GEOLOGIJA 46/1, 123–128, Ljubljana 2003
https://doi.org/10.5474/geologija.2003.012

Chemical composition of cave sediment in Potočka zijalka, Mt. Olševa, North Slovenia

Kemična sestava jamskega sedimenta v Potočki zijalki na gori Olševi

Polona KRALJ & Bernarda BOLE
Geološki zavod Slovenije, Dimičeva 14, 1000 Ljubljana

Key words: cave sediments, clastic sediments, trace elements, Slovenia
Ključne besede: jamski sediment, klastični sedimenti, sledne prvine, Slovenija

Abstract

Potočka zijalka was a station of Aurignatien hunters and the site of rich fossil remains of Pleistocene large mammals. Clastic sediments were deposited in Würm and are an intimate mixture of gravel, sand, silt and clay occurring in various proportions. The fractions form distinct populations, which were transported by different agents, like rock-fall, flowing water, ephemeral torrent flows and cryoturbation. The sediment constituents are petrologically rather diverse and indicate that they were derived from different parent rocks - Mesozoic limestone, Permian-Carboniferous shales, Tertiary fine-grained sediments and fluvial pebbly deposits.

Bulk chemical composition is strongly influenced by the limestone component, but the majority of trace elements, like Ti, Li, V, Fe, Co, Zn, Ga, Y, REE, Zr, Nb, Cs, Hf and Th originates from clay and fine silt, and Mn, Pb, Ni, Cu and Sn mainly from the heavz minerals in the sand fraction. Ca, Mg, Br, Rb, Sr and U show strong correlation with the amount of carbonate component. Rare earth elements, normalised to PAAS are not appreciable fractionated and show light positive europium anomalies.

Kratka vsebina

Potočka zijalka je bila postaja aurignacienskih lovcev in je zato tudi bogato nahajališče fosilnih ostankov velikih pleistocenskih sesalcev. Klastični sediment je nastal v würmu in predstavlja mešanico grušča, proda, peska, melja in gline v najrazličnejših razmerjih. Frakcije vsebujejo populacije, ki so bile transportirane z različnimi dejavniki transporta kot so prosti pad, tekoča voda, občasni hudourniški tokovi in krioturbacija. Sediment sestoji iz drobcev, ki izvirajo iz različnih vrst kamnin – mezozojskih apnencev, permokarbonskih skrilavcev, terciarnih drobnozrnatih sedimentov in rečnih prodov.

Na celotno kemično sestavo močno vpliva primes karbonatov. Večina slednih prvin, kot so Ti, Li, V, Fe, Co, Zn, Ga, Y, prvine redkih zemelj, Zr, Nb, Cs, Hf in Th izvira iz gline in melja, Mn, Pb, Ni, Cu in Sn pa iz težke frakcije peskov. Ca, Mg, Ba, Rb, Sr in U so vezani na karbonatno sestavino sedimenta. Prvine redkih zemelj, normalizirane na PAAS, ne kažejo močne frakcionacije, temveč le manjšo pozitivno evropijevo anomalijo.

Introduction

Potočka zijalka is located on southwestern flanks of Mt. Olševa in the Karavanke mountain range (Fig. 1). The cave became famous after the remains of Pliocene mammals, particularly the cave bear, and the traces of Aurignacien culture were found in its

Fig 1. The location of Potočka zijalka.

Sl. 1. Polo'aj Potočke zijalke.

sediment (Brodar 1939; Brodar & Brodar 1983). During the last excavation campaign, which lasted from 1997 to 2000, clastic deposits have been sampled also for sedimentological, mineralogical, petrological and geochemical analyses, in order to obtain more data about their provenance, the mode of transport and deposition, and early diagenetic alteration (Pohar & Pacher 1999).

Clastic cave sediment overlies basal rockfall composed of Upper Triassic limestone. The limestone is partially dolomitised and strongly tectonised. Grain-size analyses confirmed extremely poor sorting of the cave sediments, and the existence of distinct populations, which were transported by different transporting agents. Petrology of gravel and pebbles, and mineralogical composition of heavy minerals have shown several rocks sources - Upper Triassic limestone, Permian-Carboniferous shales, metamorphic rocks, Tertiary fine-grained sediments. Bulk chemical composition is strongly dependent on the ratio of carbonate and illitic clay.

