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Characterization of sediments from Voglajna and Savinja rivers – preliminary results

Karakterizacija sedimenata rijeka Voglajne i Savinje – preliminarni rezultati

Stanislav FRANČIŠKOVIĆ-BILINSKI[1*], Halka BILINSKI[1], Darko TIBLJAŠ[2], Darko HANŽEL[3] & Alenka MERTELJ[3]

[1]Department of Physical Chemistry, Ruđer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia; [*]corresponding author, e-mail: francis@rudjer.irb.hr
[2]Division of Mineralogy and Petrology, Department of Geology, Faculty of Science, University of Zagreb, Horvatovac bb, HR-10000 Zagreb, Croatia
[3]Jožef Stefan Institute, Jamova 39, SI-1001 Ljubljana, Slovenia

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Ključne riječi: riječni sedimenti, Voglajna, Savinja, Slovenija, mineralni sastav, koncentracija željeza, mikroelementi, ICP-MS, Mössbauerova spektroskopija

Abstract

Preliminary mineralogical, geochemical and Mössbauer studies of six surface sediments (fraction <63 μm) from Voglajna and Savinja rivers (Slovenia) are reported for the first time. The location was chosen because of two reasons. One was possible pollution due to industry in Celje. Another was presumed high concentration of iron (later found 2.8 – 5.6 %), easily studied by Mössbauer spectroscopy. XRD data showed that quartz is present in all samples. Other minerals are different in different locations. Iron can be present in Fe-chlorite and in montmorillonite, found by XRD as trace minerals. Microelements were determined by ICP-MS method. Sediment of Voglajna near Štore contain the highest concentrations of S, P, Cr, Ni, Pb, Cu, Mo, Sb, W and Hg. Sediment of Savinja at Tremerje contain the highest concentrations of Zn, Cd, Ag and Au. These results indicate industrial pollution around Celje. Further characterization of Fe (II) and Fe (III) was performed by ^{57}Fe Mössbauer spectroscopy at room temperature. Spectra were fitted with two and in one case with three doublets. In addition to the presence of two doublets, two magnetic sextets are present in the sediment of Voglajna at Štore, suggesting minor quantity of Fe_3O_4. The Fe (III) / Fe (II) ratio decreases downstream the Voglajna river. The work is in progress on additional sampling stations.

Kratak sadržaj

Prvi puta su izvršena preliminarna mineraloška, geokemijska i spektroskopska (Mössbauer) istraživanja šest površinskih sedimenata (frakcija <63 μm) iz rijeka Voglajne i Savinje (Slovenija). Lokacija je odabrana iz dva razloga. Jedan je moguće zagađenje zbog industrije u Celju. Drugi je pretpostavljena visoka koncentracija željeza (kasnije nađeno 2,8 – 5,6 %), koja se može jednostavno studirati Mössbauerovom spektroskopijom. Rezultati rendgenske difrakcije na prahu su pokazali da je kvarc prisutan u svim uzorcima, dok su ostali minerali različiti na različitim lokacijama. Željezo može biti prisutno u Fe-kloritu i u montmorilonitu, koji su nađeni u tragovima. Mikroelementi su određeni metodom ICP-MS. Sediment Voglajne kraj Štora sadrži najviše koncentracije S, P, Cr, Ni, Pb, Cu, Mo, Sb, W i Hg. Sediment Savinje kod Tremerja sadrži najviše koncentracije Zn, Cd, Ag i Au. Ovi rezultati ukazuju na industrijsko zagađenje u okolici Celja. Daljnja karakterizacija Fe (II) i Fe (III) je provedena metodom ^{57}Fe Mössbauerove spektroskopije na sobnoj temperaturi. Spektri su prikazani s dva, a u jednom slučaju s tri dubleta. U sedimentu Voglajne kod Štora osim dva dubleta prisutna su dva magnetska seksteta, koji ukazuju na manju količinu Fe_3O_4. Omjer Fe (III) / Fe (II) se u Voglajni smanjuje nizvodno. Rad je u tijeku na dodatnim postajama uzorkovanja.

Introduction

Present work is a part of the joint bilateral project between Slovenia and Croatia. Multidisciplinary research on river sediments is going on in different geological settings. The aim of the work is to investigate surface sediments, which reflect weathering products of surrounding rocks and also possible anthropogenic influence. Because most of the rivers contain grains from gravel to clay sizes, for better comparison only silt + clay fraction (f < 63 µm) was analyzed. This fraction is also easily transportable downstream. For possible application of Mössbauer spectroscopy, we have been looking for locations where iron is rather abundant.

