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Clay mineralogy of the Boda Claystone Formation (Mecsek Mts., SW Hungary)

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Abstract: Boda Claystone Formation (BCF) is the host rock of the planned site for high level nuclear waste repository in Hungary. Samples representing the dominant rock types of BCF were studied: albitic claystone, claystone with high illite content, and analcime bearing claystone. Clay minerals in these three rock types were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and thermal analysis (DTA-TG), and the results were discussed from the point of view of the radionuclide sorption properties being studied in the future. Mineral compositions of bulk BCF samples vary in wide ranges. In the albitic sample, besides the dominant illite, few percent of chlorite represents the layer silicates in the clay fraction. Illite is the dominating phase in the illitic sample, with a few percent of chlorite. HRTEM study revealed that the thickness of illite particles rarely reaches 10 layers, usually are of 5–6 TOT layer thick. Illite crystals are generally thicker in the albitic sample than in the illitic one. The significant difference between the clay mineral characteristics of the analcimous and the other two samples is that the former contains regularly interstratified chlorite/smectite beside the dominant illite.

Based on the structural and chemical data two illite type minerals are present in the BCF samples: 1M polytype containing octahedral Fe and Mg besides Al, 2M polytype illite generally is free of Fe and Mg. Close association of very thin illite plates and nanosized hematite crystals is typical textural feature for BCF.

The goal of this study is to provide solid mineralogical basis for further studies focusing on radionuclide sorption properties.

Keywords: illite polytypes; HRTEM; nuclear waste repository; analcime; hematite

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1 Introduction

Investigations on Boda Claystone Formation (abbreviated in the following as BCF) as a potential rock formation for high level nuclear waste (HLW) disposal began in 1989 and goes on up to present in several research stage in the '90s and 2000s. During the first years, research was supported by Paks Nuclear Power Plant. Since 1998 Public Limited Company for Radioactive Waste Management (PURAM) as a Hungarian governmental agency has the responsibility and financial funds for the coordination of the studies. PURAM considers BCF as suitable rock formation for HLW since 1999. Favourable properties which support the suitability of BCF based on the studies [1–4] are the followings: BCF is a massive, homogeneous rock body with significant extension and thickness (700–900 m); it has low bulk-porosity (0.6–1.4%) and very low permeability 10^{-11} – 10^{-13} m/s, referring to diffusion-dominating transport conditions; the hydrogeological and flow system has long term stability; high proportion of clay minerals and analcime provide good adsorptive properties; it has favourable geotechnical features due to the subordinate amount of swelling clays and high amount of albite. Disadvantage is the presence of abandoned tunnels and cavities of a closed uranium mine.

Physical and chemical properties of clay minerals, such as sorption, sealing and isolation capacity are important from the point of view of radionuclide migration in rocks. All of these properties are function of the crystal chemical and structural, as well as textural features of clay

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minerals. Therefore, characterization of clay minerals in details is crucial in the evaluation of the technical properties of a given rock formation. Despite the extensive study of BCF since two decades, till now, there is no any work studying its clay mineralogy from this aspect. Our goal is to give a detailed mineralogical characterization of the most typical BCF samples, in order to provide a mineralogical basis for the radionuclide sorption studies. Moreover, the results are discussed from the point of view of presumable radionuclide sorption properties of the claystone.

2 The Boda Claystone Formation

2.1 Geologic setting

The following paragraphs summarize the knowledge on the geological setting, petrology and mineralogy of BCF accumulated hitherto.

The sedimentary sequence of the Upper Permian Boda Claystone Formation is located in Western Mecsek Mountains, southern Transdanubia, SW Hungary (Figure 1). The Mecsek Mts. is part of the Tisza Megaunit comprising the basement of the south-eastern half of the Pannonian Basin. The continental sedimentation in the Mecsek Mts. began in the Early Permian (Korpád Sandstone Formation) and terminated in the Lower Triassic [5]. The BCF is part of this about 2000–4000 m thick siliciclastic sequence (continental red beds). On the basis of data from boreholes and geological mappings the extension of BCF is around 150 km², and only 15 km² area outcrop exposed at the Boda village region in W Mecsek Mts. (Figure 1). Two occurrences of BCF are known: 1. perianticlinal structure of the W Mecsek Mts (WMA); 2. so called Gorica block. In the Gorica block outcrop of BCF is not known, in this block several deep drillings reached the BCF, but only the borehole Ib-4 recovers sequence of BCF in significant thickness (between 494.2 and 709 m). On the basis of the deep drillings total thickness of BCF is estimated to be about 700–900 m in the perianticlinal structure (WMA) whereas according to our knowledge its thickness is smaller in the Gorica block (about 350 m).

The BCF sediments are dominantly red and reddish brown in color, reflecting the dominantly oxidative environment during sedimentation and early diagenetic processes [2, 6–10]. According to our present-day knowledge the middle part of BCF has only one reductive interbedding (greyish black albitic claystone containing pyrite and finely disseminated organic matter), its thickness is about 3–4 m. However, several reductive thin layers (green,

greenish-gray claystone, siltstone) can be observed in its lower and upper transitional zones (Figure 2).

The BCF deposited in a shallow-water salt lake environment surrounded by dry to saline mudflat, under semi-arid to arid climatic conditions [7–9, 11].

2.2 Mineralogy and petrology

The main rock-forming minerals of the BCF in the perianticlinal structure (WMA) are clay minerals (dominantly illite-muscovite and chlorite, associated with minor; smectite, kaolinite, vermiculite), authigenic albite, detrital quartz, carbonate minerals (calcite, dolomite) and hematite [2, 8, 9, 12]. In addition, some barite, anhydrite, authigenic K-feldspar and detrital constituents (muscovite, biotite, chlorite, zircon, rutile, apatite, ilmenite, Ca-bearing plagioclase) were always also identified in trace amounts. The authigenic albite is present as albite cement (typical for all rock types of BCF), and few millimetre sized irregular vesicles filled with albite and carbonate minerals (typical for albitic claystone), and albite replacement of detrital feldspars in sandstone beds [2, 8, 12]. Carbonate minerals (fine-grained and sparry calcite and euhedral rhombohedral dolomite) and authigenic K-feldspar are always present in these vesicles. Electron microprobe analyses of these pore-lining carbonates show that they always contain Mn and Fe (Mn > Fe). On the basis of their morphology these albite-, carbonate- and K-feldspar-lined vesicles are interpreted as replacement of the previous halite crystals ("hopper halite") [11].

The BCF recovered by borehole Ib-4 (Gorica block) differs in its mineralogical composition. The BCF at Gorica block contains abundant analcime in addition to above listed minerals [10, 13]. Same as the authigenic albite, analcime is present as cement and pore-filling material. According to mineralogical investigations, amounts of analcime range between 8 and 25 wt%. Further mineralogical difference between the two facies is that the BCF in Gorica Block does not contain authigenic K-feldspar, and dolomite is absent or it is subordinate in the studied samples.

The formation has undergone a multistage and complex diagenetic process from the dissolution of the primary evaporite minerals (halite, gypsum, anhydrite) to the formation of authigenic albite and K-feldspar, or calcite- and albite-bearing pseudomorphs after gypsum and anhydrite. Present-day mineral assemblages and rock types are the result of these multistage processes.

