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GEOCHEMICAL–MINERALOGICAL CHARACTERISTICS OF SPRING SEDIMENT OF THE IRON–SULFATE MINERAL WATER LJEPOTICA NEAR SREBRENICA (RS)

by

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The Srebrenica area in Eastern Bosnia (Republika Srpska) is characterized by numerous Pb–Zn sulfide ore bodies and several iron–sulfate mineral water springs. The spring Ljepotica appears in the central part of the area and has similar water composition and spring sediment "limonite" mass like nearby the famous medical iron–arsenic water spring Crni Guber. The sequential chemical analysis of iron and XRD–studies of the relative shortly aged spring sediment showed that it is composed by ferrihydrite, jarosite and some goethite. The ratio Fe_{dit}/Fe_{tot} of 0.76 indicates that jarosite appears as a main constituent, in contrast to the Crni Guber spring sediment in which occurs irregularly and in traces. Trace elements pattern is characterized by appearance of As, Pb, Sb, and Sr as the most abundant (>5000 and up to 1450, 780, and 210 ppm, respectively), small contents of Cr, Cu, Ti, V, and Zn (up to 60 ppm), and traces of Mn, Ni and Sc (below 10 ppm). Chemical analysis of the sediment indicates that jarosite is of the jarosite–hydronium jarosite type.

Key words: geochemistry, mineralogy, spring sediment, ferro–sulfate mineral water, ferrihydrite, jarosite, redox processes, Ljepotica spring, Srebrenica, Eastern Bosnia, Republika Srpska.

Подручје Сребренице у Источној Босни (Република Српска) карактеришу бројна Pb–Zn–сулфидна рудна тела као и низ извора гвожђевито–сулфатних минералних вода. Извор Љепотица се налази у централном делу подручја и одликује се сличним саставом воде и "лимонитским" масама изворског седимента као код оближњег извора чувене лековите воде Црни Губер. Секвенцијална хемијска анализа гвожђа и рендгенска проучавања узорака релативно мало "остарелих" изворских седимената показала су да изворски седимент изграђују ферихидрит, јарозит и нешто гетита. Количник Fe_{dit}/Fe_{tot} је 0,76 и указује да је јарозит главни минерал изворског седимента, насупрот изворском седименту Црног Губера у коме се јарозит појављује нерегуларно и у траговима. Асоцијацију микроелемената карактеришу високи садржај As, Pb, Sb и Sr (>5000 и до 1450, 780 и 210 ppm=mg/kg, респективно), нижи садржаји Cr, Cu, Ti, V и Zn (до 60 ppm) и трагови Mn, Ni и Sc (<10 ppm). Хемијска анализа седимента указује да је јарозит типа јарозит–хидронијумјарозит.

Кључне речи: геохемија, минералогија, изворски седимент, минерална феро–сулфатна вода, ферихидрит, јарозит, редокс процеси, извор Љепотица, Сребреница, источна Босна, Република Српска

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INTRODUCTION

The broader area of the town of Srebrenica, in Republika Srpska, in the eastern Bosnia, is a well known mining area, having a mining history longer than two thousand years. It is situated at the boundary with Serbia and belongs to the Tertiary Serbo–Macedonian eruptive and Pb–Zn metallogenic province. In the Roman time, as having been an important producer of silver and lead, the Srebrenica area was the center of the large mining province Dalmatia. In the Medieval, it was also an important mining and lead and silver producing area. The modern mining started about 40 years ago and the ore is using as a source of lead, silver zinc and cadmium.

