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1 Modal abundance, density and chemistry of micrometer-sized assemblages by 2 advanced electron microscopy: application to chondrites

3
4 P-M. Zanetta^{1,2}, C. Le Guillou¹, H. Leroux¹, B. Zanda^{2,3,4}, R.H. Hewins^{2,3}, E. Lewin⁵ and S. Pont².

5 1. Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET - Unité Matériaux et Transformations, F-
6 59000 Lille, France ; 2. IMPMC, Sorbonne Université, MNHN, UPMC Paris 06, UMR CNRS 7590,
7 75005 Paris, France ; 3. EPS, Rutgers Univ., Piscataway, NJ 08854, USA ; 4. Observatoire de Paris,
8 IMCCE, 75014 Paris, France ; 5. ISTERRE (OSUG : Univ. Grenoble Alpes & INSU-CNRS), Grenoble,
9 France. (Pierre.marie.zanetta@gmail.com)

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11 matrices;

12 Abstract

13 Numerous geosciences samples display a multi-scale mineralogical heterogeneity for which it is challenging
14 to obtain spatially resolved quantitative chemical data. It is the case for chondritic meteorites, which can
15 contain up to 10 different phases with grain size ranging from the nanometer to the millimeter. We
16 developed a method providing multiple physical and chemical information by advanced scanning electron
17 microscopy (SEM), hyperspectral energy dispersive X-ray spectroscopy (EDX) and electron probe micro-
18 analyses (EPMA). The method includes: i) infra-micrometric low-voltage EDX mapping and innovative
19 post-acquisition hyperspectral data analysis (based on both clustering and multiple linear least square fitting)
20 which allow phase mapping and quantification of the modal abundances; ii) EPMA of chemical end-
21 members to upgrade the phase map into a quantified chemical map; iii) physical modelling of the EDX
22 background, used as a proxy of the density. Density maps can be obtained with a precision of ~10%; iv)
23 determination of the bulk sample composition by combining modal abundances, chemical analysis and
24 density measurements.

25 The approach is applied to three well-known chondrites (Murchison, Paris and Orgueil), showing
26 heterogeneous grain sizes and mineralogy. Areas of ~ 250*250 μm^2 were mapped with a pixel size of 250
27 nm to determine the modal abundances, size distribution, circularity and densities of all phases, as well as
28 the matrix bulk compositions. Taking bulk wet chemistry data as reference, ACADEMY leads to a better
29 match than published defocused beam EPMA measurements. We demonstrate that choosing a Fe-rich,
30 hydrated standard (a biotite) to quantify phyllosilicate by EPMA improves the quantification by up to 10%,
31 and we ultimately retrieve the Mg/Si ratio with a 1% precision. We called this method ACADEMY for
32 Analyzing the Composition, the modal Abundance and the Density using Electron Microscopy. A code
33 was developed and was made available online so that ACADEMY can be applied to other materials.

34 1. Introduction

35
36 The petrological and chemical description of natural samples is fundamental in Earth and Planetary Science.
37 It permits us to constrain transformation processes which have shaped the matter and to reconstruct scenarios
38 of rock formation. A number of these rocks consist of a fine-grained heterogeneous assemblage comprising
39 various minerals (primary or secondary), cracks, porosity and filled veins. To analyze these samples
40 properly, it is necessary to have at least access to the chemical bulk composition, the mineralogy (nature

41 and composition of phases) and the petrofabrics (grain size, composition of phases, texture and structure).
42 For this purpose, conventional tools such as scanning electron microscopy (SEM) and electron probe micro-
43 analysis (EPMA) are used. These techniques offer a wide range of possibilities of routine studies, both for
44 imaging, and chemical or structural analysis.

45
46 In their basic configuration, electron microscopy techniques have limits in terms of spatial resolution,
47 especially in microanalysis. Difficulties arise when the scale of the study reaches the micrometer. SEM
48 imaging is performed routinely with an accelerating voltage optimized for the targeted emission. A
49 resolution of 1 to 10 nanometers is easily accessible by using secondary electron emission (SE).
50 Backscattered electron (BSE) images, which give information on the average atomic number Z, display a
51 lower resolution with a range between 100 and 500 nanometers (Brisset, Repoux, Grillon, & Robaut, 2008)
52 (Goldstein, et al., 2017). Lastly, when adapted for geological samples (taking into account the surface effects
53 and the absorption characteristics), cathodoluminescence (CL) can be used with a maximum resolution of
54 about 100-200 nanometers (Chen, Xu, & Chen, 2015). Those imaging techniques are often combined with
55 chemical characterization. Methods based on X-Ray emission such as energy dispersive X-ray spectroscopy
56 (EDX) or wavelength dispersive X-ray spectroscopy (WDX) are used in a systematic way. However,
57 working conditions of microanalysis are not well suited for fine-grained samples. Accelerating voltages of
58 15-20 kV are usually used and lead to a spatial resolution of the order of a micrometer for the X-ray
59 emission, which is much higher than that associated with the electronic imaging. A comparison of the
60 volume probed is quite informative: for instance, for quartz (density 2.62 g/cm³) studied with an accelerating
61 voltage of 15 keV, previous studies and Monte-Carlo simulations reveal that SE and BSE signals typically
62 probe a volume of ~1E-6 μm³ and ~0.125 μm³ (Goldstein, et al., 2017) respectively while the volume probed
63 by the X-Ray corresponds to ~5 μm³ (Drouin, et al., 2007). This spatial resolution limitation can be
64 problematic for the ϕ(ρz) correction in case of strong density variation and beam overlapping of phases.

65
66 In addition to the spatial resolution limitation for microanalysis, fine-grained materials can introduce some
67 difficulties related to the quantification procedure. Three major issues have been identified dealing with
68 fine-grained material:

69 - to obtain high resolved quantitative data over large area in a reasonable amount of time, the choice
70 of the electron beam technique and its parametrization is a fundamental and a complex problematic. Both
71 EDX and WDX provide chemical mappings over large areas with high number of pixels and they can be
72 used in low –voltage condition to gain in spatial resolution. But those techniques have specificities that can
73 put some restraints on their utilization. On the one hand EDX is fast and enables the measurement of all
74 elements simultaneously. However, routine EDX is less adapted to a quantitative approach due to the peak
75 overlap and a relatively low signal to noise ratio. On the other hand, WDX provides more accurate chemical
76 composition (no peak overlap and better S/N ratio) but requires a longer acquisition time.

77 - the quantitative mineralogy SEM-EDX and EPMA techniques provide X-ray data cubes and many
78 software programs (PETROMAP®, XRMapAnal®, QEMSCAN®, Zeiss®, MAPS Mineralogy®,
79 XMapTools®) or published thresholding methods (Tovey & Krinsley, 1991); (Berrier, Hallaire, & Curmi,
80 1999); (Pret, et al., 2010) allow us to construct phase maps and to retrieve the texture of grains. However,
81 such data treatments remain generally applied to simple cases such as coarse-grained assemblages. In the
82 case of fine-grained assemblages, the entanglement of the different minerals can lead to mixing zones under
83 the beam and bias the modal abundances. Moreover, in natural samples, phases do not always display pure
84 end-member compositions and the usual data treatments cannot be easily applied to solid solutions.

85 - An additional difficulty encountered with a heterogeneous fine-grained assemblage is the
86 variability of density which can have a significant effect on the determination of the average sample
87 composition. The different constituents of the material have their own chemistry and their own abundances
88 in a given area but the combination of these two parameters is insufficient to obtain the bulk composition.

89 Chemical analyses have to be weighted by the density of the different phases to correctly measure the
90 composition of the sample (Ichinokawa, Kobayashi, & Nakajima, 1969), (Warren, 1997), (Nazarov,
91 Ignatenko, & Shevaleevsky, 1982), (Zanda, Lewin, & Humayun, 2018). In natural samples, a wide range of
92 phase density can be encountered in a single sample, from $\sim 2 \text{ g/cm}^3$ for fibrous and highly porous material
93 to $7\text{-}9 \text{ g/cm}^3$ for metallic phases. In meteorites, most phases have a known density (for forsterite, metal,
94 sulfides for instance), but the density of very fine-grained regions, consisting of a mixture of amorphous
95 phases, phyllosilicates, porosity, and nanophases can be difficult to estimate. Numerous methods exist to
96 quantify the porosity (Hellmuth, Siitari-Kauppi, & Lindberg, 1993) (Landry, 2005) (Oila, Sardini, Siitari-
97 Kauppi, & Hellmuth, 2005) (Anovitz & Cole, 2015) (Liu, King, Huis, Drury, & Plümper, 2016). Most of
98 these methods have a spatial resolution not adapted to textural analyses of fine-grained rocks such as
99 claystones, siltstones or primitive chondrites. They also require more powerful facilities than common
100 electron microscopy or worse, might damage the sample. The porosity measurement method developed by
101 (Pret, et al., 2010) based on the sum of oxide weight concentrations and measured using EPMA comes close
102 to this resolution with a conventional tool. Even so, this method cannot be applied if organic matter or
103 amorphous (non-stoichiometric) phases are part of the material constituents.

104
105 Here we propose a method named **ACADEMY** (**A**nalyzing the **C**omposition, the modal **A**bundance and the
106 **D**ensity using **E**lectron **M**icroscop**Y**), which combines the advantages of two conventional and easily
107 accessible techniques (SEM and EPMA) and the development of data treatment procedures, in order to
108 improve the characterization of natural samples with fine-grained assemblages. This method aims to
109 produce quantitative chemical maps with improved spatial resolution in combining the EDX spectrum,
110 density and proxy EPMA analysis for each pixel. The method includes the following main steps:

- 111 - To decrease the volume of interaction and reach a higher spatial resolution, the hyperspectral maps
112 are acquired with a lower accelerating voltage than conventional SEM-EDX working conditions.
- 113 - Complementary deconvolution procedures are added to the clustering method allowing us to obtain
114 accurate modal abundances. These supplementary procedures deal with the problem of extreme
115 mixing of micrometer-sized assemblages and the compositional variation existing in some mineral
116 phases due to solid solutions.
- 117 - Quantitative chemical compositions of each phase are obtained by coupling SEM-EDX datasets
118 with EMP point analyses (normal conditions 15 keV) allowing more accurate standard calibrations
119 and correct $\phi(\rho z)$ corrections.
- 120 - The density of the material is determined based on the modeling of the EDX background of the
121 hyperspectral signal.
- 122 - The bulk chemical composition is retrieved through the combination of modal abundance and
123 specific phase chemistry and density.

124 This thorough methodological development leads to a complete petrological description of the sample with
125 an improved spatial resolution. This method is illustrated by examples of fine-grained matrices of primitive
126 chondrites. Their investigation has been so far complicated by the extremely fine-grained nature, the
127 mineralogical and compositional heterogeneity (including amorphous and partially altered phases), the wide
128 range of density and the nano-porosity of the assemblage (Scott & Krot, 2003). This method should yield
129 more accurate description of those objects and better constrain processes which have shaped matter in the
130 early Solar System.

131 **2. Samples and analytical conditions**

132 **2.1. Samples**

133

134 The different steps of the ACADEMY method are described using fine-grained primitive chondrites as test
135 samples. These meteorites consist of varied amounts of chondrules (droplets of igneous silicates), refractory
136 inclusions (minerals condensed from the gas) and fine-grained interchondrule ‘cement’ named matrix.
137 Although their formation mechanisms are not yet well established, chondrules and refractory inclusions
138 have been extensively studied, e.g., (Hewins, 1997) (Russell, Connolly Jr, & Krot, 2018) (Krot, et al., 2009).
139 They are typically several hundred micrometers to millimeter objects, rendering their study relatively easy
140 by various techniques (optical microscopy, SEM, EPMA, ion probe, ICPMS). The matrix is much more
141 difficult to study because it consists of submicron grains entangled with each other, extremely
142 heterogeneous in terms of compositions, structural states and densities. Matrices carry information on the
143 origin and the evolution of the dust in the protoplanetary disk and have been mainly studied by transmission
144 electron microscopy (TEM). (Brearley, 1993), (Greshake, 1997), (Chizmadia & Brearley, 2008), (Le
145 Guillou & Brearley, 2014), (Leroux, Cuvillier, Zanda, & Hewins, 2015) (Le Guillou, Changela, & Brearley,
146 2015). Matrices consist of an unequilibrated mineral assemblage of a groundmass of amorphous silicates
147 and phyllosilicates with numerous inclusions of anhydrous silicates, sulfides, metallic Fe,Ni, sulfates,
148 carbonates and organic compounds. The size of the anhydrous silicates can vary from 0.1 to 10 μm . The
149 groundmass of amorphous silicates is intermingled with phyllosilicates down to the nanometer scale.
150 Moreover, phyllosilicates often crystallize in the form of intergrowths with a huge range of chemical
151 variation between layers. These intergrowths are commonly serpentine interlayered with saponite, or
152 tochilinite interlayered with cronstedtite (TCI), and exhibit numerous textures (Brearley, 2006). The matrix
153 also contains significant inter-granular porosity (Leroux, Cuvillier, Zanda, & Hewins, 2015). This
154 heterogeneity is due to the strong mixture of components which originate directly from the protosolar dust
155 and components formed by secondary processes on their parent body (Scott & Krot, 2003).

