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COMPARATIVE MINERALOGICAL CHARACTERISTICS OF KAOLIN SANDS FROM DOULOVO AND TERVEL REGIONS - NE BULGARIA

VIOLETA TODOROVA

Institute of Applied Mineralogy, 92 Rakovski str., 1000 Sofia, Bulgaria

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Abstract: On the basis of data from analyses (particle-size, mineralogical, morphological and morphostructural) considerable differences are observed in the mineralogical and particle-size composition of the sands. Tervel sand is more coarse-grained and unique with the presence of feldspars - microcline, orthoclase, plagioclase (up to 40 %). Doulovo sand is more fine-grained, without feldspar, but anatase, rutile and muscovite are more abundant than in Tervel sand. Kaolinite is the essential clay mineral, but smectite is determined only in the Tervel clay. The elemental composition of the clay fractions <2 μm (bulk), 1 - 2 μm and <1 μm were analyzed. In the Doulovo clay the mean Al : Si ratio is higher. Na_2O, CaO and MgO are present only in Tervel clay.

Key words: kaolin sands, clay minerals, X-ray diffraction DTA, chemical composition.

Introduction

The area covered by kaolin sand in NE Bulgaria is about 3500km^2. Kaolin sands are related to the sedimentary deposits of the Moesian Platform and overlie a denuded Early Cretaceous basement complex. The relief was formed by karstification. It is built by positive and negative forms. The textures of the carbonate rocks are complicated. The so-called "mantel" clay is located at the bottom of the industrial deposits and they follow the karst relief. The width changes from several cm up to 20 m. The "mantel" clays have high contents of kaolinite and iron minerals. The productive formation has quite a variable morphology and thickness (from several cm to 100 - 130 m). Some authors propose that the sand from Tervel region is Middle Sarmatian (Kostadinov et al. 1962) while the Doulovo deposits - Aptian or Pliocene(?). There are no paleontological data to give an explicit answer. The formation is represented by quartz sand, kaolinite clay, glauconitic sand as lens or rarely layers. There are two large zones of intensive karst processes - Vetovo-Senovo and Kaolinovo-Doulovo (Karavasteva et al. 1980). They are divided into six regions (Fig. 1):
Vetovo region, Senovo region, Kaolinovo region, Isperih region, Doulovo region (DR), Tervel region (TR).

The covering Quaternary deposits have a thickness from 1 - 2 to 30 - 35 m, and consist of loam and clayed loess.

Materials and methods

The object of present study is to determine the differences and resemblances between the kaolin sands from the TR and DR. Nine borehole samples from the Doulovo and Tervel regions were chosen for this study. The particle-size analysis based on Krumbein's ϕ-scale and classification of Wentworth were used when the particle size composition was determined. The following fractions were separated: <0.002, 0.002 - 0.004, 0.004 - 0.008, 0.008 - 0.016, 0.016 - 0.032, 0.032 - 0.063, 0.063 - 0.125, 0.125 - 0.250, 0.250 - 0.50, 0.50 - 1.00, 1.00 - 2.00 and >2.00 mm. The clay fraction below 0.002 mm was separated by sedimentation, dried at 80 °C.

The heavy constituent part was extracted from fractions 0.063 - 0.125 and 0.125 - 0.250 mm. The mineralogical composition of the obtained fraction was determined by X-ray powder diffraction on DRON, CoKα, while the light fraction was characterized by optical microscope MIN.

Mineralogical compositions of the clay fraction were determined by X-ray diffraction. A DRON-1, CoKα radiation at 35kV and 30mV was used to analyze six randomly oriented specimens sedimented on glass slate. The <2 μm (bulk), 1 - 2 μm or <1 μm fractions were examined in air dried state, saturated with ethylene glycol and heated at 550 °C for 2h. The relative abundance of the clay minerals was determined according to the methods and data of Thorez (1975).

A SEM-Philips 515 was used to study the surface texture and morphometric parameters of the quartz particles. The degree of sphericity was determined by using the program image analyzer SEM (Weibel 1980) was determined a degree of sphericity

$$\sigma = \frac{4\pi\ A}{P^2}$$

where A is the area of a particle, P is the perimeter of a grain. When $\sigma = 1$, the particle has a spherical form.