In the WMA block six main rock types of BCF can be defined based on mineralogical, geochemical and textu-

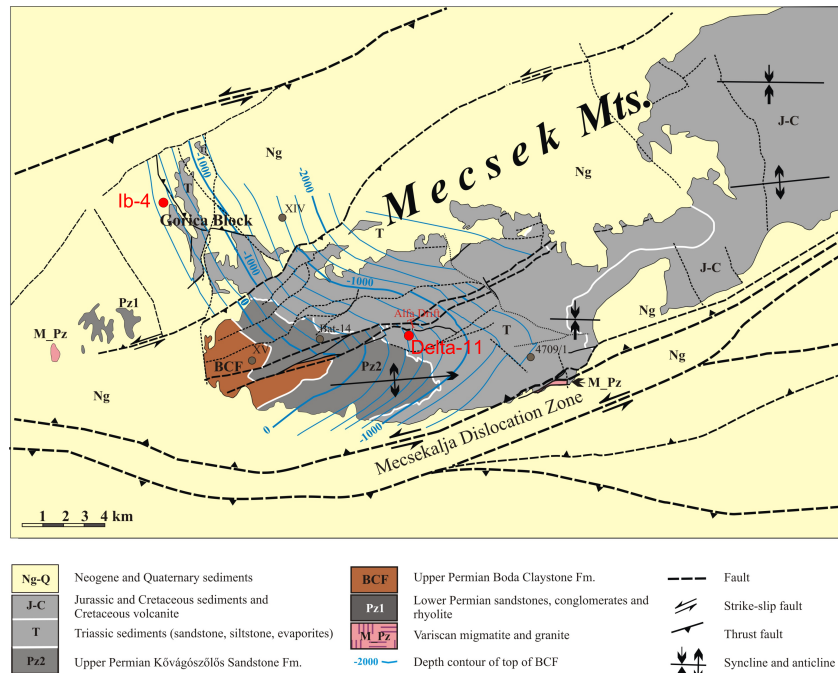


Figure 1: Geological map with depth contour of the top of the Boda Claystone Formation and studied objects after [14] (red circles: studied boreholes: Ib-4, Delta-11). Reddish brown BCF designate the W Mecsek perianticlinal structure.

ral considerations: albitic claystone, albitolite, "true" siltstone, dolomite interbeddings, sandstone and conglomerate. Gorica Block is built up by albite- and analcime-bearing claystone, "true" siltstone, sandstone and conglomerate, dolomite interbeddings are infrequent [2, 7, 8, 10, 12–14]. In both blocks the dominant rock type of the formation is the albitic (albite- and analcime-bearing in Gorica Block) claystone.

On the basis of the thickness of overlying strata in WMA the formation was located at least at 3.5 to 4 km burial depth in the Middle Cretaceous. Illite and chlorite crystallinity as well as vitrinite reflectance data indicate late or deep diagenesis, with a maximum temperature of 200–250°C [8, 12]. Relatively higher absolute values of illite and chlorite crystallinity indices were determined in the core samples of the deep drilling Ib-4 (Gorica block) than the mean phyllosilicate crystallinity indices in WMA, suggesting that BCF in Gorica block underwent lower grade diagenesis [8, 15].

ies based on the previous mineralogical study of 73 samples. The three studied samples represent the most typical rock types of the two facies of BCF (Figure 1). The sample G-12458 is a reddish-brown, unbedded, authigenic albite-bearing claystone from borehole Delta-11, 39.78–40.20 m. This sample represents the dominant rock type of BCF in the WMA block. Albite is present as cement in groundmass and in albite-, carbonates- and K-feldspar-lined vesicles. The sample G-12459 derives from the upper transitional zone of BCF in the Gorica block (borehole Ib-4 510.5–510.6 m). It is a reddish-brown, unbedded claystone with high illite content. It does not contain authigenic albite and analcime. The sample G-9945 representing also Gorica block (borehole Ib-4 540.32–540.37 m), however, it is a reddish-brown, unbedded claystone with authigenic analcime and albite, being present both as cement in groundmass, and as pore-filling associated with various carbonates.

Clay mineralogical studies were carried out on the clay fraction (less than 2 μm) which was obtained by sedimentation of the ground and well washed samples in distilled water.

3 Materials and methods

3.1 Sampling

Samples representing the three most prevalent lithologies were selected for detailed clay mineralogical stud-

3.2 X-ray powder diffraction (XRD)

The mineral composition was determined by X-ray powder diffraction (XRD) analysis performed on a Philips PW-

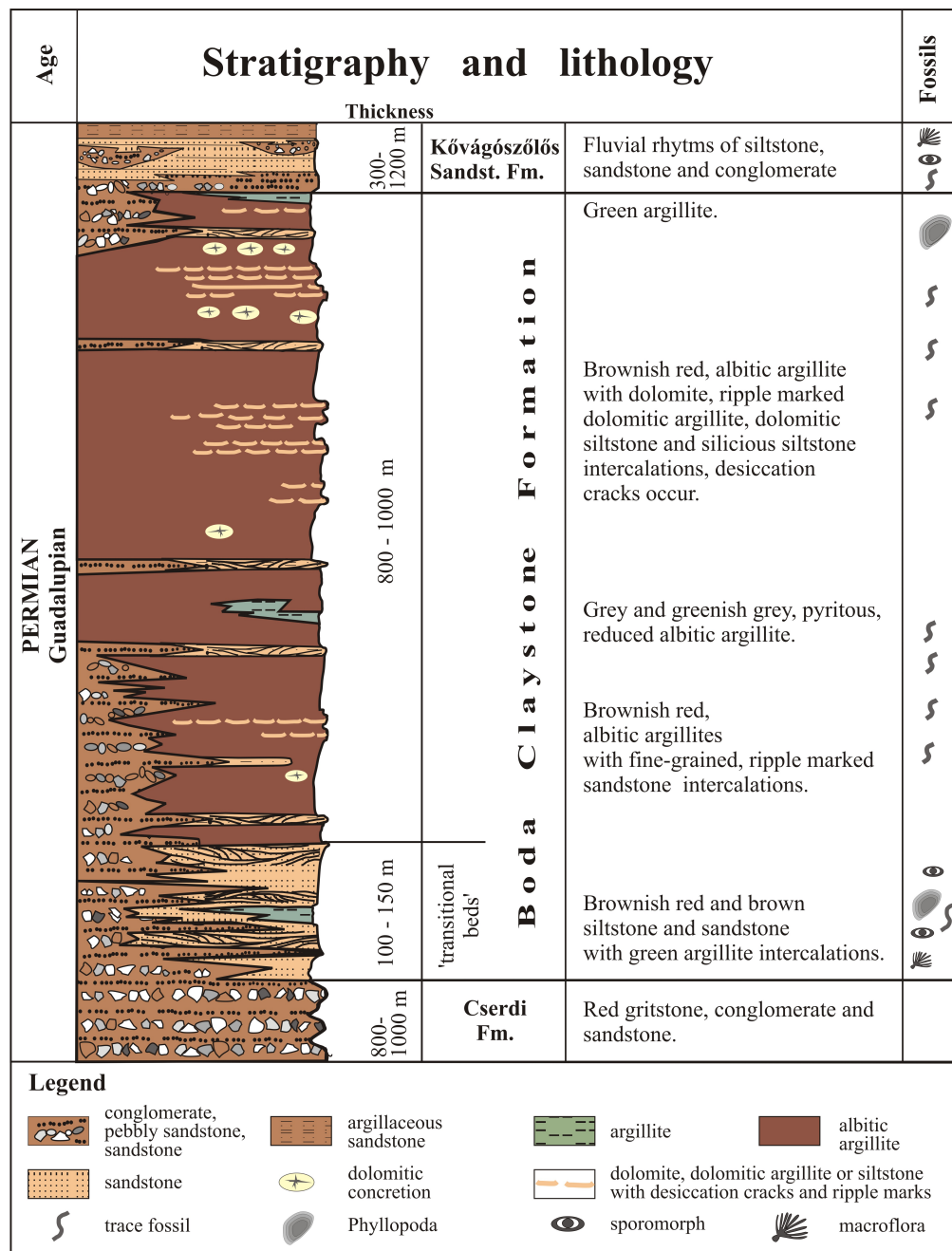


Figure 2: Idealised lithological column of Boda Claystone Formation [14].

