Theses of the PhD Dissertation

RESULTS OF MINERALOGICAL, PETROLOGICAL AND GEOCHEMICAL INVESTIGATION OF BODA CLAYSTONE FORMATION

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The aims of the thesis

In the last twenty-five years' of Hungarian geological investigations the Boda Claystone Formation owns an outstanding place (the new name of the formation given by the Paleozoos Subcommittee of the Hungarian Stratigraphic Committee in 2011, its previous name is Boda Siltstone Formation). Within professional circles its short name, BAF is widely accepted. The formation is the deep substratum of the U-ore sequence in Mecsek Mts. (Kővágószőlős Sandstone Formation), therefore it did not gain much attention during the 40 years of uranium ore mining. Consequently there are only a few mineral-petrographic and chemical data about this period (Barabás, 1956; Nagy, 1959; Jámbor, 1964; Fazekas, 1987; Barabás and Á. Barabásné Stuhl, 1998). In the last quarter of the century there has been a major change in the knowledge according to the formation. The thought or proposal that the Boda Claystone Formation could be suitable for establishing the deep-geological storage of the radioactive waste of the nuclear power plant of Paks was conceived in 1983 (Mátrai et al, 1983). The actual researches started in 1989, and the work is ongoing till nowadays with shorter-longer pauses in the financing of PURAM. The Short-Term Research Program's detailed professional planning and professional coordination was made by Mecsek Ore Campany (MÉV), and by its successor MECSEKÉRC Ltd. In the later research phases MECSEKÉRC was and is the Prime Contractor. As the colleague of MÉV and then of MECSEKÉRC Rt. I am taking part in the research programs of BAF since 1990, as a project leader responsible for the laboratory tests. Besides the administrative activities I had important tasks in assembling the laboratory programs for the better understanding of the mineral-petrographic, geochemical, sedimentological features, the formation relationships and the diagenesis degrees of BAF. My PhD research was an integral part of it, and my aims are the following:

- Describing the mineral-petrographic and geochemical features of BAF, highlighting the uncovered facies in the Block of Gorica by Ib-4 deep drilling. The sunk deep drillings of Gorica from the '60s and '70s uncovered only a few ten meters of the claystone, and there were no examinations about them. The Ib-4 drilling, which uncovered the BAF in large thickness, the comparison of the detailed examination of its core material with the anticline faces is inevitable for the coherent characterization of BAF.

- Based on the mineral composition, the texture types, the rock types and geochemical features and on the comparison of them with the help of the analogies of today and of different ages, determining the early and later diagenetic transformation of the formation environment (facies, climate) of the Boda Claystone Formation.
- The evaluation of the results in the light of the aspects of establishing the future deep geological storage.

Relating to the research programs the realization of the pursued objectives of my research was done by detailed thin section study on the chosen samples of the deep drilling's core material, different in their macroscopic nature, and by the joint assessment of the results of further phase analytical and geochemical examinations.

Applied examination methods

Petrographic examinations

In the completion of the set objectives, petrographic examinations were of high importance. During the thin section examinations I defined the mineral components which had a yet determinable size with the help of a polarization microscope, I characterized the defined mineral phases, and I described in detail the texture and structure characteristics of the examined samples.

Instrumented examinations

Mineralogical composition definitions

Based on the macroscopic features and thin section examinations the determinative mineralogical components are clayminerals, carbonates, iron oxide phases; their recognition and the definition of their quantity rates was made by X-ray powder diffraction (XRD) and thermal (DTA) examinations. The main part of the XRD measurements were done in the MTA Earth Science Research Center's Geochemistry Laboratory, then in its successor, the MTA's Astronomy and Earth Science Research Center's Geological and Geochemical Institute (later CSFK GKI).

The thermal examinations were done partly in the Thermal Laboratory of the Geological Institute of Hungary and partly in CSFK GKI.

The definition of feldspar and carbonate mineral types and generations, the chemical composition of the analcime (Gorica block), and the mineral composition of the fine-

grained material separated during the thin section, XRD and thermal examinations were done with electron microprobe analyses in CSFK GKI.

In order to understand the chemical composition, the structure, the potentially intervening layers, the potential transformations in the tectonic zones better, electron microscope examinations (TEM) were made in ELTE's Department of Mineralogy and in CSFK GKI.

