Combining wavelets with statistical inference to map the mineralogical composition of pedological features from synchrotron X-ray diffraction data

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Abstract

Clay translocation is among the most widespread processes in soils. It is generally identified by the presence of clay coatings at the macroscopic or microscopic scales. Nevertheless, several authors demonstrated that clay coatings have different origins, which renders the attribution of individual coatings to a particular process difficult. Therefore, their characterization at the microscopic scale is necessary. Modern synchrotron techniques allow mapping of the mineral composition of soil thin sections by X-ray diffraction with a lateral resolution of a few micrometers that is compatible with the size of the clay coatings. However, the use of this technique raises a certain number of technical difficulties when clay minerals and small pixel size are considered. Therefore, a preliminary feasibility analysis was performed on soil coating obtained experimentally in a soil column experiment. We developed a mathematical/statistical method to automatically identify and map the minerals present in synchrotron X-ray diffraction maps. This method combines a subtraction of the background signal, an identification of the diffraction peaks and the attribution of the obtained peaks to the different minerals phases. The robustness of the method was tested for the two first steps that were critical. We then showed that most of the minerals present in the considered samples could be identified, including clay minerals and Fe oxides; however, their relative proportions were difficult to estimate within the experimental conditions. As a conclusion, we proposed here a new mathematical method for the data treatment of synchrotron X-ray diffraction. Our study shows that this method could be applied on natural heterogeneous samples with data of poor quality to perform robust qualitative analysis. Moreover, with the recently available fast data acquisition schemes, large amounts of datasets (diffractograms) can be rapidly acquired and are expected to benefit the automatic data treatment approach proposed here.

Keywords Signal processing · Filtering · Mineralogy · Clay translocation · Pedogenesis

Mathematics Subject Classification 92F99 · 62-07 · 60G35 · 65D10

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1 Introduction

Clay translocation is among the most widespread processes in soils. This process is defined as a substantial vertical transfer of particles from a horizon, called eluviated horizon, to another horizon referred to illuviated horizon. Lessivage is generally identified in soils by the presence of clay coatings and fillings at the macroscopic or microscopic scales [16, 17, 19, 26, 47]. Clay translocation has been considered as occurring mostly under boreal conditions and consequently as a fossil process in temperate conditions [50]. Recent research, however, clearly demonstrated that this process is still active nowadays in temperate climate [32, 39] and that its intensity is particularly sensitive to anthropic or climatic global changes [29, 33]. As increasing intensity of clay translocation may correspond to increasing risks of erosion and compaction in surface soil horizons, to increasing transfer of soil contaminants associated with eluviated soil particles but also to increasing long-term C sequestration in subsoil horizons [48], it seems thus necessary to better understand its mechanisms notably at the microscopic scale.

Indeed, while few studies deal with the characterization and quantification of clay coatings by image analysis to our knowledge [36, 39, 40, 46], none of them proposes a mineralogical characterization of illuvial clay features. Clay coatings being generally 60–200 μm thick [8, 40, 47], the selective sampling of clay coatings to characterize their mineralogical composition with laboratory X-ray diffractometers is generally not feasible. The mineralogical composition of clay coatings and fillings therefore remains largely unknown, making it impossible to specify the mineralogical selectivity of the translocation process or its dependence on the conditions of formation of clay coatings. Micromorphological studies have, however, demonstrated that the composition of clay coatings and infillings depends on their deposition conditions. Pure micro-laminated and limpid clay coatings are associated with a homogeneous and low energy flow of water under permanent plant cover, while “dusty” clay coatings containing organic and silt-sized particles are associated with a flow of high-energy water under cultivation [13, 20, 21]. Modern synchrotron techniques allow mapping mineral composition on soil thin sections by (monochromatic) X-ray diffraction (XRD) with a lateral resolution of a few micrometers that is compatible with the size of the clay coatings. Classically in the literature, synchrotron XRD is either used on powder to detect mineral phases that are hardly detectable by laboratory XRD apparatus, as iron oxides for example [23, 41, 44, 49, 53], or in association with micro-X-ray fluorescence (XRF) or micro-EXAFS to identify phases bearing trace elements

on thin sections [9, 10, 12, 25, 42, 43, 45], among others. While dealing with small investigated volumes (small X-ray beams and thin section samples), the probed sample cannot be anymore assimilated to a random orientated powder. As a consequence of the few number of illuminated crystallites (Gueriau et al. [15], in press), the Bragg diffraction condition is scarcely satisfied and not all the peaks are recorded for a given mineral phase [25, 42, 43]. To solve this problem, most authors sum up individual XRD pattern on a chemically homogeneous zone of interest (Sutton et al. [45], among others) or use larger X-ray beams, e.g., of size of several tenth of μm [9, 10, 45] in order that the probed volume resembles more to a random orientated crystalline powder. Also, XRD maps are rarely presented with the notable exception of De Nolf et al. [9] who used a 60 μm pixel size. In addition, while clay minerals as kaolinite and illite were detected by synchrotron XRD, mainly on powder samples [25, 34, 49], in the case of orientated clay coating, depending on the orientation axis, detection of these mineral might be more challenging. At last under these conditions (few number of crystallites in the X-ray probed volume), classical data treatment approaches as Rietveld refinement and other full pattern fitting methods that were proved very efficient to quantify the mineral composition of a sample cannot be used as mentioned by Siebecker et al. [42] “often, peak-matching is challenging because minerals can have overlapping peaks, and the number and intensity of the peaks can be disproportionate to the reference database”. In addition, due to the large amount of XRD patterns acquired automatic processing procedure is required if mapping mineral is one of the pursued objective. The aim of this paper was thus to study the feasibility of mapping the mineralogy of clay coatings by synchrotron X-ray diffraction. To this aim, we analyzed coatings from thin sections obtained in an experiment of in vitro pedogenesis on soil columns, performed by Cornu et al. [7]. Due to the high number of diffractograms acquired, we developed an automatic processing procedure that combines a subtraction of the background signal (both from thin section mount and from mathematical modeling), an identification of the diffraction peaks and an attribution of the obtained peaks to different minerals phases in order to draw various contrasts maps.

2 Material and methods

2.1 Experimental design

Cornu et al. [7] performed clay translocation laboratory experiments on two E-horizons of Luvisols developed in

loess with contrasting pH and clay mineralogy. For eluviation, an E-horizon, called *L1*, containing smectites and with a pH of 6.2 was chosen, while for illuviation, a E-horizon, called *L2*, containing no smectite and with a pH of 7 was chosen. Undisturbed cylinders (with height and diameter of 15 cm) were sampled at a depth between 35 and 50 cm. To monitor illuviation (particle deposition), complex columns were built consisting of an undisturbed *L1* cylinder overlaying an undisturbed *L2* cylinder. Thirty rain events were applied to the soil columns using a rain simulator. The considered *L2* cores contained quartz, feldspars, kaolinite, illite, chlorite, iron oxides (goethite, ferrihydrite notably) and accessory minerals, and eventually smectite coming from the upper *L1* cylinders. For more details, see Cornu et al. [7].

