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A baseline study of mineralogical and morphological properties of different size fractions of illite du Puy

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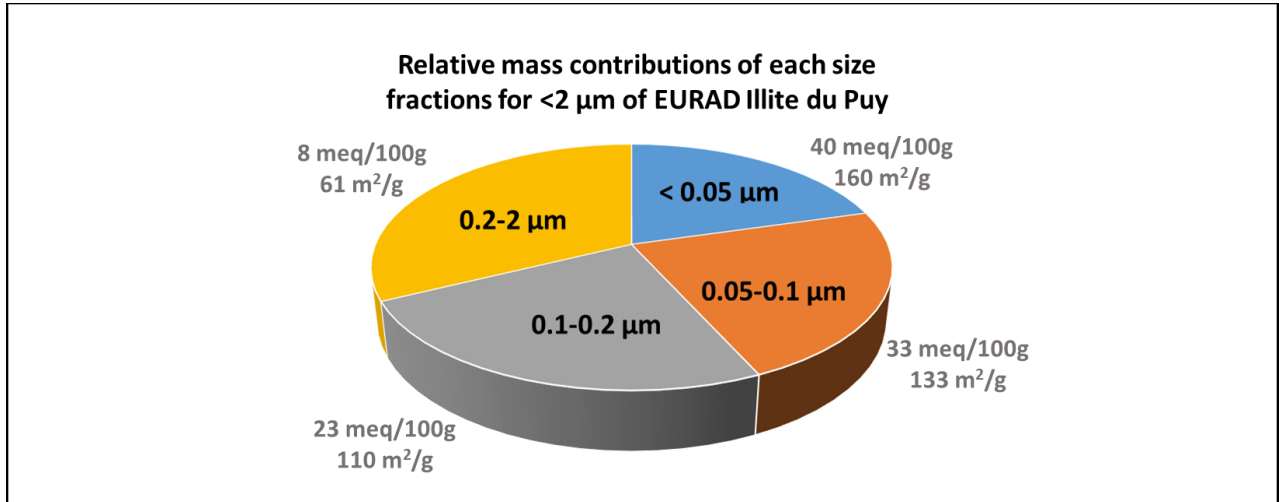
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25 **Table of Content**



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29 **Highlights**

- 30
- Providing a baseline study of the illite du Puy used in an ongoing European project
- 31
- Geological setting is responsible for the mineralogical variability found in the literature
- 32
- Particles in the subfractions display similar crystal chemistry and aspect ratios
- 33
- The grain density of the illite du Puy particles was revisited and refined

34 **Abstract**

35 The objective of this study is to revisit the mineralogical and physico-chemical properties of
36 illite du Puy material (Puy-en-Velay, France), which is envisaged as a model clay system in the
37 European Joint Programme on Radioactive Waste Management (EURAD) project. This illite
38 material is compared to the raw illite material commonly extracted from the Velay ore site.
39 Both materials were collected and separated into different subfractions (i.e., <0.05, 0.05-0.1,
40 0.1-0.2, and 0.2-2 μm) to examine the mineralogical heterogeneity. The X-ray diffraction bulk
41 analyses indicated that the observed variability in the literature, in terms of the nature of
42 accessory minerals and the presence of kaolinite, was directly related to the locations of
43 geological sampling. Moreover, the respective mass contributions of the different subfractions
44 were similar for the two materials.

45 Further analyses were performed on the subfractions of the illite used for the EURAD project
46 by utilizing a suite of different techniques. The clay mineralogy was refined as an illite–smectite
47 mixed-layer mineral with a small amount (<5%) of smectite layers. No significant changes in
48 chemical properties or particle lamellarity were observed between the different subfractions.
49 However, the different subfractions displayed a wide range of specific surface areas (i.e., N_2
50 BET surface) and cation exchange capacity values, the latter of which increased by factors of
51 ~ 3 and ~ 5 from the 0.2-2 μm to the <0.05 μm size fractions, respectively. The EURAD illite
52 and associated subfractions can be considered appropriate material models to be used for the
53 refinement of our understanding of the adsorption and diffusion processes of solutes in porous
54 media made from charged clay particles.

55

56 **Keywords:** illite du Puy, size fractions, mineralogical and morphological properties.

57

58 **1. Introduction**

59 For the past two decades, purified and conditioned illite du Puy (IDP) has been considered
60 an analogous clay model of more complex clayey rocks (i.e., argillite) envisaged as potential
61 host rocks for the geological disposal of nuclear wastes. Numerous studies have focused on
62 sorption/diffusion of ions and water in this material (Poinssot et al., 1999; Rajec et al., 1999;
63 González Sánchez et al., 2008; Bradbury and Baeyens, 2009; Diaz, 2009; Glaus et al., 2010;
64 Altmann et al., 2015; Rajyaguru, 2018). In these works, the physio-chemical properties of IDP,
65 i.e., mineralogical composition, cation exchange capacity (CEC), specific surface area, and
66 geometrical properties of IDP particles (the relative amount of lateral and basal surfaces; Bardot
67 et al., 1998; Rajec et al., 1999; Hassan et al., 2005) represented key input parameters for the
68 interpretation of anionic exclusion and sorption reactions for solutes (e.g., Bradbury and
69 Baeyens, 2005, 2009; Rabung et al., 2005; González Sánchez et al., 2008; Glaus et al., 2010,
70 2015; Altmann et al., 2015; Chagneau et al., 2015). Despite the large number of studies devoted
71 to IDP, significant differences in the composition and thus reactive properties of this material
72 can be found in the literature. For example, Poinssot et al. (1999) reported the presence of
73 kaolinite at ~5% and 7% in raw and purified Na⁺-saturated IDP, respectively, as observed by
74 X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR). In contrast,
75 Bradbury and Baeyens (2009) and Altmann et al. (2015) reported a composition of Na⁺-
76 saturated IDP of 88 wt.% illite and 12 wt.% sanidine (K-feldspar), which was also deduced
77 from XRD measurements. Even though some of the reported variations in CEC and specific
78 surface area can be induced by the differences in the processes used to purify the raw material
79 (e.g., size separation and removal of accessory minerals), another reason for these differences
80 may be the variation in the mineralogical properties of the raw material in relation to the
81 geological setting and sampling strategy.

82 IDP originates from the Velay basin, which consists in Oligocene lacustrine sediments of
83 approximately thirty kilometers in length located at le Puy-en-Velay (Haute-Loire) in the
84 Massif Central region in France. The first mineralogical study of this basin was carried out by
85 [Gabis \(1963\)](#), who divided the central area of this geological formation into three series: upper,
86 lower, and medium series (30-80 m thick). According to this author, deposits from these series
87 are predominantly composed of ferruginous illite that results from the illitization of detrital
88 montmorillonite in alkaline lakes. In addition to illite, associated clay minerals may include
89 (i) kaolinite in a proportion up to 20% in the bottom of the series, this percentage decreasing
90 moving upward until kaolinite diminishes in the upper portion ([Gabis, 1963](#)); (ii) illite-smectite
91 mixed-layer minerals with low smectite contents (~20 to 30%; [Altmann et al., 2015](#)); and (iii)
92 smectite, which is mainly present in the upper portion. Other non-clay accessory minerals
93 include potassic feldspars (mainly sanidine ([Bradbury and Baeyens, 2009](#))), carbonates, and
94 quartz, in varying proportions from 0 to 40%. In addition to their presence at the clayey levels,
95 carbonates also exist in the banks of gray marl and calcite streaks, intercalating with the clay-
96 rich levels. Some of these latter in the medium series exhibit remarkable mineralogy that is
97 solely composed of illite. Overall, and although illite is the dominant mineral through the
98 stratigraphic profile, the other associated minerals in IDP material may vary significantly with
99 the location and sampling strategy applied in the field.