156
157 We used two polished sections of the Orgueil meteorite, one section of the Murchison meteorite and one
158 section of the Paris meteorite provided by the Muséum National d’Histoire Naturelle (Paris). They were
159 chosen to test the robustness of the method on different objects and also because they are extensively
160 described previously in the literature. The Orgueil meteorite is an extensively altered CI chondrite (Scott &
161 Krot, 2003). This type of chondrite contains neither chondrules nor refractory inclusions and has generally
162 been considered as pure matrix material. Orgueil is composed almost entirely of serpentine and saponite
163 phyllosilicates and inclusions of ferrihydrite, magnetite, Ca–Mg carbonate, and pyrrhotite as main minerals
164 (Bostrom & Fredriksson, 1965) (Nagy, Meinschein, & Hennessy, 1963) (Nagy & Andersen, 1964) (Bass,
165 1971) (Reid, Bass, Fujita, Kerridge, & Fredriksson, 1970) (Kerridge & Macdougall, 1976) (Tomeoka &
166 Buseck, 1988). The composition of Orgueil has been quantified by wet chemistry (Jarosewich, 1990)
167 (Jarosewich, 2006) (Lodders, Palme, & Gail, 2009) and falls close to the composition of the solar
168 photosphere for all but the lightest and strongly volatile elements. This sample will allow us to validate the
169 quantification method. Murchison is a CM2 chondrite which principally exhibits a mixture of Mg-serpentine
170 with cronstedtite. Principal mineral inclusions identified are pyrrhotite, carbonate or sulfate, pentlandite,
171 olivine and pyroxene (Kvenvolden, et al., 1970) (Barber, 1981) (Bernatowicz, et al., 1996). Murchison is a
172 partially altered sample (Clayton & Mayeda, 1984), but the matrix is exceptionally complex at the nanoscale
173 and displays heavily aqueously altered minerals in close contact with anhydrous ones (Fuchs, Olsen, &
174 Jensen, 1973) (Mackinnon, 1980) (Mackinnon & Zolensky, 1984) (Le Guillou, Bernard, Brearley, &
175 Remusat, 2014) (Trigo, Vila-Ruaix, Alonso-Azcárate, & Abad, 2017). The Paris meteorite (CM2 chondrite)
176 exhibits two lithologies of different alteration degree (Hewins, et al., 2014). The least altered matrix areas
177 consist mostly of amorphous silicate grains with abundant porosity which enclose numerous Fe-sulfide
178 nanograins but also crystalline Mg–silicates (forsterite and enstatite), Ni-rich sulfides and carbonaceous
179 material (Marrocchi, Gounelle, Blanchard, Caste, & Kearsley, 2014) (Leroux, Cuvillier, Zanda, & Hewins,
180 2015) (Vinogradoff, et al., 2017) (Vacher, Marrocchi, Verdier-Paoletti, Villeneuve, & Gounelle, 2016)
181 (Piani, Yurimoto, & Remusat, 2017). In more aqueously altered areas, the matrix consists mostly of a

182 mixture of amorphous material and Fe-rich, crystalline phyllosilicates. The porosity fraction is less abundant
183 and the mixed amorphous-fibrous material frequently forms a continuous groundmass (Leroux, Cuvillier,
184 Zanda, & Hewins, 2015) (Pignatelli, Marrocchi, Mugnaioli, Bourdelle, & Gounelle, 2017). This sample will
185 allow us to assess how much the density variation affects the quantification of composition.

186
187 Those samples have been embedded in an epoxy resin, mechanically polished and coated by a thin carbon
188 layer (~10-15 nm). Sections were first examined by optical microscopy and SEM in order to select areas for
189 EDX mapping. Matrix was distinguished from fragments of chondrules, CAIs and other components by
190 their distinctive sizes, shapes, and textures. Suitable matrix zones for EDX were selected in regions without
191 wide fractures and without relief due to differential polishing.

192
193 Seven areas are studied in this paper. Areas in Murchison and Orgueil have been selected by choosing
194 mineral distributions representative of the whole sample. Conversely, in the case of the Paris meteorite,
195 different areas have been chosen as a function of their degree of alteration.

196 **2.2. Analytical conditions**

197 **2.2.1. Scanning electron microscopy**

198 The first objective is to enhance the spatial resolution of the analyses in order to reach the sub-microscale
199 of grains in chondrite matrices. During EDX acquisition the X-ray generation volume is directly linked to
200 the electron accelerating voltage. The lateral and depth resolution are improved as the accelerating voltage
201 is reduced. In the case of fine-grained materials such as matrices of primitive chondrites, the decreasing of
202 the electron accelerating voltage significantly improves the minimum grain size detectable. Various
203 experimental conditions have been tested to reach an equilibrium between a maximal number of counts, a
204 minimal X-ray volume interaction, a sufficient peak to background ratio of useful X-ray lines and an area
205 sufficiently large to be representative of the whole sample. An accelerating voltage of 5 keV was chosen
206 with a probe current of 1.2 nA to limit potential damage under the beam. However, reducing the accelerating
207 voltage gives rise to two important issues: i) The number of counts is much lower than that obtained with
208 conventional working conditions of 15 kV - 20 kV. ii) For a number of elements of interest, the K-series is
209 not excited at low voltage (here 5 keV) or has significantly lower intensities. Elements with their K-line
210 higher than the acceleration voltage see only their L-lines excited. This is the case for Fe - Ti - Ni - Cr - Mn
211 and requires us to work only on those lines which are concentrated below a few keV. For these elements,
212 we used the L-alpha lines and a Gaussian deconvolution procedure to measure intensities. This approach
213 will be discussed in more detail in the next section (3.4).

214
215 Hyperspectral maps were acquired using a FEG-SEM JEOL JSM-7800F LV at the University of Lille
216 equipped with an EDX/EBSD Aztec system from Oxford Instruments and a silicon drift detector (SDD
217 XMaxN) of 80 mm². The development of field emission gun (FEG) sources over the past 25 years has
218 permitted the production of electron beams which are smaller in diameter, more coherent and with greater
219 current density. Thanks to this technical improvement, hyperspectral map can be performed with lower
220 accelerating voltage in order to resolve small grains while maintaining a sufficient X-ray signal, an adequate
221 peak to background ratio and a relatively short acquisition time.

222
223 All hyperspectral EDX maps were collected with an acquisition time of about 12-14 hours including a dead
224 time of 18%, a mean input count rate of 50000 cps and an output of 40000 cpc. We set a process time of 3
225 on the Aztec software in order to obtain a full width at half maximum (FWHM) of the manganese K α peak
226 of ~ 135 eV for the different maps. Monte Carlo simulations were performed using NIST-DTSAII software
227 (Ritchie, 2009) to estimate the interaction volume at 5 keV. Depth resolution variations with those
228 conditions are contained in a range between 100 nanometers (for Fe-rich metal grains) and up to ~300
229 nanometers (based on the Fe L-alpha line) for porous phyllosilicates (compared to 300 nm and 1.5 μ m
230 respectively for a 15 keV accelerating voltage). Again the comparison of the probed volumes is interesting:

231 it is contained between [0.003 – 0.040 μm^3] for the 5 keV conditions while the range becomes [0.3 – 10
232 μm^3] for the 15 keV conditions (also based on the Fe L-alpha line). The resolution of X-ray maps has been
233 defined by the width of the interaction volume. Pixel size is then fixed to 260 nm to avoid over-sampling
234 and such that each interaction volume is always approximately contained in one pixel. Each map consists
235 of a typical rectangular matrix of 1024 by 832 pixels corresponding to a region of 270 μm by 220 μm . A
236 working distance of 10 mm, a dwell time of 200 μs , and an energy range of 10 keV for 2048 channels (5 eV
237 per channel) were used. The total number of counts obtained with those conditions was typically 1-2 billion
238 in the whole map, which corresponds to 1500 - 2000 counts per pixel and to 125 summed frames. During
239 acquisition, a drift correction was used, based on a BSE image with double the size of the analyzed region.
240 After the acquisition the maximum drift correction recorded was 750 nm, with a mean drift of 230 nm (i.e.
241 about one pixel).
242

243 **2.2.2. Electron probe microanalysis**

244 To reduce errors during EPMA and obtain precise compositions, new standards have been carefully
245 mounted. A series of standards provided by the Smithsonian Institution, Department of Mineral Sciences
246 and by the SARM (Service d'Analyse des Roches et des Minéraux), have been used (fayalite, diopside,
247 hornblende, biotite, siderite, magnetite, and plagioclase samples). Major and minor element concentrations
248 were measured by a CAMECA SX 100 at the University of Lille, using an accelerating voltage of 15 keV
249 and an intensity of 10 nA for most minerals, and slightly defocused (3 μm) for carbonates and phyllosilicates
250 which are more sensitive to the electron beam.

251 $K\alpha$ peak intensities for Si, Al, Na and Mg were collected on a TAP crystal, the Fe, Ni intensities on a LiF
252 crystal and other elements K, S, Ca, P, Ti, Cr on a LPET crystal. The oxygen concentration was calculated
253 by stoichiometry. We used a counting time of 20 seconds to obtain quantitative point analysis for all
254 elements but a loss compensation model has been applied to the Na and K intensities. The background
255 subtraction has been achieved by averaging the bremsstrahlung counts in two identical windows on either
256 side of the characteristic peaks. In few cases, one of the two windows was inaccessible due to another peak.
257 In that case only, one window has been used and a slight slope (between 1 and 1.2) is used to compensate
258 the lack of the other window.
259

3. Analyzing the Composition, the modal Abundance and the Density using Electron Microscopy (ACADEMY)

We used low-voltage EDX hyperspectral maps combined with EPMA and established a method to obtain modal abundance, density maps and bulk composition of heterogeneous phase assemblages.

The procedure can be divided into five parts steps which are summarized in Fig. 1. These steps include background modelling and peak fitting of EDX spectra, phase map, EPMA chemical quantification, density map and quantification.

- Elemental maps were created from the raw EDX hyperspectral data thanks to the development of a background model which is fitted together with Gaussians for the different X-ray lines.
- Elemental maps were analyzed by a classification algorithm in order to obtain a high-resolution phase map. Linear combination of end-member spectra was used to account for mixing of grains smaller than the pixel size. We thus obtained accurate modal abundances.
- These data were turned into quantitative maps using EPMA data as calibration.
- The density of each phase was determined by analyzing the bremsstrahlung background, which is a function of density. Determining the density is a requisite for obtaining bulk composition.
- The bulk composition of the entire region of mixed fine-grained materials was calculated by combining modal abundance, phase composition and density information.

Most data are processed using Hyperspy, an open source library for analysis of multidimensional data (De la peña, et al., 2017). A first phase classification is performed using XmapTools (Lanari et al., 2014) and corrected afterwards by manual thresholding. The background modeling approach has been implemented in HyperSpy and can be performed automatically on any dataset. A script allowing to reproduce the whole procedure is available at: <https://github.com/ZanettaPM/Demo-ACADEMY>.

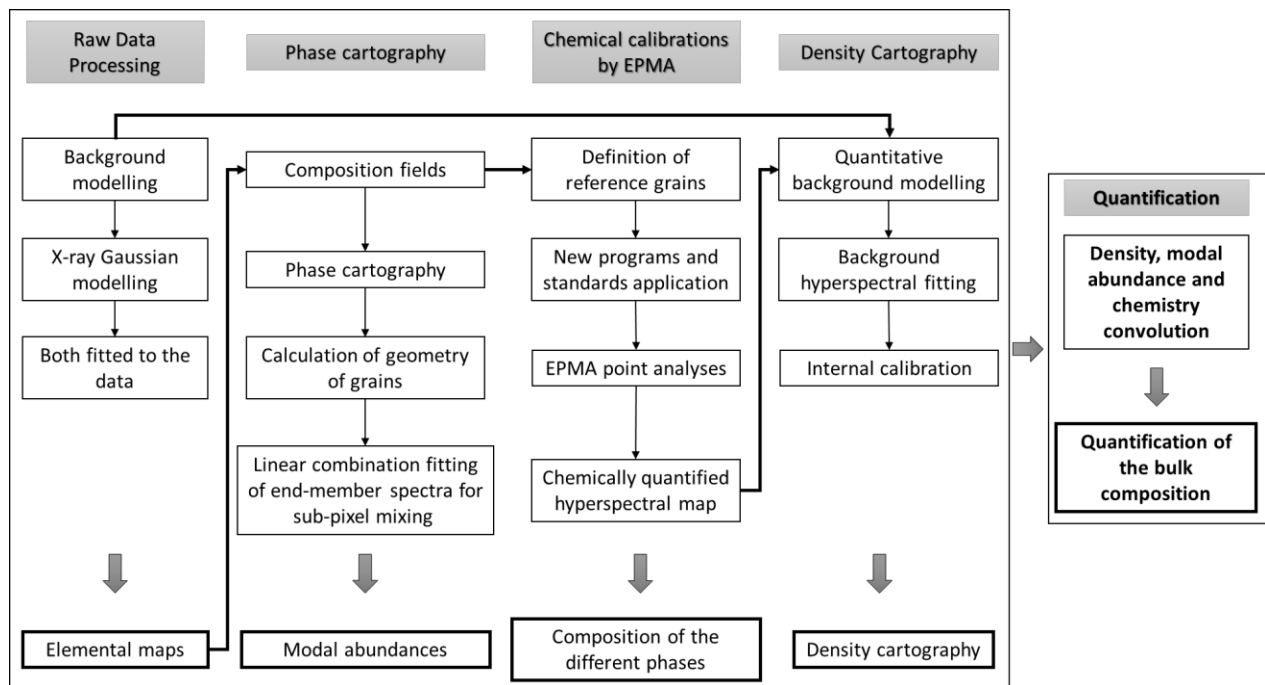


Fig 1: ACADEMY operating diagram schematizing the structure of the method. The final result of the entire method is the convolution of resulting parameters to obtain the local and global quantitative chemistry.

