

## HIGH TEMPERATURE TRANSFORMATION OF FE-BEARING MINERALS IN BENTONITE – MÖSSBAUER SPECTROSCOPY STUDIES

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### Abstract

Bentonite is widely used in various branches of industry due to its special properties like low hydraulic conductivity, high sorption capacity, low permeability. High temperature stability of bentonite determines its usefulness for industrial applications. The thermal stability of the bentonite from Lower Silesia region (Wilków, Pogórze Kaczawskie, SW Poland) has been tested at various temperatures between 100°C and 800°C. Raw bentonite sample contained montmorillonite (47%), magnesioferrite (30%), orthoclase (11%) and goethite (8%). Decomposition of bentonite at high temperatures was followed by Mössbauer spectroscopy investigations. The changes in the Mössbauer spectra well reflected various phases of decomposition and transformation, because Fe-bearing minerals make up the majority (89%) in all present phases of the investigated bentonite. At a temperature of 400°C the process of dehydroxylation of montmorillonite started, and continued up to 700°C. The recrystallization of montmorillonite to illite was observed in a temperature above 700°C. In a temperature range from 400°C to 500°C conversion of goethite to hematite took place. Mössbauer spectrum obtained after heating at 800°C showed hematite as the main iron oxide phase with approximately the same relative ratio of iron oxides and hydroxides as in the starting material.

**Keywords:** Bentonite, high temperature affects, Mössbauer spectroscopy, Fe-bearing minerals

### 1. INTRODUCTION

Bentonite is defined as a naturally occurring material that consists predominantly of the clay mineral, montmorillonite [1]. Bentonite may also contain a small amount of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum, or pyrite and various iron oxides/hydroxides [2]. However, the presence of smectites determines the suitability of bentonite for industrial applications [1,3,4]. The main physical properties of montmorillonite include low hydraulic conductivity [5], high sorption capacity [6], and low permeability [7]. High temperature affects changes in cation-exchange capacity, pore structure, and catalytic activity as well as the chemical composition of the particles and the mineralogy of bentonite. Therefore, a thermal stability of bentonite as well as changes in microstructure determine the usefulness of it for industrial practice [9,10]. In practice, there are a lot of various methods typically used for the bentonite thermal stability determination. One group of the methods is based on application of instrumental analytical methods, DTA/TGA analysis and/or X-ray diffraction analysis in particular [3,8,9]. However, there are only a few studies of bentonite in which Mössbauer spectroscopy was used [10-12] and practically, there are no studies which use this technique to investigate high temperature properties of bentonite.

Knowledge about thermal stability of bentonite and, precisely speaking, all its components, is important for industrial applications. For this reason, the purpose of this study is to investigate the mineralogy and high temperature transformations of bentonite under oxidative (in air) conditions. For these studies the <sup>57</sup>Fe Mössbauer spectroscopy will be used. It is well known that the Mössbauer spectroscopy method as a local

probe technique [13,14] is very sensitive to the local atomic structure, its local deformation, and atomic or lattice defects when treating the Fe nucleus as a probe of its local surrounding.

## 2. MATERIALS AND METHODS

A native bentonite originating from the Lower Silesia region (Wilków, Pogórze Kaczawskie, SW Poland), which forms the eastern part of the Central European Volcanic Province and supplied by PGP "BAZALT" SA. The material was divided by manufacturer into three groups with different granulations: 0-0.063 mm, 0-2 mm and 2-5 mm. These granulations are commonly used by the manufacturers because it is useful for filling various holes (for example). The sample with 0-2 mm granulation was chosen for thermal investigation. Sample was heated for three hours in an electric furnace on air atmosphere under static conditions in temperature range from 100°C to 800°C. After each heating treatment, the Mössbauer measurement was taken.

The chemical composition was determined by the use of X-ray fluorescence (XRF) from ZSX Primus II Rigaku spectrometer. The spectrometer, equipped with the 4 kW, 60 kV Rh anode and wavelength dispersion detection system, allowed for the analysis of the elements from Be to U. No external standards were necessary, only the internal standards coupled with the fundamental parameters method (theoretical relationship between the measured X-ray intensities and the concentrations of elements in the sample) were implemented.