100 In the context of nuclear waste disposal facilities, and before the analysis of sorption and
101 diffusion properties of water and ionic tracers in IDP material, a particular attention must be
102 paid to the sampling and to the associated characterization of these material. In fact, these
103 properties may vary due to the variability in mineralogical composition of IDP raw material
104 when sourced from different geological settings. In the framework of the European Joint
105 Program on Radioactive Waste Management (EURAD, 2019-2024), a large set of studies

106 involving adsorption and diffusion measurement of a large set of tracers using the same IDP
107 raw material stresses the need for a baseline analysis of IDP mineralogical and physico-
108 chemical properties. Hence, this study aims to (i) elucidate the differences in mineralogy
109 between the IDP material used in EURAD and typical sampling in the Velay ore used in
110 previous works and then (ii) to determine the mineralogy, crystal chemistry, and geometric
111 characteristics of the IDP particles used in the current EURAD project as an analogous illite
112 model. An initial quantitative mineralogical analysis of both IDP raw materials will be
113 performed for these purposes. Afterward, both raw materials will be purified and size-
114 fractionated (i.e., <0.05, 0.05-0.1, 0.1-0.2, and 0.2-2 μm) to highlight the mineralogical
115 heterogeneity between the different size fractions. After a mineralogical comparison between
116 the two IDP samples, a detailed characterization that focuses on the different subfractions of
117 the IDP sample used in the EURAD project will be provided, including (i) clay structure
118 identification and smectite quantification by profile modeling of XRD 00 ℓ reflections, (ii)
119 structural formula and grain density calculations based on microchemical analysis by scanning
120 electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX), (iii)
121 specific surface area measurements and associated geometrical features of particles from low-
122 pressure N₂/Ar adsorption at 77 K and (iv) CEC measurements from K⁺-saturated samples. The
123 results from this work will be compared to the literature data to establish a baseline source of
124 physico-chemical data of interest for the use of IDP as a model material to expand our
125 understanding of the transport properties of solutes in the context of nuclear waste disposal
126 facilities.

127

128

129 **2. Materials and Methods**

130 *2.1. Illite du Puy materials*

131 Three raw IDP samples were considered for this study, all originating from Oligocene
132 lacustrine sediments in le Puy-en-Velay (Haute-Loire, France). The Argile du Velay company
133 (www.argileduvelay.com) provided the first IDP sample collected from the clay ore during
134 industrial sampling. The second IDP sample was provided by the Paul Scherrer Institute (PSI,
135 Villigen, Switzerland) from its sampling campaign and corresponded to the reference illite used
136 in their own work (González Sánchez et al., 2008; Bradbury and Baeyens, 2009), in the CatClay
137 European project (Glaus et al., 2010, 2015; Altmann et al., 2015 among others) and in the
138 ongoing European Joint Project EURAD. The third IDP material was provided by the
139 Commissariat à l'énergie atomique (CEA, Université Paris-Saclay, France) from their sampling
140 campaign, which was used in previous works (Poinssot et al., 1999). However, different
141 previous mineralogical analyses on this last sample revealed a similar composition to the Velay
142 IDP (data not shown). Consequently, only a comparison between data obtained with the Velay
143 and EURAD IDP will be presented here.

144 For sample homogenization of raw materials before bulk mineral quantification using X-
145 ray diffraction (XRD) on randomly oriented powder, the Velay and EURAD IDP samples
146 (referred to as V-IDP and E-IDP materials, respectively) were gently crushed in an agate mortar
147 and dry sieved at 50 μm . To perform other analyses, raw IDP samples were purified and size-
148 fractionated. The purification procedure consisted of removing carbonate and sparingly soluble
149 minerals by mixing clay dispersion in hydrochloric acid (pH=1, room temperature). Carbonate
150 dissolution was considered complete when the pH of the clay/acid suspension reached 5.5. A
151 confirmation of the complete removal of carbonates was obtained by recording the XRD
152 patterns (not shown) of the decarbonated material. The < 50 μm particle size fraction of the

153 decarbonated IDP was obtained by wet sieving after several cycles of centrifugation with
154 distilled water to remove the remaining acidic solution. Then, the Na⁺ saturation of IDP samples
155 was achieved by performing three saturation cycles with a 1 M NaCl solution followed by
156 removing excess salt by dialysis using a 6-8 KD membrane until the test with silver nitrate was
157 negative. Different size fractions were obtained from the dispersion of the Na⁺-saturated IDP
158 samples by adapting the protocol of sequential fractionation developed by [Reinholdt et al.](#)
159 [\(2013\)](#). The <2 μm fraction was first separated using a Thermo Scientific legend XFR
160 centrifuge from Fisher Scientific®. Then, 5 g of <2 μm IDP were divided between 6
161 centrifugation tubes (38.5 mL polypropylene tubes), dispersed in Milli-Q® pure water by
162 sonication, and centrifuged using an Avanti J 301 centrifuge (swinging bucket rotor JS-24.38)
163 from Beckman Coulter®. The sequential fractionation process started with extraction of the
164 finest fraction (i.e., <0.05 μm), and five centrifugation cycles were performed until the
165 supernatant became clear. Then, extractions of the coarser size fractions (0.05-0.1 and 0.1-0.2
166 μm) were performed using the same steps until the IDP material remaining in the tubes
167 corresponded to the 0.2-2 μm fraction. Three aliquots of dispersion (1 mL) from each fraction
168 were dried at ambient humidity and weighed to calculate the mass proportions. The
169 centrifugation parameters and the yield of each size fraction are reported in [Table 1](#).

170 After size separation, the obtained dispersion of each fraction was divided into three
171 portions. Two of them were saturated with Ca²⁺ and K⁺ for XRD and CEC measurements,
172 respectively, by following the same procedure described above for saturation with Na⁺. The
173 Ca²⁺- and K⁺-saturated IDP samples were stored in suspension at 4 °C. The last portion, which
174 corresponded to the remaining Na⁺-saturated dispersion, was lyophilized for gas adsorption
175 measurements as described in [Section 2.5](#).

176

177 **Table 1.** Centrifuging parameters for size fractioning of the Velay and EURAD illite du Puy
 178 samples (V-IDP and E-IDP, respectively) and the relative mass contributions of each size
 179 fraction.

Fraction (μm)	Time (min)	Speed (rpm)	Acceleration (g)	% Mass contribution ^a	
				V-IDP	E-IDP
<0.05	20	20000	72128	19.5	18.2
0.05-0.1	15	12500	28175	23.8	20.1
0.1-0.2	14	6500	7619	22.1	21.7
0.2-2	-	-	-	22.0	28.6
<2	3	1000	-	-	-
2-50	-	-	-	6.0	6.5
Total Yield %				93.4	95.1

180 ^a Uncertainties in relative mass contributions are estimated at ~10% (based on replicate measurements).

181

182 **2.2. Bulk mineral quantification using XRD refinement on randomly oriented powders**

183 The XRD randomly oriented mounts for V-IDP and E-IDP bulk materials were prepared
 184 by filling the sample holder using the side-loading technique as in [Kleeberg et al. \(2008\)](#).
 185 Acquisition of XRD patterns of these samples was performed with a Bruker D8 Advance
 186 operating in Bragg–Brentano geometry using a copper source with $\text{CuK}\alpha_{1+2}$ wavelength and
 187 with a LYNXEYE detector for a step size of $0.02^\circ 2\theta$ over the $2\text{--}65^\circ 2\theta$ $\text{CuK}\alpha$ angular range. A
 188 40 kV voltage and 40 mA intensity were used for the analytical conditions. Crystalline phase
 189 quantification was carried out using the open-source Rietveld refinement program BGMN
 190 interfaced with Profex ([Doebelin and Kleeberg, 2015](#)). In both refinements, illite was modeled
 191 using a combination of both disordered and ordered 1M polytypes with a chemical composition
 192 that matched the structural formula reported in the present study. The presence of K-feldspars
 193 was modeled by considering a mixture of sanidine and microcline ([Gabis, 1963](#); [Bradbury and](#)
 194 [Baeyens, 2009](#)). Other minerals included Na-rich plagioclase (oligoclase; ([Gabis, 1963](#))),

195 calcite, with trace amounts of quartz, anatase and apatite. The R_{wp} goodness of fit parameter
196 was used for the refinement (Howard and Preston, 1989).

197 **2.3. Quantification of clay mineralogy using profile modeling of XRD 00 l reflections**

198 The characterization of the clay phases in the different E-IDP size fractions was obtained
199 by XRD analysis of the oriented clay mounts. An aliquot of the Ca^{2+} -saturated clay dispersion
200 was dropped onto a glass slide and dried at room temperature. The XRD patterns were recorded
201 using a Panalytical X'Pert Pro MPD diffractometer equipped with an X'Celerator detector
202 operating with an angular aperture of 1.021° . The scanning parameters included a step size of
203 $0.033^\circ 2\theta$ and 6 s for the counting time per step throughout the $2-50^\circ 2\theta$ $CuK\alpha_{1+2}$ angular range.
204 The divergence slit, the anti-scatter slit, and the two Soller slits were 0.125° , 0.25° , 2.3° , and
205 2.3° , respectively. For all samples, XRD patterns were recorded in air-dried (AD) conditions
206 and after ethylene glycol (EG) saturation of the clay mounts in an EG atmosphere at $40^\circ C$ for
207 24 h.