286 **3.1. Background modeling and spectrum fitting strategy**

287 SEM-EDX spectra are characterized by an important background, especially at energies below 2.5 keV and
 288 it was necessary to develop a background model including bremsstrahlung to obtain accurate peak intensities
 289 for weakly abundant elements.

290 To model the background, two different phenomena must be considered, the bremsstrahlung emission and
 291 the x-ray absorption in the sample and the detector (eq. 1). The bremsstrahlung phenomenon generates X-
 292 rays as a result of the deceleration of electrons due to the Coulombic fields of the different atoms. Then, this
 293 radiation is absorbed within the sample (Statham P. J., 1976) (Small, Leigh, Newbury, & Myklebust, 1987).
 294 In our model, we combined physical expressions of these phenomena from different sources. Continuous
 295 X-ray emission by a thick target is modelled using electron scattering cross sections by the Thomas-
 296 Whiddington law (Kramers, 1923).

297
$$I_{Br} = K Z \frac{(E_0 - E_v)}{E_v} \quad (1)$$

298 where I_{Br} is the intensity produced by the energy of the incident electrons E_0 , E_v is the energy of the
 299 bremsstrahlung x rays, K is Kramer's constant, and Z is the mean atomic number of the ionized atoms.
 300 Absorption of the emitted X-rays within the sample and the detector are taken into account based on
 301 (Statham P. J., 1976) (Ritchie, 2009). The theoretical absorption correction F can then be written as:

302
$$F(\chi) = \int_0^{\infty} \varphi(\rho x) e^{(-\chi \rho x)} d\rho x \quad (2)$$

303 where ρ is the density, x the depth, $\varphi(\rho x)$ is the ionization density as a function of depth, $\chi = \mu/\rho * \sin(\theta)$,
 304 with μ/ρ the mass absorption coefficients and θ the take-off angle. A simplified model (square model) has
 305 been proposed by (Sewell, Love, & Scott, 1985) that allows the simplification of the $\varphi(\rho x)$ distribution term.
 306 A top-hat profile representing the mean value of the distribution of the X-ray emission is assumed. This
 307 simplification allows one to consider a constant distribution which does not depend on the depth. We used
 308 their formulation:

309
$$I_{Br} = KZ \frac{(E_0 - E_v)}{E_v} * \frac{1 - e^{-2\chi \rho x}}{2\chi \rho x} * C * W \quad (3)$$

310 The parameters C and W represent the absorption taking place in the thin-layer coating of the sample and
 311 in the polymer window of the EDX detector, respectively. The mass absorption coefficients, which are
 312 function of energy, can be calculated according to:

313
$$\mu/\rho(E) = \sum_{i=1}^n W_i \mu_i \quad (4)$$

314 where W_i and μ_i are the weight fraction and mass absorption coefficients for element i in a compound with
 315 n elements. We used the mass absorption coefficients database of Chantler et al. (2005). Weight fractions
 316 are known a priori, and two options are available in the Hyperspy module of our model: i) by default, weight
 317 fractions are estimated by integrating EDX peaks or ii) when they are known, the phase compositions can
 318 be provided as inputs to obtain a more precise model (see section 3.3).
 319

320 Absorptions due to the thin coating layer (C) and by the polymer window (W) must be taken into account
 321 because the efficiency of low-energy X-ray collection has a major impact on background modeling. The
 322 coating layer parameter is computed using the Love and Scott model:
 323

324

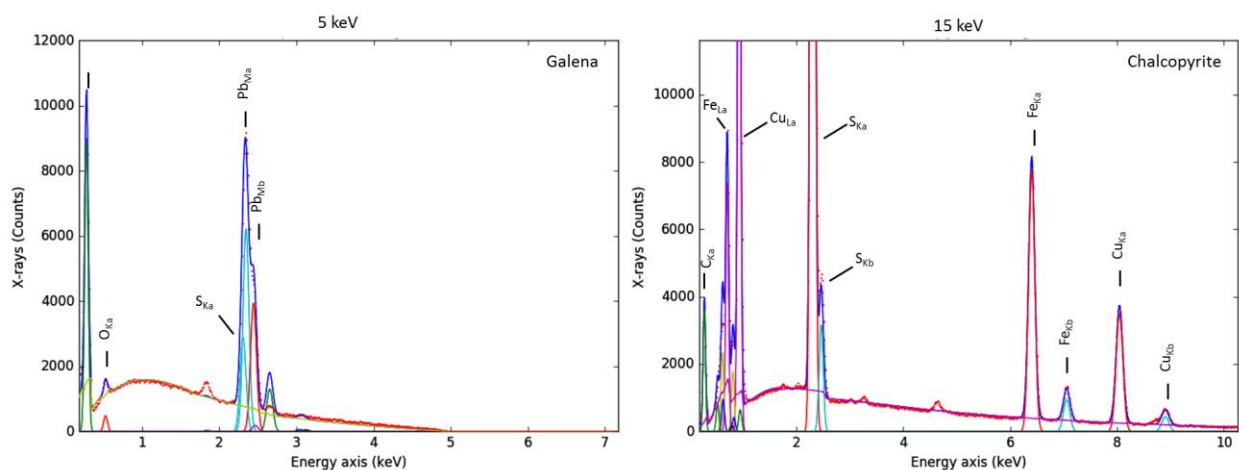
$$C = \frac{1 - e^{-2\chi\rho x}}{2\chi\rho x} \quad (5)$$

325

326 We used values for ρ and x of 1.9 g/cm^3 and 15 nm for the sample coating (100 wt% of C). For the W
327 parameter we used the ultra-thin polymer window curve proposed in (Schlossmacher, Klenov, Freitag,
328 Harrach, & Steinbach, 2010). The two main absorption edges are the carbon absorption edge (280 eV) and
329 the oxygen edge (520 eV). The minor absorption edge below 2 keV is due to the thin aluminum coating
330 used for the UV, IR and visible light rejection. (see supplementary materials 1)

331

332 The unknowns which must be fitted are “KZ” and the mass depth ‘ ρx ’. K is a constant for all pixels in a
333 given hyperspectral map. The KZ value could be perfectly fitted using the higher energy range of the spectra
334 ($> 2.5 \text{ keV}$, Fig.2), where absorption is negligible (Statham, Penman, & Duncumb, 2016). The mass-depth
335 parameter ‘ ρx ’ is fitted on the low energy part of the spectrum ($< 2.5 \text{ keV}$).



336

337 **Fig 2** Gaussian fitting and background modeling using Hyperspy. The first spectrum is Galena measured with a 5 keV
338 accelerating voltage while the second spectrum is chalcopyrite measured at 15 keV. The background is modeled at two
339 different beam energies. Each pixel/spectrum of the hyperspectral map was fitted using this background model.
340

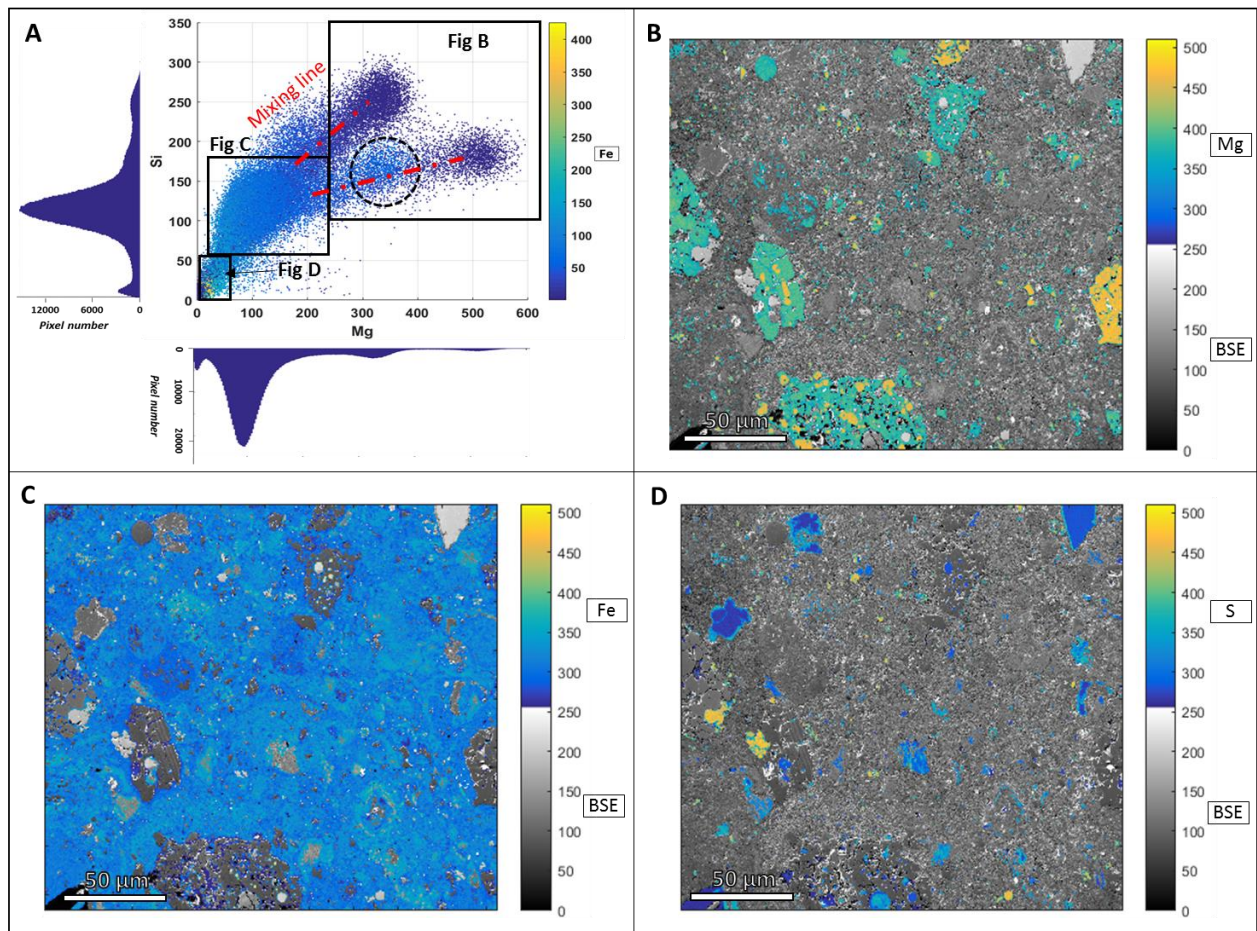
341 We fitted the data using a linear combination of the different components (i.e background and Gaussians)
342 and a least square minimization method (Fig.2). Net peak counts are given by the Gaussian areas which
343 allows us to obtain maps for 12 elements: C, O, Na, Mg, Al, Si, P, S, K, Ca, Fe, and Ni. At 5 keV, for some
344 elements, only the L lines are available (Fe –Ni). These lines are present at low energy (below 1 keV) and
345 their deconvolution can sometimes be ambiguous. Some elements were below detection level, such as Ti –
346 Cr – Mn (but were accessible by EPMA; see section 3.3).

347 **3.2. Phase mapping and modal abundances**

348 **3.2.1. Phase recognition and pixel classification**

349
350 The phase map is established in two steps. The first one consists of identifying the various phases present
351 using compositional fields. It is a “training stage” which is necessary to define “reference” grains. The
352 second step uses those reference grains for the supervised classification of all pixels, performed thanks to
353 the XMapTools software (Lanari et al., 2014). The X-ray intensities are plotted to reveal compositional end-
354 members and mixing lines (Fig. 3A). Those composition fields are directly extracted from the elemental
355 count map, where each datapoint corresponds to one pixel. Each cluster represents a phase of a given
356 composition (but from randomly distributed grains). We use these plots (Matlab®) to select pixels of similar
357 composition and reveal the localization of the different “objects” (minerals, mineral boundaries and
358 fractures).

359 In an Mg vs. Si plot (Fig. 3A), pixels with high Mg counts correspond to forsterite and enstatite (all phases
360 are confirmed by later EPMA quantification, see section 3.3). The sharp boundaries of grains match with
361 the BSE images and exhibit a geometry typical of fragmented silicate inclusions found in chondrite matrices
362 (Fig. 3B). Pixels of intermediate compositions (Fig 3.C) correspond to finer scale mixtures of amorphous
363 silicates and phyllosilicates with other embedded grains such as sulfides. There are more chemical
364 heterogeneities in these clusters and their limits are not as clear as for single crystals. It is known that
365 phyllosilicates in primitive chondrites are commonly serpentines, a family of minerals showing a solid
366 solution series between Fe and Mg end-members (Tomeoka & Buseck, 1985) (Zolensky, et al., 1997)
367 (Lauretta, Hua, & Buseck, 2000). In order to better describe this solid solution, we defined two end-
368 members, an Fe-rich fraction and an Mg-rich fraction. Pixels between the two clusters of Fig 3.B and 3.C
369 exhibit intermediate compositions and correspond to the boundaries of anhydrous silicates (i.e. where the
370 beam probes two different phases) or to mixing of grains smaller than the pixel size. Pixels low in both Mg
371 and Si (Fig.3.D) correspond to phases such as troilite, pentlandite, carbonate or metal and can be identified
372 using other composition fields (Fe, S, Ca and Ni). The BSE map acquire simultaneously to the X-ray data
373 can also be plotted in composition field versus the different elements since it contains a mean Z information,
374 but also give a spatial information (grains location, boundaries etc.).

