GEOLOGIJA *46/1*, 113–116, Ljubljana 2003

Chemical composition of Kiscellian silty sediment (sivica) from the Trobni Dol area, Eastern Slovenia

Kemična sestava sivice s Trobnega Dola, vzhodna Slovenija

Polona KRALJ & Miha MIŠIČ
Geological Survey of Slovenia, Dimičeva 14, 1000 Ljubljana, Slovenia

Key words: Kiscellian silt, sivica, geochemistry, Pannonian basin, Slovenia
Ključne besede: kiscellijski melj, sivica, geokemija, Panonski bazen, Slovenija

Abstract

Kiscellian marine silt termed »sivica« is widely developed in Tertiary basins of Eastern Slovenia. Chemical composition is rather uniform and reflects the dominance of filosilicates (mainly illite/muscovite, chlorite and montmorillonite) and carbonates. PAAS normalised REE and Y abundances are slightly depleted for La, Ce, Pr and Nd, very close to PAAS for Sm, Eu, Gd and Tb, and depleted for Y, Ho, Er, Tm, Yb and Lu.

Kratka vsebina

Kiscellijski morski sediment imenovan »sivica« je močno razprostranjen v terciarnih bazenih vzhodne Slovenije. Kemična sestava je precej enotna in odraža prevladujoč delež filosilikatov (illita/muskovita, klorita in montmorillonita) in karbonatov. Na PAAS normalizirane vsebnosti prvin redkih zemelj kažejo nekoliko nižje vrednosti za La, Ce, Pr in Nd, skoraj enake za Sm, Eu, Gd in Tb, in nižje za Y, Ho, Er, Tm in Lu.

Introduction

The Trobni Dol area (Fig. 1) forms a part of the Laško basin – a Tertiary depression, which belongs to the system of Pannonian basins. The Laško basin is moderately folded and composed of a number of synclines and anticlines (Aničić & Juriša 1985a,b), where pre-Tertiary basement and Tertiary sediments ranging in age from Kiscellian to Pannonian outcrop (Aničić et al. 2002).

Sivica is a poorly lithified fine-grained marine sediment which was commonly termed as marly clay or clayey marl in the past. Sivica is very similar to Kiscellian clay in Hungary according to lithological characteristics and foraminifera fauna (Rijavec 1978, Jelen et al. 1992). Our studied samples belong to silts, which contain up to 30% of clay and some fine sand. Mineral composition is rather uniform, although the content of minerals is variable. The following minerals were recognised: illite/muscovite with attached mixed layered clay minerals, chlorite with attached mixed layered clay minerals, kaolinite, Ca-montmorillonite, quartz, plagioclase, calcite, dolomite and pyrite. Details of clay mineral

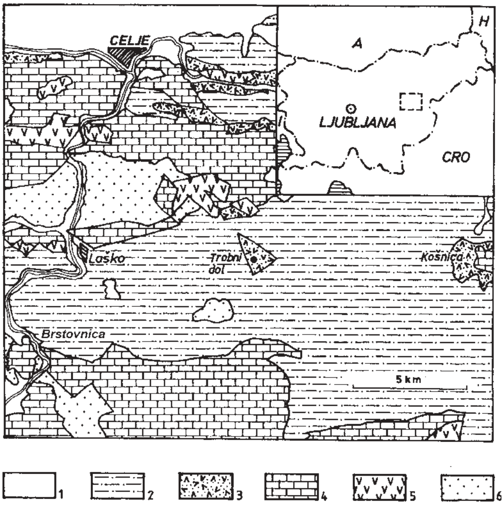

Fig. 1. Simplified geological map of the Trobni Dol area (modified after Buser 1977). 1, Quaternary; 2, Mio-Pliocene clay, silt, sand and gravel; 3, Oligocene volcaniclastics; 4, Mesozoic carbonates; 5, triassic keratophyre and tuffs; 6, Permian and Carboniferous clastic rocks

Sl. 1. Shematska geološka karta območja Trobnega Dola (prirejeno po Buserju 1977). 1, kvartar; 2, mio-pliocenski sedimenti – glina, melj, pesek in prod; 3, oligocenski vulkanoklastiti; 4, mezozojski karbonati; 5, triasni keratofir in njegov tuf; 6, permijski in karbonski klastiti

composition are treated in Mišič and Kralj (2002).

This contribution is focused on chemical composition of Kiscellian clastic sediments and its comparison to a widely used post-Archean Australian Shale composite (PAAS) as they are supposed to represent average crustal relative abundances (Taylor & McLennan 1985). Furthermore, the studies of PAAS (Nance & Taylor 1976) reveal remarkable uniformity of rare earth element distribution. Departures from typical PAAS pattern of rare earth elements, however, can result in tectonically active systems (McLennan et al. 1990), and in diagenesis, weathering and sorting during transport of heavy minerals (Sethi et al. 1998).

