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Combined X-ray microanalytical study of the Nd uptake capability of argillaceous rocks

Annamária Kéri^{1*}, János Osán¹, Margit Fábíán¹, Rainer Dähn², Szabina Török¹

¹Hungarian Academy of Sciences, Centre for Energy Research, P.O. Box 49, H-1525 Budapest, Hungary

²Laboratory for Waste Management, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

*Corresponding author. E-mail: keri.annamaria@energia.mta.hu

Abstract

Argillaceous rocks are considered as suitable host rock formation to isolate the high-level radioactive waste (HLW) from the biosphere for thousands of years. Boda Claystone Formation, the possible host rock formation for the Hungarian HLW repository, has geologically and mineralogically been studied in detail, but its physico-chemical parameters describing the retention capability of the rock needed further examinations. Studies were performed on thin sections subjected to 72-hour sorption experiments using inactive Nd(III). Nd(III) has been used as a chemical analogue for transuranium elements of the radioactive waste to examine the ion uptake capability of the micrometre size mineral phases occurring in the rock. The elemental mapping of synchrotron radiation based microscopic X-ray fluorescence (micro-XRF) combined with scanning electron microscopy energy dispersive X-ray analysis (SEM/EDX) has sufficient sensitivity to study the uptake capability of the different mineral phases on the microscale without the necessity of applying radioactive substances. Elemental maps were recorded on several thousand pixels using μm magnitude spatial resolution. By interleaving micro-XRF and SEM/EDX data sets from the same sample area and applying multivariate methods, calcite and clay minerals could be identified as main mineral phases responsible for Nd(III) uptake without using additional microscopic X-ray diffraction (micro-XRD) mapping. It should be highlighted that the ion uptake capability of dolomite containing calcium and magnesium could be distinguished from the characteristics of calcite only by the interleaving of micro-XRF and SEM/EDX data sets. The presence of minerals was verified by applying micro-XRD point measurements.

Keywords: microscopic X-ray fluorescence (micro-XRF); scanning electron microscopy energy dispersive X-ray analysis (SEM/EDX); microscopic X-ray diffraction (micro-XRD); positive matrix factorization (PMF); cluster analysis (CA); argillaceous rock; sorption; radioactive waste

1. Introduction

In Hungary, deep geological disposal was found to be the most suitable placement for high level radioactive waste (HLW) that is consistent with the international recommendations [1]. The storage site can be placed into several different formations of mineralogical origin (crystalline, clay and salt rock) [2]. In most of the radioactive waste management research programs, clay formations were found to be suitable for high level radioactive waste storage [3,4,5]. It is known that argillaceous rocks have several suitable properties of which the most advantageous are the homogeneity, the chemical buffering capacity, the low groundwater flow, the self-healing capability by crack swelling and the radionuclide retardation related to sorption [3,4]. The main goal of these experiments is to determine the partition coefficient (R_d) between the mobile (dissolved in water) and the sedentary (solid) phase [4,6,7,8]. These bulk experiments are necessary but inadequate to describe the sorption process in detail, thus sorption experiments involving thin sections and microscopic studies are needed.

In microscopic studies, the samples are treated with different solutions containing key radionuclides in order to study the sorption capability of the different mineral phases present in the rock. The key radionuclides, represent transuranium elements, fission and corrosion products, are not present in the rock. They can be substituted with their inactive or natural analogues without requiring high activity radioisotopes. The chemical conditions present at the depth of the planned repository as the concentrations of the elements of interest in the solutions involved should be sufficiently low in order to avoid precipitation. Therefore, the element of interest will be present in minor or trace concentration level heterogeneously distributed in the sample after the sorption experiment [9,10]. Nd(III) was used as a chemical analogue for trivalent transuranium elements of the radioactive waste to examine the ion uptake capability of the micrometre size mineral phases occurring in the rock.

