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MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF SILICA-CARBONATE GEMSTONE VEINS FROM GAJ-LAZINE (CENTRAL SERBIA)

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A b s t r a c t: Gemstone deposit Gaj-Lazine is located in central Serbia, 70 km south from Belgrade. Buff brown and red jaspers and colourless chalcedony are the main gemstone types, with subdued magnesite and quartz. Complex veins consisting of these minerals are filling up the fractures and vugs within the host serpentinite rock. The host rock is intensely altered – listwenitized, due to the circulation of hydrothermal solutions from which the gemstone veins have formed via sol phase. As geological features of the gemstone deposit Gaj-Lazine with its economic significance have been previously published in detail, further laboratory examinations' results are shown here. Microscopic analysis has shown that magnesite and jasper have formed contemporaneously. X-ray powder diffraction analyses have shown that the red jasper consists of quartz (crypto- to microcrystalline silica) with minor hematite, while the altered serpentinite host rock consists of quartz, dolomite, smectite clay and serpentine minerals. The results of atomic absorption spectrophotometric analysis have indicated the presence of the elements originating from the ophiolite sequence, Cretaceous limestones and clay minerals.

Key words: gemstone; silica-carbonate veins; jasper; chalcedony; central Serbia

INTRODUCTION

As described in [1], in Gaj-Lazine locality, around 70 km south from Belgrade, in central Serbia, gemstone silica-carbonate veins of the complex composition were found and their geologic features examined in detail. Additional laboratory explorations were performed during 2014 and 2015, aiming to establish the succession of mineral formation within these veins and the colouring agent of red jasper. A long period of geologic exploration facilitated by the rarely deep erosional level of this deposit make it the most interesting locality for establishing the trial genetic model, not only for this particular deposit, but also for all the conjugate deposits in the Vardar zone ophiolitic sequence of central Serbia.

It is evident from all gemstone deposits of this type in central Serbia that the chalcedony veins are younger than magnesite and jasper both, so it has been established that there were two main phases of hydrothermal activity [1, 2], where the first gave the jasper veins and, after an inter-phase with intense tectonic activity, the second phase of hydrothermal activity gave colourless chalcedony veins with sporadic equant quartz geodes. It was impossible to determine the mutual relations between jasper and magnesite, however, since we weren't able to find any samples where the direct contact of the two could be observed. This sample was finally obtained in 2014, and here are presented the results of its microscopic examination.

GEOLOGICAL SETTING

The geological setting is shown in great detail in [1]. In short, the gemstone deposit Gaj-Lazine is situated within the Central Vardar zone ophiolite belt serpentinite, i.e. its hydrothermally altered part bordering with the surrounding younger Cretaceous sediments. Serpentinite belt cannot be traced continuously at the surface, for north of Stragari and south of Dobrača it is covered by Miocene sediments. The same general tectonic trend has caused both the formation of the Miocene lake basins [3] and the initiation of the magmatic activity that eventually led to gemstone deposit formation.

The distribution of the silica-carbonate veins is typical for hydrothermally altered serpentinite and is therefore much more restricted than that of serpentinite body itself. The general geotectonic motion and processes that caused the formation of this and all the other silica gemstone deposits in the central Serbia [4] are described in detail in [1, 2].

The present gemstone types are: A. chalcedony (a. opaque, i.e. jasper and b. translucent i.e. colourless chalcedony). Less frequent are quartz (rock crystal) and magnesite (can be regarded as gemstone when silicified). These appear forming complex veins and stockworks within the hydrothermally altered – listwenitized and disintegrated host serpentinite rock.

LABORATORY EXAMINATIONS

The laboratory examinations performed include microscopic examination, powder X-ray diffraction analyses and atomic absorption spectrophotometric analysis.

Microscopic examination

Microscopic examinations and photomicrograph capturing are performed in Stone and Aggregate Laboratory of Institute for Materials Testing – Belgrade, on stereo-microscope type ZEISS Stemi 2000-C type with digital camera AxioCam ERc 5s. After many years of examining silica gemstone deposits of central Serbia, the authors have found the sample that can reveal the answer to a long-existing question: what are the mutual time relations between jasper and magnesite. Therefore, this most important sample of a complex silica-carbonate vein has been examined in detail to reveal their mutual relations (Figs. 1 to 6).

