GEOLOGIJA 60/2, 223-234, Ljubljana 2017
https://doi.org/10.5474/geologija.2017.016

Mineralogical and geochemical characteristics of mudstones in the Jersovec chert deposit

Mineraloške in geokemične značilnosti muljevcev iz nahajališča rožence Jersovec

Simona JARC[1], Simon JERINA[2], Miloš MILER[3] & Nina ZUPANČIČ[1,4]

[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva 12, SI-1000 Ljubljana, Slovenia, e-mails: simona.jarc@ntf.uni-lj.si; nina.zupancic@ntf.uni-lj.si
[2]Aškerčeva ul. 8, SI-8000 Novo mesto, Slovenia, e-mail: simon.jerina@gmail.com
[3]Geological Survey of Slovenia, Dimičeva ulica 14, SI-1000 Ljubljana, Slovenia, e-mail: milos.miler@geo-zs.si
[4]Ivan Rakovec Institute of Paleontology, ZRC SAZU, Novi trg 2, SI-1000 Ljubljana, Slovenia

Prejeto / Received 11. 9. 2017; Sprejeto / Accepted 26. 10. 2017; Objavljeno na spletu / Published online 22. 12. 2017

Key words: mudstone, chert, geochemistry, SEM/EDS, Jersovec
Ključne besede: muljevec, roženec, geokemija, SEM/EDS, Jersovec

Abstract

Jersovec chert deposit is a part of the transitional zone between the internal and the external Dinarides. Tethyan cherts are often interlaid with fine-grained material, as is also the case in Jersovec, where chert beds interchange with several thin, up to 10 cm thick layers of fine-grained sedimentary rocks. The source of this material is often questionable and interpreted to be terrigenous, volcanogenic or even combination of both. In order to determine origin and depositional environment of fine-grained material, detailed mineralogical and geochemical analyses were performed.

Fine-grained sedimentary rocks were characterised by X-ray diffraction (XRD), scanning electron microscopy/ energy dispersive X-ray spectroscopy (SEM/EDS) and inductively coupled plasma emission spectroscopy (ICP-ES) and mass spectroscopy (ICP-MS). All samples are mineralogically very similar but differ in mineral ratios. They contain quartz and clay minerals, predominantly illite/muscovite and chlorite group minerals. SEM/EDS analysis additionally revealed zircon, monazite, Ti-oxide (probably rutile) and iron oxides/hydroxides in all samples, whereas chromite, ilmenite, xenotime, apatite and baryte were found only in some of them. The average sizes of accessory minerals range from 3–20 μm. Two samples differ from the others by their brown colour and higher Fe_2O_3 and lower SiO_2 contents. All other samples are green. Chemical analysis showed that they consist mostly of SiO_2 (46.3–69.3 %), Al_2O_3 (15–24.1 %) and minor contents of K_2O (2.8–3.4 %), Fe_2O_3 (2.1–8.4 %), MgO (1.6–2.3 %), TiO_2 (0.5–0.7 %), CaO (0.3–1.4 %), Na_2O (0.1 %) and P_2O_5 (up to 0.5 %).

Position of all samples in the Zr/TiO_2 vs. $(V+Ni+Cr)/Al_2O_3$ diagram points to terrigenous origin and sedimentation on the continental margin. According to the chemical weathering indices (CIA and CIW) material has been subjected to the intense and long weathering, supported also by the index of compositional variability (ICV), which corresponds to the compositionally mature material, and by rounded zircon and ilmenite grains.

Izvleček

Nahajališče rožence Jersovec se nahaja v prehodni coni med Zunanjimi in Notranjimi Dinaridi. V nahajališču so med roženci tanke, do 10 cm debele plasti drobnozrnatih sedimentnih kamnin. Takšne sedimentne kamnine z roženci so zelo značilne na območju Tetide. Izvor medplastovnega materiala je pogosto vprašljiv in ga razlagajo kot terigen ali vulkanski ali kombinacijo obeh. Je pomemben indikator sedimentacijskega okolja. Z geokemičnimi in mineraloškimi analizami smo skušali določiti izvor teh sedimentov.

Mineralno sestavo smo določili z metodo rentgenske difrakcije (XRD) in z vrstično elektronsko mikroskopijo v kombinaciji z energijsko disperzijsko spektroskopijo rentgenskih žarkov (SEM/EDS), geokemično sestavo z metodo induktivno vezane plazme z emisijsko spektrometrijo (ICP-ES) in masno spektrometrijo (ICP-MS). Vsi vzorci imajo podobno mineralno sestavo. Prevladujejo kremen in glineni minerali, med njimi največ illita/ muskovita in mineralov kloritove skupine. SEM/EDS analiza je poleg omenjenih mineralov v vseh vzorcih pokazala še prisotnost cirkona, monacita, Ti-oksida (najverjetneje gre za rutil) in železovih oksidov/hidroksidov, medtem ko smo kromit, ilmenit, ksenotim, apatit in barit našli le v posameznih vzorcih. Povprečne velikosti akcesornih mineralov so med 3 in 20 μm. Dva vzorca se od preostalih razlikujeta po rjavi barvi in večji vsebnosti Fe_2O_3 in manjši vsebnosti SiO_2. Ostali vzorci so zelene barve. Kemijska analiza je pokazala, da v vseh vzorcih prevladujeta SiO_2 (46,3–69,3 %) in Al_2O_3 (15–24,1 %), sledijo K_2O (2,8–3,4 %), Fe_2O_3 (2,1–8,4 %), MgO (1,6–2,3 %), TiO_2 (0,5–0,7 %), CaO (0,3–1,4 %), Na_2O (0,1 %) in P_2O_5 (do 0,5 %).

Položaj vseh vzorcev na diagramu Zr/TiO2 vs. $(V+Ni+Cr)/Al_2O_3$ kaže na terigen izvor materiala in sedimentacijo na kontinentalnem robu. Indeksa kemičnega preperevanja (CIA in CIW) kažeta na intenzivno in dolgo preperevanje, kar potrjuje tudi indeks spremenljivosti sestave (ICV), ki skupaj z zaobljenostjo zrn cirkona in ilmenita kaže na zrelost sestave materiala.

Introduction

Sedimentary rocks with cherts are very common Mesozoic pelagic sediments of the entire Tethys (Baumgartner, 2013). In Slovenia, they are found in the transitional zone between the internal and the external Dinarides. The stratigraphy of several Tethyan chert outcrops has been extensively studied, whereas the studies on the fine-grained clastics, interbedded with cherts, are not very common (Barrett, 1981; Baltuck, 1982, Amodeo, 1999; Di Leo et al.,2002a, b; Halamić et al., 2005; Peh & Halamić, 2010, Skobe et al., 2013). The origin of the fine-grained material could be either terrigenous and/or volcanogenic; it reflects the depositional environment, ranging from a shelf to a mid-ocean ridge or continental margin (Boström, 1973; Murray, 1994; Girty et al., 1996; Andreozzi et al., 1997; Di Leo et al., 2002a). Therefore, it helps to interpret the palaeoenvironmental and palaeogeographic position of the area in Tethys realm.

In Jersovec deposit in Dolenjska region, chert is still being quarried. Here, chert beds interchange with thin, up to 10 cm thick layers of fine-grained sediments. The origin of this fine-grained material has not been determined yet. In the vicinity, very similar clastic material of Jurassic age has been found and studied in the abandoned quarry near Izvir village in Krško depression (Skobe et al., 2013), in Italy, where the interbedded material is also of Jurassic age (Barrett, 1981), and in Croatia, where the clastics are of Triassic and Jurassic age (Peh & Halamić, 2010).