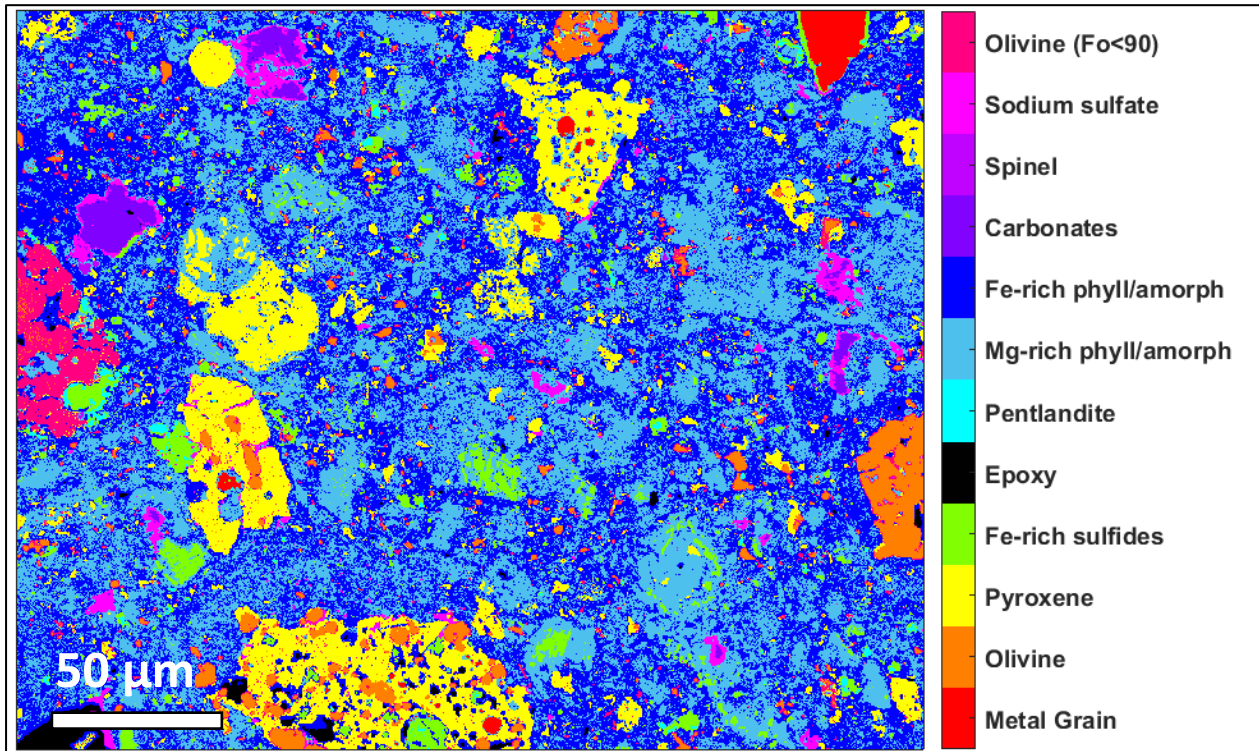


375

Fig 3: A: X-ray intensities of Mg and Si peaks, combined with Fe intensity (colorbar). Each point corresponds to one pixel (Paris Zone 2). Pixels of identical composition form clusters. B: forsterite and enstatite map based on the selection of the corresponding cluster. C: This cluster corresponds to a fine-grained mixture of amorphous silicates, phyllosilicates with sulfides and anhydrous silicate inclusions. D: Map of the remaining pixels after thresholding for Mg and Si. This selection contains Mg and Si-free phases, such as metal grains, sulfides, etc. Unselected pixels are displayed as a secondary electron image or back-scattered electron image.

376

377 We used the XMapTools software to build phase map (Lanari, et al., 2014). However, this classification
 378 could also be done using open source python libraries. XMapTools is a MATLAB©-based graphical user
 379 interface dedicated to electron microprobe X-ray image processing (Lanari, et al., 2014). It uses K-means
 380 clustering to classify pixels into classes of similar compositions. The K-means procedure identifies clusters
 381 and allocates pixels to these clusters by minimizing the distance in the compositional space between each
 382 pixel and the center of gravity of each cluster (Saporta, 2006). As for other supervised classification
 383 methods, the user needs to define reference pixels as initial guesses for each group on the chemical map.
 384 The compositions of these pixels are used as starting cluster centroids.



385 **Fig 4:** Phase map of the matrix of the Paris meteorite (Zone 2) after manual adjustment; 11 different phases were
 386 found. Grains down to 500 nanometers are visible and well classified.
 387

388 We chose to use the “normalization” function which considers the mean values of the elemental maps such
 389 that all elements have the same weight and only the variances are compared. A map is generated displaying
 390 the principal phases, which have higher abundances and largest chemical differences between them (Figure
 391 4). Regions of anhydrous silicates, phyllosilicates, fractures and sulfides are clearly revealed.

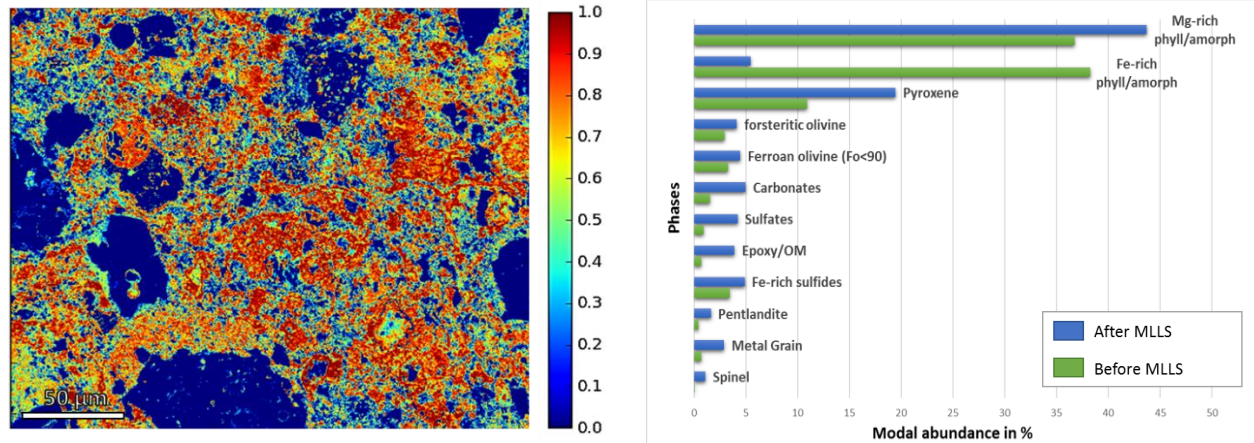
392 However, phases represented by only a few pixels and weak chemical difference in comparison to some
 393 other more abundant phase are neglected most of the time. After the first map proposed by XMapTools it is
 394 necessary to go back to the composition field step, to manually check that no artefacts have appeared and
 395 add new phases, whenever appropriate. This step allows separating into two phases pixels which may have
 396 been mistakenly grouped together. It produces maps that are more accurate but it does not change the modal
 397 abundances, which only depends on the MLLS procedure (see next section).

398 **3.2.2. Fitting linear combination of spectra to unravel phase mixing at the pixel scale**

399 It has been shown that matrices of carbonaceous chondrite are made of a heterogeneous assemblage of
 400 grains smaller than 1 µm which cannot be resolved with a pixel size of 300 nm. To refine the modal
 401 abundance determinations, we deconvolved spectra of mixed fine-grained materials using linear
 402 combination of “end-member” spectra. Reference spectra were defined by considering only the pixels from
 403 the center of the clusters which are considered as “pure” (Fig.3.A). A non-negative linear combination is
 404 fitted using Hyperspy by scaling coefficients (mixing proportions) to the experimental spectrum by means
 405 of least-square optimization (Leapman & Swyt, 1988) and can be expressed as the following formulation.

$$406 \quad E_s = \sum_{j=1}^n (\alpha_j * S_{ref_j}) \quad (6)$$

407 Where E_s is the experimental spectrum, α are mixing coefficients, S_{ref} are the spectra of the end-members
 408 and j is the number of phase. We used the denomination “MLLS” for “Multiple Linear Least Square fitting”
 409 to refer to this procedure.



410 **Fig 5:** Example of a MLLS deconvolution. **A:** Map of the proportion of the Mg-rich phyllosilicate in the fine-grained
 411 matrix. **B:** Modal abundances before and after correction provided by the MLLS fitting. Forsterite olivine has Mg>98
 412 % while ferroan olivine has typically around 15 % of Fe
 413

414 This step led to significant improvements of the modal abundances. About 25% of the total volume initially
 415 classified as “Fe rich phyllosilicates/amorphous silicates” was re-assigned to other phases. In contrast, the
 416 abundances of sub-micrometer grains of pyroxenes, olivine and sulfides embedded within the
 417 “phyllosilicate/amorphous silicates” were initially under estimated. However, the fact that the
 418 amorphous/phyllosilicate material contains a low amount of S can be problematic. The deconvolution of the
 419 nano-sulfides will be based on the variation of a peak with a small number of counts. This weak count
 420 statistic is visible in Fig 5.B, and the modification by the MLLS step of the abundance of sulfides is relatively
 421 small compared to what can be expected from TEM studies (Zolensky, Barrett, & Browning, 1993)
 422 (Brearley, 2006) (Leroux, Cuvillier, Zanda, & Hewins, 2015). This poor constrain on the S peak can lead to
 423 an underestimation of the nano-sulfides and impacted the final matrix composition.

<i>Phase</i>	<i>Abundances in %</i>	<i>Relative error (1σ) in %</i>
<i>Forsteritic Olivine</i>	4.46	0.64
<i>Pyroxene</i>	21.05	2.88
<i>Pentlandite</i>	1.77	1.19
<i>Pyrrhotite</i>	5.28	0.84
<i>Metal grain</i>	3.12	1.82
<i>Mg-rich phyll/amorph</i>	47.24	12.99
<i>Fe-rich phyll/amorph</i>	5.89	8.19
<i>Spinel</i>	1.20	1.75
<i>Sulfates</i>	5.37	2.84
<i>Carbonates</i>	4.61	3.10
<i>Ferroan olivine</i>	4.82	0.71

424 **Table 1:** modal abundances obtained with phase map in the matrix of the Paris meteorite (zone 2) and associated
 425 relative error due to the variation of the mixed phase proportions among the different pixel of the map.

426 Errors in the attribution have been estimated by the means of the multinomial statistic law (Dirichlet law).
 427 Only pixels for which the non negative constraint imposed by the MLLS fitting had a very low impact

428 (around 85 % of the fine matrix), and therefore when the statistic χ^2 law was applicable, were considered.
429 The modal abundances given by the MLLS procedure correspond to a mean value. This mean value is
430 calculated based on the proportion of the different phase in each pixel. In order to calculate the error in the
431 attribution, we calculate the standard deviation around these mean values for the considered pixels. For a
432 random mixing and a sufficient number of pixel, the standard deviation should be low and the value of most
433 of the pixels should draw near the mean value. We make the assumption that the deviation is therefore linked
434 to an error in the attribution of the different phase by the MLLS procedure.

435 Table.1 represents the relative error compared to the abundance of the phase. This estimation leads to errors
436 below 3 % for most of the phases. Phyllosilicate which has the most varied proportions in the whole map
437 has the largest error. The standard deviations for the Mg-rich part and the Fe-rich part of the fine material
438 have been calculated separately since two clear population of the mixture could be distinguished. The coarse
439 grains previously masked are considered to be perfectly attributed to the right class and we assume that their
440 errors are negligible. Thanks to the low-voltage of the acquisition and the high resolution of the map, errors
441 stay below a few percent (8-12%) and seem appropriate for fine-grained material application.

442 **3.3. Quantitative chemical calibrations by EPMA**

443 In order to obtain quantified compositional maps, we coupled the high spatial resolution maps obtained by
444 SEM-EDX with EPMA. We use the phase map to identify the largest grains of each different phases and
445 use them as an internal calibration. Reference grains were selected as follows: 1) They have to be large
446 enough for the EPMA probe ($> 2\text{-}3\ \mu\text{m}$), 2) they have to correspond to pixels from the center of the clusters
447 (i.e. end-members). Numerous EPMA standards were prepared in order to be as close as possible to the
448 chemistry and the density of the phase to quantify. In particular, an iron-rich biotite (ref: 12:119-201
449 (Govindaraju & Roelandts, 1988)) was used for the Mg-Fe-Si quantification of the amorphous/phyllosilicate
450 material, since they have $\text{Fe/Si}=0,56$ and mean density of $3\ \text{g/cm}^3$ which are close to each other, a point
451 which is crucial for precise absorption correction calculation.

452
453 The effect of the water contained in the amorphous/phyllosilicate material has also been taken into account
454 for quantification. Bulk water content values have been taken from (Jarosewich, 1990) (Jarosewich, 2006)
455 for Orgueil and Murchison and from (Vacher, Marrocchi, Verdier-Paoletti, Villeneuve, & Gounelle, 2016)
456 for Paris. We made the assumption that most water is carried by the amorphous/phyllosilicate material,
457 which contains 18.3 % H_2O (wt. % oxide) for Orgueil, 18.2 wt. % for Murchison and 17.5 wt. % for Paris.
458 These values have been added to the quantification sheets of the phyllosilicate reference grains in the EPMA
459 software to allow accurate $\phi(\rho z)$ correction.

