GEOLOGIJA *46/1,* 117–122, Ljubljana 2003

Geochemistry of Upper Pliocene silty and sandy sediments from the well Mt-7, Moravci Spa, North-Eastern Slovenia

Geokemične značilnosti zgornjepliocenskih meljastih in peščenih sedimentov iz vrtine Mt-7 v Moravskih Toplicah

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Key words: silts, sands, Upper Pliocene, geochemistry, Pannonian basin, Slovenia
Ključne besede: melji, peski, zgornji pliocen, geokemija, Panonski bazen, Slovenija

Abstract

Bulk chemical composition of Upper Pliocene silts and sands, cored in the well Mt-7, is strongly controlled by mineralogy – the abundance of quartz, carbonates and phyllosilicates in the sediments. Trace elements are in general more abundant in silts than in sands (Li, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Sb, Cs, REEs, Th and U), except for Y, Zr, Hf and Ba. The majority of yttrium probably originates from xenotime, Zr and Hf from zircone and Ba from alkali feldspars and the traces of barite. YREE patterns, normalised to PAAS show very similar shapes, although the abundance in sands are lower. Positive europium anomalies can be ascribed to the presence of plagioclase feldspars, and positive cerium anomalies to the presence of monazite. Sm/Nd ratios are relatively close and do not differ very much from Kiscellian marine siltstones termed »sivica« from Kozjansko, indicating that the source rocks for sediments probably did not change significantly.

Kratka vsebina

Kemična sestava zgornjepliocenskih sedimentov iz jedrovanih odsekov vrtine Mt-7, odraža vpliv mineralne sestave – vsebnosti kremena, karbonatov in filosilikatov v sedimentih. Sledne prvine so v splošnem bolje zastopane v meljih kot v peskih (Li, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Sb, Cs, prvine redkih zemelj, Th in U), razen za Y, Zr, Hf in Ba. Glavnina yttrija verjetno izhaja iz ksenotima, cirkonija in hafnija iz cirkona in barija iz alkalnih glinencev in sledov barita. Yttrij in prvine redkih zemelj, normalizirani na PAAS, kažejo podobno razporeditev, četudi so v peskih zastopani v manjših količinah. Pozitivne evropijeve anomalije so najverjetneje vezane na prisotnost plagioklazov, in pozitivne cerijeve na prisotnost monazita. Razmerja Sm/Nd so podobna in se ne razlikujejo od tistih v sivici s Kozjanskega in kažejo, da so bile izvorne kamnine sedimentov podobne.

Introduction

Moravske Toplice (Moravci Spa) in North-Eastern Slovenia are well known healing and recreation centre, which produces thermal water from an Upper Pliocene intergranular aquifer termed »Thermal I« (Kralj & Kralj 2000). The water belongs to the sodium-chloride-bicarbonate hydrogeochemical facies with total dissolved solids amounting to about 1 g/l (Kralj, Pe. 2001). Prior to 1993, six wells were drilled yet in Moravci Spa; they were primarily designed for oil exploration and later used for exploitation of thermal water. The well Mt-7 was intended and designed for reinjection. The first 300 m were drilled vertically, and the following 711,2 m under the angle of declination of 57°.

Two sections were cored – the first from 925,20 to 929,00 m, and the second from 1004,20 to 1011,20 m. The cores were studied sedimentologically, paleontologically and geochemically in order to obtain more data about the Upper Pliocene depositional environment in North-Eastern Slovenia. The present contribution is focused on geochemical issues, related to the differences in grain-size and mineral composition. By a comparison with older, Kiscellian sediments, we tried to recognise the changes, which could be caused by the change in sediment provenance.