Petrographic thin sections are prepared from the geological samples. After treatment, these highly heterogeneous samples are most often studied with microscopy techniques [11]. Microscopic X-ray fluorescence (micro-XRF) spectroscopy is a suitable tool to detect simultaneously the distribution of the sorbed elements and the main elements corresponding to the rock-forming minerals [12]. Although, it has several advantageous properties, micro-

XRF performed in air is not capable to detect major light elements (e.g. Na, Mg), therefore it is inadequate to ascertain mineral phases containing elements only with low atomic number (e.g. dolomite, albite) [9,12]. The missing additional information can be obtained with the elemental mapping of the same sample area using micro-XRF in vacuum mode or with a helium flush around the sample to avoid its damage. However, in order to excite the major light elements effectively, a modified setup employing a lower excitation energy is necessary. Another measurement technique that can be applied, is scanning electron microscopy energy dispersive X-ray analysis (SEM/EDX) employing a laboratory-size equipment. SEM/EDX is a well suited measurement technique for detecting the major elements of mineral phases but it is inappropriate to detect the elements representing key radionuclides because of their usually high atomic numbers and low concentrations.

Although, the differently measured data sets can be treated individually, more accurate information can be obtained if the data sets of different measurements are combined [13,14]. The interleaving of existing data sets of light element concentrations determined from SEM/EDX measurements as well as minor and trace element concentrations obtained from micro-XRF can be applied for this purpose.

Multivariate methods such as factor analysis (FA) and positive matrix factorization (PMF) are used to handle large data matrices. Although, the result of FA is explicit, the expression of factors in the original variables (factor loadings) can contain negative values expressing anticorrelation with original variables (concentrations of chemical elements) [15]. This problem can be overcome by application of PMF, commonly used in air pollution studies, where the factors should contain only non-negative values [16,17]. PMF was successfully applied to process three-dimensional data sets answering questions related to other topics [9,18]. However, no applications of PMF on combined micro-XRF and SEM/EDX data sets have been reported to date. Segmentation of the data set can be performed using cluster analysis based on the similarity (distance) of the pixels in the abstract space defined by elemental concentrations. The most commonly used method is the non-hierarchical K-means clustering algorithm [19,20,21].

The aim of the present study was to obtain quantitative information on the sorption capacity of the mineral phases responsible for the uptake of Nd(III). Due to the heterogeneity of the rock, microscopic studies (micro-XRF and SEM/EDX measurements) were necessary on the representative geological samples. Multivariate methods were applied on the interleaved data set to handle the large data matrix. Microscopic X-ray fluorescence spectroscopy combined

with microscopic X-ray diffraction [12,22] was applied at selected representative positions to verify the results.

2. Materials and methods

2.1. Samples

The petrographic thin sections were prepared from geochemically characterized cores from drillings of Boda Claystone Formation (BCF). The Upper Permian sedimentary sequence of the BCF, which is the possible formation for HLW repository in Hungary, is located in Western Mecsek Mountains, SW Hungary. The sediments of the BCF are dominantly red and reddish brown in colour reflecting the oxidizing nature of the depositional and early diagenetic environments. BCF was deposited in a shallow-water salt lake environment surrounded by dry to saline mudflat, under semi-arid to arid climatic conditions [1,23,24]. Two distribution areas of BCF are known in West-Mecsek Mountains: the perianticlinal structure of the West-Mecsek Anticline (WMA) Block and the Gorica (G) Block [25].

The rocks are highly heterogeneous on the microscale, two major regions can be distinguished, the clayey matrix and the fracture infillings. The clayey matrix is formed by high amount of clay minerals (around 50 m/m% illite, chlorite, kaolinite and mixed structure clay minerals) as well as albite cement (and analcime cement for G Block) [23,24,25]. The most important clay mineral is illite containing potassium and iron. Nanometre size hematite crystals are wedged between the illite plates [26]. The fracture infillings consist of mostly authigenic albite (or analcime for G Block), carbonate minerals (calcite and dolomite) and authigenic potassium feldspar. The absolute dominant rock type of the formation is albitic claystone in the WMA Block and albite- and analcime-bearing claystone in the G Block [25]. In previous studies, the differences in the ion uptake of G Block and WMA Block have been examined [24,25,26]. The results pointed out that only in WMA Block a new mineral phase was formed with high ion binding capability for the case of uranium and neodymium treated samples [9]. Therefore hereinafter only samples from WMA Block will be discussed [9].