2.2 Thin sections fabrication and observation by optic microscope

On four *L2* cores (named R, S, AR and P), undisturbed blocks (80 mm × 50 mm) were sampled both at the top and at the bottom of the core (named /T and /B, respectively), for thin sections. The blocs were air-dried for 2 months, then oven-dried at 40 °C for 2 weeks and impregnated under a vacuum of − 5 kPa with a polyester resin diluted to 30% by volume with a styrene monomer [3]. Eight uncovered thin sections, 50 × 50 mm in size and 25 µm thick, were prepared on a glass slide and observed by using a petrographic microscope Nikon Eclipse 50ipol optical microscope in both plane polarized light (PPL) and crossed polarized light (XPL) at the magnification of 20×, 40×, 100× and 200×. Three different microscopic units (MU) are observed: the soil matrix (skeleton and plasma), voids and voids coating made of fine material, and of varying thickness. The skeleton is composed of sandy and silty particles embedded in a finer brownish silty-clay plasma containing some fine brown organic particles common in E horizons. The dark hue of the matrix is typical of Fe and/or Mn oxides. The skeleton includes mainly quartz grains. Pores are mainly channels, which are the traces of burrowing by soil macrofauna and roots, and vughs.

Three types of coatings may be distinguished: a dark brown, dusty and slightly birefringent one (DSB) (Fig. 1a), a limpid and birefringent one (LB) (Fig. 1b), and a highly birefringent laminated one (HBL) (Fig. 1c). Increasing birefringence is interpreted as increasing orientation of the clay particles inside the clay coatings or infillings and is linked to decreasing energy of the water flows. Limpid and dusty coatings are, respectively, associated with pure and impure clay deposits. Impure clay coatings contain mineral or organic particles mobilized from the soil surface. The DSB and LB coatings are generally thin and may be observed from the top to the base of the soil column

Fig. 1 Micromorphology of **a** a dusty and **b** a clear clay coating surrounding a pore, and **c** a clay cutan with internal lamination. The yellow squares are the regions-of-interest that have been scanned with μ XRD

(Table 1), suggesting that they may have been formed during rain simulations and thus may contain smectites. Their boundaries are diffuse as the clay fills the irregularities of the edge of the pores. Highly birefringent, thick and microlaminated coatings and infilling with iron staining (HBL) are mostly observed at the base of the soil column and are typical of illuviated horizons, suggesting that they may have been formed under field conditions.

On each thin section, zones containing the portions of the different MU: matrix, pore and one particular kind of clay coating, were selected for X-ray diffraction characterization. Three thin section zones are more specifically studied here in order to target the different kinds of clay coatings and finally identify potential relationships between clay coatings morphology, conditions of deposition and mineralogy. Image analysis (supervised classification) allowed the segmentation of the zones in the three MU as already performed by Montagne et al. [30].

2.3 Synchrotron μ XRD and μ XRF analysis

The three selected zones of coatings were mapped by coupling μ XRD and μ XRF on the DiffAbs beamline of the SOLEIL Synchrotron (France) in transmission mode at 17.2 keV X-ray photons energy (i.e., $\lambda = 0.72 \text{ \AA}$), and a beam of 10 µm per 6 µm (FWHM, horizontal × vertical direction) with a photon flux of several 10¹⁰ ph./s in the focused beam. The experimental setup is sketched in Fig. 2a: The sample (see details above) was placed vertically on a YZ scanner stage (µm accuracy), with its surface normal rotated by about 20° with respect to the incident X-ray beam, to avoid shadowing effects for measuring the XRF signal. This small

Fig. 2 **a** Illustration of the synchrotron setup for XRD and XRF mapping with an X-ray microbeam: The sample is mounted on a micron-accuracy scanner stage and surrounded, as shown, by the two detectors. The schematics of the XPAD detector (modules and chips assembly) are also shown, after Mocuta et al. [28]; powder diffraction data acquired on a powder sample ($< 2 \mu\text{m}$ fraction of the L2 soil) using the XPAD detector, for three 2θ positions (of about 3.5, 13.5 and 23.5 degrees, respectively) and the data conversion procedure, to obtain XRD Intensity vs. 2θ datasets: **b** raw XPAD images (Log10 color scale, from blue to red); **c** the previous images are first transformed to mask the inter-module gaps and broader inter-chip pixels; **d** then the angular coordinates of each pixel are

calculated from the known particular geometry and reported in maps with the horizontal axis being the scattering angle (2θ) and the vertical one being ψ , the azimuth measured on the XRD ring, zero being its apex point, situated in the xz plane (cf. panel **a**). In this representation, the XRD rings appear as vertical lines ($2\theta = \text{constant}$). The borders of the 3 XPAD images/datasets patched to generate this figure are shown by the colored contours (black, blue and red, respectively); **e** the XRD (I vs. 2θ) curve is obtained from each dataset by performing a ψ azimuthal regrouping (histogram like) and shown using the previously mentioned colors (black, blue, red)

angle has as a consequence a slight increase in the beam footprint on the sample, in the horizontal direction, by about 6.5 percents.

The XRF silicon drift detector (SDD, Vortex-EM X-ray Detector from Hitachi, with 50 mm^2 active area) is placed in the horizontal plane, at 90° from the incident X-ray beam. Since the X-ray beam is polarized in the horizontal plane, this particular geometry insures that the elastic scattering is minimized (zero in theory). The area detector used for μ

XRD analysis is a hybrid pixel area detector, XPAD 3.2, that works in a single-photon-counting pixel mode. It consists of 8 modules assembled as shown in Fig. 2. Each module consists of 7 hybrid integrated circuits (chips) on a single $500\text{-}\mu\text{m}$ -thick silicon sensor [27] which has its rear face pixelized and each pixel is coupled via “bump-bonding” to an electronic counting device in a dedicated circuit. Each chip consists of 80×120 pixels of $130 \mu\text{m}$ size, except the first and last columns if situated at the junction with the next

chip. They have a size precisely 2.5 times larger along the neighbor chip direction. Due to the module assembling on a flat plane, an inter-module gap of about 27 pixels (about 3.5 mm of dead area) is observed. Thus, the total area covered by the detector is $75.1 \times 149.3 \text{ mm}^2$. Knowing this detector geometry in detail, and combining it with reference X-ray diffraction images (ex. XRD taken on calibration powders), reliable image and geometry corrections can be carried out to extract the position in space, and then in the angular space, for each pixel (Fig. 2). The detail of these corrections is described in several references [18, 22, 28]. For this experiment, the sample–detector distance used was of 369.9 mm, yielding an angular opening of about 0.02° per pixel. For all the reported results on thin sections, a counting time of 4 s was used; XRD and XRF data are acquired simultaneously, thus on precisely same region of the sample. The choice of the acquisition time is a compromise between signal statistics (for detecting XRD, mostly) and total duration to measure one sample, in order to remain compatible with the possibility of measuring several samples during the allocated beamtime at synchrotron. Since the XPAD detector-analyzed angular domain is of about $10\text{--}15^\circ$, three different acquisitions were performed for $3.5\text{--}17$, $9.3\text{--}24.7$ and $19.3\text{--}33.4$ degrees ranges in 2θ . Glass plus resin areas were also analyzed to have a background signal as well as $< 2 \mu\text{m}$ fraction samples in powder, in order to verify that the peak of interest was detected in the analytical configuration used (see “Methodological test on the $< 2 \mu\text{m}$ fraction of the considered soil” in Appendix 1). All the XPAD data were preprocessed for image correction as mentioned above [22, 28]. The 2D diffraction patterns (XPAD images) were transformed into diffractograms (intensity vs. 2θ curves) using Python codes (Fig. 2). “Background” like signal (obtained on glass and resin alone) was systematically subtracted. One can note that both the XRD signal and the “background” have rather noisy baselines, so this subtraction is generally insufficient and further processing of the data was necessary (see below).