Determination of chemical composition

The full rock chemical analyses (main oxide components) were made with X-ray fluorescence methods (XRF) in the accredited laboratory of ISD DUNAFERR Zrt.'s Spectrometric Material Testing Department. In order to recognize the changings in the in formation oxidation-reduction relations and to recognize the carbonate content, their ferrous iron concentration values and CO2 contents were determined in the Geological Institute of Hungary. The loss on ignition value was measured in the accredited Chemical Laboratory of MECSEKÉRC Zrt.

The trace element analyses were made by ICP MS (As, Rb, Y, Zr, Nb, Mo, Cs, Rare Earth Elements, Pb, Th, U, Cd, Hf, Ta), and by ICP OES (Ba, Sr, Co, Cr, Cu, Ni, V, Zn, Li) methods in the Geological Institute of Hungary with LiBO2 excavations.

In order to understand the facies of BAF more thoroughly boron analyses were made from the most representative rock types with PGAA method in the MTA Energy Research Center's Nuclear Analytical and Radiographic Laboratory.

Summary of the new scientific results

1. I verified the albite authigenic formation in the area of the anticlinal formation area (Boda block) by the detailed petrographic analysis of the core of the BAT-4 borehole, supplemented with samples from new drillings deepened during the new research programs and from the BAF section uncovered by Alfa-1 tunnel, and I described its various forms of appearances for the first time, which are the following:

- The matrix material is impregnated by fine-grained albite, which is present in all rock types of the formation in various quantities.
- The reddish brown claystone is the key member of the material which fills in the combined mineral's different shaped and sized pores.

- The anhydrite veins which appear at the lower section of BAT-4 and BAT-5 bores connect with the thin albite layer made of twinned semi-detached, slatted albite crystals with the different rock types of BAF.
- Between the bigger sized mica sheets' cleavage planes is autigene albite.

2. In the anticlinal area I detected the authigenic K-feldspar's presence besides the autigene albite for the first time ever in the pores of the reddish brown pore filling claystones, which is younger than the albite based on the texture natures.

Based on the tissue stamps the albite and K-feldspar formation is the result of early diagenetic processes.The huge albite-content supplies the very favorable mining properties of the formation.

3. Based on the detailed petrographic, mineralogical and geochemical examinations made on the core material of Ib-4 deep bore, I defined the mineral composition, the petrographic and geochemical characteristics of the BAF Gorica block's formation. The main mineral components are: clay minerals (illite/muscovite are the dominant, and besides them chlorite is an always present layered silicate), quartz, albite, analcime, carbonates (calcite is the dominant, dolomite is only present in the interlayers in larger amount), hematite. Analcime is missing from the front side approximately 25,0 m in the transition zone (this features the albite as well), it is present in the approximately 140 m middle section (its maximum value is 15-20 weight percent), and it disappears in the lower, sandstone dominated section. The albite-content is growing gradually downwards, in the bottom sandstone dominated section it's quantity reaches 40 %, which is well signed by the chemical analyses as well. These data prove Na-metasomatism in the Gorica formation.
4. I made the comparison of the BAF sequence's two formation areas. The most important difference in the mineral composition is that in the area of the anticlinal, analcime is missing from the BAF mineral composition, while on the contrary this is the dominant component of the BAF in the area of Gorica block. Analcime has two appearances:

- Fine-grained analcime, which impregnates the matríx material.
- The pore fillings' independent, nearly regular shaped crystals or crystal groups on the wall of the pores.

The other main difference is, that in the Gorica block the autigene K-feldspar is missing, while in the anticlinal area it is a typical member of the reddish brown claystones pore filling mineral combination. Dolomite, as a mineral phase is much inferior in the area of the Gorica block, dolomite interlayers are much rarer, its lack or its minimal presence in the claystones is particularly striking. The results summarized in points 3. and 4. raise the possibility that the two formations of BAF may not relate to the same shallow salt lake (see Conclusions).

5. Based on the quantity rate of the petrographic nature and of the main mineral components (clay minerals, quartz, albite, carbonates and hematite) I separated the following main rock types.

Anticlinal of West-Mecsek:

Reddish brown pore filling ("**albite cavitied**", an often used marker) **claystone**, which is one of the most recognizable rocks and it is separable from the others.

