



## Geochemistry of bentonite clays from the Eastern Rhodopes (SE Bulgaria): preliminary results

### Геохимия на бентонитови глини от Източни Родопи (ЮИ България): предварителни резултати

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#### Introduction

Voluminous explosive volcanism took place in the Eastern Rhodopes (SE Bulgaria) during Paleogene and large amounts of tephra were accumulated. Both acid and intermediate in composition glass-rich pyroclastic rocks were widely affected by processes of zeolitization and argillization resulting in formation of large zeolite (Djourova, Aleksiev, 1984; Raynov et al., 1997; Yanev et al., 2006, etc.) and bentonite deposits (Atanassov, Goranov, 1988). Bentonite clays originated by transformation of both acid and intermediate glasses as several deposits and many occurrences have been identified (Atanassov, Goranov, 1962; Atanassov et al., 1964, Atanassov et al., 1972, etc.). Bentonite clays associated with acid tuffs (known as first Oligocene acid phase) like Zlatna Livada and Enchets deposits, we refer here as A-bentonites. Bentonite clays developed on the expense of intermediate volcanic glass like Propast-Dobrovolets deposit hosted by the second intermediate volcanic phase, are referred as I-bentonites, respectively. Due to their wide application in the industry bentonite clays in Bulgaria have been an object of intensive studies since 60s of the last century but there are no published data on their trace and rare-earth elements contents. In this work we report data from LA-ICP-MS analyses of 7 bentonite samples from the Eastern Rhodopes as three of the samples come from two bentonite deposits – Zlatna Livada and Propast-Dobrovolets.

#### Material and methods

The two analysed samples (A-ZL and A-Ba) from A-bentonites have been collected in a small quarry

located to the north-east of Zlatna Livada village (Chirpan district) and to the south of the town of Kardzhali, near Balabanovo village. The I-bentonites have been sampled to the east and south of the town of Kardzhali. Two samples (I-PD<sub>i</sub> and I-PD<sub>b</sub>), collected near Sedlovina village and just to the south of Kardzhali suburbs, represent respectively the topmost and lowermost parts of the interval hosting Propast-Dobrovolets deposit. The three additional samples (I-Gr, I-Gl and I-Sv) were collected further south near the villages of Gruevo, Gluhar and Svoboda. Whole-rock samples have been analysed for major oxides using XRF spectroscopy in Bureau Veritas Mineral Laboratories (Canada). Trace elements have been measured in the Geological Institute, Bulgarian Academy of Sciences. The LA-ICP-MS system used consists of a 193 nm ArF excimer laser (ATLEX-SI, Germany) linked with an ELAN DRC-e ICP-MS instrument (Perkin Elmer, Canada). The analyses were performed with 100 µm ablation pits on fused pellets with lithium tetraborate at 1050°C. External standardization on NIST glass standard SRM-610 allows linear drift correction of the spectrometer and provides relative element concentrations. These element concentrations were transformed into true values by internal standardization (a known concentration of Si, determined by XRF) using “Sills” program (Guillong et al., 2008) for data reduction. The XRD measurements have been carried out in the Geological Institute, Bulgarian Academy of Sciences using HUBER Image Plate Guinier Camera G670 (40 kV and 40mA, step size of 0.005 2θ with Ge monochromator on primary beam providing pure Cu Kα<sub>1</sub> radiation; diffraction data were collected in the range of 4–100 °2θ,

simultaneously) and Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, using D2 Phaser – Bruker AXS Bragg-Brentano diffractometer operated at 30 kV and 10 mA with a step size of 0.05 2 $\theta$  and a counting time of 1 s/step.

## Results

The analyzed samples display differences in major-element abundances between bentonites developed on acid and intermediate volcanic precursor as well as noticeable variation within the group of I-bentonites. Except being richer in SiO<sub>2</sub> (up to 73.73%), A-bentonites are depleted in TiO<sub>2</sub> (0.08–0.19%), Fe<sub>2</sub>O<sub>3</sub> (0.78–1.65%), MgO (1.69–1.81%) and P<sub>2</sub>O<sub>5</sub> (0.14%). I-bentonites show variable contents of Fe<sub>2</sub>O<sub>3</sub> (5.76–9.54%), MgO (2.89–5.18%), K<sub>2</sub>O (1.72–5.19%) and Na<sub>2</sub>O (0.13–3.03%). Two samples (A-Ba and I-Gr) have high LOI values (16.1% and 14.7%), and display lower SiO<sub>2</sub> contents – 50.49% and 50.38%, respectively. These two samples are enriched in CaO, especially A-Ba – 17.5%. The variations in major-elements abundances are due to differences in precursor glass composition, some diversity of primary and authigenic mineral assemblages (Table 1) as well as possible variation in composition of the major rock-forming phase – montmorillonite (Atanassov, Goranov, 1988; Yanev et al., 2004; Ilieva, 2007). For example, samples rich in CaO contain calcite; zeolites fix some more sodium in sample I-Sv (Na<sub>2</sub>O – 3.03%).