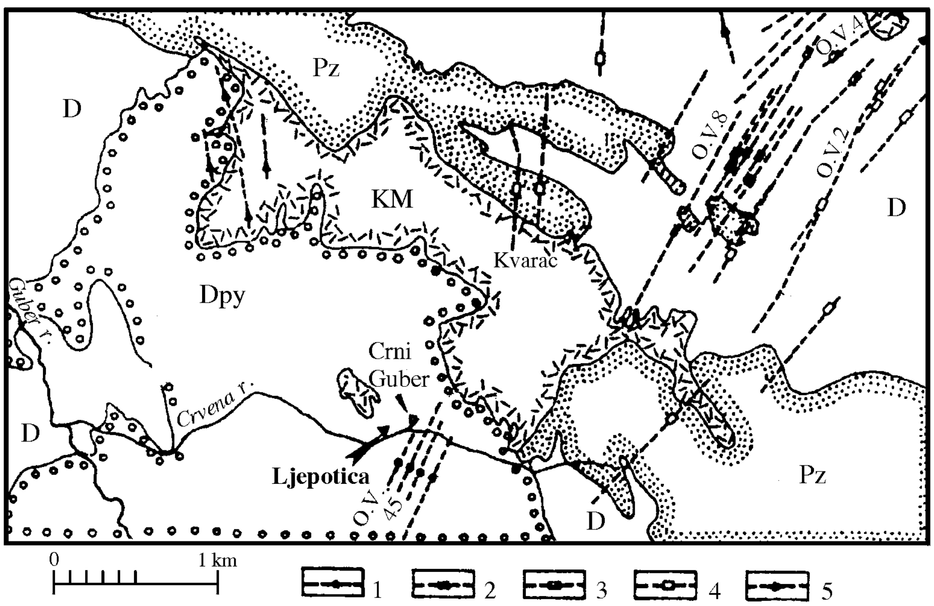

Fig. 1. Geological map of central parts of the Srebrenica eruptive and ore–bearing area. D= dacite, Dpy= pyritized dacite (andesite), KM= contact–metamorphic rocks, Pz= Paleozoic schists; 1–5 ore veins: 1. quartz–pyrite–pyrrhottite, 2. quartz–pyrite–Pb–Zn, 3. siderite–quartz–Pb–Zn, 4. quartz–Sb–(Zn, Pb), 5. quartz–pyrite.

Сл. 1. Геолошка карта централних делова еруптивног и рудног подручја Сребренице. D= дацит, Dpy= пиритисан дацит (андезит), KM= контактно–метаморфне стене, Pz= палеозојски шкриљци; 1–5 рудне жице: 1. кварц–пиритско–пиротинске, 2. кварц–пирит–Pb–Zn, 3. кварц–сидерит–Pb–Zn, 4. кварц– Sb–(Zn, Pb), 5. кварц–пиритске.

The Srebrenica area is also well known due to a famous mineral water spring Crni Guber (Fig. 1), with water of the unique iron–arsenic–sulfate composition (Ludwig, 1890; Miholić, 1955; Dangić & Dangić, 1989). The spring is situated near the town of Srebrenica and based on medical applications of its water there exists the Guber spa for several tens of years. At the Crni Guber spring a larger mass of spring sediment was formed and for a long time it was treated as a "limonite mass". Detail mineralogical–geochemical studies (Dangić & Dangić, 1982; 1983a; 1983b; 1989; 1992) showed that the mass is of specific mineralogical and geochemical characteristics. It is composed of ferrihydrite and goethite but sporadically contains also some jarosite. It was found that "jarosite" has rather specific mineralogical and geochemical features – it is represented by more than one member of the jarosite group and is enriched by several trace elements (Dangić & Dangić, 1982; 1989; 1992; 1996; 1998).

Nearby the Crni Guber spring few other mineral water springs appear. Among them, the spring Ljepotica has some similarities with the Crni Guber spring in the water composition and spring sediment formation. The paper presents geochemical–mineralogical studies of the Ljepotica spring sediment and its comparison with the Crni Guber spring sediment.

BASIC GEOLOGY

The Srebrenica eruptive and ore–bearing area appears to be a western part of the Podrinje district which makes the NW part of the Tertiary eruptive and metallogenic Serbo–Macedonian Province (Dangić, 1994). It is characterized by andesite–dacite––quartzlatite volcanic and subvolcanic masses and masses of their pyroclastics, localized in/on Paleozoic schists, as well as quartz–tourmaline rocks appearing in the central part of the eruptive area.

In both igneous rocks and schists numerous hydrothermal sulfide ore assemblages appear, forming either typical ore veins or disseminated mineralizations (Ramović, 1963; Dangić, 1979–80). Hydrothermal activity in the area started with a pneumatholityc–hydrothermal stage, producing disseminated mineralization and quartz–tourmaline veins in the central part of the area, and has continued by formation of ore veins up to a low temperature stage. In all ore veins quartz and Fe–sulfides (pyrrhotite, pyrite, marcasite) are present and in most of them galena and sphalerite are abundant, but several other minerals appear in some of hydrothermal stages. Due to high content of silver in the ore, the area was in the Roman and Medieval times known as important producer of silver and lead. Both Roman and present names of town/area Argentaria and Srebrenica, respectively, are derived from the noun silver. At the present, the ore is also a source of zinc and cadmium.