Albitolite. It's most important feature is the albite content, which exceeds 50 %. According to the thin section and electron microprobe examinations the albite pore filling appears only occasionally, almost 100% of the autigene albite is present in the form of impregnation in the rock.

"**Real aleurolite**". The albite pore filling is only rarely observable, the autigene, the very fine-grained albite, and calcite impregnates the stone, and it is present as a binder. The most typical separating stamp of this rock type is the texture, besides the mineral composition. It is always laminar stratified (parallel and cross-stratification). On the border of the laminas very small sized heavy mineral sands can be found.

Dolomite interlayers, which appear in the whole facies of the formation. Besides the dolomite they contain autigene albite varying within wide limits. Their most typical macroscopic feature besides their color and layered structure is desiccation cracks.

Sandstone interlayers. They are typical of the whole formation, but their frequency increases sharply in the transition zone facing the lying Cserdi Formation (Őrházi Member). Their grain size varies from fine to middle. The parallel, flazered, wave ruffled, arched oblique stratification and cross stratification is typical as well. On the border of the layers erases also appear here with very small size.

Gorica block

The Gorica facies of BAF is constructed by rock types similar to the ones that appear in the anticlinal block. **Reddish brown pore filling** ("**Analcime cavitied**", an often

used marker) **claystone** is the prevailing. It is one of the most recognizable to the eye, and it can be well separated from the other rocks. The **dolomite interlayers** are much more rarer in it then in the Gorica facies. Albitolite as a rock type cannot be separated, but the rate of the **aleurolites** and of the **sandstone** (from fine grained to large grained) layers increase heavily. The bottom transition section's sandstones are free from analcime, while the autigene albite's quantity, which impregnates the rock, increases heavily.

6. I detected that on both facies area the pore fillings, which are the characteristics of claystones, the albite, carbonate, K-feldspar (Anticlinal) after rock salt crystals and analcime, carbonate (Gorica) are pseudomorphs filled with mineral combinations. The hematite free fine-grained carbonate and albite based lens, and the sets composed of irregular shaped tubers, prismatic sections are gypsum or after anhydrite pseudomorphs. The dolomite crystals of the dolomite space-settlements based on their characteristic shapes (saddle-shaped crystals, romboeders distorted in the direction of the peaks, distorted and regular star shape) are also after rock salt pseudomorphs. These characteristic tissue elements are clear evidences of the rock salt and sulphate layers' formation, then it's re-dissolution, and they mark the semi-arid-arid climate of the area.

Conclusions

The petrographical (e.g. the pores of claystones, the dolomite layers' dolomite crystals pseudomorphs after rock salt, gypsum, pseudomorphos of albite and carbonate material after andrihite, drying cracks), mineralogical (e.g. analcime, rock salt proved by the pseudomorphs, presence of gypsum), geochemical (e.g. high B and Na2O contents) features prove clearly the formation environment of the Claystone Formation of Boda. The BAF piled up in a shallow salt lake sulphate environment (playa lake, playa mud plains) in a closed basin with no outlets inside the continent in an arid-semi-arid climate. The differences in the mineral composition of the two areas may refer to a basin, in which there were many salt lakes. Today analogies on Earth: e.g. Thar-desert and Lake Lewis in Australia. It can be stated that this environment is not equal to the present East-African salt lakes with alkaline nature (e.g. Natron-lake). The large thickness of the sequence indicates the gradual sinking of the basin. The

upper features prove, that the present rock types separated based on the tissue characteristics, the mineral components and their quantity rates, are the results of complex, multi-staged, diagenetic (mainly early) and soil formation processes. The rock salt gypsum and andrihite layers, crusts went through a re-dissolution process and in their place in many cases dolomite crystals were formed preserving their original shapes, and in the pore fillings pseudomorphs were formed from albite and carbonate. The formation environment, paleoclimate, which is based on the petrographic, mineralogical and geochemical features of BAF, fits well in the Permian palaeogeographic and climatic relations, arid-semi-arid climated basins far from oceans, with no outlets of Middle-Europe outlined by Roscher and Schneider (2006). My results contribute to the refinement of the Tisza Unit's Upper-Paleozoic palaeogeographic picture.

In addition to all of this my results contribute to find the most suitable block for receiving the deep geological storage in the dispersal area of BAF. The mineral-petrographical, geochemical, facies doctrine, tissue, and sedimentological features are basic input parameters of the models, which are parts of the formation's security assessment.

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