460
461 We identified that the principal source of error in the EPMA results is the counting statistic which depends
462 on the concentration of each element, with the error ranging from $\sim 0.4\%$ for Mg to 15 % for Na in olivine
463 (see supplementary material 2). We minimized other errors by carefully defining our working conditions
464 according to (Lifshin & Gauvin, 2001).

465 **3.4. Density determination through bremsstrahlung modelling**

466 **3.4.1. Validation of the method using reference materials**

467 Bremsstrahlung is a function of the material density and modelling and fitting it can therefore be used to
468 determine the density of a material based on its EDX spectrum (see section 3.1). However, the proxy
469 obtained by curve fitting is the mass-depth (i.e. ρx) and not directly the density itself. In order to determine
470 the respective contribution of the density and the emission depth, which are non linearly coupled, we used

standards covering a large range of compositions and densities. The following standards were measured at 5 and 15 keV: Albite, Almandine, Anhydrite, Apatite, Arsenopyrite, Barite, Benitoite, Biotite, Calcite, Chalcopyrite, Chlorite, Chromite, Diopside, Dolomite, Galena, Hematite, Jadeite, Magnetite, Olivine Orthoclase (see supplementary material 3). For background modelling, the absorption correction relies on the estimation of the phase composition. Here, instead of estimating composition based on peak fitting as done for unknown materials (see section 3.1), we used the composition of the standards as direct inputs to be as accurate as possible.

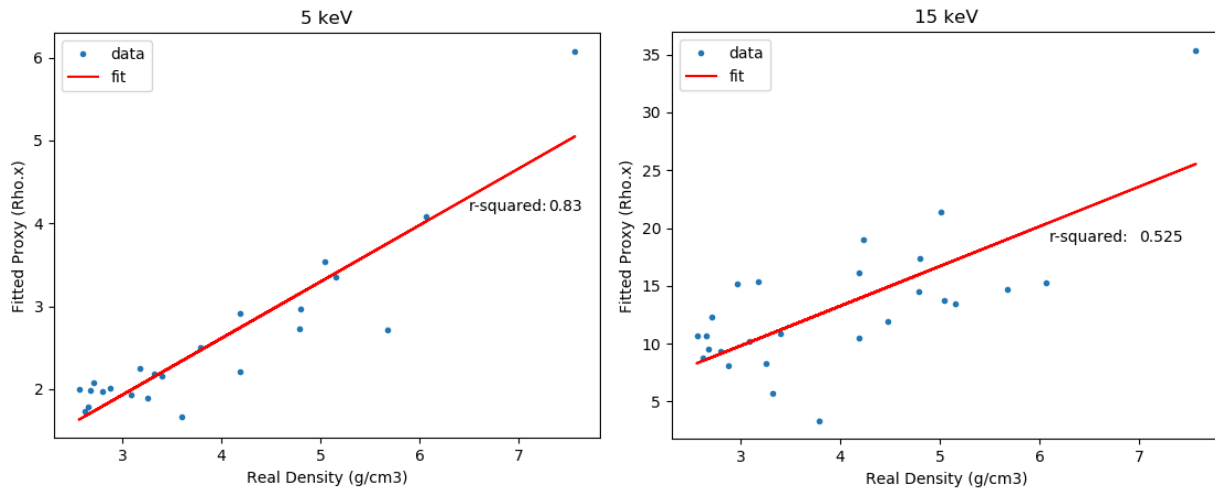
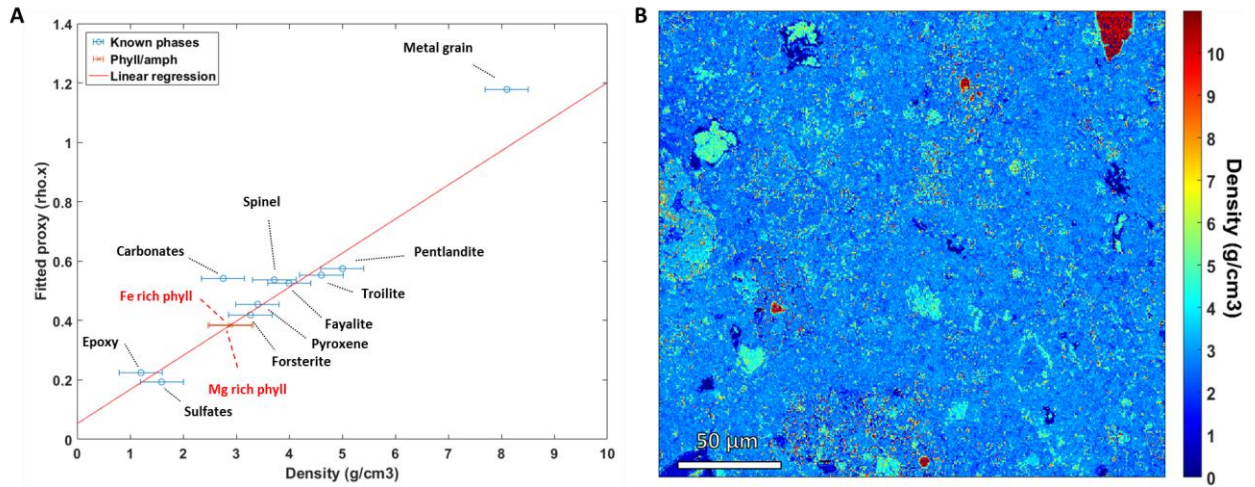


Fig 6: Plots of the ‘ ρ_x ’ proxy obtained by least square minimization of eq. (4) versus the real density of the standards.

Our results demonstrate that the fitted ρ_x parameter is correlated with density (Fig. 6) and thus that background modelling allows the determination of the density of unknown samples (Fig. 7) whereas the emission depth only induces second order variations. We obtain a mean absolute percentage error (MAPE) of 10% for the 5 keV conditions and 24 % at 15 keV (Fig.6). Errors related to the fitting procedure are negligible. At 5 keV, the correlation is better because interaction volumes decrease at lower voltage and thus, for the same density range, the variability of the emission depth is smaller. The principal uncertainty is the variability of the emission depth. Indeed, based on Monte-Carlo simulations, the variations of mean emission depth at 5 keV can be around 20% (Ritchie, 2009). Nonetheless, uncertainties on the mass absorption coefficients and approximation linked to the chosen model might also have a strong effect on the background modelling. At low energy (below 1 keV), values of mass attenuation coefficients found in different databases (Heinrich, 1986) (Henke, Gullikson, & Davis, 1993) (Chantler, et al., 2003) are poorly constrained which could explain part of the uncertainties. This parameter is critical in many aspects of modeling X-ray transport and the improvement of these databases is necessary (Lepy, Mantler, & Beckhoff, 2008). Conversely, the background model is an evolutionary code which could be easily improved in the future. For instance, monte-carlo simulations could be implemented for the determination of the X-ray emissions allowing to not use the Love & Scott simplification anymore.

3.4.2. 2D density and porosity mapping of heterogeneous assemblages

In chondrites, the density of fine-grained regions, made of a porous mixture of amorphous silicate, phyllosilicates and sulfides, is unknown. In this case, we then used the known density of the surrounding phases (Troilite, Pentlandite, Olivine..., including the epoxy which embed the samples) to establish an internal calibration. We obtained an excellent correlation with a mean absolute percentage error of MAPE=8% which allows us to determine the density of the amorphous/phyllosilicate regions (Fig. 7.A) and to produce a density map (Fig. 7.B).



504
 505 **Fig 7: A.** Mean proxy values (Paris zone 2) for all pixels of each different phase versus their nominal density. The
 506 error bars represent the mean absolute error (MAE=0.41) calculated in the previous section. **B:** resulting density map
 507 produced by this approach.

508 The mean density of the amorphous/phyllsilicates mixed with nano-inclusions is 2.9 ± 0.32 g/cm³ for the
 509 Fe-rich part and 2.8 ± 0.31 g/cm³ for the Mg-rich part. Considering the abundance of sulfide nano-inclusions
 510 the iron content of the phyllosilicate and the nano-porosity, these values are coherent.

511
 512 From this result it is possible to calculate the density of the phyllosilicate itself without the contribution of
 513 the other phases. We calculated a mean density map of the inclusions based on the MLLS results:

514

$$D_{inclu} = \sum_{j=1}^n (\alpha_j * D_{nom j}) \quad (8)$$

515 Where α are mixing coefficients, D_{nom} is the nominal density of the different phases and j the number of
 516 inclusions embedded in the phyllosilicate material. The difference between the density map calculated using
 517 background modeling and the density of inclusion phases gives a residual. This residual represents the
 518 density of the phyllosilicate material with a variable amount of porosity.

519

$$D_{Phyll} = \frac{D_{App} - D_{Inclu}}{\alpha_{Phyll}} \quad (9)$$

520 Where D_{app} is the apparent density found thanks to the background modeling and α_{Phyll} is the mixing
 521 coefficient of the Fe-rich and Mg-rich amorphous/phyllsilicate material. Values found for Paris are 2.35
 522 g/cm³ for the Mg-rich part and 2.44 g/cm³ for the iron rich part. Now, if a nominal density of 2.8 g/cm³ for
 523 the Fe-rich part and 2.6 g/cm³ for the Mg-rich part (deduced from their Fe/Mg ratio) is assumed and if all
 524 the porosity is considered to be filled by epoxy, then, mean porosities of 22% and 18% are needed to explain
 525 respectively the apparent density of the Mg-rich part and the Fe-rich part (see supplementary materials 4).

526 3.5. Calculation of the bulk composition and related uncertainties

527 We combine the modal abundance, the chemical composition and the density of each phase to calculate the
 528 bulk composition of the analyzed region using the following equation:

529

$$[I] = \sum_{j=1}^n (M_j * [I]_j * \rho_j) \quad (10)$$

530 where I is the concentration of a given element, j a given phase, n the number of phases, M is the abundance
 531 of a phase in vol.%, and ρ is the density. The area abundances have been directly converted into volume
 532 fractions according to (Cuzzi & Olson, 2017). The density used for the known phases (olivine, pyroxene,
 533 etc..) are taken from the literature (accounting for their compositions) whereas the density for the
 534 amorphous/phyllosilicate phase is determined based on background modelling. By computing each relative
 535 error previously discussed, we can also determine an associated error. We first determined a relative error
 536 per phase and per element to obtain afterwards errors on the global composition (table.3).

	<i>Paris Zone 2</i>	<i>Absolute error</i>
<i>Na</i>	0,78	0,05
<i>Mg</i>	23,32	0,87
<i>Si</i>	27,14	0,97
<i>Fe</i>	28,49	1,00
<i>Al</i>	2,63	0,11
<i>K</i>	0,13	0,01
<i>S</i>	10,01	0,40
<i>Ca</i>	4,56	0,18
<i>P</i>	0,29	0,02
<i>Ti</i>	0,07	0,00
<i>Cr</i>	0,41	0,02
<i>Ni</i>	2,16	0,09
Total	100	

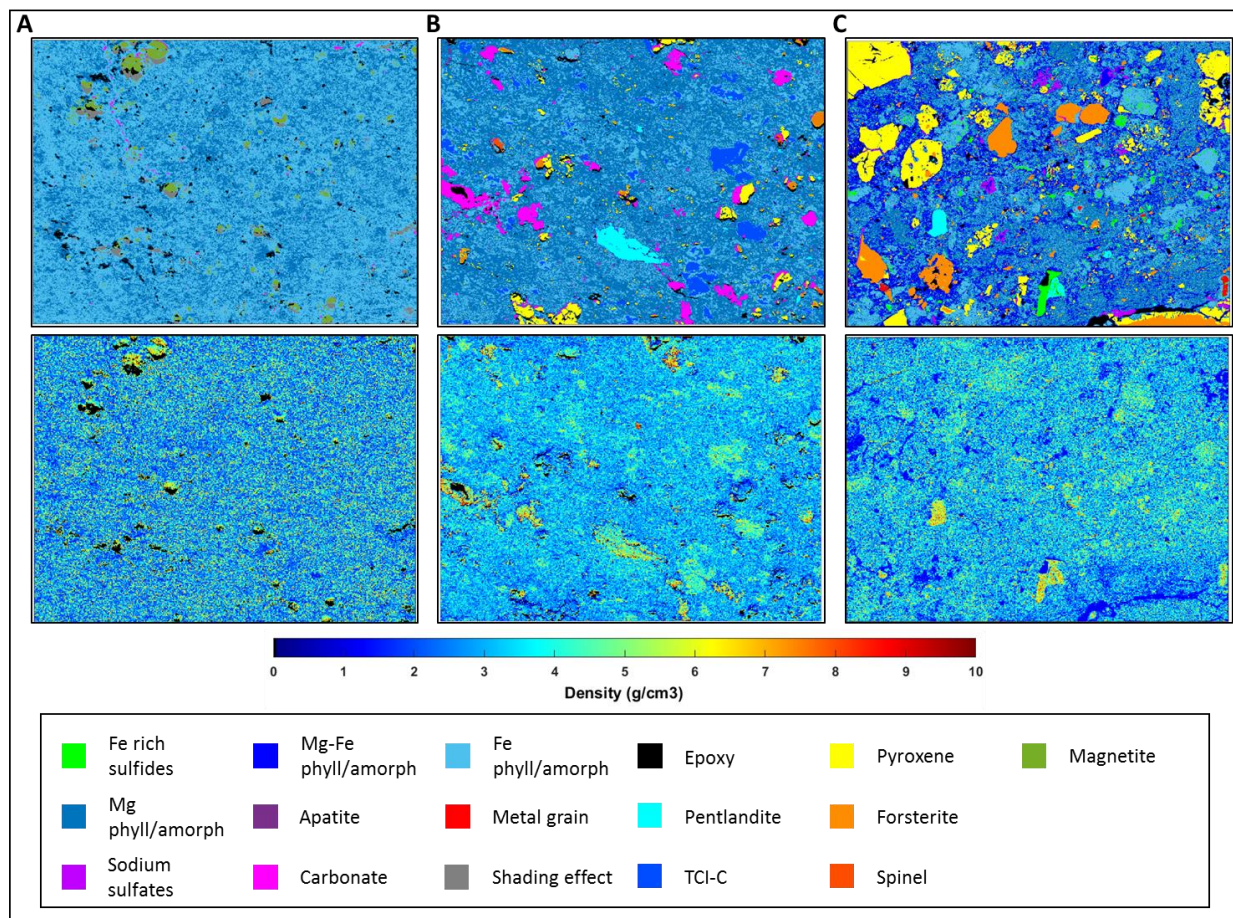
537 **Table 2:** Bulk composition of the matrix of Paris in at%. Absolute errors linked to the entire method are indicated in
 538 percent for the Paris meteorite (zone 2).