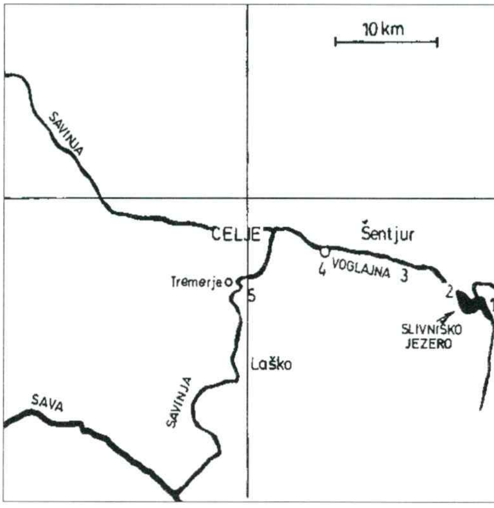

Fig. 1. Study area with numbers of sampling stations 1 – 6. Sediments were collected in August 2001.

Study area

Fig. 1 represents positions of sampling locations in a sketch-map of Voglajna and Savinja rivers, located in eastern part of Slovenia. Geology of Slovenia is very interesting because it is of high diversity, as described by Pirc (2001). The geology of the Voglajna region was described in detail by Nosan (1963). The northern border of the Laško syncline east the Savinja River was studied by Hamrla (1954). To our knowledge, these two rivers were poorly studied in terms of geochemistry. Samples 1 – 6 described in this report were taken in August 2001, during extremely dry season. Additional samples, not yet studied, were collected in August 2002, during rainy period, with high water levels.

Experimental

Sediment samples were wet sieved and then dried at 80 °C. Sediment fraction containing silt and clay (< 63 µm) was further analyzed. Mineralogical composition was determined by an X-ray diffractometer (Philips, X Pert MPD). Major crystalline phases have been identified using a Powder Diffraction File (1997). Elemental content was determined in Actlabs, Canada, in aqua regia extracts of sediment fraction < 63 µm, by inductive coupled plasma – mass spectrometry (ICP-MS), using Ultratrace 2 program. For determination of Ti, P and S, Perkin Elmer Optima 3000 ICP was used. It should be mentioned that this digestion is not total (silicates will not dissolve). Total mercury was determined using a flow injection technique (FIMS) and atomic absorption spectrometer.

Poorly crystalline iron phases were studied by Mössbauer spectroscopy at 300 K. For all experiments we used a ^{57}Co source with an activity of ~10 mCi in a Rh matrix. The velocity scale was calibrated by metallic Fe which was also used as a reference for the isomer shift parameters. The speciations were computer fitted by assuming Lorentzian or Voigt shapes for the resonance lines.

Results and discussion

XRD results of sediments (fraction <63 µm) from Voglajna and Savinja rivers are presented in Table 1. Quartz predominates as a major mineral in all sediment samples. Of other major minerals, feldspar was found in locations 1 and 3, muscovite in location 2, calcite in locations 4, 5 and 6, and dolomite only in location 6. Depending on location, there are several minor and trace minerals. Among minerals which could contain iron in the structure are montmorillonite and Fe-chlorite which were present as trace minerals. Chemical weathering can

Table 1. Mineralogical composition of sediment fraction f < 63 μm from Voglajna and Savinja rivers

No	Major minerals	Minor minerals	Trace minerals
1	quartz feldspar (sanidine, albite)	muscovite	montmorillonite kaolinite clinoenstatite
2	quartz muscovite	feldspar (albite)	kaolinite Fe-chlorite montmorillonite Mg-calcite calcite dolomite
3	quartz feldspar (sanidine, albite)	calcite	muscovite kaolinite Fe-chlorite Mg-calcite dolomite montmorillonite
4	quartz calcite	muscovite	feldspar (albite) Fe-chlorite montmorillonite kaolinite dolomite
5	quartz calcite	muscovite	dolomite Fe-chlorite feldspar (albite)
6	quartz calcite dolomite	muscovite	feldspar (albite) Fe-chlorite Mg-calcite

