Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 80 (8) S278–S285 (2015)
Supplementary material

SUPPLEMENTARY MATERIAL TO

Geochemical investigation as a tool in the determination of the potential hazard for soil contamination (Kremna Basin, Serbia)

TAMARA PERUNOVIĆ[1], KSENIJA STOJANOVIĆ[1*#], MILICA KAŠANIN-GRUBIN[2], ALEKSANDRA ŠAJNOVIĆ[2#], VLADIMIR SIMIĆ[3], BRANIMIR JOVANČIĆEVIĆ[1#] and ILIJA BRČESKI[1]

[1]*University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia,* [2]*University of Belgrade, Center of Chemistry, ICTM, Njegoševa 12, 11000 Belgrade, Serbia and* [3]*University of Belgrade, Faculty of Mining and Geology, Djušina 7, 11000 Belgrade, Serbia*

J. Serb. Chem. Soc. 80 (8) (2015) 1087–1099

AREA AND SAMPLING LOCATION

The Kremna Basin covering an area of 15 km^2 is a lacustrine basin of the Zlatibor complex and is located in southwest Serbia, about 200 km from Belgrade (Fig. S-1). Zlatibor Mountain is one of the largest serpentinite massifs on the Balkan Peninsula and is an ecologically exceptional area with 960 plant species, 280 insect species, 10 amphibians and reptiles, 150 bird species and 54 mammal species.[1]

Kremna Basin landscape is hilly–mountainous with pastures, meadows and agriculture as the dominant vegetation type (Fig. S-1). The area is sparsely populated with mountain villages, which are dispersed and mostly isolated. The main water supplies for the villages are springs.

Due to its very interesting geological setting, this basin has been explored for magnesites and borates. During the last few decades, the Kremna Basin was studied for presence of searlesite in the magnesite deposit,[2] magnesite and dolomite[3,4] and sepiolite and palygorskite clays.[5] The total thickness of sediments is about 350 m, and their age is of Lower Miocene, between 19 and 17 Ma.[6,7]

Obradović and Vasić (2007)[8] distinguished two main sedimentation series, alluvial and lacustrine, and the latter was further divided into marginal and intrabasinal facies. The alluvial series consists of conglomerates and sandstones containing fragments of ultramafic rock,[8] while the marginal lacustrine and intrabasinal lacustrine facies consists of carbonate sediments.[9]

* Corresponding author. E-mail: ksenija@chem.bg.ac.rs; xenasyu@yahoo.com

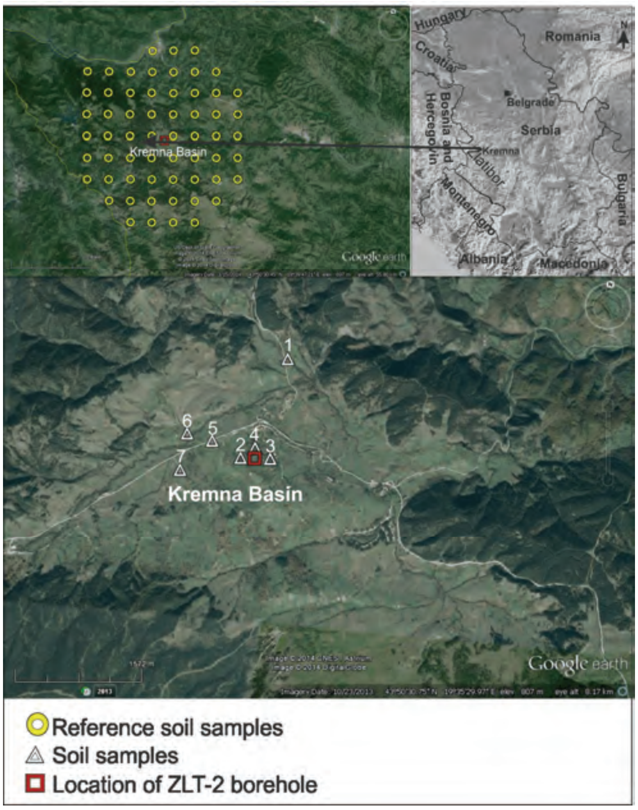

Fig. S-1. Locations in the Kremna Basin, borehole ZLT-2, reference soil samples and soil samples (1–7).