The aim of the paper is to characterise the fine-grained material from Jersovec deposit, to establish its provenance and depositional environment, and to compare it with similar rocks from neighbouring deposit near Izvir in Krško depression.

Geological setting

The investigated area is located in the south-eastern Slovenia, in the vicinity of Mirna and Trebnje, Dolenjska region. The area is a part of the transitional zone between the internal and the external Dinarides (Fig. 1). In the area several outcrops of cherts are reported, the closest one to Jersovec is Izvir (Fig 1).

The rocks from Jersovec deposit are of upper Triassic age, the so called »transitional« beds (the expression is used for rock of indefinable age, laying between upper Triassic and lower Cretaceous beds), lower Cretaceous and Quaternary age (Šolar, 1991). Upper Triassic beds are characterised by light grey »Bača dolomite« with chert nodules and beds, and crisscrossed with calcite veins. Upper parts of the dolomite are strongly weathered (Šolar, 1991). The transitional beds are represented by dolomite-chert breccia, bedded and laminated cherts and beds of muddy sandy to sandy muddy chert gravel. Cretaceous beds consist of quartz sandstones, shales and micritic limestones transiting to calcarenites and containing chert nodules and beds. The youngest is Quaternary alluvium (Šolar, 1991).

Jersovec quarry is intersected by the NW-SE (Dinaric) fault and therefore the rocks have been tectonically deformed. Also, the older faults with W-E direction had caused some minor deformations (Šolar, 1991).

Between the chert beds there are very thin, at most up to 10 cm thick layers and lenses of fine-grained green to brown sediments. The colour is interpreted as a result of different degree of oxidation of some iron mineral(s) (Šolar, 1991). No mineralogical and geochemical studies of these fine-grained materials have been performed yet.

Materials and methods

Altogether, 7 samples were taken at two sites, located about 50 m from each other (Figs. 2 and 3). All samples were dried at 50 °C for two weeks and afterwards pulverised by hand in agate mortar to a grain size of <0.063 mm for geochemical and XRD analysis. Fragments of original rock samples were also prepared for SEM/EDS analysis. Heavy mineral fraction was prepared from one sample (Je-01) using bromoform (density 2.89 g/cm^3) and then inspected by SEM/EDS.

Mineral composition of all samples was determined by powder X-ray diffraction (XRD) at the Faculty of Natural Sciences and Engineering, Department of Geology, University of Ljubljana. XRD measurements were conducted using a Philips PW3710 diffractometer (PANalytical B.V.) equipped with CuKα radiation and a graphite monochromator. The X-Ray radiation was generated at a voltage of 10 kV and a current of 10 mA. Data were recorded in the range $2° \leq 2\Theta \leq 70°$. Mineral compositions of the samples were determined by X'pert Highscore Plus database.

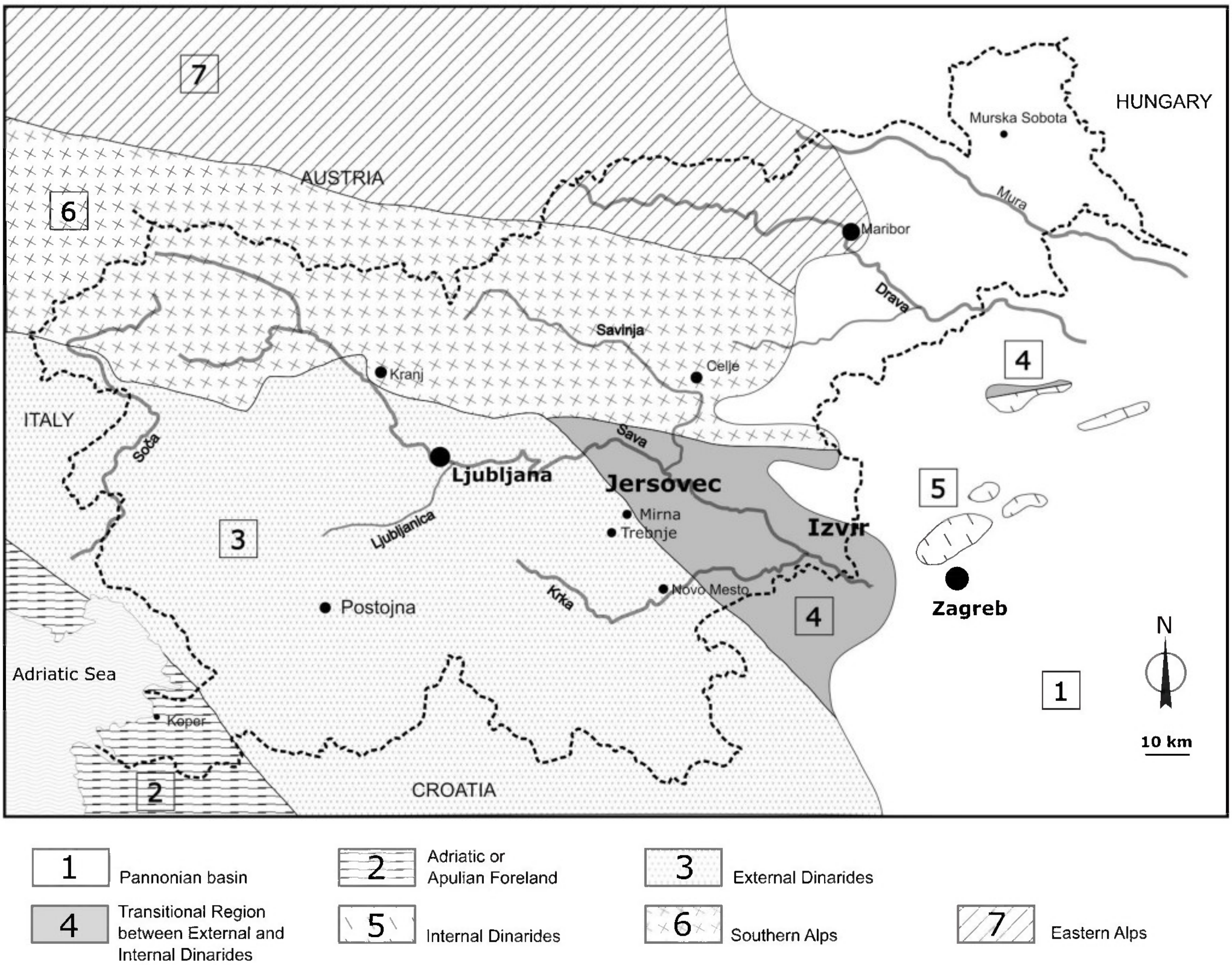

Fig. 1. Location map of the Jersovec deposit within main geotectonic units (after Placer, 1999; Skobe et al., 2013).

Fig. 2. Position of first sample Je-01; measuring rod equals 1.8 m; photo: S. Jerina.