2.4 Automatic identification of XRD peaks (pixel scale)

As mentioned in the Introduction, at the pixel scale, only few, if any, XRD peak may be encountered, which may be very small in intensity. Their automatic identification thus requires the identification of relevant peaks, after removing both the noise and the baseline.

2.4.1 Removal of the remaining baseline

To detect the peaks, the remaining part of the background signal either linked to the glass slide mount or

to the detection apparatus had to be removed. At first sight, this is similar to what was done by Antoniadis et al. [1, 2] for mass spectrometry data. These authors modeled each spectrum Y by the equation:

$$Y(x) = L(x) + S(x) + \varepsilon \quad (1)$$

where x is the molecular mass, L is the baseline (some smooth function), S is the genuine signal (peaks associated with proteins) and ε is a white noise. Technically, [1, 2] used first the stationary wavelet transform algorithm [24, Sect. 10.2.3] to pick out the noise, and then the R package of penalized quantile smoothing spline COBS [35] to estimate the baseline. We adapted their method to the specific nature of our data. Unlike Antoniadis et al. [1, 2], who considered mass spectrometry peaks having a quantitative meaning, the peaks in XRD patterns have a semi-quantitative meaning. In addition, the signal-to-noise ratio of our data is much lower than in Antoniadis et al. [1, 2].

To detect significant peaks, we propose a two-step strategy:

1. baseline correction, thanks to COBS: $Y \mapsto (Y - \hat{L})$, where $\hat{L}$ denotes the baseline estimate
2. stochastic denoising, thanks to an original method (see Sect. 2.4.2):

$$(Y - \hat{L}) \mapsto (Y - \hat{L}) - \hat{\varepsilon} \approx S. \quad (2)$$

Like in Antoniadis et al. [1, 2], the smoothing parameter λ of COBS [35] was automatically chosen according to the Schwartz information criterion, but we chose as a quantile level $\tau = 0.5$ (median regression).

Remark 1 For the first angular domains, ranging from 3.5 to 17 degrees of angles, because of the steepness of all the associated patterns near the origin (see Fig. 5), it was impossible to obtain a satisfying fit with median regression in a standard way. This case has been processed in a special way detailed in “Background removal in the case of the first angular domain” in Appendix 2.

While [1, 2] chose a rather large number of knots ($K = 60$) for fitting L (adapted to the length of their series: about 18,000 points [5]), we used smaller values: $K = 10$ for the angular domains ranging from 9.3 to 24.7 and 19.3 to 33.4 degrees of angle, respectively, and $K = 20$ for the angular domain ranging from 3.5 to 17 degrees of angles (remember that K controls the smoothness of L). We could this way determine a sufficiently smooth estimate $\hat{L}$ of the baseline and separate it from $S + \varepsilon$ (see Eq. 1). We finally obtained for each angular domain and

pixel i the **detrended XRD signal** $\mathcal{D}_i := Y_i - \hat{L}_i$ from the original diffractogram Y_i .

2.4.2 An inference method to identify significant peaks in $\mathcal{D}_i$

Due to the size of the analyzed pixel, each diffraction signal Y_i as well as the detrended one $\mathcal{D}_i$ was noisy and of low intensity. We thus considered as a diffraction peak only those higher than a given number of times the standard deviation of the noise. Consequently, we had to estimate the standard deviation (SD) σ of the noise ε before eliminating it thanks to the three- σ rule evoked by Pukelsheim [37].

2.4.2.1 Stage 1: estimation of σ We drew from each zone a random sample of N pixel positions and obtained the required estimate of σ , **for each angular domain**, according to the following algorithm (detailed in “Estimation of σ ” in Appendix 3):

1. remove the noise from each detrended signal, thanks to stationary wavelets denoising: $\mathcal{D}_i \mapsto \mathcal{D}_i - \hat{\varepsilon}_i$
2. check the normality of the noise
3. robustly estimate its standard deviation σ .

A typical distribution of noise is displayed in Fig. 3. The normality of the noise was practically never rejected (Cramér–von Mises test of level 0.05), in accordance with model (1); consequently, the general hypothesis

$$(H) : \varepsilon^m = \mathcal{N}(0, \sigma^m)$$

of a Gaussian noise affecting each angular domain m , for each pixel, was accepted.

Fig. 3 Kernel density estimate of the noise distribution (in black), for a fixed pixel from a zone and a fixed angular domain; the associated Gaussian distribution ($\mu = 0$, $\sigma = 0.0400082$) is plotted in red and $\eta = 0.716156$ is the P value of the Cramér–von Mises test

2.4.2.2 Stage 2: binarization Impulse noise can be observed on the XRD pattern and must thus be discarded. Thus, once the SD of the noise affecting the m th angular domain of the studied zone, σ^m , had been estimated, we binarized the detrended XRD patterns by using the following two-step algorithm.

1. Detect **stochastic peaks under (H)** by binarizing each $\mathcal{D}_i$ thanks to formula (6) of “Stochastic binarization of detrended patterns” in Appendix 4, according to some fixed threshold η_0 .
2. Keep only those stochastic peaks which can be **simultaneously** considered as local maxima of the smoothing cubic spline $\mathcal{S}(\mathcal{D}_i, \hat{\sigma}^m)$ whose smoothing parameter λ is determined from $\hat{\sigma}^m$ by minimizing the unbiased risk estimate of Wahba [51], implemented in R by Wang and Ke [52].

Remark 2 In the first step above, we fixed $\eta_0 := P(|Z| > 3\hat{\sigma}^m)$ as a threshold (three- σ rule of Pukelsheim [37]), where $Z = \mathcal{N}(0, \hat{\sigma}^m)$ and $\hat{\sigma}^m$ is the robust estimation provided by Stage 1; this may seem severe, but notice that high-energy physicists, for instance [4], currently use 5σ as a threshold.

Finally, each $\mathcal{D}_i = \{(a_1^i, d_1^i), \dots, (a_j^i, d_j^i)\}$ was binarized according to the rule:

$$\mathcal{D}_i \mapsto \mathcal{B}_i := \{(a_1^i, b_1^i), \dots, (a_j^i, b_j^i)\}$$

where $b_k^i = 1$ if a_k^i is the position of some retained peak and otherwise $b_k^i = 0$.

2.5 From peaks to images of minerals: presence indicators

The method proposed above allowed to identify the XRD peaks for each pixel. These peaks must then be associated with minerals (through “theoretical” binary reference spectra (see “The intervals of $\mathcal{T}$: their exclusiveness and exclusiveness” and “The operator Λ^m associating $\mathcal{T}$ with angles of the m th angular domain” in Appendices 5.1 and 5.2) associated with minerals), and mapped.