208 The algorithms developed initially by Sakharov and coworkers were used to model the
209 00 l reflections for the $2-50^\circ 2\theta$ $CuK\alpha$ range using a trial-and-error approach (Sakharov et al.,
210 1982a, 1982b, 1983). Instrumental and experimental factors, such as horizontal and vertical
211 beam divergences, goniometer radius, and length and thickness of the oriented slides, were
212 measured and introduced without further adjustment. The mass absorption coefficient was set
213 to $45\text{ cm}^2/\text{g}$ (Moore and Reynolds, 1997). For each XRD pattern, a single illite–smectite
214 interstratified structure was used. Structural parameters, such as the proportion of illite layers,
215 layer-to-layer (LLT) distance of illite layers, and coherent scattering domain size (CSDS) along
216 the c^* axis (which was characterized by a lognormal distribution around a variable mean value
217 (N) and a maximum CSDS value set to 80 layers (Drits, 1997)), were adjusted to fit the

218 experimental XRD patterns. The z-coordinates for all atoms within the 2:1 layer framework
219 were set as suggested by Moore and Reynolds (Moore and Reynolds, 1997). The chemical
220 composition was introduced according to the IDP structural formula reported in this work. The
221 interlayer configuration of smectite was systematically constituted by 2 layers of water or EG
222 molecules in AD (LLT=15 Å) and EG conditions (LLT=16.9 Å), respectively.

223

224 **2.4. Microchemical analysis by electron microscopy**

225 Microchemical analysis was performed on compressed pellets of clay powders from the
226 E-IDP subfractions using a JEOL JSM IT500 scanning electron microscope (SEM) equipped
227 with a Bruker Lynxeye Energy Dispersive X-ray spectrometer (EDX) with an XFlash 4030
228 silicon drift detector. The acquisition parameters for quantitative EDX analysis were as follows:
229 acceleration voltage 15 kV, current beam 1 nA, counting time 50 s, working distance 11 mm,
230 and analytical area of ~ 2 µm. The quality of the EDX quantitative analysis was confirmed by
231 a series of standards consisting of albite (Na, Al, Si), almandine (Mg, Fe), diopside (Ca),
232 orthoclase (K), and spessartite (Mn). Matrix corrections were performed using the integrated
233 program PhiRhoz correction. The reproducibility of the standard analyses was 1.5% for all
234 chemical elements, except Na, for which the reproducibility was 3%.

235

236 **2.5. Low-pressure nitrogen and argon adsorption at 77 K**

237 Low-pressure nitrogen (N₂) and argon (Ar) adsorption measurements of the E-IDP
238 fractions were performed at LIEC (Laboratoire Interdisciplinaire des Environnements
239 Continentaux) Nancy-France. The experimental procedure consists on the recording of high-
240 resolution adsorption isotherms on a lab-built automatic quasi-equilibrium volumetric setup,

241 described elsewhere (Michot et al., 1990; Villieras et al., 1997; Bardot, 1998). The quasi-
242 equilibrium technique is based on the adsorbate introduction with a slow, constant, and
243 continuous flow rate through a micro leak. High-resolution adsorption isotherms were recorded
244 at least up to the BET domain, corresponding to the formation of the first adsorbed layer.

245 Before adsorption measurements, the E-IDP size fractions were flash-frozen by
246 immersion in slush nitrogen (SN₂) for 2-5 min and dried by lyophilization at – 40 °C. All
247 samples were first outgassed at a 10⁻⁵ Pa residual pressure for at least 12 h at 110 °C to remove
248 surface impurities. The use of two probe molecules, argon and nitrogen, and the capacity of the
249 experimental setup to record approximately 3000 adsorption points (i) allows for cross-
250 validation of the overall surface area of the particles while (ii) giving access to morphological
251 properties of the clay particles, such as the area of basal/lateral surfaces and the aspect ratio (the
252 ratio between the particle thickness and diameter).

253 Due to a large number of experimental data points, the experimental derivative adsorption
254 isotherms can be calculated as a function of the logarithm of relative pressure, $\ln(P/P_0)$, which
255 corresponds to the adsorption energy expressed in kT or RT units. These isotherms were
256 analyzed by the derivative isotherm summary (DIS) procedures introduced by Villieras et al.
257 (1992) and later improved by others (Villieras et al., 1997; Bardot et al., 1998). This procedure
258 allows for the study of energetic surface heterogeneity in highly heterogeneous materials such
259 as clay particles. DIS is performed by fitting the experimental derivative isotherm to local
260 theoretical isotherms that correspond to different adsorption energy domains (basal and lateral
261 faces). Each local derivative isotherm is defined by three parameters (Bardot, 1998): the
262 interaction energy between the solid and the adsorbed molecule, which is deduced from the
263 peak position of $(\ln P/P_0)$, the lateral interaction between two adjacent gas molecules (ω), and

264 the monolayer capacity (V_m) of the domain, which can be used to calculate the surface area by
265 taking into account cross-sectional areas of 13.8 \AA^2 and 16.2 \AA^2 for argon and nitrogen
266 molecules, respectively.

267 Mean particle thickness (h) and basal diameter (l) were calculated by considering IDP
268 particles as regular hexagonal plates using the equations reported in [Hassan et al. \(2005\)](#):

$$269 \quad h = \frac{2}{\rho \times BSA} \quad (1)$$

$$270 \quad l = \frac{8}{\sqrt{3} \times \rho \times LSA} \quad (2)$$

271 where BSA and LSA are the basal and lateral surface areas from low-pressure Ar
272 measurements, respectively, and ρ is the grain density of the Na^+ -saturated E-IDP particles,
273 which is calculated for the different subfractions by using structural formulas and crystal
274 structure parameters derived in this study from the XRD structural refinements.

275 **2.6. Cation exchange capacity (CEC) measurements**

276 The first attempts to measure the CEC values from Na^+ -saturated samples and Ca^{2+} -for-
277 Na^+ exchange proved unsuccessful. Indeed, the results showed a decrease in CEC with
278 decreasing size fraction. This behavior was attributed to the difficulty in saturating the edge
279 sites of IDP particles with Na^+ cations at neutral pH because of the higher selectivity of H^+ over
280 Na^+ for this type of sites ([Tertre et al., 2011b, 2011a](#)). Thus, to ensure sufficient saturation of
281 edge sites in these conditions, the CEC values were obtained from K^+ -saturated samples and
282 Sr^{2+} -for- K^+ exchange ([Viennet, 2015](#)). Known masses of the K^+ -saturated size fractions
283 (ranging from ~ 30 mg for the finest size fraction to ~ 100 mg for the coarsest fraction) were
284 dispersed in 100 mL of 1 M SrCl_2 prepared with Milli-Q[®] pure water ($18 \text{ M}\Omega \cdot \text{cm}$). The

285 dispersions were mechanically agitated and allowed to react for one week. The clay slurry was
286 then retrieved by centrifugation at 34000 g for 30 min (Centrifuge Avanti J 301, rotor JLA-
287 16.250 from Beckman Coulter®) to ensure that no fine particles were left in the supernatant.
288 The K^+ concentrations of the collected supernatants were measured by atomic absorption
289 spectroscopy (AAS, Varian AA240FS). For analysis, the supernatants were diluted with 2%
290 HNO_3 , and were prepared in 2 g/L $CsNO_3$ solution to account for possible interference during
291 acquisitions. The measured K^+ concentrations ranged between 1-3 mg/L, which fell within the
292 linear absorption range of K^+ for this device (between 0 and 5 mg/L). The excess $SrCl_2$ salt
293 present in each clay slurry was removed by dialysis in Milli-Q® pure water using a 6-8 KD
294 membrane until the test with silver nitrate was negative. Then, the rinsed clay slurry was dried
295 at 60 °C to determine the dry clay mass, which was found to be similar to the initial mass of the
296 solid from the original dispersion with an uncertainty of ~6 wt%. Measuring the solid mass
297 before and after CEC measurements allowed us to discard any influence of mineral dissolution
298 during the dialysis procedure. Such uncertainty, combined with the one from aqueous
299 concentrations measured by AAS (i.e., 5%), led to a global uncertainty value of approximately
300 10% for each calculated CEC value.