The ferrous–arsenic–sulfate mineral water spring Crni Guber occurs in the central part of the area, which is characterized by several sulfide ore veins, mostly of higher temperature, and disseminated mineralizations (Fig. 1). Sulfide assemblages are localized in volcanics and quartz–tourmaline rocks (former Paleozoic schists) and a few patterns of the wall–rock (hydrothermal) alteration are found around ore veins (Dangić, 1977; 1979–80). The mineral water comes out from an ancient (Roman or Medieval) mining work (tunnel) draining underground works which collect descending water mineralized by sulfide ore oxidation (Dangić & Dangić, 1984). This underground reservoir is enough large to enable that water is of the constant composition at the spring (Dangić & Dangić, 1989). At the spring, a large mass of "limonite" is formed due to a rapid oxidation of ferrous–ion in the water–air interaction. It is composed of ferrihydrite, goethite and, sporadically, jarosite (Dangić & Dangić, 1982; 1983a; 1983b; 1989).

The Ljepotica mineral water spring is situated nearby the Crni Guber spring and is characterized by similar water composition but with higher iron content (237 and 125.2 ppm, rcspectively). At the spring, a "limonite" mass like that at the Crni Guber is forming.

MATERIAL AND METHODS

The spring sediment of the mineral water Ljepotica was studied in an appropriate profile as thick as 0.8 m. In the profile, few samples of the spring sediment material were taken. Based on macroscopic and other preliminary studies, two samples, representing the lower and upper parts of the profile, were selected for detailed geochemical–mineralogical studies.

The study of samples included: X–ray diffraction analysis (XRD), sequential chemical analysis of iron (determination of oxalate– and dithionate–soluble iron and total iron), partial chemical analysis (Fe_2O_3, Na_2O, K_2O, PbO, SO_3), and trace element analysis.

In the XRD study, the powder diffraction patterns were obtained on a Philips PW–1050/25 diffractometer equipped with a CuKα radiation, and a graphite monochromater.

In the analyses of oxalate– and dithionate–soluble iron, the procedure of sample treatment was that described elsewhere (Dangić & Dangić, 1982; etc.) and iron concentrations were measured by atomic absorption spectrophotometry (AAS). Chemical composition of samples was analyzed by a combination of AAS, spectrophotometric (SPH), and classical methods of chemical analysis. In AAS and SPH a Perkin–Elmer 373 equipment (and the flame technique) and a "Zeiss" UV VIS SPECORD were used, respectively. Trace elements were analyzed by the emission spectrography (ES), using a EST–1 spectrograph with crossed dispersion and the d.c. arc in a controlled atmosphere ($Ar+O_2$). In ES, 30 elements were analyzed and average precision and accuracy, controlled by the internal standards (Ge and Pd) and geochemical (international) referent standards were ±12%.

RESULTS AND DISCUSSION

The spring sediment of the Ljepotica mineral water is represented by "limonitic" masses at and bellow the spring, which looks to be almost similar to those formed at the Crni Guber spring. It is composed by rather porous brown–yellowish to brown materials, mostly of laminar texture. The freshly precipitated material is softer and brown–yellowish, but aged material (in the lower parts of the profile) is harder and more brownish. The more complexly investigated samples, from the upper (sample #54) and the lower (#52) parts of the spring sediment profile, represent a younger and an aged sediment material, respectively.

Mineral composition of investigated samples was identified by both appropriate sequential chemical analysis of iron and XRD analysis.

Sequential chemical analyses of iron involved determination of oxalate– and dithionate–soluble iron and total iron and their ratios. In this type of material, these ratios may indicate presence/quantity of ferrihydroxide/ferrihydrite, goethite and jarossite. It was found that the Ljepotica spring sediment (sample #54) is characterized by the high total iron content, as high as 30.68%, and relative lower contents of the oxalate– and dithionate soluble iron (Table 1). The Fe_{ox}/Fe_{tot} and Fe_{dit}/Fe_{tot} ratios indicate the follows: ferrihydrite appears to be a main constituent of the sediment, goethite is present in the small amount, and an other phase which may be jarosite is significantly abundant.

Table 1. Ratio of oxalate–soluble iron (Fe_{ox}) and total iron (Fe_t) in the Ljepotica mineral water spring sediment and related phases (sample #54).
Табела 1. Секвенцијална хемијска анализа гвожђа у изворском седименту минералне воде Љепотица и одговарајуће минералне фазе (узорак #54).