Geological outline of the Mura basin

Moravci Spa is located in the Mura basin (Fig. 1), which forms a part of a widespread system of Pannonian basins. The Mura basin is infilled with clastic sediments ranging in age from Early Neogene to Quaternary, and although its formation started as early as Carpathian stage, the main subsidence occurred during Late Pliocene and Quaternary. This subsidence is closely related to tectonic activity which produced deep-seated strike-slip faults. Two of them are particularly important: the northeast-southwest trending Radgona fault in the north and the east-west trending Ptuj-Ljutomer fault in the central part. Along the faults two depressions developed, separa-

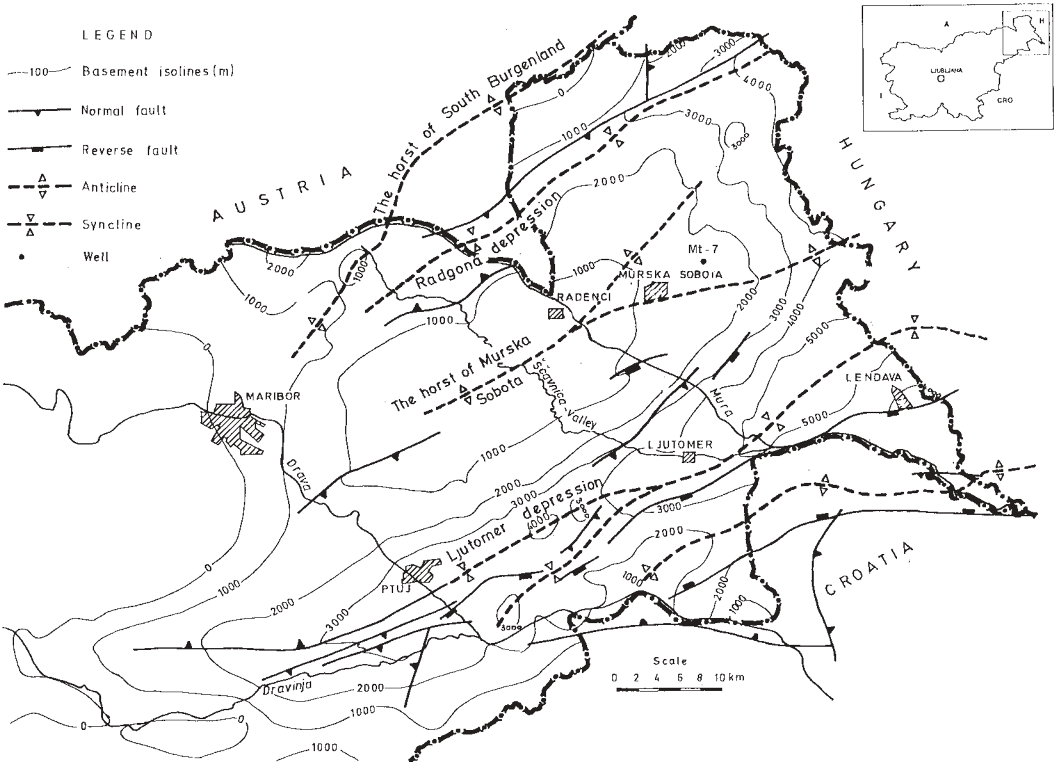

Fig. 1. Simplified tectonic map of the Mura basin (adapted from Ina-projekt OOUR KGI & Geološki zavod Ljubljana, TOZD GGG, 1986)

Sl. 1. Poenostavljena tektonska karta Murskega bazena (prirejeno po Ina-projekt OOUR KGI & Geološki zavod Ljubljana, TOZD GGG, 1986) ted by the horst of Murska Sobota. They were named after the faults – the Radgona and Ljutomer depressions. The Radgona depression is separated in the north from the adjacent Graz basin by the horst of South Burgenland, where pre-Tertiary metamorphic basement outcrops. The basement deepens towards the south and the east, so that in Moravci Spa, metamorphic it occurs at a depth of 1417,0 m.