301

302 **3. Results and discussion**

303 ***3.1. Mineralogy comparison between V-IDP and E-IDP raw materials***

304 **Fig. 1** a shows a comparison between the XRD patterns from randomly oriented powders
305 of the raw V-IDP and E-IDP materials. Both XRD patterns exhibit the typical reflections of
306 illite and K-feldspars, while the V-IDP pattern presents additional reflections for kaolinite and
307 calcite. Full pattern Rietveld refinement (**Fig. 1** b) shows that the raw E-IDP sample is mainly

308 composed of 1M illite polytype (~83%), with ~15% feldspars (plagioclase, sanidine, and
309 microcline). This sample also contains small quantities of quartz with the addition of <1% each
310 of anatase, halite, and apatite. The raw V-IDP samples are also dominated by 1M illite (~81%),
311 with a small quantity of quartz, anatase, and apatite. The main differences found in the raw V-
312 IDP sample are a lower amount of feldspars (7.5%) and significant contributions of calcite and
313 kaolinite of ~5 and 4%, respectively. Phase quantification, particularly the absence of calcite
314 and kaolinite in the E-IDP sample, allows us to consider this sample similar to the material used
315 by previous authors (Tessier, 1984; Bardot, 1998; Bardot et al., 1998; Rajec et al., 1999; Hassan
316 et al., 2005; Bradbury and Baeyens, 2009; Altmann et al., 2015). By comparison, the
317 mineralogical composition of the V-IDP sample with large amounts of kaolinite corresponds to
318 that of the sample used by Poinssot et al. (1999), Diaz (2009), and Rajyaguru (2018). By
319 comparing the experimental XRD patterns reported in Gabis (1963) to those obtained in this
320 work, it was found that both IDP samples come from the middle series of the central zone of
321 the Velay sedimentary basin (Fig. 2). More precisely, the E-IDP sample likely belongs to the
322 “green clay” level, which alternates with the marl banks in the middle of this series. In addition,
323 according to Gabis (1963), this level does not contain calcite minerals, unlike the beds just
324 above or below it. The presence of kaolinite in the raw V-IDP sample suggests that it comes
325 from the “versicolored clayey banks” below the “green clay” level, where illite and kaolinite
326 form a mixture that contains 5-10% calcite (Fig. 2).

327 With more than 80% of their mass being illite mineral, both of the raw IDP samples are
328 appropriate candidates for reference illitic material. Naturally, the removal of the other non-
329 illitic minerals is necessary. A simple and widely used method for purifying clay materials is
330 size separation after dispersion and removal of soluble minerals (e.g., calcite). In this work, the
331 results from sequential fractionation indicate (i) that both IDP samples are widely dominated

332 by $<2\ \mu\text{m}$ particles (values normalized to the total yield at 94 and 93% for V-IDP and E-IDP
333 samples, respectively; [Table 1](#)), and (ii) that each of the $<2\ \mu\text{m}$ subfractions has a significant
334 mass contribution of more than 18%. However, the $0.2\text{--}2\ \mu\text{m}$ size fraction has $\sim 5\%$ higher mass
335 contribution in the E-IDP sample ([Table 1](#)). As commonly observed in natural clay samples
336 ([Hubert et al., 2012](#); [Viennet et al., 2015](#)), the XRD patterns of the fine $<0.2\ \mu\text{m}$ subfractions
337 ([Fig. 3](#)) indicate that both IDP samples are almost entirely constituted from clay phases, while
338 the accessory silicates remain concentrated in the $0.2\text{--}2\ \mu\text{m}$ fraction. However, this method did
339 not allow to separate kaolinite from the different subfractions of the V-IDP sample, given that
340 kaolinite persists even in the finest fraction that was investigated (i.e., $<0.05\ \mu\text{m}$). It is worth
341 noting that kaolinite traces remained even in $<0.02\ \mu\text{m}$ fraction for the V-IDP sample (results
342 not shown). In contrast, the $<0.2\ \mu\text{m}$ subfractions of the E-IDP sample exhibit only 00ℓ
343 reflections of illite, and a quasi-monomineralic sample of illite is thus obtained. Therefore, the
344 minimal shifts of the 00ℓ reflections of illite after ethylene glycol solvation indicate that the
345 illite phase of both IDP samples is most likely an illite–smectite mixed-layer mineral (MLM)
346 mainly composed of illite layers with a marginal proportion of smectite layers ([Fig. 3](#)). This
347 illite–smectite mixed-layer mineral is present in all size fractions. The broadening of its 00ℓ
348 reflections with decreasing particle size is most likely because of the decrease in the coherent
349 scattering domain size, as previously observed for size fractionation of vermiculite ([Reinholdt](#)
350 [et al., 2013](#)).

351 The mineralogical results show that a large amount of quasi-monomineral illite material
352 can be obtained easily from raw E-IDP by size fractionation at $<0.2\ \mu\text{m}$ (representing $\sim 60\%$ of
353 raw E-IDP mass). Note that removing other clay minerals, such as kaolinite, from the $0.2\ \mu\text{m}$
354 and other subfractions is not achievable by using the approach used here based on size
355 fractionation.

356 In line with the main objectives of this work, the following sections provide further
357 analysis of the subfractions of the E-IDP used in the EURAD project. These analyses include
358 information on the crystal structure, grain density, particle morphology, CEC, and crystal
359 chemistry of these size fractions.

360

361 ***3.2. Chemical properties and geometrical characterization of subfractions from the*** 362 ***E-IDP sample***

363 *3.2.1. Crystal structure of illite–smectite MLM in E-IDP size fractions*

364 The crystal structure of the illite phase in the different size fractions of E-IDP material
365 was determined by profile modeling of the 00 l reflections on XRD patterns recorded after AD
366 and EG treatments (Fig. 4). A single R0 illite–smectite MLM was sufficient to reproduce the
367 experimental XRD profiles of the 00 l reflections in the different subfractions and for both
368 treatments. As reported in Table 2, this illite–smectite MLM contains an overwhelming
369 proportion of illite layers with a very low proportion of smectite layers, which is lower than 5%
370 irrespective of the size fraction. Except for the marginal increase of 1% of smectite layers, the
371 main evolution of crystal structure with the decrease of particle size is the aforementioned
372 gradual decrease of the mean CSDS, from 14 layers (in the EG state) for the coarsest 0.2-2 μm
373 fraction to ~ 7 layers for the $<0.05 \mu\text{m}$ size fraction. Note that the slight increase in the smectite
374 layer content after EG saturation is consistent with the swelling of smectitic layers that were
375 initially collapsed in the AD state (Ferrage et al., 2011).

376 The different size fractions of the E-IDP sample are thus composed of a single type of
377 clay mineral, i.e., an R0 illite–smectite MLM. Compared to materials mentioned in previous
378 studies that contain a proportion of smectite layers that can reach nearly 20 to 30% (Altmann
379 et al., 2015), the illite–smectite MLM of the E-IDP sample is particularly rich in illite layers

380 with less than 5% smectite layers. Moreover, the crystal structure of the illite–smectite MLM
 381 is notably stable despite the changes in particle size. Indeed, only a decrease in CSDS is
 382 correlated with a particle size decrease, as generally previously observed (Hubert et al., 2012;
 383 Viennet et al., 2015; Bakker et al., 2019).

384

385 **Table 2.** Structural parameters for the modeling of experimental 00ℓ XRD reflections of Ca²⁺-
 386 saturated fractions of EURAD illite du Puy (E-IDP) in air-dried conditions (AD) and after
 387 ethylene glycol saturation (EG).

Fraction (μm)	AD			EG		
	% I/S ^a	N ^b	LLT Illite ^c	% I/S	N	LLT Illite
<0.05	97/3	7	9.97	96/4	7.6	9.97
0.05-0.1	97/3	8.2	9.98	96/4	9	9.98
0.1-0.2	97/3	9.3	9.99	97/3	10	9.99
0.2-2	98/2	12	10	97/3	14	10

^a relative proportion of illite and smectite layers. ^b Coherent scattering domain size value (in layers). ^c Layer-to-layer distance of illite layers (in Å).

388

389 3.2.2. Structural formulas and grain densities of E-IDP size fractions

390 Energy dispersive spectrometric (EDS) measurements of the compressed pellets of dry
 391 powder from the different fractions of the E-IDP sample were obtained by scanning electron
 392 microscopy. All size fractions, which were initially Ca²⁺-saturated for mineralogical
 393 characterization, were Na⁺-saturated, except for the <2 μm fraction. The structural formula for
 394 each fraction is reported in Table 3. During SEM observations of the compacted pellets, a
 395 dispersion of small grains of titanium oxides between clay particles was detected. Therefore,
 396 TiO₂ quantities were removed from the calculation of the structural formula. Moreover, as both
 397 the 0.2-2 and the <2 μm fractions contain feldspar impurities, the reported chemical

398 composition does not correspond to pure illite minerals but corresponds more closely to a
 399 mixture of phases for these two size fractions.

400

401 **Table 3.** Structural formulas and grain densities for different size fractions of EURAD illite du
 402 Puy (E-IDP).