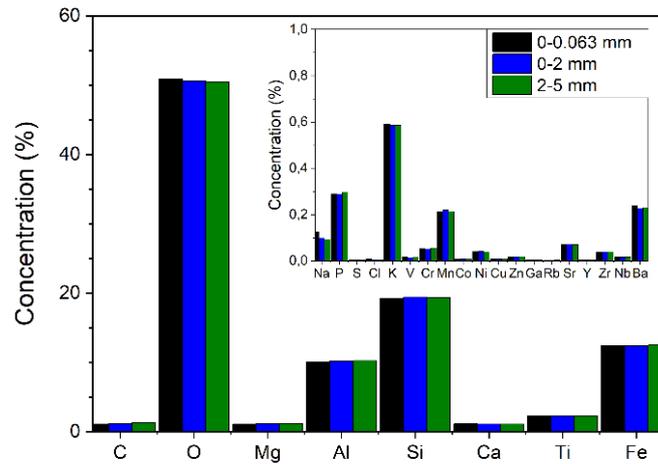
To confirm presence of montmorillonite structure in the investigated samples and identify other minerals in the samples after the heating procedure, the XRD studies were done. X-ray diffraction studies were conducted at room temperature by the use of a Siemens D5000 X-ray diffractometer and  $\text{CuK}\alpha$  radiation. Rietveld refinement was performed in a licensed Xpert High Score Plus with PDF-4 crystallography database.

$^{57}\text{Fe}$  Mössbauer transmission spectra were recorded at room temperature with an MS96 Mössbauer spectrometer. The spectrometer was calibrated with a 30  $\mu\text{m}$  thick  $\alpha\text{-Fe}$  foil. Numerical analysis of the Mössbauer spectra was performed by means of the WMOSS4F program (Ion Prisecaru, WMOSS4 Mössbauer Spectral Analysis Software, www.wmoss.org, 2009-2016) based on least squares fitting of Lorentzian lines. The analysis made it possible to determine both hyperfine parameters of individual components and relative contribution from the spectral areas of each of them.

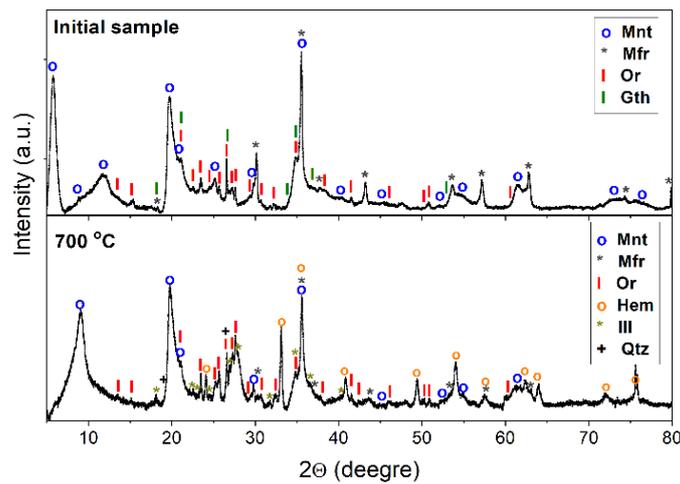
## 3. RESULT AND DISCUSSION

**Figure 1** presents contents of the elements in the investigated bentonites with different granulation determined by X-ray fluorescence (XRF) method. These analysis indicated that chemical composition of all the investigated bentonites is almost the same and does not depend on the granulation. The analyzed materials contained mainly Si (~19.46 mass%), Fe (~12.48 mass%) and Al (~10.12 mass%) which, just as C, Mg, Ca or O, are elements of minerals present in bentonite.

