

## Factors contributing to the formation of carbonated mineral water systems in Serbia

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**Abstract.** There are more than 65 occurrences of carbonated mineral water (CMW) within the territory of Serbia. More than 93 % of these systems are found in the geotectonic unit referred to as the Vardar Zone and on the fringes of nearby units. To the east, west and north of the Vardar Zone, CMWs are either rare or non-existent. The area featuring CMWs is characterized by Tertiary magmatism, a complex geology and deep neotectonic structures. Based on  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  and  $\text{HCO}_3^-$  in several CMWs in Serbia, and also in carbonates and  $\text{CO}_2$  from liquid inclusions in several hydrothermal deposits around the world, it was concluded that  $\text{CO}_2$  in the lithosphere of Serbia could originate from hydrothermal carbonates, and carbonates from sedimentary, metamorphic and magmatic rocks. The findings clearly showed that the main generators of  $\text{CO}_2$  are located in the Vardar Zone and that  $\text{CO}_2$  degasification is accomplished through temperature metamorphosis of carbonates (dolomite, calcite). Based on the carbonate transformation temperatures and the temperature conditions in the lithosphere of Serbia, the  $\text{CO}_2$  might be the result of temperature-induced carbonate transformation below a depth of 3 km. Therefore, the conclusion of the study of CMWs in Serbia is that the formation of CMW systems in the lithosphere depends on the geochemical, temperature, and the magmatic and structural-neotectonic conditions.

**Key words:**  $\text{CO}_2$ , mineral waters, magmatism, geochemistry, neotectonic structures, Serbia.

**Апстракт.** На територији Србије је регистровано 65 појава угљокиселих минералних вода (УМВ). Од овог броја је чак 93% формираних система УМВ везано за познату геотектонску јединицу Вардарска зона и маргине суседних јединица према овој зони. Са удаљавањем од Вардарске зоне, источно, западно и северно, појаве УМВ су ретке или их уопште нема. Исто подручје доминантног распрострањења појава УМВ се карактерише и терцијарним магматизмом, сложеном геолошко-структурном грађом и дубоким неотектоонским структурама. На основу вредности  $\delta^{13}\text{C}$  у слободном угљен диоксиду и хидрокарбонатима и карбонатима и угљен диоксиду у течним инклузивима, констатовано је да у литосфери Србије угљеник може да води порекло из карбоната хидротермалних процеса, карбоната седиментних и метаморфних стена и карбоната магматских стена. Постигнути резултати су јасно показали да се у домену Вардарске зоне налазе главни генератори угљен-диоксида и да се дегазација одвија кроз процесе температурне метаморфозе карбоната (калцита, доломита). На основу познатих температура трансформације карбоната, при којима се ослобађа угљен-диоксид и геотемпературних услова у литосфери Србије, закључено је да угљен-диоксид у домену Вардарске зоне може да се генерише испод 3 км дубине. Тако је у резултату истраживања УМВ Србије закључено да формирање система УМВ зависи, пре свега, од геохемијских, геотемпературних, магматских и структурно-неотектонских услова.

**Кључне речи:** угљен-диоксид, минералне воде, магматизам, геохемија, неотектонске структуре.

### Introduction

In Serbia, most of the registered occurrences of carbonated mineral water (CMW) are found in the cen-

tral part of southern Serbia. Several isolated occurrences have been registered away from this area, but there are no such occurrences in the northern, eastern and south-eastern parts of Serbia. Within the territory

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of Serbia, CMWs are grouped such that they reflect the different regional geological structures (anticlines, fault zones, and the like). There are only a few published papers which consider these mineral waters in Serbia. PROTIĆ (1995) addressed all the mineral waters in Serbia and grouped most of the CMWs according to their genetic link with metamorphites, and a small number based on their contact with volcanism and sedimentary basins. The same author briefly described the geological makeup of the near surrounding of the occurrences, presented the physical and chemical properties, the gas compositions and the radioactivity of the CMWs, and described major documented investigations.