1730 diffractometer equipped with a graphite monochromator using Cu-K α radiation at 45 kV and 35 mA with 1° divergence slit and 1° receiving slit. Scanning rate was 0,05°2 θ per minute from 3°, to 70°. The determination of the semi-quantitative mineral composition is based on XRD. Net peak area of the corresponding reflections obtained on random powder samples was measured and the composition was calculated by the modified method of Bárdossy [16]. Although semi-quantification of mineral composition is based on XRD, DTA-TG data were also used for the quantification. Identification and characterization of clay minerals on oriented aggregates involved all necessary diagnostic methods used in XRD: ethylene-glycol solvation, glycerol solvation of Mg-saturated sample for smectite-vermiculite differentiation at 60 and 90°C, respectively, overnight; and heating at 350 and 550°C for one hour. Layer charge of swelling clay minerals was estimated by potassium saturation. Tetrahedral or octahedral origin of layer charge was determined based on the Green-Kelly test. XRD phyllosilicate parameters (Kübler (illite) and Árkai (chlorite) indices) were measured on sedimented specimens following Peter Árkai's method and instrumental conditions, as well as standardization and calibration procedures described in [17].

3.3 Transmission electron microscopy (TEM)

The sub-micron textural, crystal structural and crystal chemical characteristics of the mineral phases in BCF were revealed by HRTEM imaging, electron diffraction and analysis.

For TEM, high resolution TEM (HRTEM) and analytical TEM (ATEM) studies thin section of the bulk rock samples were cut and attached to a 3 mm copper ring. Then these areas were detached and further thinned by Ar ion mill. The TEM studies were carried out applying a FEI Tecnai G² transmission electron microscope operating at 200 kV, equipped with an EDAX energy dispersive X-ray spectrometer. Powdered samples were studied also as sedimented samples on a lacey-carbon covered copper grid. In this case the analysis was performed with a Philips CM20 transmission electron microscope used at 200 kV accelerating voltage and equipped with a Noran energy dispersive system (EDS).

3.4 Thermal analysis (DTA-TG)

Differential thermal (DTA) and thermogravimetric analyses (TG) were carried out on \approx 200 mg of sample by a MOM

Derivatograph Q instrument in air atmosphere in corundum crucible at a heating rate of 10°C/min to 1000 °C, using corundum powder as reference material. Before thermal analysis samples were kept under controlled humidity (20-25 RH%) in a desiccator to assure similar humidity environment and thus to avoid errors emerging from adhesive and adsorbed water.

4 Results and discussions

4.1 Whole rock mineral composition

Hardness, compactness, reddish colour, and fine particle size are common properties of the three studied samples. Interestingly, behind this macroscopic similarity significant differences exist in the mineralogy of the samples. Semiquantitative mineral compositions of the studied bulk samples determined using XRD and thermogravimetry data are given in Table 1. Total clay mineral content of BCF (35-70%) is similar to that of other clayey rocks in Europe being candidates to a host for high level nuclear waste, such as Boom Clay in Belgium [18], Opalinus Clay in Switzerland [19], and Tournemire argillite in France [20]. High feldspar (albite) content, significant hematite content and presence of analcime are the main features which differentiate BCF from the above potential clayey formations. However, BCF has other peculiar mineralogical features, concerning its clay mineralogy and iron-oxide content.

4.2 Mineralogy of the clay fraction

4.3 Albitic sample (G-12458)

Besides the dominant illite (10 and 5 reflections), a few percent of chlorite - as revealed by the 7 reflection and by the appearance of a peak at 13.9 upon 550°C heating - represents the layer silicates in the clay fraction (Figure 3). The basal reflection of illite did not change considerably (see Kübler indices, FWHM, Table 2) due to ethylene-glycol solvation, cation saturation or heat treatment, suggesting that illite does not contain more than 5 % swelling (smectite) component. Non-clay minerals, such as hematite and albite are present in significant amount in the fine fraction, but the calcite content is low.

Among the studied samples the albitic one has the lower weight loss due to water release at low temperature (Figure 4). It indicates not only the smaller amount of clay minerals, but the low amount of water bound by adsorp-

Table 1: Semiquantitative mineral composition of the samples, based on XRD, TG and chemical composition (wt%).

sample	10	chlorite	analcime	quartz	albite	calcite	dolomite	hematite
G-12458	36	1		4	35	6	6	13
G-12459	71	2		6	5	9	1	4
G-9945	51	1	13		12	13		9

tion on illite [21]. Low adsorbed water content and/or interlayer H_3O^+ content is in agreement with the illite crystallinity data $\text{IC} = 0.39 \Delta^\circ 2\theta$ obtained, namely that this illite represents the highest grade of diagenesis (Table 2).

TEM image shown in Figure 5 represents the typical sub-micron textural features of albitic BCF. Euhedral albite crystals indicating its evident authigenic origin from direct precipitation of 1–2 μm size are floating in a matrix composed of packets of illite plates and some accessory minerals, such as hematite.

As revealed by TEM and HRTEM images taken in parallel view to the stacking of the layers, illite crystallites are relatively thick. Illite crystallite thickness varies around 30 nanometres. This thickness is in accordance with the measured crystallinity indices determined by XRD (Table 2). Concerning the crystal chemistry of this illite, ATEM data revealed that it contains Mg and Fe besides Al in the octahedral sheet.

4.3.1 Illitic sample (G-12459)

Intense and relatively broad peaks at 10 and 5 clearly indicate that illite is the predominating phase in this sample. The weak 7 and 14 reflections (this latter enhanced upon 550°C heating) is assigned to a few percent of chlorite (Figure 6). The amount of non-clay minerals is significantly less than in the albitic sample, both in the bulk rock and the clay fraction. Half-width of 001 illite reflection is the largest in this sample. Since the basal reflection did not change considerably upon glycolation (Table 2), the broadening of the peak is not related to smectite interstratification but rather it is the consequence of the very small crystal thickness. HRTEM study showed that the thickness of illite particles generally does not reach ten nanometres, they are usually of 5–6 nm thick, which corresponds to 5–6 layers of TOT unit. The sharpening of the basal peak upon heating to 350 and 550°C suggests significant weakly bound adsorbed water content in the interlayer space and/or the presence of interlayer H_3O^+ . This is supported by the 2.7 % weight loss between 35–235°C, which is the highest among the three samples (Figure 7). Based on thermal analysis dehydroxylation of illite occurs

at 595°C, which is typical for illites. Weight loss at around 800°C is assigned to different carbonate minerals.