Small pieces of the selected core samples were ground and mounted onto 350 µm thick high purity silicon wafers and polished by 0.25 µm diamond paste. The samples were reacted for 72 hours with Nd(III) in porewater and a 0.1 M NaCl solution as background electrolyte. The ionic strength of this latter solution was similar to the porewater while the pH was set to 7.0 to avoid precipitation of Nd phases. Hereinafter only samples treated with NaCl solution will be discussed, because this electrolyte ensured a sufficient loading of the element of interest to

match the sensitivity of micro-XRF while avoiding precipitation in the solution itself [9]. The concentrations of the key element to be applied for the sorption experiments based on the sorption isotherms measured and modelled for Eu(III) on illite taking into account the clay content of the BCF samples (around 40%) as well as the solid-to-liquid ratio [7]. The applied Nd(III) initial concentrations were $3.6 \times 10^{-6} - 3.6 \times 10^{-5}$ M, resulting in equilibrium concentrations of $10^{-6} - 10^{-5}$ M [7].

2.2. SEM/EDX and micro-XRF measurements

A JEOL JSM-5600LV scanning electron microscope (SEM) equipped with an Oxford Si(Li) energy dispersive detector with atmospheric thin window was employed for the SEM/EDX measurements. The system allowed the detection of light elements down to carbon. A 25 kV accelerating voltage and a 1 nA beam current was used for the measurements. Although, the SEM was operated in high-vacuum mode, no conductive coating was necessary for the examinations. Elemental maps of 128×95 pixels were collected with a resolution of $4.5 \times 4.8 \mu\text{m}^2$. In order to decrease sample damage due to the electron beam, the area was scanned ten times with a 150 ms dwell time at each position.

Since all major elements except hydrogen could be detected using the SEM/EDX method, the concentrations of major elements were determined for each pixel of the elemental maps using a standardless iterative method based on Monte Carlo simulations for electrons [27].

The micro-XRF experiments were performed at the FLUO beamline of ANKA. The white beam of a bending magnet was monochromatized by a W/Si multilayer double monochromator (energy resolution $\Delta E/E = 10^{-2}$). Because of the high iron content of the rock sections, micro-XRF elemental mapping was performed at an energy of 7.1 keV below the Fe-K α absorption edge. A Fresnel zone plate was used as focusing element, providing a $3 \times 8 \mu\text{m}^2$ spot size. A silicon-drift detector was applied to collect fluorescence spectra. Characteristic X-ray intensity maps were recorded for the adsorbed element (Nd-L α) as well as for the major and minor elements of the rock (e.g. K-K α , Ca-K α , Mn-K α) using a $5 \mu\text{m}$ step size and 4–10 s counting time per pixel [9]. The net characteristic X-ray intensities were determined by processing the full X-ray spectra collected at each pixel using the AXIL software [28].

2.3. Interleaving of micro-XRF and SEM/EDX data sets

First, the interleaving of micro-XRF and SEM/EDX data sets was prepared for the further evaluation. Potassium and calcium micro-XRF as well as SEM/EDX elemental maps had sufficiently good statistics for the basis of the interleaving. The micro-XRF and SEM/EDX measurements were not carried out at the same time, therefore small deviation could be seen on the elemental maps representing the distribution of the same element. The obvious differences were corrected comparing the potassium and the calcium elemental maps measured by micro-XRF and SEM/EDX, respectively. The relatively rotated and/or slipped maps were combined taking into account only the overlapping area after the rotation and shift. The two measurement methods had different lateral distribution, therefore the better one was resized with interpolation. This resulted that the corresponding pixels on the elemental maps indicated the same area on the sample (Figure 1).

Afterwards the minor and trace elemental concentrations were calculated for each pixel in the interleaved data set based on the micro-XRF net characteristic X-ray intensities. Standardless fundamental parameter method [29] was used for the calculations, which takes into account the absorption of the exciting X-ray beam, the production of fluorescence in the sample and the absorption of the outgoing fluorescence X-rays as they propagate towards the detector. This mathematical method requires an accurate energy spectrum of the exciting radiation and geometric factors in order to reach reliable quantification. Since monochromatic excitation was applied, the geometric factors, the XRF production cross sections and the detector efficiency could be canceled out through the measurement of a standard reference material (NIST SRM 613) [30, 31]. The method also requires a relevant estimation of the composition of elements without a detectable characteristic X-ray line in the measured spectra (the so-called dark matrix). The X-ray spectra recorded in air and 7.1 keV excitation energy do not contain information about elements with lower atomic number than that of silicon. Therefore, the composition of the dark matrix was obtained from the SEM/EDX measurements. The thickness of the sample was 50 μm and the average density of the rock was 2.7 g/cm^3 . Higher order interactions were not considered for the calculations.