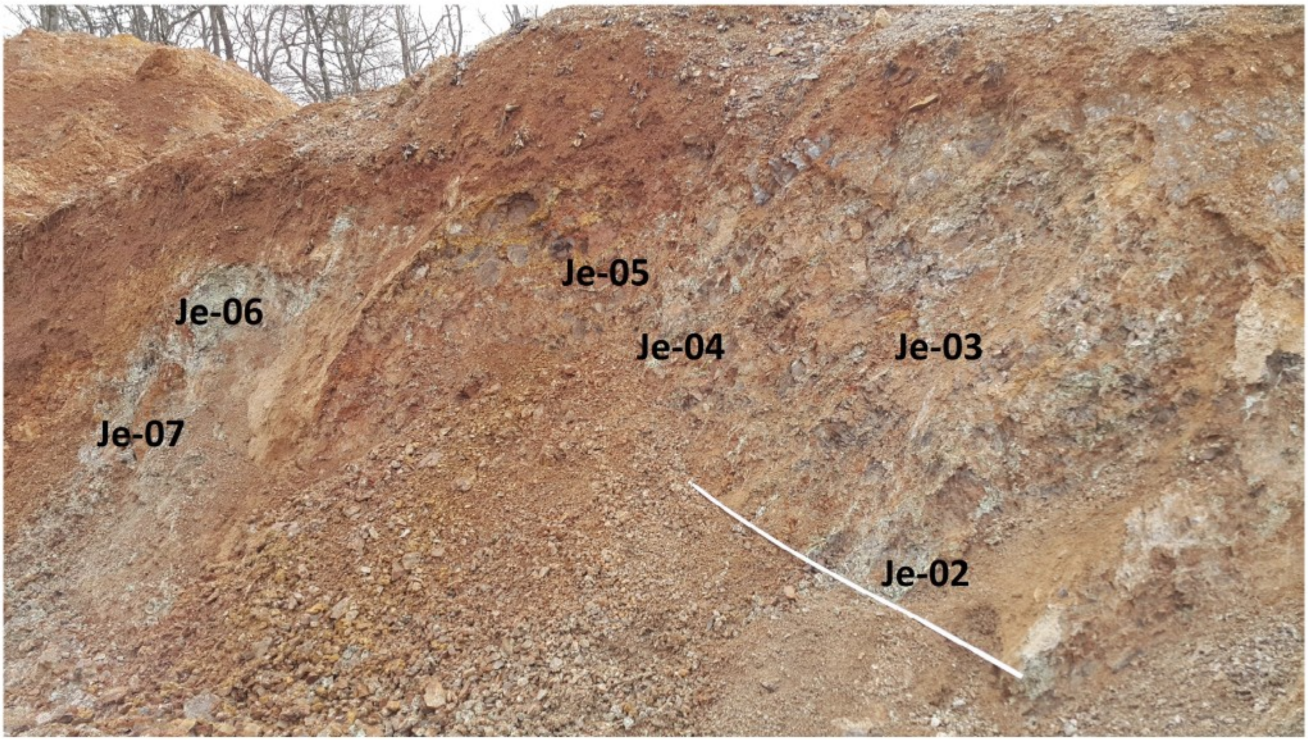

Fig. 3. Position of samples Je-02, Je-03, Je-04, Je-05, Je-06 in Je-07; measuring rod equals 1.8 m; photo: S. Jerina.

A whole rock geochemical analysis of major oxides and several trace elements, including rare earths was carried out by inductively coupled plasma emission spectroscopy (ICP-ES) and mass spectroscopy (ICP-MS) at Bureau Veritas Commodities Canada. The analytical quality based on international standards and one replicate sample (Je-06-1) is satisfactory, with the precision and accuracy error below 10 %. Precision error >10 % was established for CaO, Cu, Hg, Pb, Sn, Ta, U, W and Zn, due to their low content. These elements, and additionally Sb and total sulphur (TOT/S), whose contents were below detection limit (0.1 and 0.02 %), were omitted from further study. Also contents of MnO were below detection limit in some samples. As MnO is necessary for one of the used discriminant diagrams, half of the detection limit value was used for the calculation.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) of original rock fragments and one sample of heavy mineral fraction was carried out at Geological Survey of Slovenia. The samples were coated with carbon and then observed in high vacuum, in backscattered electron (BSE) mode by JEOL JSM 6490LV SEM, coupled with an Oxford INCA EDS at an accelerating voltage of 20 kV, working distance 10 mm and acquisition time of 60 s. Minerals were determined using known mineral databases (Anthony et al., 2009; Barthelmy, 2010).

Results and discussion

Macroscopically, the colour of the samples varies from green and greenish grey (5GY 7/2, 5GY8/1) to brown (5YR 5/6, 5YR 3/4). The mineral compositions of all samples are very similar (Fig. 4) with prevailing quartz and illite/muscovite (illite and muscovite cannot be distinguished), and possible minor presence of chlorite group minerals. Samples differ only in mineral ratios. The sample Je-05 contains less quartz than others and also seems to be of lower crystallinity, whereas samples Je-02 and Je-06 contain the maximum content of quartz.

SEM/EDS analysis supports the results of XRD analysis and additionally reveals the presence of some accessory minerals (Table 1). Quartz grains are the most abundant in all samples, followed by clay minerals. The average grain size of quartz is approximately 15 µm. Also, clay minerals are abundant in all samples. Micas, most probably muscovite, and minerals of chlorite group, are around 10 µm in size with frequently pseudohexagonal shapes. In all samples, zircon, iron oxides/hydroxides, monazite and Ti-oxide mineral, most probably rutile, have been detected. Rutile grains are euhedral, sometimes elongated, prismatic and around 7 µm in size (Fig. 5a). They are more abundant in samples Je-01, Je-02, Je-03 and Je-07 (Table 1). Iron oxides/hydroxides are around 5 µm in size and more

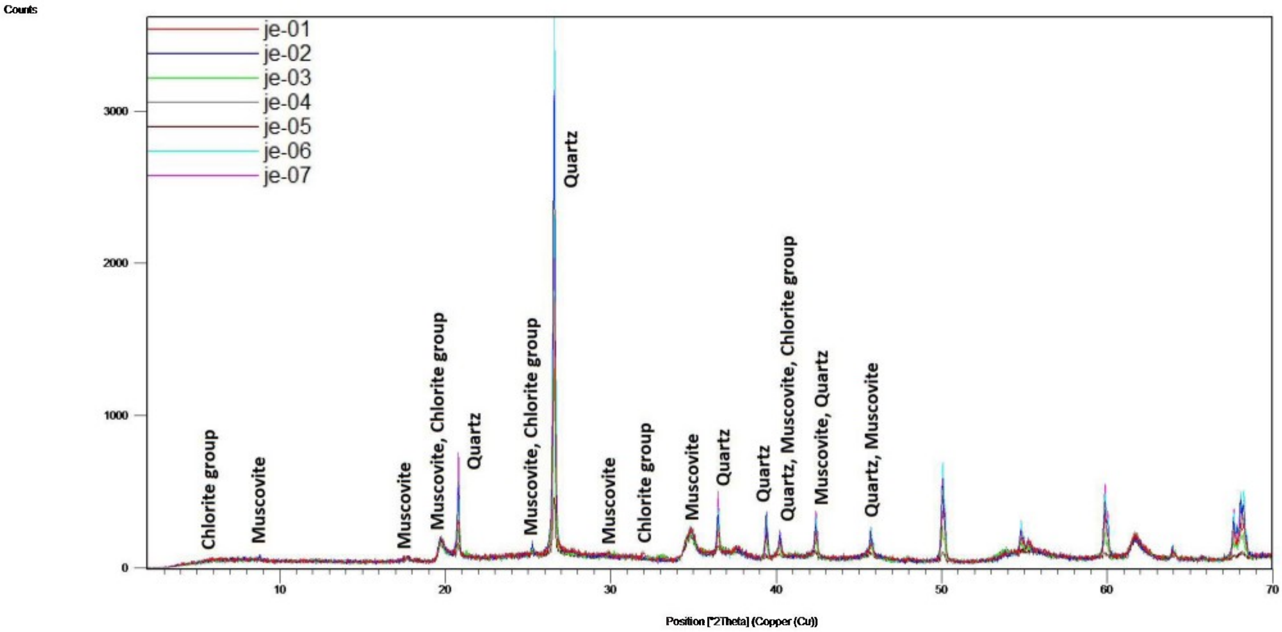

Fig. 4. XRD patterns of the investigated mudstone samples from Jersovec chert deposit.