Figure 8 shows the typical sub-micron texture of illite rich BCF with more or less uniformly thick packets of illite plates forming a fishbone parquet pattern. It can be seen in lattice-fringe images that these packets are built up by thin individual illite platelets of 5–10 layers of 10 periodicity (Figure 9). TEM (electron diffraction, HRTEM) and ATEM studies revealed that two kinds of illitic mineral can be distinguished based on their crystal structures and chemical composition. Figure 10a shows relatively thick illite crystals (up to 20 layers) exhibiting electron diffraction characteristic of a two-layer monocline polytype structure (2M illite) according to 20 diffraction spots along c^* axis in SAED patterns. Based on the EDX spectra (Figure 10b), the chemical composition of 2M illite in BCF are normally close to ideal dioctahedral composition, containing only Al as octahedral cation. Besides this, a one-layer polytype (1M) is also present in this BCF sample (Figure 11a). The Fourier-transform of the selected area in the HRTEM image (encircled in the Figure 11a) prove the 1M polytype structure. As compared to 2M polytype, this 1M mica-like mineral tend to contain considerable amount of octahedral Fe and Mg, alike in the aluminoceladonite (Figure 11b).

Small amount of chlorite have been detected by XRD. Based on TEM study chlorite forms relatively large packets (100–200 nm), not rarely occurring as triangular junction with a 20 nm cavity in the middle (Figure 12a). EDX spectrum of chlorite (Figure 12b) indicates some potassium content. Potassium derives from illite interstratification, which is also proven by electron diffraction patterns and HR lattice fringe images.

4.3.2 Analcime bearing sample (G-9945)

Figure 13 shows the X-ray diffractograms of the clay fraction after the different diagnostic treatments. Besides 10 reflection of illite, there are peaks at 14.5 and at 7 indicating the presence of some chlorite. Upon glycolation 14.5 reflection shifted to 15.5, and when heated to 550°C a part of it moved to 13.8 and a new peak appeared at 12, undoubtedly indicating the presence of interstratified

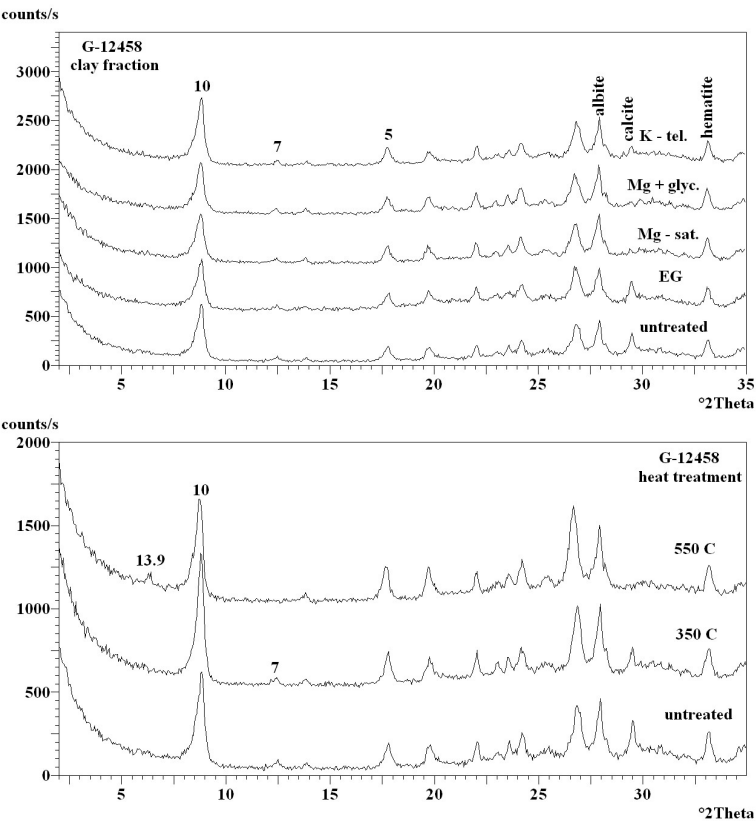


Figure 3: XRD patterns of the clay fraction of albitic BCF (G-12458) after the different diagnostic treatments. Numbers on the peaks indicate corresponding *d* values in Å.

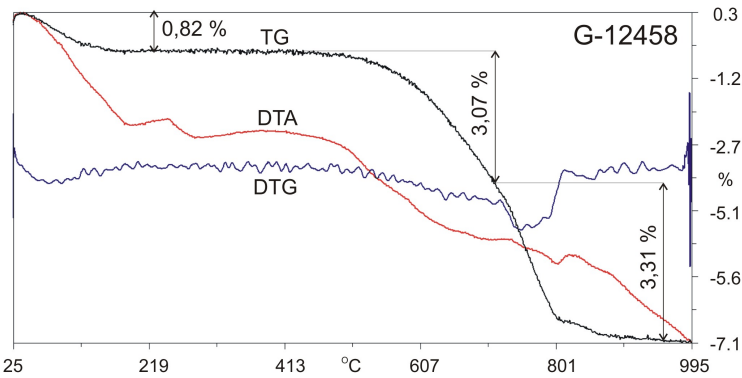


Figure 4: Thermal analysis curves of the albitic BCF (G-12458).

Table 2: Illite crystallinity (Kübler) indices of BCF samples expressed in $\Delta^{\circ}2\theta$ units. AD = air dried; EG = ethylene-glycol solvated; 350 = heated at 350°C. WMA = West Mecsek perianticlinal structure, Gorica = Gorica block.

sample	mineralogy	locality	AD	EG	350
G-12458	albitic	WMA	0.39	0.41	0.36
G-12459	illite-rich	WMA	0.77	0.75	0.59
G-9945	analcimous	Gorica	0.68	0.635	0.55

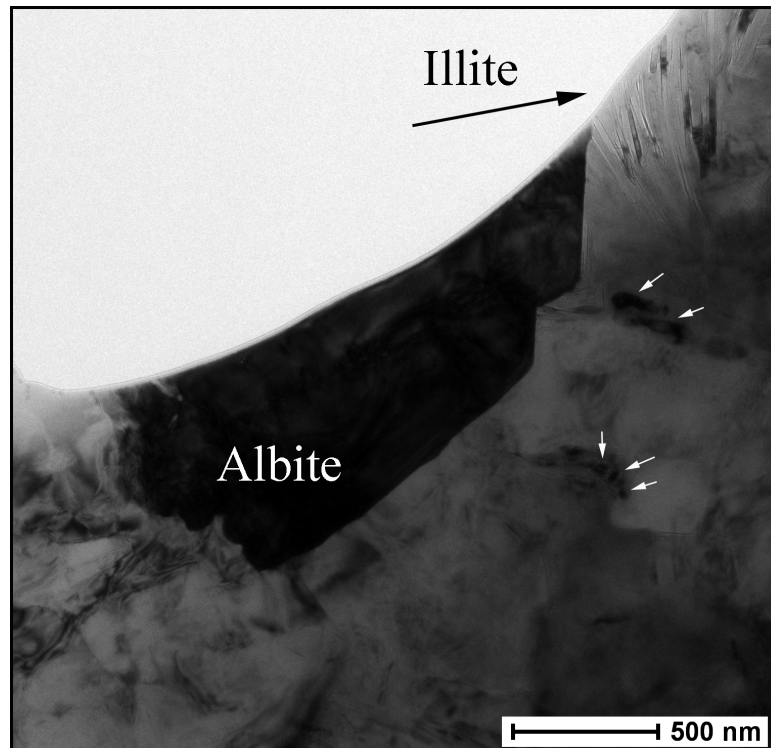


Figure 5: Low magnification TEM image of the albitic BCF with euhedral albite surrounded by illite. The white arrows point to some iron oxide particle.