Figure 1. Potassium (a and b) and calcium (c and d) elemental concentration maps from an area of $0.3 \times 0.27 \text{ mm}^2$ on a thin section measured by scanning electron microscopy energy dispersive X-ray analysis (a and c) and microscopic X-ray fluorescence (b and d). The elemental maps are presented as max–min normalized, where black representing the minimum and white the maximum intensity.

2.4. Micro-XRD measurements

The micro-XRD experiments were performed at the FLUO beamline of ANKA. At several selected positions of interest, micro-XRD images were collected by a 130 mm diameter CCD detector using a modified setup applying a 17.5 keV excitation energy. In this case, a compound refractive lens was used as focusing element, providing a $2 \times 5 \text{ }\mu\text{m}^2$ spot size. The calibration for the micro-XRD measurements was performed by measuring of standards (corundum, silicon, PbCO_3 . $\text{Pb}(\text{OH})_2$). The beam position on the XRD images was determined using the XRDUA software [32]. The least distorted circular rings were obtained using the parameters of -5° tilt and 25° rotation. XDB software [33,34], which allows full interpretation of a sample diffractogram and helps generate initial concentrations of identified minerals

based on a standardless approach, was applied for the phase identification and quantification. Due to the increased width of reflection lines as a result of the low energy resolution of the multilayer monochromator and the existence of large crystallites compared to the beam size, only semi-quantitative information could be obtained on the mineral phases. XDB software helped to refine the final phase composition applying the mass balance procedure. After the phase identification, the quantitative phase composition was calculated based on the reference intensity method. The phase proportions were derived from the weight parameters of the profile fit corrected with their respective reference intensity – I/I_c – coefficient. The calculated phase proportions, depended on the particle size of the components and the absolute amounts (phase percentages), are normalized to the sum of the phases, while the reliability of the results greatly depended on the distribution of the intensities to the identified phases.

2.5. Multivariate methods

Multivariate data analyses are usually used in environmental chemistry to handle large scale data matrices. The aim of their application in this study was to obtain new information from the estimation of the number and composition of factors (latent variables) describing the original data set. For this, factor analysis (FA), positive matrix factorization (PMF) and cluster analysis (CA) were found to be the most suitable methods. As these mathematical methods can treat only 2D matrices (variables–observations), the 2D elemental maps for each element (variable) were unfolded into 1D vectors. The resulting factor or cluster maps were created after refolding the resulting data into 2D matrices.

Standard FA employing varimax rotation was performed using the IDAS software package [35]. The number of factors present in the data set was determined using the 95% limit of the explained variance. The concentration values were scaled using autoscaling (Equation 1) in order to take the variables into consideration with similar weights but assigning higher weight to data with smaller statistical error [36].

$$z_{ij} = \frac{x_{ij} - \bar{x}_j}{s_j} z_{ij} = \frac{z_{ij} - \bar{z}_j}{s_j} z_{ij} = \frac{x_{ij} - \bar{x}_j}{s_j} \sum_{i=1}^m \sum_{j=1}^n \left(\mathbf{X}_{ij} - \mathbf{X}_{ij}^{(h)} \right)^2 \mathbf{X}^{(h)} = \sum_{k=1}^h \mathbf{u}_k \mathbf{s}_k \mathbf{v}_k^T \quad (1)$$

where $\bar{x}_j$ is the average of the measurement results connected to the given variable j and s_j is the corresponding standard deviation.

PMF decomposes the data matrix into two non-negative matrices in the following way:

$$e_{ij} = x_{ij} - \sum_{k=1}^p g_{ik} f_{kj} \quad e_{ij} = x_{ij} - \sum_{k=1}^p g_{ik} f_{kj} \quad X = GF + EX = GF + E = GTT^{-1}F + E = \bar{G}\bar{F} + EX \approx GFX^{(h)} = \sum_{k=1}^h u_k s_k v_k^T \quad (2)$$

where e_{ij} is the element of the residual matrix, x_{ij} is the element of the input data matrix at sampling point i and variable j , g_{ik} and f_{kj} are the elements of the left and right factor matrices and p is the number of factors [37].

The objective function should be minimized based on Equation 3 retaining the elements of the factor matrices positive to obtain the best PMF decomposition.