be confirmed by the presence of montmorillonite (from weathered albite) and of kaolinite (from weathered chlorite), as described by Murakami et al. (1996). Mineralogical analysis of sediments (f < 63 μm) reflects cumulative effects of parent rocks, chemical weathering, hydraulic sorting and abrasion, according to Nesbitt et al. (1987). Complex mineralogical composition could be expected owing to the position on the contact of several geotectonic units. Location of sample 1 is on rock from torton (Miocene). In the catchment area of sample 2 occur rocks of Middle and Upper Oligocene in the north and Carboniferous and Permian in the south. In the catchment area of sample 3 are sands and gravel containing sheets of sandy clay of upper Pliocene and partly Pleistocene. The youngest alluvion belongs to Holocene and recent deposits (samples 3 and 4). Voglajna inflows to Savinja in Celje. Location of sample 5 is on rocks of Triassic and of sample 6 is on rocks of Triassic and Tertiary.

Table 2 shows results of ICP-MS analysis of 52 elements. Fe and Ca are the most abundant. Ca and Mg concentrations are significantly higher in Savinja (samples 5 and 6) than in Voglajna. Al and K are similar in all samples. From microelements the highest concentrations of S, P, Cr, Ni, Pb, Cu, Mo, Sb, W and of Hg were found in sample 4. Sample 5 from Savinja at Tremerje, downstream of Celje, shows the highest concentrations of Zn, Cd, and also of Ag and Au, suggesting influence of industry in Celje. This result regarding Zn and Cd is in support to reported calculated mass balance of Zn and Cd in Celje region (Žibret, 2002).

To get more information about iron, which is known as a carrier of numerous trace elements, further characterization was performed by ^{57}Fe Mössbauer spectroscopy. Spectra obtained at room temperature for samples 1 – 6 are presented in Fig. 2, fitted with two doublets in samples 1, 2, 3 and 5, with three doublets in sample 6, and two doublets and two sextets in sample 4. Two sextets can be ascribed to minor quantity of Fe_3O_4. Hyperfine parameters, such as isomer shift (IS) and electric quadrupole splitting, together with the relative resonance area (A in percent of total iron) are presented in Table 3. Mössbauer spectroscopy can provide quantitative information about the relative population of the iron species, together with specific properties of the individual iron sites. The Fe (III) / Fe (II) ratio was calculated and included in Table 3. It is higher in Voglajna than in Savinja. Fe (III) can be retained in the silicate sites or precipitated as finally divided iron oxide (Schwertmann & Cornell, 1991). For Fe (II) we assume that it is contained in chlorite.

Conclusions

Conclusions at this stage can be only preliminary. Voglajna and Savinja rivers were chosen as example of iron rich and trace element-loaded rivers.

From mineralogical analysis it was concluded that quartz is present in all samples. Other minerals are different in different locations. Iron can be present in Fe-chlorite and in montmorillonite, found by XRD as trace minerals. Additional tests are necessary to detect kaolinite with certainty.

Microelements show the highest concentrations of S, P, Cr, Ni, Pb, Cu, Mo, Sb, W

Table 2. Concentrations (in ppm) of 52 elements in approximately decreasing order in sediments (fraction < 63 μm) of Voglajna and Savinja rivers (Slovenia)