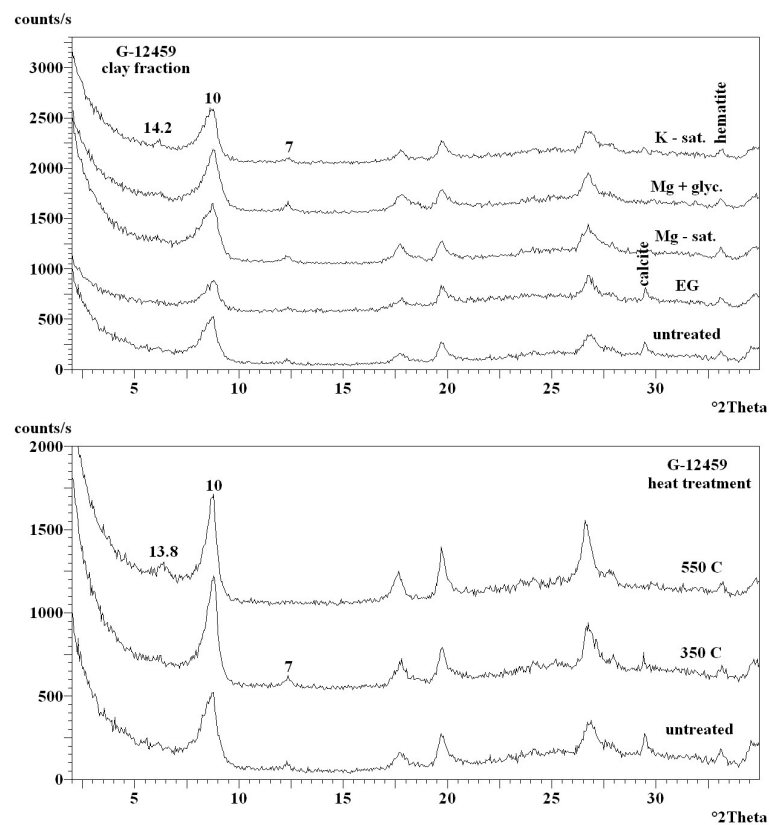


Figure 6: XRD patterns of the clay fraction of illite-rich BCF (G-12459) from Gorica block after the different diagnostic treatments. Numbers on the peaks indicate corresponding d values in Å.

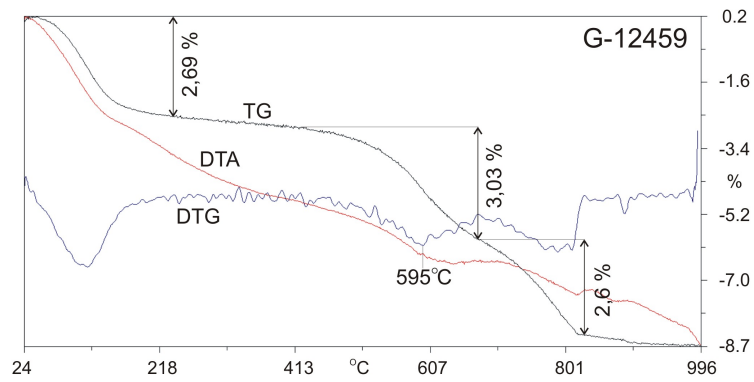


Figure 7: Thermal analysis curves of the illite-rich BCF (G-12459) from Gorica block.

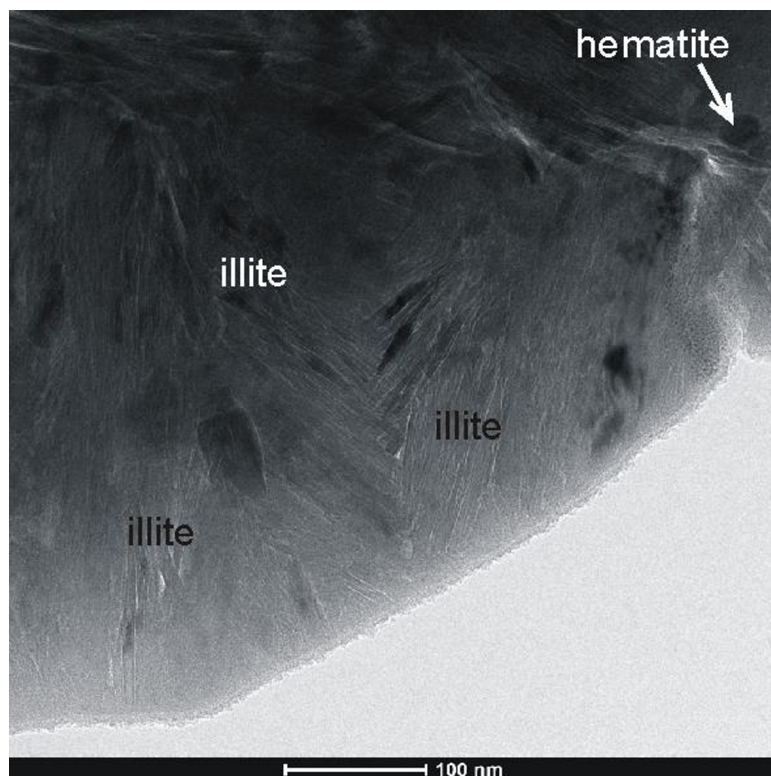


Figure 8: Texture of illitic BCF (G-12459) with illite plates and hematite crystals less than 100 nanometres.

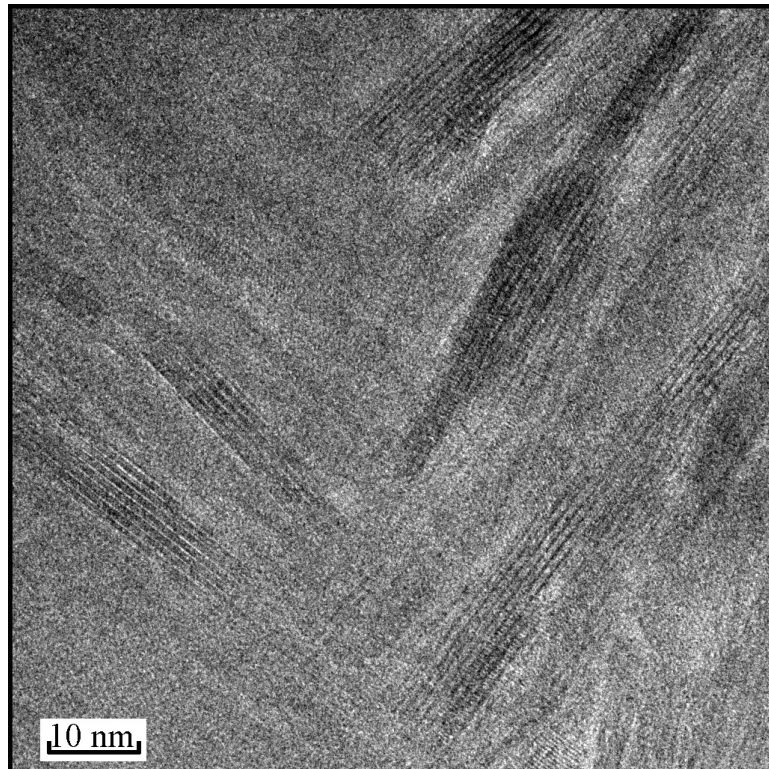


Figure 9: High resolution detail of the image in the Figure 8 showing 4-9 TOT layer thick 2M illite crystallites.

