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Original scientific paper

GEMSTONE SILICA VEINS IN KREMENJAČA VOLCANIC ROCKS (SERBIA)

Lidja Kurešević, Snežana Dević

Institute for Materials Testing,
Bulevar vojvode Mišića 43, Belgrade, Serbia
lidja.kuresevic@institutims.rs

A b s t r a c t: The Ješevac volcanic complex located in central Serbia is made up of various Tertiary volcanic rocks. Kremenjača hill is situated on the SW rim of the Ješevac volcanic complex. Silica veins found in this site are made up of chalcedony varieties and crystalline quartz. Jasper veins are examined more thoroughly in this paper. Microscopic analysis has shown it is made up of cryptocrystalline silica with fluidal structure. X-ray powder diffraction analysis of the samples has shown crystalline silica-quartz, ruling out the presence of amorphous silica-opal. The results of spectrochemical analysis have indicated the presence of colouring agents originating mostly from ultramafic and mafic rocks.

Key words: gemstone; silica veins; jasper; dacite

INTRODUCTION

Volcanic complex of Ješevac (Borač) is located in the cCentral Serbia, SE from Gornji Milanovac and NE from Čačak cities. Kremenjača site with silica gemstone occurrence is located on the slopes of Kremenjača hill, on south-western flanks of Ješevac volcanic complex (Fig. 1).

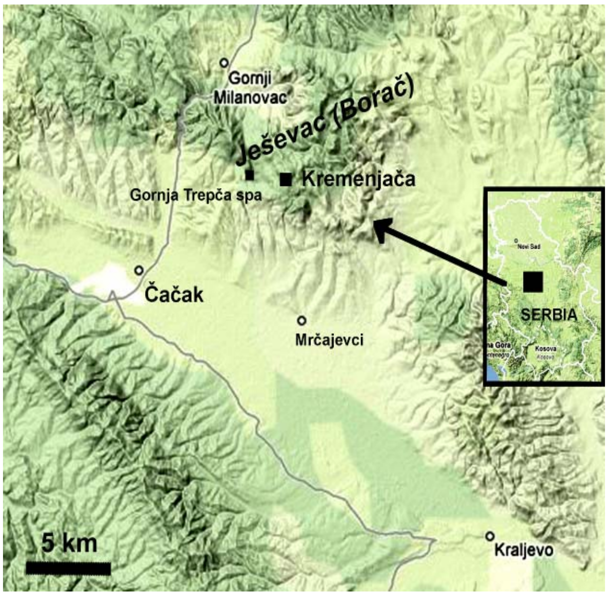

Fig. 1. Geographic location of Kremenjača site.

During the period 1982–1984, special prospecting works have been conducted in central Serbia (Šumadija district), aiming to find new occurrences of gemstone [6]. In Ješevac complex, it resulted in discovering of a very rare type of agate named "fish agate" in diluvium material on the Kremenjača hill slopes. Silica veins also appear on other locations in Ješevac. As these can be used economically as a gemstone raw material, further special prospecting work has been conducted in this locality during 2004. These new works resulted in discovering types of siliceous gemstones unknown in this area before [8].

GEOLOGICAL SETTING

Many authors have given abundant data on geologic setting of Ješevac complex. The most detailed study is given in [1, 2, 3, 4, 7]. Ješevac volcanic complex belongs to Rudnik-Ješevac-Kotlenik volcanic province, as a part of Late Paleogene-Neogene volcanic formation of the central axis of the Balkan Peninsula [5].

The oldest neighbouring rocks are serpentinites, which rarely crop out, due to overlying massive Tertiary volcanic rocks. The Ješevac complex is made up of effusive and pyroclastic rocks of Egerian to Egenburgian age (23–20 Ma, [2]). These comprise dacite, quartzlatite, ignimbrite, andesite and lamprophyre (Fig. 2). Central part of the Kremenjača hill is made up of dacite and dacitic tuff. Tectonic setting of the site is marked by North-South and NNW-SSE trending faults. Through some of these faults, in Gornja Trepča spa (streams Besni potok and Banjska reka) thermal waters, as probable remains of hydrothermal activity, still emerge. Teofilović and Vujanović [12] have proved the juvenile origin of these waters.