539 Large uncertainties are found for elements with minor concentrations (Ti, P, K, Na, Cr). This is due to the
 540 low counting statistics of EPMA acquisition. Conversely, the errors for major elements (i.e. Mg, Fe, Si)
 541 depend on the modal abundance error and the density error. Indeed, the amorphous/phyllosilicate domains
 542 which carry a large fraction of these elements, display tortuous edges, mixing of phases and are
 543 heterogeneously porous.

544 4. Applications of ACADEMY to fine-grained assemblages from chondrite matrices

545 4.1. Density, modal abundances and bulk composition

546 We applied ACADEMY to several areas (220*270 μm) of the Orgueil, Paris and Murchison chondrites.
547 Different areas in Paris have been selected because they display different degrees of alteration: zone number
548 2 is located in a fresh area where chondrules exhibit large metal grains with only thin oxidized rims on their
549 borders. Zone 3 is located in a more aqueously altered area showing phyllosilicates. Zone 1 is intermediate
550 between the zones 2 and 3.

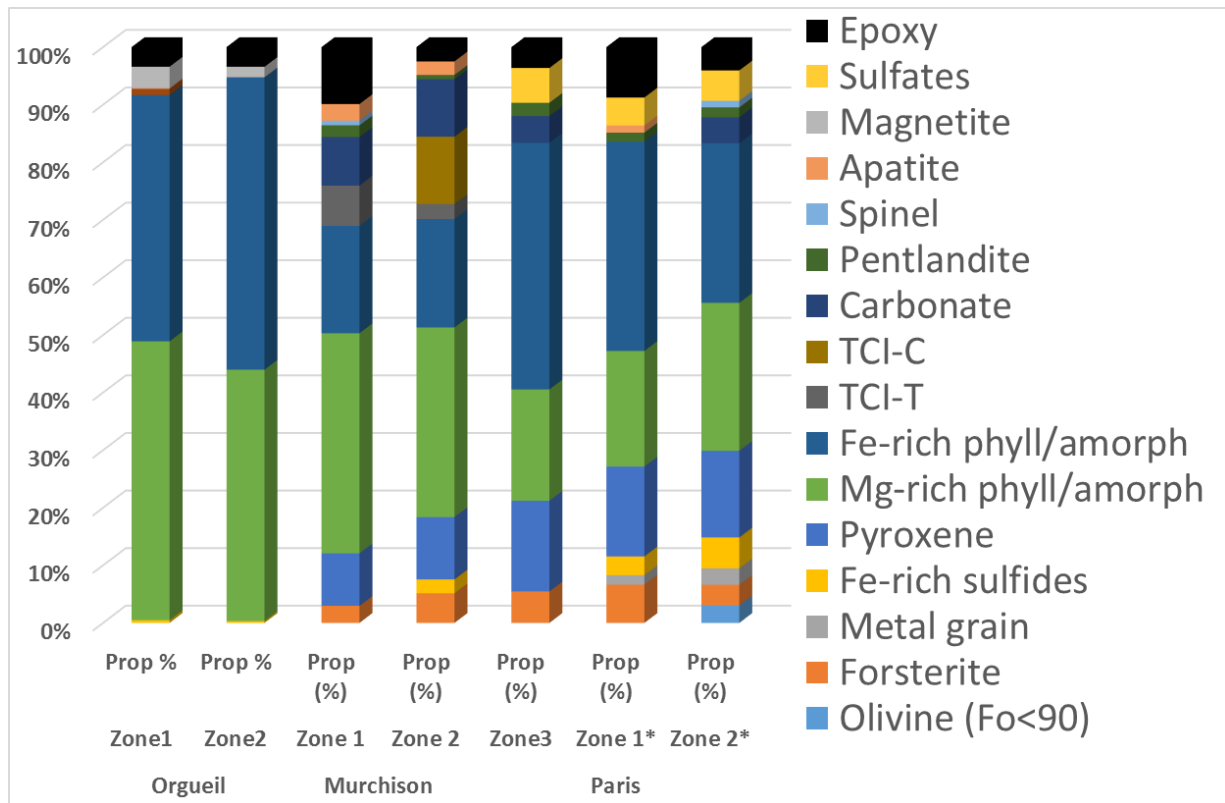


551 **Fig 8:** Phase map (top), and density map (bottom) are displayed. Three matrices of different meteorites are compared:
552 A: Orgueil; B: Murchison; and C: Paris Zone 1. Each map consists of region of 270 μm by 220 μm .
553

554 ACADEMY allows us to quantitatively compare modal abundances of heterogeneous matrices (Fig.8 and
555 9). In the case of Zone 1 and Zone 2 of the Paris meteorite, large chondrule fragments were ignored. Matrices
556 are dominated by a mixture of amorphous silicates and phyllosilicates that ranges from $55.7 \pm 5.9 \%$ in
557 Paris, $67.0 \pm 7.1\%$ in Murchison and up to $94 \pm 9.9\%$ in Orgueil. Conversely, anhydrous silicates represent
558 $14.1 \pm 0.2\%$ of the matrix of Murchison and reach $23.0 \pm 0.6\%$ for the unaltered part of the matrix of Paris (0
559 $\%$ in Orgueil). In Paris, the amount of amorphous silicates/phyllosilicate varies between $49.1 \pm 5.2\%$ for the
560 unaltered parts and $62.8 \pm 6.7\%$ for more altered regions. Also, anhydrous silicates vary from $23 \pm 0.6\%$ to
561 $21 \pm 0.3\%$ between these two regions respectively (see supplementary material 5).

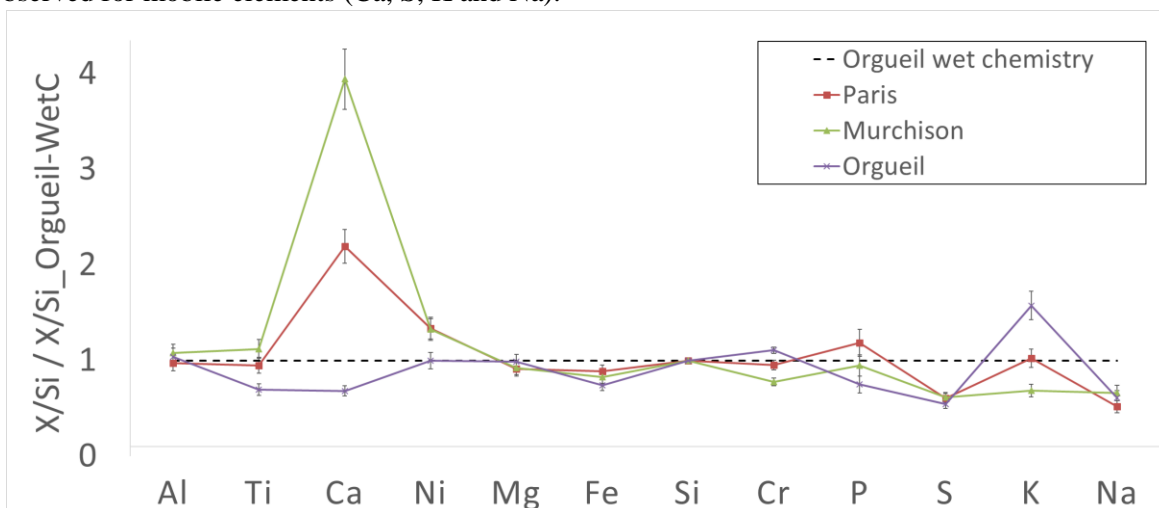
562 The mean density of the phyllosilicates mixed with nano-phases varies from 2.60 g/cm^3 for Paris to 3.15
563 g/cm^3 for Murchison and 3.24 g/cm^3 for Orgueil. The accuracy is lower for Orgueil since there was not as

564 many phases of known density available to establish the internal calibration. Paris has a more heterogeneous
 565 and higher density than Orgueil (Fig. 8).



566
 567 **Fig 9:** Modal mineralogy of the different matrices as determined by phase mapping and MLLS fitting. For phases
 568 other than phyllosilicates, relative errors range from 0.5 to 3%. This error is larger for phyllosilicates (8-12 %). Zones
 569 with a symbol "*" indicate areas from which large chondrule fragments were ignored (see supplementary materials 6).
 570

571 Finally, we calculated the matrix bulk composition for the three meteorites. The deduced composition falls
 572 close to chondritic values and deviations in major elements (Mg – Si – Fe) are small. A stronger variability
 573 is observed for mobile elements (Ca, S, K and Na).



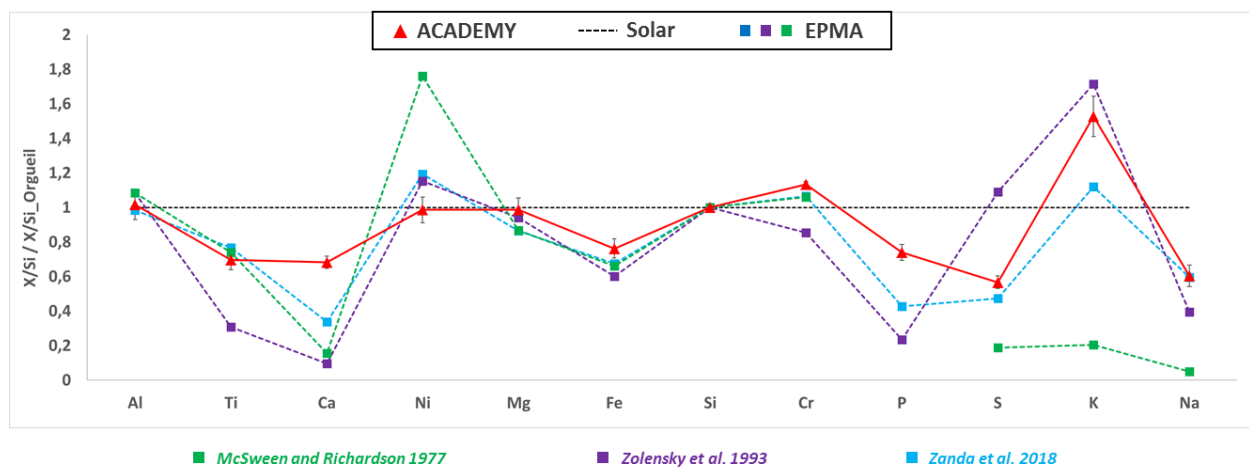
574
 575 **Fig 10:** Bulk compositions of matrices (atomic ratios) calculated by ACADEMY (average of all analyzed regions)
 576 normalized to silicon and to the composition of Orgueil determined by wet chemistry (Lodders & Palme, 2009). (See
 577 supplementary materials 7)

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4.2. Comparison to wet chemistry and EPMA data

ACADEMY compared to wet chemistry for Orgueil

Orgueil is the only meteorite for which the bulk composition of the matrix has been quantified by wet chemistry (Jarosewich, 1990) (Jarosewich, 2006) (Lodders, Palme, & Gail, 2009). A good correlation is found between the wet chemistry and ACADEMY values ($R^2 \sim 0.96$; Fig. 11). Considering major elements only, the match is even better. Deviations are mainly due to the scale of the analysis. Sulfides, carbonates and phosphates, which occur as large patches and are not perfectly sampled at this scale, biases the concentrations of Fe, Ca, P and S. We calculated that a depletion of 5 % of sulfides and 1 % of carbonates could explain the lower Fe, S and Ca contents. For minor elements such as K, Na, Cr or Ti, additional deviations could be linked to their low concentrations within their carrier (<1 at. %) which leads to higher uncertainties. In the case of published EPMA measurements, a part of the deviation could also be due to non-representative sampling of carbonates and sulfides.



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Fig 11. Bulk matrix compositions obtained by ACADEMY and EPMA compared to data obtained wet chemistry (Lodders, Palme, & Gail, 2009). EPMA data are from (McSween Jr & Richardson, 1977), (Zolensky, Barrett, & Browning, 1993), (Zanda, Lewin, & Humayun, 2018).

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The role of EPMA standard, water content and phase specific density weighing.

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In chondrites, because matrices and chondrules cannot be easily separated for independent measurement by wet chemistry, “bulk” matrix compositions have been mainly determined by EPMA using a defocused beam of five to a few tens of microns. Here we discuss the technical advantages of ACADEMY and we compare our matrix composition results to the EPMA data of previous studies.