Pedogenic factors influenced the formation of humus silicate soil type on serpentinites in the Zlatibor region.[10] These soils vary in color from black to brown with a dominant silt component and fairly stable aggregates.[11] The humus silicate soils in the investigated area are shallow with depth varying between a few cm up to 20–30 cm. Usually only the A–R profile is developed on these soils, but the A–AC–R profile can also really be observed.

There were two main criterions for soil sampling location: proximity to the borehole and outcropping sediments bellow soil. Only seven locations filled one or both of these criterions (Fig. S-1; Table I). Soil sample 1 was taken above the outcropping coal layer about 1.4 km north from the borehole site ZLT-2. At this location, the soil is very thin, up to 10 cm. Samples 2, 3 and 4 were taken in the central part of the basin, close to the location of the borehole ZLT-2. Sample 2 was taken 20 m west from the borehole, sample 3, 30 m east from the borehole, and sample 4 at the borehole site. Sample 5 was taken about 600 m, and sample 6 about 1 km northwest from the borehole site. Both soils are thin and light brown.

Sample 7 was taken about 1 km west from the borehole site and it is darker with more organic matter present.

The reference soil sample (Table I) was determined by a statistical method. The contents of trace elements in the reference soil sample were calculated based on data for sixty soil samples (at depths up to 30 cm) surrounding the Kremna Basin (Fig. S-1), reported by the Agency for Environmental Protection, the Ministry of Energy, Development and Environmental Protection of the Republic of Serbia,[12] using the following approach: for every element the mean ±2 standard deviation were used to eliminate the top and bottom outlying data.[13]

For studying of the Kremna Basin sediments, 43 core samples (5–10 cm in length) were taken from the ZLT-2 borehole, located in the central part of the Basin (Fig. S-1), at depth from 11.5 to 343 m (Table S-I). The borehole samples were taken for two purposes. The first one was the reconstruction of the origin and geological evolution of the sediments based on the determination of the qualitative mineral composition, content of major and several trace elements, which are important for understanding sedimentation processes, as well as a detailed investigation of the sedimentary organic matter. These results are given in a previous paper.[14] The second purpose of the sampling was to determine background levels of heavy metals in the Kremna Basin. For this purpose, the contents of heavy metals interpreted in this study (As, Cr, Cu, Hg, Ni, Pb and Zn) were determined, whereas the contents of the major elements used for the calculation of the weathering parameters were taken from a previous paper.[14] As was already mentioned, this location was chosen due to its importance as a potential evaporite (magnesite) deposit and boron occurrence, as well as because of its proximity to the Tara National Park. In the ZLT-2 borehole, the Lower Miocene sediments are more than 340 m thick. The borehole ends in weathered serpentinite, which is characterized by the occurrence of rare fragments of serpentinite, sepiolite and small amounts of quartz and dolomite. Background levels of heavy metals in the Kremna Basin sediments were calculated using the same statistical method as for the reference soil sample.[13]

TABLE S-I. Contents of heavy metals (mg kg^{-1}) and several major compounds (%) in sediment samples from ZLT-2 borehole of the Kremna Basin, reference standard values and values of weathering indices