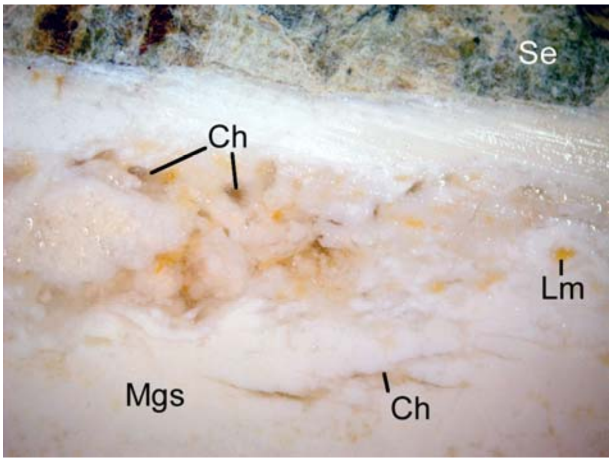

Fig. 1. Silica-magnesite vein in an altered host serpentinite (6.5× magnification). Further explanation in the text.

Figure 1 shows the relations between jasper silica and magnesite in a complex silica-carbonate vein in an altered host serpentinite. Silica and magnesite phases are incompletely segregated from the sol of a complex composition. Previous polarizing microscope examinations [4] have shown that this silica is cryptocrystalline, proving it was formed from the gel, while all XRD analyses have confirmed that no traces of opal are left due to the solid-state transformation into quartz. Here it can be observed that the first-phase silica is actually chalcedony seen in a thin layer, but due to numerous limonite inclusions it is perceived as opaque, i.e. jasper when in thick layer.

Figures 2 and 3 show magnesite globules in jasper silica. Macrodimensions of these globules range up to 1 mm.

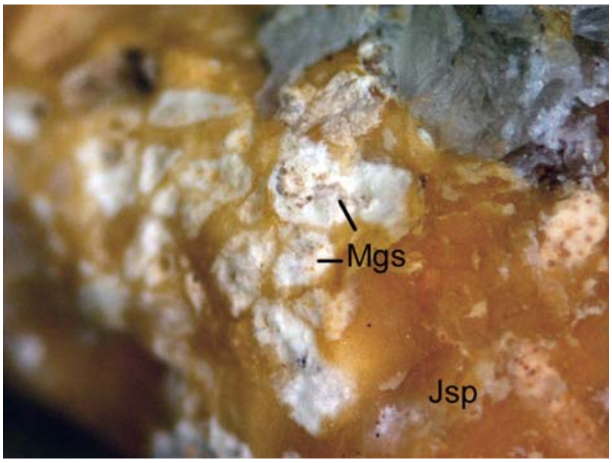

Fig. 2. Magnesite globules in jasper silica, natural break-surface (32× magnification).

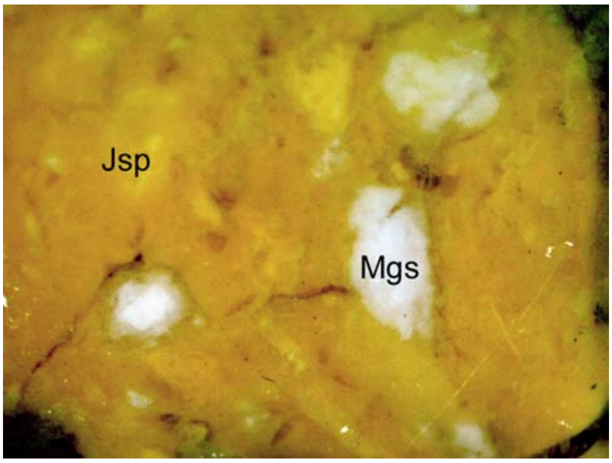

Fig. 3. Magnesite globules in jasper silica, honed surface (32× magnification)

Figure 4 shows segregation of jasper silica globules from magnesite, while at the same time there are minute magnesite globules in jasper silica seen in the jasper globule lower left and lower right. The vein was tectonically broken apart during the inter-phase; in the second phase of hydrothermal activity, colourless chalcedony vein with macrocrystalline quartz in a geode was formed. Figure 5 gives a better view of the quartz geode.