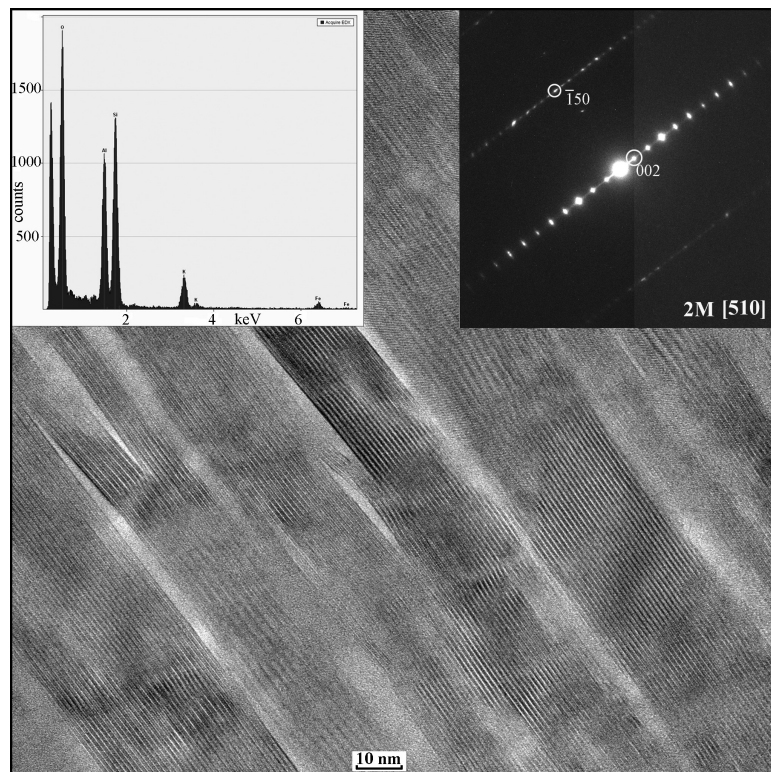


Figure 10: Lattice-fringe image of thicker 2M illite crystallites (SAED patterns inset) (a) and EDX spectrum of an individual 2M illite crystal (b).

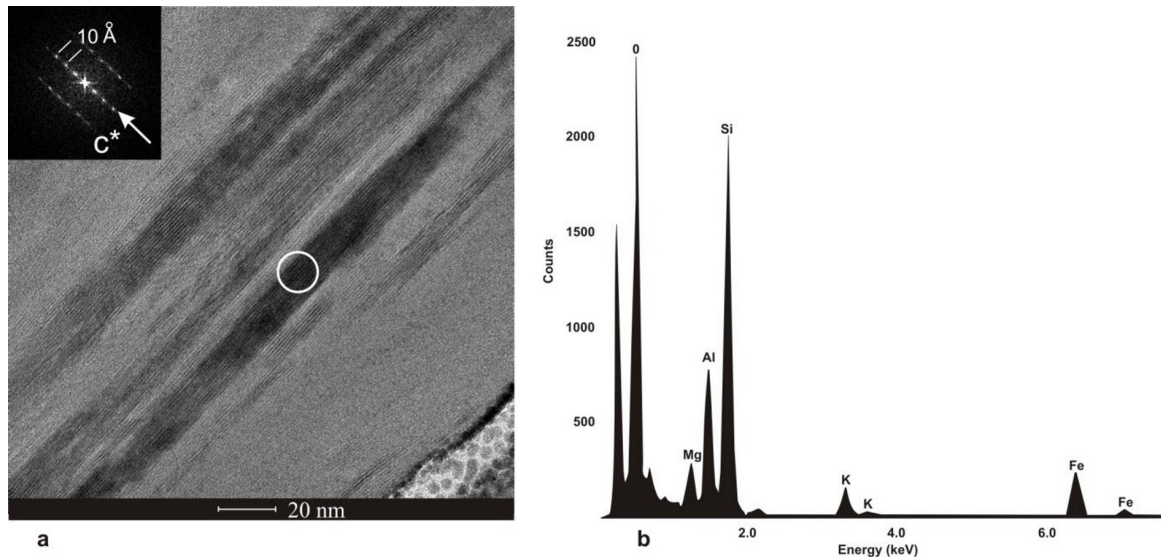


Figure 11: Lattice-fringe image and FFT pattern of the selected circle (inset) of 1M polytype, Fe- and Mg containing illite (a) and its EDX spectrum (b).

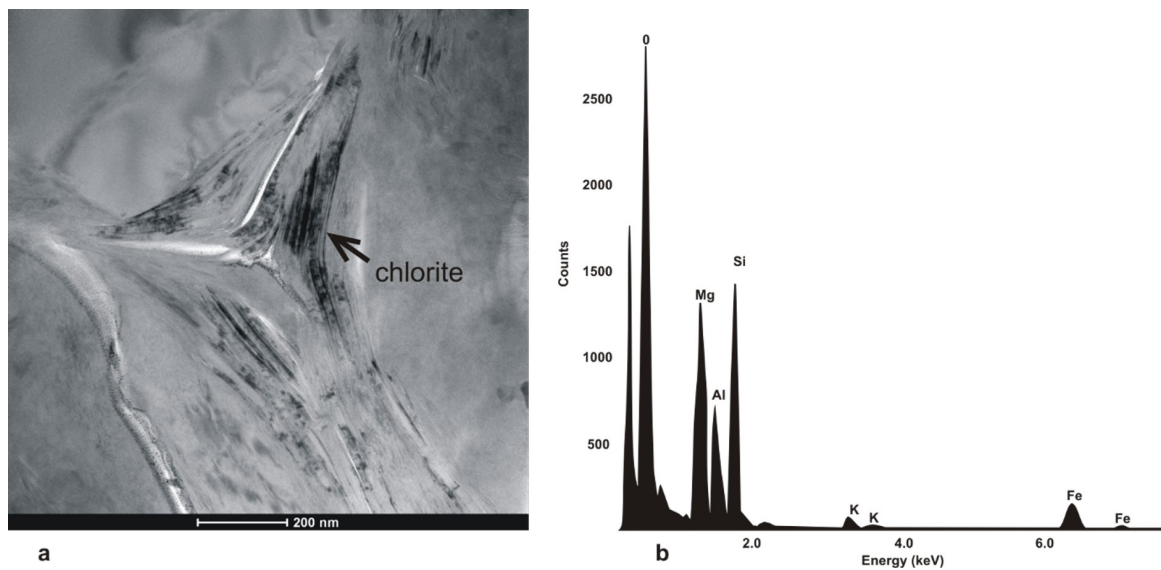


Figure 12: TEM image (a) and EDX spectrum (b) of chlorite in BCF.

swelling component in chlorite. Expansion upon glycerol solvation and that the basal reflection remained at 14.5 after potassium saturation suggest that this swelling component is smectite. According to the Green-Kelly test the layer charge of the swelling component (smectite) is originated from the tetrahedral sheet, so it has beidellitic character. The amount of swelling component in chlorite/smectite mixed layer mineral is around 50 %, as it is suggested also by the formation of a 32 superstructure (16 and 8 reflections occurred too belonging to this phase). The moderate sharpening of the basal 10 reflection of illite upon glycolation suggests the presence of some smectite interlayering, but presumably it does not contain more than 10-15% swelling component. The most important difference between the clay mineral characteristics of the analcimous sample and the other two rock types is the presence of this interstratified chlorite/smectite in amount of 10-20 wt% beside the dominating illite.