Allochtonous component of the cave sediment was brought into the cave by water currents, in the beginning that could be fluvioglacial waters, and latter, ephemeral torrent flows draining steep slopes of Mt. Olševa.

Grain-size and mineralogical composition of the cave sediment

Typical cave sediment is extremely poorly sorted mixture of gravel, sand, silt and clay (Kralj & Pohar 2001). Locally, pebbles with Tertiary fossils also occur. Grain-size has been analysed by wet sieving method and with laser particle sizer Fritsch Analysette for grains < 100 µ m. Average composition of the studied samples is 20 % of clay, 18 % of silt, 12 % of sand and 50 % of gravel, but it is still an approximation as commonly, the largest cobbles were not included in the sample composition.

Clay and silt fraction is dominated by silicate minerals, mainly illite/muscovite, whereas quartz and iron oxides are less abundant. Sand fraction is dominated by very angular grains that mainly belong to limestone fragments detached from the cave walls and cieling, and were decomposed to smaller grains by physical agents, as for example freezing. Heavy mineral fraction is dominated by opaque minerals, which are heavily oxidised. Among rock-forming heavy minerals, garnets predominate over somewhat less abundant amphyboles, pyroxenes and zircone. In subordinate amounts, tourmaline, staurolite, disthene, zoisite, clinozoisite, epidote, apatite, topas, sphene, chlorite and biotite occur. Some well rounded sand grains have mainly silicate composition and belong to detritus, which could have be transported by flowing water or wind.

In the gravel fraction, angular grains of limestone predominate. Limestone fragments mainly originate from the cave wall and cieling. The edges of some fragments, however, are slightly rounded and could indicate short transport from nearby screes by torrential currents. A small part of gravel fraction belongs to the fragments of Permian-Carboniferous shales which underwent only very short transport and obviously originate from the vicinity of the cave. Today, the nearest location is Sv. Duh, about 300 m below Potočka zijalka, but the situation was probably different in the past.

Cave sediment locally includes well rounded and well sorted pebbles of various colour. Grain-size determined by Brodar & Brodar (1983) has shown that over 92% of the grains have diameters ranging from 4 mm to 10 mm. Pebbles have mainly carbonate composition. Fragments of muscovite-rich rocks are very rare. The fragments could originate from metamorphic rocks or pegmatites. Carbonate pebbles consist of micritic or microsparitic limestone while oolitic limestone is less abundant. In the pebble-rich layers, well preserved and only rarely broken molluscan shells of Miocene age occur. The occurrence of those fragile fragments and well rounded pebbles is inconsistent with assumed high energy of transporting agent. Some molluscan shells, however, are still infilled with fine–grained silty sediment. The fossils could have been protected by a coating of silty sediment during the transport, but only in a very short distance.

In addition to molluscan shells, heavy mineral assemblages, separated from the sand fraction of the cave sediment indicate the origin from Tertiary deposits, too. Today, Tertiary deposits do not occur in the area but we suppose that they probably covered the area before the Mt. Olševa uplift, which could cause their erosion.

Chemical composition of the cave sediment

As carbonate forms an essential part of the cave sediment, it is not surprising, that calcium ions predominate in the chemical composition (Table 1). Absolute abundance ranges from 24,8% of CaO to 40,1% CaO, which corresponds to 36,8% and 71,2% of the $CaCO_3$ content, respectively. Although some calcium ions must be related to silicate minerals, too, a negative correlation between the abundance of calcium ions and the content of clay fraction can be observed.

A great part of magnesium is related to carbonate, as the limestone belongs to a Mg-calcite variety. Another part of magnesium originates from clays. Absolute abundance ranges from about 1000 ppm to nearly 9000 ppm.

Aluminium originates from alumosilicate minerals, which form a part of clay, silt and sand fractions. Absolute values range from about 12000 ppm (2,3% Al_2O_3) to almost 26000 ppm (19,6% Al_2O_3). The samples that contain the largest proportion of the clay fraction (PZ 158a and PZ 344). The influence of silt and particularly sand fraction can be observed for the sample PZ 162a, which is very low in clay, but very rich in silt and sand.