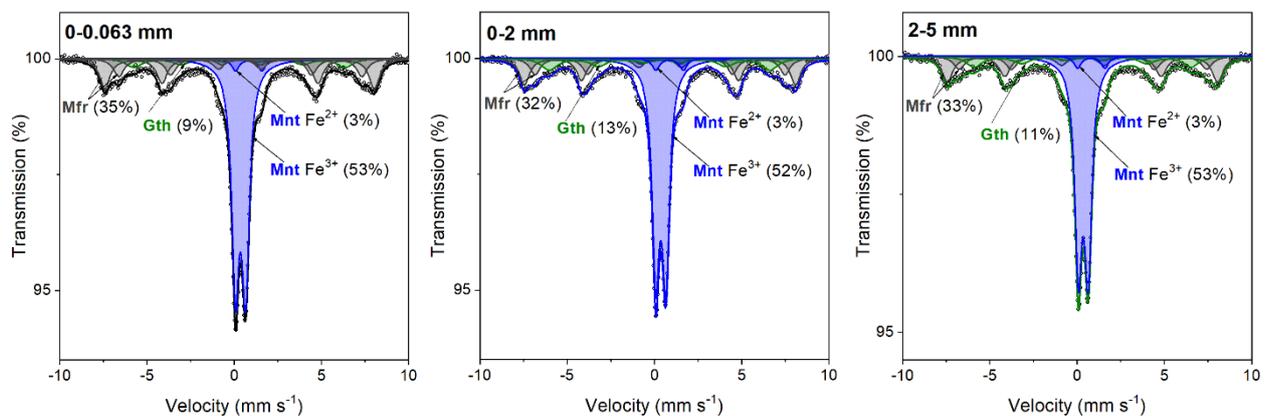
**Figure 2** presents X-ray diffraction patterns obtained for the sample with 0-2 mm granulation of raw material and after heating at temperature 700°C. Montmorillonite accounts for about 47%, magnesioferrite 30%, orthoclase 15% and goethite 8% of the whole sample. After heating at 700°C the peak at  $2\theta = 5.74^\circ$  (the initial sample), which corresponds to 001 basal reflection in montmorillonite, disappeared and the distinct peak at  $9.16^\circ$  is observed. This peak indicates dehydrated phase [15]. This peak is broad and its intensity is low compared with the previous one. Since the peak intensity is a precise indicator of the surface extent and of the number of atoms of this surface, it makes it possible for the crystallinity of a clay mineral to be assessed by the intensity of the 001 reflection [16]. Thus, high temperature might be responsible for the formation of a wide variety of smaller plans randomly orientated by fragmentation of 001 plans or even partial decomposition of montmorillonite structure what can confirm diffraction lines connected with illite (Ill) and quartz (Qtz). Also, after heating bentonite sample at 700°C one can observe diffraction lines attributed to hematite as a product of goethite dehydration and magnesioferrite transformation. After heating at this temperature, montmorillonite averages 31%, hematite 21%, orthoclase 14%, magnesioferrite 13%, quartz 13% and illite 8%.



**Figure 1** Elements concentration higher than 1 mass% and smaller than 1 mass% (insert) of the investigated bentonite samples with different granulation.

