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Mineralogy and geochemistry of Upper Miocene pelitic sediments of the Zagorje Basin (Croatia): implication for evolution of the Pannonian Basin

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Abstract: According to X-ray powder diffraction analyses of Upper Miocene pelitic sediments from the Zagorje Basin all of the samples contain same mineral species, but in significantly different quantities. Calcite is a dominant component in most of the samples (31–74 wt. %), clay minerals (18–50 wt. %), quartz (5–21 wt. %) and feldspars (1–5 wt. %) are less abundant, while dolomite and pyrite are present only in a few samples. Among clay minerals, in < 2 μm insoluble residue fraction, smectite, illite, chlorite and kaolinite were determined. The dominant constituents in 0.09–0.16 mm fraction, as determined by optical microscopy, are quartz, feldspars, rock fragments (chert, quartzite and schists) and micas. Chlorite, limonite, pyrite, garnet, tourmaline, zircon, epidote and staurolite are present as heavy minerals. Pelitic sediments within older (Upper Pannonian) investigated sediments are, in accordance with the mineral composition of insoluble residue and $CaCO_3$ content, classified as marls, while those in the younger (Lower Pontian) sediments are silty marls. The observed gradual decrease in carbonate content, and simultaneous increase of clayey-silty component, going from older to younger deposits, is the result of the gradual increase of terrigenous influence. Mineral composition of marls together with elemental ratios critical of provenance (SiO_2/Al_2O_3, K_2O/Na_2O, Eu/Eu*, La/Sc, Th/Sc, Th/Co, Th/Cr and La/Co) and source rock discrimination diagrams (Fe_2O_3-K_2O-Al_2O_3 and La-Th-Sc), point out that source rocks were from the Upper Crust and remarkably felsic in nature. The chemical composition of the sediments and modal composition of silt-size fraction indicate Alpine provenance of the clastic material.

Key words: Upper Miocene, Zagorje Basin, chemical composition, clay minerals, marl, X-ray diffraction.

Introduction

The composition and provenance of the detrital material, which was deposited during Late Miocene in the Croatian part of the Pannonian Basin System (PBS), were studied in detail by Šćavničar (1979), Šimunić & Šimunić (1987), Kovačić (2004) and Kovačić et al. (2004), Kovačić & Grizelj (2006). However, due to the fact that their investigations were focused on medium- to coarse-grained clastic sediments, the petrology, mineral composition and provenance of Upper Miocene pelitic sediments from the Croatian part of the PBS is still obscure.

On the contrary, numerous investigations dealt with mineral composition, provenance and diagenesis of pelitic layers within the Hungarian part of the PBS. These investigations (Varsányi 1975; Viczián 1975, 2002; Tanács & Viczián 1995) showed that pelitic sediments contain illite, smectite, illite/smectite, chlorite and kaolinite. According to Viczián (2002) in the Great Hungarian Plain clay mineral composition was basically the same: a polymineral detrital clay mineral suite displaying slight systematic regional differences, with no significant differences in composition of different stratigraphic horizons in the time span from Late Pannonian to Late Pliocene–Pleistocene. Detrital clay minerals were transported from neighbouring Carpathian and Alpine areas. Sub-basins may differ in degree of disorder and quantitative proportion of clay minerals and quantitative relations of other phases like calcite, dolomite, quartz and feldspars depending on relatively permanent source areas and transport direction.

The aim of the work was to investigate mineral and geochemical characteristics of Upper Miocene pelitic sediments from the Zagorje Basin, a sub-basin located in the south-western marginal area of the PBS, in the north-western part of Croatia (Fig. 1). Investigations were performed on the samples collected from two localities, Pušća and Kupljenski Hruševec (Fig. 2). The stratigraphic attributions given in Fig. 2, which are used in the article, have doubtful chronostratigraphic value due to the fact that age determination of the sediments was based on their fossil content.

The main aim of the paper was determination of the mineral composition of pelitic sediments and reconstruction of their provenance based on their mineral and chemical characteristics. Correlation of the results with those obtained in the neighbouring, Hungarian part of the PBS is planned.

Geological setting

The Miocene deposits of the Zagorje Basin belong to the south-western marginal belt of the PBS. The PBS, which belongs to the Central Paratethys, comprises several

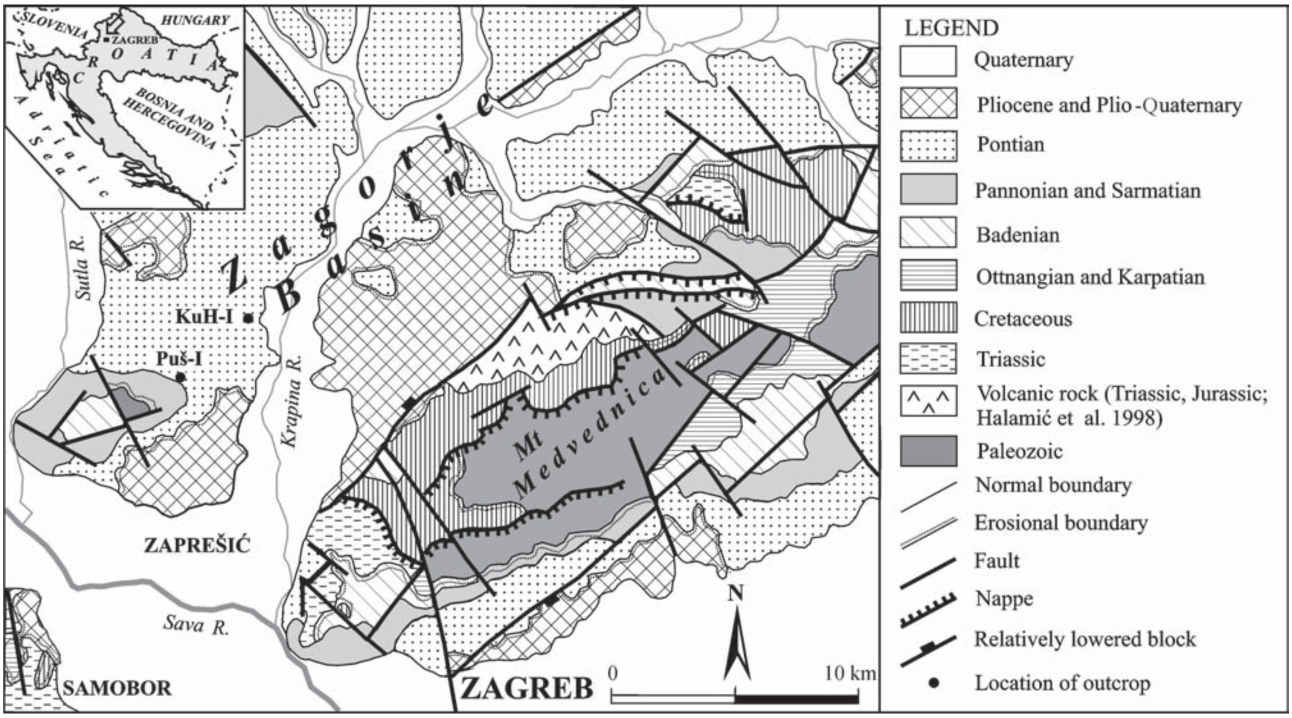

Fig. 1. Geological sketch-maps of Hrvatsko Zagorje and Mt. Medvednica with locations of Pušća (Puš-I) and Kupljenski Hruševec (KuH-I) outcrops (based on the 1:300,000 Geological Map of the Republic of Croatia, Institute of Geology, Zagreb).

smaller sub-basins separated by relatively shallowly laid basement rocks (Royden 1988). It is surrounded by the Alps, Carpathians and Dinarides (Fig. 3).

The basin evolved during the Tertiary simultaneously with the Alpine-Carpathian orogen, as a result of back-arc extension due to continental rifting and collision of the European and African plates.

In the paleogeographical sense the PBS occupied major part of the Central Paratethys, a sedimentation area which was several times connected and separated from the world seas during its evolution. The PBS was definitely isolated from other parts of Paratethys at the end of Middle Miocene, what resulted in formation of the brackish Pannonian Lake (Rögl & Steininger 1983; Rögl 1998). During the Late Miocene, because of clastic systems progradation, the area of the lake was gradually diminished while land areas simultaneously enlarged (Bérczi & Phillips 1985; Pogácsás et al. 1988; Mattick et al. 1998; Juhász & Magyar 1992; Vakarcs et al. 1994; Kovačić et al. 2004; Kovačić & Grizelj 2006).

Sedimentation of the Upper Miocene deposits in the investigated part of the Zagorje Basin shown on Fig. 2, started by, usually continuous, deposition of Lower Pannonian Croatica Beds, thin-bedded clayey limestones and calcite-rich marls, on the Sarmatian beds in a littoral zone of the low-salinity lake.

The Upper Pannonian Banatica Beds, represented almost exclusively by marls with equal shares of clayey and carbonate components, were continuously deposited on the Croatica Beds within the deepened sedimentation basin (Šikić et al. 1978, 1979; Kovačić 2004). They were continuously covered by Lower Pontian marly layers. Marl deposition was occasionally interrupted by deposition of sandy and silty detritus originating from the basin margin. Such deposition resulted in the Abichi Beds, alternating beds of sands, silts and silty marls. Due to further increase of clastic material input and simultaneous decrease of basin subsidence, the sedimentation basin became shallower, so in the Upper Pontian Rhomboidea Beds, sandy-silty sediments, were deposited in a shallow lake.

