$_3$ in ferroan olivines or Raman spectroscopy for a rapid characterization of the alteration state of a chondrite, and the detection of the most primitive meteorites. Finally, the combination of XRD and TEM allows for the detection of all primary and secondary phases and represents an ideal methodology for the characterization and detailed study of primitive chondrites and the different types of incipient aqueous alteration.

1 Introduction

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

Although chondrites are nearly all affected by secondary processes (e.g., Barber, 1981; Zolensky and McSween, 1988; Stöffler et al., 1988; Scott et al., 1992; Buseck and Hua, 1993; Brearley, 2006; Marrocchi et al., 2021), the search for the least processed samples has been a long-standing one in meteoritics, as such material would provide access to the physico-chemical conditions in the solar nebula. From this perspective, it is necessary to constrain secondary processes based on robust qualitative and quantitative parameters. Thermal metamorphism leads to known modifications in some carbonaceous chondrites, such as partial or complete dehydration of hydrous minerals (Nakamura, 2005), changes in composition and/or texture of Fe-Ni metal and sulfide phases (Kimura et al., 2008, 2011), and changes of the structure of organic matter (Bonal et al., 2016, 2020). Those modifications can be evidenced by using numerous proxies, such as petrographic characteristics (e.g., Rubin et al., 2007), chemical and isotopic compositions, as well as infrared (IR) and Raman signatures (Tonui et al., 2014; Bonal et al., 2016; Hanna et al., 2020). The latter indicates a temperature range of thermal metamorphism in some carbonaceous chondrites from < 250°C to > 750°C (Nakamura, 2005; Tonui et al., 2014). The source and timing of thermal metamorphism through decay of the short-lived radionuclide $^{26}$Al and/or impact is hard to identify in carbonaceous chondrites (McSween et al., 1988; Grimm and McSween, 1989; Rubin, 2015; Huss et al., 2006; Tonui et al., 2014; Vacher et al., 2018). Besides long term thermal metamorphism through $^{26}$Al decay, some carbonaceous chondrites show evidence of shock metamorphism, which can be observed in deformation and/or transformation of minerals inside chondrites and creates localized melting, metal-troilite mixtures, and changes of abundances of rare gases and volatile trace elements (Bischoff and Stöffler, 1992).
In addition to thermal and shock metamorphism, assessing the extent and nature of aqueous alteration in carbonaceous chondrites is necessary to understand the secondary processes in primitive asteroids. Aqueous alteration of chondrites may have taken place before final accretion (Barshay and Lewis, 1976; Grossman and Larimer, 1974; Lewis, 1972; Prinn and Fegley, 1989; Metzler et al., 1992, Bischoff 1998; Ciesla et al., 2003; Toppani et al., 2005) on temporary protoplanetary bodies, subsequently broken by collisions, scattering the altered materials into the nebula and mixing them with unaltered, anhydrous materials; or after accretion on a parent body formed by unaltered nebular materials (Brown et al., 2000; Browning et al., 1996; Bunch and Chang, 1980; Hanowski and Brearley, 2000, 2001; McSween, 1979a; Tomeoka and Buseck, 1985; Trigo-Rodriguez et al., 2006; Zolensky et al., 1993). The temperature at which aqueous alteration took place is still debated and could range from -10°C to 250°C (Baker et al., 2002; Benedix et al., 2003; Clayton and Mayeda, 1984; Guo and Eiler, 2007; Verdier-Paoletti et al., 2017; Vacher et al., 2019a; Zolensky et al., 1993). Moreover, different mechanisms, such as direct precipitation (Morse et al., 1997) or interface dissolution-precipitation (Morse et al., 1997, 2007; Putnis and Putnis, 2007; Ruiz-Agudo et al., 2014) could be at the origin of aqueous alteration products. These reactions can produce a variety of secondary products (Krot et al., 2021): carbonates (Horita, 2014; Morse et al., 1997, 2007), phyllosilicates, tochilinite-cronstedtite-intergrowths (TCIs), sulfides (and sulfates), magnetite (Pignatelli et al., 2016; Rubin et al., 2007), fayalite (Doyle et al., 2015) and kirschchteinite (MacPherson et al., 2017).

In addition, deciphering the composition of the fluids responsible for the aqueous alteration is not straightforward. Indeed, temperature, oxygen fugacity ($fO_2$), pH, water/rock ratio, as well as the chemical composition of the primary phases, can have an impact on the kinetics of the reactions and the secondary products. For example, formation of tochilinite in CM chondrites requires alkaline conditions, low $fO_2$ and low temperature (Zolensky and McSween, 1988; Vacher et al., 2019b). Indeed, localized variations in geochemical conditions, particularly
in pH, are present in CM chondrites, called “microchemical environments” (Brearley, 2006), as
for example, the alteration fluids in the fine-grained rims and matrix of CM chondrites are
thought to be more alkaline than those in the interior of chondrules (e.g., Chizmadia and
Brearley, 2008, Brearley, 2006). Most CM chondrites are also considered to be complex breccias,
comprising multiple lithologies that preserve differing hydration conditions (e.g., Lentfort et al.,
2020), making classification of their alteration state challenging.

Efforts to quantify the degree of secondary processing in chondrites have resulted in the
definition of a scale, called petrologic type. In 1967, Van Schmuss and Wood proposed a
secondary classification of chondrites based on mineral chemistry (olivine and pyroxene
homogeneity, water and carbon content, Ni in sulfides), petrography (low-Ca pyroxenes
crystallinity, feldspar modal abundance) as well as matrix and chondrule textures. This
classification splits chondrites into 6 petrographic groups, scaling from 1 to 6, with type 3
indicating the most primitive chondrites, based on their aqueous alteration and thermal
metamorphism. This scale is independent of shock metamorphism, which is classified with its
own scale (Stöffler et al., 1988, Scott et al., 1992). Types from 3 to 1 present increasing degrees
of aqueous alteration. Types from >3 to 6 show increasing degree of thermal metamorphism. This
single digit scale is the accepted classification framework for petrologic types used to date, as
attribution of a type for meteorites requires necessary simplification. Nonetheless, this
classification has the disadvantage of separating thermal metamorphism and aqueous alteration,
whereas numerous studies prove they can both occur within a single chondrite (Buseck and Hua,
1993; Kerridge and Bunch, 1979; Krot et al., 1998; Tomeoka and Buseck, 1985; Zolensky and
McSween, 1988; Zolensky et al., 1997; Nakamura, 2005; Tonui et al., 2014). Other
classifications based on various characteristics, such as petrography, textures and chemistry
(Browning et al., 1996; Rubin et al., 2007), bulk element composition (H, C and N) (Alexander et
al., 2013), and/or phyllosilicate content (Howard et al., 2015) can also be used to classify chondrites, but are usually not established for all chondrite groups.

Subtypes of the type 3 chondrites have been defined by Sears et al. (1980) using thermoluminescence parameters. These subtypes can also be separated using the Cr$_2$O$_3$ content of ferroan olivine (Grossman and Brearley, 2005), or Raman spectral properties of the fine-grained matrix (Bonal et al., 2006, 2016). Subtypes between 2 and 3 have also been established for CM chondrites based on petrologic criteria (Rubin et al., 2007; Rubin, 2015; Kimura et al., 2020).