Table 1. Minerals detected by SEM/EDS and their relative abundances;
Legend: *** – very frequent; ** – frequent; * – rare.

Mineral	Sample						
	Je-01	Je-02	Je-03	Je-04	Je-05	Je-06	Je-07
Quartz	***	***	***	***	***	***	***
Clay minerals	***	***	***	***	***	***	***
Mica	***	***	***	***	***	***	***
Iron oxides/hydroxides	**	**	***	**	***	**	**
Rutile (TiO_2)	**	**	**	*	*	*	**
Zircon	*	*	*	**	**	**	*
Monazite	*	*	*	*	*	*	*
Chromite	*			*		*	*
Ilmenite	*			*		*	
Xenotime						*	*
Apatite	**						
Baryte				*			

abundant in samples Je-03 and Je-05. The majority of zircon grains are around 20 μm in size, but sometimes larger grains are also present (>150 μm) – some rounded grains point to long transportation (Fig. 5b). Zircon grains are more abundant in samples Je-04, Je-05 and Je-07 (Table 1). Monazite is frequently found in clusters of 5 μm (Fig. 5c). Chromite is detected in some samples (Je-01, Je-04, Je-06 and Je-07) – it is angular and about 5 μm in size (Fig. 5d). Ilmenite was detected only in samples Je-01 and Je-04. It has an average grain size of 10 μm, with the exception of one rounded grain (sample Je-01) larger than 150 μm, which could indicate a long transportation (Fig. 6a). About 3 μm large xenotime grains were found in samples Je-06 and Je-07 (Fig. 6b). Apatite, most probably fluorapatite of 70 μm in size, has been found only in one sample (Je-01; (Fig. 6c), and one very small baryte grain (~ 2 μm) in sample Je-04. The heavy minerals in sample Je-01 represent approximately 0.95 % of the total sample weight. According to mineral compositions and grain sizes all investigated samples are mudstones.

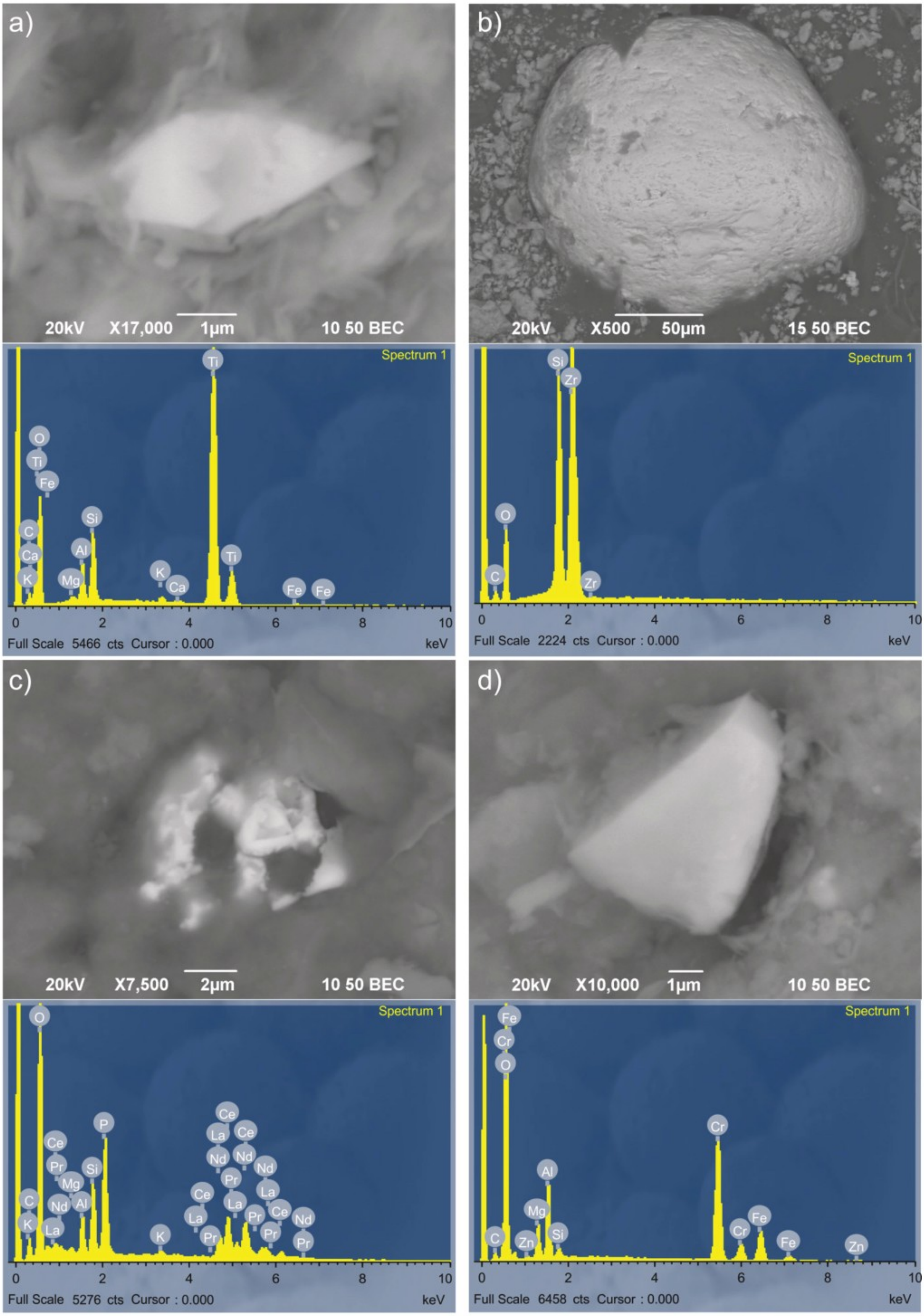

Fig. 5. SEM (BSE) images and EDS spectra of: a) rutile (sample Je-01); b) rounded zircon grain in heavy mineral fraction (sample Je-01); c) monazite (sample Je-04) and d) chromite (sample Je-04).