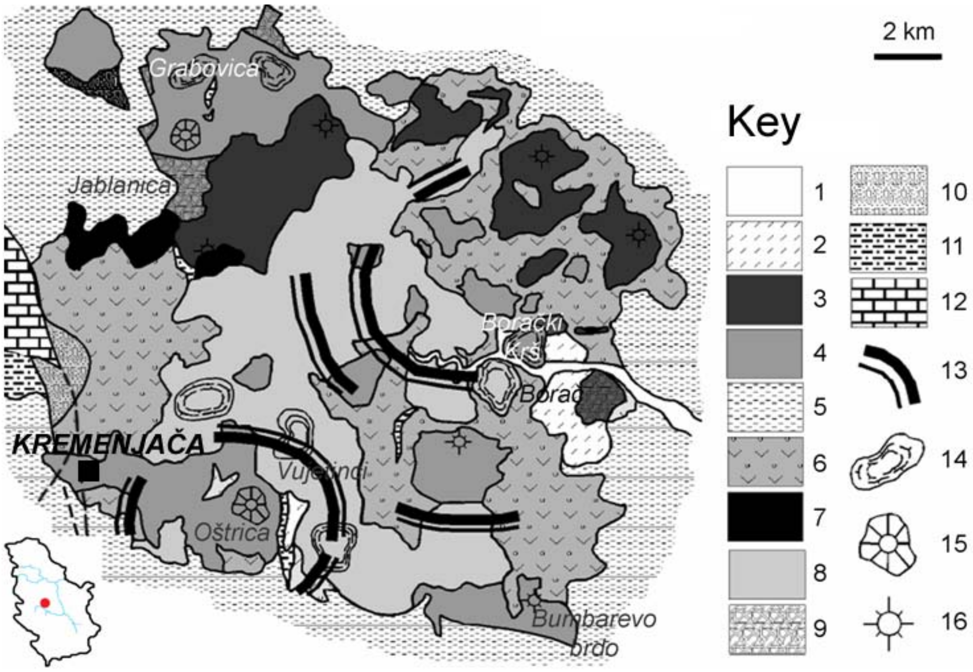

Fig. 2. Geologic map of Ješevac complex with location of Kremenjača site (according to [3]; modified). Lower left – location in Serbia.
Key. 1. alluvium; 2. diluvium; 3. andesite; 4. quartzlatite; 5. sediments of Middle Miocene; 6. pyroclastite; 7. lamprophyre; 8. dacite; 9. autoclastite in situ; 10. redeposited autoclastite; 11. sediments of Lower Miocene; 12. Cretaceous sediments; 13. caldera relicts; 14. lava domes; 15. volcano necks; 16. inferred centres of volcanic activity.

FIELD STUDY

Silica veins in Kremenjača site appear as small, irregular-shaped fracture fillings and stockworks in weathered dacite. The following silica types are found to be present: chalcedony varieties (jasper, purple and colourless chalcedony, carnelian, sard, chalcedony onyx and agate) and quartz variety rock crystal (Fig. 3). All cited translucent to transparent chalcedony varieties, and jasper as opaque variety, appear in the same, comparatively narrow belt-shaped zone, trending approximately ENE-WSW. The belt is about 50 m wide, while the length of this belt is not easily determinable due to soil and vegetation cover and the presence of village on it. All varieties are interchanging in more narrow subbelts: the southernmost is the dark green jasper subbelt, which grades into translucent to transparent chalcedony varieties subbelt towards the North. This subbelt gradually passes into dark red and grey jaspers subbelt further North.

Jasper (Fig. 3a-c), namely grey and mottled red-grey varieties form veins filling fractures of irregular shape, up to 7 cm thick. Green jasper is rarer and appears as veins up to 1 cm thick. All varieties tend to appear as stock works rather than single veins. Fractured jasper surfaces are characteristically conchoidal and smooth.