element	1	2	3	4	5	6
Fe	38900.0	55300.0	51900.0	56500.0	29500.0	28400.0
Al	13900.0	13400.0	10600.0	12100.0	11700.0	11500.0
Mg	6200.0	5600.0	5900.0	9000.0	12700.0	20800.0
Ca	5700.0	13000.0	31400.0	49000.0	84800.0	94400.0
K	1300.0	1500.0	1200.0	1500.0	1200.0	900.0
Mn	708.0	10370.0	1140.0	1490.0	1030.0	643.0
P	320.0	850.0	1720.0	1810.0	1100.0	410.0
S	230.0	860.0	1170.0	3230.0	2860.0	1470.0
Na	120.0	190.0	300.0	400.0	360.0	210.0
Ba	67.1	238.0	125.0	166.0	274.0	64.9
Zn	67.8	111.0	136.0	489.0	2760.0	66.0
Ce	46.7	40.3	40.3	47.8	24.3	18.4
Ni	56.9	61.2	55.4	68.2	46.5	36.3
V	41.0	44.0	36.0	34.0	24.0	26.0
Cr	39.2	35.5	43.9	71.8	42.2	19.4
Sr	23.6	55.2	101.0	120.0	134.0	126.0
Cu	22.9	24.2	30.5	139.0	52.5	19.8
Co	19.5	24.7	20.4	19.4	17.9	11.6
La	23.9	19.1	19.4	23.0	11.6	8.4
Nd	22.1	18.1	18.8	20.7	10.9	9.1
Li	20.5	18.3	14.1	15.2	18.7	18.9
Rb	17.7	17.2	13.5	14.9	12.5	10.1
Pb	17.4	33.9	43.9	133.0	66.7	23.9
As	10.9	28.6	16.6	18.1	13.1	10.9
Y	14.5	14.3	15.5	17.1	9.8	8.9
Ga	5.91	4.94	3.79	3.97	3.33	3.38
Sm	4.7	4.0	4.2	4.7	2.5	2.3
Th	4.0	3.7	3.1	2.5	0.5	1.1
Cs	1.5	0.9	0.9	1.0	1.2	1.0
Zr	1.2	1.7	1.1	1.4	1.1	1.0
Be	1.1	1.2	1.1	1.1	0.7	0.7
Yb	1.1	1.1	1.1	1.2	0.7	0.6
Eu	1.0	0.8	0.9	0.9	0.5	0.5
U	1.0	0.8	0.9	0.9	0.6	0.6
Mo	0.78	1.49	1.75	6.28	1.14	0.71
Sb	0.57	0.78	0.83	6.71	1.07	0.75
Nb	0.5	0.4	0.4	0.4	0.5	0.4
Sn	0.47	0.82	8.49	5.40	1.71	0.81
Tb	0.6	0.5	0.6	0.6	0.4	0.3
W	0.4	0.4	0.4	2.8	0.7	0.5
Bi	0.34	0.40	0.35	0.79	0.47	0.28
Se	0.3	1.1	1.2	1.4	1.6	0.9
Cd	0.2	0.8	0.7	2.7	3.8	0.3
Tl	0.2	0.23	0.19	0.26	0.28	0.16
Lu	0.2	0.1	0.2	0.2	0	0
Hg	0.178	0.304	0.606	0.914	0.569	0.333
Te	0.05	0.11	0.07	0.10	0.10	0.09
In	0.04	0.05	0.04	0.08	0.06	0.03
Ag	0	0.09	0.46	0.55	3.32	0.11
B	0	0	0	2	2.6	0
Re	0	0	0.002	0.006	0.002	0
Au	0	0.0032	0.0163	0.027	0.106	0.0016