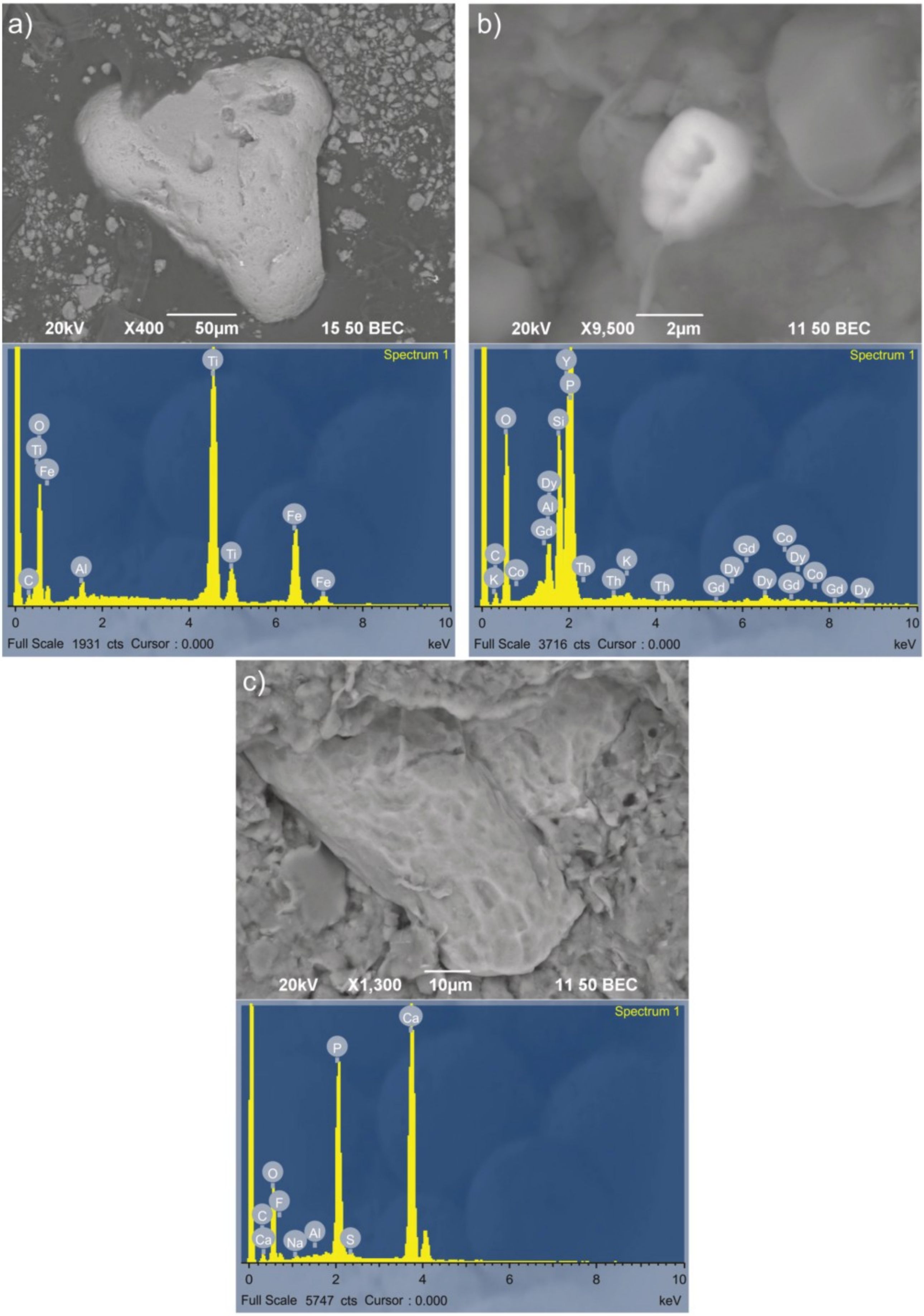

Fig. 6. SEM (BSE) images and EDS spectra of: a) rounded ilmenite grain in heavy mineral fraction (sample Je-01); b) xenotime (sample Je-06) and c) apatite (sample Je-01).

The layers and lenses of fine-grained sedimentary rocks from Jersovec are macroscopically quite similar to up to 2 cm thick shale intercalations from the closest chert outcrop at Izvir. However those from Jersovec do not have fissile structure. Mineralogically, fine-grained materials from both Jersovec and Izvir consist of quartz, clay minerals (illite and minor chlorite); however K-feldspar was found additionally in some samples from Izvir (Skobe et al., 2013).

The geochemical composition of all the samples is generally similar (Table 2). In all samples SiO_2 prevails, with the contents ranging from 46.3 % (Je-05) to 69.3 % (Je-06), followed by Al_2O_3 (15 % in Je-06-1 to 24.1 % in Je-05) and K_2O (2.8 % in Je-02 to 3.4 % in Je-05). The content of Fe_2O_3 is very variable, from 2.1 % in Je-06-1 to 8.4 % in Je-05. The content of MgO is from 1.6 % (Je-02) to 2.3 % (Je-05). The content of CaO is <1 %, except in sample Je-01 (1.4 %). The values of Na_2O, TiO_2, P_2O_5 and MnO are all <1%.

Table 2. Chemical compositions of the mudstone from the Jersovec chert deposit.

wt %	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	TOT/C
Je-01	59.06	19.20	2.80	2.23	1.40	0.13	3.32	0.63	0.34	<0.01	10.70	0.04
Je-02	66.93	16.38	2.40	1.63	0.43	0.11	2.76	0.47	0.04	<0.01	8.70	0.02
Je-03	53.61	20.13	6.68	1.91	0.47	0.12	3.18	0.67	0.48	0.04	12.20	0.23
Je-04	64.25	17.49	2.67	1.79	0.49	0.11	3.02	0.52	0.06	<0.01	9.40	<0.02
Je-05	46.32	24.12	8.42	2.29	0.57	0.11	3.36	0.53	0.26	0.12	13.60	0.14
Je-06	69.25	15.16	2.19	1.62	0.39	0.10	2.94	0.57	0.07	<0.01	7.50	0.03
Je-07	66.16	16.77	2.60	1.66	0.34	0.11	3.03	0.57	0.04	0.07	8.50	0.02
Je-06-1	69.00	15.04	2.13	1.63	0.84	0.10	3.00	0.57	0.07	<0.01	7.40	0.11

mg/kg	As	Cr	Ba	Co	Cs	Hf	Nb	Ni	Pb	Sc	Sr	Ta
Je-01	0.8	212	240	7.4	37.3	3.7	11.6	125.8	6.3	17	61.2	1.0
Je-02	<0.5	137	216	5.4	31.7	2.9	8.4	104.2	2.9	16	52.0	0.7
Je-03	15.5	171	959	8.3	34.6	3.5	13.1	132.3	45.4	31	324.4	1.0
Je-04	<0.5	164	280	6.5	36.2	3.2	9.8	122.8	3.6	15	70.9	0.7
Je-05	21.3	178	361	9.7	45.0	3.2	10.2	152.0	11.4	30	89.7	1.2
Je-06	<0.5	129	251	4.7	25.2	2.9	10.1	79.9	6.3	14	61.2	1.4
Je-07	1.2	123	240	13.0	28.2	3.3	10.0	68.5	4.7	16	54.3	0.8
Je-06-1	<0.5	137	251	4.9	25.2	3.1	10.2	73.1	5.3	14	64.8	1.1

mg/kg	Th	U	V	W	Y	Zn	Zr	Bi	Hg	Sn	Rb	Cu
Je-01	12.6	5.3	198	2.2	35.3	120	137.0	0.3	0.08	3	186.1	41.2
Je-02	10.6	3.9	140	1.8	69.2	129	106.4	0.2	0.06	3	160.9	43.9
Je-03	15.6	17.9	231	1.7	136.0	149	135.9	0.6	0.36	4	172.2	103.7
Je-04	11.9	4.6	157	2.1	82.0	147	124.9	0.2	0.06	3	171.0	52.4
Je-05	15.0	9.2	219	1.3	114.7	154	108.4	0.6	0.43	4	187.5	101.1
Je-06	10.8	6.4	133	2.1	58.8	114	115.1	0.2	0.05	2	144.8	44.5
Je-07	10.5	3.8	133	1.9	54.1	91	115.1	0.2	0.06	3	154.2	37.3
Je-06-1	10.2	4.3	133	1.8	57.8	98	116.5	0.2	0.04	3	147.0	40.2

mg/kg	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Je-01	53.1	65.9	10.0	36.7	6.8	1.4	5.9	0.8	4.8	1.0	2.9	0.4	2.8	0.4
Je-02	51.0	51.5	9.4	35.0	6.4	1.5	7.3	1.1	6.9	1.6	4.8	0.7	4.2	0.7
Je-03	290.9	213.0	70.1	305.6	52.8	10.7	41.5	4.7	23.1	3.8	9.4	1.2	7.2	1.0
Je-04	75.6	73.4	16.8	67.7	12.0	2.7	11.5	1.6	9.5	1.9	5.6	0.8	4.9	0.8
Je-05	131.4	88.1	25.9	105.5	20.4	4.6	20.6	2.6	15.1	2.9	8.4	1.1	7.3	1.1
Je-06	72.3	66.6	14.3	54.8	9.5	2.0	8.7	1.2	7.3	1.5	4.4	0.6	3.9	0.6
Je-07	56.9	63.5	11.7	44.3	7.8	1.8	7.8	1.1	6.9	1.5	4.4	0.6	4.0	0.6
Je-06-1	70.6	64.2	14.0	53.8	8.8	1.9	8.7	1.2	7.0	1.5	4.3	0.6	4.0	0.6