Colourless (Fig. 3f,g) to pale purple (Fig. 3d) chalcedony is translucent. It occurs in veins, most often up to 1 cm thick. Sometimes it forms thicker veins, up to 7 cm, with visible botryoidal inner surfaces. Sard (Fig. 3e) and carnelian (Fig. 3i), transparent to translucent chalcedony varieties, of orange-brown and orange-red colours respectively, have been found only as small fragments in diluvium material. Chalcedony onyx (Fig. 3h) is another chalcedony variety, more rare in nature. Unlike agate, its bands are not concentrically round but perfectly straight (Liesegang rings). It has been discovered in Serbia for the first time in 2004 [8]. Macroscopically, white translucent to opaque bands interchange with translucent to transparent brown-coloured bands.

Quartz is present as small, densely packed crystals filling up the central parts of chalcedony geodes. This form of quartz is not regarded as gemstone, except with chalcedony base, market-named "drusy quartz".

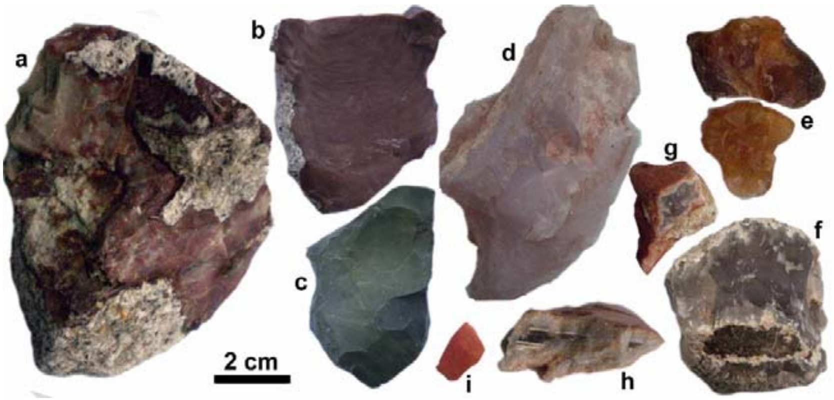

Fig. 3. Silica gemstone varieties found during fieldwork (**a** – mottled grey-red jasper, **b** – red jasper, **c** – green jasper, **d** – pale purple chalcedony with drusy quartz on upper right side of the specimen, **e** – sard, **f** – colourless chalcedony, **g** – ibid., with red crust, **h** – chalcedony onyx, **i** – carnelian).

LABORATORY EXAMINATIONS

In this paper we have focused the laboratory examination works on jasper specimens. As occurrences of jasper in red hues are abundant in central Serbia and green jasper is very rare, the spectrochemical examinations were focused on green jasper specimens, in order to establish the possible colouring agents.

Microscopic examination in transmitted light

Microscopic examinations and photomicrograph capturing are performed in Petrology Department of the Faculty of Mining and Geology – Belgrade University, Serbia, on polarizing microscope for transmitted light type Leica DMLSP with digital camera.

Dacite has massive structure and porphyritic texture. It is impregnated with secondary silica (Fig. 4) in botryoidal aggregates with fluidal structure.

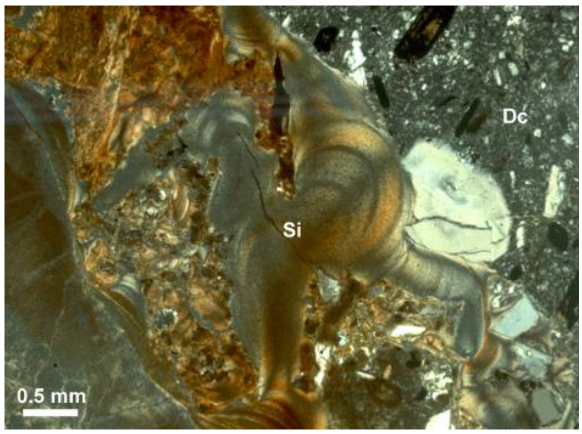

Fig. 4: Photomicrograph of the silica vein in dacite (crossed polars).
Key: Si – silica vein; Dc – dacite host rock

POWDER X-RAY DIFFRACTION ANALYSES

These analyses have been performed in the Petrochemistry Laboratory of the Faculty of Mining and Geology – Belgrade. The results are shown in Figs. 5 and 6.

The X-ray examinations of the samples were performed by the X-ray powder diffractometer type PHILIPS PW 1710 with Cu anode with radiation wave-length of CuKα = 1.54178 Å and a graphite monochromator.