The goal of the research reported in this paper was to determine the main factors contributing to CMW formation and thus identify the laws of nature which govern their extent and depth in Serbia's lithosphere. The study of these factors included the results of modeled geotemperature conditions in Serbia's lithosphere, the outcomes of CMW  $\delta^{13}\text{C}$  tests and the results of isotope tests of the infiltration origin of the CMW (MILIVOJEVIĆ 1989). To define the depth of favorable geotemperature conditions for geochemical oxidizable carbonate transformation processes and the release of  $\text{CO}_2$ , the results of investigations by *in-situ* methods conducted at boreholes in the Yellowstone Park in the USA (PATRICK & WHITE 1968) were used.

A spatial link of Serbia's CMW systems was established with the geostructural unit of the Vardar Zone, Tertiary magmatism and regional neotectonic structures. It was then determined that the origin of carbon is primarily associated with oxidizable forms of carbonates in Proterozoic, Paleozoic and Mesozoic sedimentary and metamorphic rocks, and that  $\text{CO}_2$  is generated in the Vardar Zone below a depth of 3 km or, in other words, at depths where favorable geotemperature conditions exist for geochemical processes of temperature-induced metamorphism of carbonates and the release of  $\text{CO}_2$ . The findings led to the conclusion that the main contributors to the formation of CMW systems in Serbia's lithosphere are geochemical, geotemperature, magmatic and structural-neotectonic factors.

## Results and discussion

### Extent of CMW systems in geostructural terms

A CMW system is a unit of geological inter-connected porous water-bearing structural elements in the lithosphere, between the recharge zone, the blending zone of infiltrated water and  $\text{CO}_2$ , and the CMW drainage zone.

The extent of the CMW systems relative to known geological tectonic units within the territory of Serbia (DIMITRIJEVIĆ 1995) is shown in Figs. 1 and 2. Based

on the number of occurrences in geological tectonic units, 57 % of them are found in the Vardar Zone (VZ), 26 % in the Gneiss Complex (GNC) of the Serbo-Macedonian Massif (SMM), 11 % in the zone of the Drina-Ivanjica Element (DIE), 4 % in the Ophiolitic Belt (OB), and 1.5 % in both the East Durmitor Block (EDB) and the Carpathian-Balkan Region (CB). It follows from the above, as shown in Fig. 2A, that 93 % of the occurrences are within the VZ and on the fringes of nearby units.

This means that  $\text{CO}_2$  is generated in the deeper reaches of Serbia's lithosphere within the VZ and that, while migrating toward the surface, the  $\text{CO}_2$  is distributed to neighboring tectonic units *via* younger tectonic zones. This is analogous to the observation of WEINLICH *et al.* (2003) in connection with the Western Eger Rift, namely that  $\text{CO}_2$  from the deeper reaches of the lithosphere migrates to the surface along so-called Y-structures. In the present case, the CMW systems are rooted in the deeper reaches of the lithosphere within the VZ. For these reasons, the majority of the CMW occurrences in Serbia are found in the VZ and the border zones with adjacent geotectonic units. The directions of the younger tectonic structures that distribute the  $\text{CO}_2$  away from the VZ are quite distinct within the belt between the VZ and the SMM (Figs 1 and 2B).

A schematic representation of the noted linear directions of the CMWs is presented in Fig. 2B. It is a well-known fact that most tectonic faults are characterized by limited permeability or virtual impermeability. The greatest fault permeability is found in the moving zones of the Earth's crust, particularly in its stretching parts (STEPANOV 1989). Consequently, considering all relevant aspects, it follows that the linear directions in Serbia's lithosphere are the directions of neotectonic movements. These are also the privileged pathways of  $\text{CO}_2$  distribution from the deeper reaches of the lithosphere to the surface and open structures for the easy infiltration of meteoric and surface waters for CMW recharge. According to the schematic representation in Fig. 2B, the directions of these neotectonic structures vary but are approximately northwest-southeast, east-west and northeast-southwest. It is also apparent in Fig. 2B that many of the CMW occurrences are grouped along the southern edge of the Pannonian Basin. This suggests a connection between these occurrences and the tectonic structures formed by the cascading descent of the Pannonian Basin and the parallel ascent of the Vlašić-Bukulja Anticlinorium and other structures south of the Pannonian Basin.