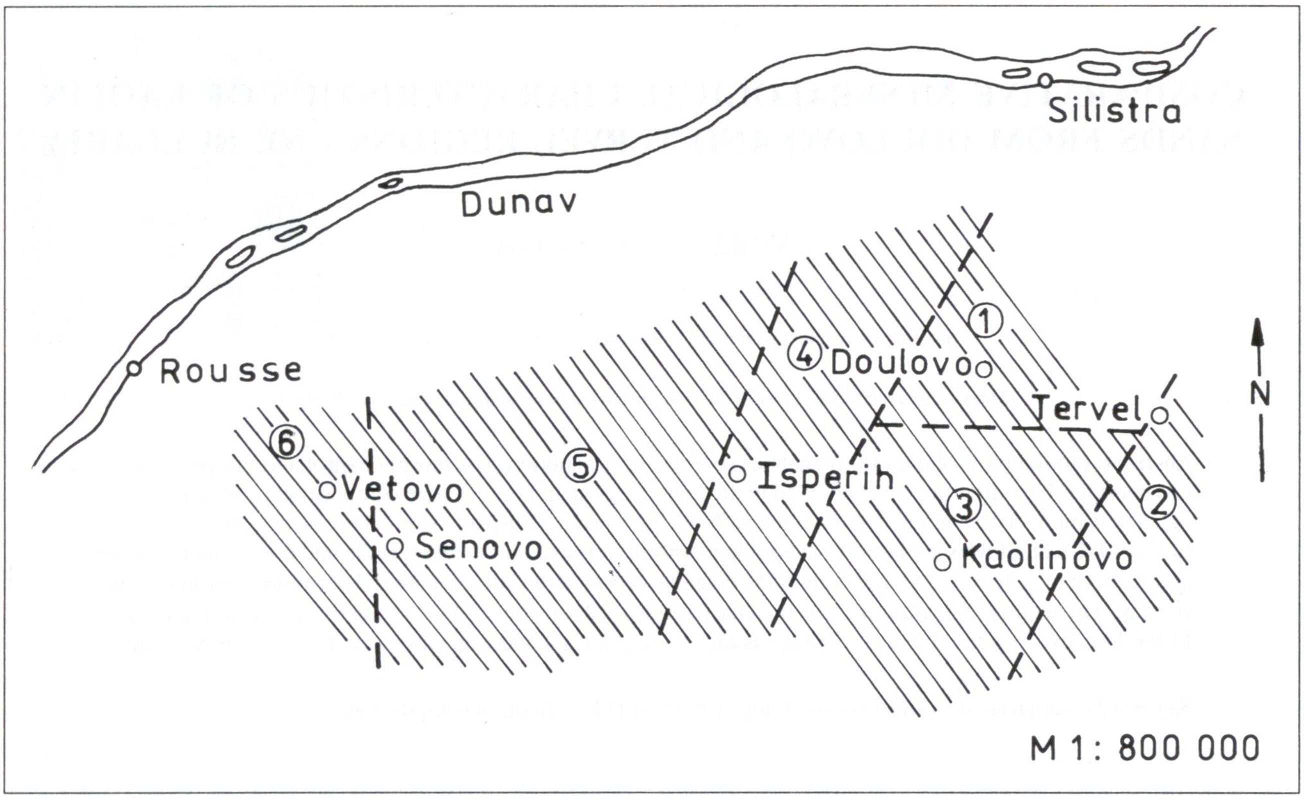

Fig. 1. Simplified map of kaolin sand deposits in NE Bulgaria.
1 - Doulovo region, 2 - Tervel region, 3 - Kaolinovo region, 4 - Isperih region, 5 - Senovo region, 6 - Vetovo region.

The <2 μm fractions were chemically analyzed by SEM-Philips 515 equipped with an appliance EDAX analyzer.

The DTA and TG curves were obtained simultaneously using STA-1500, Stanton Redcroft, apparatus with a heating rate of 10° min^{-1}.

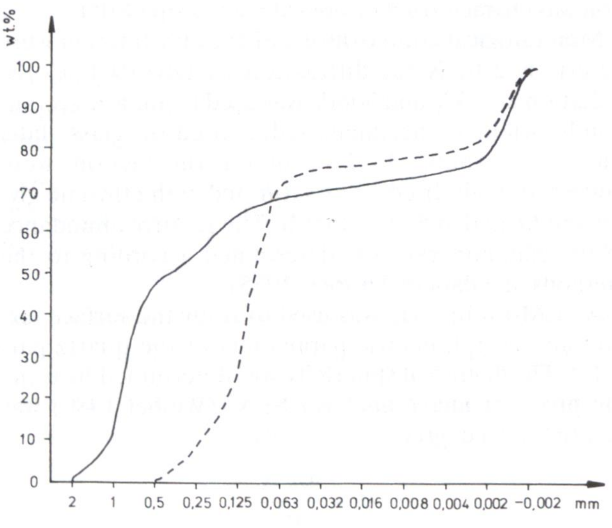

Fig. 2. Particle size distribution curves.
— Tervel region, - - - Doulovo region.