In the Radgona depression, Tertiary sedimentation started in Carpathian, in a marine environment. Marine environment persisted during the following Badenian and Sarmatian stage (Pleničar 1970). Except for Badenian, the sediments are developed as clastics – clays, marls, silts and sands. During Pannonian and Early Pontian, brakish conditions prevailed. In Late Pontian and Quaternary, the environment changed into continental – fluvial and liminic. Along the horst of South Burgenland, systems of alluvial fans developed, and further on, they evolved into braided rivers (Kralj, Po. 2001). In the river channels, sands and pebbly sands accumulated, whereas in the adjacent flood basins, finer-grained sediments and organic matter deposited. About 3 million years ago, alkali basaltic volcanism occurred (Kralj, Po. 2000a, b) producing thin lava flows, tuff cones and rings, which were devastated by subsequent hydrovolcanic explosions, lahars, debris flows and fluvial currents.

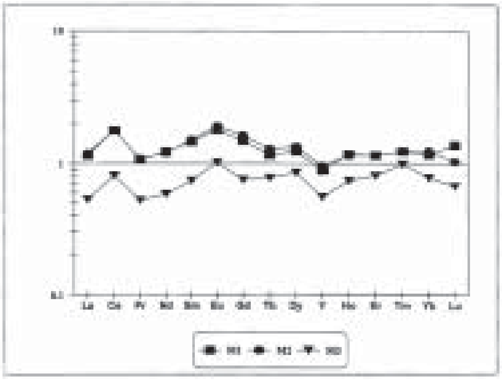

Fig. 2. PAAS normalised YREEs for the studied samples from Mt-7 well core (M1 – 925,20 m; M2 – 926,30 m; M3 – 1005,00 m)

Sl. 2. Na PAAS normalizirane vsebnosti prvin redkih zemelj in yttrija iz jedra vrtine Mt-7 (M1 – 925,20 m; M2 – 926,30 m; M3 – 1005,00 m)

On the horst of Murska Sobota and in the Ljutomer depression, tertiary sedimentation began in the Sarmatian stage in a marine environment. A thin layer of basal breccia is overlain by the sequences of interstratified clays, marls, shales, sands and sandstones. The overlying Pannonian and Pontian sediments are clays, silts and silty sands, deposited in a brakish environment. Upper Pontian and Quaternary sediments are continental.

Studied sediments from the Mt-7 well were deposited in the Upper Pliocene fluvial environment, in the river channels, and food basins suitable for preservation of organic matter and the formation of coal.

Petrology and mineralogy of sediments

Sediments from both cored sections were studied sedimentologically (grain-size analysis, the content of carbonate – lime and dolomite, light and heavy mineral fraction), mineralogically by the means of X-ray diffraction, and geochemically. Grain-size analyses have shown that the samples from the upper cored section from 925,20 m to 929,00 m belong to silts, which contain 5-20 % of sand and 2-20 % of clay. The sediments from the lower cored section from 1004,20-1011,20 are sands, which contain from 10 - 15 % of silt and up to 2 % of clay. Sandy sediments of the lower section contain fragments of coal. Silt with clay occurs in the form of laminae interlayered with the sands.

Simple wet chemical analysis has shown that the silty sediments of the upper section contain from 10,4 to 23,4 of carbonate, mainly in the form of dolomite and magnesian calcite. Sandy layers of the lower section are carbonate-poor, as they contain from 1,0 to 1,9 % of carbonate only.

Silty sediment from the upper cored section is - with respect to the grain-size - relatively rich with heavy mineral fraction as it amounts to 1,2 %. The assemblage of heavy minerals is dominated by chlorite and iron oxides. Among rock-forming minerals, garnets predominate, while the others occur only in subordinate amounts (epidote, kyanite, zoisite, amphiboles, tourmaline). Light mineral fraction is dominated by muscovite, and the rest consists of quartz and feldspars.