Meteorites with subtype 3.0 to $\geq$3.7 show evidence of both metamorphism and aqueous alteration (Sears and Dodd, 1988; Sears et al., 1995; Bonal et al., 2020). One ambiguity of the current classification is that chondrites considered to be the most primitive are found between types 2.9 and 3.00 (Hewins et al., 2014; Kimura et al., 2020). Also, detecting aqueous alteration is the intrinsic proprieties of the meteorites (e.g., porosity, permeability) and may thus be found only in specific parts of a meteorite (Bland et al., 2009). In addition, the nature and composition of the fluid can vary (e.g., water, calcium rich fluids, partial pressure of CO$_2$ (pCO$_2$) abundance, supercritical fluids), and thus induce a variety of alteration products, making the use of a trans-group aqueous alteration scale difficult. As it depends on the variety of effects of thermal metamorphism and/or aqueous alteration, identifying the most primitive chondrites turns out to be a challenge. In addition, many previously classified chondrites have not been studied in detail according to the most recent classification criteria, implying the existence of potential misclassified meteorites (e.g., Marrocchi et al., 2020). The study of aqueous alteration in meteorites is also of interest in relation to the Hayabusa2 and Origins, Spectral Interpretation, Resource Identification, and Security-Regolith Explorer (OSIRIS-REx) spacecraft to asteroids (162173) Ryugu and (101955) Bennu, respectively. Both missions showed that surface materials from those asteroids were hydrated (Hamilton et al., 2019; Kitazato et al., 2019; Lauretta et al., 2019; Pilorget et al., 2021).
Beyond the limitations of classification scales, the definition of aqueous alteration in chondrites remains vague. There are no widely accepted unique criteria to estimate if a chondrite has suffered aqueous alteration or not. In this paper, we review different methods used to estimate the extent of aqueous alteration in chondrites and apply them to the study of four ungrouped carbonaceous chondrites showing very little aqueous alteration and thermal metamorphism: Chwuchiya 002, El Medano (EM) 200, Northwest Africa (NWA) 12957 and NWA 11750. We discuss whether the detection of aqueous alteration in these chondrites depends on the technique used or the investigation scale. We then propose the most reliable methodology to identify chondrites with no trace of metamorphism and low degree of aqueous alteration. We also compare the chondrites of this study to the chondrites long considered as the least aqueously altered and metamorphosed and show that three of the four chondrites in this study could be part of the most primitive material in the current meteorite collection.

2 Methodology

2.1 Samples

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

2.2 Petrography

Optical maps of the four meteorites were made with a Leica DM2500P petrographic microscope, using reflected light on thick polished sections. Backscattered Electron (BSE) images were taken with a scanning electron microscope (SEM) for all meteorites with a Hitachi S3000-N at the Centre Européen de Recherche et d’Enseignement en Géoscience de l’Environnement (CEREGE). Higher-resolution SEM images and element maps were made with a Field Emission Gun
(FEG) microscope Jeol JSM 7900F equipped with an EDS (Energy-dispersive X-ray spectroscopy) XFlash 6/60 detector at Centre Interdisciplinaire de Nanoscience de Marseille (CINaM) laboratory. Elemental maps were done using a probe current of 10 nA, an acceleration voltage of 5 kV and 20 min counting time.

Focused Ion Beam (FIB) sections were extracted from Chwichiya 002 at IEMN, University of Lille, using a dual-beam Thermo-Fisher Strata DB235 workstation; and NWA 11750 and EM 200 FIB sections were extracted at CP2M (Centre Pluridisciplinaire de Microscopie Électronique et de Microanalyse) Marseille using a dual-beam FIB (FEI Helios 600 Nano Lab), with a Gallium (Ga⁺) ion beam, starting with 30 keV current. To limit the damage and amorphization of the slide faces under the ion beam, the current is reduced to 5 keV for thinning and then 1 keV for final cleaning. TEM observations of the FIB sections were made on a Thermo-Fisher Titan Themis S/TEM at the microscopy platform of the University of Lille for HAADF imaging and EDS mapping. Elemental maps were obtained using a four-quadrant, windowless, super-X SDD EDS detector with a probe current of 300 pA, an accelerating voltage of 300 keV, and a counting time of ~20 min. The uncertainties are of the order of 3% for major elements in silicates (O, Si, Mg and Fe-, and ~20% for the minor elements (Al, Ca, Mn, Cr).

High-resolution TEM (HR-TEM), and selected area electron diffraction (SAED) patterns were made on a TEM Jeol JEM-2010 at CINaM laboratory.

2.3 Modal abundances

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

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

2.5 Bulk major and trace elemental analyses

Around ~50 mg of powdered samples were divided in 3 fractions to evaluate the possible chemical heterogeneity of the samples. Each subfraction was mixed with ~0.3 g of a 4:1 ultrapure metaborate-tetraborate mixture. The mixture was heated in a graphite crucible at 1000° C for 10 minutes. After cooling down, the bead was dissolved in 50 ml of 2N HNO$_3$ with a stirring magnet for 5 hours. Major element oxide concentrations were determined by measuring solutions on an ThermoScientific iCAP 7000 Series inductively coupled optical emission mass spectrometer (ICP-OES) at Laboratoire G-Time at ULB. Yttrium was used as internal standard and the calibration curves
were obtained on artificial multi-element standards. Natural standards from USGS (BHVO-2, RGM-2) were used for quality control. The external reproducibility expressed as relative standard deviation (RSD) for individual oxide, based on 5 replicates of BHVO-2 and RGM-2 was better than 2%, except for K2O (<10%) and P2O5 (<13%).

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

2.6 Infrared (IR) spectroscopy

IR reflectance spectroscopy was performed at the Institut de Planétologie et d’Astrophysique de Grenoble (IPAG), using the SHADOWS instrument (Potin et al., 2018). The instrument was used in normal standard mode as well as in a μ-beam mode enabling measurements of IR reflectance spectra of areas of ~3 mm². Spectra were measured under nadir incidence and with an observation angle of 30°. Spectra were normalized to infragold™ and spectralon™. Each spectrum was measured from 0.3 µm to 2.6 µm, with a step of 20 nm.

Infrared transmitted spectra were obtained at IPAG at Grenoble France, using a Bruker Hyperion 3000 infrared microscope and a Vertex 70V Fourier transform infrared spectroscopy (FTIR) spectrometer. The infrared beam was focused through an 15x objective, creating a spot on the sample of 50x50 µm². Spectra were measured at 4 cm⁻¹ spectral resolution over a range of 4000-650 cm⁻¹. Matrix pieces were chosen under binocular microscope (~50 µm) and transferred onto a 3×0.5 mm type IIa synthetic diamond window. The pieces were then crushed by another diamond window. Spectra of the four chondrites were also acquired from powdered samples. The window containing the most crushed pieces with optical shapes was analyzed in an environmental cell enabling exposure
of the sample to a vacuum (10^{-6} \text{ mbars}). Infrared transmission spectra were acquired under vacuum at
20°C, at 100°C and 250°C or 300°C, in order to progressively remove the effect of adsorbed ambient
water and study the meteorites under “dry conditions” (Beck et al., 2010).

2.7 \textbf{Raman spectroscopy}

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

2.8 \textbf{Magnetic analyses}

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

2.9 \textbf{X-ray Diffraction (XRD)}

XRD analyses were conducted on both a polished section and bulk powder for NWA 11750
and NWA 12957, in order to see differences between the two sample preparation methods. For EM
200, analyses were made on a polished section, and for Chwitchen 002 on a powdered sample.
Classical XRD analyses were carried out with an X'Pert Pro MPD diffractometer (Panalytical)
equipped with a cobalt tube (\lambda = 1.79 \text{ Å}) operating at 40 kV and 40 mA, with a \theta - 20 goniometer, at
CEREGE. A rotation of the samples (powders and sections) in the horizontal plane at 15 rpm was
used in order to improve the counting statistics. The powders were placed on Si supports (non-
diffracting), using a few drops of ethanol, in order to obtain a thin and homogeneous layer of crystals,
and the polished sections were fixed on circular supports. Analytical conditions were for powders,
counting from 5° to 75° (2θ) in steps of 0.033°, for a total counting time of 4 hours; for the polished
sections, from 4° to 75° (2θ) in steps of 0.033°, and a total counting time of 5 hours. Mineral identification was done using the X’Pert Highscore Plus (Panalytical) software and the ICDD’s PDF2 database.