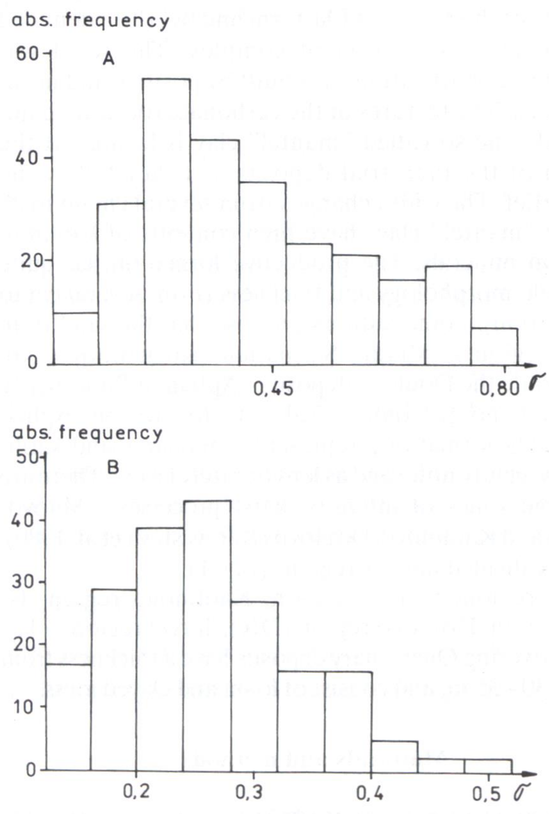

Fig. 3. Histogram morphometry ofquartz grain fomrs.
A - Tervel region, **B** - Doulovo region.