2.5.1 Mineral phases: identification and image

For each analyzed thin sections, XRD patterns were averaged by (MU pore, matrix, clay coating or cutan), based on the attribution of each pixel to one of these features by image analysis, as described above. The obtained XRD

patterns were then interpreted classically, and a list of XRD peaks encountered was established and reported in Table 1. Peaks that were common to several minerals were differentiated from peaks belonging to a single mineral, also called exclusive peaks (Table 1). Each mineral is characterized by a family of diffraction peaks, which were defined as **characteristic intervals** (because of possible experimental shift). Since these intervals are different from one mineral to another, it was necessary to construct a common system $\mathcal{T}$ of **disjoint** intervals such that any original spectrum could be reconstituted in $\mathcal{T}$. (The construction of $\mathcal{T}$ is detailed in “The intervals of $\mathcal{T}$: their exclusiveness and exclusiveness” in Appendix 5.1). In concrete terms, $\mathcal{T}$ consists in this study of 442 intervals. Since some XRD peaks may be associated with several minerals while other may be exclusive of a single mineral, a ponderation was applied to give more weight to exclusive peaks than to peaks shared by several minerals (see “The intervals of $\mathcal{T}$: their exclusiveness and exclusiveness” in Appendix 5.1). We then defined indicators assigning to each peak a weight depending on the number of minerals that shares it. This point is detailed in “The presence indicators associated with minerals” in Appendix 5.3, where are defined the **Presence Index** of some mineral s at some position (x_i, y_i) , $PI(s; x_i, y_i)$, and its **Weighted Presence Index**, $WPI(s; x_i, y_i)$, which takes into account the **exclusiveness** of each peak.

2.6 Computational aspects: a digest

In Fig. 4, we synthesize by a flowchart the sequence of processing proposed. The left side of this figure corresponds to a *Mathematica* package, calling two R packages: COBS [35] for baseline removing and assist [52] for fitting the residual of COBS by some smoothing spline. A second *Mathematica* package has been dedicated to the right part of Fig. 4: conversion of binarized DRX data into maps of presence indicators of minerals of interest, thanks to reference spectra provided by experts. Another preliminary *Mathematica* package has been written, to build the family $\mathcal{T}$ of intervals (see “The generating family $\mathcal{T}$ of intervals, the associated tables, and presence indicators” in Appendix 5) associating 2θ coordinates with characteristic intervals. The whole processing lasts around an hour per image (depending on its size, its signal-to-noise ratio, etc).

3 Results and discussion

3.1 Stability of the peak detection and identification process

In the above-described approach, two key steps were identified: the background removal method and the choice of the number of σ as a threshold for peak detection.

Fig. 4 First part (left side): sketch of processing at the pixel level, for each angular domain; the resulting binary curves are then merged and compared with reference spectra of minerals of interest (right side)

Fig. 5 Two examples of XRD patterns. Raw data (dots) and fitting of the background by COBS of angular domains 1 (yellow), 2 (green) and 3 (red)

3.1.1 Removal of the background

As shown in Fig. 5, the background of the obtained XRD pattern may be quite complex and varies according to the angular domain considered.

It comprises a decrease in exponential type of the signal from 3 to 5° in 2θ and a large bulge ranging from 7 to 15° in 2θ (Fig. 5). The exponential decrease in small angles is classical (principally due to air and small particles scattering and other phenomenons like Compton scattering and fluorescent radiation [14]). The bulge corresponds to the signature of the glass slide (amorphous material) on which the soil thin section was mounted. The subtraction of an experimental XRD pattern obtained for a zone of the thin section containing only the resin from the raw XRD patterns before pre-treatment was used to remove this bulge. It, however, results in an increasing noise. That is why a supplementary mathematical removal of the background was performed. Both the exponential decrease and the residual bulge were thus removed mathematically from the XRD signal for the automatic analysis of the XRD patterns of the individual pixels as shown in Fig. 5 in

red, green and yellow. As seen on this figure, the chosen algorithm was robust enough to remove the background whatever its shape for the different angular domains considered.

3.1.2 Binarization strategy: choice of the threshold $k\sigma$

In order to differentiate diffraction peaks from noise, the results of Pukelsheim [37] was used for determining stochastic peaks. This type of threshold is classical in signal analysis but can range from as high as five SD, as in high-energy physics Collective [4], or as low as two sigmas in geochemistry. In Fig. 6, we reported the peaks identified for two XRD patterns using 2, 3 or 3.5σ as a threshold.

Some of the peaks identified with 2σ do not really come out of the background level and would not have been interpreted as peaks by an expert. (See, for example, peaks at 21.2, 28.2 and 31.5 degrees in 2θ in Fig. 6a and at 10.8, 11, 18.2, 21.8, 22.8 and 23.2 degrees in two-theta in Fig. 6b.) Two sigmas seemed thus an insufficient threshold for diffraction peak detection. Using 3σ , for the two considered pixels, only significant diffraction peaks were selected (see Fig. 6c and d). Moving to a 3.5σ threshold, small peaks considered as significant by an expert, as the peak at 11.7 degrees in 2θ in Fig. 6f, are not identified anymore by our procedure. At last, while considering 4σ , no peak is detected, in both cases (results not shown). We thus conclude that 3σ was the optimal threshold to be used for the peak detection.

3.2 Identification of the mineral on the mean XRD patterns of the different soil microscopic units for the three studied zones

Average XRD patterns for the analyzed zones show that the main notable feature of these XRD patterns is a bulge for 2θ values ranging from 7 to 17° that is characteristic of the glass slide on which the thin sections are mounted. Few small peaks are also observed. They may be considered either as artifacts due notably to an underestimation of the noise in certain zones, or resulting from an overestimation of the pore surface by the image analysis including grains located at the edges of these areas. The mineral maps of the two zones including pores (Figs. 7 and 8c–e) also show that almost no minerals are detected in the zones considered as pores with some exceptions of very small intensity. For other zones, however, more peaks were detected due to an overestimation by image analysis of the pore zone (see pore zones of P/T, S/B and R/T-2 in Table 1). The total number of peaks detected remains, however, largely lower than in the matrix or in the clay coatings (Table 1).

Fig. 6 Peaks detection for two diffractograms (columns). On each panel are superimposed: the detrended data (black points) $\mathcal{D}$, the smoothing spline $\mathcal{S}(\mathcal{D}, \hat{\sigma}^m)$ (green) and the neighborhoods of stochastic peaks (red strips)

The average XRD patterns of the matrix always exhibit a large number of peaks, many of them being associated with feldspars and quartz (Figs. 7j–9j and Table 1). Kaolinite and goethite are also systematically observed on the average XRD patterns of the matrix, while illite is only encountered in the matrix of some of the analyzed zones. Peaks of feldspar are the most numerous with the highest intensities; this might be due to the fact that feldspar is a mineral family with a high amount of possible diffraction peaks (150, see Table 1); it is also a mineral common in the studied soil. Surprisingly, quartz that is known to represent about 80 percents in mass of these soils was

not dominating the XRD signal, probably due to the much lower number of possible diffraction peaks in the angular domain of 3.5 to 33.4 in 2θ (Table 1) and the difficulty in detecting the crystallite size of the quartz with the small size beam used for mapping with X-ray synchrotron as already observed by others (Stroh et al. [43], Siebecker et al. [42], Supplementary materials 2 and 3). Smectite is rarely detected without ambiguity, as expected for the matrix of this soil chosen to be depleted in smectite.