Operating voltage U = 40 kV, current intensity I = 30 mA. Samples are examined within 5–60°2θ with 0.02° step and time-hold 0.5 s on each step (goniometre speed). Obtained data of diffraction peak positions (°2θ), interplanar spacings d (Å) and intensities are compared with literature data and JCPDS standards.

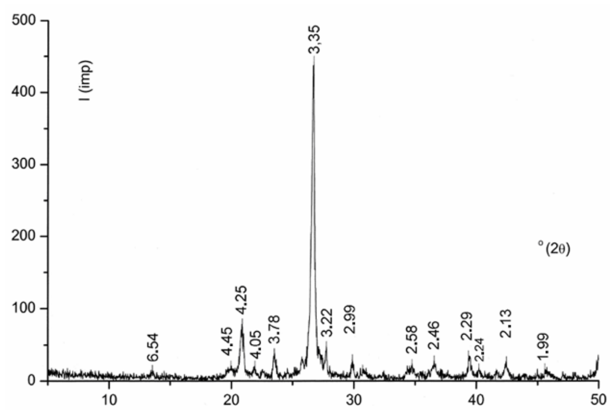

Fig. 5: Powder X-ray diffraction analysis diagram of dark green jasper

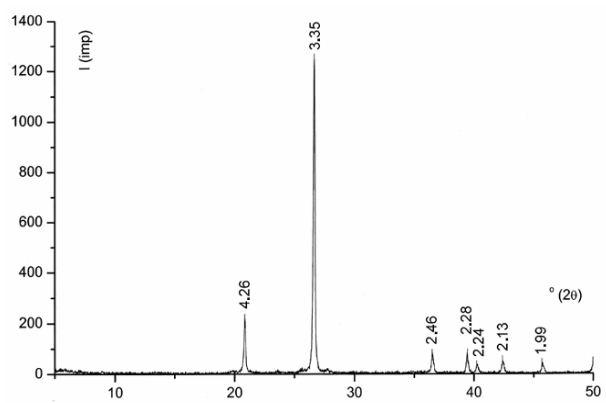

Fig. 6. Powder X-ray diffraction analysis diagram of red-grey mottled jasper

SPECTROCHEMICAL ANALYSIS

Spectrochemical analysis is performed by Geoinstitute – Belgrade Laboratory. Recording of the previously prepared sample is performed on the high dispersion spectrograph type LITROU-HILGER E-478 in visible and UV light spectrums (2700–9000 Å). Sample ignition is carried out in DC electric arc by current intensity of 8 A. Maximum electric arc temperature is 3000–7000°C. The sample mixture with carbon powder (1:1) is completely burned during 3 minutes. Inner standards used are Germanium and Palladium. Quantitative determination is done by work-sheets in logarithmic scale with concentration span 0.0001–1.0% (1–10000 ppm). Determination absolute error is ±15–20%.

The results are shown in Table 1.

T a b l e 1

The results of spectrochemical analysis of green jasper

Element	Content (ppm)	Element	Content (ppm)
Al	> 10 000	V	60
Fe	> 10 000	Cu	12
Mg	2 500	Zr	150
Ca	6 000	Ni	75
Ti	1 600	Co	10
Mn	95	Sc	9
Ga	traces	Cr	50
Ba	210	Sr	230

RESULTS AND DISCUSSION

Microscopic study of a jasper vein shows that dacite is veined with secondary silica in botryoidal aggregates with fluidal structure. This type of fabric points to amorphous silica-opal.

Powder X-ray diffraction analysis on opaque silica (jasper) specimens has shown the predominance of quartz, with most intensely pronounced peak on 3.35 Å and smaller ones on 4.26, 2.46, 2.28, 2.24, 2.13 and 1.99 Å. Minor amounts of feldspar (small peaks on 2.99, 3.22, 4.05 and 6.54 Å) and clay (small peaks on 2.58 and 4.45 Å) in green jasper sample come from the host rock, which couldn't be avoided due to small thickness of the silica vein. Presence of clay points to advanced phase of weathering or hydrothermal alteration of the host rock.