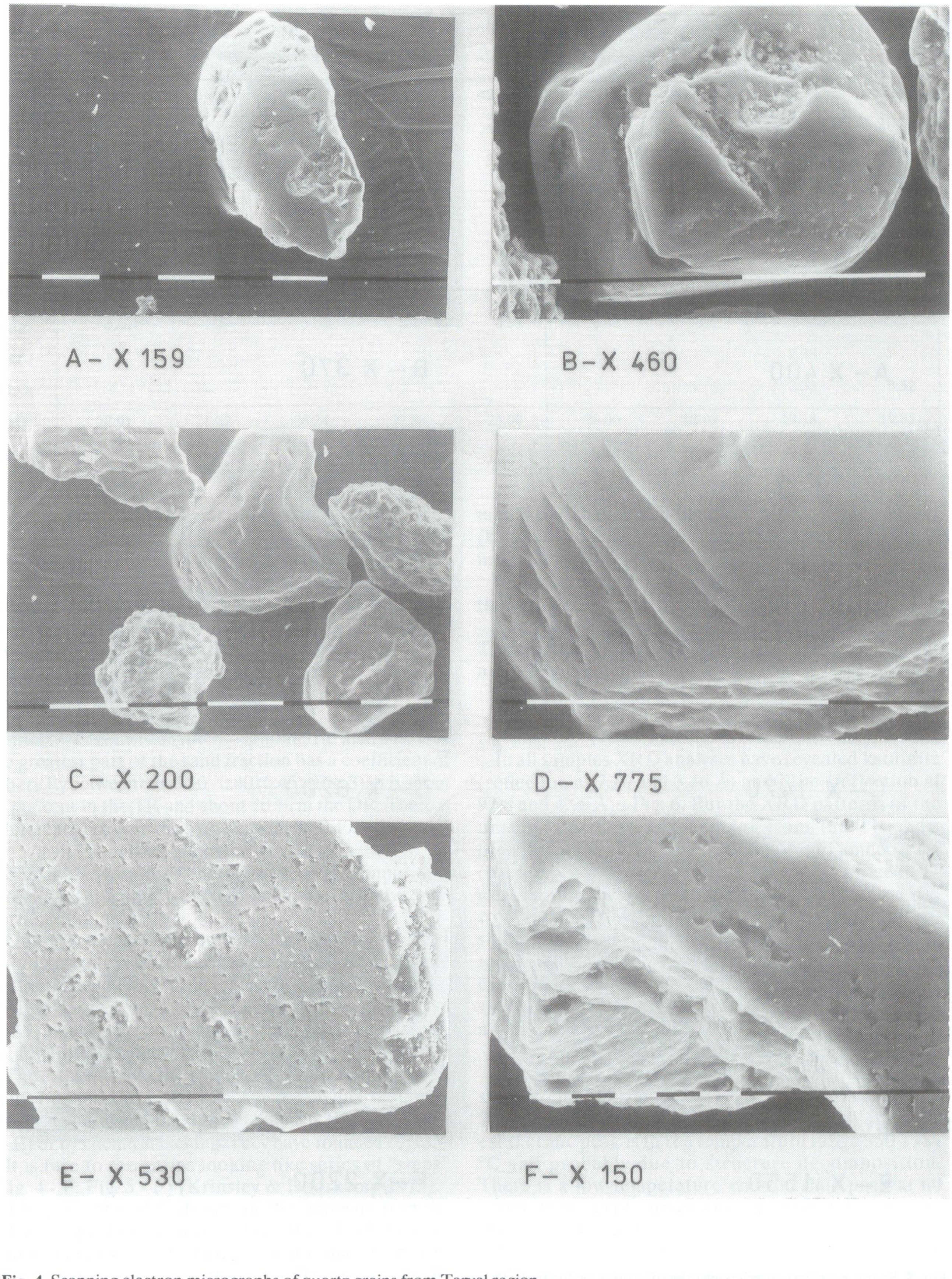

Fig. 4. Scanning electron micrographs of quartz grains from Tervel region.