In the coating zones, the average XRD patterns show a comparable number of diffraction peaks to that observed for the matrix with the notable exception of R/T-1 (Table 1)

Fig. 7 Analysis of a dusty clay coating surrounding a pore from S/T: **a** micromorphology picture; **b** classification of the different considered zones (pore, coating, matrix) by image analysis; **c–i** maps of the probability of presence of the different minerals WPI of different minerals identified on **l**, the average XRD patterns for the different considered zones, with **c** feldspars; **d** quartz, **e** goethite; **f** maghemite; **g** kaolinite; **h** illite; **i** smectite. The green lines represent the borders between the different pedological features (pore, coating and matrix). Blue stands for the absence of the mineral when orange is its maximal probability of presence. Maps **j** and **k** are μ XRF maps for Fe and Zn, respectively

that is very thin with probably a small amount of matter on the section according to the optic microscopy observations (data not shown). As for the matrix, feldspars and kaolinite were systematically detected in the coatings, whereas goethite, illite and quartz are observed in most of them. Finally, smectite is rarely unambiguously detected (Table 1). No clear distinction is observed between the mineral composition

of the two types of coatings, while dusty coatings (DSB) were thought to be richer in grains (feldspars and quartz, Fedoroff and Courty [13], Jongmans et al. [20] and Kuhn et al. [21]). In addition, while it was expected to identify more clay minerals in coatings than in the matrix, this was not clearly observed (Table 1). These two surprising results may be due to changes in the relative abundance of the

Fig. 8 Analysis of a limpid clay coating surrounding a pore from R/T-3: **a** micromorphology picture; **b** classification of the different considered zones (pore, coating, matrix) by image analysis; **c–i** maps of the probability of presence of the different minerals identified on **l**, the average XRD patterns for the different considered zones, with **c** feldspars; **d** quartz; **e** goethite; **f** maghemite; **g** kaolinite; **h** illite; **i** smectite. The green lines represent the borders between the different pedological features (pores, coating and matrix). Blue stands for the absence of the mineral when orange is its maximal probability of presence. Maps **j** and **k** are μ XRF maps for Fe and Zn, respectively

mineral species but not in the presence/absence of specific minerals and possibly to imprecisions in the segmentation of images MUs. In the case of the laminated coating (HLB), only a few peaks were identified (Table 1 and Fig. 9j) despite the clear evidence of a large amount of matter on the considered zones of the thin sections (see Fig. 8a). The number of peaks associated with feldspars is, for example, close to those observed in pores and considerably lower than those of the soil matrix (Table 1), suggesting that the diversity and

very likely the abundance of feldspar are limited in the HLB. Quartz shows a similar behavior (Table 1). Contrastingly, peaks associated with clay minerals and more particularly with kaolinite are more systematically detected than in pores (Table 1). Smectite, that has been only very rarely detected, seems entering in the mineralogical composition of the AR/B HLB. These combined results suggest that HLB is very likely enriched in various clay minerals and impoverished in quartz and feldspar grains as expected. It is, however, clear that the

Fig. 9 Analysis of a laminated coating from AR/B: **a** micromorphology picture; **b** classification of the different considered zones (pore, coating, matrix) by image analysis; **c–i**: maps of the probability of presence of the different minerals identified on **l**, the average XRD patterns for the different considered zones, with **c** feldspars; **d** quartz; **e** goethite; **f** maghemite; **g** kaolinite; **h** illite; **i** smectite. The green lines represent the borders between the different pedological features (pores, coating and matrix). Blue stands for the absence of the mineral when orange is its maximal probability of presence. Maps **j** and **k** are μ XRF maps for Fe and Zn, respectively

total number of peaks detected in the HLB remains surprisingly low. This is interpreted as resulting from the marked orientation of the clay minerals in HLBs as deduced from its high level of birefringence (Fig. 9a). Therefore, due to their orientated nature, it seems very difficult to characterize with certainty the nature of the clay minerals contained in HLBs, while the same minerals being randomly orientated when present in the matrix may be identified with the same technique [23, 41, 44, 49, 53].

3.3 Spatial distribution of the XRD pattern in the different soil microscopic unit (MU) of the three studied zones

The μ XRD maps confirm reasonably well the analysis obtained from the different MU average XRD patterns:

the pore, the matrix and the coatings (Figs. 7, 8 and 9c–i). Pores are almost free of mineral (Figs. 7 and 8c–i) as already observed from average XRD patterns and in good coherence with the very low Fe and Zn concentrations (Figs. 7 and 8j and k) used here as geochemical tracers for iron oxides and for the clay minerals, respectively, as already demonstrated in comparable studies [6]. The matrix is characterized by the highest abundances in feldspar and quartz (Figs. 7, 8 and 9c and d) and by a patchy distribution of clay minerals like kaolinite and illite and of iron oxides, especially maghemite (Figs. 7, 8 and 9e–i). The coatings, unsurprisingly rich in clay minerals as suggested by high Zn concentrations (Figs. 7–8k), are characterized by (1) the presence of kaolinite, illite and of most of the detected smectite in the HLB (Figs. 7, 8 and 9g–i); (2) almost no feldspar nor quartz but in the dusty coating (DSB) or at the borders of the limp

Table 1 Number of peaks observed experimentally for each mineral on all the studied thin sections in the angular domain 3.5–33.4 degrees in 2θ ($\lambda = 0.72 \text{ \AA}$) and number of peaks observed experimentally for each mineral for the different zones

Feature type	Studied zone	Kaolinite	Goethite	Illite	Feldspars	Quartz	Smectite	Tot. no. of obs. peaks
No. of peaks observed exp.	All	52 (30)	14 (7)	17 (11)	150 (119)	12 (7)	6 (1)	
Limpid coating	R/T-1	1 (0)	0	0	7 (0)	0	0	7
	R/T-2	16 (9)	2 (0)	4 (2)	22 (15)	7 (5)	0	42
	R/T-3	3 (3)	1 (1)	1 (0)	15 (12)	3 (3)	0	22
	S/B	7 (4)	3 (1)	9 (7)	30 (23)	3 (3)	3 (1)	30
Laminated coating	AR/B	3 (2)	1 (0)	2 (1)	8 (8)	1 (1)	1 (0)	14
	P/B	5 (2)	0	0	7 (4)	0	0	9
Dusty coating	AR/T	6 (5)	3 (2)	0	11 (11)	1 (1)	1 (0)	22
	P/T	10 (4)	2 (1)	3 (2)	23 (18)	2 (2)	1 (0)	31
	S/T	11 (7)	2 (1)	2 (1)	18 (13)	1 (1)	2 (0)	31
Matrix	AR/B	8 (3)	3 (1)	0	15 (13)	3 (3)	0	30
	AR/T	10 (8)	3 (2)	0	14 (12)	4 (4)	1 (0)	30
	P/B	9 (5)	1 (1)	1 (1)	12 (8)	1 (1)	0	20
	P/T	5 (2)	3 (2)	1 (1)	30 (28)	3 (3)	0	41
	R/T-1	8 (3)	2 (0)	2 (0)	29 (21)	4 (3)	0	36
	R/T-3	6 (3)	2 (0)	3 (3)	18 (17)	2 (2)	0	31
	S/B	10 (7)	4 (1)	1 (1)	35 (28)	4 (3)	1 (0)	53
	S/T	6 (2)	4 (3)	3 (1)	20 (13)	2 (2)	3 (1)	33
	P/T	0	0	1 (1)	8 (8)	2 (2)	0	11
	R/T-1	0	0	0	4 (2)	0	0	4
Pore	R/T-2	2 (2)	2 (1)	3 (2)	3 (2)	1 (0)	0	9
	R/T-3	0	0	0	3 (3)	0	0	3
	S/B	3 (2)	1 (0)	1 (1)	5 (4)	2 (1)	0	11
	S/T	1 (1)	0	0	1 (1)	0	0	4