Based on the present observations, it is important to emphasize that the considered mineral water occurrences are associated not only with magmatic massifs, but also with younger tectonic structures, as is clearly shown by their linear distribution (Figs. 1 and 2). With regard to chemical types of the CMWs, there is only

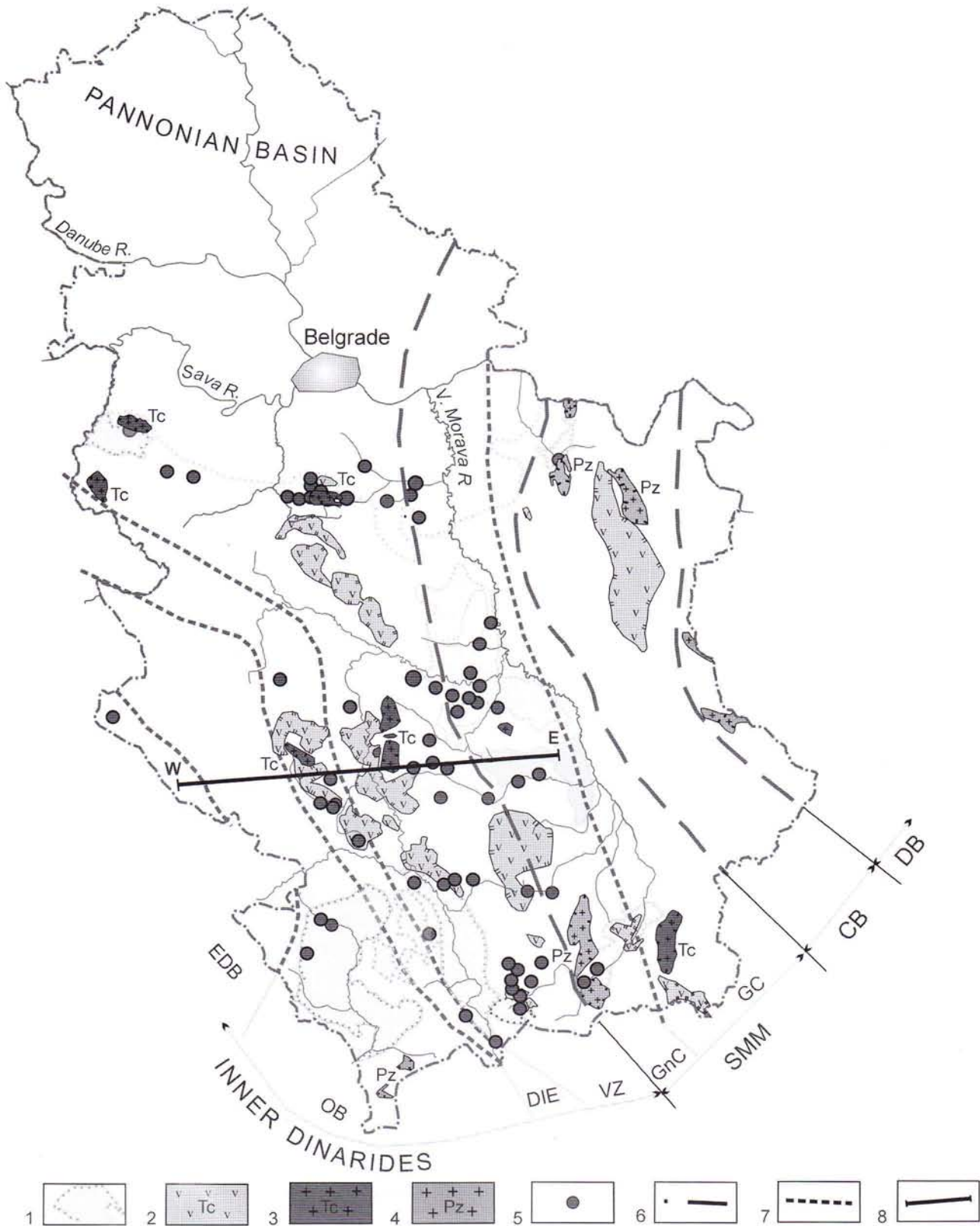


Fig. 1. CMW occurrences in Serbia in respect to granitoid intrusions (Tertiary and Paleozoic) and igneous rocks (Tertiary) of the Serbian lithosphere. **1**, Tertiary sedimentation basin; **2**, Tertiary igneous rocks; **3**, Tertiary granitoid intrusion; **4**, Paleozoic granitoid intrusion; **5**, CMW occurrence; **6**, Geological-structural unit boundary; **7**, Geological-structural sub-unit boundary; **8**, Geological cross-section (Geology reprinted from the Geological Map of Yugoslavia, Scale 1:500.000; produced by Federal Geological Institute, Belgrade, 1970). Geological-structural units: **CB**, Carpathian-Balkan Region; **SMM**, Serbian-Macedonian Massif; **GnC**, Gneiss complex; **GC**, Greenrock complex; **VZ**, Vardar Zone; **DIE**, Drina-Iva-njica Element; **OB**, Ophiolite Belt; **EDB**, East-Durmitor Block.