The Upper Miocene deposits are overlain by Pliocene siliciclastic deposits accumulated in small fresh-water lakes, swamps and rivers (Pavelić et al. 2003).

Materials and methods

Thirteen samples of massive marls of homogeneous structure were investigated. According to fossil mollusc and ostracod associations samples 1 to 6 are of Late Pannonian age, while samples 7 to 13 are of Early Pontian age.

The distribution of major and trace elements in the clay size fraction is strongly influenced by rock mineral composition (Refaat 1993), therefore analyses were performed on insoluble residue and its clay size fraction ($<2\ \mu m$). Samples were prepared by carbonate fraction dissolution by acetic acid with an ammonium acetate ($1\ mol \cdot dm^{-3}$) buffer of pH 5 (Jackson 1956) followed by separation of the $<2\ \mu m$ fraction by normal gravity settling according to Stoke's law.

X-ray powder diffraction (XRPD) patterns were recorded on random and oriented mounts of air dried material, and after glycol treatment, heating to 400 °C and 550 °C (Starkey et al. 1984) using a Philips vertical X-ray goniometer (type X'Pert) equipped with Cu tube and graphite crystal monochromator, with the following experimental conditions: 40 kV, 40 mA, primary beam divergence 1/4°, continuous scan (step 0.02 °2θ/s). In order to distinguish kaolinite and chlorite several additional tests were used, namely the XRD pattern was recorded after boiling the sample in 2 N HCl (Starkey et al. 1984) as well as after dimethyl-sulfoxide (DMSO) treatment (Calvert 1984). Quantitative analysis was performed according to Schultz (1964).

IR spectra were recorded on Perkin Elmer Spectrum One instrument. Approximately 0.03 g of <2 μm fraction of sample insoluble residue was mixed and homogenized with 0.2 g of KBr in an agate mortar. The mixture was pressed at 5 tons. The spectra were recorded over the range 4000–450 cm^{-1}, but the conclusion about the presence of kaolinite was based on spectrum appearance in the OH-stretching region (Russell & Fraser 1994).

Chemical analyses of insoluble residue and its <2 μm mineral fraction were performed in ACME Analytical Laboratories LTD, Vancouver, Canada. Major elements content was determined by inductively coupled plasma emission spectroscopy (ICP-ES), while trace elements were measured on an inductively coupled plasma mass spectrometer (ICP-MS). For both of the methods most of the elements were analysed after melting of samples with lithium-metaborate ($LiBO_2$), while noble and base metals were analysed from solutions prepared by dissolution of samples in aqua regia. The content of $CaCO_3$ was determined by EDTA (ethylenediamine tetra acetic acid) titration.

Composition of the sandy-silty fraction of samples was determined on a polarizing microscope by quantitative modal

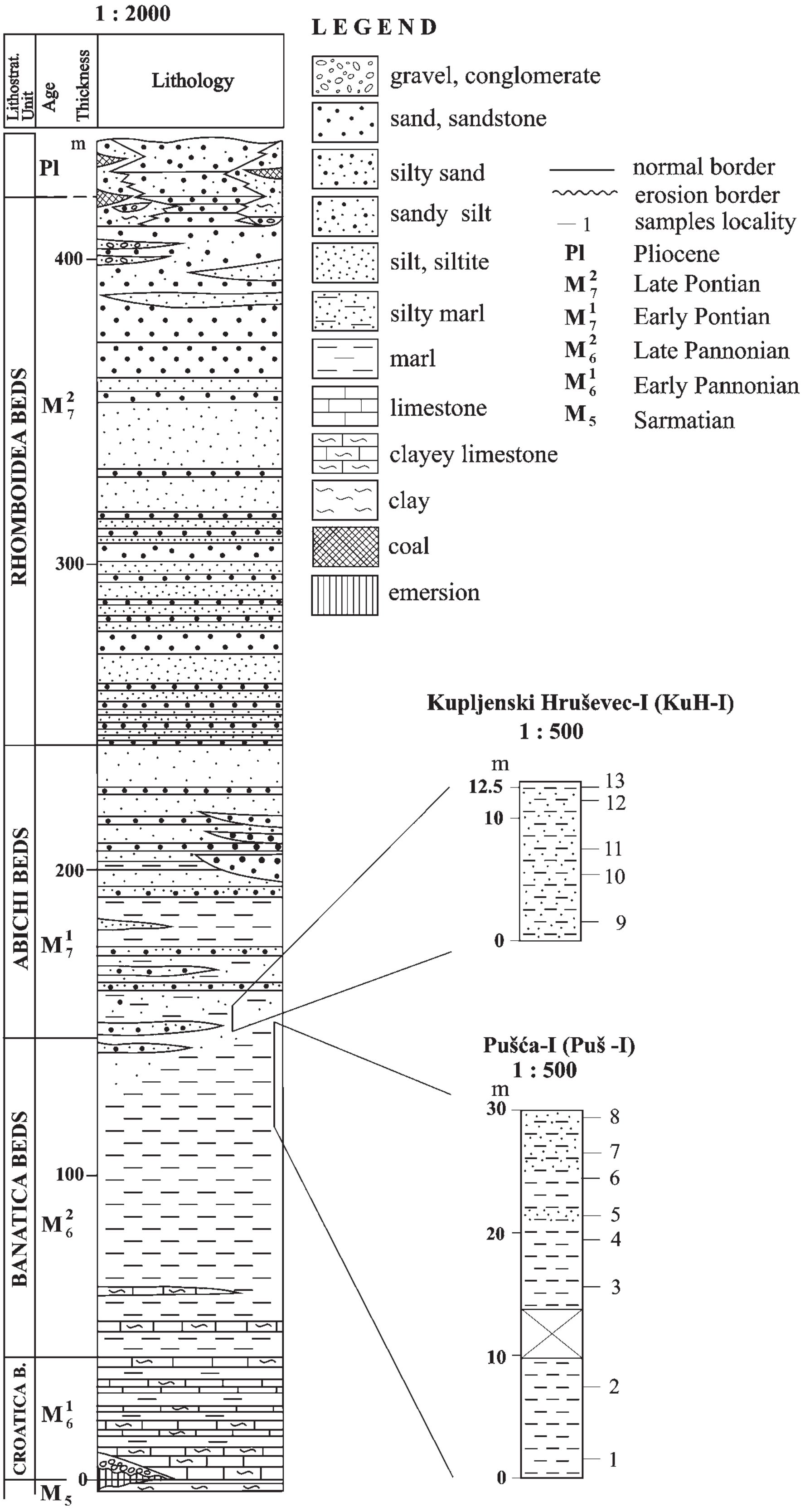

Fig. 2. Lithostratigraphical column of the Upper Miocene succession of the Zagorje Basin (1:2,000) (after Kovačić 2004) with lithological columns recorded on Pušća and Kupljenski Hruševec outcrops (1:500).

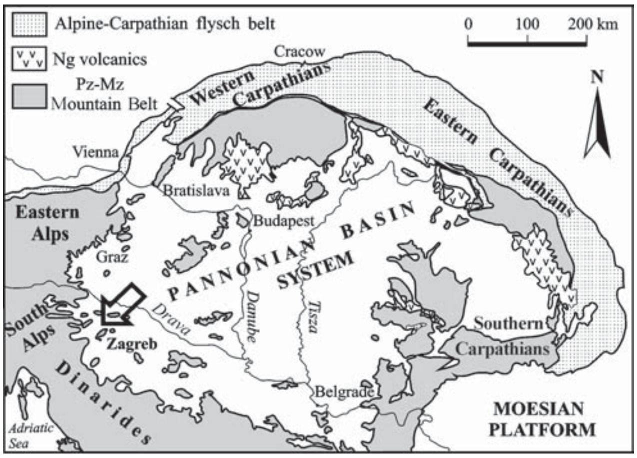

Fig. 3. Tectonic sketch of the Pannonian Basin and its surroundings with location of the Zagorje Basin (marked with arrow). After Royden (1988).

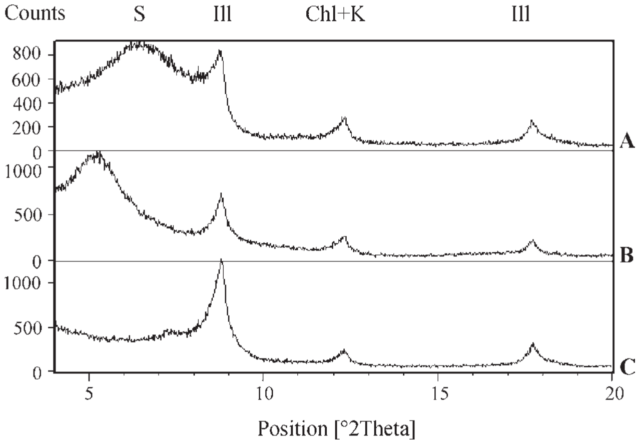

Fig. 4. XRD pattern of untreated sample 3 (A), in comparison with patterns recorded after ethylene glycol treatment (B) and heat treatment at 550 °C (C).

analysis of the 0.09–0.045 mm mineral fraction after removal of calcite by 4 % cold hydrochloric acid.