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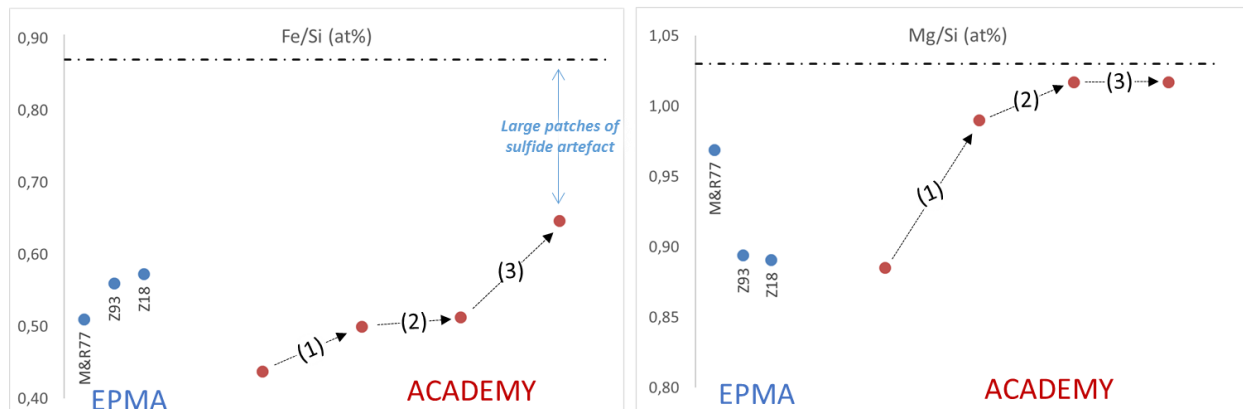
Accurate quantification by EPMA requires: (1) performing $\phi(\rho z)$ corrections on a homogeneous material, which becomes complicated when different phases are mixed together; (2) the use of specific standards that are chemically and in density close to the mineral to quantify; (3) all elements present in the sample have to be taken into account for the $\phi(\rho z)$ correction, including hydrogen and oxygen from water. In addition, to obtain accurate bulk composition, the modal abundance of each phase has to be pondered by their density. In matrices of primitive chondrites, the infra-micrometric grains-size, the presence of water, and the variable densities precludes an ideal EPMA measurement, especially when a defocused EPMA probe is used.

613
614

To evaluate improvements due to these different parameters (Fig. 12), we compared the bulk Fe/Si and Mg/Si ratios: i) using two different EPMA standards to quantify the Mg-Fe-Si concentrations of the

615 amorphous/phyllsilicate material; ii) by adding the water to the $\phi(\rho z)$ correction (post-measurement); iii)
 616 weighting by the density of the different phases. Compared to previously published EPMA data,
 617 ACADEMY provides composition much closer to the wet chemistry data.

(1) Standard closer in composition (2) Including H₂O in ZAF calculation (3) Wheighing modal abundances by specific densities



618
 619 **Fig 12.** Fe/Si and Mg/Si (at. %) ratios for the Orgueil meteorite obtained by previous results and compared to
 620 ACADEMY. The effect of different parameters on the results of ACADEMY are presented, i.e. the use of two different
 621 standards, the addition of H₂O content for the $\phi(\rho z)$ correction, and the density ponderation. These analytical
 622 improvements increases the Fe/Si and the Mg/Si ratio by about 22 and 12 % respectively which are ultimately very close
 623 to the wet chemistry data (dashed line; from (Lodders & Palme, 2009)). EPMA ratios are taken from (McSween
 624 Jr & Richardson, 1977), (Zolensky, Barrett, & Browning, 1993) and (Zanda, Lewin, & Humayun, 2018).
 625

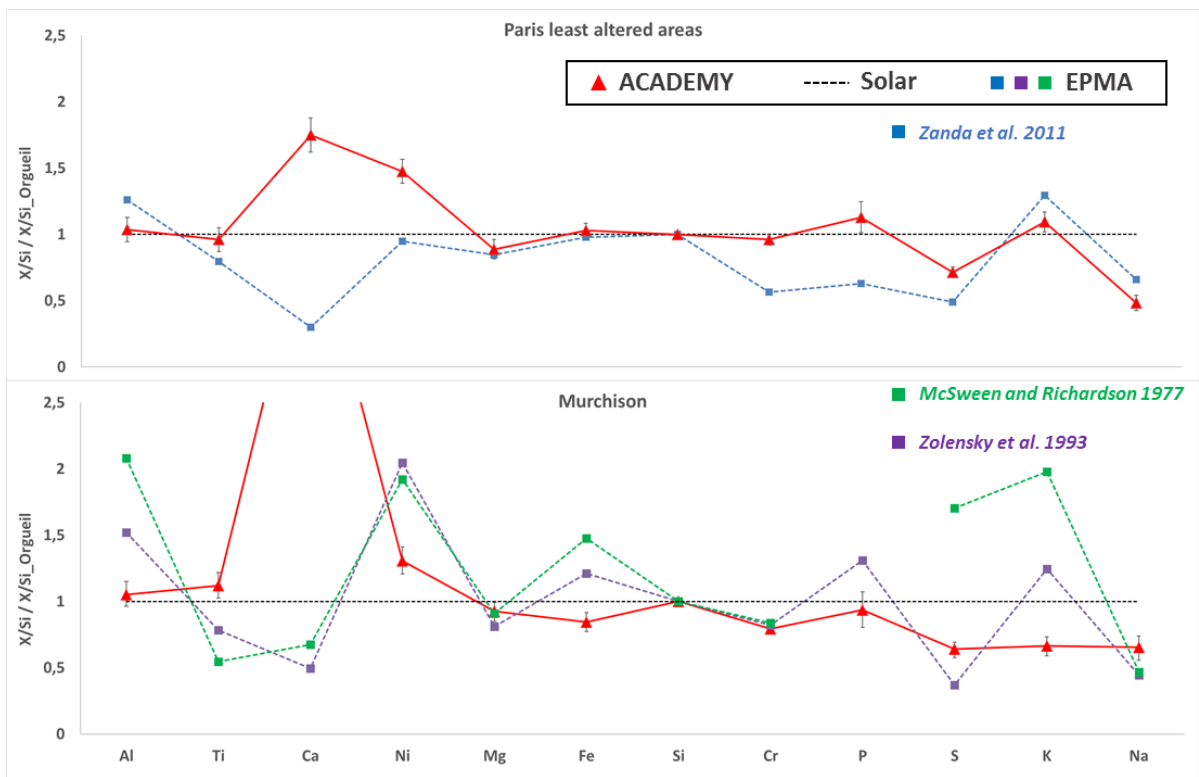
626 Usually, EPMA measurements are obtained using standards such as Mg-rich silicate (forsterite or diopside)
 627 for Mg and Si and hematite for Fe. Here, we compared a Mg-rich hornblende and a Fe-rich biotite and
 628 demonstrate that using the biotite improves the Fe/Si and Mg/Si ratios by about 7 % and 10 % respectively
 629 (Fig. 12). Iron in the amorphous/phyllsilicate material induces a differential absorption between the Mg
 630 and the Si peak which is not well corrected by the $\phi(\rho z)$ procedure and leads to an underestimation of the
 631 Mg content. It is thus crucial to choose a standard which is chemically close to the targeted phase (i.e. the
 632 Fe-rich biotite).
 633

634 One limit to analytical accuracy of the EPMA measurements of chondrites is that water and hydroxyl groups
 635 in the phyllsilicate are not taken into account (the “totals” never reaches 100%). This underestimation of
 636 the oxygen content ultimately generates errors in the absorption corrections. By adding about ~20% H₂O
 637 (wt.% oxide) to the EPMA quantification procedure, the Fe/Si and Mg/Si ratios are improved by 1.5 and
 638 2.6 %, respectively (Fig. 12).
 639

640 Previous works have pointed out that EPMA data show deviations compared to bulk analytical methods
 641 because the quantification results are not balanced by the density of the different phases (Ichinokawa,
 642 Kobayashi, & Nakajima, 1969), (Warren, 1997), (Nazarov, Ignatenko, & Shevaleevsky, 1982), (Zanda,
 643 Lewin, & Humayun, 2018). Thanks to the high resolution of the maps and because the different phases are
 644 considered independently, ACADEMY allows to apply a density ponderation as a final step. In Orgueil,
 645 the density ponderation improved the Fe/Si ratio by about 13% (Fig.12). This is due to the fact that iron is
 646 carried by various phases of different densities (sulfides and magnetites are denser than phyllsilicates).
 647 There is no improvement for the Mg/Si ratio (Fig.12) since the phyllsilicates are the only carrier of this
 648 element in Orgueil.
 649

650 *Comparison with previous works on Paris and Murchison*

651



652
 653 **Fig 13.** Bulk matrix compositions obtained by ACADEMY and compared to EPMA data from (Zanda, Humayun,
 654 Barrat, Bourot-Denise, & Hewins, 2011) for Paris, and (McSween Jr & Richardson, 1977), (Zolensky, Barrett, &
 655 Browning, 1993) for Murchison.

656
 657 General trends are similar for both EPMA and ACADEMY (Fig. 11, 13) but compositions are generally
 658 closer to the chondritic value for ACADEMY. As for Orgueil, Mg/Si and Fe/Si ratio of Murchison and Paris
 659 fall nearer to the chondritic composition. Higher deviations are observed for mobile and/or volatile elements
 660 (Na, K, Ca, Fe, S) which are susceptible to be in too low concentration, redistributed in the matrix or carried
 661 by small grains (i.e. Nanosulfides <150 nm (Barber, 1981) (Leroux, Cuvillier, Zanda, & Hewins, 2015)).

662

5. Conclusions

The ACADEMY method provides quantitative mineral maps with high spatial resolution of a few hundred nanometers (linked to the low-voltage X-ray emission volume) on representative areas for infer-micrometric assemblages. It presents several advantages: (1) Thanks to a high resolution and a thorough deconvolution procedure, it considers independently the different entities present in matrices; (2) it provides superimposed maps; (3) it permits a statistical analysis of the grains which constitute the region of interest (size distribution, circularity, Appendix 1.); (4) it provides a global composition taking into account the density parameter and allow to apply specific standards for the EPMA correction. This new method therefore appears to be most adapted for the analysis of micrometer-sized assemblages and has demonstrated its robustness for different samples of matrices of primitive chondrite.

Comparison to bulk wet chemistry data of Orgueil demonstrates that the Fe/Si and Mg/Si ratios given by ACADEMY are closer to the real composition than previously published EPMA defocused beam data. We found a deviation of 25 % and only 1 % respectively (compared to 35% and 13% for defocused EPMA). Given that Paris and Murchison are more homogeneous in terms of grain sizes, densities and chemistry than Orgueil, the precision enhancements allowed by ACADEMY for their matrix measurement should be even larger (alternative data are not available at this point) which opens new avenues for the study of their condition of formation. Improved chemical and mineralogical characterization achieved with this new approach will be used in the future to improve our understanding of chondrite matrix origin and evolution. We made available an open source code allowing to execute all the different steps to offer the possibility to apply ACADEMY to study any submicrometric mineral assemblages (silt porosity measurements, analyses of growth or reaction rims, shock effects on minerals, and the nature of breccias).

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700 **Supplementary materials**

701 **1. Modelisation of the detector efficiency curve**

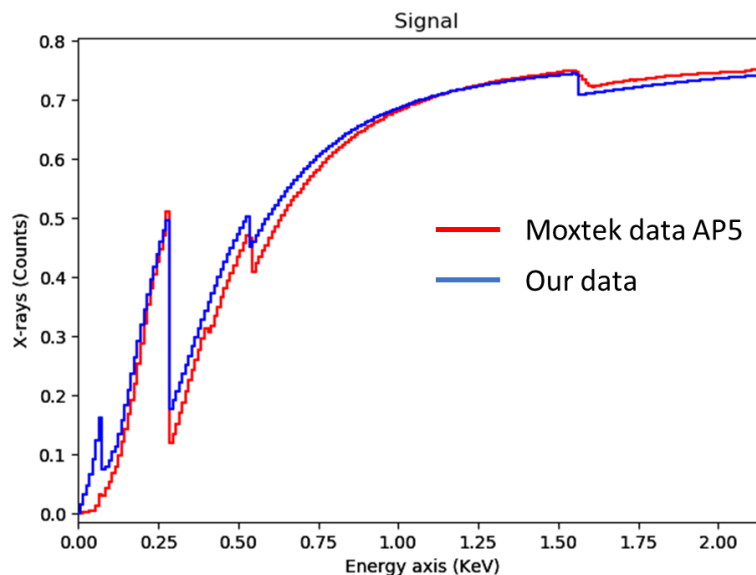
702
703 Since the manufacturers rarely communicate the exact characteristics of the detectors we tried to model
704 the detector efficiency curve of a typical polymer window using the Love & Scott model. We hope that this
705 work could be useful for other groups.

706 We considered two different layers:

- 707 - The first one represents the polymer window itself and we used a density of 2 g/cm^3 and a thickness
708 of 200 nm. Composition: C – 70% - O – 30 %
- 709 - The second layer correspond to the thin aluminum coating used for the UV, IR and Visible light
710 rejection. We used the following values: $\rho = 2.7 \text{ g/cm}^3$ and $x=50 \text{ nm}$ (Al = 100 %)

711 We also considered a shadowing effect of 20% due to the carbon grid, which produces an efficiency loss
712 over the entire energy range. The major effects are the absorption by the polymer window (i.e. C and O)
713 and the shadowing loss. This model reproduces well the detector efficiency curve proposed by the
714 manufacturer (here compared to the AP5 model available at moxtek.com). Other detector efficiency curves
715 could therefore be modeled using this few information.