Fe fraction[1] Фракција Fe[1]	Fe (%)	Fe_{ox}/Fe_{tot}	Fe_{dit}/Fe_{tot}	Mineral phases[2] Минералне фазе[2]
Fe_{ox}	21.30	0.694		Fh
Fe_{dit}	23.16		0.755	Fh, Gt
Fe_t	30.68			Fh, Gt, J

[1]– Fe_{ox}= oxalate (оксалатно) Fe; Fe_{dit}= dithionate (дитионатно) Fe; Fe_t = total (укупно) Fe.
[2]– J= jarosite (јарозит); Fh= ferrihydrite (ферихидрит); Gt= goethite (гетит).

The XRD study showed that spring sediment contains jarosite, which appears to be a relative abundant constituent. Indeed, in XRD patterns of samples, jarosite appears as only detectable crystal phase. The XRD patterns (diagrams) of bulk samples are characterized by several jarosite lines (peaks) but also there are some very weak bands which may be indications of presence of a non/short crystalline phase like ferrihydrite. In the pattern of more aged material (sample #52) there is a very weak band which may be the indication of presence of goethite in traces (?). In XRD patterns even of bulk spring sediment for both samples, jarosite is represented by numbers of lines (the most intense are given in Table 2). There is not any significant difference in jarosite patterns between studied samples. They are characterized by d–values and peak intensities similar to those of jarosite from the Crni Guber spring deposit and the synthetic jarosite (Table 3).

Table 2. X–ray powder diffraction data for jarosites from the Ljepotica springs deposit.
Табела 2. Параметри рендгенског дијаграма праха (d вредности и интензитети пикова) јарозита изворског седимената извора Љепотица.

d (Å)	I	hkl[1]	d (Å)	I	hkl
5.941	21	101	2.868	25	006
5.742	24	003	2.548	19	024
5.111	43	012	2.292	35	107
3.658	14	110	1.982	33	033
3.109	62	021	1.826	32	220
3.078	100	113	1.540	14	226
2.969	12	202	1.511	19	0,2,10

[1]– According (према): Brown (1980).

Table 3. Selected X−ray powder diffraction data for jarosites from Ljepotica and Crni Guber spring deposits and syntethic jarosite.
Табела 3. Карактеристичне вредности рендгенског дијаграма праха за јарозите изворских седимената Љепотице и Црног Губера и синтетички јарозит.

hkl	Ljepotica (Љепотица)		Crni Guber[1] (Црни Губер)[1]		Synthetic jarosite[2] (Синтетички јарозит)[2]	
	d (Å)	I	d (Å)	I	d (Å)	I
101	5.941	21	5.93	45	5.917	30
012	5.111	43	5.09	70	5.076	45
113	3.078	100	3.08	100	3.076	100
107	2.292	35	2.287	40	2.285	33
033	1.982	33	1.977	45	1.977	38

[1]– Dangić & Dangić (1982); [2]– Brown (1980)

The sample representing younger sediment (L–54) was chemicaly analyzed. In partial chemical analysis, components relevant to jarosite composition: Fe_2O_3, Na_2O, K_2O, PbO, and SO_3, were analyzed (Table 4). It was found that chemical composition of spring sediment is characterized by a very high content of ferric–oxide, high SO_3, relative high potassium and low sodium and lead oxide contents. Contents of Fe_2O_3, SO_3, and K_2O are as high as 43.87%, 14.27% and 1.75%, respectively. Contents of Na_2O and PbO are 0.08% and 0.09%, respectively. Molecular and related atomic abundances of these components and atomic ratios against sulfur are also calculated and presented in the Table 4.

Table 4. Partial chemical composition of the Ljepotica spring sediment and atomic relations of ions relevant to jarosite composition (sample L–54).
Табела 4. Парцијални хемијски састав изворског седимента Љепотице и атомски односи јона важних за састав јарозита (узорак L–54).