Results

The mineral composition of the insoluble residue and clay mineral content of its <2 µm fraction are shown in Tables 1 and 2 respectively. The mineral composition of the whole rock (Table 3) was calculated on the basis of the mineral composition of its insoluble residue and $CaCO_3$ content, and accordingly rocks were classified after Konta (1973). Table 4 shows the modal composition of 0.09–0.045 mm fraction obtained by polarizing microscope. Fig. 4 shows the XRD pattern of untreated sample 3 (A), in comparison with patterns recorded after ethylene glycol treatment (B) and heating at 550 °C (C), while Fig. 5 gives its IR spectra. An absorption band at 3698 cm^{-1} is typical of kaolinites (Russell & Fraser 1994). Kaolinite presence was also confirmed by DMSO treatment. Fig. 6, on powder pattern of sample 2, shows a peak shift from 7.15 to 11.2 Å, as a result of kaolinite swelling with DMSO.

Results of the chemical analyses of insoluble residue and <2 µm fraction are shown in Tables 5 and 6.

By comparison of the main element content of insoluble residue and its clay fractions, it is evident that the whole insoluble residue is enriched in Si, Na, K, Mn and Ti. On the other hand Al, P and loss on ignition (LOI) are enriched in clay fraction, while Ca, Mg and Fe are present in similar concentrations in the whole residue and its fine-grained fraction. The elevated Si, as well as Na and K concentrations in the whole insoluble residue are in accordance with the results of the XRPD and modal analyses by polarizing microscope that revealed the presence of quartz and feldspars respectively. The higher Ti concentrations are most probably due to the rutile that was determined in the silty fraction of the insoluble residue. The elevated contents of Al and LOI in clay fraction could be correlated with clay minerals, in which Al is one of the main components, and the water could be structural, pore or adsorbed on particle surfaces (Weaver & Pollard 1973; Newman & Brown 1987).

Table 1: Quantitative mineral composition (in wt. %, + — traces) of insoluble rock residue. The analyses were made by XRPD according to the procedure described by Schultz (1964).

Sample	Clay minerals	Quartz	Feldspar	Dolomite	Pyrite
1	79	17	4		
2	75	23	3		
3	79	17	4		
4	73	22	5		+
5	62	21	9	9	+
6	81	16	3		+
7	76	16	5	3	+
8	74	19	7		+
9	55	26	9	11	
10	56	36	8		+
11	74	17	9		+
12	71	19	10		
13	68	22	9		

Table 2: Semi-quantitative content of clay minerals in the <2 µm fraction of insoluble rock residue. The analyses were made by XRPD according to the procedure described by Schultz (1964). **** — dominant (60–100 %), *** — abundant (30–60 %), ** — considerable (10–30 %), * — subordinate (1–10 %), + — traces.

Sample	Illite and/or muscovite	Chlorite	Kaolinite	Smectite
1	**	*	+	****
2	***	*	+	****
3	**	*	+	****
4	**	*		****
5	***	*		***
6	***	**		***
7	***	*		***
8	***	*		***
9	****	***		*
10	***	**		***
11	***	*		***
12	**	*	+	****
13	***	**		***

Table 3: Quantitative mineral composition (in wt.%, + — traces) and classification of pelitic sediments according to Konta (1973).

Sample	$CaCO_3$	Clay minerals	Quartz	Feldspar	Dolomite	Pyrite	Classification
1	62	30	6	2			marl
2	63	28	8	1			marl
3	56	35	7	2			marl
4	74	19	6	1		+	marl
5	70	18	6	3	3	+	silty marl
6	60	32	7	1		+	marl
7	51	37	8	3	1	+	silty marl
8	49	38	10	3		+	silty marl
9	55	25	12	4	4		silty marl
10	39	34	22	5		+	silty marl
11	31	51	12	6		+	silty marl
12	54	33	9	4			silty marl
13	57	29	10	4			silty marl

Table 4: Semi-quantitative mineral composition of 0.09–0.045 mm fraction determined by polarizing microscope. **Op** — opaque minerals, **Dol** — dolomite, **Chl** — chlorite, **Tur** — tourmaline, **Zrn** — zircon, **Rt** — rutile, **Am** — amphibole, **Ap** — apatite, **Ep** — epidote, **Zo** — zoisite, **Grt** — garnet, **Ky** — kyanite, **St** — staurolite, **Ttn** — titanite, **X** — undetermined grains, **Qtz** — quartz, **Pl** — plagioclase, **Kfs** — K-feldspar, **S** — rock fragments (chert, quartzite and schists), **Ms** — muscovite. *** — abundant (30–60 %), ** — considerable (10–30 %), * — subordinate (1–10 %), **+** — traces.

Sample	Op	Dol	Chl	Tur	Zrn	Rt	Am	Ap	Ep	Zo	Grt	Ky	St	Ttn	X	Qtz	Pl	Kfs	S	Ms
1	**	+	+	+					+		+	+	+		+	***		*	***	+
2	***	+			+		+				+		+			***		*	**	
3	***		+		+	+		+				+	+		+	***		*	**	+
4	***	+	+	+	+			+	+		+					**	+	*	**	+
5	***	*	+				+	+		+			+			***		*	**	
6	***	+	+	+	+				+	+	+					***		**	**	+
7	**	+	*	+	+					+					+	***		**	***	+
8	**	+	+		+				+	+	+		+			***		*	***	+
9	*	*	*	+	+	+	+		+		+		+	+	+	***	+	**	**	+
10	*	*	*	+	+	+	+		+		+		+		+	***		**	**	+
11	**	*	+	+					+		+		+		+	***	+	**	**	+
12	*	*	+	+	+	+			+		+	+	+		+	***	+	**	**	*
13	***	*	+	+	+	+			+		+					***	+	*	**	+

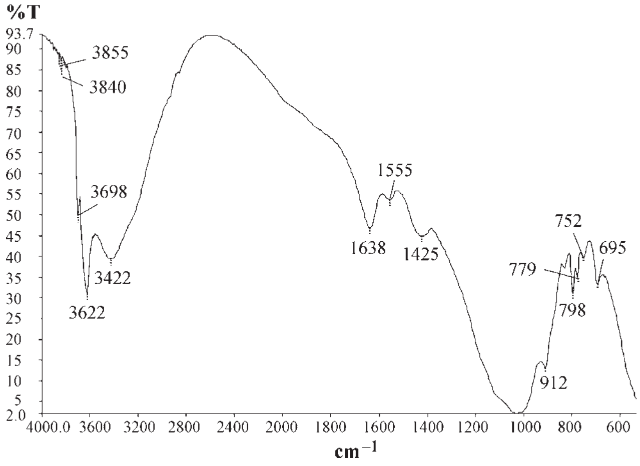

Fig. 5. IR spectrum of sample 3.

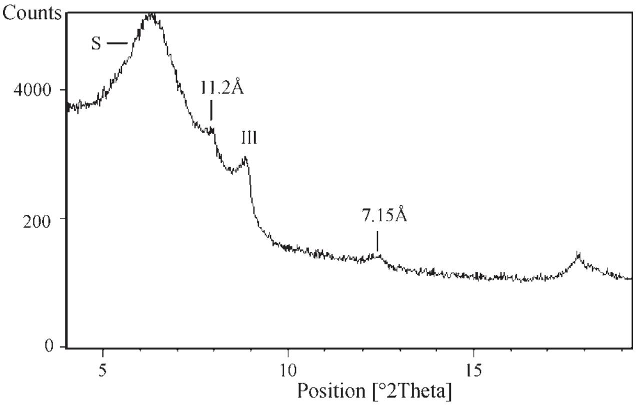

Fig. 6. X-ray powder diffraction pattern of sample 2 after DMSO-treatment.

The higher contents of Ca and Mg in samples 5, 7 and 9 are the consequence of the presence of dolomite (Table 1), which can also contain some Fe. Mg and Fe are also present in clay structures, they can replace Al in octahedral sheet (Weaver & Pollard 1973; Newman & Brown 1987). Iron is bound to pyrite, limonite and eventually present amorphous component, but also enters the structure of some transparent heavy minerals (garnets, epidote, tourmaline) that are present in the silt fraction.

The major, as well as, the trace element content of the analysed samples was compared with the values for Post-Archaean Australian Shale (PAAS) (Taylor & McLennan 1985) (Fig. 7a). The Zagorje samples are explicitly enriched with LOI and depleted in MnO, CaO and Na_2O.

Table 5: Chemical composition of insoluble rock residue. Major elements (wt. %) and several trace elements, marked with star sign (ppm) were determined by ICP-AES, and other trace elements (ppm, except Au in ppb) by ICP-MS. The CIA, chemical index of alteration of Nesbitt & Young (1982), is calculated as $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]\times100$, oxides are expressed in molar proportions, CaO* is the amount of CaO in siliciclastic minerals only i.e. excluding carbonates and apatite.