Under bracket, the number of peaks experimentally detected and not shared among several minerals (called thereafter exclusive peaks)

(LB) and the HLB coatings (Figs. 7, 8 and 9c and d) and (3) few goethite and almost no maghemite (Figs. 7, 8 and 9e, f) despite very high Fe contents (Fig. 7, 8 and 9j). The DSB is characterized by the identification of quartz and feldspars grains, which is in good agreement with microscopic observations made for this type of coatings (see Sect. 2.2) and with their conditions of formation [13, 20, 21]. Smectite is in addition more frequently detected in this coating than in LBs (Figs. 7 and 8i). Since DSBs are supposed to develop after rains on bare soils [13, 20, 21], which correspond to the conditions of the rain experiment performed, and since this coating contains smectite that is absent from the surrounding matrix, it could have been formed by eluviation of material coming from the upper core that contains smectite during the rain experiment. More systematic analysis of this type of coating should be performed in order to definitely conclude on that point. Finally, the ability of μ XRD to detect clay minerals in clay coatings decreases from DSBs to LBs and finally to HLBs despite similarly high Zn contents (Figs. 7, 8 and 9k). It is very likely related to an increasing orientation of clay particles as shown by increasing birefringence

and resulting from conditions of formation characterized by slower water flows. the μ XRD maps were relatively successful in identifying changes in the mineralogical composition not only between the soil matrix and soil features like but also between DSB and LB coatings. On the contrary, only few Fe-bearing minerals were identified in the different clay coatings despite homogeneously high Fe concentrations in clay coatings and despite the identification of patches of goethite or maghemite in the soil matrix for lower Fe concentrations (Figs. 7, 8 and 9j). This apparent contradiction results from the fact that in this type of soil, a large part of Fe is mainly present as poorly crystalline oxides as shown by sequential extractions by Montagne et al. [31] and that maghemite is more of an inherited mineral present in parent loess material and thus in the matrix.

4 Conclusion

Synchrotron μ XRD on thin sections of soils resulted in mineralogical maps of high complexity due to the small size of the analyzed pixel compared to the size of the mineral grains and the orientated nature of the clay coatings that partially extinguish the diffraction peaks of the clay minerals. It leads to the detection of a few diffraction peaks in the most favorable case. Despite this complexity, our approach, combining various signal processing methods (wavelets, quantile regression, smoothing splines, statistical inference), was shown to be efficient and robust enough to automatically identify and map minerals from synchrotron XRD large datasets obtained on naturally highly heterogeneous soil materials. Most of the minerals present in the considered samples could be identified, including clay minerals with the notable exception of smectite that was rarely identified with certainty. μ XRD mapping was found to be complimentary to average XRD patterns and particularly helpful to characterize changes in mineralogical assemblages. Although mostly qualitative, the approach proposed here successfully differentiated the mineralogical composition of the soil matrix from that of soil features like clay coatings. It results in one of the first characterization of the spatial variability of clay mineral assemblages in clay coatings. In the studied case, the clay coatings were found to contain not only smectite as generally hypothesized but also kaolinite and illite. It suggests that the clay translocation process, if selective of clay minerals species, is not selective enough to produce monospecific clay coatings. The development of quantitative approach thus seems necessary to definitively state on the potential clay mineral selectivity of the translocation process. The mineralogical composition of clay coatings was found to be sensitive to their conditions of formation as shown by dusty coatings richer in feldspar, in quartz or in smectite than the limpid ones.

Moreover, the recently available fast data acquisition schemes, yielding now large amounts of datasets (e.g., several $10^4 - 10^6$ diffractograms), require automatic methods dedicated to the automatic identification and mapping of minerals as the one developed in this study.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Appendices

Notations and special terms

In this part, $\#E$ will denote the number of elements of some finite set E . We will say that a matrix is of size $r \times c$ if it has r rows and c columns, and the Hadamard (i.e., elementwise) product of two vectors of dimension p will be denoted: $u \circ v := (u_1 v_1, \dots, u_p v_p)$. As usual, $\mathbb{N}$ will denote the set of positive integer numbers, $\mathbb{Q}$ the set of rational numbers and $\mathbb{R}$ the set of real numbers, and the logical connectors **and** (resp. **or**) will be denoted $\wedge$ (resp. $\vee$).

Appendix 1: Methodological test on the $< 2 \mu\text{m}$ fraction of the considered soil

The fraction $< 2 \mu\text{m}$ of the soil was analyzed in powder mode by synchrotron XRD in the same configuration than the studied thin section in order to test whether the mineral of interest, notably the clay minerals, could be detected in the configuration used. Two main differences with respect to the thin section analysis are to be noted: (a) longer XRD acquisition time (100 s) and (b) during the acquisition, the sample is continuously moved laterally in the Y- and Z-directions over a $\pm 500 \mu\text{m}$ range. As a consequence, more crystallites are potentially brought into diffraction condition, i.e., the sample resembles more to a random powder (i.e., with a sufficient statistic for all possible orientation that is not obtained at the pixel size even for $< 2 \mu\text{m}$ randomly orientated particles) (Fig. 10).

This explains the much more ring-like XRD features on the XPAD images (see e.g., Fig. 2). Clay mineral peaks are detected; however, the 001 peaks, traditionally used to identify clays, are very small despite their important concentration in this fraction. Quartz is also clearly detected

Fig. 10 Synchrotron XRD pattern of the $< 2 \mu\text{m}$ fraction (in powder) of the L2 core (acquisition time: 100 s)

despite its small amount in this $< 2 \mu\text{m}$ fraction. Small peaks of feldspars and goethite are also observed. This first analysis demonstrated the feasibility of our approach when randomly orientated particles are considered. In the case of thin sections, very few peaks are observed because of the discrete orientation of the crystals in the illuminated sample volume (their volume is comparable with the illuminated sample volume).