Additional PSD-XRD analyses were conducted on powder samples for all four meteorites at the Natural History Museum, London. For each meteorite, ~50 mg of powder was packed into an aluminum sample holder and analyzed using an Enraf-Nonius PDS120 X-ray diffractometer with an INEL curved 120° position-sensitive-detector (PSD-XRD). Cu-Kα₁ radiation was selected with a Ge <111> monochromator, and the size of the primary beam on the sample was restricted to 0.24×2.00 mm using a set of post-monochromator slits. Samples were rotated throughout the analyses and XRD patterns were collected from each meteorite for 16 hours, and from terrestrial mineral standards under the same analytical conditions for 30 minutes. Mineral abundances in the meteorite powders were determined using a profile-stripping method that has previously been described in detail (Bland et al., 2004; Howard et al., 2009; King et al., 2015). Briefly, the XRD pattern of a mineral standard was scaled to the same measurement time as the meteorite analysis (i.e., ×32) and then reduced by a factor in order to match its intensity in the pattern of the meteorite. The standard XRD pattern was then subtracted, leaving a residual meteorite pattern. This process was repeated for all phases identified in the meteorite until there were zero counts remaining in the residual and the sum of the fit factors was one. Fit factors were corrected for relative differences in X-ray absorption to give a final volume fraction in the meteorite (Cressey and Schofield, 1996). Uncertainties in the mineral abundances are typically <1% (King et al., 2015).

2.10 Thermogravimetric analysis (TGA-DSC)

Thermogravimetric and Differential Calorimetry analysis (TGA-DSC) were performed using a Mettler-Toledo TGA-DSC3+ instrument at the Institute des Sciences de la Terre (ISTerre, Grenoble, France). 50 mg of each sample was manually crushed with an agate mortar in order to obtain a fine powder. 35mg of this powder was then measured in a 70 µL alumina crucible under a 50mL/min inert
N$_2$ atmosphere. The temperature was increased from 25°C to 1075°C at a heating rate of 10°C/min. FTIR spectra of the degassed species were measured every 23 s over a period of 120 min. From the resulting TGA mass loss curve, the first derivative (DTG) curve can be calculated, which allows for a better visualization of temperature regions associated with strong mass losses. This, coupled with the IR spectra measured of the degassed phases, provides information about the quantity and type of hydrated mineral in the sample. The IR spectra are interpreted by integrating over wavelength ranges of specific chemical compounds of interest and looking at the evolution of these peak areas over time. The wavelength ranges of interest used here are CO (2240-2040 cm$^{-1}$), CO$_2$ (2450-2240 cm$^{-1}$), CH (3000-2800 cm$^{-1}$), H$_2$O (4200-3000 cm$^{-1}$) and SO$_2$/SO$_3$ (1420-1330 cm$^{-1}$). For correction of background noise, several measurements of empty crucibles were performed and later subtracted from the TGA curves of the samples. To get boundaries on the evolution of the chemical compound peak areas in the IR spectra, the same wavelength ranges as mentioned above are assessed for the empty crucible, and the average and standard deviation are determined for each compound. This is done for all empty crucible measurements, and an average standard deviation is determined. The boundaries are shown as green dotted lines in the plots (Fig. S4-7).

### 2.11 X-ray computed tomography

Two chips of NWA 11750 were imaged on a Zeiss Versa 620 XRM at 100 kV and 12 W at the University of Texas High Resolution X-ray CT (UTCT) facility. For the smaller chip, 3001 views were collected on the 0.4× objective with an acquisition time of 5s per view. A LE2 filter was used and a beam hardening correction of 0.3 was applied during reconstruction and the final voxel size was 3.00 µm. The larger chip was imaged using the flat panel detector with 9001 views and a 0.05 s acquisition time per view. A LE3 filter was used and a beam hardening correction of 0.25 was applied during reconstruction with a final voxel size of 4.50 µm.
Carbonate oxygen isotopic compositions were analysed using a CAMECA IMS 1270 E7 at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) laboratory in Nancy, France. A Cs+ primary ion beam (~15×10 µm spot area) with a current of ~5 nA was used in order to collect $^{16}$O–, $^{17}$O– and $^{18}$O– secondary ions in multi-collection mode using three Faraday cups (L’2, FC2 and H1). Charge compensation was applied using a normal-incidence electron gun. Mass Resolving Power (MRP = M/ΔM) was adjusted to ~7000 to resolve interference from $^{16}$OH– on the $^{17}$O– peak and achieve maximum flatness on the top of the $^{16}$O– and $^{18}$O– peaks (entrance and exit slits of FC2 were adjusted to ~70 µm and ~170 µm, respectively). $^{16}$O– and $^{18}$O– secondary ions were collected on L’2 and H1, respectively (slit 1, MRP ≈ 2500). Pre-sputter on a large area (~20×20 µm) was applied before each measurement during 60 s, to remove carbon coating at the surface of the calcite grains. Acquisition time was set to ~5s, and measurements were repeated over 30 cycles to achieve counting statistics ~0.2‰ (1σ) for δ$^{18}$O and ~0.3‰ for δ$^{17}$O. Isotope ratios ($^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O) are presented in per mil (‰) relative to Standard Mean Ocean Water (SMOW):

$$\delta^x_{\text{SMOW}} (\text{‰}) = \left( \frac{x_{\text{Sample}}}{x_{\text{SMOW}}} - 1 \right) \times 1000 \quad (1)$$

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

3.1 Petrographic description

The petrographic characteristics of the studied chondrites are reported in Table 1. Chwichiya 002, NWA 11750, and NWA 12957 show overall CM-like petrography (Fig. 1), with high matrix abundance (63.3-74.0 vol%), low chondrule abundance (12.9-26.0 vol%), and small chondrule apparent diameter (average in the range 240-480 µm) (Table 1), but differ from CM chondrites in their bulk oxygen isotopic compositions and lack of evidence for significant aqueous alteration (Gattacceca et al., 2020). No amoeboid olivine aggregate (AOA) or calcium-aluminum rich inclusions (CAIs) were observed in those meteorites. They were approved as type 3.00, based on the absence of detectable phyllosilicates in XRD patterns and IR transmission spectra, as well as Raman spectroscopy of the fine-grained matrix polyaromatic carbonaceous matter reflecting a peak metamorphism temperature lower than that for Semarkona (LL3.00) (Bonal et al., 2016). They show a high FeO content in their matrices: 34.86 wt% for NWA 12957, 34.30 wt% for NWA 11750 and 39.39 wt% for Chwichiya 002 (Table 1). A distinguishing feature of NWA 11750 is the presence of large carbonate veins cutting through the matrix and as cracks in the fine-grained rims all around chondrules (Fig. S1). The position of the carbonate veins around the chondrules suggests hexagonal shapes, resembling desiccation patterns, an observation confirmed by CT data (Fig. S2). Carbonates in NWA 11750 have $\delta^{18}$O values of ~30-40 ‰, with slightly negative $\Delta^{17}$O (average -0.63 ‰) (Fig. 2). Although the carbonate O-isotopic compositions plot within errors on the TFL, they show do not show $\delta^{18}$O and $\delta^{17}$O values close to 0‰ as commonly observed for carbonates resulting from terrestrial weathering (Tyra et al., 2007). Due to the low permeability of CM chondrites (Bland et al., 2009), contamination by the terrestrial water occurs only in fractures, and can be associated with evaporite minerals. The veins in NWA 11750 contain only calcite, with no gypsum. The oxygen
isotopic composition of the calcite at the locations analyzed suggests that it is extraterrestrial in origin. EM 200 (C3 with affinities with CO3) (Ruzicka et al., 2015) has a smaller amount of matrix (44.1 vol%), a high proportion of magnetite (10.7 vol%) and a small chondrule size (130±80 µm) (Table 1). It is classified as a type 3 based on similar characteristics as Chwichiya 002, NWA 11750 and NWA 12957 and shows a lower concentration of FeO in its matrix (23.79 wt%) (Table 1). Because these four chondrites show a similar primitive petrologic type as the ungrouped chondrite Acfer 094, with limited secondary alteration, we followed the protocol in Abe et al. (2017) to look for cosmic-symplectites (COS). We used a polished section of Acfer 094 to verify our method enabled us to identify COS using Fe-S-O EDS mapping. We were able to identify COS in Acfer 094, but no COS was observed in the four chondrites of this study.