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{\sigma_{ij}} \right)^2 \quad Q = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{\sigma_{ij}} \right)^2 \quad Q(E) = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{E_{ij}}{\sigma_{ij}} \right)^2 \quad (3)$$

where σ_{ij} is the uncertainty of each data point and variable [37].

In the weighting of the data matrix, the uncertainty of the data points is also utilised allowing the separate treatment of the matrix elements (Equation 3). As a consequence values measured under the detection limit can also be taken into the data set avoiding data loss. In this work the EPA PMF 3.0 software package was used to perform calculations on the interleaved data set. The PMF problem is solved by using multistage iteration method starting from pseudorandom initial values. The number of runs and factors had to be given as input parameters which were assumed from FA results of the same set of elemental maps. Elements could be categorized in three different groups based on the signal/noise ratio of their concentrations. Elements with high signal-to-noise ratio were categorized as “strong” including every element that could possibly be a component of the mineral phases occurring in the sample (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe), as well as the element added in the sorption experiment (Nd). Elements with small intensities and high uncertainties (e.g. Ba) were in the group of “weak”. Oxygen was also classified to this group not to create a separate factor. The output factor profiles were calculated by the software considering that the average factor contribution is equal to unity. The output factor profiles were normalized to their maximum because in the present case the factor contribution cannot be higher than one at each measured pixel.

Non-hierarchic CA is generally applied for data matrices containing numerous measurement points [38]. In this work the k -means algorithm was used that classifies every object (measurement point) to a cluster whose centroid is the closest to the given object. CA was performed using the built-in routine of PAST software [39].

3. Results and Discussion

3.1. Elemental concentration maps

The elemental concentration maps (Figure 2) themselves already bear information on the distribution of minerals on the microscale, based on the mineral phase composition of the corresponding crushed bulk sample determined by powder XRD [9,26]. The regions where K and Fe were present together, were considered as clayey matrix. This mineral aggregation contains phyllosilicates (mainly illite with 6% K, 1.5% Fe, 1.9% Mg, 9% Al, 25.3% Si), ilmenite (FeTiO_3), nanocrystalline ($<200\text{ nm}$) hematite (Fe_2O_3), fine grained albite ($\text{NaAlSi}_3\text{O}_8$) and rutile (TiO_2) [23,26]. As it can be seen on the K map (bottom and top-right regions), the clayey matrix contains medium concentration of K ($\sim 6\text{ wt.}\%$) homogeneously distributed. The correlation between K and Fe was reduced due to the presence of micrometre size ($1\text{--}10\text{ }\mu\text{m}^2$) hematite grains that could be separated by SEM/EDX [9,23,26]. The studied scanned area was selected such a way that it contained fracture infilling regions in addition to the clayey matrix regions. Pixels on the elemental maps with high K, Al and Si concentrations could be related to the fracture infilling potassium feldspar (KAlSi_3O_8) [9,23,26]. Fracture infilling carbonate may be present as calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and different phase Mn-carbonate, respectively [9,23,26].

Figure 2. Elemental concentration maps from a $0.3 \times 0.27\text{ mm}^2$ scanned area. The elemental maps are presented as max–min normalized, where black representing the minimum and white the maximum concentration. Concentration maps of Na, Mg, Al, Si and Fe were generated from scanning electron microscopy energy dispersive X-ray analysis, while those of K, Ca, Ti, Mn and Nd were based on microscopic X-ray fluorescence data sets.

Comparing of the concentration distribution maps of major elements and Nd (Figure 2), a homogeneous distribution of Nd was obtained at the clayey matrix regions, while enhanced Nd concentrations were observed at or around Ca-rich phases. Figure 3 shows that a good correlation ($r = 0.68$) was observed between K and Nd concentrations when only the clayey matrix region was selected, while the concentrations of the two elements were practically uncorrelated ($r = 0.04$) when all pixels of the scanned area were considered.

Figure 3. Scatter plot of K and Nd concentrations for all pixels (black) and pixels belonging to the clayey matrix (red).

Thus, the role of the clayey matrix in the Nd uptake could be highlighted using elemental concentration maps and inter-elemental correlations. However, the application of multivariate methods and micro-XRD was necessary in order to obtain quantitative information about the sorption capacity of the clayey matrix and the identification of additional mineral phases responsible for the uptake.