Size fraction (μm)	Structural Formula ^a	Interlayer charge (per O ₂₀ (OH) ₄)	Calculated grain density (g.cm ⁻³)
<0.05	[Al _{2.69} Mg _{0.78} Fe _{0.60}] _{Σ4.08} (Si _{7.24} Al _{0.76}) O ₂₀ (OH) ₄ (K _{1.19} Na _{0.08} Ca _{0.02})	1.30	2.79
0.05-0.1	[Al _{2.51} Mg _{0.80} Fe _{0.79}] _{Σ4.10} (Si _{7.07} Al _{0.93}) O ₂₀ (OH) ₄ (K _{1.16} Na _{0.08} Ca _{0.09})	1.42	2.82
0.1-0.2	[Al _{2.46} Mg _{0.79} Fe _{0.81}] _{Σ4.06} (Si _{6.98} Al _{1.02}) O ₂₀ (OH) ₄ (K _{1.31} Na _{0.19} Ca _{0.05})	1.60	2.83
0.2-2 ^b	[Al _{2.52} Mg _{0.74} Fe _{0.76}] _{Σ4.02} (Si _{6.95} Al _{1.05}) O ₂₀ (OH) ₄ (K _{1.55} Na _{0.06} Ca _{0.05})	1.71	2.84
<2 ^b	[Al _{2.50} Mg _{0.75} Fe _{0.80}] _{Σ4.04} (Si _{7.02} Al _{0.98}) O ₂₀ (OH) ₄ (K _{1.33} Na _{0.02} Ca _{0.11})	1.57	2.83

^a Fe is considered as Fe³⁺
^b samples contain minor amounts of K-feldspars

403

404 The deduced structural formulas are typical of ferruginous illitic material (Gabis, 1963;
 405 Tessier, 1984) with an increased Fe³⁺ occupation in the octahedral sheet that correlates to a
 406 decrease in Al³⁺ content. There is a slight increase in Si⁴⁺ in the tetrahedral sheet upon
 407 comparison to what is reported in the literature (Wilson, 2013). In addition, the octahedral
 408 occupancy is slightly higher than 4, which can be attributed to the presence of small
 409 trioctahedral domains. Finally, for the three <0.2 μm fractions, which are more representative
 410 of a pure illitic phase, note that the layer charge decreases with decreasing size fraction (Table
 411 3). Such a decrease of this value for the finest illitic clay fraction was previously reported for

412 illite material collected from soil environments (Robert et al., 1991). This observation can be
413 tentatively assigned to the formation conditions of the particles and the slight increase in
414 smectite contribution in the finest fractions (Table 2). Another observation is the remaining
415 Ca^{2+} amount, which can be tentatively associated to adsorption sites in the smectite or illite
416 interlayers and on the external surface of particles (Table 3). Overall, the structural formulas
417 obtained for all subfractions are consistent with those reported in the literature and derived from
418 different methods (Gabis, 1963; Tessier, 1984; Bardot, 1998; Poinssot et al., 1999; Altmann et
419 al., 2015). Minor differences can be assigned to the selection of the size fractions and sampling
420 region in the ore site.

421 Grain densities for the different subfractions were calculated based on the structural
422 formula (Table 3) and cell parameters derived in this study. Densities for both ordered and
423 disordered illite were calculated by taking into account a and b parameters obtained from the
424 bulk refinement for each of these polytypes (i.e., $a = 5.165 \text{ \AA}$ and $b = 8.996 \text{ \AA}$ for ordered illite
425 and $a = 5.2269 \text{ \AA}$ and $b = 9.049 \text{ \AA}$ for disordered illite), and densities values reported in Table
426 3 are averaged values based on the contribution of these two polytypes in each subfraction. For
427 these calculations, layer-to-layer distances reported in Table 2 for each subfraction and
428 corresponding to c^* parameters were used. The calculated grain densities show no noticeable
429 variation with particle size (Table 3). A mean grain density value of the $<2 \mu\text{m}$ fraction at 2.83
430 $\text{g}\cdot\text{cm}^{-3}$ can be calculated based on the relative proportion of the different subfractions. This
431 value is slightly higher than the grain density of $\sim 2.7\text{-}2.79 \text{ g}\cdot\text{cm}^{-3}$ that was reported in the
432 literature (Tessier, 1984; Bardot, 1998; Poinssot et al., 1999; Altmann et al., 2015) based on
433 generic compositions and structural parameters.

434

435 3.2.3. *Specific surface area and associated geometrical features of particles in E-IDP size*
436 *fractions*

437 The derivative isotherms of low-pressure argon adsorption at 77 K and the DIS
438 decomposition for the different size fractions of Na⁺-saturated E-IDP are shown in Fig. 5. The
439 parameters used for the DIS modeling are reported in Table S1 (see Supplementary Data
440 (S.D.)). The lateral, basal, and total specific surface areas (LSA, BSA, and TSA, respectively)
441 from the DIS decomposition are reported in Table 4. This table also includes the mean values
442 for the height (*h*) and basal length (*l*) of the clay particles, which were calculated according to
443 Eqs. 1 and 2, respectively, based on the grain densities reported in Table 3.

444 The experimental derivative isotherms are similar for all size fractions, and the
445 decomposition procedure leads to the definition of 6 and 5 energy domains for the <0.1 μm and
446 >0.1 μm fractions, respectively (Table S1). These different domains are attributed to either
447 lateral (green dashed line; Fig. 5) or basal (red dashed line; Fig. 5) surfaces (Michot et al., 1990;
448 Villieras et al., 1992, 1997; Bardot et al., 1998; Chemedda et al., 2021). The overall TSA values
449 expectedly increase with decreasing size fraction and are consistent with the N₂ adsorption
450 results (Table 4) upon consideration of the differences between the acquisition methods
451 (continuous vs. point-by-point method for N₂ and Ar, respectively).

452 Mean particle lengths and heights derived from the DIS decomposition are found to
453 decrease with decreasing size fractions. The obtained mean particle dimensions are in fair
454 agreement with those reported by Rajec et al. (1999) and Hassan et al. (2005) for the same
455 material, although no size fractionation was performed in these previous studies. The aspect
456 ratio of ~0.1 obtained for <0.2 μm size fractions in this study is also in good agreement with
457 the results of these previous studies (Rajec et al., 1999; Hassan et al., 2005). Note that the aspect
458 ratio value is slightly higher for the 0.2-2 μm size fraction, which can be associated to the

459 presence of non-clay accessory minerals (Fig. 1b). Interestingly, the aspect ratio for the <0.2 μm
460 size subfractions is similar to that obtained for Santa Olalla vermiculite by Reinholdt et al.
461 (2013). These authors indeed reported an aspect ratio of 0.08 and a TSA value of $\sim 108 \text{ m}^2 \cdot \text{g}^{-1}$
462 for the dried Na^+ -saturated 0.1-0.2 μm size fraction of vermiculite, which is in good agreement
463 with the results obtained for the same size fraction of E-IDP. This finding is of particular interest
464 in the scope of investigating the influence of interlayer porosity on a given process (e.g.,
465 adsorption or diffusion of solute species in porous clay media) for specific particle sizes and
466 morphologies.

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483 **Table 4.** Physico-chemical characterization of Na⁺-saturated size fractions of EURAD illite du
484 Puy (E-IDP) with relative mass contributions to the <2 μm size fraction, cationic exchange
485 capacity values, and geometrical properties. Surface measurements include the total specific
486 surface area determined by both N₂ and Ar adsorption. Particle geometry analysis includes
487 lateral and basal specific surface areas (LSA and BSA, respectively) and the height (*h*) and basal
488 length (*l*) of clay particles obtained by low-pressure Ar adsorption and DIS decomposition.

Sample	This study						Hassan et al. (2005) ^e	Rajec et al. (1999) ^f	
	<0.05 μm	0.05-0.1 μm	0.1-0.2 μm	0.2-2 μm	<2 μm	<2 μm ^{calc.}	IDP	IDP	
Relative mass contribution to <2 μm (%) ^a	0.21	0.23	0.24	0.32	-	-	-	-	
CEC ^b (meq/100 g at pH = 7)	39.5	32.7	22.8	8.4	21.2	24.0	-	-	
N ₂ TSA (m ² .g ⁻¹) ^c	184.6	153	114.1	60.8	123.6	120.8	-	-	
Ar specific surface area (m ² .g ⁻¹) ^c	Total (TSA)	158.2	133.2	109.2	60.7	-	-	171	233
	Lateral (LSA)	30.4	27.3	16.7	15.6	-	-	38	29
	Basal (BSA)	127.8	105.9	92.5	45.1	-	-	133	
Geometrical parameters of particles from DIS decomposition	<i>h</i> (nm) ^d	5.5	6.5	7.4	16.4	-	-	5.7	3.6
	<i>l</i> (nm) ^d	53.1	58.3	94.7	109.7	-	-	46.4	52.0
	aspect ratio (<i>h/l</i>)	0.10	0.11	0.08	0.15	-	-	0.12	0.07

^a uncertainties calculated at ~10% (based on replicate measurements), ^b uncertainties calculated at ~10% (taking into account uncertainties on sample dry mass and measured aqueous concentration), ^c uncertainty on external specific area values of ± 1 m².g⁻¹, ^d calculated using Eqs. 1 and 2, ^e & ^f calculated from fixed cations per O₁₀(OH)₂.