3.2 Metamorphic state

The Raman parameters of the structural order of the polyaromatic matter in the matrices show that the studied chondrites appear to be less heated than the least heated type 3 ordinary chondrite Semarkona (LL3.00). Comparison of the Raman spectral parameters with the data from Quirico et al. (2018) show that the four studied meteorites do not show evidence for protracted metamorphic heating due to $^{26}$Al decay observed in type 3 chondrites, but are rather similar to type 2 meteorites such as Murchison with only minor short-term heating probably due to shock (Fig. 3). EM 200 shows a larger variability of heating compared to the other three meteorites, with potentially slightly more heated zones. The ferroan olivine show Cr$_2$O$_3$ content of 0.27 ± 0.12 wt% (n=31) for NWA 11750, 0.32 ± 0.10 wt% (n=16) for NWA 12957, 0.36 ± 0.10 wt% (n=42) for Chwichiya 002 and 0.36 ± 0.24 wt% (n= 30) for EM 200. The mean and standard deviations for Chwichiya 002 and NWA 12957 are close to the data for Acfer 094 (C2-ung) (Newton et al., 1994), while the data for NWA 11750 are close to the Y-81020 (CO 3.0), Colony (CO 3.0), and Paris (CM2) meteorites (Fig. 4) (Grossman and Brearley, 2005; Hewins et al.,
EM 200 has a higher standard deviation for Cr$_2$O$_3$ content of ferroan olivine, setting it apart from the carbonaceous chondrites trend, and close to type 3.1 ordinary chondrites (Fig. 4).

### 3.3 Bulk mineralogy

#### 3.3.1 Bulk compositions

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

#### 3.3.2 Visible near infrared reflectance

The visible-near-infrared (VIS-NIR) reflectance spectra show no strong absorption bands, with only very broad and shallow absorptions around 1 µm (Fig. 6). They do not display 2 µm absorption bands indicative of olivine and pyroxene and have a flat spectral VIS-NIR slope. They all show a reflectance maximum around 600 nm, with a slight positive slope from 1 µm to longer wavelengths. These dark and featureless spectra can be attributed to the high abundance of matrix (44.1, 63.0, 73.4 and 74.0 vol%) rich in phases producing no spectral features (carbonaceous matter, opaques) that can mask silicate absorption bands (Table 1). They are also consistent with the low abundance of chondrules (12.9 – 35.2 vol%), rich in silicates, that would produce deep absorption bands around 1 µm and 2 µm (Table 1). The absorption bands of phyllosilicates
(combination of the $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ absorptions at 0.7, 0.9, 1.1 $\mu$m, $\text{H}_2\text{O}$ absorption at 1.9 $\mu$m, and 2.3 $\mu$m absorption of -OH) are absent from the IR reflectance spectra of the studied samples. Thus, no significant aqueous alteration products can be detected by VIS-NIR reflectance spectroscopy in those meteorites, agreeing with a type 3 classification for all meteorites. Although the absence of large absorption bands is also found in CM chondrite spectra, the overall spectra of the studied meteorites are very different from spectra of CM chondrites (Fig. 6).

**3.3.3 X-ray diffraction**

Semi-quantitative modal abundances were calculated from the XRD and PSD-XRD patterns (Table 3). Errors are around 5 vol% for XRD and 1 vol% for PSD-XRD, depending on the phase and crystallinity. Only modal abundances of crystalline phases could be extracted from XRD patterns and all abundances are normalized to a total of 100 wt%. However, even when amorphous phases could not be quantified in the modal abundances, some were clearly detected on the XRD patterns of Chwihya 002 and NWA 12957, leading to overestimation of the abundances of crystalline phases. The PSD-XRD measurements enabled the estimation of amorphous phase modal abundances by using Cu K-$\alpha$1 radiation. Iron-bearing components influence the fluorescent background, and thus after removing other crystalline phases from the XRD patterns, the contribution of any Fe-bearing amorphous phases can be approximated (Howard et al., 2015; King et al., 2015). For all of the meteorites, XRD patterns of polished sections and powdered samples showed similar minerals phases. Only the semi-quantitative abundances slightly vary, by no more than 5 vol%, depending on the sample preparation. This is within the error due to quantitative analysis of the patterns, as these abundances are only semi-quantitative. Primary phases such as olivine, pyroxene, and clinopyroxene are detected in all meteorites in variable abundance. Metal was not detected in EM 200 and Chwihya 002, in contrary to NWA 11750 and NWA 12957 where small metal abundances were detected (Table 1). NWA 12957 shows a high abundance of amorphous phases (23 vol%), phyllosilicates (Fe-
rich serpentine) (6 vol%), and minor carbonates (3 vol%), magnetite (2 vol%), pyrrhotite (2-5 vol%) and troilite (1 vol%). Chwuchiya 002 shows a high abundance of amorphous phases (12 vol%), with phyllosilicates (Fe-serpentine) (2-5 vol%) and minor carbonates (1-7 vol%), magnetite (2 vol%), pyrrhotite (3 vol%) and troilite (3 vol%), resembling NWA 12957. The NWA 11750 XRD patterns indicate the presence of carbonate (2-6 vol%), pyrrhotite (2-6 vol%), troilite (1-5 vol%), metal (kamacite) (1-3 vol%), and phyllosilicates (serpentine) (2 vol% from the PSD-XRD pattern). EM 200 is composed of a high abundance of magnetite (16-20 vol%), troilite (6 vol%), and low abundances of pyrrhotite (1 vol%) and phyllosilicates (Fe-serpentine) (2 vol%). Pentlandite was not detected by XRD in any of the samples.

### 3.3.4 Thermogravimetric analysis

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

Between 0-200°C, all meteorites show loss of adsorbed and loosely bound water that are commonly attributed to terrestrial contamination but could also originate from interlayer water in smectite. As XRD patterns did not detect any smectite in the studied meteorites, we believe this temperature range is only associated with terrestrial contamination. Surprisingly, no meteorites showed IR signature of H₂O at <200°C, which will be discussed in section 4.1.1. The second part of the TGA between 200-400°C is supposedly due to release of H₂O and OH from (oxy)hydroxide minerals, usually linked to terrestrial weathering, although organic matter in the matrix can also increase the mass loss in this temperature range (Gilmour et al., 2019). EM 200
shows a total mass loss of 13.43 wt%, with a signature of CH gases on the IR spectra, probably due to a high concentration of organic matter in the matrix. In this temperature range, NWA 12957 shows a mass loss of 2.96 wt%, with an IR signature of CO₂, which can also be attributed to organic matter. Chwichiya 002 and NWA 11750 show a mass loss of around 3.24 wt% and 1.50 wt% respectively, with no signature on IR, probably due to loss of hydroxyl groups (-OH) from (oxy)hydroxides, according to their more weathered condition. The 400-770°C temperature range is directly correlated to abundance of phyllosilicates, due to the release of hydroxyl groups (-OH) (Garenne et al., 2014), but SO₂ from sulfides, as well as CO₂ and CH from organics in the matrix increase the mass loss. NWA 11750 shows a significant mass loss of 8.55 wt%, with a signature of CO₂/CO and CH, from organics; EM 200 has a mass loss of 7.56 wt% with a signature of CO₂/CO and SO₂, due to sulfides and abundant organics; and Chwichiya 002 and NWA 12957 show a mass loss of 6.81 wt% and 4.85 wt% with an IR signature of CO₂/CO from organics. Finally, the temperature range 770-900°C is assigned to the CO₂/CO release from carbonates (Garenne et al., 2014). EM 200 shows a mass loss of 5.68 wt% at this temperature and the other three meteorites show minimal mass losses < 1.0 wt%.