	Weight/Теж. (%)	Molecul. abundan. (Молекул. колич.)	Atoma (Атома)		Atoms based on 4 S (Атома на бази 4 S)
Fe_2O_3	43.87	0.2747	Fe^{2+}	0.5494	12.332
Na_2O	0.08	0.0013	Na^+	0.0026	0.058
K_2O	1.75	0.0186	K^+	0.0372	0.835
SO_3	14.27	0.1782	S^{6+}	0.1782	4.000
PbO	0.09	0.0004	Pb^{2+}	0.0004	0.009

Trace element analyses showed that spring sediment contains several trace elements and that their distribution is relative homogenous, as the both analyzed samples have similar trace element patterns (Table 5). The following elements were detected in both samples: As, Cr, Cu, Mn, Pb, Sr, Ti and V, and Ni, Sb, Sc, and Zn were detected only in one sample. If one excludes arsenic, the most abundant trace elements are lead, with contents 810–1450 ppm, antimony, with contents up to 780 ppm, and strontium, with contents of 90–210 ppm. Chromium, copper, titanium, vanadium, and zinc appear in contents bellow 60 ppm, and manganese, nickel, and cadmium in contents bellow 10 ppm.

Table 5. Trace elements in samples of the Ljepotica, and Crni Guber spring sediments (in ppm).
Табела 5. Микроелементи у узорцима изворских седимената Љепотице и Црног Губера (у ppm=10^{-4} %).

Element (Елемент)	Ljepotica (Љепотица) L–52	Ljepotica (Љепотица) L–54	Ljepotica (Љепотица) mean–средње	Crni Guber (Црни Губер) n=2
As	>5000	>5000	>5000	>5000
Cr	60	10	35	8–15
Cu	15	8	11	9
Mn	9	3	6	–3
Ni	7	<		–
Pb	1450	810	1130	185–520
Sb	780			1410–3800
Sc	6	<		–
Sr	210	90	150	–
Ti	26	45	35	?
V	32	40	36	160
Y	<6	<6	<6	<6–17
Zn	66	<30	43	<30
Ag B Ba Be Bi Co Ga	–[1]	–	–	–
La Mo Nb Sn W Zr	–	–	–	–

[1]– Bellow detection limit (Испод границе детекције) – ppm: Ag<1, B<8, Ba<6, Be<1, Bi<8, Co<3, Ga<4, La<10, Mo<1, Nb<15, Sn<3, W<1, Zr<18.

The trace element pattern of the Ljepotica spring sediment is rather similar to that of the Crni Guber spring sediment (Dangić & Dangić, 1982). However, the Crni Guber sediment has significantly higher contents of antimony, zinc, and vanadium (1410–3800, 115–290, and 160 ppm, respectively), and lower contents of lead and strontium (185–520 and <10 ppm, respectively).

In the Crni Guber spring sediments, two types of jarosite were identified, both appearing to be transition members of solid solution series: jarosite–hydronium jarosite and jarosite–plumbojarosite (Dangić & Dangić, 1992; 1996). Similar types of jarosite may be also expected in the Ljepotica spring sediment. Based on data in Tables 4 and 5, composition and type of jarosite mineral in this spring sediment may be recognized.

Assuming that in the spring sediment all sulfate, potassium, sodium, and lead appear to be bounded in jarosite, a formula of this mineral may be calculated. The atomic abundances in the Table 4 are normalized against 4S, according to an ideal formula of jarosite: $K_2Fe_6(SO_4)_4(OH)_{12}$. The iron atomic content is expected to be much higher than in the jarosite ideal formula, as most of iron is bounded in ferrihydrite. Potassium atomic content is 0.893, less than in jarosite, as in the jarosite structure, potassium may be substitued by Na^+, H_3O^+, Pb^{2+}, and some other ions. In our case, the sum of K^+, Na^+, and Pb^{2+} is as high as 0.902 and the sum of their charge is 0.911. This indicates that in an ideal case 1.089 of the hydronium (H_3O^+) ion may be present. Based on this, mineral of the jarosite group appearing in the Ljepotica spring sediment appears to be a transition member of the jarosite–hydronium jarosite solid solution series. Its structural formula is:

$$(H_3O^+{}_{1.089}\ K^+{}_{0.884}\ Na^+{}_{0.009}\ Pb^{2+}{}_{0.009})\ Fe_6\ (SO_4)_4\ (OH)_{12}$$

According to the formula, it is hydronium jarosite–jarosite. However, in this type of materials considered components may be present also partly in ferrihydrite and some others (as As) in jarosite (Dangić & Dangić, 1982; 1983b; 1996). Taking that into accaunt, a little higher proportion of the hydronium–jarosite component is possible.