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490 3.2.4. The cation exchange capacity of E-IDP size fractions

491 The measured CEC values of the different size fractions of E-IDP, reported in Table 4,
492 show an expected increasing trend with decreasing particle size. In that regard, the CEC, mainly
493 originating from the sorption sites on the particle external surfaces, agrees with the evolution

494 of the N₂ or Ar TSA values. To further validate our results, the obtained CEC values for the
495 <2 μm size fraction can be successfully compared to the calculated values (<2 μm^{calc.}) based on
496 the relative proportion and associated CEC values of each subfraction (Table 4). This very good
497 agreement between the experimental and calculated CEC values is also obtained for N₂ TSA
498 values between <2 μm and <2 μm^{calc.} fractions, further confirming the consistency of the results
499 derived for the different subfractions (Table 4).

500 The results obtained in this study for E-IDP can be compared to those obtained by
501 Altmann et al. (2015) using similar materials. These authors reported a CEC value of 19
502 meq/100 g and an N₂ TSA value of 110 m².g⁻¹ for the Na⁺-saturated sample. Both values are in
503 good agreement with our results, although Altmann et al. (2015) reported a different mineralogy
504 of the clay phase with a large amount of smectitic layers (20-30% vs. <5% in the present study).
505 In contrast, the lower CEC and N₂ TSA values reported by Poinssot et al. (1999) for V-IDP
506 (13.2 meq/100 g and a N₂ TSA value of 97 m².g⁻¹, respectively) can be tentatively assigned to
507 the higher content of kaolinite in the V-IDP material.

508

509 **4. Concluding remarks and perspectives**

510 The results obtained in this study confirm that illite du Puy is a suitable model clay system
511 almost solely constituted by illite clay mineral. Most of the variability in the characterization
512 data found in the literature originates from mineralogical variation that results from the different
513 locations of geological sampling. However, the particle size distribution between the different
514 subfractions is similar irrespective of the sampling location.

515 Precise sampling in the sedimentary Velay clay-rich formation allows for the extraction
516 of almost pure illite with a minor amount of non-clay phases. Using a suite of different
517 techniques, different size fractions of this illitic material used in the ongoing EURAD project

518 were fully characterized. This sample was found to be an illite–smectite mixed-layer material
519 with an extremely low amount of smectite layers (<5%). No significant changes in crystal
520 chemistry or particle aspect ratios were found between the different subfractions. These
521 different subfractions displayed a wide range of specific surface areas (i.e., N₂ BET surface)
522 and cation exchange capacity values, increasing by factors of ~3 and ~5 from the 0.2-2 μm to
523 the <0.05 μm size fractions, respectively. EURAD illite and associated subfractions can thus
524 be considered good models to better understand the adsorption and diffusion of solutes in clay-
525 rich materials. The size fraction can be chosen to tune the specific surface area and thus enhance
526 or reduce the anionic exclusion and adsorption effects of solutes in the case of diffusion studies
527 of ionic tracers within compacted samples (Ochs et al., 2001; Sato and Suzuki, 2003; Van Loon
528 et al., 2003, 2007; Appelo and Wersin, 2007; González Sánchez et al., 2008; Melkior et al.,
529 2009; Glaus et al., 2010, 2011; Mazurek et al., 2011; Savoye et al., 2012, 2015; Altmann et al.,
530 2015; Bestel et al., 2018). Such a variation is also important to experimentally highlight the role
531 played by the electrical double layers located around particles in the diffusion of cations and
532 anions. Finally, the similar aspect ratios and TSA values obtained for illite and vermiculite
533 (Reinholdt et al., 2013) subfractions with comparable external CEC values represent key assets
534 for the investigation of the influence of interlayer porosity on solute transport properties in
535 porous media made of these two types of particles for a given particle size and morphology.

536

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547

548 **Supplementary Data (S.D.)**

549 Table S1 reports the main parameters of Na⁺-saturated EURAD illite du Puy (Na-EIDP) size
550 fractions obtained by using the DIS method applied to low-pressure Ar adsorption isotherms.

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564 **Captions**

565

566 **Fig. 1.** (a) Experimental X-ray diffraction patterns (black crosses) of randomly oriented Na⁺-
567 saturated bulk powders of Velay illite du Puy (V-IDP) and EURAD illite du Puy (E-IDP)
568 together with calculated patterns obtained by BGMN Rietveld refinement (red solid lines). (b)
569 Quantitative mineralogical composition (in wt. %) for the two types of samples as determined
570 from Rietveld refinement with I: illite, K: kaolinite, K-Fd: potassium feldspar, Plag:
571 plagioclase, Qz: quartz, Cal: calcite, Hal: halite, Ap: apatite, and Ana: anatase.

572

573 **Fig. 2.** Lithological section of the central zone of the Velay basin (adapted from [Gabis, \(1963\)](#)),
574 illustrating the potential sampling locations of the two samples investigated in the present study.
575 The experimental X-ray diffraction pattern from [Gabis \(1963\)](#) obtained for green clays
576 alternating with gray marl banks, shown as an insert, is similar to that obtained in this study for
577 the EURAD illite du Puy (E-IDP; top) considering the absence of kaolinite and calcite. The
578 XRD pattern collected for Versicolor clays at the bottom of the middle series by [Gabis \(1963\)](#),
579 also shown as an insert, with kaolinite and calcite as accessory minerals, is similar to the pattern
580 obtained in this present study for Velay illite du Puy (V-IDP; bottom).

581

582 **Fig. 3.** Experimental X-ray diffraction patterns of oriented Ca²⁺-saturated preparations for the
583 different subfractions of Velay illite du Puy (V-IDP, left) and EURAD illite du Puy (E-IDP,
584 right). In black, the patterns are recorded under air-dried conditions, whereas the patterns after
585 ethylene glycol saturation are shown in gray. I and K stand for illite and kaolinite reflections,
586 respectively. Non-indexed reflections are associated with accessory minerals.

587

588 **Fig. 4.** Comparison between the experimental (crosses) and calculated (solid red lines) XRD
589 patterns of oriented Ca^{2+} -saturated preparations recorded in air-dried (AD) and after ethylene
590 glycol (EG) saturation for the different subfractions of EURAD illite du Puy (E-IDP). The
591 structural parameters of the illite–smectite mixed-layer minerals are reported in [Table 2](#).

592

593 **Fig. 5.** Experimental low-pressure Ar derivative adsorption isotherms (open circles) were
594 obtained at 77 K for the different Na^{+} -saturated subfractions of EURAD illite du Puy (E-IDP).
595 Derivative isotherm summation (DIS) decompositions are reported as dashed lines (red and
596 green for domains associated with Ar adsorption on basal and lateral surfaces, respectively).
597 The sum of the different DIS contributions is shown as a solid blue line.