3.4 Matrix petrography

3.4.1 Electron microscopy

A combination of FEG-SEM, STEM, HR-TEM and SAED was used to identify phases, as well as to document textures and to determine modal abundances in the matrices of the four chondrites. SEM-EDS maps of the four meteorites have been acquired in order to document modal abundances in the matrix at a larger scale (crystals > 100 nm) (Fig. 7). A total of three SEM-EDS maps of ~225 μm² were studied for EM 200, Chwichiya 002 and NWA 12957, and five maps of ~225 μm² for NWA 11750. As all meteorites show heterogeneity in their matrices, we chose the most representative zone for each meteorite to extract the FIB sections used for TEM studies (Fig. S3). For Chwichiya 002, EM 200 and NWA 11750, one FIB section of ~60
μm² for each meteorite was extracted from the matrices in order to conduct High-angle annular
dark-field imaging (HAADF) observations and STEM-EDS mapping. Modal abundance
calculated from SEM-EDS and STEM-EDS maps are reported in Table 5.

On SEM-EDS images, Chwichiya 002 and NWA 12957 show broadly similar textures
with micrometric forsterite and enstatite fragments, troilite, pentlandite, magnetite, and abundant
micrometric TCIs aggregates, all set in a fine nanoscale grained matrix, named here “fine-grained
mix” (Table 5, Fig. 7a and Fig. 7c). The difference in secondary phases between the two
meteorites is the modal abundance of TCIs with 22.0 vol% and 5.3 vol% for Chwichiya 002 and
NWA 12957; and sulfides with 4 vol% and 13.0 vol% for Chwichiya 002 and NWA 12957,
respectively, with both Fe-Ni dominant sulfides. In addition, a minor abundance of metal, mostly
kamacite, is observed in both meteorites. Chwichiya 002 shows a small amount of phosphates
and brucite is observed in NWA 12957. Using STEM-EDS, the observation of the “fine-grained
mix” in Chwichiya 002 allows the distinction of the different phases unresolved by SEM. It is
composed of amorphous materials, TCIs, and a low abundance of forsterite, enstatite, metal, Fe-
oxide, and pentlandite (Fig. 8a, Fig. 9a). Nanosized crystals of troilite are present in low
abundance. The presence of amorphous material is confirmed using SAED that shows patterns
typical of an amorphous material with characteristic diffuse rings (Fig. 10 A3). These amorphous
phases contain abundant metal and sulfide inclusions (Fig. 10 A1, A2). The elemental
composition of the amorphous component in Chwichiya 002 is on average O (63 at%), Si (16
at%), Fe (9.2 at%), Mg (7.3 at%), Al (1.9 at%) and Ca (1.3 at%) (n=5). The assemblage of
amorphous material with inclusions of metal and sulfide resembles Glass with Embedded Metal
and Sulfide (GEMS)-like material. The modal abundances are similar to the ones found in SEM-
EDS maps, except that the STEM-EDS maps show higher porosity in the matrix of Chwichiya
002 (Table 5).
On SEM-EDS maps, NWA 11750 shows micrometric grains of silicates (Mg-rich olivine and enstatite), troilite, kamacite, and tetrataenite grains and micrometric diffuse patches of carbonates and serpentine (Fig. 7d, Fig. S3b). Some larger silicate grains, that may well represent chondrules fragments, can be found with sizes from 10 μm to 1 mm. These grains are set in a large abundance of nanoscale fine-grained mix (Table 5). Pentlandite is found as traces in some matrix zones, although too small to be analyzed. STEM-EDS maps reveals that the “fine-grained mix” of NWA 11750 is composed of carbonates finely intermixed with abundant olivine, a few enstatite grains, Mg-rich serpentine, and subhedral to euhedral taenite metal grains (Fig. 8b, Fig. 9b). The studied FIB section STEM-EDS map shows two types of olivine: small nanoscale olivines (Fa~25) forming aggregates with an engrained texture (Fig. 10 B1, B3), and a porous aspect with nanometric sulfides inclusions; and larger micrometric to millimetric grains of olivine (Fa~10) (bottom of the section Fig. 8b). Traces of troilite, sulfates and Ca-phosphates are also observed in STEM-EDS maps. A difference between SEM-EDS and STEM-EDS abundances in NWA 11750 is the modal abundance of carbonates. This phase is well intermixed with olivine and pyroxene, as observed on STEM-EDS maps (32.6 vol%). Therefore, on SEM-EDS maps, only the larger veins of carbonates are observed (3.66 vol%), while the small, intermixed carbonates are “lost” in the “fine-grained mix”.

SEM-EDS images of the matrix of EM 200 show micrometric silicates and magnetite, with submicrometric troilite, pentlandite, and metal (taenite) grains, all set in a nanosized “fine-grained mix”. No TCIs were found on FEG-SEM images (Fig. 7b, Fig. S3d). On STEM-EDS maps, the “fine-grained mix” is composed of olivine, pyroxene, metal, magnetite, troilite and pentlandite, embedded in a nanocrystalline phyllosilicates and organic matter assemblage (Fig. 8c, Fig. 9c). We observed Mg-rich olivine (Fe~10-35) as well as Ca-rich and Ca-poor pyroxene. Most of the FIB section shows recrystallization in fine lamellar nanoscale phyllosilicates and organic matter (Fig. 10 C1, C2), but silicate crystal borders do not show traces of alteration. EM
200 TEM maps also show thin and straight lamellae of TCIs, with dominant cronstedtite (Fig. 10 C1, C2), and rare grains of phosphates and chromite. Rare amakinite Fe(OH)₂ is observed interlayered inside one exceptionally large TCI (Fig. S8). The large modal abundance of magnetite identified from the bulk analyses (Table 1) is not observed at the scale of the matrix FIB section. This shows that magnetite is distributed heterogeneously in micrometric crystals rather than in nanometric grains in the matrix. The modal abundances between SEM and TEM were not different within errors (Table 5), except for the porosity estimated abundance, higher on STEM, showing a nano-sized porosity.

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

Figure 11 and Table 6 show the analytical total of the electron microprobe (EMP) analyses in the matrix of the four studied meteorites compared to the main carbonaceous chondrite groups. EMPA totals are lowered by the presence of volatiles (OH, H₂O, H) in the phyllosilicates or in the amorphous materials or by the carbon content (both in organic matter (OM) and carbonates), which were not measured during the EMPA. CV chondrites, known to have experienced metamorphism, have the highest totals in the matrix (highest frequency around 95-100 wt%). CM chondrites, most of them classified as CM2, have more aqueous alteration phases in their matrix and therefore lower EMPA totals in their matrix (highest frequency around 80-85 wt%). The most aqueously altered carbonaceous chondrites, the CI chondrites, show the lowest EMPA total in their matrices with a highest frequency around 75-80 wt%. The four chondrites show a large spread in their analytical EMPA totals. EM 200 shows the lowest total (72.34 wt%), at the bottom of the range of CI and CM. NWA 11750 has the highest total (96.45 wt%), close to CO and CV chondrites (Fig. 11, Table 6).