The Ljepotica spring sediment is forming by a rapid oxidation of ferrous ion at the spring, in the contact of the ferrous–sulfate water with air, in the same way like it is forming the spring sediment of the Crni Guber water (Dangić & Dangić, 1983a; 1989). The investigations of synthesis of ferrioxide minerals from ferrosulfate solution (Dangić, 1984) indicated that in systems which correspond to the studied mineral waters, rather small changes of pH and iron activity my favor formation of jarosite or ferrihydrite. Some differences between these spring sediments appear due to the differences in their water geochemistry (ferrous ion is near twice more abundant in the Ljepotica water than in the Crni Guber water).

CONCLUSIONS

The Ljepotica iron–sulfate mineral water spring in the Srebrenica area is characterized by the deposition of spring sediment in the form of "limonitic" masses. These masses appearing at/bellow the spring consist of rather porous brown–yellowish to brown materials, mostly of laminar texture.

The ratios of oxalate– and dithionate–soluble Fe/total Fe and XRD–studies showed that spring sediment is composed by ferrihydrite and jarosite with traces of goethite and that jarosite is a rather abundant phase. Chemical composition of the sediment is characterized by very high iron, high sulfate and relative high potassium contents. Among trace elements, arsenic, lead and antimony appear to be most abundant.

Relations of jarosite–relevant ions in the sediment indicate that the jarosite mineral is the most probably a transition member of hydonium jarosite–jarosite solid solution series, with a little prevalence of the hydronium–jarosite component.

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РЕЗИМЕ

ГЕОХЕМИЈСКО–МИНЕРАЛОШКЕ КАРАКТЕРИСТИКЕ ИЗВОРСКОГ СЕДИМЕНТА ФЕРО–СУЛФАТНЕ МИНЕРАЛНЕ ВОДЕ ЉЕПОТИЦА КОД СРЕБРЕНИЦЕ (РС)

Шире подручје Сребренице у источној Босни, у Републици Српској, припада Подрињској области терцијарне Српско–македонске магматске и Pb–Zn металогенетске провинције и важно је рударско подручје још од античког доба. Сем тога веома је познато и по бањи Губер, са извором минералне воде Црни Губер, јединственог гвожђевито–арсенско–сулфатног састава и изванредних лековитих својстава. На извору је формирана већа маса изворског седимента која је раније

означавана као "лимонитска" маса, а детаљнијим минералошко–геохемијским истраживањима (Dangić & Dangić, 1982; 1983b; 1989; 1992; 1996) је утврђено да је изграђују ферихидрит, гетит и нешто јарозита, као и да је јарозит представљен са два варијетета. Извор Љепотица налази се у близини Црног Губера и сличан му је по саставу воде и изгледу изворског седимента. Рад приказује резултате геохемијско–минералошких истраживања седимента овог извора и разматра одговарајуће генетске импликације.

Минерални извор феро–сулфатне воде Љепотица се налази у централном делу еруптивног и рудног подручја Сребренице, у коме су заступљене бројне рудне сулфидне пиритско–полиметаличне рудне жице, дацити, измењени дацити и контактно метаморфне стене (сл. 1). Минерална вода Љепотице се вероватно као и вода оближње минералне воде Црни Губер формира у старим (римским ?) рударским радовима. Извор Љепотица се карактерише образовањем изворског седимента у облику "лимонитских" маса. Ове масе, образоване на извору и испод извора састоје се од доста порозног материјала мрко–жућкасте до мрке боје, који је већином ламинарне текстуре.

Проучавања изворског седимента минералног врела Љепотица су изведена на профилу дебљине око 0,8 m. Узет је већи број узорака седимента а на основу макроскопских и неких других прелиминарних проучавања за детаљнија геохемијско–минералошка истраживања одабрана су два, од којих један репрезентује нижи, а други виши део профила.

Секвенцијална хемијска анализа гвожђа и рендгенско–дифракциона проучавања релативно млађег (не много старог) изворског седимента показују да га изграђују ферихидрит и јарозит са нешто гетита. Количник Fe_{dit}/Fe_{tot} од 0,76 указује да је јарозит заступљен као главни минерал за разлику од изворског седимента Црног Губера у коме се појављује нерегуларно и у траговима. Седимент се одликује релативно високим садржајем SO_3 и K_2O и ниским Na_2O. Најобилнији микроелементи су As, Pb, Sb и Sr (>5.000, до 1.450, 780 и 210 ppm, респективно), мање заступљени су Cr, Cu, Ti, V и Zn (до 60 ppm), а веома мало Mn, Ni и Sc (<10 ppm). Односи релевантних компоненти у седименту указују да је јарозит представљен прелазним чланом серије чврстог раствора јарозит – хидронијум–јарозит.