716



717
718 Fig. Comparison of the modelled detector efficiency curve using Love and Scott model and the AP5 curve
719 proposed by moxtek ©.

720
721

2. Relative error in percent attached to the EPMA quantification

722 Estimated uncertainty is derived from counting statistics on each point (of the different phases) in the matrix
723 of Paris meteorite (zone 2).

<i>Phase</i>	<i>Na</i>	<i>Mg</i>	<i>Si</i>	<i>Fe</i>	<i>Al</i>	<i>K</i>	<i>S</i>	<i>Ca</i>	<i>P</i>	<i>Ti</i>	<i>Cr</i>	<i>Ni</i>
<i>Olivine</i>	15.06	0.4	0.45	1.58	2.98	6.36	3.22	2.16	13.14	3.73	2.16	4.51
<i>Pyroxene</i>	16.36	0.47	0.37	1.41	2.36	6.49	5.44	1.88	12.29	3.64	1.67	4.84
<i>Pentlandite</i>	10.8	3.34	2.12	0.39	4.35	4.18	0.43	1.16	11.95	3.28	2.05	1.26
<i>Fe-rich sulfides</i>	16.36	1.96	1.42	0.45	3.37	4.9	0.98	2.96	9.43	3.12	1.78	1.6
<i>Metal grain</i>	18.62	3.58	2.27	0.51	3.97	5.03	5.53	2.6	7.83	2.97	1.41	2.1
<i>Fine matrix</i>	7.82	0.67	0.49	0.63	1.6	4.74	1.57	2.06	8.77	3.32	1.98	2.57
<i>Spinel</i>	8.32	0.8	0.52	0.54	1.47	4.63	1.8	2.58	9.86	3.57	2.28	2.53
<i>Sulfates</i>	12.22	0.74	0.52	0.65	0.77	5.3	1.34	0.83	11.25	2.73	2.03	2.9
<i>Carbonates</i>	6.03	0.77	0.55	0.82	1.29	3.23	1.03	0.54	11.47	3.14	2.25	3.02
<i>Ferroan Olivine (Fo<90)</i>	16.36	7.22	4.99	2.84	6.37	5.89	4.2	0.25	8.6	4.46	3.11	5.67

724

725

726

3. Analyzed standard compositions and densities for the bremsstrahlung modeling

<i><u>Name</u></i>	<i><u>Formula</u></i>	<i><u>Density g/cm³</u></i>
Albite	NaAlSi ₃ O ₈	2,62
Almandine Garnet	Fe ₃ Al ₂ Si ₃ O ₁₂	4,19
Anhydrite	CaSO ₄	2,97
Antimony Telluride	Sb ₂ Te ₃	6,50
Apatite	Ca ₅ (PO ₄) ₃ F	3,18
Arsenopyrite	FeAsS	6,07
Barite	BaSO ₄	4,48
Benitoite	BaTiSi ₃ O ₉	3,60
Biotite	K(Fe,Mg) ₃ AlSi ₃ O ₁₀ (OH) ₂	3,09
Calcite	CaCO ₃	2,71
Chalcopyrite	FeCuS ₂	4,19
Chlorite	Mg ₅ AlSi ₃ O ₁₀ (OH) ₈	2,80
Chromite	CrFe ₂ O ₄	4,79
Diopside	MgCaSi ₂ O ₆	3,40
Dolomite	MgCa(CO ₃) ₂	2,88
Galena	PbS	7,20
Hematite	Fe ₂ O ₃	5,04
Jadeite	NaAlSi ₂ O ₆	3,25
Magnetite	Fe ₃ O ₄	5,15
Olivine	(MgFe) ₂ SiO ₄	3,32
Orthoclase	KAlSi ₃ O ₈	2,56
Pentlandite	(Fe,Ni) ₉ S ₈	4,80
Periclase	MgO	3,79
Plagioclase	(Ca,Na)Al(Al,Si)Si ₂ O ₈	2,68
Pyrite	FeS ₂	5,01
Quartz	SiO ₂	2,65
Rutile	TiO ₂	4,23
Cubic Zirconia	ZrO ₂	5,68

4. Porosity map

Thanks to the assumptions made in the section 3.4.2 we calculated a map of the porosity in the amorphous silicate/phylosilicate part of the matrix. Although the density determination method shows non-negligible errors, it is useful to determinate localized relative variations of porosity which can be already observed on the apparent density map.

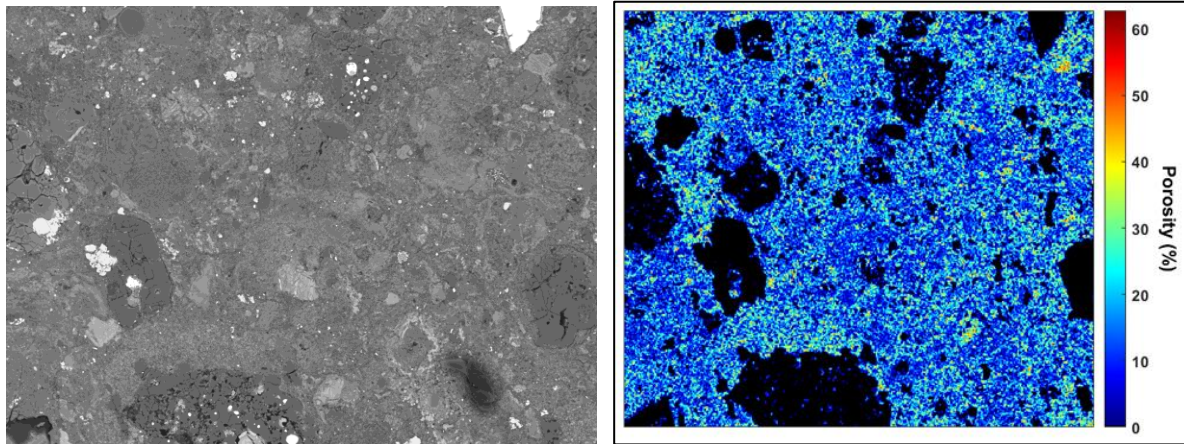


Fig. A. BSE image of the zone 2 of Paris. **B.** Porosity map of the fine grained material in percent. Zonations of the porosity are observed on particular granular areas.

5. Modal abundances of the different zones corrected by the MLLS procedure.

Column indicated with ‘*’ represent areas where chondrule fragments that were too large were removed

Phases	Orgueil		Murchison		Paris				
	Zone1	Zone2	Zone 1	Zone 2	Zone3	Zone 1*	Zone 2*	Zone1	Zone2
	Prop %	Prop %	Prop (%)	Prop (%)	Prop (%)	Prop (%)	Prop (%)	Prop (%)	Prop (%)
Olivine (Fo<90)	0	0	0	0	0	0	3.04	0	4.6
Forsterite	0	0	3.11	5.04	5.53	6.56	3.55	8.03	4.26
Metal grain	0	0	0	0	0	1.62	2.86	1.62	2.97
Fe-rich sulfides	0.48	0.318	0	2.36	0	3.24	5.34	3.14	5.03
Pyroxene	0	0	9.54	10.6	15.91	15.42	14.98	17.73	20.08
Mg-rich phyll/amorph	48.9	43.65	40.01	32.3	19.55	19.85	25.61	18.94	22.41
Fe-rich phyll/amorph	43.21	50.76	19.53	18.47	43.28	35.92	27.61	34.95	24.28
TCI-T	0	0	7.32	2.54	0	0	0	0	0
TCI-C	0	0	0	11.46	0	0	0	0	0
Carbonate	0.08	0.02	8.82	9.79	4.7	0	4.47	0	4.39
Pentlandite	0	0	2.14	0.73	2.33	1.55	1.73	1.52	1.69
Spinel	0	0	0.84	0	0	0	1.14	0	1.14
Apatite	0.2	0.03	3.02	2.3	0	1.22	0	1.22	0
Magnetite	3.68	1.8	0	0	0	0	0	0	0
Sulfates	0	0	0	0	6.11	4.82	5.26	4.77	5.13
Epoxy	3.45	3.42	10.36	2.44	3.67	8.65	4.03	8.55	3.91

6. Grain size analysis

After the classification of all phases, the map can be considered as a combination of different masks. Numerous functions in Matlab® allow the measurement of properties (grain areas, grain perimeters, centroid etc.) of each pixel neighborhood (grains) contained in the different mask, yielding quantitative petrography for each phase in the sample. Thanks to those properties, a histogram of grain size distribution, a map of areas of grains, the circularity of grains and mean composition for each phase as a function of grain size can be displayed afterwards. Grain areas are calculated in pixels and recalculated in microns knowing the pixel size. The circularity is calculated knowing the perimeter P and the area A from:

$$f_{circ} = \frac{4\pi A}{P^2}$$

The circularity of a circle is 1, and becomes much less than one for grains with tortuous or angular edges. This grain analysis of each phase strengthens the mineralogical study of the different matrices.

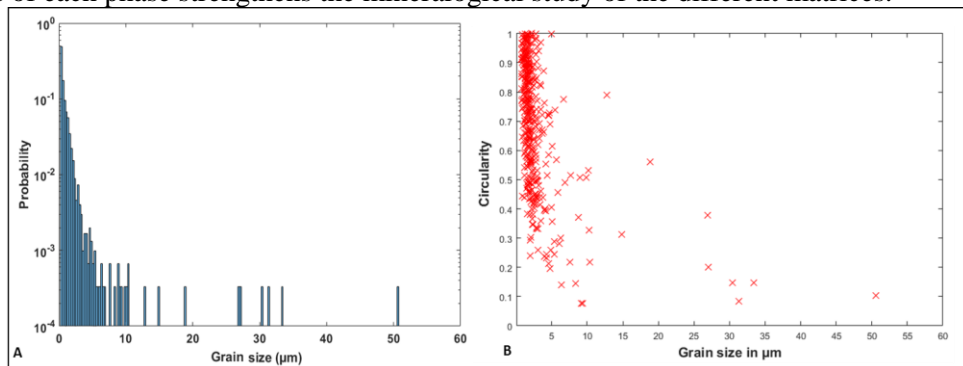


Fig. Analysis of physical parameters of grains of only two phases (olivine and pyroxene) in the matrix of the Paris meteorite (zone 1). A. Histogram of the grain size distribution of the anhydrous silicates in μm . B. Circularity of grains as a function of their size.

Grain size thresholding and composition

Concerning the Paris meteorite, many coarse grains (anhydrous silicates and metal) were dispersed in the matrix and suggest the presence of chondrule fragments. It was difficult to select areas without these angular silicate grains. It was therefore interesting to use the grain size parameter obtained with the phase map to mask all silicates and metal grains above a specific size (i.e. $4\mu\text{m}$) and recalculate a new global composition without chondrule fragments.

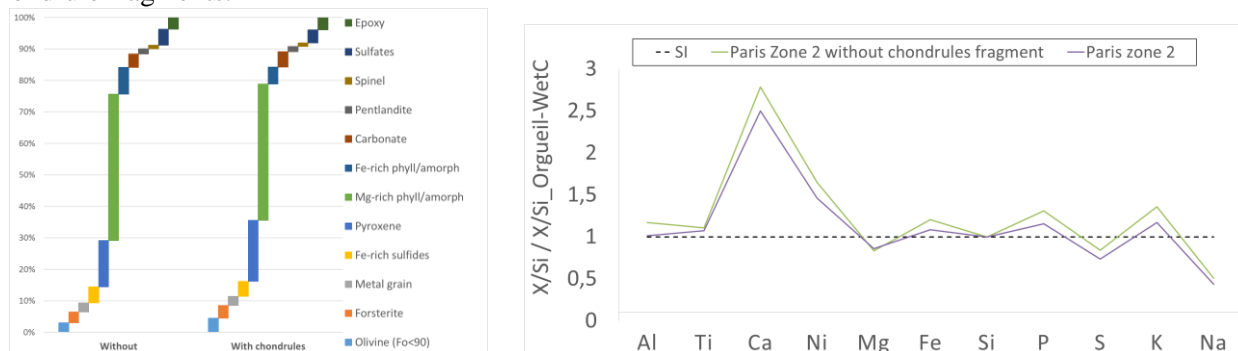


Fig. Bulk chemistry of the matrix of the Paris meteorite (zone 2) recalculated after masking chondrules fragments present in the matrix.

7. **Global compositions obtained with the Academy method.** Composition are in (At%/Si)

	Na	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Fe	Ni
Orgueil	0,035	1,017	0,086	1,000	0,006	0,239	0,006	0,041	0,002	0,015	0,646	0,048
Paris Zone 1	0,027	0,969	0,079	1,000	0,008	0,233	0,003	0,043	0,002	0,010	0,697	0,065
Paris Zone 2	0,029	0,859	0,097	1,000	0,011	0,369	0,005	0,168	0,003	0,015	1,050	0,080
Paris zone 3	0,033	0,993	0,066	1,000	0,010	0,193	0,003	0,186	0,002	0,013	0,564	0,049
Murchison zone 1	0,045	0,911	0,100	1,000	0,011	0,308	0,003	0,201	0,003	0,010	0,769	0,087
Murchison zone 2	0,030	0,994	0,079	1,000	0,005	0,232	0,002	0,276	0,003	0,011	0,667	0,041

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