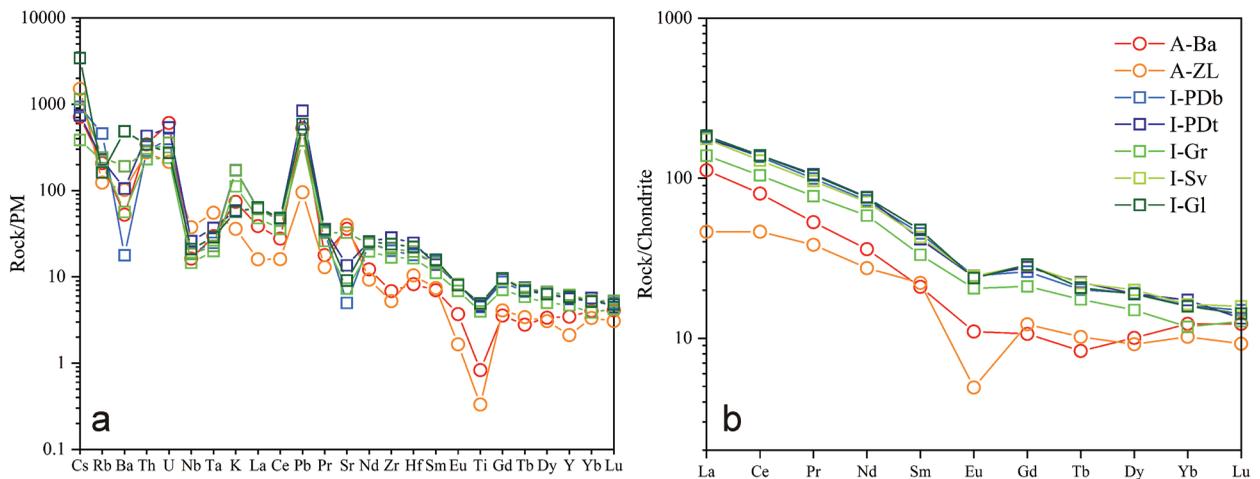
Trace elements distribution patterns of the studied samples have downward-sloping primitive mantle-normalized profiles with LILE enrichment, negative Ti anomaly and positive U-Th and Pb anomalies (Fig. 1a). The negative Ba anomaly is not well expressed in all samples and is even missing in sample I-Gl. Chondrite-normalized profiles are LREE enriched compared to HREE, with negative Eu anomaly (Fig. 1b), which is stronger

in A-ZL. The contents of the compatible in the magma processes elements (Ni, Cr, Co, Sc, Eu<sup>2+</sup>) are low and relatively uniform. The highest contents of Ni and Cr are registered in A-bentonites, 18.5 ppm (in A-Ba) and 86.4 ppm (in A-ZL), respectively. The I-bentonites are slightly enriched in Co (11.6–17 ppm), Sc (12.8–18.9 ppm) and Eu (1.15–1.38 ppm). The other transitional elements as Cu and V are also enriched in I-bentonites. Some of the incompatible elements (Ba, Sr) behave as compatible in respect to some primary magmatic minerals (Bt, Fsp) present in the studied samples. The contents of Ba are higher in the samples enriched in crystal clasts, and especially, of lava lithics (I-Sv – 1335 ppm, I-Gl – 3405 ppm), while Sr is more abundant in A-bentonites (758–837 ppm). Rubidium and Cs are highly incompatible during magma crystallization and the results obtained indicated they remain incompatible during the bentonitization of the volcanic glass: the contents registered are low and relatively uniform (Rb 78–150 ppm; Cs 3–27 ppm). It seems they prefer other secondary minerals (as adularia and clinoptilolite) present in small amounts in some of the studied samples (Table 1). Accordingly, some minor enrichment of Rb (290 ppm) is registered in sample I-PD<sub>b</sub>, that contains some adularia (Yanev et al., 2004). However, the highest value of Cs (27 ppm) was not measured in the richest in zeolites sample. The behavior of HFS elements in magmas is controlled by accessories and, respectively, the I-bentonites are relatively enriched in Zr (187–318 ppm), Hf (5–7.6 ppm), and REE ( $\Sigma$ REE 150–199 ppm). The other HFS element (U, Th, Nb, Ta) are present in detectable amounts in all samples but their variation seems mostly random (U 4.5–12.7 ppm; Th 19–36 ppm; Nb 10–26 ppm; Ta 0.8–2.3 ppm). The only exception is A-NZ sample, showing highest contents of both Nb and Ta. The highest  $\Sigma$ REE value (199 ppm) is obtained for I-Gl and it is probably due to amphibole presence.

Table 1. Mineral assemblages in the studied samples based on XRD data of bulk samples and microscopic observations of thin sections

Sample	Pl	Kfs	Bt	Qz	Amp	Lithics	Mnt	Cpt	Anl	Cal	O-CT	Php?	Ilt	Adl
A-Ba	+	+		+	+	+	+	+		+	+		+	
A-ZL	+			+			+	+			+			
I-PD <sub>b</sub>	+			+			+	+		+			+	+
I-PD <sub>t</sub>	+	+					+	+		+				
I-Gr	+	+	+				+		+					
I-Sv	+	+				+	+	+	+		+			
I-Gl	+	+		+	+	+	+		+	+			+	

Notes: the primary magmatic components are shaded; O-CT, Opl±Crs±Trd; the mineral name abbreviations are after Whitney, Evans (2010)



**Fig. 1.** *a*, primitive mantle-normalized trace-element spider diagram; *b*, chondrite-normalized REE diagram of bentonite clays from the Eastern Rhodopes. The normalization values are from Sun and McDonough (1989).

## Conclusions

The obtained results show no significant accumulation of trace elements in the studied samples. Their overall chemical composition is strongly influenced by the volcanic glass chemistry, the presence and abundance of magmatic minerals and lithic clasts and to lesser extent by secondary authigenic mineral associations. Respectively, their trace element signature is similar to that of the unaltered extension-related orogenic volcanic rocks in the Eastern Rhodopes. No correlation between any of the trace elements measured and the relative montmorillonite abundance (in samples A-ZL and I-PD) have been established. Nevertheless, these data complete the knowledge of bentonite clays from the Eastern Rhodopes; they can shed more light on the connection between volcanic precursors and alteration products and can provide deeper insight into the process of glass transformation.

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