Sample No.	Depth m	Litology	As	Cr	Cu	Hg	Ni	Pb	Zn	Al_2O_3	CaO	Na_2O	P_2O_5	*CPA*[a] %	*CIW*[b] %
1	11.5	Clayey carbonates	18.50	103.77	8.59	0.05	159.86	1.21	9.10	0.94	8.88	0.12	0.01	82.49	70.20
2	13.5	Clayey carbonates	11.90	117.28	12.50	0.03	179.07	0.91	8.07	1.02	22.19	0.09	0.01	87.21	77.33
3	27	Marly dolomite	5.14	103.41	6.55	0.05	119.09	3.12	15.11	3.03	21.58	0.11	0.02	94.33	89.27
4	32	Marly dolomite	3.13	48.42	4.04	0.04	45.29	1.72	10.11	1.87	22.43	0.11	0.01	91.09	83.64
5	42.5	Marlstone	27.07	89.85	9.80	0.06	152.24	2.93	11.11	3.04	37.64	0.07	0.02	96.32	92.89
6	54	Silty Mg-marlstone	79.35	119.56	18.81	0.12	159.83	5.24	26.72	6.80	9.24	0.08	0.01	98.05	96.18
7	55.5	Marly dolomite	30.05	62.73	8.25	0.04	105.64	1.94	11.21	1.97	18.86	0.08	0.03	93.62	88.00
8	64.5	Marly dolomite	6.64	6.88	1.91	0.02	22.62	0.50	4.02	0.61	23.15	0.08	0.01	82.25	69.86
9	70	Marlstone	35.29	105.28	10.67	0.08	114.07	5.03	17.44	6.04	27.70	0.06	0.01	98.35	96.76
10	78	Dolomitic marlstone	34.86	27.66	3.94	0.04	55.58	2.12	8.08	2.09	32.77	0.13	0.01	90.64	82.87
11	80	Dolomitic marlstone	37.89	20.85	4.88	0.07	34.84	1.63	10.16	2.38	36.77	0.11	0.02	92.82	86.60
12	83	Marlstone	35.42	48.88	5.21	0.09	43.27	2.96	17.35	3.31	41.81	0.15	0.04	92.92	86.78
13	96	Marlstone	64.70	90.49	13.12	0.10	136.83	3.66	20.35	3.18	42.84	0.13	0.11	93.60	87.98
14	111	Marlstone	47.50	48.61	7.31	0.08	75.52	2.64	12.18	2.59	36.33	0.14	0.15	91.72	84.70

3 TABLE S-I. Continued

Sample No.	Depth m	Litology	As	Cr	Cu	Hg	Ni	Pb	Zn	Al_2O_3	CaO	Na_2O	P_2O_5	*CPA*[a] %	*CIW*[b] %
15	113	Marlstone	32.32	265.12	17.74	0.06	156.11	8.97	24.47	5.46	35.35	0.20	0.04	94.21	89.05
16	127	Marlstone	31.41	195.39	18.77	0.07	270.37	6.94	18.36	5.18	38.01	0.25	0.04	92.51	86.06
17	137.5	Marlstone	11.69	55.16	6.35	0.04	72.85	1.91	5.04	1.18	44.58	0.15	0.06	82.58	70.33
18	150	Marlstone	7.78	112.00	10.85	0.06	240.02	3.99	11.25	1.87	32.43	0.16	0.01	87.42	77.66
19	164	Marlstone	8.00	131.69	9.32	0.04	245.54	2.94	8.10	1.82	43.88	0.20	0.12	84.55	73.23
20	185	Dolomitic marlstone	4.55	76.05	7.58	0.03	75.18	1.82	10.11	1.04	29.38	0.23	0.07	73.13	57.65
21	189.5	Dolomitic marlstone	9.06	130.86	9.36	0.04	174.05	2.72	13.09	1.39	26.89	0.22	0.05	79.22	65.59
22	216	Silty Mg--marlstone	3.30	162.47	4.03	0.03	203.59	0.93	5.16	0.31	13.46	0.41	0.01	31.31	18.56
23	219	Marly magnesite	3.04	180.02	4.65	0.02	227.08	1.32	6.07	0.85	5.99	0.29	0.01	63.78	46.82
24	224	Marly dolomite	11.60	323.14	10.27	0.02	440.66	2.77	12.32	1.79	17.10	0.45	0.01	70.62	54.58
25	238	Mg-clay	10.19	87.11	1.80	0.01	261.33	10.40	23.34	4.89	2.36	1.24	0.01	70.54	54.49
26	243.5	Marly magnesite	2.44	138.93	4.97	0.04	189.85	1.12	9.14	0.94	6.29	1.19	0.01	32.58	19.46
27	245	Marly magnesite	4.11	555.53	4.21	0.02	604.73	0.92	8.22	0.73	4.79	0.69	0.01	39.18	24.36
28	248.3	Marly magnesite	1.63	208.73	4.37	0.02	276.49	1.02	6.10	0.66	6.50	2.28	0.01	14.99	8.10
29	255	Marly magnesite	1.83	340.85	3.36	0.02	263.83	0.92	6.10	0.60	4.58	0.70	0.01	34.20	20.63