Similar dependence on the content of clay fraction can be observed for almost all trace elements: titanium, lithium, vanadium, iron, zinc, gallium, yttrium, rare earth elements, zirconium, niobium, caesium, hafnium, thorium and uranium. The clay fraction and a part of the silt fraction seem to be the main carriers of the above mentioned trace elements. For these 28 elements, the ratio between the highest and the lowest abundance is very similar; it ranges from 1,79 to 2,09, averages to 2,03, and is strongly dependent, although not directly proportional to the clay content. Yet, a direct proportionality can not be achived as all fractions, even the clay fraction, contain some carbonate.

The majority of lithium must be related to illite and muscovite, as they are the most abundant alumosilicate minerals in the clay, silt and sand fractions. Iron content shows a good correlation with the content of clay, but it also seems to be influenced by the content of sand, actually its heavy mineral fraction, which is dominated by iron-rich opaque minerals. Sand also seems to be a strong carrier of lead, manganese, nickel, copper and tin, the metals, which are the most probably concentrated in opaque minerals of the heavy sand fraction. Zinc, cobalt and gallium are the most abundant in the clay rich-, and the less abundant in the clay-poor samples, but the ratios are not directly comparable. Tungsten can not be correlated with any of parameters; the concentrations are strongly scattered ranging from 0,34 ppm to 4,64 ppm in a clay rich sample from the surface (PZ 344). Molibden and tallium were under the detection limit for all analysed samples, except for a clay rich one (PZ 158a), but berillium, cadmium, antimony, silver, gold and quick silver were under their detection limits in all analysed samples.

It is surprising that zirconium also shows very strong dependence on the content of clay fraction. Although in general, heavy mineral zircon is supposed to be the most important source, sand fraction does not seem to have any detectable influence on the abundance of zirconium. Zirconium/hafnium ratio is rather constant in the analysed samples and ranges from 36,8 to 37,1.

The main source of niobium and tantalum is the clay fraction, too.Tantalum is above the detection limit only in the clay-rich sample PZ 158a; the calculated Nb/Ta ratio amounts to 15,4 which is very close to the

Table 1: Chemical composition of cave sediments in Potočka zijalka

Tabela 1: Kemična sestava jamskega sedimenta iz Potočke zijalke

Element	Unit	PZ 158a	PZ 162a	PZ 163a	PZ 164a	PZ 165a	PZ 344
CaO	%	24,8	40,1	37,4	31,5	30,05	28,56
MgO		0,58	0,49	0,55	0,41	0,18	0,41
Al_2O_3		19,6	2,3	2,6	2,9	2,5	14,7
Li	ppm	23	11,4	16,0	15,8	13,6	20,1
Sc		2,2	n.d.	n.d.	n.d.	n.d.	1,4
Ti		1135,4	621,6	632,3	747,6	676,5	912,2
V		32,2	15,2	18,1	20,2	16,2	23,7
Cr		6,8	1,9	2,9	n.d.	1,6	5,5
Mn		274,9	254,1	169,7	189,9	168,1	226,5
Fe		14213	7032	7197	8371	7402	10614
Co		3,1	1,5	1,8	2,9	2,1	3,6
Ni		13,5	8,1	7,8	10,4	6,4	7,8
Cu		73,6	35,9	33,2	37,9	31,5	51,8
Zn		1320	675	731	896	828	1312
Ga		6,2	2,8	3,0	3,7	2,9	4,0
Rb		42,5	30,0	34,3	35,5	25,8	35,1
Sr		195,8	161,0	156,4	190,3	190,9	209,1
Y		10,2	5,5	6,3	7,1	6,2	7,9
Zr		60,2	30,1	30,6	38,4	34,3	45,6
Nb		4,9	2,5	2,5	3,2	2,8	3,8
Mo		1,6	n.d.	n.d.	n.d.	n.d.	n.d.
Sn		0,98	0,62	0,53	0,60	0,49	0,65
Cs		3,73	2,05	2,36	2,62	2,11	2,98
Ba		153,7	107,2	94,2	109,9	92,2	130,6
La		12,10	6,04	6,81	8,14	6,42	9,08
Ce		23,75	12,00	13,52	15,53	12,61	17,90
Pr		2,79	1,40	1,62	1,87	1,49	2,17
Nd		10,62	5,40	5,96	7,23	5,48	7,94
Sm		2,03	0,96	1,14	1,41	1,13	1,57
Eu		0,44	0,22	0,24	0,30	0,24	0,34
Gd		1,75	0,91	1,00	1,11	0,97	1,44
Tb		0,28	0,15	0,16	0,19	0,17	0,21
Dy		1,61	0,87	1,01	1,15	0,94	1,20
Ho		0,33	0,17	0,20	0,23	0,20	0,26
Er		0,92	0,50	0,57	0,63	0,55	0,70
Tm		0,14	0,07	0,08	0,09	0,08	0,11
Yb		0,86	0,49	0,47	0,63	0,59	0,62
Lu		0,126	0,067	0,078	0,091	0,085	0,107
Hf		1,62	0,82	0,81	1,06	0,96	1,24
Ta		0,32	n.d.	n.d.	n.d.	n.d.	n.d.
W		0,53	0,35	0,34	2,12	1,66	4,64
Tl		0,38	n.d.	n.d.	n.d.	n.d.	n.d.
Pb		6,33	8,79	3,28	3,73	2,71	4,20
Th		3,82	1,92	2,05	2,53	1,91	2,80
U		1,97	1,05	1,19	1,42	1,19	1,36
Th/U	ratio	1,94	1,83	1,72	1,78	1,61	2,06
Zr/Hf		37,1	36,8	37,8	36,2	35,8	36,7
Zr/Nb		12,2	12,0	12,4	12,1	13,2	12,1
Nb/Ta		15,4	15,3	16,1			
Ce/Yb		27,6	24,5	28,2	24,7	21,4	28,9