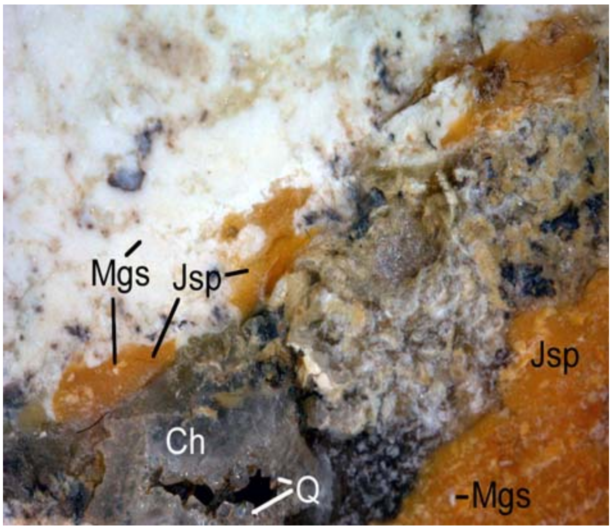

Fig. 4. Jasper globules in magnesite vein, honed surface (12.5× magnification)

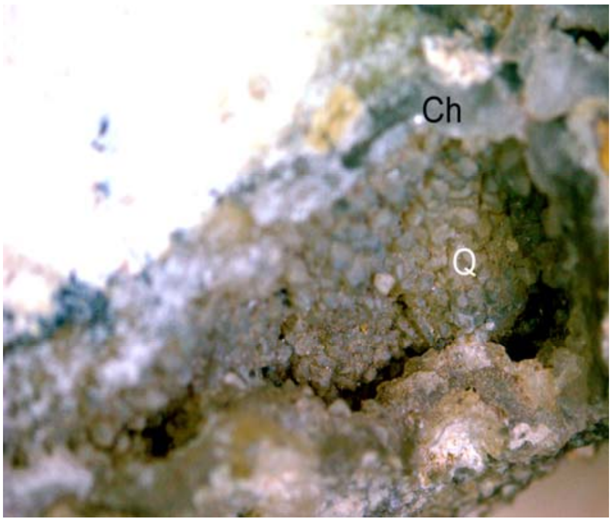

Fig. 5. Equant quartz crystals in a geode (10× magnification)

Figure 6 shows a non-sharp transition between magnesite and jasper silica in great magnification. Also, green zone in the centre of the lower half of the figure is opalized serpentinite, such as that described in detail in [5].

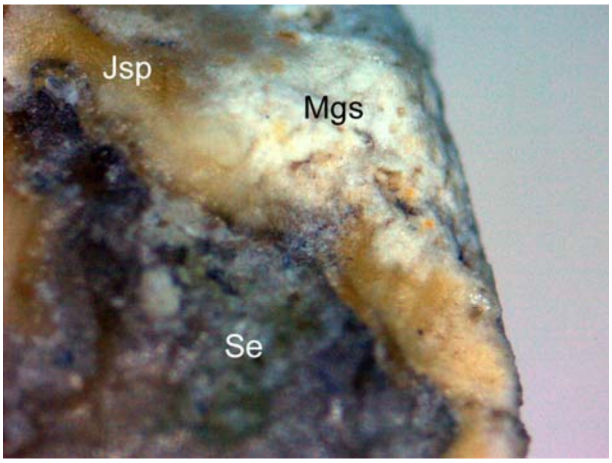

Fig. 6. Non-sharp transition from magnesite into jasper silica, natural break-surface (40× magnification)

Key (Figs. 1 to 6): Ch – chalcedony, Mgs – magnesite, Jsp – jasper silica, Lm – limonite, Se – serpentinite host rock, Q – quartz crystals.

Powder X-ray diffraction analyses

These analyses have been performed in the Petrochemistry Laboratory of the Faculty of Mining and Geology – Belgrade. The first sample is a piece from the vein of dark red jasper and the second one is a piece of the host rock – hydrothermally altered serpentinite. The results are shown in Figs. 7 and 8. The X-ray examination of the samples is performed by the X-ray powder diffractometer type PHILIPS PW 1710 with Cu anode with radiation wave-length of CuK α =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 JCPD standards.