Chemical composition of sivica

Two samples from the Trobni Dol area have been analysed (Fig. 1) – from Trobni Dol, near the TDp-1/84 borehole, and from Brstovnica at Rimske Toplice. Both are surface samples. Chemical composition of the studied sivica samples is rather uniform (Table 1), although minor discrepances in abundance of some major oxides and trace elements were observed. Among major oxides, the content of sodium, manganese and total sulphur is somewhat different. With respect to the high mobility of sodium and manganese, and participation of sulphur in biosphere, the observed differences are not surprising. Bulk chemical composition reflects the dominance of filosilicates and carbonates in the sivica, and relatively low abundance of quartz and plagioclases.

Significant difference in trace element abundance occur only at chromium and nickel, and to some extent at zirconium. Yttrium and rare earth elements (REE) show rather similar content. Some trace elements can be compared to the abundance in PAAS (Taylor & McLennan 1985). Rubidium, lead, uranium and REEs are close to the abundance in PAAS, but many other trace elements differ significantly (Table 1). The strontium content is much higher in the sivica samples than in PAAS, and that can be ascribed to the presence of carbonate, which occurs mainly in the form of foraminifera shells. The content of zirconium, hafnium, niobium, barium and thorium is higher in PAAS, and also, the Zr/Hf ratio, but not the U/Th ratio, which is lower than in the sivica samples (Table 2).

Table 1:Chemical composition of two sivica samples

Tabela 1: Kemična sestava dveh vzorcev sivice

Oxide/ Element	Unit %	Trobni Dol	Brstovnica
SiO_2		043,57	45,13
TiO_2		0,60	0,63
Al_2O_3		13,92	13,61
Fe_2O_3		5,42	5,40
Cr_2O_3		0,014	0,019
FeO		2,8	2,6
MnO		0,17	0,07
MgO		2,70	3,08
CaO		12,99	11,74
Na_2O		0,45	0,18
K_2O		3,01	2,69
P_2O_5		0,10	0,13
TOT/C		3,58	3,45
TOT/S		0,37	0,67
L.O.I.		16,9	17,1

Element	Unit ppm	Trobni Dol	Brstovnica
Sc		12	12
V		138	132
Co		19,1	15,3
Ni		129	94
Cu		26,9	21,6
Zn		76	69
Ga		22,1	17,7
As		5,4	7,3
Rb		166,3	149,1
Sr		348,6	364,5
Y		24,3	25,5
Zr		109,1	123,3
Nb		11,0	11,5
Ag		0,1	<0,1
Cd		0,3	0,1
Sn		2	2
Sb		0,2	0,1
Cs		11,5	11,9
Ba		269	264
La		31,6	33,3
Ce		60,7	64,4
Pr		6,77	7,38
Nd		27,5	29,0
Sm		5,8	5,7
Eu		1,08	1,12
Gd		4,65	4,68
Tb		0,73	0,79
Dy		4,23	4,39
Ho		0,80	0,76
Er		2,19	2,32
Tm		0,34	0,41
Yb		2,33	2,14
Lu		0,39	0,38
Hf		3,1	3,8
Ta		0,9	0,8
W		1,6	1,4
Au		0,7	0,5
Hg		0,09	0,09
Tl		0,1	<0,1
Pb		19,1	19,7
Bi		0,3	0,3
Th		10,8	10,2
U		2,8	3,6

Table 2: Some trace element ratios for the studied sivica samples

Tabela 2: Nekatera razmerja med slednimi prvinami v preiskanih vzorcih sivice

Ratio	Trobni Dol	Brstovnica
Zr/Hf	37,15	36,48
U/Th	0,26	0,26
Nb/Ta	16,16	15,19
Sm/Nd	0,20	0,20
La_N/Yb_N	1,00	1,15
Eu/Eu*	0,99	1,01
Ce/Ce*	0,98	0,97

Rare earth elements (REE) and yttrium, normalised to PAAS (Fig. 2), have shown slight depletion of some light REEs (from La to Nd). Most of the middle REEs – Sm, Eu, Gd and Tb – are close to the PAAS values, and from Dy to Lu, a negative fractionation dominates again. For this reason, the La_N/Yb_N ratio, which is commonly used as a measure for fractionation of LREEs against HREEs (Sethi et al 1998) shows no fractionation in the sample from Trobni Dol, and only slight fractionation of LREEs over HREEs in the sample from Brstovnica. The depletion of light rare earth elements can be ascribed to the weathering processes. There is practically no europium anomaly in the studied samples, as the Eu/Eu* are close to 1 and to the PAAS value (1,00). Cerium anomalies are also insignificant and slightly exceed that in PAAS which amounts to 0,95. The ratio Sm/Nd, widely used as an indicator of the change in provenance, is constant for both analysed samples.