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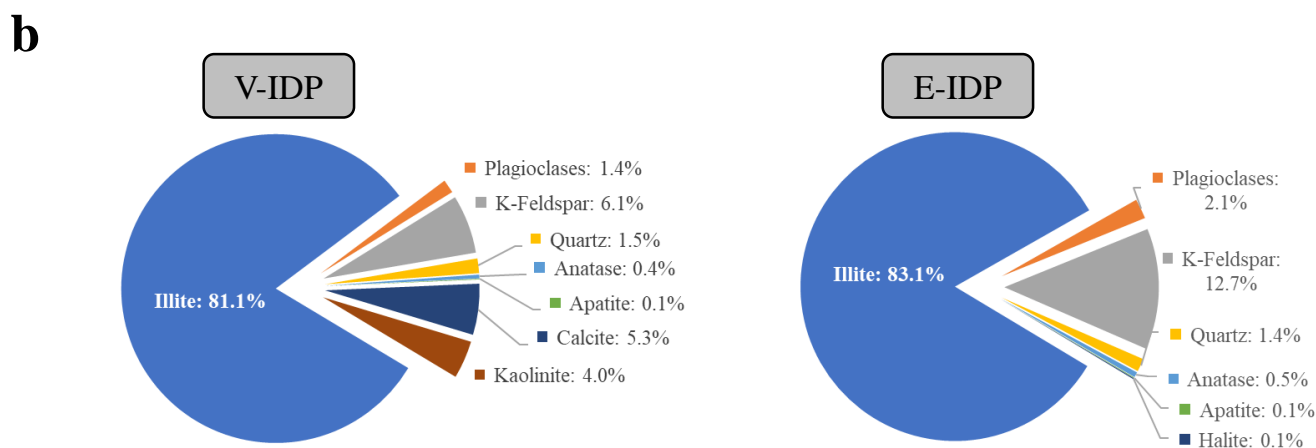
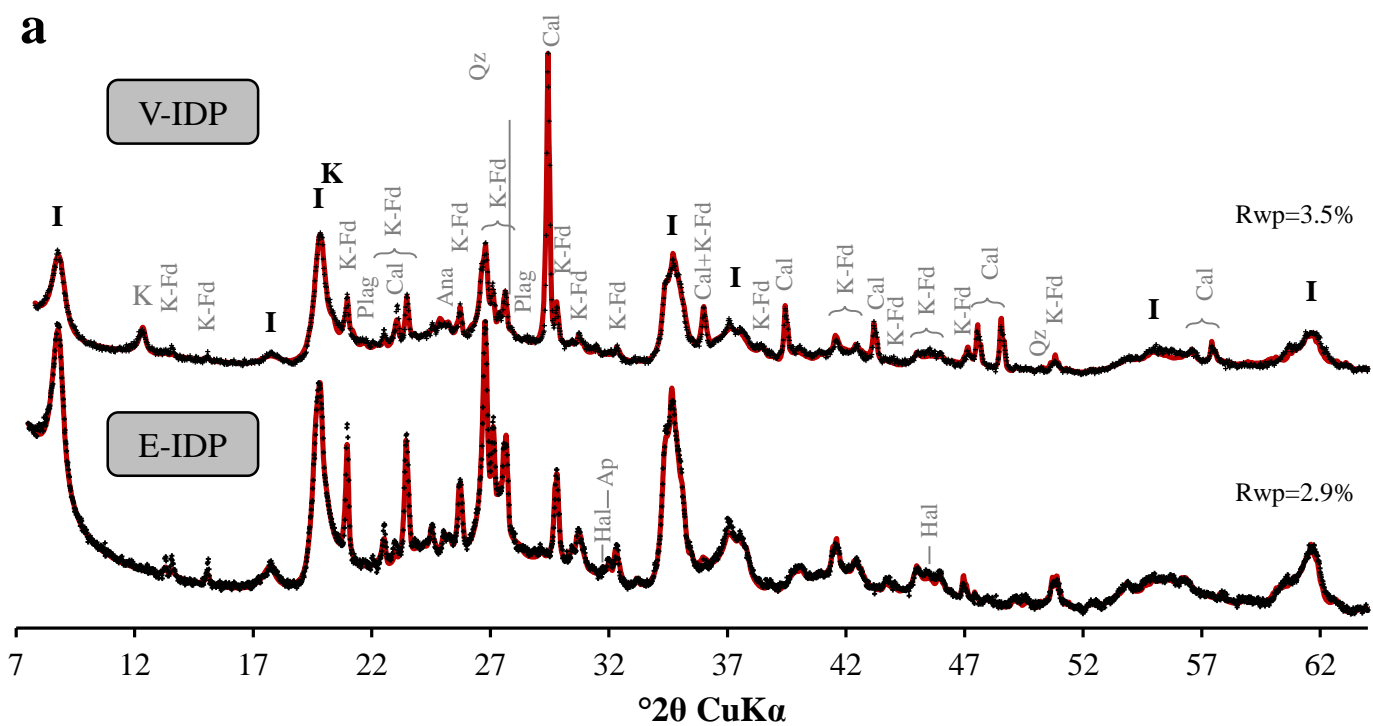


Fig. 1.

Central zone of Velay basin

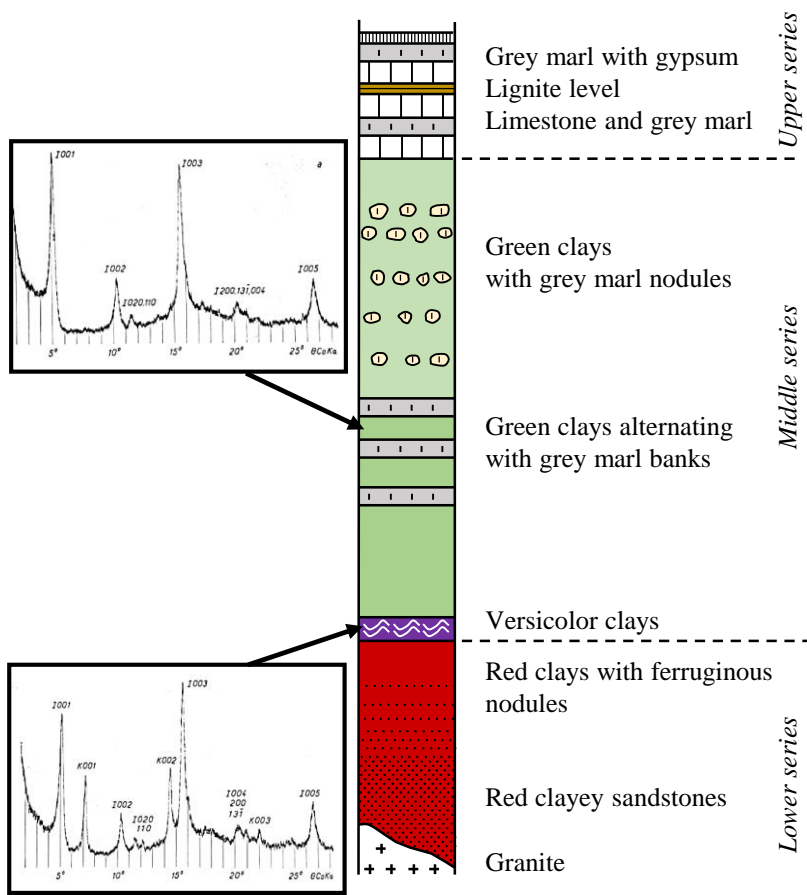


Fig. 2.

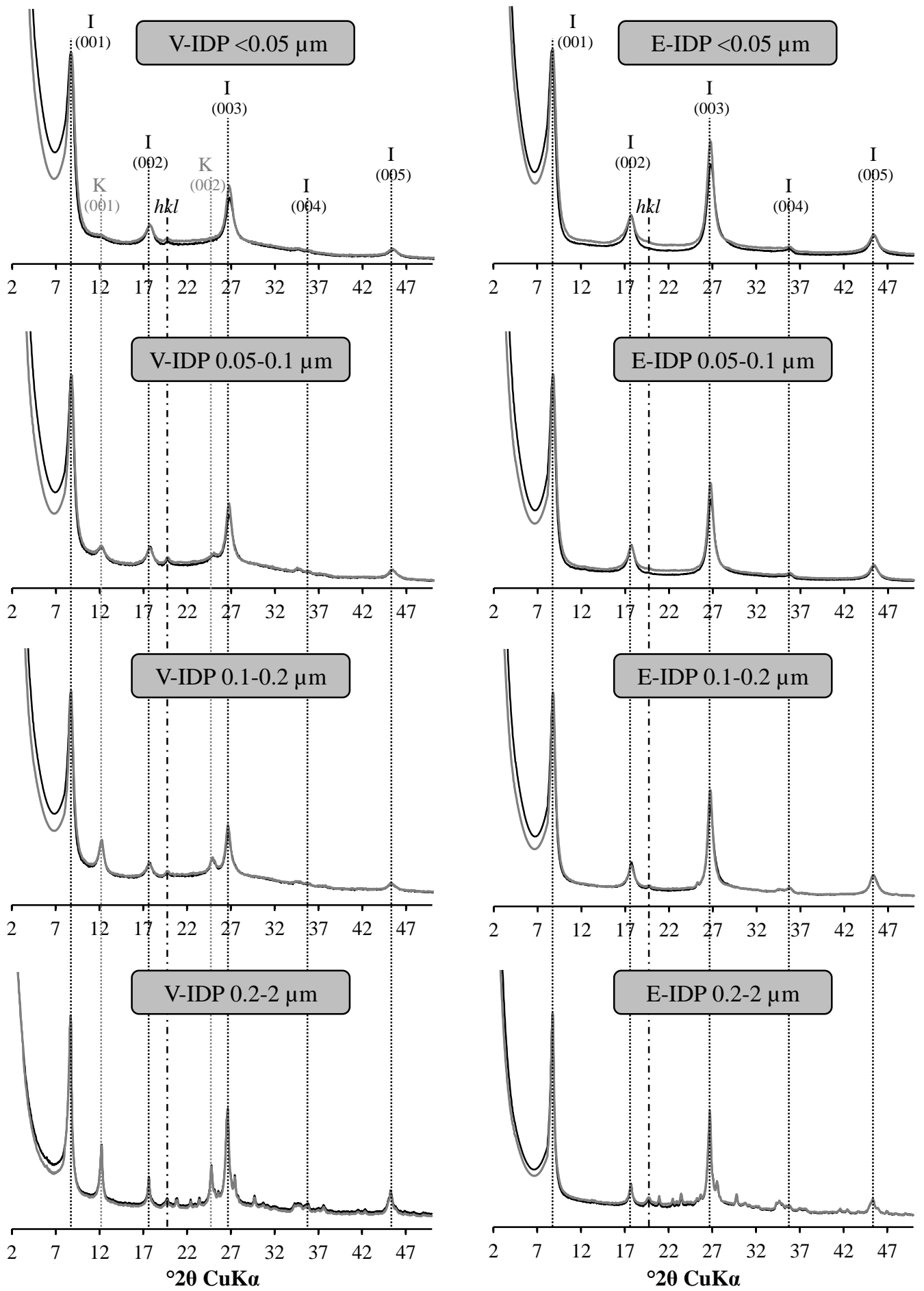


Fig. 3.