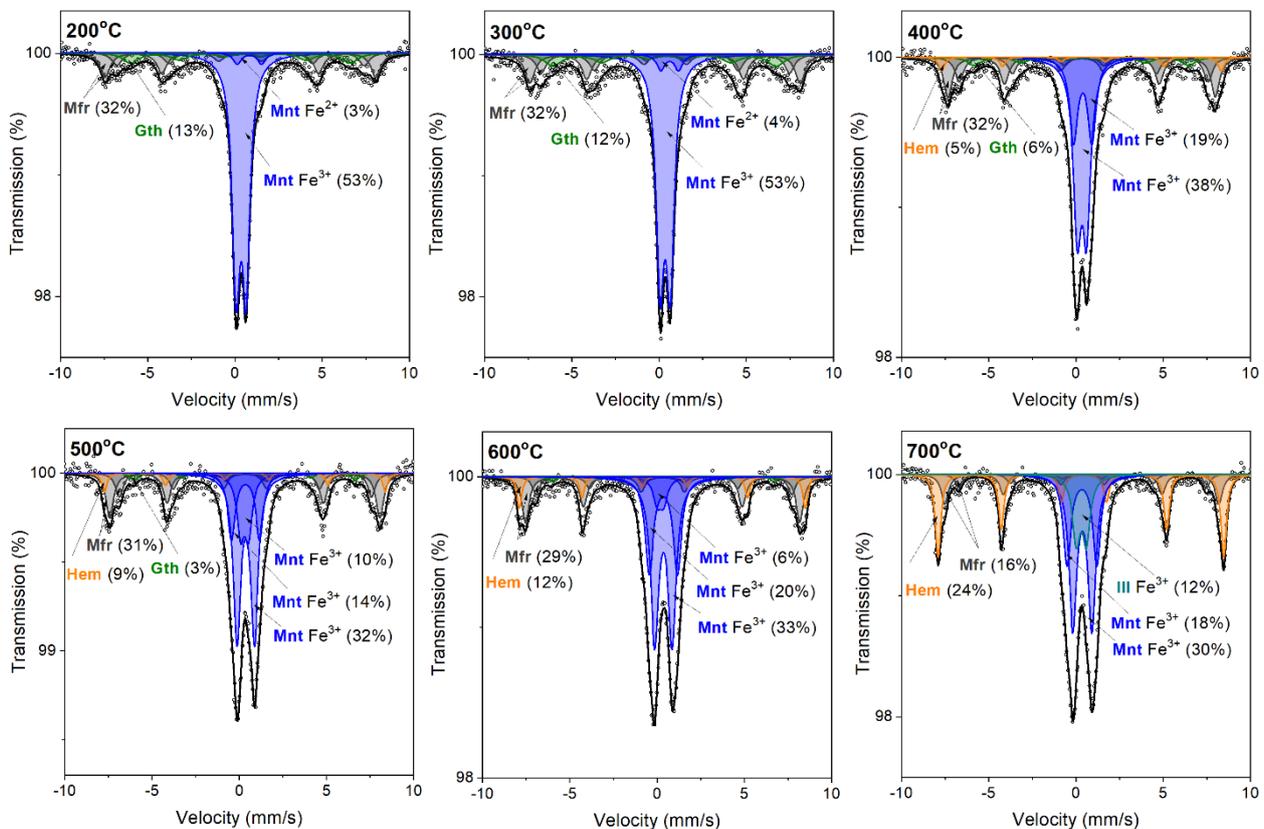


**Figure 2** XRD patterns of the initial and heated at 700°C bentonite sample. Symbols: Mnt – montorillonite, Mfr – magnesioferrite, Gth – goethite, Or – orthoclase, Hem – hematite, Ill – illite, Qtz – quartz.



**Figure 3** Mössbauer spectra obtained for raw bentonite samples with different granulation. Fitted components, their assignment and contributions are indicated on the spectra.

The results of the Mössbauer analyses (**Figure 3**) of the row bentonite samples show three magnetic  $\text{Fe}^{3+}$  sites and two non-magnetic,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , sites. Granulation of the sample almost did not influence on contribution of fitted components. Two sextets with hyperfine magnetic field of about 44 T and 48 T are connected with magnesioferrite [17] and result from  $\text{Fe}^{3+}$  on the tetrahedrally (A) sites and  $\text{Fe}^{3+}$  on the octahedrally (B) sites (respectively) of its spinel structure [18]. The Mössbauer hyperfine parameters of the third sextet, with hyperfine magnetic field  $\sim 38\text{T}$ , could be interpreted to goethite [17,18]. The main component on all the Mössbauer spectra is a ferric quadrupole doublet with isomer shift value of about 0.36 mm/s and quadrupole splitting  $\sim 0.57$  mm/s associated with  $\text{Fe}^{3+}$  ions located in trans-OH octahedral sites in montmorillonite structure [11,12,17]. Second doublet, with very low intensity, is probably connected with  $\text{Fe}^{2+}$  ions also located in montmorillonite structure. As can be seen, the investigated bentonites contain quite a large fraction of magnetic phases ( $\sim 45\%$ ) in comparison to these present in literature [12]. Such differences in composition can be a result of the geochemical conditions during formation of bentonite.



**Figure 4** Mössbauer spectra obtained after heating of bentonite sample at definite temperatures. Fitted subspectra, their assignments and contributions are visible on the spectra.

**Figure 4** shows room temperature Mössbauer spectra obtained for the sample heated up to temperature 800°C. There is no significant change of Mössbauer spectrum up to a temperature of 400°C. However, after heating at this temperature a decrease in contribution of goethite is observed and on Mössbauer spectrum appears a sextet with hyperfine magnetic field of 49.4T associated with hematite [17]. In this temperature starting conversion of goethite to hematite. Dehydration of goethite involves removal of hydrogen and one quarter of the oxygen, without disturbing the network of the remaining oxygen, and atomic rearrangement of  $\text{Fe}^{3+}$  to form hematite [19]. This process takes place in a wide temperature range, and up to a temperature 500°C small remainder of goethite was still observed. The concentration of montmorillonite is almost constant up to temperature 600°C but a detailed analysis of Mössbauer spectra indicates changes, which take place