3.2. Multivariate methods

Based on the 95% limit of the explained variance, six factors (latent variables) were found to describe the interleaved data set of SEM/EDX and micro-XRF concentrations by FA. According to the diagram of factor loadings (correlation of factors with the elemental concentrations; Figure 4), strong correlation was observed between elements present in the same mineral phases, e.g. Ca and Mn (Factor 1) in carbonates, Ti and Fe (Factor 2) mostly in the clayey matrix, and Al and Si (Factor 5) as aluminosilicates. A strong anticorrelation was observed between Na and K (Factor 3) as albite and K-feldspar are separated in the fracture infilling regions. A separate factor (Factor 4) was formed for the element of interest Nd with a complete anticorrelation indicating that its distribution was different from that of the main rock-forming minerals. The determination of ion binding capability of the mineral phases would need quantitative information about the elements present together with Nd. FA provides negative loading values (Figure 4), therefore multivariate methods with non-negativity constraint are needed for quantitativity [40]. However, the application of FA is necessary in order to provide the appropriate number of factors describing the data set.

Figure 4. Factor loadings of the interleaved scanning electron microscopy energy dispersive X-ray analysis and microscopic X-ray fluorescence data set representing correlations between the factors and the elemental concentrations. The results were obtained using factor analysis on elementally maximum normalized and autoscaled concentrations.

PMF was performed on the interleaved data set of the maximum normalized elemental concentration measured by SEM/EDX and micro-XRF to identify the mineral phases and to estimate their ion binding capability. From the result of the PMF evaluation (*G* and *F* matrices), the composition of the factors expressed as elemental concentrations (factor profiles) and the values of the factors at each measured pixel (factor contributions) could be created, the latter ones visualized as factor distribution maps (Figure 5a). From the factor profiles expressed in elemental concentrations (Figure 5b) and from the comparison of the factor distribution maps (Figure 5a) and the elemental maps (Figure 2), information on the mineral phases present could be obtained despite the fact that factors could not be identified as single mineral phases.

The highest Nd uptake capability could be evaluated as 1200 $\mu\text{g/g}$ in Factor 4 (Figure 5b) representing the clayey matrix based on its Al, Si and Fe content. Almost the same amount of Nd (1100 $\mu\text{g/g}$) was bound to a calcium rich mineral phase representing calcite (Factor 3), while the ion uptake capability of dolomite (Factor 2) was orders of magnitude lower. It should be highlighted that the ion uptake capability of dolomite, containing calcium and magnesium, could be distinguished from the very diverse characteristics of calcite only by the interleaving of micro-XRF and SEM/EDX data sets. For both mineral phases non-negligible but different amount of manganese was bound corresponding to the two phase manganese-carbonate.

Figure 5. Factor contribution maps (a) and profiles expressed as elemental concentrations (b). The factor contribution maps are presented as max–min normalized, where black representing the minimum and white the maximum contribution. The results were obtained using positive matrix factorization on maximum normalized elemental concentrations from interleaved microscopic X-ray fluorescence and scanning electron microscopy energy dispersive X-ray analysis results taking into account the corresponding standard deviation in each pixel.

As multiple mineral phases or chemical elements can be present together, several factors can contribute to the composition at the same pixel. It was the reason for applying PMF for relation of abstract factors to mineral phases. CA is a different approach, where one pixel can only belong to one cluster based on the main mineral phase present in the given pixel. It means that CA is capable to provide information on the ion uptake capacities of different main mineral phases.

CA was carried out on the interleaved micro-XRF and SEM/EDX data set taking into account only those elements which were dominant in the factors obtained as the result of PMF. The number of clusters was chosen as the number of factors, because the number of separable mineral phases and mineral aggregations (clayey matrix) is the same for both cases as the same data set was studied. Before carrying out CA, every variable was normalized to its maximum to contribute with the same weight defined by the concentration of the chemical elements in the calculation of the distance between the objects. As a result, the assignment of pixels to each of the six clusters is presented as cluster maps (Figure 6). The representative average composition of each cluster could be determined from the average of the elemental concentration of the pixels classified to it. The average Nd and Ca concentrations of the clusters are tabulated into Table 1.

Figure 6. Cluster maps based on the result of interleaved, maximum normalized scanning electron microscopy energy dispersive X-ray analysis and microscopic X-ray fluorescence concentrations; white pixels are assigned to the given cluster.