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	54.76	54.13	53.89	53.25	50.03	53.83	52.05	54.23	51.92	55.75	55.43	56.30	55.46
Al_2O_3	19.29	19.45	19.36	19.52	18.09	19.57	18.52	19.23	17.76	19.68	19.80	19.05	18.63
Fe_2O_3	7.60	8.55	8.52	8.71	7.59	8.16	7.40	7.30	7.82	7.27	7.16	8.09	7.87
MgO	2.03	1.97	2.00	2.01	2.93	2.16	2.59	2.29	3.27	2.54	2.82	2.37	2.40
CaO	0.65	0.56	0.70	0.66	2.12	0.47	1.18	0.27	2.2	0.40	0.56	0.28	0.33
Na_2O	0.39	0.39	0.50	0.51	0.53	0.51	0.71	0.73	0.76	0.72	0.88	0.71	0.81
K_2O	2.92	2.93	2.95	3.04	2.75	3.00	2.84	2.90	3.02	3.18	3.33	3.04	3.08
TiO_2	0.85	0.81	0.86	0.83	0.80	0.85	0.88	0.89	0.78	0.87	0.87	0.84	0.83
P_2O_5	0.27	0.17	0.20	0.30	0.27	0.21	0.16	0.14	0.22	0.13	0.12	0.19	0.19
MnO	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.03	0.04	0.04	0.04	0.04	0.03
LOI	10.9	10.7	11.0	10.2	14.6	11.1	12.9	11.9	12.1	9.2	9.0	9.5	9.9
total	99.68	99.68	100.00	99.05	99.74	99.89	99.27	99.91	99.89	99.78	100.01	100.41	99.53
TOT/C	0.98	1.09	0.81	1.13	3.26	1.73	3.02	2.65	1.35	0.45	0.57	0.70	1.49
TOT/S	0.03	0.03	<0.01	0.04	1.66	0.61	1.68	1.13	0.01	0.01	<0.01	0.01	0.07
Ag	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2
As	30.2	36.4	31.0	35.9	30.9	34.2	30.4	33.0	26.2	17.2	18.0	24.7	27.0
Au	3.9	4.1	3.6	3.6	3.0	4.1	2.3	2.2	4.3	3.1	3.3	3.8	3.2
Bi	0.5	0.6	0.6	0.6	0.5	0.7	0.5	0.6	0.6	0.7	0.6	0.7	0.6
Ba*	394	398	427	409	370	454	479	418	456	488	514	442	626
Cd	0.1	0.1	0.1	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	0.1
Ce	62.5	64.8	67.2	63.2	65.7	71.8	65.4	68.2	73.9	77.7	73.6	69.3	69.4
Co	8.4	9.2	8.8	8.2	17.2	11.4	15.0	12.5	14.1	15.8	15.4	12.5	12.8
Cr*	123	110	123	110	136	100	123	116	136	123	140	95	130
Cs	15.1	15.9	13.9	14.5	13.4	13.6	11.6	13.5	11.7	13.0	12.2	12.2	12.9
Cu	55.7	67.5	57.3	68.2	55.4	56.6	50.9	55.2	54.2	52.2	47.0	62.0	59.9
Dy	4.05	3.76	4.23	3.83	4.30	4.45	5.03	4.91	4.34	4.49	4.22	3.80	3.95
Er	2.53	2.47	2.62	2.51	2.65	2.82	3.00	3.02	2.61	2.49	2.51	2.38	2.42
Eu	1.00	1.02	1.03	0.94	1.06	1.09	1.18	1.25	1.12	1.03	1.03	0.98	0.99
Ga	25.3	26.8	26.9	25.0	24.9	25.3	23.0	25.8	25.0	26.5	26.7	25.7	27.4
Gd	4.73	4.28	4.90	4.03	4.49	5.38	5.50	5.28	4.58	4.72	4.40	4.09	4.47
Hf	3.4	3.6	4.2	3.9	3.9	3.5	3.9	4.0	4.1	4.1	4.1	4.3	4.5
Hg	0.20	0.17	0.15	0.16	0.18	0.24	0.15	0.16	0.09	0.12	0.11	0.11	0.10
Ho	0.85	0.84	0.88	0.80	0.85	0.95	0.98	1.01	0.89	0.89	0.84	0.80	0.86
La	31.3	33.4	33.4	31.3	31.6	35.0	31.4	33.4	34.5	35.2	34.2	33.6	34.9
Lu	0.36	0.34	0.37	0.37	0.34	0.37	0.38	0.41	0.35	0.35	0.34	0.35	0.35
Mo	3.3	2.1	1.7	2.9	2.8	2.5	3.5	2.8	0.9	1.0	0.5	1.1	1.1
Nb	15.0	14.8	15.8	15.1	14.3	14.8	14.1	14.9	15.4	17.6	16.4	16.2	16.1
Nd	27.3	28.1	29.3	27.3	28.0	31.3	29.6	30.9	30.0	30.2	29.1	27.5	29.0
Ni	59.1	67.8	54.5	51.5	60.5	53.4	47.7	56.6	45.0	71.9	70.3	49.9	47.7
Ni*	76	86	70	85	86	82	69	59	64	96	95	57	66
Pb	24.6	26.5	25.6	30.8	25.2	32.3	21.8	25.4	25.7	26.4	25.7	26.3	23.8
Pr	6.93	7.42	7.69	7.14	7.52	8.33	7.57	8.11	8.27	8.39	8.08	7.70	7.66
Rb	169.4	166.9	163.7	167.3	157.3	165.0	147.8	162.0	159.8	169.4	168.8	160.3	168.3
Sb	1.1	0.9	0.9	0.9	0.8	1.1	0.8	1.0	0.8	0.7	0.5	0.7	0.9
Se	0.8	1.2	<0.5	1.1	1.8	3.2	1.7	1.9	1.4	<0.5	0.5	<0.5	2.3
Sc*	16	15	15	17	18	17	19	16	17	18	18	15	17
Sm	5.4	5.7	5.7	5.5	5.7	6.4	6.1	6.5	6.0	5.9	5.9	5.5	5.5
Sn	4	5	4	4	2	3	2	3	4	4	5	4	5
Sr	98.3	95.3	98.0	93.3	100.9	90.1	92.6	81.3	95.5	93.9	62.7	90.5	91.7
Ta	1.0	1.1	1.1	1.1	1.0	1.0	0.9	1.0	1.1	1.1	1.1	1.0	1.1
Tb	0.72	0.67	0.81	0.72	0.74	0.76	0.82	0.85	0.78	0.77	0.73	0.66	0.71
Th	13.1	13.2	14.2	14.7	14.6	16.2	13.5	15.9	16.2	14.1	16.5	13.9	13.8
Tl	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Tm	0.38	0.35	0.40	0.36	0.36	0.40	0.39	0.39	0.40	0.36	0.36	0.34	0.39
U	4.7	3.4	3.1	3.5	3.4	4.4	3.9	3.8	3.2	2.6	2.5	2.8	3.1
V	169	161	158	157	147	154	134	146	139	154	151	147	160
W	2.3	2.6	2.7	2.7	2.4	2.5	2.3	2.5	2.6	2.9	2.5	2.3	2.8
Y	26.2	23.5	25.4	24.1	26.0	26.6	28.1	27.3	25.5	25.1	24.2	23.6	24.2
Yb	2.41	2.47	2.40	2.24	2.51	2.45	2.66	2.57	2.38	2.29	2.42	2.16	2.43
Zn	128	131	119	148	91	124	98	117	116	131	125	126	119
Zr	129.7	118.7	137.2	130.1	123.1	122.5	124.1	128.7	137.1	136.5	135.3	137.7	149.9
SiO_2/Al_2O_3	2.84	2.78	2.78	2.73	2.77	2.91	2.81	2.82	2.92	2.83	2.81	2.95	2.98
K_2O/Al_2O_3	0.22	0.22	0.22	0.23	0.22	0.22	0.22	0.22	0.24	0.23	0.24	0.23	0.24
Eu/Eu*	0.61	0.63	0.60	0.61	0.71	0.63	0.64	0.66	0.66	0.60	0.62	0.63	0.61
Th/Sc	0.82	0.88	0.94	0.86	0.81	0.95	0.71	0.99	0.95	0.78	0.92	0.93	0.81
La/Sc	1.95	2.23	2.23	1.84	1.75	2.33	1.65	1.75	2.03	1.95	1.9	2.24	2.05
La/Co	3.73	3.63	3.79	3.82	1.84	3.07	2.09	2.67	2.45	2.23	2.22	2.69	2.73
Th/Co	1.56	1.43	1.61	1.79	0.85	1.42	0.90	1.27	1.15	0.89	1.07	1.11	1.08
Th/Cr	0.11	0.12	0.12	0.13	0.11	0.16	0.11	0.14	0.12	0.11	0.12	0.15	0.11
ICV	0.65	0.69	0.69	0.70	0.85**	0.68	0.75**	0.65	0.91**	0.66	0.67	0.70	0.72
CIA	79	80	78	78	70**	79	74**	80	68**	78	77	79	78

Table 6: Chemical composition of the <2 µm fraction of insoluble rock residue. Major elements (wt. %) and several trace elements, marked with star sign (ppm) were determined by ICP-AES, and other trace elements (ppm, except Au in ppb) by ICP-MS.