inside its structure influenced by high temperature. After heating at 400°C the contribution of the main doublet decreases and the second doublet with high quadrupole splitting (QS) value of 1.04 mm/s appears. Two of the observed doublets, in place of one, on the Mössbauer spectrum do not correlate with the two different crystallographic sites but depend on a number of different cation arrangements around a crystallographic site. The increase in the quadrupole splitting relates to an increase in the electric field gradient at the iron nuclei that may be caused by the distortion of the symmetry of the Fe octahedra due to local cation environments around these cations. On the basis of this observation we can assume that at this temperature the process of dehydroxylation, where the adjacent OH groups are replaced with a single residual oxygen atom, starts. Relatively low observed temperature of dehydroxylation let classify investigated bentonite as formed by weathering of other minerals (primarily micas) [7] while those which undergo dehydroxylation at 700°C originating from the weathering of volcanic. After heating at temperature 500°C on Mössbauer spectrum doublet connected with trans-OH octahedral sites was not visible, but a doublet with larger (1.60 mm/s) quadrupole splitting come up. Presence of such doublet proclaims that the octahedral positions are completely distorted. After heating at 500°C and 600°C on the Mössbauer spectra appear doublets with the values of isomer shift of about 0.28 and 0.19 mm/s, which are characteristic for Fe<sup>3+</sup> in tetrahedral coordination. Additionally, on the basis of the literature data [20] we can assume that at this temperatures range migration of octahedral cations takes place, notably the migration of Al cations from the trans-sites to vacant pentagonal prisms. It can indicates that above these temperatures remodelling of some octahedral polyhedrons take place. This process progresses up to a temperature of about 700°C. On the Mössbauer spectrum obtained after heating the sample at temperature 700°C doublet with isomer shift 0.31 mm/s and quadrupole splitting 0.57 mm/s is visible. This doublet is related to illite [17] and appears as a result of recrystallization of montmorillonite to illite. Mössbauer spectrum obtained for the sample heated at 800°C contains hematite as main magnetic component (35%). Hyperfine magnetic field for this sextet is equal ~51T. The presence of illite indicate that above a temperature of 700°C decomposition of montmorillonite took place. Doublet related to illite is the main (~31%) non-magnetic component visible on the spectrum after heating the sample at 800°C. The second doublet represents a remnant of the montmorillonite (~29%). However, its hyperfine parameters (IS = 0.31 mm/s and QS = 1.05 mm/s) differ from these obtained from initial and even dehydroxylated montmorillonite what showing the loss of structure by it.

#### 4. CONCLUSIONS

The paper illustrates high temperature transformation of Fe-bearing minerals in bentonite using Mössbauer spectroscopy technique. The temperature, above which decomposition of crystal phases present in bentonite take place, determine its usefulness in various branches of industry. The raw bentonite sample contained montmorillonite, magnesioferrite, orthoclase and goethite. High temperature studies show that all of Fe-bearing phases remained unchanged up to a temperature of about 300°C. It can be important for the potential use of this material as bentonite buffer and for its waste repositories function. Heating the sample at a temperature higher than 300°C converts goethite and magnesioferrite to hematite but this process takes place in a wide temperature range (above 700°C). Dehydroxylation process of montmorillonite starts at a relatively low temperature, namely above 400°C, and the breakdown of the clay structure takes place at about 700°C. Such knowledge about high temperature stability of clay-mineral fraction is important for the production of foundry sand, ceramic or in civil engineering. Above this temperature the recrystallization of montmorillonite to illite starts. Hematite is the main iron oxides phase above 700°C.