one occurrence of the  $\text{SO}_2$ -CaMg type, while all the other registered occurrences are of the  $\text{HCO}_3^-$ -type based on their anion composition, and with regard to their cation composition, they are mostly of the Na-type, rarely of the C-type and very seldom of the Mg-type.

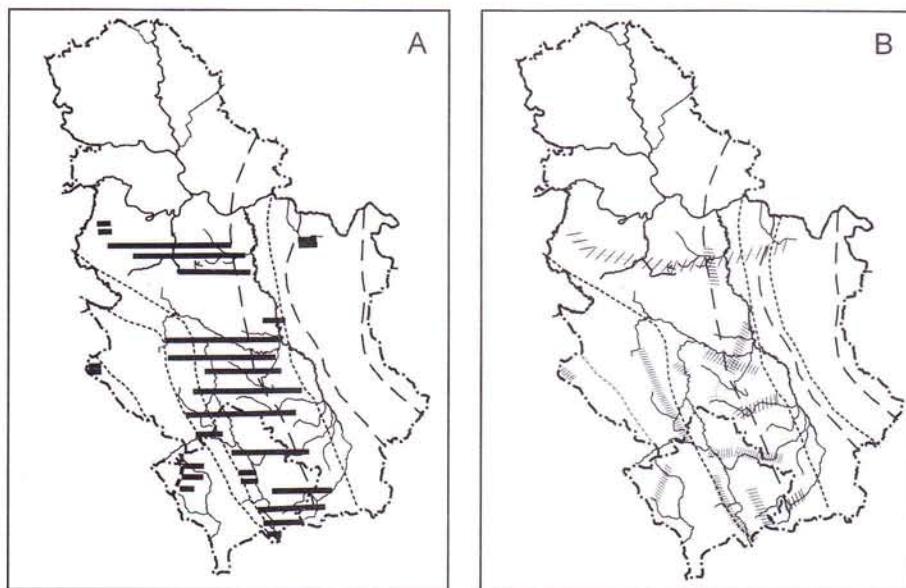


Fig. 2. Schematic representation of (A) the region of CMW occurrences and (B) noted linear distributions of the occurrences as potential directions of deep tectonic structures.

Based on the above, it is safe to assume that the VZ, characterized by a complex geological and tectonic makeup and Tertiary magmatism, holds the main  $\text{CO}_2$  generators and that the distribution of  $\text{CO}_2$  and the infiltration of surface water occur along regional neotectonic discontinuities which are rather pervious. Neotectonic vertical movements cause an enormous mass of carbonate-rich rock to become gradually exposed to elevated geotemperatures and, as a result, there is ongoing exposure of new masses to thermometamorphic geochemical processes. Consequently, the neotectonic units both predispose porous tectonic zones to  $\text{CO}_2$  migration and expose new masses of the substrates of this gas to favorable geotemperatures for the transformation and release of  $\text{CO}_2$ .

### Origin of carbon in carbonated mineral waters

For a number of CMW occurrences in Serbia, the values of the  $\delta^{13}\text{C}$  isotope in free  $\text{CO}_2$  were found to be in the range from  $-8.5$  to  $-2.5$  ‰, that is  $-10.03$  to  $+1.78$  ‰ in  $\text{HCO}_3^-$  (MILIVOJEVIĆ 1989). If this range of values detected in Serbia is compared with the values of the  $\delta^{13}\text{C}$  isotope in the carbonates and  $\text{CO}_2$  of

liquid inclusions determined at several hydrothermal sites in the world (Fig. 3), a very good match is apparent. This supports the assumption that some CMWs in Serbia are traceable to carbonates *via* hydrothermal processes (either ended or still active, but in the “quenching” stage). Oxidizable forms of carbon in hydrothermal fluids can originate from magmatic sources, but can also be formed as a result of oxidation of reducible forms of carbon and leaching of sedimentary carbonates (OMOTO & RYE 1982).