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	49.54	51.52	48.78	50.84	48.20	48.73	47.93	43.83	50.56	51.46	51.58	51.50	50.97
Al_2O_3	20.47	21.18	20.81	20.96	19.79	20.53	20.29	17.94	19.44	20.39	20.60	19.32	19.17
Fe_2O_3	7.88	8.09	9.67	8.53	6.63	7.91	5.97	5.60	9.54	7.97	8.08	8.50	8.74
MgO	2.23	2.20	2.24	2.28	2.94	2.38	2.69	2.19	2.49	2.49	2.74	2.41	2.44
CaO	0.76	0.64	0.90	0.73	2.54	0.60	1.21	0.24	0.18	0.17	0.19	0.16	0.17
Na_2O	0.18	0.23	0.21	0.24	0.21	0.25	0.25	0.25	0.34	0.29	0.38	0.28	0.32
K_2O	2.82	3.45	2.96	3.33	2.90	2.97	3.02	2.83	2.91	2.86	2.92	2.70	2.73
TiO_2	0.71	0.84	0.72	0.78	0.72	0.69	0.77	0.66	0.66	0.69	0.69	0.62	0.62
P_2O_5	0.32	0.22	0.30	0.32	0.31	0.28	0.16	0.21	0.26	0.17	0.14	0.21	0.21
MnO	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.02
LOI	14.9	12.0	13.6	12.0	16.0	15.6	17.3	21.0	13.2	12.7	12.8	14.0	14.2
total	99.83	100.39	100.21	100.03	100.26	99.96	99.62	94.77	99.6	99.21	100.15	99.72	99.59
TOT/C	1.56	1.38	1.42	1.62	4.55	3.25	4.36	4.98	1.37	1.08	1.49	1.58	2.40
TOT/S	0.04	0.03	0.04	0.05	0.62	0.41	0.37	0.75	0.02	0.02	0.04	0.03	0.02
Ag	0.3	0.1	0.1	0.2	0.3	0.2	0.2	0.2	0.2	1.1	0.5	0.7	0.7
As	30.2	30.8	33.0	28.5	18.7	25.4	16.6	23.0	27.0	38.1	21.0	30.5	29.6
Au	7.1	10.3	8.5	8.2	9.4	8.8	5.1	11.4	3.2	4.2	3.3	5.5	5.9
Bi	0.5	0.7	0.8	0.7	0.7	0.7	0.6	0.6	0.6	0.9	0.6	0.9	0.7
Ba*	330	411	376	394	331	559	439	332	352	353	383	320	320
Cd	0.9	0.2	0.3	0.2	0.2	0.3	0.2	0.5	0.1	0.3	0.7	0.3	0.3
Ce	58.7	74.1	61.6	62.5	63.9	65.2	71.5	67.3	69.4	58.0	60.0	58.9	53.4
Co	10.4	9.4	9.0	8.4	17.1	12.4	16.8	12.4	12.8	9.8	10.1	13.9	8.7
Cr*	150	123	123	116	123	140	150	136	140	130	178	140	130
Cs	19.9	19.0	17.1	17.6	16.3	17.0	16.6	17.0	12.9	15.1	16.0	15.2	15.2
Cu	71.3	69.4	85.2	108.4	90.7	91.2	85.5	87.1	59.9	83.5	79.5	77.5	86.9
Dy	3.47	3.84	3.44	3.41	3.88	3.79	5.10	4.21	3.95	2.78	2.82	3.01	2.53
Er	2.31	2.49	2.11	2.06	2.36	2.27	2.76	2.50	2.42	1.68	1.77	1.72	1.64
Eu	1.00	1.14	0.95	0.91	1.05	1.06	1.34	1.20	0.99	0.78	0.82	0.79	0.67
Ga	30.3	30.1	28.9	30.1	27.5	29.1	28.9	28.3	27.4	28.9	27.3	27.6	26.7
Gd	3.61	4.06	3.53	3.71	4.80	4.21	5.64	5.08	4.47	3.30	3.03	3.57	2.93
Hf	3.1	3.3	3.1	3.4	3.0	2.8	3.0	3.0	4.5	2.5	2.4	2.5	2.8
Hg	0.22	0.15	0.19	0.14	0.14	0.22	0.15	0.22	0.10	0.17	0.24	0.25	0.27
Ho	0.76	0.76	0.71	0.68	0.81	0.72	0.96	0.86	0.86	0.57	0.58	0.59	0.51
La	29.9	39.7	31.6	32.8	33.8	34.1	37.0	35.9	34.9	31.4	31.4	29.7	27.8
Lu	0.32	0.36	0.29	0.32	0.34	0.31	0.39	0.34	0.35	0.26	0.28	0.26	0.21
Mo	4.7	1.6	1.9	2.9	3.2	2.8	4.9	5.5	1.1	1.2	1.0	0.8	1.3
Nb	13.2	16.7	13.2	15.3	14.1	13.0	13.9	13.7	16.1	13.6	13.2	13.3	12.0
Nd	24.3	32.2	26.2	25.8	29.1	28.8	31.7	30.4	29.0	24.4	23.6	24.5	21.3
Ni	64.8	75.5	65.2	55.1	63.3	59.9	55.9	59.1	47.7	48.1	76.0	84.7	47.6
Ni*	87	98	85	77	80	95	79	78	85	95	108	72	75
Pb	22.2	30.3	34.4	27.0	32.0	30.1	25.5	26.9	23.8	32.4	24.5	31.4	27.7
Pr	6.60	8.52	7.06	7.07	7.59	7.59	8.29	7.97	6.54	6.71	6.62	6.08	6.07
Rb	204.2	212.9	185.2	204.0	185.8	200.5	195.3	199.0	180.3	177.4	180.0	169.2	161.3
Sb	1.1	0.8	0.9	0.7	0.8	0.9	1.0	1.3	0.8	0.5	0.6	0.8	0.9
Se	0.8	1.2	0.7	1.3	1.9	3.0	1.3	1.6	2.0	0.5	1.0	0.6	2.8
Sc*	17	18	18	17	17	19	21	17	17	19	18	15	16
Sm	4.9	5.8	4.9	4.9	5.9	5.9	6.9	6.3	4.1	4.3	4.6	4.2	3.9
Sn	5	5	5	5	4	5	4	5	4	4	4	4	4
Sr	108.3	125.2	104.7	109.6	121.5	100.8	130.6	90.1	74.4	77.9	73.7	70.9	66.8
Ta	0.9	1.1	1.0	1.0	1.0	0.8	0.9	0.8	1.0	0.9	0.9	0.8	0.8
Tb	0.63	0.73	0.58	0.59	0.70	0.69	0.92	0.78	0.50	0.52	0.51	0.48	0.44
Th	14.3	15.2	16.9	15.8	15.5	14.8	16.1	14.5	12.7	11.7	13.3	11.0	12.5
Tl	0.3	0.4	0.2	0.3	0.2	0.3	0.1	0.3	0.1	0.2	0.2	0.2	0.2
Tm	0.35	0.35	0.34	0.33	0.36	0.33	0.45	0.40	0.29	0.32	0.29	0.27	0.24
U	5.1	3.1	2.9	3.1	3.5	4.4	4.4	3.7	2.5	2.2	2.5	2.3	2.5
V	213	194	191	191	183	191	186	186	176	173	171	157	160
W	2.5	3.1	2.5	2.8	2.6	2.3	2.3	2.8	2.9	2.6	2.2	2.4	2.3
Y	23.8	24.5	21.2	21.3	24.6	22.8	29.7	25.2	16.2	16.7	16.5	15.0	15.1
Yb	2.35	2.32	2.27	2.21	2.46	2.13	2.92	2.43	1.90	1.92	1.69	1.55	1.67
Zn	165	168	180	180	133	170	125	155	152	155	159	148	146
Zr	99.8	105.9	96.0	105.1	94.9	90.5	97.6	94.7	81.1	80.3	76.7	76.9	76.1

They have slightly lower contents of SiO_2, TiO_2 and K_2O, while Al_2O_3, FeO and MgO are present in similar concentrations as in the PAAS. Samples with dolomite (5, 7, 9) are expectedly enriched with CaO and MgO in comparison to other samples and the PAAS. Comparison of trace element content in whole insoluble residue and its clay fraction showed that insoluble residue is enriched with: Ba, Ce, Dy, Er, Eu, Hf, Ho, La, Lu, Nb, Nd, Pr, Sm, Ta, Tm, Zr, Y and Yb (Tables 5 and 6). Relative to the PAAS, the Zagorje samples contain comparable amounts of Sc, V, Cr, Ni, Rb, Y, Nb and Th, however they are enriched with Zn, Cu, Ga, and depleted in Co, Sr, Zr and Ba (Fig. 7b).