With regard to SiO_2 and Al_2O_3, samples Je-01, Je-03 and Je-05 differ from others, as they are poorer in SiO_2 and enriched in Al_2O_3. However, with respect to Fe_2O_3 content and content of majority of other elements, sample Je-01 differs from Je-03 and Je-05 and is more similar to the other samples. On the contrary, Je-03 and Je-05 have more Fe_2O_3 and also elevated contents of some trace elements, i.e. As, Ba, Ni, Pb, Sr, U, V and REE, and higher values of loss on ignition (LOI). Both samples macroscopically differ from others by their brown colour. Colour and geochemical characteristics could indicate more intense weathering. Further, the results of SEM/EDS analysis have shown the highest abundance of iron oxides/hydroxides in mentioned samples.

In a discrimination diagram of ANDREOZZI et al. (1997) and DI LEO et al. (2002a, b), Jersovec samples plot in the field of terrigenous sediments (Fig. 7).

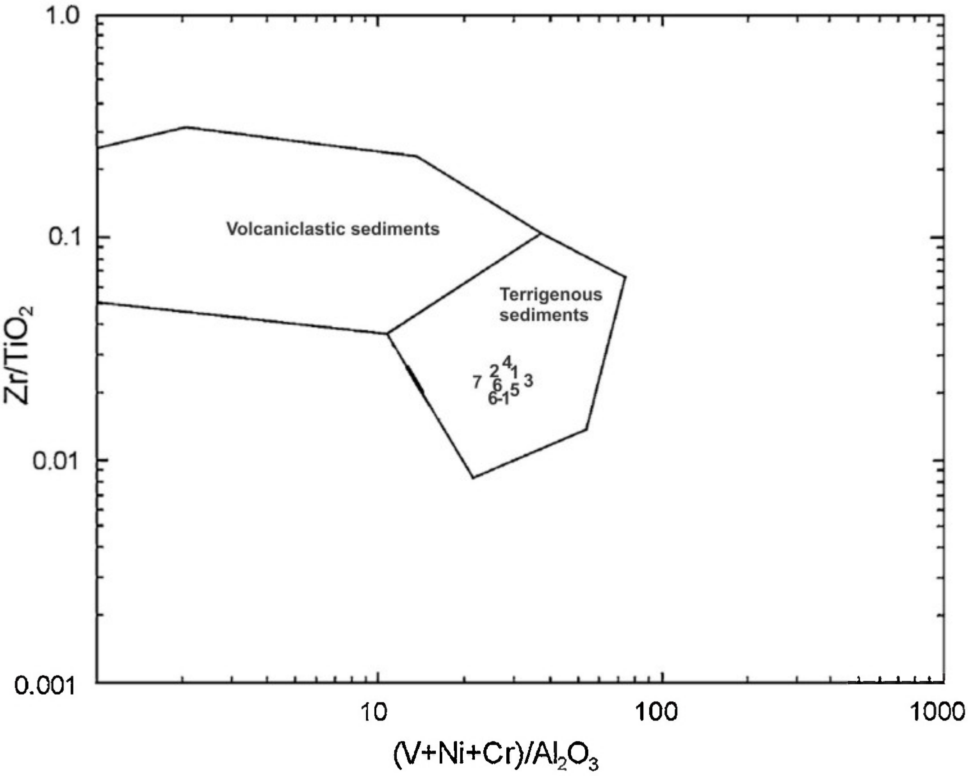

Fig. 7. Plot of the Jersovec mudstone samples in the discrimination diagram for the volcanogenic *vs.* terrigenous origin of the material (according to ANDREOZZI et al., 1997; DI LEO et al., 2002a, b).

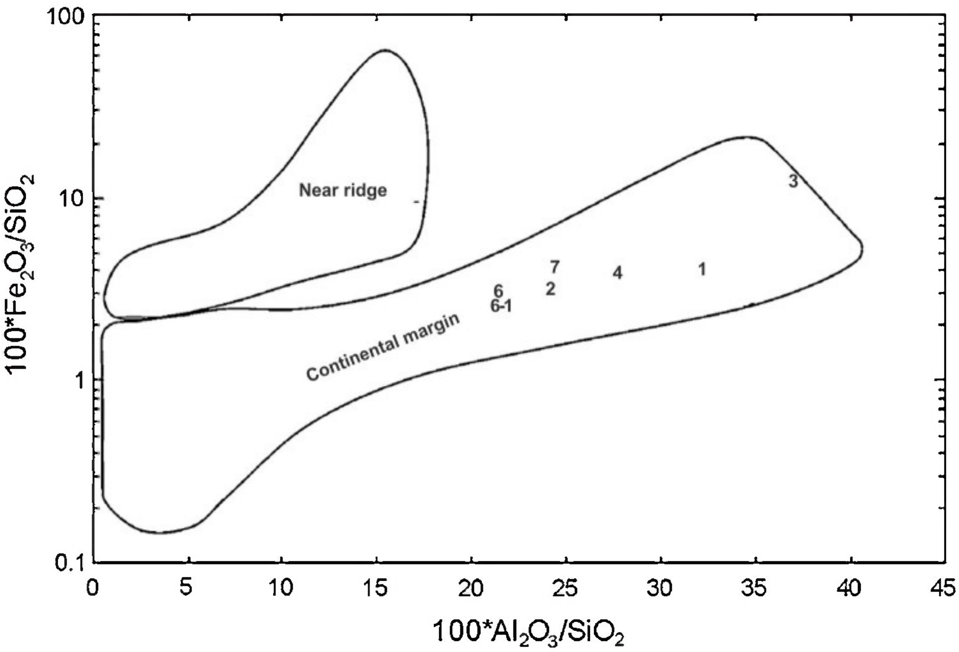

Fig. 8. Plot of investigated mudstone samples from Jersovec chert deposit in the discrimination diagram $100\times Fe_2O_3/SiO_2$ *vs.* $100\times Al_2O_3/SiO_2$ (after MURRAY, 1994).

According to $100 \times Fe_2O_3/SiO_2$ - $100 \times Al_2O_3/SiO_2$ discriminant diagram (MURRAY, 1994), depositional environment of the material is continental margin (Fig. 8). Exception is sample Je-05, which is placed outside the diagram due to its high Fe_2O_3 and low SiO_2 content.

All samples plotted on the discriminant diagram Fe_2O_3/TiO_2 - $Al_2O_3/(Al_2O_3+Fe_2O_3)$ (Fig. 9) also display the values typical for continental margin and old continental crust provenance (MURRAY, 1994; GIRTY et al., 1996).

The fine-grained clastics from the Jersovec are not hydrothermally altered as can be seen from the Fe_2O_3/TiO_2 *vs.* $Al_2O_3/(Al_2O_3+Fe_2O_3+MnO)$ diagram (BOSTRÖM, 1973) where they plot close to the material of terrigenous to basaltic origin (Fig. 10).