Spectrochemical analysis of green jasper has shown the presence of colour-giving elements. Alumina and iron contents are above detection limits for this method. The intense green colour can be caused by the presence of iron, chromium and nickel. Some of the present elements point to connection with ultrabasic (Cr, Ni, Co) and basic (Cu, V) rocks, which is a characteristic of all the gemstone deposits in the Vardar zone of central Serbia.

In deposit type division by Paradis et al. [9], this occurrence belongs to Hydrothermal silica veins in volcanic host rocks type ("IO7"), closely related to Hydrothermal volcanic-hosted opal ("Q11"), agate ("Q03") and jasper ("Q05"), but also to Hydrothermal silica-carbonate Hg deposits ("I08"), to which belong all the other silica gemstone deposits found in the Vardar zone of central Serbia (the difference being the host rock – serpentinite in the latter case).

Geologic setting on the regional scale is the complex geotectonic evolution of the Vardar zone [11]. Connected with the closure of the Tethys Ocean through collision and thrusting occurred the Tertiary sincollisional to postcollisional magmatic activity of the Vardar zone, predominantly of calc-alkaline character, exerted along regional and splay faults. Ješevac volcanic rocks, including Kremenjača dacite are formed as its part. As extension phases within the predominantly collisional setting were short-lived, huge portions of molten magma did not reach the field surface. Thus formed the hidden plutons, which have caused hydrothermal activity in the overlying rocks.

Ore controls are the open spaces and other permeable zones open to silica-bearing solutions. Volcanic-hosted veins are associated with major faults related to crustal extension which control the ascent of hydrothermal fluids to suitable sites for silica deposition, in this case most probably due to cooling. The fluids are believed to be derived from calc-alkaline intrusions of Tertiary age. Also the cooling magma can cause the formation of extensive meteoric waters heating and circulation system. This locality was in the close neighbourhood of the so-called Čačak-Kraljevo lake, which existed in Miocene, and this is a common characteristic for all the silica gemstone deposits found in the Vardar zone of central Serbia.

Most authors exploring hydrothermal silica agree on the fact that relations between crypto- to microcrystalline silica (chalcedony) and crystalline silica (quartz) precipitated from hydrothermal solutions depend on relations of silica saturation, temperature and pressure (e.g. [10]). The formation of crystalline quartz at higher temperatures has been noted, while at lower temperatures, solution saturation has more influence on the silica precipitates' crystallinity degree. Oversaturated solutions give amorphous silica, which by solid-state transformation over geological time gives chalcedony. On the other hand, after the silica surplus has precipitated from the solution, quartz forms from the undersaturated solution (in the closed system). This is the reason why in all silica gemstone occurrences of this type in the Vardar zone of central Serbia, chalcedony veins are covered by drusy quartz crystal crusts [8].

The results of our analyses have proved that one type of analysis is not reliable enough for characterization of silica precipitates. Microscopic examination has shown silica to be amorphous, i.e. opal. X-ray diffraction analyses have shown silica to be crystalline, i.e. quartz. Rapid cooling of silica-bearing solutions near the field surface, in the open system, has caused rapid precipitation, producing amorphous silica, which, through the processes of the solid-state transformation over geological time gained an ordered crystalline lattice. As this silica still appears amorphous under microscope, it is identified as chalcedony-cryptocrystalline silica variety; in this case – jasper, macroscopically opaque chalcedony.

Presence of the elements typical for ultrabasic (Cr, Ni, Co) and basic (Cu, V) rocks in jasper indicated by spectrochemical analysis points to circulation paths of hydrothermal fluids through ophiolite sequence typical for Vardar zone, although it does not crop out at this part of terrain.

Considering significant amounts of dark red and mottled red-grey, and minor amounts of dark green jaspers in the Kremenjača site and their quality, this site has economic importance for gemstone raw materials, although jasper is generally considered a lower value gemstone named "semi-precious" or "ornamental" [9]. Other present gemstone types (translucent to transparent chalcedony varieties and rock crystal) do not have economic importance as gemstone on this site due to inappropriate morphological characteristics and scarcity.

REFERENCES

[1] Brković T. et al.: *Explanatory booklet of the Basic geological map of Yugoslavia*, sheet Čačak, 1:100000., Savezni geološki zavod – Beograd, p. 64 (1978).