n.d. –non defined, below the detection limit ratios observed the above mentioned Tertiary Mura and Rogatec basins. The Nb abundance seems to be influenced by pyroxenes, amphyboles, biotite, ilmenite and sphene, the heavy minerals which incorporate Nb in their structure as a trace element.

Yttrium and lanthanides show very good dependence on the clay content. That can be well seen from the plots of chondrite and PAAS (post-Archaean Australian Shales) normalised abundance (Fig. 2, 3). The plot shapes are almost identical but differ in in absolute abundance of all rare earth elements, which means that the source is the same, and only the proportion of these REE carriers is different in the analysed samples.

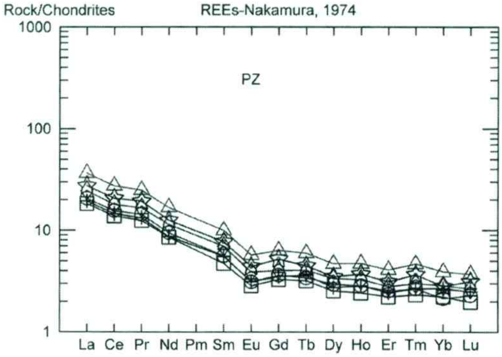

Fig. 2. Chondrite-normalised REE patterns of cave sediment samples.

Sl. 2. Na hondrite normalizirane vsebnosti prvin redkih zemelj v vzorcih jamskega sedimenta.

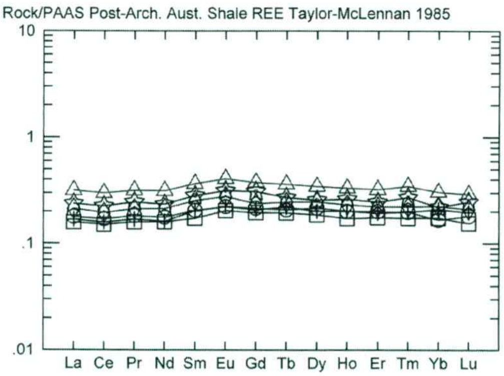

Fig. 3: PAAS normalised (Taylor & McLennan 1985) REE patterns of cave sediment samples.

Sl. 3. Na PAAS normalizirane vsebnosti prvin redkih zemelj (Taylor & McLennan 1985) za vzorce jamskega sedimenta.

Chondrite normalised REE plots (Fig. 2) show strong fractionation of LREE and HREE, which can be seen as an approximately ten-fold enrichment of LREE against HREE. The samples show negative europium anomaly. PAAS normalised (after Taylor & McLennan 1985) REE patterns indicate weak fractionation of heavy rare earth elements over light rare earth elements and weak positive europium anomalies. REE normalised values are lower than PAAS, mainly owing to the carbonate admixture.