Peaks at 2.7, 3.03 and 3.2 on the XRD pattern of the clay fraction prove the presence of hematite, calcite, and albite, respectively. Moreover, 5.59 and 3.42 reflections indicate significant amount of analcime in the clay fraction. Potassium saturation caused the shift and intensity changes of analcime reflections, suggesting that sodium have been exchanged to potassium during the treatment.

The relatively high weight loss up to 220 °C is due to the adsorbed water and/or H_3O^+ content of illite and to the presence of mixed layer chlorite/smectite. Slight weight loss at around 250-300°C can be attributed to analcime [21] (Figure 14).

Based on their morphology, crystal structure and chemical composition, various mineral phases can be distinguished in the analcimous sample by TEM. Illitic clay mineral occurs as 50-150 nanometres sized, thin, irregular flakes (Figure 15) with K deficiency (3.5 at%), as well as with various Mg (6-10 at%) and Fe content (3-6 at%). The Si/Al ratio varies between 1.98-2.15, which is similar to mixed layer illite/smectite containing small amount of swelling component. Its mixed ring-like and spot-like diffraction patterns also suggests this (Figure 15).

Large platy illite crystals with mica-like diffraction pattern lack of turbostratic features can be also observed. The diameter of the plates is around 250 nm, and the thickness of them is in the 10-20 nm range, that is they are built up by 10-20 TOT unit layer. The Si/Al ratio is small (1.6), its potassium content is high (7.6 at%). Additionally, the sample contains uniformly sized illite plates (laterally 250 nm and 10-20 nm thickness), but with disordered structural stacking along the c-axis. It contains less potassium (4.4 at%), at the same time has higher Mg (5% at%) and Fe (10 at%), content associated with higher Si/Al ratio (1.82).

4.3.3 Hematite

Hematite appears not only in the whole rock in 5-10%, but it is a substantial component of the clay-sized fraction too. Presence of hematite supports the oxidative environment during the sedimentation and diagenesis. The presence of hematite differentiate BCF from other claystone formations being potential HLW host rocks. Based on TEM studies, hematite forms 100-200 nm sized euhedral hexagonal tabular crystals. In addition, really nanosized hematite flakes (5-30 nm diameter and 2-5 nm thickness) are closely associated with illite (Figure 16). Hematite flakes lie between packets of clay minerals in parallel to their (001) face. Based on ATEM chemical analysis of individual crystals, hematite contains 0.65 to 2.5 at% titanium.

5 Aspects concerning radionuclide sorption properties

Nature of clay minerals is at least, if not even more important from viewpoint of safe disposal of radioactive waste than their quantity. Considerable volume of BCF is abundant in clay minerals. As mentioned above, the sum of clay mineral content is similar to other potential host rock formations. The clay mineral character of Boda Claystone is fundamentally illitic. Although swelling clay minerals, such as smectites and vermiculites have the largest cation exchange and adsorption capacity among clay minerals [22], illite has special sorption property for large cations with low hydration energy, such as caesium [23]. Illite and other mica-like minerals are excellent caesium adsorbents from low concentration solutions due to the presence of weathered, hydrated crystallite edges [24], the so called frayed edges. Caesium cation is selectively and strongly adsorbed at these frayed-edge sites of illite, but smectites adsorb more Cs^+ [25]. Boda Claystone contains various kind of illite. According to Komarneni and Roy [26], who found that dioctahedral micas are better adsorbent for caesium than trioctahedral ones, Fe and Mg-bearing illite presumably has lower selectivity for Cs, than aluminium-illite in BCF. Nevertheless, illite and illite/smectite expectedly may be good adsorbent for large radioactive cations, such as Cs and Sr. Extreme thinness of illite crystals enhances the uptake of all kind of cations due to the increased specific surface area. Voids which can be seen in Figures 16 and 13a between illite plates partially filled with hematite, and in the centre of triple junction shaped chlorite grains can also improve sorption capacity. Analcime due to its zeolitic structure with large pores also can be a good adsorbent for Cs^+

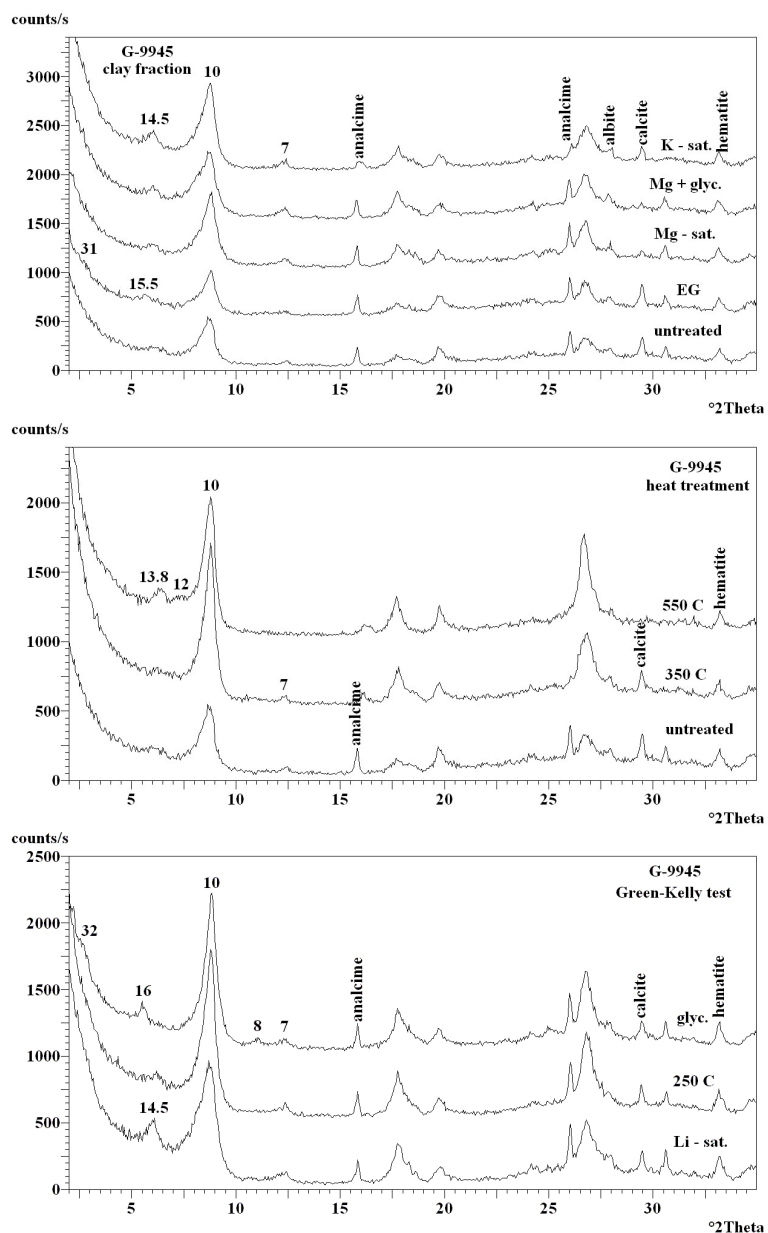


Figure 13: XRD patterns of the clay fraction of analcime-bearing BCF (G-9945) from Gorica block after the different diagnostic treatments. Numbers on the peaks indicate corresponding d values in .