The degree of weathering has been established by three different indices. The chemical index of alteration (CIA) – $Al_2O_3/(Al_2O_3+Na_2O+CaO+K_2O) \times 100$ (NESBITT & YOUNG, 1982) is on the average 79.4, indicating weathered material. Sample Je- 01 has the lowest index of alteration (CIA; 75.1), and sample Je-05 has the highest (83.2). The chemical index of weathering (CIW) – $Al_2O_3/(Al_2O_3+Na_2O+CaO) \times 100$ (HARNOIS, 1988) ranges from 87.4 (sample Je-01) to 95.5 (sample Je-07), with an average value of 93.3 demonstrating intense and prolonged weathering (BARBERA

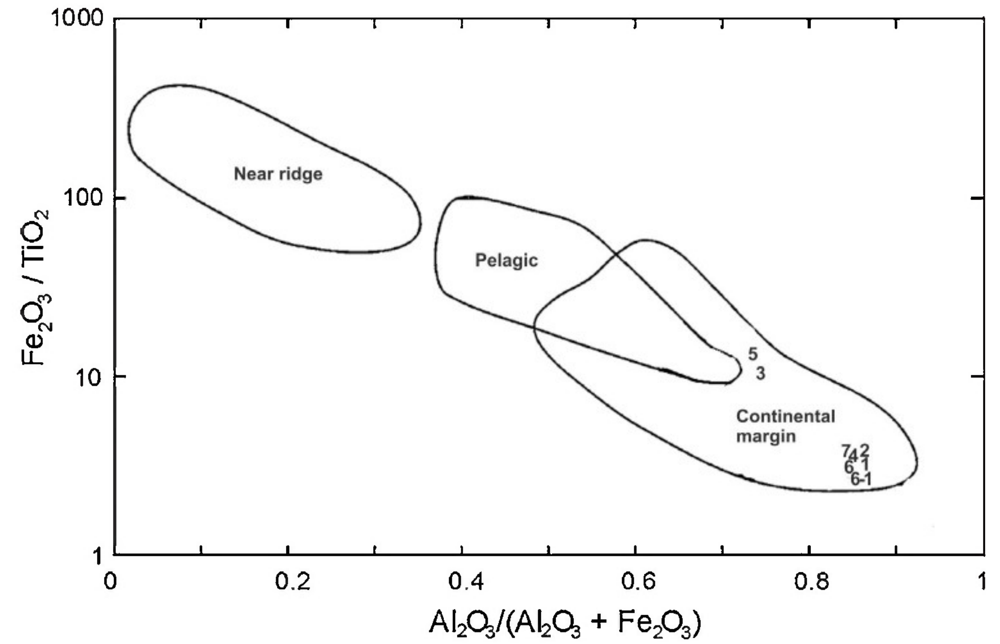

Fig. 9. Plot of the Jersovec mudstone samples in the Fe_2O_3/TiO_2 *vs.* $Al_2O_3/(Al_2O_3+Fe_2O_3)$ diagram (according to MURRAY, 1994; GIRTY et al., 1996).

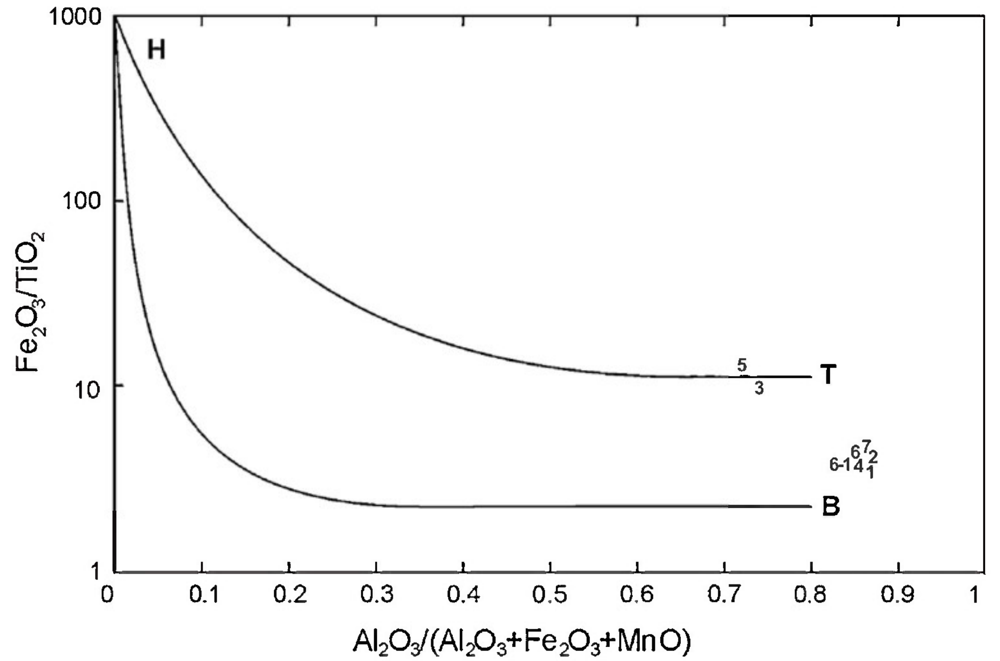

Fig. 10. Plot of the Jersovec mudstones in Fe_2O_3/TiO_2 *vs.* $Al_2O_3/(Al_2O_3+Fe_2O_3+MnO)$ discrimination diagram according to BOSTRÖM (1973); abbreviations: T – terrigenous material, B – basaltic material; H – hydrothermal end-member

et al., 2006). The brown coloured samples Je-03 and Je-05 have also very high CIW values, 95.0 and 95.2 respectively. The average value of the ICV (index of compositional variability): (Fe_2O_3+K_2O+Na_2O+CaO+MgO+TiO_2)/Al_2O_3 (Cox et al., 1995) is 0.54, and points to compositionally mature sediments (Cullers & Podkovyrov, 2000; Barbera et al., 2006). Also, the rounded grains of some accessory minerals (i.e. zircon, ilmenite) point to terrigenous origin of the material.

The Jurassic bedded cherts from Izvir are the closest to the investigated area. Comparison of Jersovec mudstones with the Izvir shales shows similar geochemical characteristics. The differences are in higher content of K_2O in Izvir shales reflecting the presence of K-feldspar. In Izvir area, the mixing of marine and meteoric waters during late diagenesis caused alteration of K-minerals, which were already present in sediments, into K-feldspars (Skobe et al., 2013). This process has not been detected in Jersovec. According to geochemical analysis, the material from Izvir is of terrigenous and not volcanic origin. Sediments in Izvir area, which is also part of the transitional zone that formed by rifting of thinned (micro)continental margin (Rižnar, 2005), were deposited on a Tethyan passive margin due to rapid subsidence, originally as silica-rich carbonate beds intercalated with mud (Skobe et al., 2013). As is in the case of Jersovec mudstones, the hydrothermal origin is also excluded for Izvir shales (Skobe et al., 2013). The average chemical index of weathering (CIW) is 95.7 and is similar to Jersovec samples. It indicates an intense and prolonged source of weathering. Also, index of compositional variability (ICV) points to compositionally mature material (Skobe et al., 2013).