У изворском седименту врела Црни Губер откривена су два типа јарозита, а оба представљају прелазне чланове серија чврстих раствора: јарозит–хидронијум јарозит и јарозит–плумбојарозит (Dangić & Dangić, 1992; 1996). Слични типови јарозита могу такође да се очекују и у изворском седименту извора Љепотица. На основу резултата приказаних у табелама 4 и 5 могу да се детаљније размотре вероватни састав и тип јарозитског минерала у овом изворском седименту.

Претпостављајући да су у изворском седименту сав сулфат, калијум, натријум и олово везани за јарозит, може да се прорачуна приближна формула тог минерала. Атомске количине у табели 4 су нормализоване на 4S, према идеалној формули јарозита:

$$K_2F_6(SO_4)_4\,(OH)_{12}$$

Атомска количина гвожђа је много већа од оне у идеалној формули јарозита, стога што је већи део гвожђа везан за ферихидрит. Атомска количина калијума је 0,893 и мања је него у јарозиту, зато што у јарозитској структури калијум може да буде замењен Na^{+}, H_3O^{+}, Pb^{2+}, као и неким другим јонима. У овом случају, збир количина јона K^{+}, Na^{+}, и Pb^{2+} је 0,902, а збир њихових набоја (валенци) 0,911. Ово указује да би у идеалном случају могло да буде заступљено 1,089 хидронијум (H_3O^{+}) јона. На основу изнетог, минерал јарозитске групе заступљен у изворском седименту извора Љепотица био би прелазни члан серије чврстих раствора јарозит–хидронијум јарозит. Његова приближна структурна формула је:

$$(H_3O^{+}{}_{1.089}\ K^{+}{}_{0.884}\ Na^{+}{}_{0.009}\ Pb^{2+}{}_{0.009})\ Fe_6\ (SO_4)_4\ (OH)_{12}$$

Према овој формули, минерал је хидронијум јарозит–јарозит. Ипак, у овом типу материјала анализиране компоненте могу да буду присутне такође делом и у ферихидриту, а неке друге (као As) у јарозиту (Dangić & Dangić, 1982; 1983b; 1996). Ако се ово узме у обзир, могућа је нешто већа заступљеност хидронијум–јарозитске компоненте.

Изворски седимент извора Љепотица образује се брзом оксидацијом феро–јона при контакту феро–сулфатне воде са ваздухом, на исти начин како се формира и изворски седимент извора Црни Губер (Dangić & Dangić, 1983a; 1989). Проучавањем синтезе фериоксидних минерала из феросулфатног раствора (Dangić, 1984) је утврђено да у системима који одговарају проучаваним минералним водама релативно мале промене pH и активности феро–јона могу да фаворизују образовање јарозита или ферихидрата. Извесне разлике између изворских седимената Љепотице и Црног Губера проузроковане су разликама у геохемији минералних вода (феро–јон је скоро двоструко обилнији у води Љепотице него у води извора Црни Губер).

ЗАКЉУЧАК

Извор минералне гвожђевито–сулфатне воде Љепотица у подручју Сребренице се одликује депоновањем изворског седимента у облику "лимонитских" маса. Ове масе се појављују уз извор и испод извора а чине их доста порозни материјали, мрко–жуте до мрке боје, претежно ламинарне текстуре. Количници оксалатно–растворног према укупном и дитионатно–растворног према укупном гвожђу (Fe_{ox}/Fe_{total}, Fe_{dit}/Fe_{total}) као и рендгенска проучавања показују да се изворски седимент састоји од ферихидрита и јарозита са нешто гетита и да је јарозит доста обилно заступљен. Хемијски састав седимента се карактерише врло високим садржајима гвожђа и сулфата и релативно високим садржајем калијума. Међу микроелементима најобилнији су арсен, олово и антимон.

Међусобни односи јона значајних за састав јарозита присутних у седименту указују да је јарозитски минерал вероватно прелазни члан серије чврстог раствора хидронијум јарозит–јарозит, са малом преваленцијом хидронијум–јарозитске компоненте.