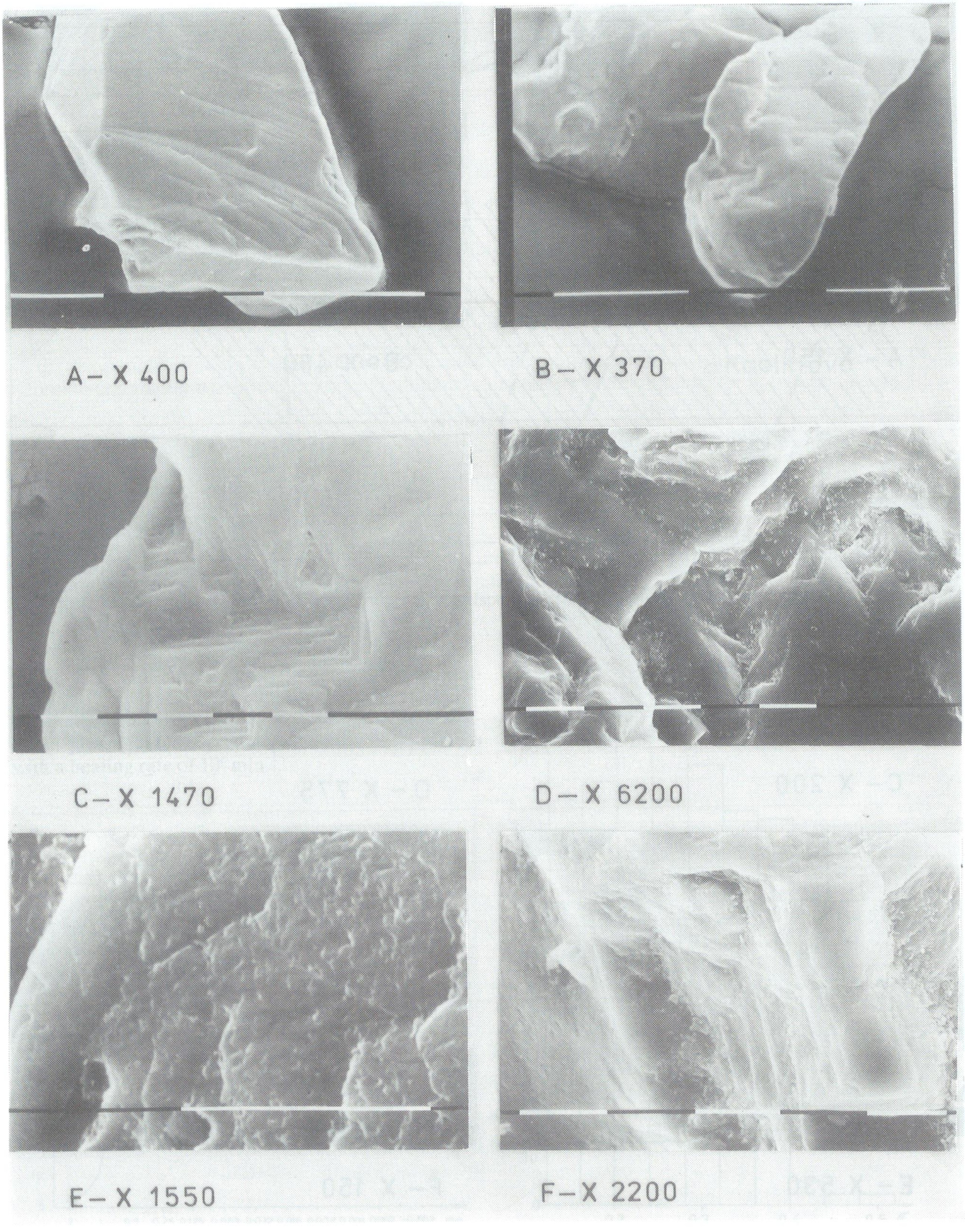

Fig. 5. Scanning electron micrographs of quartz grains from Doulovo region.

Table 1: Chemical composition of clays.

	Doulovo region					Tervel region			
	1	2	3	4	5	1	2	3	4
wt.%	<1μm	1-2μm	<1μm	<2μm	<2μm	1-2μm	<1μm	<2μm	<2μm
SiO_2	43.69	44.58	41.81	40.30	42.63	61.35	49.86	53.52	46.26
Al_2O_3	31.97	32.34	31.35	31.36	31.70	15.80	25.58	21.91	29.29
Fe_2O_3	0.87	0.77	0.30	-	-	1.69	3.43	-	3.05
TiO_2	0.12	-	-	-	-	0.49	0.54	0.28	-
CaO	-	-	-	-	-	-	0.42	-	-
MgO	-	-	-	-	-	-	1.27	-	0.58
K_2O	0.84	1.09	0.30	0.45	0.66	0.66	0.81	0.40	0.64
Na_2O	-	-	-	-	-	-	-	2.38	-
Cl_2O_7	-	-	-	-	-	-	-	2.33	0.32
H_2O	22.91	21.22	26.24	27.88	25.00	20.00	18.09	19.18	19.85
Al:Si	0.87	0.86	0.88	0.92	0.88	0.30	0.60	0.48	0.75

Results and discussion

The grain-size distribution is shown on the cumulative curves (Fig. 2). The sand fromthe TR is classified as a course sand but it is fine-grained in the DR. The aleurite component (0.063 - 0.002 mm) has a relatively low content while clay fraction increases sharply.

Sand fraction

It can be seen from the morphometric analysis, that the greatest part of the sand fraction has a coefficient of sphericity between $\sigma = 0.10 - 0.40$ (0.45) (Fig. 3). It is about 60 per cent in the TR and about 70 % in the DR. There is a difference between the particles with $\sigma > 0.40$. It decreases to 15 % in TR but it is approximately 30 % in the TR.

The investigation of the mineralogical composition shows a significant distinction in the quantitative proportion of minerals.

Quartz is the main mineral in both regions with identical disturbances of its surface texture (Figs. 4, 5). The disturbances of the surface texture have negative and positive forms (Fig. 4 - A, B, C, D; Fig. 5 - A, B, D). On some of quartz grains relatively well preserved conchoidal fracture is noticeable (Fig. 4 - A, B).

The other characteristic features are numerous V-shaped patterns irregularly distributed on quartz surface. Probably they are formed by the impacts (Fig. 4 - E; Fig. 5 - E) or by chemical etching. They have rounded edges.

It is rare to see grains looking like series of "steps" (Fig. 4 - F; Fig. 5 - F) (Krinsley & Doorkamp 1973).

The presence of feldspars in the deposits fromthe TR distinguishes them from the other. Feldspars are found everywhere but their content ranges from 1 to 40 %. Orthoclase, microcline and plagioclase are established. They are affected by secondary processes (kaolinitization and sericitization) the intensity of which increases w ith depth.

Quantitatively, there is more muscovite in the DR than in the TR.

The heavy minerals are identified in both regions. They are zircon, rutile, anatase, iron minerals (magnetite, pyrite), iron-rich biotite.

Clay fraction

In all samples XRD analyses have revealed kaolinite (reflection at 7.20 and 3.56 Å) and illite (reflection at 9.98 and 4.98 Å) - Fig. 6. But the XRD patterns of the untreated oriented specimens from the TR show broad peak at 14,41 Å. It may belong to smectite or chlorite. That is why, different treatment procedures were very important for the identification of these two components. Samples treated with ethylene glycol show reflection at 16,99 Å. The layer spacing decreases to 9.98 Å after heat treatment at 550 °C. Therefore, the clay mineral association of the Tervel area is kaolinite, smectite and illite, but at Doulovo - kaolinite and a small admixture of illite.