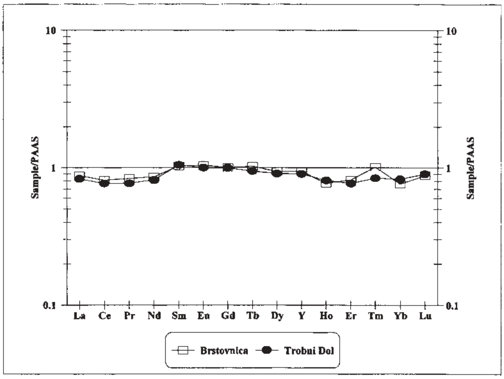

Fig. 2: PAAS normalised REE + Y patterns for the studied sivica samples

Sl. 2: Na PAAS normalizirane vrednosti prvin redkih zemelj in yttrija za preiskane vzorce sivice

Conclusions

Chemical composition of both studied sivica samples, from Trobni Dol and Brstovnica, is rather similar. If compared with PAAS, rubidium, lead, uranium and REEs are close to the abundance in PAAS, but many other trace elements like strontium, zirconium, hafnium, niobium, barium and thorium differ significantly. Strontium is practicaly the only trace element, which is much higher in sivica than in PAAS, and that can be ascribed to the carbonate content. Rare earth elements (REE) and yttrium, normalised to PAAS have shown slight depletion of some light REEs (from La to Nd). Most of the middle REEs – Sm, Eu, Gd and Tb – are close to the PAAS values, and from Dy to Lu, a negative fractionation dominates again. For this reason, the La_N/Yb_N ratio, which is commonly used as a measure for fractionation of LREEs against HREEs shows no fractionation in the sample from trobni Dol, and only slight fractionation of LREEs over HREEs in the sample from Brstovnica. The depletion of light rare earth elements with respect to PAAS can be ascribed to the weathering processes. There is practically no europium anomaly in the studied samples, as the Eu/Eu* are close to 1 and to the PAAS value (1,00). Cerium anomalies are also insignificant and slightly exceed that in PAAS which amounts to 0,95. The ratio Sm/Nd indicates that provenance of the sivica sediments probably did not change appreciably. The studies of REEs in Kiscellian andesitic to rhyolitic tuffs of the Kozjansko area (Kralj, 2002) indicate that the contribution of volcanic material in the sivica composition slightly enlarges the abundance of REEs in sivica, so that the normalised values can lie above the PAAS line, but does not influence significantly the shape of REE + Y distribution patterns.

References

Aničić, B. & Juriša, M. 1985a: Osnovna geološka karta SFRJ, list Rogatec 1:100.000. – Zvezni geološki zavod, Beograd.

Aničić, B. & Juriša, M. 1985b: Osnovna geološka karta SFRJ, list Rogatec 1:100.000 – Tolmač za list Rogatec. – Zvezni geološki zavod, Beograd.

Aničić, B., Ogorelec, B., Kralj, P. & Mišič, M. 2002: Litološke značilnosti terciarnih plasti na Kozjanskem. – Geologija *45/1*, 213–246, Ljubljana.

Buser, S. 1978: Osnovna geološka karta SFRJ, list Celje. – Zvezni geološki zavod, Beograd.

Grad, K., Dozet, S., Petrica, R. & Rijavec, L. 1996: Pseudosocka beds with coal in borehole Tdp-1/84 Trobni Dol (Eastern Sava Folds, Slovenia). – Geologija *39*, 97–118, Ljubljana.

Jelen, M., Aničić, B., Brezigar, A., Buser, S., Cimerman, F., Drobne, K., Monostori, M., Pavšič, J. & Skaberne, D. 2002: Model of positional relationship for Upper Paleogene and Miocene strata in Slovenia. In: Interdisciplinary Geological Conference on Miocene Epoch, 1992, IUGS Subcommission on Geochronology, Ancona, Abstracts and field trips, 71–72, Ancona.

Kralj, P. 1999: Volcaniclastic rocks in borehole Tdp1/84 Trobni Dol, Eastern Slovenia.– Geologija *41*, 135–155, Ljubljana.

Kralj, P. 2002: Dacitic glassy lava flow from Trlično at Rogatec, Eastern Slovenia.– Geologija *45/1*, 139–144, Ljubljana.

McLennan, S. M., Taylor, S. R., McCulloch, M. T. & Maynard, J. B. 1990: Geochemistry and Nd-Sr isotopic compostion of deep-sea turbudites: Crustal evolution and plate tectonic associations. – Geochim. Cosmochim. Acta *54*, 2015–2050.

Mišič, M. & Kralj, P. 2002: Mineral composition of Kiscellian sediments from the Trobni Dol area, Eastern Slovenia.– RMZ – Materials & Geoenvironment *49*, 521–535, Ljubljana.

Nance, W. B. & Taylor, S. R. 1976: Rare earth element patterns and crustal evolution – I: Post-Archean sedimentary rocks.– Geochim. Cosmochim. Acta *40*, 1539 –1551.

Rijavec, L. 1978: Tortonska in sarmatska mikrofavna v zahodnem delu Slovenskih goric.– Geologija *21/2*, 209–238, Ljubljana.

Sethi, P. S., Hannigan, R. E., Leithold, E. L. 1998: Rare-earth element chemistry of Cenomanian-Turonian shales of the North American Greenhorn Sea, Utah. – In: J. Schreiber, W. Zimmerle & P. Sethi (eds.), Shales and Mudstones II, Schweizerbartsche, Verlagbuchhandlung, Stuttgart.

Taylor, S. R. & McLennan, S. M. 1985: The continental crust: Its composition and evolution. – Blackwell Scientific Publications, 186 pp.