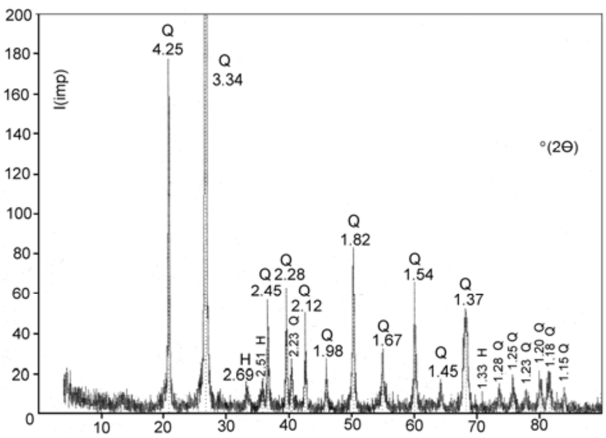

Fig. 7. Powder X-ray diffraction analysis diagram of red jasper (Q – quartz; H – hematite)

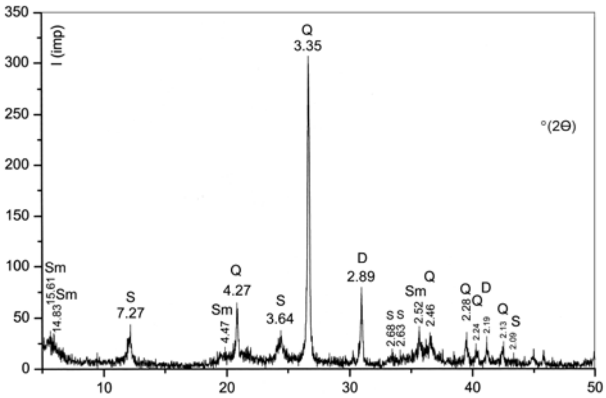

Fig. 8. Powder X-ray diffraction analysis diagram of altered serpentinite host rock (Q – quartz; S – serpentine; Sm – smectite; D – dolomite).

Atomic absorption spectrophotometric analysis

The analysis is performed by Geoinstitute – Belgrade, 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). The results are shown in Table 1.

Table 1

The results of atomic absorption spectrophotometric analysis of colourless chalcedony

Element	Content (ppm)	Element	Content (ppm)
Al	160	Ti, Mn, V	tr. 10*
Fe	2 000	Ni	50
Mg	500	Sc	15
Ca	3 200	Cr	22

Note: An asterisk marks the elements whose content in the sample is near the lower detection limit of this method.

DISCUSSION

Microscopic study of silica-carbonate vein has shown that both magnesite and jasper silica have been formed in the first phase of hydrothermal activity as segregations from the sol of the complex composition. What was known from the previous studies [1] is that after the first phase had started the inter-phase with intense tectonic activity which had resulted in tectonisation of the solidified jasper and magnesite veins. After this tectonic activity inter-phase, the second phase of hydrothermal activity had occurred, in which chalcedony veins have been formed, sporadically containing minute equant quartz crystals where the system remained closed and the medium had returned from sol into a true solution i.e. from silica-oversaturated into silica-undersaturated disperse system.

Powder X-ray diffraction analysis on opaque silica (red jasper) specimen has shown the predominance of quartz, with most intensely pronounced peaks on 3.34 and 4.25 Å and smaller ones on 2.45, 2.28, 2.23, 2.12, 1.98, 1.82, 1.67, 1.54, 1.45, 1.37, 1.28, 1.25, 1.23, 1.20, 1.18 and 1.15 Å. Minor amounts of hematite (peaks on 2.69, 2.51 and 1.33 Å) account for the red colouring of jasper silica.

Powder X-ray diffraction analysis on hydrothermally altered serpentinite host rock specimen has shown the presence of quartz (peaks on 4.27, 3.35, 2.46, 2.28, 2.24 and 2.13 Å), dolomite (peaks on 2.89 and 2.19 Å), smectite clay group mineral (peaks on 16.61, 14.83, 4.47 and 2.52 Å) and serpentine (peaks on 7.27, 3.64, 2.68, 2.63 and 2.09 Å). This generally points to listwenitization of serpentinite host rock.