The group of actinides, thorium and uranium have been determined. Th and U abundance range from 1,91 to 3,82 and 1,05 to 1,97, respectively. The majority of Th and U seem to be related to the clay fraction, although the distribution of U is less consistent than of Th. The Th/U ratio ranges from 1,61 to 2,06 and is much lower than in Tertiary sediments from the Mura and Rogatec basins. The reason is very possibly in the presence of carbonate. For Th, clays and heavy silicate minerals are the only significant source, but U is easily incorporated in carbonate minerals and carbonate skeletons of organisms. Lower Th/U ratios could therefore be related to the contribution of U from carbonate constituent of the cave sediment.

Barium, rubidium and strontium are also enriched in the clay-rich samples, but their abundance must have been influenced by the carbonate constituent of the cave sediments, too. The most strongly scattered are the Ba concentrations. But for Rb and Sr, they do not differ significantly, as all three major sources – clays, sands and carbonate fragments contributed to the bulk composition.

Discussion and conclusions

The sediment in Potočka zijalka which contains the remains of Pleistocene mammals and traces of Aurignacien culture, was deposited in Middle Würm, above the basal rockfall. Its thickness is variable, attaining some ten decimetres to nine metres. Grain-size analysis has shown the sediment is a mixture of various proportions of clay, silt, sand, gravel and locally pebbles. The sediment is extremely poorly sorted and consists of more than on population, transported by different transporting agents and from different parent rocks or sediments.

The most abundant are the grains of carbonate composition. The majority of them was detached from the cave walls and cieling. Some fragments could also originate from gravel deposits in the vicinity of the cave and were eventually transported into the cave by ephemeral storm flows. The fragments of Permian-Carboniferous schists must have been transported only in a short distance. In spite of their softness and poor resistance against abrasion, many grains are still very angular. Today, the nearest outcrops of Permian-Carboniferous deposits are near Sv. Duh, at the foothills of Mt. Olševa. Intensive Neogene to Pliocene tectonic activity along the Periadriatic fault zone caused the uplift of Mt. Olševa and rapid erosion of the overthrusted Permian-Carboniferous shales.

Grain-size and compositional heterogenity of the studied cave sediments is well reflected in their chemical composition. Clay fraction seems to be the major source for many trace elements: Ti, Li, V, Fe, Co, Zn, Ga, Y, REE, Zr, Nb, Cs, Hf and Th. Ca, Mg, Ba, Rb, Sr and U originate from carbonate and detritials, mainly clay. Mn, Pb, Ni, Cu and Sn seem to be the most concentrated in the heavy fraction of sands. Iron and manganese are partially authigenic in origin. Chondrite and PAAS normalised REE patterns indicate, that clays are the main REE carrier. The consistence and similarity of normalised REE patterns indicate the same source of clay minerals for all analysed samples.

Chemical composition of analysed samples is virtually strongly variable owing to different proportions of compositionally different constituents. Beyond that, no comopsitionally variability related to abrupt change in provenance, depositional environment or climate can be established.

References

Brodar, S. 1939: O stratitgrafiji Potočke Zijalke / Über Stratigraphie von der Höhle Potočka zijalka/. - Glasnik Muzejskega društva za Slovenijo, 4-33, Ljubljana.

Brodar, S. & Brodar, M. 1983: Potočka zijalka - visokogorska postaja aurignacienskih lovcev / Potočka zijalka, eine hochalpine Aurignacjäger-Station/. - Dela 1. in 4. razreda SAZU 24, 1-213, Ljubljana.

Kralj, P. & Pohar, V. 2001: Klastični sediment v Potočki zijalki.- Razprave IV. Razreda SAZU, XLII-1, 25-36, Ljubljana

Pohar, V. & Pacher, M. 1999: Izsledki novih raziskav v Potočki zijalki (Neue Forschungsergebnisse in Potočka zijalka). - Geološki zbornik *14*, 37-39, Ljubljana.

Taylor, S. R. & McLennan, S. M. 1985: The continental crust: Its composition and evolution.- Blackwell, Oxford.