Investigations involving the  $\delta^{13}\text{C}$  isotope have shown that in granites and mafic and ultramafic rocks its values vary over a much broader range than in carbonates, and that the  $\delta^{13}\text{C}$  values of carbonates in such rocks are generally from  $+2$  to  $-10$  ‰, and those of reducible forms of carbon from  $-15$  to  $-30$  ‰ (OMOTO & RYE 1982). Based on the above and the values of the  $\delta^{13}\text{C}$  isotope in free  $\text{CO}_2$  and  $\text{HCO}_3^-$  in Serbia's CMWs, it is safe to assume that the carbon in Serbia's CMWs may originate from carbonates of Proterozoic, Paleozoic and Mesozoic sedimentary and metamorphic rocks, carbonates of magmatic rocks created through assimilation of carbonates from sedimentary and metamorphic rocks, and carbonates from hydrothermal processes which could have leached from sedimentary, metamorphic and magmatic rocks. It is also safe to conclude that carbon from reducible forms cannot be a major contributor to Serbia's CMWs.

Supporting the above assumptions are estimates that about 93 % of all carbon in the Earth's crust is attributed to sedimentary and metamorphic rocks and only 7 % to magmatic rocks, while as little as 0.01 % is the sum of carbon in the atmosphere, hydrosphere and biosphere (OMOTO & RYE 1982). In Serbia's lithosphere, as schematically represented in Fig. 4, such a large proportion of carbon (in excess of 90 %), can only be found up to a depth of 5–8 km, or the depth of the complex of Proterozoic, Paleozoic and Mesozoic sedimentary and metamorphic rocks, interspersed with Tertiary magmatites. Below these depths, up to 15–20 km, in the “granitoid metamorphic layer”, a carbon content of up to 7 % may be expected.

The depths of the CMW systems in Serbia are consistent with the configuration of the VZ (Fig. 4). In this part of the lithosphere, Tertiary magmatites intersperse the entire complex of sedimentary and meta-