Atomic absorption spectrophotometric analysis of the second-phase chalcedony has shown that, although XRD analyses determine only the presence of silica (quartz), contain, in order of abundance, the following elements: Ca, Fe, Mg, Al, Ni, Cr, Sc, Ti, Mn and V.

CONCLUSION

The microscopic study of the valuable new-found magnesite-jasper sample, where their mutual direct contact is observable, has enabled the reconstruction of the genetic succession model given previously. Based on the new-found data, the previously suggested, three-phase genetic succession

[1] model needs to be redefined into a two-phase model:

1) magnesite, formed from the gel, together with silica in the form of chalcedony with limonite inclusions, appearing as colourless in thin sections but as buff-brown jasper (or red jasper where hematite inclusions are present) in thick sections and

2) colourless chalcedony with sporadic occurrence of equant quartz crystals in geodes;

– with an inter-phase between the two main hydrothermal pulses, in which the intense tectonic activity had caused the fragmentation of already formed silica-carbonate veins.

The red jasper is formed within the same phase as buff-brown jasper, since the two appear intimately intermixed in mottled jaspers, the difference being in the mineral in which the chromophore iron is bound.

The results of the XRD analysis have shown that the colouring agent of the red jasper is hematite (previous studies have shown that the colouring agent of the buff-brown jasper is limonite formed from pyrite and marcasite). The XRD analysis of the altered host rock serpentinite has shown that the predominant general alteration type is listwenitization, with the presence of quartz, dolomite, smectite clay mineral and serpentine mineral.

Presence of Ca in the second-phase chalcedony, indicated by spectrochemical analysis is explained by the circulation of hydrothermal fluids through the Cretaceous sediments (mostly limestones) over which the host ophiolite sequence has been obducted. The presence of the elements typical for ultramafic rocks (Cr, Ni, Fe, Mg) and diabase-chert formation (Mn, V, Ti) points to circulation paths of hydrothermal fluids through the Vardar zone ophiolite sequence, which is a common characteristic of all the gemstone deposits of this type examined in the central Serbia Vardar zone. Iron is released from the mafic minerals' lattices both during serpentinization of the primary ultramafic rock and listwenitization of serpentinite due to the impact of CO_2-bearing hydrothermal fluids. Presence of Al is probably due to smectite clay taken over from the altered host serpentinite. These clays also contain Ca, Mg and Fe.

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Р е з и м е

МИНЕРАЛОШКА И ГЕОХЕМИСКА КАРАКТЕРИЗАЦИЈА НА СИЛИКА-КАРБОНАТНИ ЖИЦИ ВО ЛОКАЛИТЕТОТ ГАЈ-ЛАЗИНЕ (ЦЕНТРАЛНА СРБИЈА)

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Клучни зборови: бесценет камен; силика-карбонатни жици; јаспис; калцедон; централна Србија

Наоѓалиштето на бесценет камен Гај-Лазине се наоѓа во централна Србија, 70 km јужно од Белград. Кафеав и црвен јаспис и безбоен калцедон се доминантни типови на бесценет камен, со споредно присутни магнезит и кварц. Комплексни жици од овие минерали ги заполнуваат пукнатините во карпата домаќин – серпентинит. Карпата домаќин е интензивно променета – лиственизирана, што се должи на хидротермалната активност од која се формирале и жици на бесценет камен, преку солна фаза. Бидејќи геолошките карактеристики на наоѓалиштето на бесценет

камен Гај-Лазине се претходно објавени во детали, овде се прикажани резултати од лабораториските испитувања. Микроскопската анализа покажа дека магнезитот и јасписот се формирани истовремено. Анализите со рендгенски зраци врз спрашен примерок покажаа дека црвениот јаспис се состои од кварц (крипто- до микрокристален силикат) со мали нечистотии од хематит, а изменетата карпа домаќин – серпентинитот, се состои од кварц, доломит, смектитска глина и серпентински минерали. Резултатите од анализата на атомска спектрофотометриска апсорпција покажаа присуство на елементи кои потекнуваат од офиолитските карпи, кредните варовници и глински минерали.