The clay fraction also contains quartz.

All the DTA curves of the clay fraction from the TR show an endothermic effect between 507 - 513 °C (Fig. 7). The peak indicates dehydration of minerals. The exothermic peak is in the temperature range 950 - 984 °C and probably due to structure decomposition. There is a low-temperature endothermic peak at 60 - 70 °C in the DTA curves which correspond to the separation of adsorbed water.

The clays from the DR show a typical DTA curves (Fig. 7). The endothermic peak is at around 526 - 535 °C and the

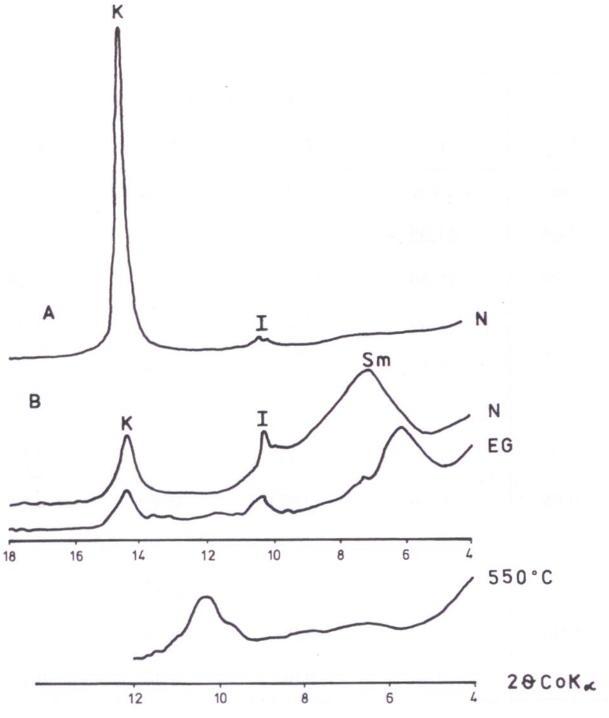

Fig. 6. XRD patterns of clay fraction. **A** - Doulovo, and **B** - Tervel region.
K - kaolonite, I - illite, Sm - smectite.

exothermic peak at 996 - 1004 °C. The differences between the DTA curves of clays fromthe TR and DR may be due to smectite and illite which are characteristic of the TR.

The chemical composition of clay component is given in Tab. 1. The Al : Si ratio is considerably higher in the DR (lower in the TR). The content of SiO_2, Fe_2O_3 and TiO_2 is higher in kaolinite from the TR while K_2O from the DR slightly outweighs that in the TR. Na_2O, CaO and MgO are reported only in clay from the TR.

Conclusion

The following conclusions can be reached, based on the results:

1 - The differences in the granulometric composition were well expressed in the sand component. The material from the TR is coarse-grained, while it is fine-grained in the DR.

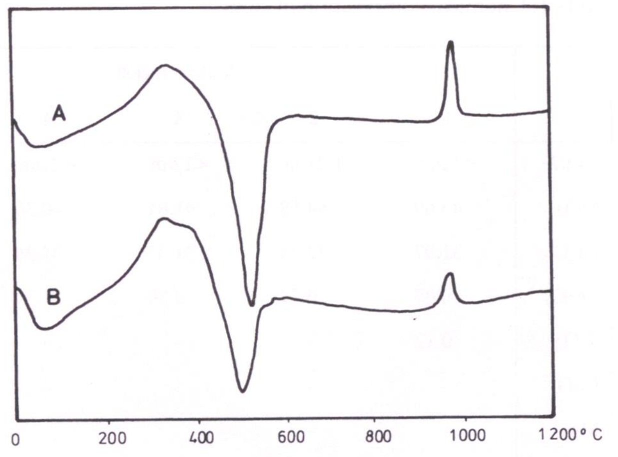

Fig. 7. DTA curve. **A** - Doulovo, **B** - Tervel region

2 - Sand from the TR have two main components - quartz and feldspar with insignificant amounts of mica and heavy minerals.

3 - The phase composition of the $<2\,\mu m$ fraction was determined and characterized by XRD and DTA. Kaolinite was found to be the dominant mineral in all samples. Illite was established as a mixture in small quantity. Smectite was present only in clays from the TR.

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