Barium as well as light rare earth elements (LREE: La, Ce, Pr, Nd and Sm) in insoluble residue are associated with

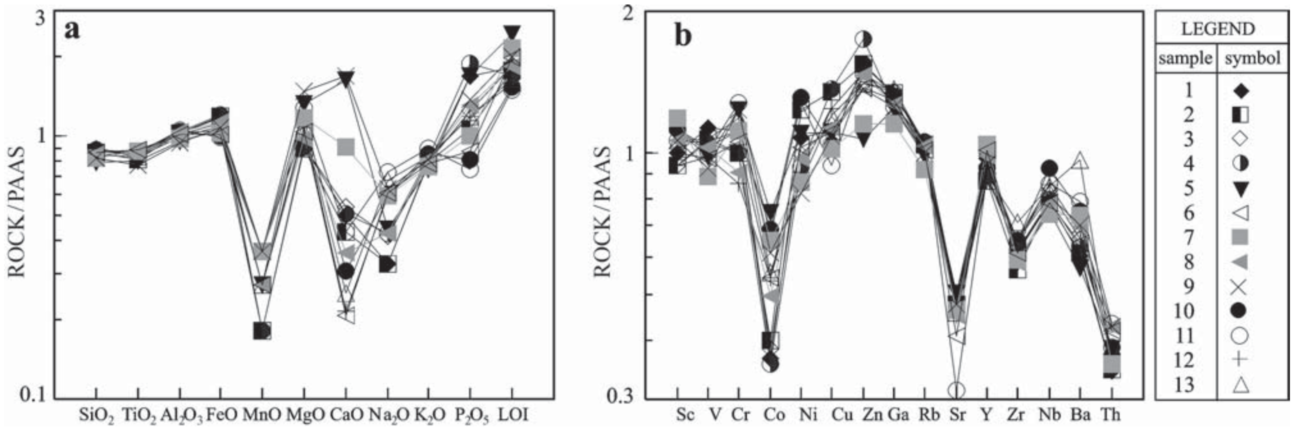

Fig. 7. Chemical composition of the Zagorje samples normalized to Post-Archaean Average Shale (PAAS) after Taylor & McLennan (1985). **a** — plot of major element oxides (wt. %). **b** — trace elements (ppm) spidergram. In legend sample numbers and corresponding symbols are given.

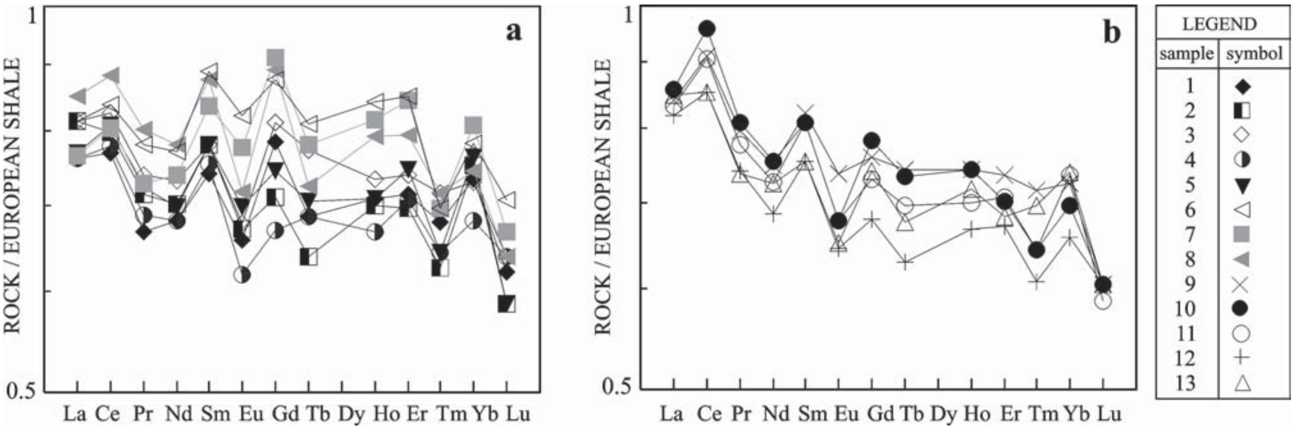

Fig. 8. Rare earth element plots of Zagorje samples normalized to average European Shale (ES) after Haskin & Haskin (1966). **a** — samples from Pušća outcrop. **b** — samples from Kupljenski Hruševec outcrop. In legend sample numbers and corresponding symbols are given.

feldspars; due to the similar ionic radii they can substitute Ca and Na in feldspar structure (McLennan 1989; Deer et al. 2001). Feldspars prefer LREE and bivalent Eu as a substitute for Ca (McLennan 1989; Prohić 1998). Dy, Ho, Er, Tm, Yb, Lu and Y are most probably incorporated in garnets and zircon which prefer heavy rare earth elements (HREE) (Henderson 1996; Prohić 1998). Most probably, Nb and Ta, which usually come together with HREE, are related to heavy minerals, too. The analysed samples are depleted in REE in comparison with the European Shale composite (ES) (Haskin & Haskin 1966) (Fig. 8a and b).

Insoluble residue enrichment with Zr and Hf is correlated with zircon; zircon usually incorporates approximately 50 % of Zr and several % of Hf present in the rock (McLennan 1989). Chondrite normalized patterns are typical for the shale in general, with enrichment of LREE relative to HREE (Fig. 9).

The clay fraction is enriched with: Bi, Cs, Cu, Ga, Hg, Pb, Rb, V and Zn (Table 6). Gallium could replace Al and Si in tetrahedral sheets of clay minerals, while Cs and Rb can be present as interlayer cations in some clay minerals (Newman & Brown 1987). Cesium also substitutes potassium in micas (Heier & Billings 1972). Copper and zinc could replace magnesium, while vanadium could replace aluminium in octahedral sheets of clay minerals (Newman

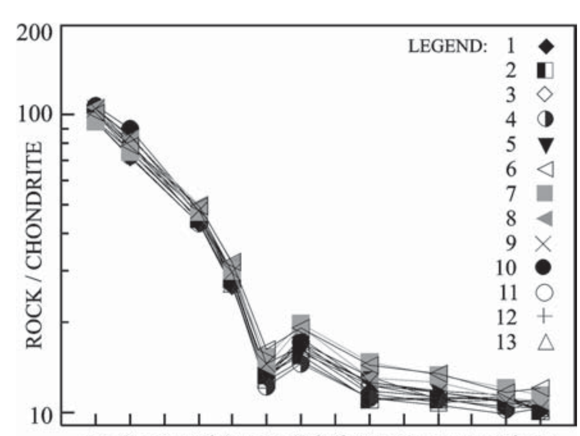

Fig. 9. Rare earth element plots of Zagorje samples normalized to chondrite after Nakamura (1974). Sample numbers and corresponding symbols are given in the legend.

& Brown 1987). Heavy metals, Hg and Pb, do not enter the structure of clay minerals, but their elevated concentration could point to the adsorption of these elements onto the surface of clay particles. It is known that sediments with a high specific area adsorb heavy metals by physical and chemical sorption (Siegel 2002). According to Ahrens & Erlank (1969) elevated Bi content in the clay fraction could indicate Bi for Ca substitution in silicates. The role of organic matter could not be excluded since the total carbon content is also elevated in the clay fraction.

Discussion

Mineral characteristics of pelitic sediments

The Upper Miocene marls of the Zagorje Basin, which comprise marls collected from the localities Pušća and Kupljenski Hruševec, were deposited in a brackish lake under hot climate conditions, and there was no significant input of coarse-grained terrigenous material (Kovačić 2004). Clay minerals were deposited from suspension, while carbonate originated in the lake. The presence of calcite and low-magnesium calcite in the marls indicate that the lake salinity was low (Reading & Collinson 1996). Nevertheless, the presence of calcite could also be explained by diagenetic transformation of primarily deposited aragonite or Mg-calcite into more stable calcite.

Comparison of calcite content in samples of different ages (Pannonian–Pontian) is represented by box and whiskers diagrams in Fig. 10. Calcite content for Pannonian samples from the Pušća outcrop varied from 49 to74 wt. %, while in Pontian ones from Kupljenski Hruševec it was between 31 and 56 wt. %. The lower calcite content in the Pontian samples could be the result of climate changes that caused carbonate production decrement, or more likely, it is due to intensified input, firstly, of clayey and later of silty-sandy clastic detritus. Gradual increase of terrigenous influence is in good agreement with sediment type change; most of the Pannonian age samples were classified as marl, while those of the Pontian age are silty marls.

In majority of the lakes clay minerals are of detrital origin and reflect the composition of source rocks (Chamley 1989; Weaver 1989). During the Late Miocene in the SW part of Lake Pannon deposition of different calcareous-marly and sandy-silty sediments took place. According to Kovačić & Grizelj (2006) the sandy-silty detritus had a terrigenous origin, most probably from the Eastern Alps.

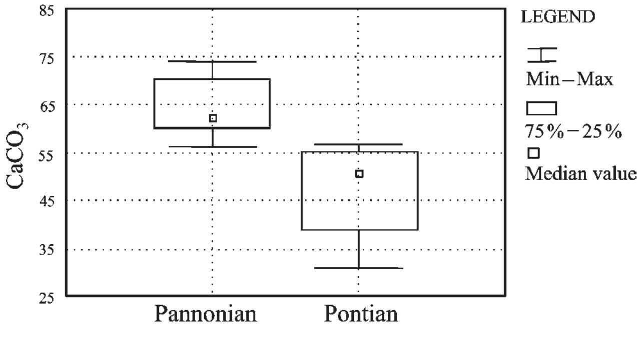

Fig. 10. Comparison of Pannonian and Pontian age samples on the basis of $CaCO_3$ (wt. %) content.