4 TABLE S-I. Continued

Sample No.	Depth m	Litology	As	Cr	Cu	Hg	Ni	Pb	Zn	Al_2O_3	CaO	Na_2O	P_2O_5	*CPA*[a] %	*CIW*[b] %
30	258	Silty Mg-marlstone	14.23	1279.03	15.29	0.05	1989.27	4.46	29.74	3.40	6.15	1.71	0.01	54.71	37.66
31	265	Marly magnesite	2.86	223.94	9.51	0.02	346.12	2.35	10.23	1.30	5.84	1.40	0.01	36.04	21.98
32	283	Magnesitic marlstone	2.59	255.57	5.71	0.01	351.32	1.97	9.34	1.35	13.79	1.16	0.01	41.37	26.08
33	286	Magnesitic marlstone	5.24	416.15	7.97	0.03	680.47	2.94	13.63	2.27	11.49	1.56	0.02	46.84	30.58
34	297.5	Magnesitic marlstone	2.91	213.55	39.12	0.08	298.48	3.54	47.86	2.09	9.19	1.53	0.01	45.39	29.36
35	309	Silty Mg-marlstone	6.64	534.03	11.39	0.03	971.31	5.06	27.42	4.62	9.25	2.23	0.02	55.79	38.68
36	317.5	Magnesitic marlstone	7.76	339.77	7.76	0.04	456.86	2.79	13.45	2.19	12.59	1.45	0.01	47.93	31.52
37	324	Silty Mg-marlstone	11.68	712.72	11.89	0.03	802.29	4.63	22.10	3.65	7.70	1.98	0.02	52.87	35.94
38	329	Silty Mg-marlstone	6.92	753.14	13.84	0.04	891.39	4.93	23.06	4.05	10.76	1.83	0.02	57.28	40.13
39	335	Magnesitic marlstone	1.79	36.09	3.38	0.06	195.15	0.42	2.11	0.06	13.48	2.11	0.02	1.79	0.90
40	336	Magnesitic marlstone	1.88	35.78	1.57	0.02	58.46	0.84	3.14	0.28	14.30	2.10	0.02	7.55	3.92
41	340	Mg-clay	9.76	674.94	11.17	0.11	1144.50	0.98	20.60	1.51	2.96	1.90	0.02	32.56	19.45
42	341	Mg-clay	11.94	995.59	11.51	0.13	1705.72	1.74	23.89	2.37	2.93	2.22	0.02	39.38	24.52

TABLE S-I. Continued

Sample No.	Depth m	Litology	As	Cr	Cu	Hg	Ni	Pb	Zn	Al_2O_3	CaO	Na_2O	P_2O_5	*CP*[a] %	*CIW*[b] %
43	343	Mg-clay	1.73	1397.25	27.12	0.13	2420.53	4.00	44.30	4.39	0.68	2.12	0.02	55.73	55.58
Local background values[c]			5.79	**113.14**	7.21	0.04	**165.69**	2.54	12.38	1.75	19.12	0.86	0.01	–	–
RS 50/2012[18]			29	100	36	0.30	35.0	85.0	140	–	–	–	–	–	–
FBiH 72/09[19]			25	125	100	1.88	62.5	125.0	250	–	–	–	–	–	–
ÖNORM S 2088-2[20]			20	100	100	1.00	60.0	100.0	300	–	–	–	–	–	–
PEL[d]			17	90	108	0.49	–	91.3	271	–	–	–	–	–	–

[a]Chemical Proxy of Alteration; *CPA* = $100Al_2O_3/(Al_2O_3 + Na_2O)$, all oxides are expressed in mole proportions;[15] [b]Chemical Index of Weathering; *CIW* = = $100Al_2O_3/(Al_2O_3 + CaO^* + Na_2O)$, where CaO* represents Ca in the silicate-bearing minerals only and all oxides are expressed in mole proportions.[16] The procedure for quantification of CaO content of silicate fraction involves subtraction of mole proportion of P_2O_5 from the molar proportion of total CaO. On subtraction, if the "remaining number of moles" is found to be less than the molar proportion of Na_2O, then the "remaining number of moles" is considered as the molar proportion of CaO of silicate fraction. If the "remaining number of moles" is greater than the molar proportion of Na_2O, then the molar proportion of Na_2O is taken as the mole proportion of CaO of silicate fraction;[17] [c]for every element mean ±2 standard deviation were used to eliminate the top and bottom outlying data;[13] [d]Probable Effect Level (*PEL*) characterizes the concentrations of pollutants that may affect the aquatic life[21,22]