Appendix 2: Background removal in the case of the first angular domain

Because of the steepness of all these patterns near the origin (see Fig. 5), it was impossible to obtain a satisfying fit with median regression in a standard way. Since COBS (Ng and Maechler [35]) is very flexible, we could impose global shape conditions to $\hat{L}_i$ (associated with the i th pixel), as well as pointwise equality constraints: The solution must run through a local maximum of the diffractogram (among its 10 first values) and must have a “right” slope at the midpoint angle. More precisely, we considered the beginning $\mathcal{D}_{\text{beg}} := \{(a_1, d_1), \dots, (a_{81}, d_{81})\}$ of the diffractogram and determined the angle a_{Max} such that $d_{\text{Max}} = \max_{1 \leq i \leq 10} d_i$. We first imposed to the output L of COBS the interpolation constraint:

$$L(a_{\text{Max}}) = d_{\text{Max}}. \quad (3)$$

Then, we considered the midpoint angle a_{41} of $\mathcal{D}_{\text{beg}}$ and the nonlinear fit of $\mathcal{D}_{\text{beg}}$ by

$$f(a; \lambda, \alpha, \beta, \gamma) := e^{-\lambda a} (\gamma + \alpha a + \beta a^2)$$

obtained for some optimal vector $(\tilde{\lambda}, \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})$. We then imposed to L , in addition to constraint (3), the slope constraint:

$$\frac{d}{da} L(a_{41}) = \frac{d}{da} f(a_{41}; \tilde{\lambda}, \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}). \quad (4)$$

Appendix 3: Estimation of σ

We drew from each zone a random sample of N pixel positions (we fixed $N \approx 1/16$ of the zone size) and obtained the required estimate of σ thanks to the following algorithm:

1. perform stationary wavelet denoising [24, Sect. 10.2.3] on each detrended signal $\mathcal{D}_i$:

$$\mathcal{D}_i \mapsto \mathcal{D}_i - \hat{\varepsilon}_i$$

- (the *SureShrink* procedure of [11] was used), and obtain the **local** estimate $\hat{\sigma}(\hat{\varepsilon}_i)$ of the SD
2. check the normality of the residual series $\hat{\varepsilon}_i$
3. robustly estimate the SD by the trimmed mean of order 0.25 of the local estimates $\{\hat{\sigma}(\hat{\varepsilon}_1), \dots, \hat{\sigma}(\hat{\varepsilon}_N)\}$; in addition, verify that the trimmed mean of order 0.25 of the local estimates of the mean, $\{\hat{\mu}(\hat{\varepsilon}_1), \dots, \hat{\mu}(\hat{\varepsilon}_N)\}$, is close to zero.

A typical illustration of the normality of residuals is shown in Fig. 3.

Appendix 4: Stochastic binarization of detrended patterns

Remember first the well-known Bienaymé–Tchebychev theorem Renyi [38].

Theorem 1 (Bienaymé–Tchebychev inequality) *Let D be a random variable with mean μ and finite standard deviation $\sigma > 0$ and $r > 1$. Then,*

$$P(|D - \mu| > r\sigma) < 1/r^2.$$

The three-sigma rule [37] came up from a kin inequality, suited for unimodal distributions and proved by Gauss.

Theorem 2 (Gauss inequality) *Let D be an absolutely continuous random variable with mode ν and $\tau := \sqrt{E((D - \nu)^2)}$. Then*

$$P(|D - \nu| > r) \leq \begin{cases} \frac{4\tau^2}{9r^2} & \text{if } r \geq \tau \sqrt{4/3} \\ 1 - \frac{r}{\tau\sqrt{3}} & \text{if } r \leq \tau \sqrt{4/3} \end{cases}. \quad (5)$$

If D is a symmetric distribution, we obtain this way $P(|D - \mu| > 3\sigma) \leq 4/81 \approx 0.05$: this is the three-sigma rule, attached to the usual excess probability 0.05. Notice that in this case the Bienaymé–Tchebychev inequality only tells us that $P(|D - \mu| > 3\sigma) < 1/9$: This is approximately twice the excess probability given by the Gauss inequality, which is consequently more accurate than the Bienaymé–Tchebychev one.

Remark 3 Of course, the accuracy is even better in the parametric setting: Suppose $D \sim \mathcal{N}(0, \sigma)$. Then, $P(|D| > 2\sigma) \approx 0.0455$, $P(|D| > 3\sigma) \approx 0.003$ and $P(|D| > 4\sigma) \approx 6.33 \cdot 10^{-5}$.

Consider now a detrended diffractogram $\mathcal{D} = \{(a_1, d_1), \dots, (a_J, d_J)\}$, where $J \in \{648, 624, 528\}$ is the length of the series and a_j is an angle. The second coordinate d_j is a realization of some random variable

$D(a_j)$; if a_j corresponds indeed to pure noise, we may agree (see Sect. 1) that $D(a_j)$ is centered Gaussian, while in other cases (when a_j is associated with some genuine signal) $D(a_j)$ should obey an entirely different distribution. Thus, we naturally postulated that D was a contaminated centered Gaussian distribution (that's the rationale of trimmed estimations in Sect. 1). We only supposed D is symmetric and unimodal, with zero as mode; in this case, $|D|$ can be controlled by Formula (5). Suppose now a risk η_0 has been fixed; thanks to inequality (5), we can associate with $\mathcal{D}$ the **binarized diffractogram** $\mathcal{B} := \{(a_1, b_1), \dots, (a_J, b_J)\}$ defined by:

$$b_j = \begin{cases} 0 & \text{if } (d_j \leq 0) \vee P(|D| > d_j) > \eta_0 \\ 1 & \text{if } (d_j > 0) \wedge P(|D| > d_j) \leq \eta_0 \end{cases} \quad (6)$$

In other words, $b_j = 1$ only if d_j is big enough. We fixed $\eta_0 = 0.0026998$, corresponding to the probability of deviation from the mean $> 3\sigma$ in the Gaussian case.

Appendix 5: The generating family $\mathcal{T}$ of intervals, the associated tables and presence indicators

To each mineral of interest s was associated a whole original family $\{I_k^s : 1 \leq k \leq N^s\}$ of not necessarily disjointed intervals (resulting from expert knowledge) such that the angles associated with s belong to $E^s := \bigcup_{k=1}^{N^s} I_k^s$. Roughly speaking, each binarized diffractogram $\mathcal{B}$ of length J^m (associated with the m th angular domain) defined in the previous subsection would give rise to S binary vectors, such that the one corresponding to s is $B^s = \{b_1^s, \dots, b_{J^m}^s\}$, where $b_j^s = b_j$ if $a_j \in E^s$ and $b_j^s = 0$ if $a_j \notin E^s$. Thus, B^s measures the similarities between $\mathcal{B}$ and the "signature" E^s of the mineral s . But two problems are met:

- **Redundancy** Because of the definition of the original intervals it is possible that for some j , $a_j \in I_k^s \cap I_{k+1}^s$; consequently, a single angle can "switch on" two intervals associated with a single s
- **Ambiguity** By construction, it is possible that $I_k^s \cap I_p^r \neq \emptyset$, or even $(I_k^s \cap I_{k+1}^s) \cap (I_p^r \cap I_{p+1}^r) \neq \emptyset$; consequently, a single angle can also switch on two (or more) intervals associated with different minerals.