[2] Cvetković V.: *Petrostructural and volcanological characteristics of Borač eruptive complex*. Unpublished Ph.D. thesis, Faculty of Mining and Geology, pp. 241, Belgrade (1997).

[3] Cvetković V. and Pécskay Z.: The Early Miocene eruptive complex of Borač (Central Serbia): volcanic facies and evolution over time. *Geologica Carpathica*, **50**, pp 91–93 (1999).

[4] Cvetković V., Poli G. and Prelević D.: Eruptive history and low-pressure evolution of the Early Miocene Borač eruptive complex (Central Serbia). *Acta Vulcanologica*, **13**, 1–2, 127–143 (2001).

[5] Cvetković V., Knežević V., Pécskay Z.: Tertiary igneous formations of the Dinarides, Vardar Zone and adjacent regions: from recognition to petrogenetic implications, *Geology and Metallogeny of the Dinarides and the Vardar*

zone (eds. S. Karamata and S. Janković) The Academy of Sciences and Arts of the Republic of Srpska, Banja Luka-Serbian Sarajevo, 245–252 (2000).

[6] Malešević N.: *Report on explorations of semi-precious gemstone in central Serbia for year 1983*. Unpublished report, Fond Geozavoda, p. 66, Belgrade (1984).

[7] Marković B. et al.: Explanatory booklet of the Basic geological map of Yugoslavia, sheet Kraljevo, 1:100000. Savezni geološki zavod – Beograd, p. 63 (1968).

[8] Marčeta L.: *Geological characteristics of gemstone occurrences in Šumadija district*. Unpublished Magisterium thesis, Faculty of Mining and Geology, p. 109, Belgrade (2005).

[9] Paradis S., Simandl G. J. and Sabina A.: Opal deposits in volcanic sequences. In: *Selected British Columbia mineral deposit profiles,* vol. **3**, Industrial minerals. Eds.: G. J. Simandl, Z. D. Hora & D. V. Lefebre. British Columbia Ministry of Energy and Mines (1999).

[10] Potapov V. V.: Formation of solid deposits of amorphous silica in a flow of hydrothermal solution. *Glass Physics and Chemistry*, **30,** 1, 82–89 (2004).

[11] Schefer S., Cvetković V., Fügenschuh B., Kounov A., Ovtcharova M., Schaltegger U. and Schmid S.: Cenozoic granitoids in the Dinarides of southern Serbia: age of intrusion, isotope geochemistry, exhumation history and significance for the geodynamic evolution of the Balkan Peninsula. *International Journal of Earth Sciences (Geol Rundschau)*, **100**, 1181–1206 (2011).

[12] Teofilović M. and Vujanović V.: The Li, Rb, Cs, Sr and other elements contents in the surrounding rocks and humus from Gornja Trepča and their genesis. *Zapisnici Srpskog geološkog društva* za 1968–70. godinu, 425–432 (1972).

Р е з и м е

СКАПОЦЕН КАМЕН – СИЛИЦИУМСКИ ЖИЦИ ВО ВУЛКАНСКИ КАРПИ НА КРЕМЕЊАЧА (СРБИЈА)

Лидја Курешевиќ, Снежана Девиќ

Институт за испитивање материјала,
Булевар војводе Мишића 43, Београд, Србија,
lidja.kuresevic@institutims.rs

Клучни зборови: скапоцен камен; силициумски жици; јаспис; дацит

Јешевац е вулкански комплекс изграден од различни вулкански карпи од терцијарна доба, кој се наоѓа во централниот дел на Србија. Ридот Кремењача се наоѓа на југозападниот раб на вулканскиот масив Јешевац. Силиконските жици кои се појавуваат на овој локалитет се изградени од варитети на халкидон и кварц. Во овој проект потемелно е испитана и се презентирани резултатите од анализата на жицата на јаспис. Микроскопскиот преглед на јаспис покажа дека се работи за криптокристална силика со флуидална текстура, а резултатите од икс-зрацната дифракција покажа дека тоа е кварц, со исклучок на присуство на аморфен силицикатен опал. Резултатите од спектрохемиска анализа покажаа присуство на компоненти со потекло од ултрабаични и базични карпи на поголема длабочина, што предизвикува боење на јаспис.