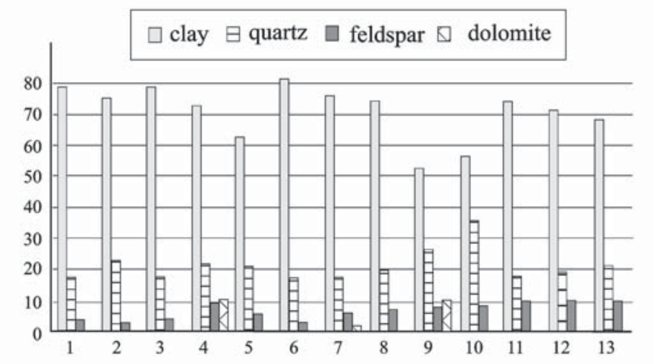

Fig. 11. Mineral composition of insoluble rock residue.

The results of the XRPD analyses of insoluble residues (Tables 1, 2 and 3) revealed that samples differ primarily by proportion of present mineral phases. All the analysed samples contain quartz, feldspars, and clay minerals (illite, smectite and chlorite, while the kaolinite is present only in a few samples), but their concentration varies significantly in particular samples. In several samples dolomite and pyrite are also present (Tables 1 and 3, Fig. 11). It is evident (Fig. 11) that clay mineral content is higher in samples from the Pušća locality, while quartz and feldspars are more abundant in the Kupljenski Hruševec samples. The higher contents of quartz and feldspars in the latter samples are in good agreement with their lithology; they are determined as silty marls (Table 3).

According to Chamley (1989) and Weaver (1989) illite and smectite constitute the dominant species in detrital supply of freshwater lake, and are as frequently encountered as quartz. Chlorite, kaolinite and mixed-layers are variously present, depending on the lake location. A general correspondence exists between the mineral composition of most freshwater lakes and average clay mineralogy of rocks and soils in the surrounding drainage basins. Chlorite, as a mineral that is not resistant to chemical weathering, is an important detrital component in areas with reduced chemical weathering (Weaver 1989). Such areas are characterized by colder climate, steeper relief, intensive erosion and faster transport. In the Pannonian and Pontian such conditions existed in the Alps, that is in the young mountain belt, the probable source region of detrital material, including chlorite, which was transported to Lake Pannon. Lower concentrations of chlorite in pelitic sediments in comparison to contemporaneous sandy-silty sediments, which were deposited to the north of investigated area (Kovačić 2004), is most probably the result of their alteration. This alteration was facilitated by the hot, humid climate that existed in the south-western part of the Pannonian Lake in Late Miocene times (Pantić 1986; Planderová et al. 1992).

Smectite and illite are more abundant than kaolinite when the water salinity is higher, as interpreted from the Gulf of Mexico example by Brooks & Ferrell (1970). Weaver (1989) thinks the same, but he recognized some exceptions such as the coastal Snuggedy Swamp. During the Late Miocene the PBS was separated from marine realm, and as a consequence, till the end of the Miocene, there was a lake area of oligohaline (Pannonian) and miohaline (Pontian) salinity characteristics (Steininger et al. 1988).

According to Chamley (1989) chlorite, illite and irregular mixed layered I/S originate directly from less weathered intrusive and metamorphic rocks, while poorly to medium-crystallized smectites are the result of weathering in mild humid areas with locally intensified volcanic activity. No evidence of volcanic activity was discovered in the investigated sediments, but such evidence exists for the Upper Miocene for other parts of the PBS (Balogh et al. 1983; Szabó et al. 1992; Pamić et al. 1995). Consequently, smectite occurrence could be correlated with volcanic activity in other parts of the basin, owing to the fact that during the eruptions volcanic material could be transported far away. Nevertheless, smectite could also originate from volcanic material that is redeposited from the older sediments as well as by weathering of other rocks. Part of the illite present in the analysed samples is probably redeposited, and the other part could be authigenic, but the presence of smectite indicates that diagenetic changes were not pronounced.

Hungarian geologists have described a similar mineral composition of pelitic sediments. Viczián (2002) claims that in the Great Hungarian Plain the mineral composition was, in principle, the same: polymineral detrital clays display slight, systematic regional differences, with no significant differences in composition of various stratigraphic horizons within the Late Pannonian to Late Pliocene-Pleistocene time span. Based on XRD, thermal and some chemical analyses he determined the dominant clay minerals in pelitic sediments of the Great Hungarian Plain: in the whole rock samples these are smectite, I/S, illite and chlorite, and in <2 μm fraction ternary-mixed-layered illite/smectite/chlorite and kaolinite with different degrees of ordering, that are absent in some samples. According to him clay minerals are essentially detrital, derived from various areas of the surrounding Carpathians and Alps. He compared several sub-basins and concluded that they differ in degree of ordering and abundance of particular clay and other minerals such as calcite, dolomite, quartz and feldspars, in dependence with constancy of source area and transport direction. Similarly, Varsányi (1975) determined montmorillonite, kaolinite, mica, chlorite, amorphous material, quartz, potassium and sodium feldspars in the <10 μm fraction of samples of Early and Late Pannonian age from boreholes in the southern part of the Great Hungarian Plain.

When the composition of the silt fraction of insoluble residue (Table 4) is compared with the composition of contemporaneous sandy-silty sediments (Kovačić & Grizelj 2006), it is evident that they are very similar: in both cases quartz and rock fragments are dominant constituents, and garnets and epidote are prevailing transparent heavy minerals. The similarity of composition suggests the same provenance of the detritus, and according to Kovačić & Grizelj (2006), most probably the Alpine. Observed differences in granulometric properties and quantity of clastic detritus are the result of distance of deposition area from the coast, since marls are deposited in more distal environments in comparison to sandy-silty sediments.

Geochemical characteristics of the pelitic sediments

The degree of chemical weathering of the source rocks can be constrained by calculating the chemical index of alteration ($CIA=[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]\times 100$, oxides are expressed in molar proportions, CaO* is the amount of CaO in siliciclastic minerals only i.e. excluding carbonates and apatite) of Nesbitt & Young (1982). According to Nesbitt & Young (1982) the CIA values for the average shale is 70–75, and for illite and montmorillonites they are 75–85. The calculated CIA values are similar for both outcrops and vary from 77 to 80 (Table 5) and suggest a high intensity of chemical weathering. CIA value for PAAS is 69. This value together with the spider diagram (Fig. 7a) enables the conclusion that Zagorje samples contain more clay minerals than PAAS.

Intense weathering of the source rocks can be also deduced from the triangular Al_2O_3-$(CaO+Na_2O)$-K_2O plot (after Nesbitt & Young 1982, 1984) on which data for average PAAS and Upper Crust (UC) given by Taylor & McLennan (1985) and North American Shale Composite (NASC) given by Gromet et al. (1984) are shown for com-

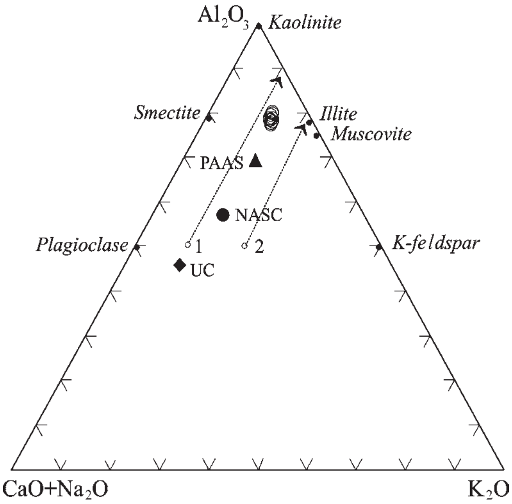

Fig. 12. Al_2O_3-$(CaO+Na_2O)$-K_2O plot of Zagorje samples (after Nesbitt & Young 1982, 1984) in comparison with the data for Post-Archaean Australian Shale (PAAS) and Upper Crust (UC) given by Taylor & McLennan (1985) and North American Shale Composite (NASC) data given by Gromet et al. (1984). Small dots are idealized mineral compositions of plagioclase, K-feldspar, kaolinite, muscovite, illite and smectite and numbers denote compositional trends of initial weathering profiles of average granodiorite (1) and average granite (2) (from Nesbitt & Young 1984).

parison (Fig. 12) together with idealized compositions of plagioclase, K-feldspar, kaolinite, illite and muscovite and trends of initial weathering profiles of granite and granodiorite (Nesbitt & Young 1984). Most of the samples plot close to the Al_2O_3-K_2O boundary and along the granodiorite weathering trend, implying that source rocks underwent intense weathering. The marl samples plot closer to PAAS than to UC or NASC.