### 3.4.3 Infrared Transmission Spectroscopy

The analyses were performed on several fragments of matrix from each meteorite to be as representative as possible. In Figure 12, we show the most representative spectra for each
meteorite at 20°C, and 250°C (or 300°C for Chwichiya 002). Those two temperature steps were chosen to demonstrate the difference of hydration and reduce the effect of adsorbed terrestrial water. The 3000 cm\(^{-1}\) absorbance is due to interlayer H\(_2\)O and -OH groups in phyllosilicates (Tuddenham and Lyon, 1959; Oinuma and Hayashi, 1965; Bishop et al., 2002), or in the water from amorphous material. Indeed, recent studies showed that amorphous silicates in Acfer 094, Paris or CMs can contain considerable water (Le Guillou et al., 2018; Ohtaki et al., 2021; Villalon et al., 2021). The position and intensity of those absorptions vary with the structure and chemical composition of the phyllosilicates. The low abundance of phyllosilicates in the studied samples does not create a sharp spectral feature from phyllosilicates in the 3000 cm\(^{-1}\) region, making it difficult to make a clear mineral identification. The 1000 cm\(^{-1}\) spectral feature is due to the absorption by Si-O groups (stretching) and reflects the silicate compositions, including secondary phases such as phyllosilicates. Extraterrestrial phyllosilicates can be recognized by a broad symmetric band around 1000 cm\(^{-1}\) (Beck et al., 2014). At 250°C, NWA 11750 matrix shows no hydration around the 3000 cm\(^{-1}\) absorption band. It shows a mixture of olivine and pyroxene (with a dominance of olivine), with no clear signs of phyllosilicates on the spectra in the 1000 cm\(^{-1}\) region. The presence of carbonates can be inferred from a band around 1440 cm\(^{-1}\), but mineral identification was not possible since the carbonate mode around 880 cm\(^{-1}\), most diagnostic of composition, could not be identified with enough accuracy. Chwichiya 002 shows a weakly hydrated matrix with a slight signature around 3000 cm\(^{-1}\) at 300°C. Silicate bands show no sign of phyllosilicates absorptions. NWA 12957 has a slightly more hydrated matrix than NWA 11750 and Chwichiya 002, with a feature at around 3000 cm\(^{-1}\) even at 250°C, and weak signatures of phyllosilicates in addition to olivine and pyroxene in the 1000 cm\(^{-1}\) region. Finally, EM 200 spectra show low hydration around 3000 cm\(^{-1}\) and low amounts of phyllosilicates in the 1000 cm\(^{-1}\) region, although higher than the other meteorites studied.
4 Discussion

4.1 Techniques for evaluating the alteration extent

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

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

4.1.1 Bulk studies

Vis-NIR reflectance spectroscopy

Vis-NIR reflectance spectroscopy can be used to detect -OH, and H$_2$O absorptions in meteorite samples, as well as on asteroid surfaces. In this work, we did not detect any hydration in the studied chondrites using Vis-NIR reflectance. The reflectance spectra are influenced by
many factors other than the hydration state of the meteorites. Indeed, temperature, texture, grain size, opaque minerals, organic phases and terrestrial weathering can change the slope of the spectra (Beck et al., 2010; Garenne et al., 2016; Johnson and Fanale, 1973; Singer and Roush, 1985; Takir et al., 2019; Hapke, 2001; Cloutis et al., 2012). A high abundance of phyllosilicates can also influence the spectral slope, in addition to having weak absorption bands around 0.7 μm, 0.9 μm, 1.1 μm and 2.3 μm, such as those detected in CM chondrites (Fig. 6). For weakly altered samples, phyllosilicates are not present in large enough amounts (Table 3) to be detected by IR reflectance spectroscopy as observed in the four studied chondrites (Fig. 6). This method is useful to find potential parent bodies of altered chondrites, through a comparison of IR reflectance spectra of meteorites and asteroid surfaces (e.g., Krämer Ruggiu et al., 2021), but this technique is not efficient to detect minor degrees of aqueous alteration.

**TGA**

In the literature, TGA data are interpreted using temperature ranges that are associated with different gases released from minerals phases (Garenne et al., 2014) (Table 4). However, in those temperature ranges, gases from other phases, such as organics or sulfides (including tochilinite from TCIs), can also be released (Table 4). The gases released at those temperature ranges show different signatures in the FTIR spectra than expected: CH and CO at 200-400°C; CH, CO, and CO₂ at 400-770°C (Table 4, Fig. S4-S7). Therefore, the mass loss abundances represent only a “maximum” of oxy-hydroxides from terrestrial alteration (200-400°C), phyllosilicates (400-770°C) and carbonate (770-900°C), all without taking into consideration the potential contribution of sulfides, TCIs, or organic matter (Table 4). Indeed, the high proportion of organic matter may explain the significant mass losses for EM 200 at 200-400°C (13.43 wt%) and at 700-900°C (5.68 wt%), as only small terrestrial alteration is observed, and no carbonates were detected with other instruments (Table 5, Table 7). In addition, the different temperature ranges do not allow for the distinction of different solid solutions of phyllosilicates, which are
important in the characterization of secondary alteration phases: TCIs (with Fe-serpentine cronstedtite) and Mg-serpentine from olivine alteration. Surprisingly, none of the studied samples showed an IR signature of H$_2$O at <200°C, which we tentatively attribute to water abundances below the detection limit of the instrument. Also, Chwichiya 002, NWA 11750 and NWA 12957 all show mass losses 1 wt% in the carbonate range (400-770°C), while showing bulk abundances of carbonates of 1-6 vol% on XRD (Table 3). Consequently, TGA associated with IR transmitted spectroscopy could represent a promising technique to measure the abundance of aqueous alteration phases, if some parameters (such as sulfides and organic matter content) are considered beforehand, and additional work on standards for the study of meteorites is made. Temperature ranges should be refined in order to precisely define the mass loss temperature for different phases. Furthermore, the organic matter content of each meteorite should be measured in order to calculate its influence in the mass loss.

**XRD**

The detection limits of our XRD analyses for quantitative modal abundances were ~ <5 vol% for most phases (Table 3). The detection limits of XRD are largely related to the composition and the crystallinity of the phases. For example, as the XRD pattern of calcite has one very intense peak, making it easily detected even in low abundances (<1 vol%), it could easily be detected in all meteorites (~2 vol%) except for EM 200, which also showed no carbonates with all other instruments (Table 7). Metal was also detected by XRD in the matrix (~1 vol%) of NWA 12957 and NWA 11750. Low abundances of magnetite were also detected (down to 2 vol% for NWA 12957) (Table 3). Sulfide detection via XRD is more complicated and depends on chemistry. Indeed, Fe-sulfides are hardly differentiated from one another because troilite and pyrrhotite have the same crystalline structure, creating only a subtle shift in the position of the peaks in XRD patterns, and could consequently be mixed or inverted. Fe-Ni-sulfides (pentlandite) were not detected by XRD in the studied chondrites because of low
abundances and peak overlap with major silicate phases. XRD patterns showed small phyllosilicate (serpentine) peaks only in Chwichiya 002 (2 vol%). Phyllosilicates had been overlooked in the analyses performed for the registration of the meteorite by the Meteoritical Society (Gattacceca et al., 2019). PSD-XRD identified poorly crystalline phyllosilicates (serpentine) in all samples (2-6 vol%). XRD and PSD-XRD “phyllosilicate” detection include the detection of both Mg- and Fe-serpentine phases, also including cronstedtite in large TCIs (with a large enough coherence domain).

Poorly crystalline phases with low intensity peaks, such as small TCIs or phyllosilicates, are harder to detect than crystalline materials. The interstratified tochilinite and cronstedtite in TCIs results in small coherence domains, making detection by XRD challenging. PSD-XRD analysis found 2 vol% phyllosilicates in EM 200 (Table 3), although TEM analyses showed a high proportion of nanoscale phyllosilicate (54 vol% of the FIB section) (Fig. 10 C1, C2). Nanoscale phyllosilicates in EM 200 have too small coherence domains to be detected in XRD patterns. Abundances of amorphous material can be deduced from PSD-XRD patterns and are important to assess the potential presence of Glass with Embedded Metal and Sulfide (GEMS)-like amorphous material in primitive chondrites (Table 7). Although we suspect most amorphous phases are GEMS-like materials in Chwichiya 002 and NWA 12957, like those we observed in STEM in Chwichiya 002 (Fig. 9a), other phases such as extremely fine-grained phyllosilicates with small coherency domains also create broad and weak diffraction peaks, increasing the estimated amorphous phase abundance. Therefore, the amorphous abundances estimated from PSD-XRD provide an upper limit of GEMS-like phases and could also include other poorly crystallized alteration phases. In conclusion, XRD provides a useful bulk technique for detecting the diversity of primary and secondary phases in the studied chondrites. XRD can detect all primary phases, as well as secondary phases (phyllosilicates, carbonates, TCIs, secondary 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
density correction should be added to improve the results (Zanetta et al., 2019). Defocused
EMPA totals can be lowered by the content of magnetite \((\text{Fe}_3\text{O}_4)\) falsely reported as \(\text{FeO}\), and the
presence of organic matter (high in the studied chondrites, even if no quantification has been
done on carbon). An additional complexity is the presence of metal counted as \(\text{FeO}\), which will
artificially increase the total. For Chwichiya 002, EM 200 and NWA 12957, this factor is
negligible as they possess a low abundance of metal \((\leq 1\ \text{vol}\%)\) but it could increase NWA 11750
EMPA totals. The totals can be corrected by using the approximative metal and magnetite
compositions and abundances, although these methods do not seem adequate for the assessment
of the aqueous alteration state of chondrites. In addition, sulfides (troilite, pyrrhotite, pentlandite)
do not influence the EMPA totals but are very sensitive indicators of secondary alteration (e.g.,
Rubin et al., 2007). In conclusion, the alteration stages defined by EMPA totals cannot reflect the
overall alteration stage, as too many factors other than secondary alteration influence the totals,
while major secondary products (sulfides) do not.