Table 1. Neodymium concentrations related to the clusters

Cluster number	Number of pixels	Ca concentration [wt.%]	Nd concentration [µg/g]
1	542	3.96	399
2	671	7.92	681
3	144	13.71	683
4	377	13.15	1140
5	1288	3.41	704
6	394	17.91	1460
Total/Average	3416	7.56	785

The main mineral phases and mineral aggregation could be identified and their ion binding capability could be estimated as the result of CA (Figure 6, Table 1). There were two separable clusters which appeared on the edge of the calcites and/or aluminosilicates which had the highest neodymium binding capability with an average Nd content of 1460 µg/g and 1140 µg/g for Cluster 6 and Cluster 4, respectively (Table 1, Figure 6). The cluster related to the clayey matrix (Cluster 5) had the second highest neodymium binding capability with lower concentration value than predicted by PMF. The results obtained by the two methods are in accordance with each other, since CA results reflect the average, while PMF results reflect the maximum uptake capacity of the clayey matrix.

For this sample, the Nd(III) equilibrium concentration was 10^{-5} M in the solution after the uptake experiment and a total Nd load of 780 µg/g was measured in the solid phase with that CA has good correlation.

3.3. Micro-XRD results

In order to verify the results obtained for the mineral phases responsible for the Nd uptake by applying multivariate methods on interleaved micro-XRF and SEM/EDX elemental maps, micro-XRD patterns were collected from several selected positions on the same sample area. When only positions representative for the clayey matrix were selected, Nd content was in a good correlation with the clay mineral (illite and montmorillonite) content (Figure 7) indicating the importance of these minerals in the Nd uptake of the rock. The azimuthally integrated diffraction patterns corresponding to positions of low and high Nd content in the clayey matrix can be seen in Figure 8.

Table 2 contains detailed results of the semi-quantitative mineral phase composition of 13 selected positions (pixels) of the scanned area. For comparison to data obtained using micro-XRF and SEM/EDX combined with multivariate methods, the corresponding Nd

concentrations, as well as CA cluster assignments and contributions to two main PMF factors are also tabulated. Positions with calcite and albite as main mineral phases were assigned well to the corresponding clusters. Micro-XRD images could not be evaluated for pixels representative for dolomite and K-feldspar due to the presence of large single crystals. The crystalline phase composition obtained for positions selected in the clayey matrix reflects well the average composition of the mineral aggregation. A strong correlation ($r = 0.91$) was observed between the contribution of PMF Factor 5, the clay mineral content (sum of illite and montmorillonite) and all selected pixels rich in clay minerals were assigned by CA to Cluster 4.

Table 2. Results of micro-XRD measurements at selected positions compared to CA cluster assignments (number of the cluster which the given pixel was assigned to) and PMF factor contributions (maximum normalized for each factor) and the corresponding Nd concentrations. (Micro-XRD images could not be evaluated for positions 3 and 4 due to the presence of large single crystals.)

Position /pixel	Mineral phase composition (wt.%)							Nd (wt.%)	Cluster number	Factor contribution		
	Albite	Illite	Mont- morillonite	Calcite	Hematite	Jacobsite	Other			Factor 3	Factor 4	
1	95							5	501	1	0.39	0.04
2	80							20	308	1	0.21	0.10
3									434	2	0.11	0.00
4									232	3	0.71	0.00
5				60	10			30	7830	4	0.54	0.04
6	40	17	34		5			4	872	5	0.06	0.38
7	23	29	25		5			18	797	5	0.07	0.48
8	42	10	33		5	5	5	5	723	5	0.01	0.36
9	25	11	30		5	5	24	608	5	0.01	0.32	
10	48	25	17		5		5	702	5	0.01	0.32	
11	23	36	20	5	5	5	6	901	5	0.09	0.39	
12	41	27	15		5		12	806	5	0.08	0.37	
13	15			58			27	2480	6	0.80	0.00	

4. Conclusions

The interleaved micro-XRF and SEM/EDX elemental mapping had sufficient information to entirely identify the main mineral phases responsible for the uptake of Nd(III) ion. The presence of minerals was verified by applying micro-XRD. With the application of multivariate methods on the interleaved data set, the ion binding capability of the mineral phases could be quantified. As the result of evaluation by positive matrix factorization, Nd was found to mostly be bound to calcite and clayey matrix. With the application of cluster analysis, basically the same results were obtained while the differences could entirely be explained by the different mathematical approach of PMF and CA, respectively.

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