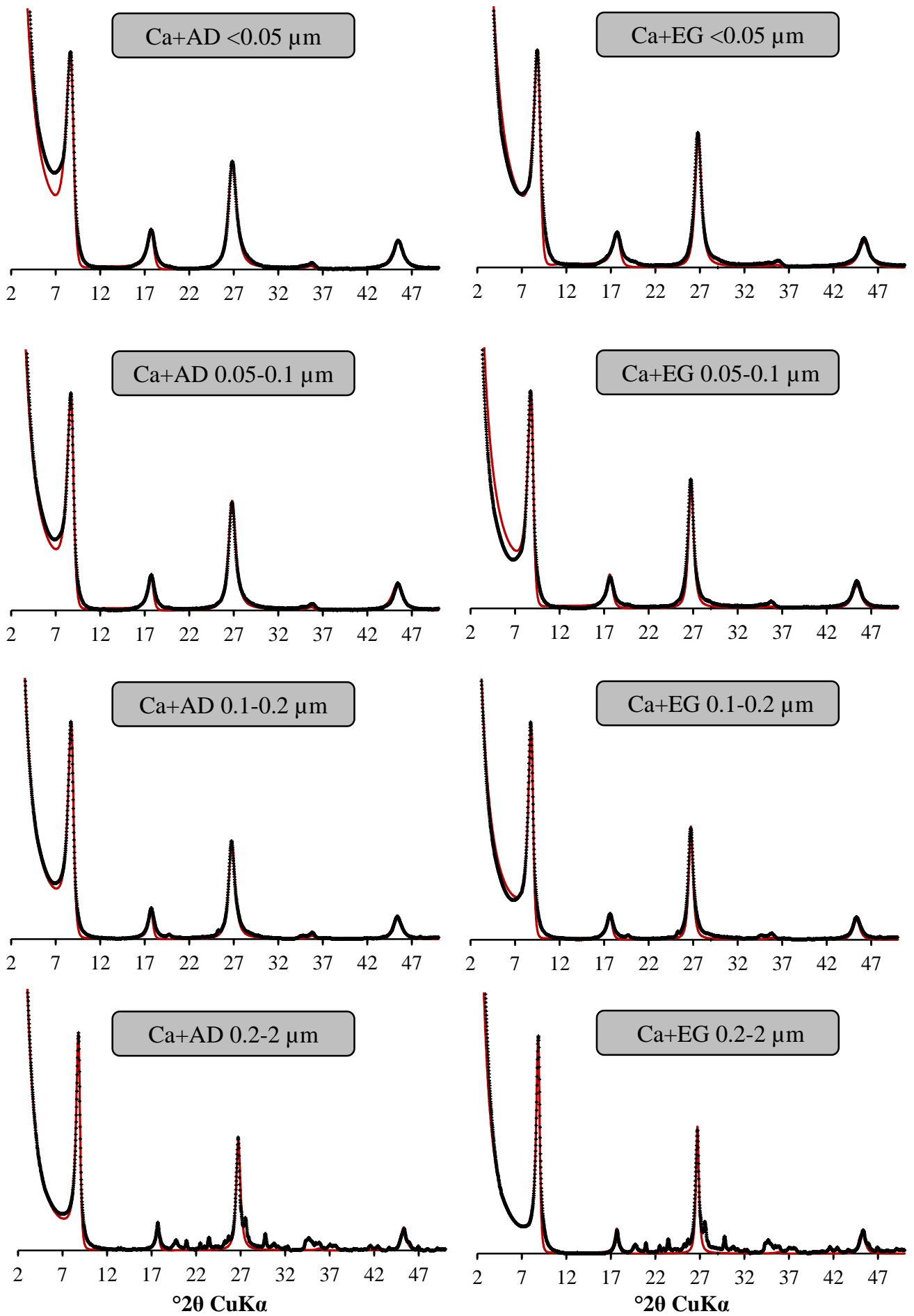


Fig. 4.

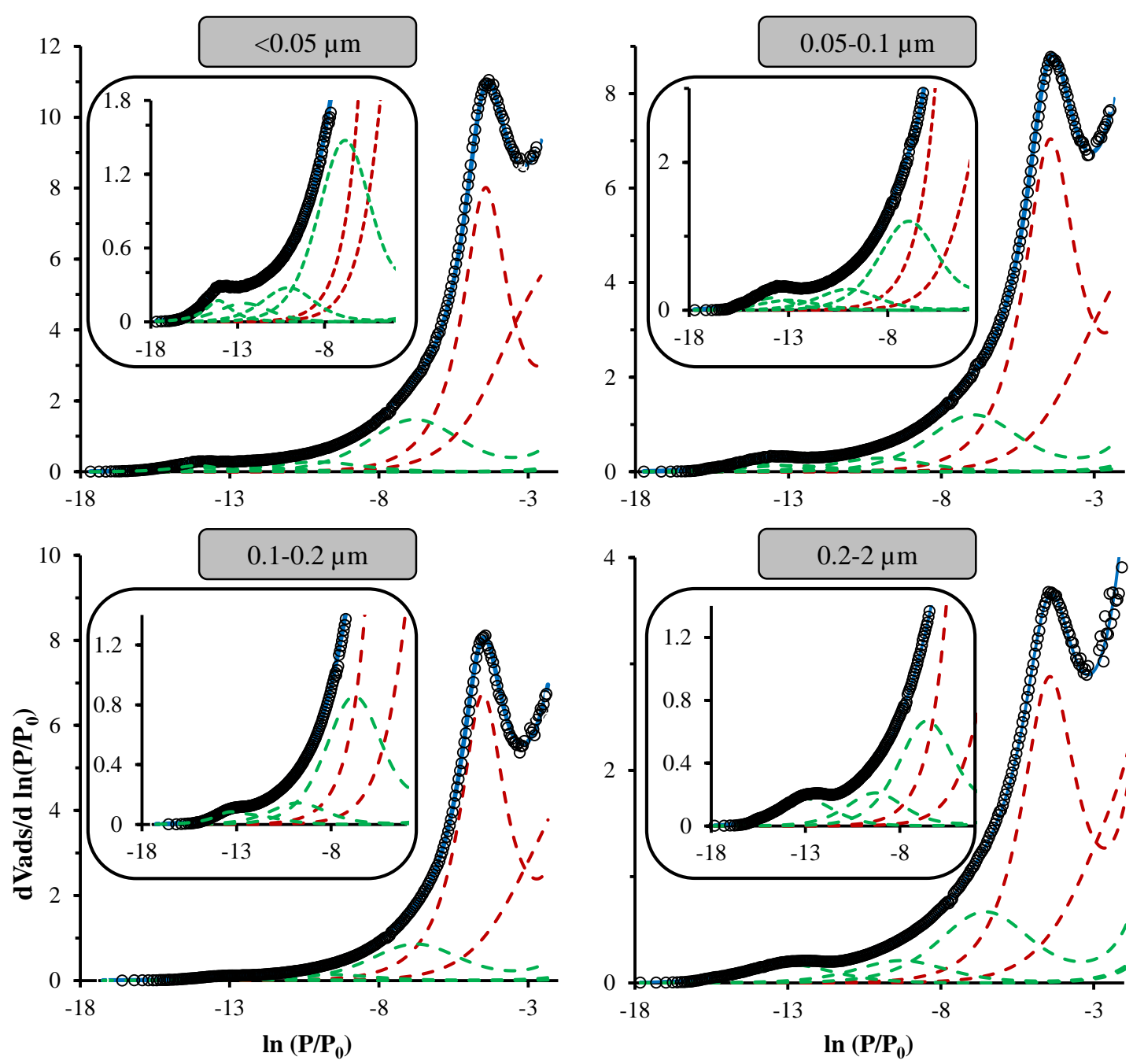


Fig. 5.