**Electron microscopy**

SEM and TEM are the only instruments that enable observation of the relationships between
the various phases and their locations *in situ*, and EDS mapping gives the chemical compositions
of all different primary and secondary phases (Fig. 9). These techniques allow identification of
metal grains, silicates, and amorphous GEMS-like material as well as incipient crystallization of
known secondary phases, including TCIs, carbonates, secondary sulfides, and magnetite. The
analyses using FEG-SEM and EDS are rapid and allow the study of multiple zones of the matrix.
Nonetheless, the modal abundances obtained from SEM- and TEM-EDS maps are directly
correlated to the spatial resolution of the techniques. The study of matrix using FEG-SEM is
limited to the observation of ca. \(>100\ \text{nm}\) crystals (at 5 kV acceleration voltage). Thus, the nano-
scale fine-grained matrix is not accessible through FEG-SEM mapping. FEG-SEM is used to
determine the most representative area of the alteration state of the chondrite but cannot identify
the nano-scale secondary phases. Thus, the modal abundances obtained from FEG-SEM maps should be taken as the modal abundances of micron-sized and larger materials with an unresolved "fine-grained mix". The TEM resolution can go down to atomic resolution providing high-definition imaging that allows the identification of the nano-sized grains in the fine-grained matrix, with the additional application of EDS and SAED techniques. It can be used to refine the results of the larger-scale SEM EDS mapping, such as the “fine-grained mix” (Fig. S3). This “fine-grained mix” was identified as mainly GEMS-like material and TCIs, with smaller abundance of magnetite, pentlandite, pyroxene, olivine and metal in Chwichiya 002; mainly carbonates and olivine crystals, with smaller abundance of phyllosilicates, sulfides, magnetite, metal and pyroxene in NWA 11750; and as mainly nanophyllosilicates and organic matter, with smaller abundance of sulfides, magnetite, metal, pyroxene and olivine in EM 200.

The use of SAED in TEM is crucial as it is the only technique allowing the clear identification of GEMS-like material, whereas the detection of amorphous material by XRD can include weakly crystalline phases, and nanoscale intermixed crystals (small TCIs or phyllosilicates). HR-TEM can also be used to look for incipient alteration of the margins of the silicate grains as evidence of incipient aqueous alteration. The limitation of TEM studies for alteration in chondrites is the area of observation related to FIB preparation techniques: typical section prepared by FIB methods are ca. 60 μm² and are rarely representative of the matrix variability present in a meteorite. Careful selection of location of the FIB sections using SEM mapping can limit this bias. However, the zones of FIB section extraction are usually chosen away from large porosities to avoid breaking during the FIB section extraction, or away from large veins or crystals, or even away from zones with unusually monomineral-rich zones, which creates a sampling bias in the modal abundances estimated from TEM observations. Thus, other bulk analyses can identify some phases missing from TEM observation, due to an absence of those phases in the extracted region of the FIB section (e.g., large magnetite grains in EM 200;
large carbonates veins in NWA 11750; carbonates in NWA 12957 and Chwichiya 002) (Table 7).

In conclusion, TEM allows the identification of all primary and secondary phases from incipient aqueous alteration, and thus the characterization of primitive chondrites, but should be used in combination with larger scale instruments such as SEM and/or XRD.

4.2 The alteration state of the studied chondrites

4.2.1 Metamorphism

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

The Cr$_2$O$_3$ content in ferroan olivine of Chwichiya 002, NWA 11750 and NWA 12957 are close to unmetamorphosed meteorites such as Acfer 094 (C2-ung), Y-81020 and Colony (both CO3.0 chondrites), and Paris (CM2.7-2.9) (Fig. 4). EM 200 shows higher standard deviation of the Cr$_2$O$_3$ contents, which is consistent with its Raman spectra parameters that show a larger variability of short-time heating (Fig. 3). Ebert et al. (2019) show that a long-term peak temperature of 400-600°C is required to dehydrate CM chondrites.

In addition, heated CMs show no hydration absorption on infrared spectroscopy, but the IR spectra (transmission in matrix) of EM 200 shows a visible 3 μm band, Chwichiya 002 and NWA 12957 show a slight 3 μm band, but NWA 11750 shows no obvious 3 μm band from
hydration (Fig. 12). Finally, the 10 μm absorption band does not reflect a high abundance of phyllosilicates, strengthening the non-dehydrated by heating hypothesis.

### 4.2.2 Aqueous alteration

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

Chwichiya 002 and NWA 12957 show similar petrography as well as similar alteration, which strengthens their potential pairing. Their potential pairing is yet to be verified, however, because their oxygen isotopic compositions ($\Delta^{17}$O=-4.59 for NWA 12957 and $\Delta^{17}$O=-3.88 for Chwichiya 002) and Raman parameters show differences (Fig. 3). They show alteration with micron-sized aggregates of TCIs (Fig. 8a, Fig. 9a), and low abundances of carbonates, magnetite, and secondary sulfides (pyrrhotite, pentlandite) (Table 5). They show abundant amorphous material on PSD-XRD analyses, with GEMS-like materials identified using SAED in Chwichiya 002, and extensive estimated porosity on TEM observations (Fig. 10, A1-A3). In addition, they have a low abundance of metal preserved from alteration ($\leq$ 1 vol%), probably dissolved or transformed into magnetite (Table 5). These meteorites suggest aqueous alteration by a fluid dissolving metal grains and troilite, while not completely altering amorphous materials to phyllosilicates, and crystalizing a low abundance of TCIs, carbonates, magnetite, and secondary sulfides (pentlandite, pyrrhotite). Small error bars of Raman parameters (Fig. 3) and small RSD of bulk major composition (Table 2) suggest homogenous alteration of the meteorites.
NWA 11750 shows abundant unaltered metal grains (3 vol% in the matrix) and primary troilite and pyrrhotite sulfides (~3 vol%), with a low abundance of phyllosilicates (serpentine), and no TCIs or magnetite (Table 5). NWA 11750 contains abundant carbonate in its matrix (Fig. 2). It does not display GEMS-like materials (Table 5) and does not show a hydration signature in IR spectra (Fig. 12). All these characteristics attest to a minimally altered matrix, except for the absence of GEMS-like materials. Besides carbonates, NWA 11750 matrix is largely composed of nanocrystals of olivine (Fig. 10 B1, B3). NWA 11750 matrix composition can be interpreted as an alteration from CO$_2$-rich aqueous fluid, dissolving any GEMS-like material that might have been present and/or converting it to phyllosilicates, while preserving metal and sulfides (troilite), and crystallizing abundant carbonates, similar to that observed in some CM chondrites (Tsuchiyama et al., 2021). NWA 11750 in an exceptional chondrite in view of its high amount of extraterrestrial carbonates in the matrix that contrasts with an overall very subtle aqueous alteration, making it a sample of choice to study CO$_2$ and Ca-rich aqueous fluid-assisted alteration, that could also give insight into the carbonate formation on CM-like asteroids such as Bennu (Kaplan et al., 2020). Both Raman parameters (Fig. 3) and bulk major composition (Table 2) suggest homogenous alteration of NWA 11750.