Table 1: Chemical composition of the studied samples – M1 (925,20 m), M2 (926,30 m), M3 (1005,00 m). Analyses were performed in XRAL Laboratories Ltd. Ann Arbor, Michigan

Tabela 1: Kemična sestava preiskanih vzorcev – M1 (925,20 m), M2 (926,30 m), M3 (1005,00 m). Analize so bile napravljene v XRAL Laboratories Ltd., Ann Arbor, Michigan

Oxide (%)	M1	M2	M3
SiO_2	40,3	45,5	80,1
TiO_2	0,65	0,63	1,02
Al_2O_3	18,0	9,0	15,2
Fe_2O_3	1,94	1,99	1,71
FeO	6,1	4,4	2,5
MnO	0,17	0,08	0,15
MgO	4,92	4,71	0,92
CaO	7,89	2,90	1,03
Na_2O	0,34	0,36	1,03
K_2O	3,39	3,70	1,03
P_2O_5	0,11	0,10	0,09
H_2O^+	5,2	6,8	1,5
H_2O^-	1,2	2,0	0,2
S	0,05	0,11	0,03
CO_2	9,20	3,60	0,04
L.O.I.	15,6	15,5	1,55
Element (ppm)	M1	M2	M3
Li	70	80	20
Be	6	7	4
B	90	100	100
Sc	16,7	15,4	11,8
V	130	150	60
Cr	110	120	64
Co	16	19	6
Ni	50	68	13
Cu	59,7	64,8	5,7
Zn	110	120	45
As	3	5	3
Rb	160	180	40
Sr	180	190	80
Y	20	10	30
Zr	90	60	170
Nb	20	30	30
Element (ppm)	M1	M2	M3
Cd	<1	<1	<1
Sn	20	10	<10
Sb	1,4	1,9	0,9
Cs	11	13	1
Ba	560	650	320
La	44,0	45,6	20,2
Ce	142	142	64,4
Pr	9,4	9,6	4,6
Nd	41,6	40,7	19,7
Sm	8,1	8,4	4,1
Eu	1,94	2,06	1,10
Gd	6,9	7,6	3,5
Tb	0,9	1,0	0,6
Dy	5,8	6,3	4,0
Ho	1,17	1,15	0,73
Er	3,3	3,3	2,3
Tm	0,5	0,5	0,4
Yb	3,3	3,5	2,2
Lu	0,60	0,45	0,29
Hf	2	1	4
Ta	1	1	1
W	4	4	<3
Au	2	7	3
Pb	15	21	<2
Bi	<3	11	10
Th	14	15	6
U	4,3	5,3	1,8

Some sandy sediments of the lower cored section were extremely rich in the heavy mineral fraction, as it amounted to 26 % in one of the studied samples. Heavy mineral fraction is dominated by garnets (up to 61 %), iron oxides (up to 17 %), and subordinate epidote, amphiboles, chlorite, kyanite, zoisite, rutile and tourmaline, and trace amounts of monazite and xenotime. Light mineral fraction is dominated by quartz, which is followed by feldspars and even less abundant muscovite.

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

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

Ratio	M1	M2	M3
Zr/Hf	45	60	43
U/Th	0,31	0,35	0,30
Nb/Ta	20	30	30
Sm/Nd	0,19	0,21	0,21
La_N/Yb_N	0,98	0,96	0,68
Eu/Eu*	1,10	1,10	1,17
Ce/Ce*	1,27	1,25	1,24

X-ray diffraction analysis was performed by M. Mišič. Average mineral composition of silty sediments from the upper cored section is the following: muscovite/illite (20 %), chlorite (17 %), kaolinite (12 %), Ca-montmorillonite (8 %), quartz (15 %), plagioclases (7 %), calcite (5 %), dolomite (14 %), the remaining are alkali feldspars and pyrite. Average composition of the sands of the lower cored section is muscovite/illite (24 %), chlorite (12 %), kaolinite (12 %), quartz (42 %), plagioclases (8 %) and pyrite (2%).