Conclusions

The fine-grained material from Jersovec chert deposit is macroscopically very similar, but different in colour, ranging from prevailing green (5GY 7/2, 5GY 8/1) to sometimes brown (5YR 5/6, 5YR 3/4). Nevertheless, mineral composition of all the samples is very similar. Quartz and clay minerals, that is illite/muscovite and minerals of chlorite group, dominate, but mineral ratios vary. Further, SEM/EDS analysis showed the presence of Ti-oxide (probably rutile), zircon and monazite in all investigated samples and chromite, ilmenite, xenotime, apatite and baryte in some of them. The average sizes of accessory minerals range from 3 to 20 µm. Larger grains of some minerals (e.g. ilmenite, zircon) are rounded due to transportation. The results of SEM/EDS analysis are strongly supported by geochemical results; the contents of SiO_2 and Al_2O_3 are the highest, followed by K_2O, MgO, TiO_2, CaO, Na_2O, P_2O_3, whereas Fe_2O_3 is variable. Two samples, Je-03 and Je-05, differ from others, as they are poorer in SiO_2 and enriched in Fe_2O_3 and some trace elements, i.e. As, Ba, Ni, Pb, Sr, U, V, REE, and Al_2O_3 and loss on ignition. Also, both samples differ from others macroscopically, as they are brown in colour. The colour and geochemical characteristics could indicate more intense weathering of the two samples as it is also proven by weathering indices. Based on the mineral compositions and grain sizes, all samples are mudstones.

According to the results of the geochemical analysis, discriminant diagrams show terrigenous origin of the mudstones from Jersovec. The material was deposited on the continental margin. The average indices of chemical alteration (CIA) and weathering (CIW) are 79.4 and 93.3, respectively. Both indicate an intense and long weathering. Weathering processes have been also confirmed by well-rounded minerals documented by SEM/EDS. The index of compositional variability (ICV; average value is 0.54) demonstrates the compositional maturity of the material. The similar results have been obtained in the clastics from the vicinity, near Izvir in Krško depression. Fine-grained material from both locations has comparable mineral and geochemical attributes, which point to terrigenous origin and the sedimentation on the continental margin. The difference is the presence of authigenic K-feldspar in Izvir samples as a result of later diagenetic processes. K-feldspars have not been detected in Jersovec samples.

Acknowledgements

We thank Kremen d.d. for enabling the access to the Jersovec quarry. Many thanks to Dr. Dragomir Skaberne and Dr. Aleksander Horvat for help with the fieldwork.

References

Amodeo, F. 1999: Il Triassico terminale - Giurassico del Bacino Lagonegrese. Studi stratigrafici sugli Scisti Silicei della Basilicata (Italia meridionale). Mémoires de Géologie, Lausanne, 33: 1–121, pls. 1–10.

Andreozzi, M., Dinelli, E. & Tateo, F. 1997: Geochemical and mineralogical criteria for the identification of ash layers in the stratigraphic framework of a foredeep; the Early Miocene Mt. Cervarola Sandstones, northern Italy. Chemical Geology, 137: 23–39, doi:10.1016/S0009-2541(96)00148-9.

Anthony, J.W., Bideaux, R.A., Bladh, K.W. & Nichols, M.C. 2009: The Handbook of Mineralogy [online]. Mineralogical Society of America. Internet: http://www.handbookofmineralogy.org/ (10.9.2016).

Baltuck, M. 1982: Provenance and distribution of Tethyan pelagic and hemipelagic sediments, Pindos Mountains, Greece. Sedimentary Geology, 31/1: 63–88, doi:10.1016/0037-0738(82)90008-2.

Barbera, G., Mazzoleni, P., Critelli, S., Pappalardo, A., Lo Giudice, A. & Cirrincione, R. 2006: Provenance of shales and sedimentary history of the Monte Soro Unit, Sicily. Periodico di Mineralogia, 75: 313–330.

Barrett, T.J. 1981: Chemistry and mineralogy of Jurassic bedded chert overlying ophiolites in the North Apennines, Italy. Chemical Geology, 34/3-4: 289–317, doi:10.1016/0009-2541(81)90118-2.

Barthelmy, D. 2010: The Mineralogy Database. Internet: http://webmineral.com/ (8.6.2016),

Baumgartner, P.O. 2013: Mesozoic radiolarites—accumulation as a function of sea surface fertility on Tethyan margins and in ocean basins. Sedimentology, 60/1: 292–318, doi:10.1111/sed.12022.

Boström, K. 1973: The origin and fate of ferromanganoan active ridge sediments. Stockholm Contributions in Geology, 27: 147–243.

Cox, R., Low, D.R. & Cullers, R.L. 1995: The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. Geochim Cosmochim Acta, 59: 2919–2940.

Cullers, R.L. & Podkovyrov, V.N. 2000: Geochemistry of the Mesoproterozoic Lakhanda shales in southern Yakutia, Russia: implications for mineralogical and provenance control, and recycling. Precambrian Research, 104/1-2: 77–93, doi: 10.1016/S0301-9268(00)00090-5.

Di Leo, P., Dinelli, E., Mongelli, G. & Schiattarella, M. 2002a: Geology and geochemistry of Jurassic pelagic sediments, Scisti silicei Formation, southern Apennines, Italy. Sedimentary Geology, 150/3-4: 229–246, doi:10.1016/S0037-0738(01)00181-6.

Di Leo, P., Giano, S.I. & Schiattarella, M. 2002b: Volcanoclastic layers in upper Triassic-Jurassic deep-sea sediments from the Lucanian Apennine, southern Italy: mineralogy, geochemistry, and palaeotectonic implications. Periodico di Mineralogia, 71: 49–63.

Girty, G.H., Ridge, D.L., Knaack, C., Johnson, D. & Al-Riyami, R.K. 1996: Provenance and depositional setting of Paleozoic chert and argillite, Sierra Nevada, California. Journal of Sedimentary Research, 66: 107–118, doi:10.1306/D42682CA-2B26-11D7-8648000102C1865D.

Halamić, J., Marchig, V. & Goričan, Š. 2005: Jurassic radiolarian cherts in north-western Croatia: geochemistry, material provenance and depositional environment. Geologica Carpathica, 56: 123–136.

Harnois, L. 1988: The CIW index: A new chemical index of weathering. Sediment Geol, 55/3-4: 319–322, doi:10.1016/0037-0738(88)90137-6.

Murray, R.W. 1994: Chemical criteria to identify the depositional environment of chert: General principles and applications. Sedimentary Geology, 90/3-4: 213–232, doi:10.1016/0037-0738(94)90039-6.

Nesbitt, H.W. & Young, G.M. 1982: Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature, 299: 715–717, doi:10.1038/299715a0.

Peh, Z. & Halamić, J. 2010: Discriminant function model as a tool for classification of stratigraphically undefined radiolarian cherts in ophiolite zones. J Geochem Explor, 107: 30–38, doi:101016/j.gexplo.2010.06.003.

Placer, L. 1999: Contribution to the macrotectonic sudivision of the border region between Southern Alps and External Dinarides. Geologija, 41: 223–255, doi:10.5474/geologija.1998.013.

Rižnar, I. 2005: Geology of the transitional area between outer and inner Dinarides, Eastern Slovenia. Ph.D. dissertation, University of Zagreb, Zagreb: 146 p, app. 5.

Skobe, S., Goričan, Š., Skaberne, D., Verbič T., Mišič, M. & Zupančič, N. 2013: K-feldspar rich shales from Jurassic bedded cherts in southeastern Slovenia. Swiss Journal of Geosciences, 106: 491–504, doi:10.1007/s00015-013-0147-3.

Šolar, V.S. 1991: Modifikacijske spremembe mineralov kremenice roženca iz nahajališča Jersovec. Magistrska naloga. Univerza Edvarda Kardelja, Ljubljana: 107 p.