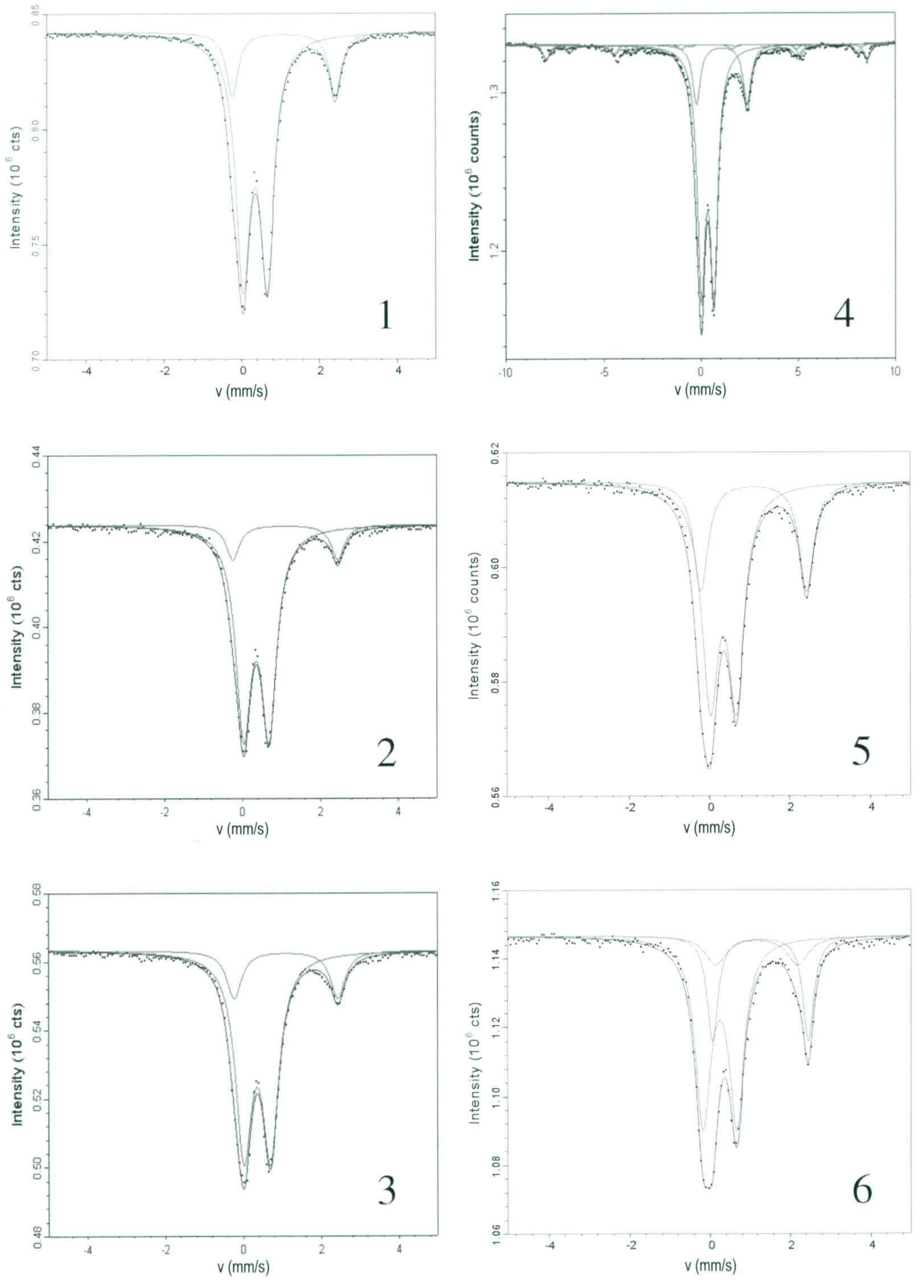

Fig. 2. Mössbauer spectra of ^{57}Fe taken at room temperature with a source of ^{57}Co in a Rh matrix: sediment fraction <63 μm of samples 1 – 6

Table 3. Hyperfine parameters of Mössbauer spectra of sediments (f < 63 µm) from Voglajna and Savinja rivers obtained at room temperature

No	sub-spectra	IS (mm/s)	QS (mm/s)	H_{eff} (kOe)	Site	A%	Fe(III)/ Fe(II)
1	du1	0.3521(19)	0.6240(31)	0	Fe(III)	81.35(60)	
	du2	1.0966(58)	2.648(11)	0	Fe(II)	18.65(70)	4.36
2	du1						
	du2	0.3536(32)	0.6481(52)	0	Fe(III)	86.75(98)	
		1.101(15)	2.686(29)	0	Fe(II)	13.3(12)	6.52
3	du1	0.3546(31)	0.6828(52)	0	Fe(III)	81.47(86)	
	du2	1.097(11)	2.655(22)	0	Fe(II)	18.5(10)	4.40
4	du1	0.3521(18)	0.6475(30)	0	Fe(III)	70.43(45)	
	du2	1.0907(65)	2.608(13)	0	Fe(II)	18.19(57)	
	se1	0.316(18)	0	511(13)		7.38(53)	
	se2	0.652(33)	0	459(24)		4.00(53)	3.87
5	du1	0.3531(52)	0.6514(84)	0	Fe(III)	68.7(12)	
	du2	1.1207(81)	2.649(16)	0	Fe(II)	31.3(14)	2.19
6	du1	0.2503(46)	0.845(11)	0	Fe(III)	61.7(13)	
	du2	1.266(11)	2.400(21)	0	Fe(II)	25.1(68)	
	du3	1.176(47)	2.05(22)	0	Fe(II)	13.3(77)	1.60

IS (mm/s), the isomer shift relative to metallic ion
QS (mm/s), the electric quadrupole splitting
A (%), relative resonance area in percent of total iron

and Hg in sediment of Voglajna near Štore and the highest concentrations of Zn, Cd, Ag and Au in sediment of Savinja at Tremerje, downstream from Celje. These results indicate industrial pollution in this region.

Mössbauer spectroscopy was used to study poorly crystalline iron compounds. This technique could provide quantitative information about the relative population of the iron species together with specific properties of the individual iron sites as oxidation states. It is suggested that Fe (III) occurs in the silicate sites or as finely dispersed iron oxide, and that Fe (II) is contained in chlorite.

Further work is in progress on new sampling locations on samples taken at different weather conditions, by additional methods for determination of clay minerals and by determination of iron minerals with Mössbauer spectroscopy.

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