On the triangular Fe_2O_3-K_2O-Al_2O_3 diagram (Fig. 13), the Zagorje samples plot in the same region as PAAS and NASC. Cox et al. (1995) proposed the Index of Compositional Variability (ICV) as a measure for characterizing the differences between samples of different provenance. ICV is defined as $(Fe_2O_3+K_2O+Na_2O+CaO+MgO+MnO+TiO_2)/Al_2O_3$ and measures the abundance of alumina relative to the other major cations in the rock or mineral. Non-clay silicates contain a lower proportion of Al_2O_3 than do clay minerals, therefore they have higher ICV. Because minerals show a relationship between resistance to weathering and ICV, the ICV may be applied to pelitic sediments as a measure of compositional maturity. Pelitic sediments with abundant clay minerals tend to have ICV's less than one and characterize tectonically quiescent or cratonic environments (Weaver 1989) where sediment recycling is active, but may also be produced by intensive chemical weathering of first-cycle material (Barshad 1966). The average ICV value for the Zagorje samples is 0.67 and suggests relative compositional maturity indicating recycled or intensely weathered first cycle sediment. Another index of pelitic sediments composition is the ratio K_2O/Al_2O_3. The ratio K_2O/Al_2O_3 can be used as an indicator of the original composition of ancient pelitic sediments (Cox et al. 1995). Ordered from high to low values, the K_2O/Al_2O_3 ratios of minerals are: alkali feldspars ~0.4 to 1, illite ~0.3, other clay minerals — nearly 0 (Cox et al. 1995). Pelitic sediments with ratios of K_2O/Al_2O_3 greater than 0.5 suggest a significant quantity of alkali feldspar relative to other minerals in the original rocks, those with ratios of K_2O/Al_2O_3 less than 0.4 suggest recycling of pelitic sediments (Cox et al. 1995). The Zagorje samples have an average K_2O/Al_2O_3 ratio of 0.23 (Table 5), suggesting minimal alkali feldspar relative to other minerals in the original pelitic sediments. The average ratio of SiO_2/Al_2O_3 =2.84 for the Zagorje samples (Table 5) suggests a relatively lower amount of quartz in relation to PAAS (SiO_2/Al_2O_3=3.32) and NASC (SiO_2/Al_2O_3=3.83), in accordance with the already discussed CIA values, spider diagram (Fig. 7a) and Al_2O_3-$(CaO+Na_2O)$-K_2O diagram (Fig. 12).

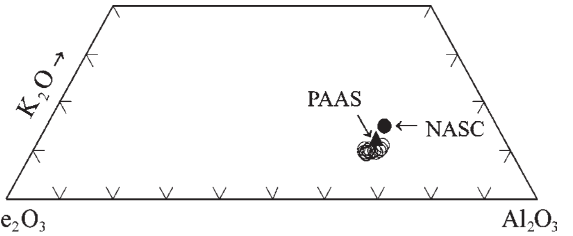

Fig. 13. Fe_2O_3-K_2O-Al_2O_3 plot of the Zagorje samples in comparison with the data for Post-Archaean Australian Shale (PAAS) data given by Taylor & McLennan (1985) and North American Shale Composite (NASC) data given by Gromet et al. (1984).

The elemental ratios of Eu/Eu*, La/Sc, Th/Sc, Th/Co, Th/Cr and La/Cr indicative of source rock composition (Cullers 2000) are in the range of those derived from silicic rather than basic source rocks (Table 5).

Plots of the Th/Sc and Cr/Th of the marl samples are shown in Fig. 14, along with the continental and mafic signatures in terms of Th/Sc and Cr/Th ratios. Th as an incompatible element is enriched in silicic rocks, while Sc and Cr are compatible elements that are enriched in mafic rocks. The plot positions show a high affinity towards a felsic component. The marl samples were also plotted on a La-Th-Sc diagram (Fig. 15) together with data for UC, PAAS, Oceanic Crust (OC) and Bulk Continental Crust (BCC) from Taylor & McLennan (1985). Our samples plot in a fairly narrow region of the Upper Crust (UC) and Post-Archaean Australian Shale (PAAS) fields.

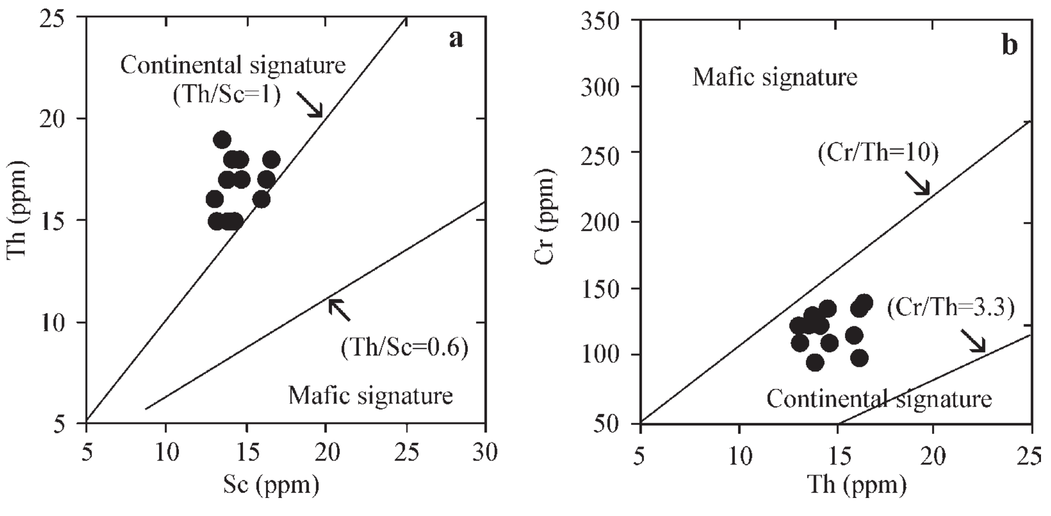

Fig. 14. a — Th versus Sc plot for the Zagorje samples. Th/Sc ratios near unity are typical of upper continental crust (UC) derivation and Th/Sc ratio near 0.6 suggest a more mafic component. **b** — Cr versus Th plot for the Zagorje samples, shown in comparison to the Upper Crust (UC) and Post-Archaean Australian Shale (PAAS) after Taylor & McLennan (1985).

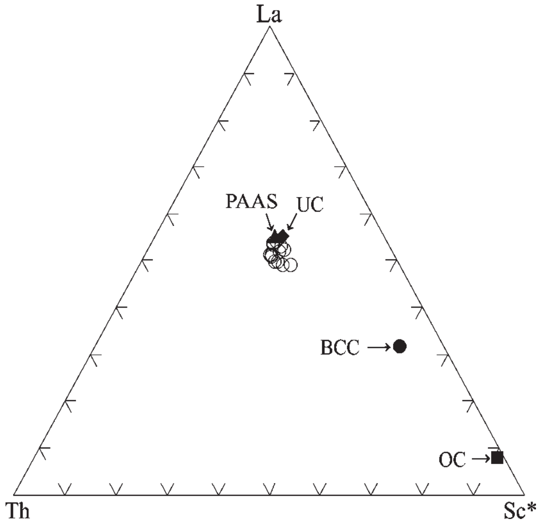

Fig. 15. La-Th-Sc plot for the Zagorje samples in comparison with the data for Post-Archaean Australian Shale (PAAS), Upper Crust (UC), Bulk Continental Crust (BCC) and Oceanic Crust (OC) from Taylor & McLennan (1985).

Conclusions

1 — XRPD analyses of marl insoluble residue revealed that most of the samples contain the same mineral species, however particular minerals are present in different quantities in different samples. Clay minerals content varied from 18 to 50 %, quartz content from 5 to 21 %, and feldspar content from 1 to 5 %. Several samples contained small quantities of dolomite and pyrite. Pannonian age marls, from the Pušća outcrop, contain higher amounts of clay minerals and calcite than Pontian marls, from Kupljenski Hruševec outcrop, that are richer in quartz and feldspars.

2 — The <2 μm insoluble residue fraction of all samples contains the following clay minerals: smectite, illite, chlorite; while kaolinite is present only in a few samples.

3 — The dominant constituents in the 0.09 to 0.16 mm fraction are quartz, feldspars, rock fragments (chert, quartzite and schists) and micas. Chlorite, limonite, pyrite, garnet, tourmaline, zircon, epidote and staurolite are present in small amounts.

4 — Sediments were classified on the basis of $CaCO_3$ content and insoluble residue mineral content; most of the Pannonian age samples were classified as marls, while the samples of the Pontian age are silty marls.

5 — Variations in chemical composition of pelitic sediments are in perfect agreement with the variations in sediment mineral composition. The CIA values of the investigated pelitic sediments (77–80) and the average ICV of 0.67 indicate relatively compositionally mature and intensely weathered first cycle sediments. Major and trace element composition, elemental ratios critical of provenance (SiO_2/Al_2O_3, K_2O/Na_2O, Eu/Eu*, La/Sc, Th/Sc, Th/Co, Th/Cr and La/Co) and source rock discriminations diagrams (Fe_2O_3-K_2O-Al_2O_3 and La-Th-Sc), suggest that the source rocks of these pelitic sediments were from the Upper Crust and remarkably felsic in nature.

6 — The chemical composition of the sediments and modal composition of the silt-size fraction indicate Alpine provenance of the clastic material.

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