Of course, these facts are not mutually exclusive. To control these problems, we built from the complete family of

intervals $\{I_k^s, 1 \leq k \leq N^s, 1 \leq s \leq S\}$ another family, $\mathcal{T}_0$, of finer **disjoint generating** intervals, such that

$$\forall s, \forall k \quad I_k^s = \coprod_{p \in P(s,k)} T_p$$

(disjoint union), where $P(s,k)$ denotes the set of indices associated with the k th original interval and the mineral s . We discarded afterward from $\mathcal{T}_0$ (538 intervals) all its "negligible" members, of width less than 0.02 degrees (angular resolution of the data), obtaining a family $\mathcal{T}$ of 442 disjoint intervals. Within this system, the redundancy phenomenon is eliminated, contrary to the ambiguity one. Nevertheless, notice that now an angle cannot switch on more than S intervals of $\mathcal{T}$.

Appendix 5.1: The intervals of $\mathcal{T}$: their exclusiveness and exclusiveness

Consider again all the angles associated with the mineral s ; they belong to $E^s = \bigcup_{k=1}^{N^s} I_k^s = \coprod_{p \in P(s)} T_p$, where $P(s)$ denotes the set of indices of members of $\mathcal{T}$ associated with s . We can thus represent some mineral s by its **binary reference spectrum** $\pi_s = (\pi_s^1, \dots, \pi_s^{442})$, where

$$\pi_s^k = \begin{cases} 1 & \text{if } k \in P(s) \\ 0 & \text{if } k \notin P(s) \end{cases}$$

and now, all the minerals are described in the common system $\mathcal{T}$! Let us now build from these binary spectra the matrix $\Pi := (\pi_1, \dots, \pi_S)$ of size $442 \times S$, where S is the number of minerals of interest. Notice that Π only depends on the experimental apparatus and that $\mu := \Pi \cdot \mathbf{1}^S \in \mathbb{N}^{442}$ gives the number of minerals associated with each interval, its **multiplicity**. The multiplicity of the 442 members of $\mathcal{T}$ is displayed in Fig. 11. It can reach 4, while there are a number of intervals of multiplicity 1, which are really exclusive of some mineral. That is why we will define the **exclusiveness** of each interval by the inverse of its multiplicity, giving rise to the positive rational vector $\Omega := \left(\frac{1}{\mu(1)}, \dots, \frac{1}{\mu(442)}\right)$.

Appendix 5.2: The operator Λ^m associating $\mathcal{T}$ with angles of the m th angular domain

Consider now the vector $A^m := (a_1^m, \dots, a_{\#T}^m)$, of length $\#T = 442$, of angles associated with this angular domain. Like Π , it is totally independent of the data, as well as the operator Λ^m of dimensions $J^m \times 442$ whose j th row is the binary vector assigning to the sampled angle a_j^m the

Fig. 11 The multiplicity μ of the members $\{T_1, \dots, T_k, \dots, T_{442}\}$ of $\mathcal{T}$

unique index $p(m, j) \leq \#\mathcal{T}$ such that $a_j^m \in T_{p(m, j)}$. We displayed in Fig. 12 the operator Λ^1 associated with the first angular domain. Notice the vertical patterns on this figure, which correspond to sequences of sampled angles belonging to a common interval of $\mathcal{T}$.

Consider finally some vector B^i of binarized responses in the angular domain m (issued from the processing of some pixel, described in Sect. 1), of length J^m . We will associate with B^i the vector of the spectra space $\Lambda^m(B^i) \in \mathbb{N}^{442}$ given by the matrix product $\Lambda^m(B^i) := B^i \cdot \Lambda^m$.

Appendix 5.3: The presence indicators associated with minerals

The binarization procedure detailed in Sect. 1 gives rise, for each pixel and the m th angular domain (with J^m angles), to some **detrended binary signal** $B^m := \{(a_1^m, b_1^m), \dots, (a_{J^m}^m, b_{J^m}^m)\}$. We then translate B^m into the $\mathcal{T}$ language, in order to evaluate the **possibility of presence** of each mineral at each pixel. Notice that the vector of first coordinates of B^m (angles), denoted A^m , only depends on the protocol, while the vector of second coordinates, B^m , actually depends on the data. The operator $\Lambda^m \in J^m \times 442$ defined in Sect. 2 associates with B^m the vector $\Lambda^m(B^m) := B^m \cdot \Lambda^m \in \mathbb{N}^{\#\mathcal{T}} = \mathbb{N}^{442}$ whose p th coordinate is the count of all the **significant angles** (i.e., a_j^m such that $b_j^m = 1$) of the detrended pattern which belong to the interval $T_p \in \mathcal{T}$. (The dot denotes the scalar product in the spectra space $\mathbb{R}^{\#\mathcal{T}} = \mathbb{R}^{442}$.)

Balancing the information bore by intervals of $\mathcal{T}$

Since some XRD peaks may be associated to several minerals while other may be exclusive of a single mineral, a

ponderation was applied to give more weight to exclusive peaks than to peaks shared by several minerals. We defined an indicator assigning to each peak a weight decreasing with the number of minerals that shares it. Consider some mineral species s , whose **binary reference spectrum** is π_s , and the vector of **exclusiveness** Ω defined too in Sect. 1; both these vectors belong to $\mathbb{Q}^{\#\mathcal{T}} = \mathbb{Q}^{442}$. While the “raw weight” of s is naturally $\bar{\pi}_s := \sum_{j=1}^{\#\mathcal{T}} \pi_s(j)$, we will define similarly its “exclusive weight” by $\omega_s := \sum_{j=1}^{\#\mathcal{T}} (\Omega \circ \pi_s)(j)$; of course, $\omega_s \leq \bar{\pi}_s$. Notice that these weights only depend on the matrices Π (defined in Sect. 1) and $\{\Lambda^m, 1 \leq m \leq 3\}$ (defined in Sect. 2), which are associated with the experimental setting, not with data.

Presence indices

Definition 3 Considering the i th “pixel” of a zone, we associate with the corresponding position (x_i, y_i) the **Presence Index** of the mineral s at this position:

$$\text{PI}(s; x_i, y_i) := \frac{1}{\bar{\pi}_s} \pi_s \cdot \Lambda^*(B^*)(x_i, y_i) \in \mathbb{Q} \quad (7)$$

where $\Lambda^*(B^*)(x_i, y_i) := \sum_{m=1}^3 \Lambda^m(B^m(x_i, y_i)) \in \mathbb{N}^{442}$.

Definition 4 Consider the i th pixel of a zone and the vector of exclusiveness Ω . We associate with its position the **Weighted Presence Index** of s :

$$\text{WPI}(s; x_i, y_i) := \frac{1}{\omega_s} (\Omega \circ \pi_s) \cdot (\Omega \circ \Lambda^*(B^*)(x_i, y_i)) \in \mathbb{Q} \quad (8)$$

with the same conventions as in Definition 3.

Fig. 12 The operator Λ^1 ; vertical patterns correspond to sampled angles belonging to a common interval of $\mathcal{I}$ (the arrows mark such cases)

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