Chemical composition of the sediments

Two samples from the upper section (925,20 m and 926,30 m), and one sample from the lower section (1005,00 m) were studied geochemically. The main difference between silts from the upper cored section arises from the content of carbonate (Table 1), although the differences in the proportion of sand also control bulk chemical composition of silty sediments. Sand from the lower cored section is appreciably richer in silica (quartz), titanium oxide (rutile) and sodium (plagioclases), but poorer in iron, magnesium, calcium, potassium, water, carbon dioxide and total ignition loss.

The majority of trace elements is appreciably higher in silty sediments than in sands - Li (muscovite/illite), V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Sb, Cs, REE, Th and U, and only few are higher – Y (xenotime), Zr and Hf (zircon), and Ba (barite and alkali feldspars).

Yttrium and rare earth elements (YREE), normalised to PAAS (Taylor & McLennan 1985), show very interesting distribution patterns (Fig. 2). The patterns have actually the same shapes, but differ only in the abundance. For silts, the abundance is higher than PAAS for almost all elements, except for Pr and Y, but for sands, the majority of YREEs lies under PAAS, except for Eu and Tm. The PAAS normalised YREE distribution indicates that the main element carriers are the same in both samples, as they do not reflect sufficiently the differences in mineral composition and grain size.

Silty sediments from the upper cored section were compared to PAAS for some other trace elements. Rubidium, barium, lead and thorium are approximately the same, strontium is slightly lower than in PAAS, zirconium, hafnium and yttrium are much lower than in PAAS, and niobium, REEs and uranium higher than in PAAS. The ratios of some trace elements (Table 2) have shown many similarities to PAAS, yet some significant differences. The Zr/Hf and U/Th ratios are somewhat higher than in PAAS. Fractionation of heavy over light rare earth elements, indicated by the La_N/Yb_N ratios, is more pronounced in the sand sample. Europium and cerium anomalies are positive. Sm/Nd ratios are very close, around 0,20.

Conclusions

Studied sediments from the Mt-7 well in Moravci Spa were deposited in the Upper Pliocene fluvial environment, in the river channels, and food basins suitable for preservation of organic matter and the formation of coal. Grain-size analyses have shown that the samples from the upper cored section from 925,20 m to 929,00 m belong to silts, which contain 5-20 % of sand and 2-20 % of clay. The sediments from the lower cored section from 1004,20-1011,20 are sands, which contain from 10-15 % of silt and up to 2 % of clay. Sandy sediments of the lower section contain fragments of coal. Silt with clay occurs in the form of laminae interlayered with the sands.

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Yttrium and rare earth elements (YREE), normalised to PAAS, have actually the same shapes for silts and sand, but differ only in the abundance. They indicate that the main element carriers are the same in both samples, as they do not reflect sufficiently the differences in mineral composition and grain size.

The ratios of some trace elements have shown many similarities to PAAS, yet some significant differences. The Zr/Hf and U/Th ratios are somewhat higher than in PAAS. Uranium could be attached to organic matter, namely coal, which occurs relatively abundantly in the sediments. Fractionation of heavy over light rare earth elements, indicated by the La_N/Yb_N ratios, is more pronounced in the sand sample. That can be ascribed to the presence of garnets which show fractionation of heavy REEs over light REEs. Europium anomalies are positive. The main carrier of europium are very possibly feldspars. Quartz originating from granite rocks shows negative europium anomaly (Götze & Zimmerle 2000), but not metamorphic quartz, which shows only strong fractionation of light REEs over heavy REEs. Positive cerium anomalies are possibly related to the presence of monazite in the heavy mineral fraction. Sm/Nd ratios are indicators for the source rocks (Sethi et al. 1998) are very close, around 0,20, and do not differ significantly from Upper Kiscellian silty sediment “sivica” from the Kozjansko area (Kralj & Mišič, this volume). That might indicate the parent rocks of fine-grained sediments did not change appreciably.

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