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

4.3 Aqueous alteration in CM-like chondrites

GEMS-like assemblage

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

Large abundance of amorphous silicates has been found in the matrices of primitive CR chondrites (Brearley 1993; Abreu and Brearley 2010; Le Guillou et al., 2015b; Le Guillou and Brearley 2014; Vollmer et al., 2020; Zanetta et al., 2022), as well as in several other carbonaceous chondrites (Brearley 1993; Vollmer et al., 2009; Nguyen et al., 2010; Nittler et al., 2013). Some of the least altered, most primitive carbonaceous chondrites show extremely fine-grained amorphous silicate with embedded metal and sulfides, resembling GEMS assemblages (Bradley 1994; Greshake 1997; Noguchi et al., 2017; Hopp and Vollmer 2018; Chizmadia and Brearley 2008), often referred to amorphous or GEMS-like materials (Barber 1981; Hewins et al., 2014; Marrocchi et al., 2014; Leroux et al., 2015; Rubin 2015; Vollmer et al., 2020; Zanetta et al., 2021; Ohtaki et al., 2021; Villalon et al., 2021). Those GEMS-like phases found in chondrites...
are comparable to the GEMS assemblages found in IDPs, i.e. they consist of an amorphous silicate with embedded metal and sulfide inclusions. GEMS-like phases identified in Chwichiya 002 are similar to GEMS-like phases found in the most primitive meteorites but differ in their higher Fe-content of the amorphous matrix, larger troilite and metal inclusions, and show larger sizes than IDPs GEMS phases.

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

**Metal**

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

**Porosity of the matrices**

The high porosity observed in the highly primitive meteorite Acfer 094 suggests that primitive chondrites may have contained a lot of water-ice-filled pores during accretion.
The matrices of the least altered chondrites consist mostly of GEMS-like or amorphous materials with high porosity (Leroux et al., 2015; Kimura et al., 2020; Suttle et al., 2021). During aqueous alteration, this porosity is filled with fine-grained to fibrous phyllosilicates or small TCIs (Leroux et al., 2015). Following Figure 15 in Leroux et al. (2015), describing the filling of the porosity around GEMS-like materials by TCIs or fine-grained phyllosilicates, Chwchiya 002 FIB section observations correspond to the second stage of incipient alteration, with fine grained TCIs forming in the porosity around the amorphous phases, with remaining porosity between the GEMS-like materials (Fig. 8a). Nevertheless, estimated porosity measurements using microscopy are highly scale dependent, which has to be taken into consideration when estimating porosity using SEM and STEM. The choice of the FIB sections for the TEM studies are usually made away from large porosity to avoid breaking during the FIB section extraction, which creates a sampling bias in the TEM porosity estimation.

**TCIs**

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

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

**Phyllosilicates**

With increasing aqueous alteration, TCIs are recrystallized into larger phyllosilicate aggregates of 20-60 µm, associated with larger secondary euhedral pyrrhotite grains (McSween, 1979b; Rubin et al., 2007). Afterward, pseudomorphic phyllosilicate crystals start to replace the anhydrous silicates (pyroxene and olivine). Ferroan olivines are altered faster than magnesian olivine (Wogelius and Walther, 1992; Hanowski and Brearley, 2001; Zolensky et al., 1993; Pignatelli et al., 2016), as ferroan olivines are altered from margin inwards, in contrast to magnesian olivine which suffer meshwork replacement, forming Fe to Mg-rich serpentine
Therefore, phyllosilicates are a major proxy for identification of chondrite subtypes (Rubin et al., 2015).

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

Carbonates

Carbonates crystallize during the earliest stages of alteration, generally in the form of calcite (e.g., Lee et al., 2014; Howard et al., 2015). First generation carbonates fill void spaces in the meteorite, whereas later carbonates replace primary anhydrous silicates and grow on already existing secondary phases. Carbonates are found in altered subtypes <2.7 chondrites (Rubin, 2015). A 12169, A 12236 and A 12085 and the most primitive Paris lithology contain rare to no carbonate, while the more altered Paris lithology contains 1-3 vol% carbonate (Table 8). EM 200 shows no traces of carbonates, similar to the referenced Asuka meteorites and the Paris primitive lithology (Table 8). NWA 12957 and Chwichiya 002 contain 1-3 vol% carbonates (estimated by XRD), comparable with the most altered Paris lithology. TEM observations of NWA 11750 contain extremely abundant fine-grained carbonates filling the porosity in between olivine along
with fine grained phyllosilicates (Fig. 8b, Fig. 9b, Fig. 10 B2). Of course, carbonates can be produced by terrestrial fluid circulation, and as shown by Tyra et al. (2007), the O-isotopic composition of carbonates precipitated from terrestrial fluids plot along the mass-dependent terrestrial fractionation line (slope 0.52) with $\delta^{18}$O and $\delta^{17}$O values close to 0‰. Large carbonates veins in NWA 11750 show $\delta^{18}$O around 30-40 ‰, with slightly negative $\Delta^{17}$O (average -0.63 ‰) (Fig. 2), thus isotopic analysis of the carbonates in NWA 11750 showed that their origin is extraterrestrial (Fig. 2). We are therefore confident that the majority of the carbonates in NWA 11750 were not formed by terrestrial alteration. Although, small terrestrial weathering observed in NWA 11760 could have produced small abundance of terrestrial carbonates.

**Other primordial and secondary phases**

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

In this study, we investigate the most representative matrix of each of the four studied meteorites. Of course, chondrites are also considered to be complex breccias, implying multiple lithologies with different alteration conditions and degrees (e.g., Lentfort et al., 2020). Therefore, a detailed investigation of potential different lithologies and the determination of presolar grain
abundances in the matrices of Chwichiya 002, NWA 12957, NWA 11750 and EM 200 should be performed in order to compare all possible lithologies to the several lithologies of Paris, A 12169, A 12236 and A 12085, to confirm their comparison.

5 Conclusion

We report on four ungrouped carbonaceous chondrites, Chwichiya 002, NWA 12957, NWA 11750, and EM 200, that show variations in both the degree and products of alteration, illustrating different alteration conditions and/or primary constituents. We find that Chwichiya 002 and NWA 12957 are among the least altered chondrites, with abundant amorphous phases, observed as GEMS-like assemblages in Chwichiya 002, and TCIs and sulfides as secondary alteration phases. They could represent primitive CM-like chondrites, similar to the A 12169, A 12269, A 12085 meteorites (CM2.8-3.0), with only incipient H2O-rich fluid alteration. NWA 11750 contains a high abundance of extraterrestrial carbonates in the matrix and is an exceptional meteorite to study incipient CO2- and Ca-rich aqueous fluid assisted alteration in the early Solar System. Its matrix contains no amorphous material, but abundant preserved nanocrystals of olivine and metal, with low abundance of magnetite, phyllosilicates and no TCIs, and we would suggest a classification as a 2.9 subtype rather than the 3.00 subtype currently used in the Meteoritical Bulletin database. EM 200 has a more altered matrix with a high abundance of magnetite and nanoscale phyllosilicates, although primary troilite is preserved. Its matrix shows no carbonate, no TCIs, and would thus suggest a classification as a 2.8 subtype rather than the 3.00 subtype currently used in the Meteoritical Bulletin database. The variety of alteration styles among the studied samples reflect the variety of primary constituents of chondrites, aqueous alteration conditions, and alteration fluid compositions.

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

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### 7 Supplementary materials

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

Figure S2: NWA 12957 TGA analyses

Figure S3: NWA 11750 TGA analyses

Figure S4: Chwichiya 002 TGA analyses

Figure S5: EM 200 TGA analyses

Figure S6: HR-TEM image (left) and EDS-TEM (right) images of tochilinite-cronstedtite intergrowths with amakinite Fe(OH)$_2$ interlayered in EM 200’s matrix.

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