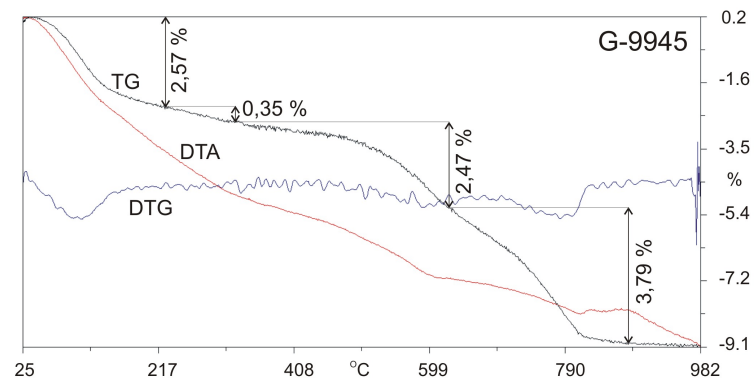


Figure 14: Thermal analysis curves of the analcime-bearing BCF (G-9945) from Gorica block.

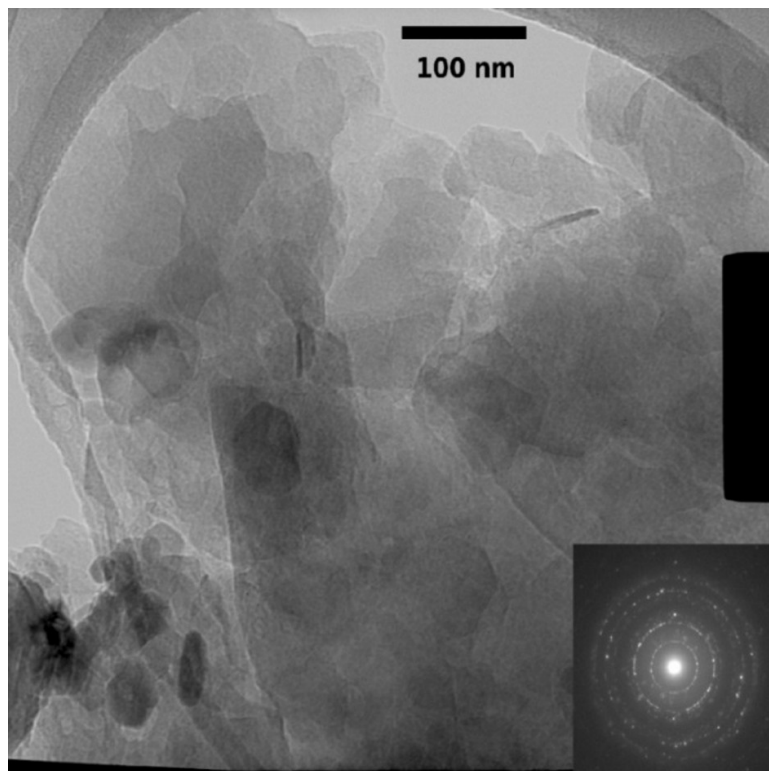


Figure 15: TEM image and SAED pattern (inset) of illite in the analcime-bearing BCF (G-9945).

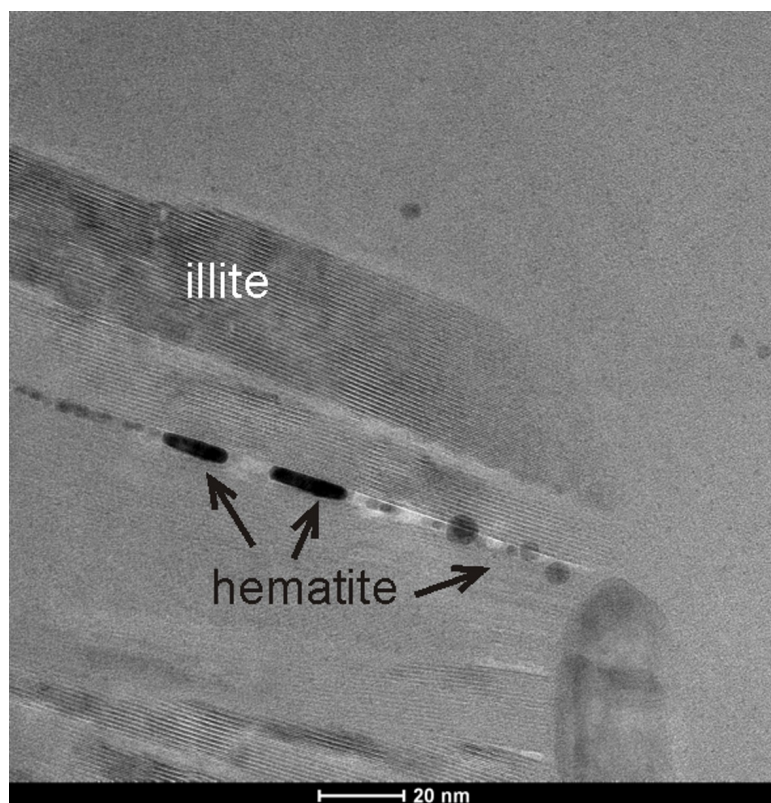


Figure 16: Interesting close association of illite and nanosized Fe-oxides (hematite) in albitic BCF (TEM image).

and Sr^{2+} by ion exchange mechanism, as it was demonstrated by Sipos and co-workers in batch adsorption experiences carried out on the analcime-bearing type of BCF [13]. Hematite probably has significant role in the sorption of iron triad elements (Fe, Co, Ni) and further heavy metals. Hematite has been found by micro-XRF to accumulate nickel in BCF [27]. As it was revealed by ATEM, hematite contains some atomic percent of titanium. Incorporation of Ti^{4+} into hematite results in extra positive charge which is compensated by OH. Consequently, surficial OH groups behave as deprotonable chemisorption sites for various metal cations.

6 Conclusions

Complex XRD, TEM and thermoanalytical studies revealed that the dominant clay mineral of Boda Claystone Formation actually covers the assemblage of various kinds of phyllosilicates: 1M Fe-Mg-illite, 2M illite, some illite/smectite mixed layer clay mineral. Thin particles with potassium deficit and probable interlayer hydronium may suggest the presence of a 10 Å K-smectite, but this must be supported by further studies. Chlorite is the sole other

clay mineral occurring in minor quantity in the WMA facies of BCF. Mixed layer chlorite/smectite is present in the analcime-bearing type of BCF in somewhat significant amount. Fine grained hematite and analcime are noteworthy constituents of the clay fraction. Peculiar feature of is the close coalescence of illite and hematite. Sorption and insulation properties of a claystone cannot be determined without detailed clay mineralogical study. Although BCF does not contain smectite as major clay mineral, it has various mineral phases which could be potentially good adsorbents for radionuclides. Such minerals are: illite, chlorite/smectite, analcime and hematite.

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