REFERENCES

1. http://www.cajetina.org.rs/sites/default/files/LBAPCajetina_0.pdf (in Serbian, last accessed October 30, 2014)
2. M. Živković, D. Stojanović, *Vatrostalni materijali* **6** (1976) 3 (In Serbian)
3. J. Obradović, J. Đurđević-Colson, N. Vasić, A. Radaković, N. Grubin, B. Potkonjak, *Ann. Geol. Penins. Balk.* **56** (1994) 177
4. J. Obradović, V. Nosik, N. Vasić, N. Grubin, *Zbornik radova Rudarsko-geološkog fakulteta* **57** (1995) 3 (in Serbian)
5. M. Kovačević, in *Proceedings of the 13th Congress of Yugoslav Geologists*, Herceg Novi, Yugoslavia, 1998, p. 753 (in Serbian)
6. V. Prysjazhnjuk, V. Kovalenko, N. Krstić, in *Geology and Metallogeny of the Dinarides and the Vardar zone*, S. Karamata, S. Janković, Eds., Academy of Sciences and Arts of the Republic of Srpska, Banja Luka, 2000, p. 219 (in Serbian)
7. N. Krstić, N. Dumadžanov, J. Olujić, L. Vujanović, J. Janković-Golubović, *Acta Vulcanol.* **13** (2001) 91
8. J. Obradović, N. Vasić, *Lacustrine Neogene basins in Serbia*, Srpska Akademija nauka i umetnosti, Belgrade, 2007, p. 123 (in Serbian)
9. J. Obradović, N., J. Đorđević-Colson, N. Grubin, in *Geology of Zlatibor*, M. D. Dimitrijević, Ed., Geoinstitute, Belgrade, 1996, p. 97
10. N. S. Miljković, *Fundamentals of soil science*, Prirodno–matematički fakultet, Novi Sad, 1996, p. 198 (in Serbian)
11. Đ. Tanasijević, N. Pavičević, G. Antonović, Đ. Filipović, Ž. Aleksić, M. Spasojević, *The soil of the Western and Northwestern Serbia*, Institut za proučavanje zemljišta, Beograd, 1966, p. 258 (in Serbian)
12. D. Vidojević, N. Baćanović, B. Dimić, *The report on the status of land in the Republic of Serbia for 2012*, Agencija za zaštitu životne sredine, Ministarstvo energetike, razvoja i zaštite životne sredine Republike Srbije, Belgrade, 2013, pp. 14, 23, 24–28 (in Serbian)
13. L. Fok, M.R. Peart, J. Chen, *Catena* **101** (2013) 212
14. T Perunović., K. Stojanović, V. Simić, M. Kašanin-Grubin, A. Šajnović, V. Erić, J. Schwarzbauer, N. Vasić, B. Jovančićević, I. Brčeski, *Ann. Soc. Geol. Pol.* **84** (2014) 185
15. B. Buggle, B. Glaser, U. Hambach, N. Gerasimenko, S. Marković, *Quatern. Int.* **240** (2011) 12
16. H.W. Nesbitt, G.M. Young, *Nature* **299** (1982) 715
17. S.M. McLennan, *J. Geol*. **101** (1993) 295
18. http://www.cis.org.rs/propisi/451?1338287527 (in Serbian, last accessed October 30, 2014)
19. http://www.uip-zzh.com/files/zakoni/poljoprivreda/72-09.pdf (in Serbian, last accessed October 30, 2014)
20. *ÖNORM S 2088-2: Austrian Standards on Contaminated Land Management: Risk assessment for polluted soil concerning impacts on surface environments*, Federal Environment Agency – Austria, 2000
21. https://www.elaw.org/system/files/sediment_summary_table.pdf (last accessed October 30, 2014)
22. *Criteria for the Assessment of Sediment Quality in Quebec and Application Frameworks: Prevention, Dredging and Remediation*, Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007, pp. 7, 8.