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**REFERENCES**

- [1] RADMILOVIĆ, N., LOGAR, M., LUKOVIĆ, J., PANTIĆ, J., MILJEVIĆ, M., BABIĆ, B., LJEVIĆ-MIHAILOVIĆ, R. Characterization of bentonite clay from "Greda" deposit. *Processing and Application of Ceramics*. 2011, vol. 5, no. 2, pp. 97-101.
- [2] WESLEY, L. *Clays and Clay Minerals: Geological Origin, Mechanical Properties and Industrial Applications*. Publisher: Nova. 2014.
- [3] JELINEK, P., DOBOSZ, S., BENO, J., MAJOR-GABRYŚ, K. The behavior of bentonite binders for the elevated and high temperatures. *Archives of Metallurgy and Materials*. 2014, vol. 59, pp. 1041-1044.
- [4] ALIU, M., KELMENDI, M., PULA-BEQIRI, L., SADIKU, M., KADRIU, S. Characterization of Karaceva bentonite by chemical composition, granulometric analysis and Mössbauer spectroscopy. *Journal of Chemical Technology Metallurgy*. 2018, vol. 53, no. 3, pp. 480-485.
- [5] BEHNSEN, J., FAULKNER, D. Permeability and frictional strength of cation-exchanged montmorillonite. *Journal of Geophysical Research: Solid Earth*. 2013, vol. 118, pp. 2788–2798.
- [6] MORROW, C., MOORE, D., LOCKNER, D. Frictional strength of wet and dry montmorillonite. *Journal of Geophysical Research: Solid Earth*. 2017, vol. 122, no. 5, pp. 3392-3409.
- [7] ŽYMANKOWSKA-KUMON, S., HOLTZER, M., GRABOWSKI, G. Thermal analysis of foundry bentonites. *Archives of Foundry Engineering*. 2011, vol. 11, no. 4, pp. 209-213.
- [8] URSU, A., JINESCU, G., GROS, F., NISTOR, I., MIRON, N., LISA, G., SILION, L., DJELVEH, G. AND AZZOUZ, A. Thermal and chemical stability of Romanian bentonite. *Journal of Thermal Analysis and Calorimetry*. 2011, vol. 106, pp. 965–971.
- [9] KRAJEWSKI, P., SUCHY, J., PIWOWARSKI, G., KRAJEWSKI, W. High Temperature Thermal Properties of Bentonite Foundry Sand. *Archives of Foundry Engineering*. 2015, vol. 15, pp. 47-50.
- [10] BENETOLI, L., DE SOUZA, C., DA SILVA, K., DE SOUZA, I., DE SANTANA H., PAESANO, A., DA COSTA, A., ZAIA, C. AND ZAIA, D. Amino Acid Interaction with and Adsorption on Clays: FT-IR and Mössbauer Spectroscopy and X-ray Diffractometry Investigations. *Origins of Life and Evolution of Biospheres*. 2007, vol. 37, pp. 479–493.
- [11] KOMLÓSI, A., KUZMANN, E., NAGY, M., HOMONNAY, Z., KUBUKI, S., KONYA, J. Incorporation of Fe in the interlayer of Na-bentonite via treatment with FeCl<sub>3</sub> in acetone. *Clays and Clay Minerals*. 2007, vol. 55, no. 1, pp. 89–95.
- [12] KOMADEL, P., ANASTÁCIO, A., ANDREJKOVIČOVÁ, S., STUCKI, J. Iron phases identified in bentonite from the Lieskovec deposit (Slovakia) by variable temperature: Mössbauer spectroscopy. *Clay Minerals*. 2008, vol. 43, no. 1, pp. 107–115.
- [13] STUCKI, J.W., GOODMAN, B.A., SCHWERTMANN, U. *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht. 1988.
- [14] DYAR, M.D., AGRESTI, D., SCHAEFER, M., GRANT, C., SKLUTE, E. Mössbauer spectroscopy of earth and planetary materials. *Annual Review of Earth and Planetary Science*. 2006, vol. 34, pp. 83–125.
- [15] KOOLI, F., MAGUSIN, P. Adsorption of cetyltrimethylammonium ions on an acid-activated smectite and their thermal stability. *Clay Minerals*. 2005, vol. 40, no. 2, pp. 233–43.
- [16] KAMP, P. Smectite-illite-Muscovite transformations, quartz dissolution, and silica release in shales. *Clays and Clay Minerals*. 2008, vol. 56, no. 1, pp. 66-81.
- [17] STEVENS, J., KHASANOV, A., MILLER, J., POLLAK, H., LI, Z. *Mössbauer mineral handbook*. Asheville, North Carolina. 2005.
- [18] ÖZDEMİR, Ö., DUNLOP, D. Intermediate magnetite formation during dehydration of goethite. *Earth and Planetary Science Letters*. 2000, vol. 177, pp. 59-67.
- [19] MULLER, F., DRITS, V., PLANCON, A., ROBERT, J-L. Structural Transformation of 2:1 Dioctahedral Layer Silicates During Dehydroxylation-Rehydroxylation Reactions. *Clays and Clay Minerals*. 2000, vol. 48, no. 5, pp. 572-585.