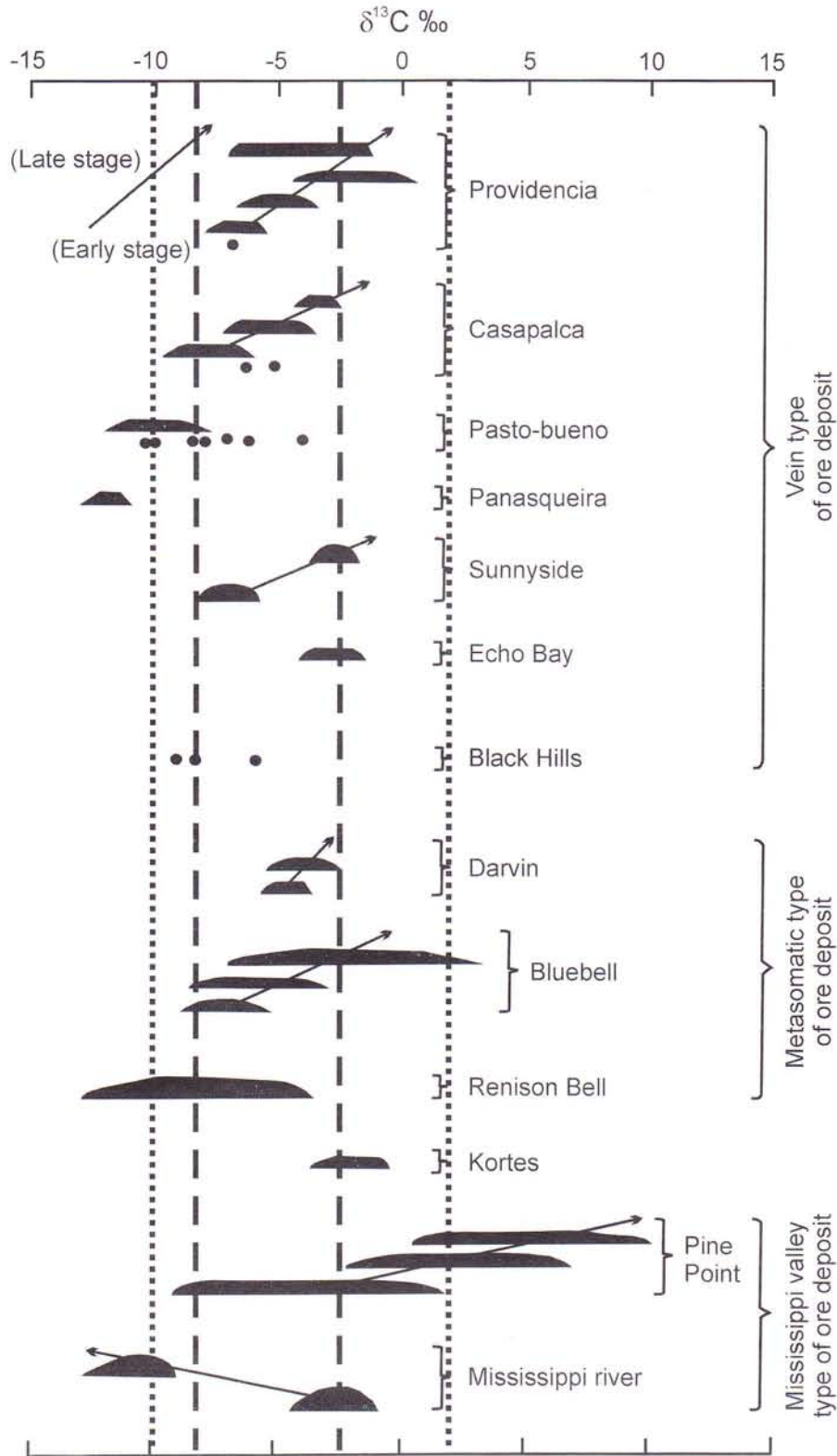


Fig. 3. Schematic representation of carbon isotope compositions of several hydrothermal ore deposits (OMOTO & RYE 1982), along with  $\delta^{13}\text{C}$  ranges of free  $\text{CO}_2$  (dashed line) and  $\text{HCO}_3^-$  (dotted line) at several CMW sites in Serbia.

morphic rocks rich in carbonates. While penetrating the complex of these rocks, the magmatites assimilated considerable amounts of carbon, which partly led

to  $\text{CO}_2$ -generating thermometamorphic processes and, in the VZ, generally brought about elevated geotemperatures. As such, the connection between the

CMW systems and the VZ is logical, since it holds the main supply channels of Tertiary vulcanites and granitoid intrusions, from the deeper reaches of Serbia's lithosphere to the surface.

### CO<sub>2</sub> generation processes in the Vardar Zone

In general, gases in the lithosphere can be generated by biochemical, metamorphic (chemical) and radioactive processes (KARTSEV & SHUGRIN 1964). As stated above, based on the  $\delta^{13}\text{C}$  values, the carbon in Serbia's CMWs cannot be traced to reducible forms, or to carbon from organic compounds and graphite. Consequently, biochemical processes are not the dominant generators of CO<sub>2</sub> in the CMWs. Although CO<sub>2</sub> is not generated as a result of radioactive processes, elevated concentrations of radioactive elements and Rn gas in the CMWs allow for a conclusion to be drawn about their joint origin associated with granitoid intrusions.

Elevated concentrations of F, Pb, As and other heavy metals suggest a connection with volcanic processes. As such, it may be concluded that the CO<sub>2</sub> in the CMWs within the VZ is generated through the chemical processes of temperature-induced metamorphism. Among the chemical processes that lead to the release of CO<sub>2</sub>, the most important are deep processes associated with intrusive and regional metamorphism (KOROTKOV 1983). It follows that an important factor for the CO<sub>2</sub>-generating processes is the geotempera-

ture of Serbia's lithosphere which, in the VZ, is governed by Tertiary volcanism and intrusive magmatism, with hydrothermal processes being the final stages of the magmatism.

According to PROTIĆ (1995), fluoride concentrations in Serbia's CMWs range from 0.1 to 14.25 mg/L (about 60 % above 1.0 mg/L), U concentrations range from 0.1 to 8.0  $\mu\text{g/L}$ , Ra from 0.06 to 1.4 Bq/L, and Rn from 7.4 to 2035 Bq/L, whereby more than 75% of the CMWs exhibit elevated concentrations of U, Ra or Rn. Based on the good match of the  $\delta^{13}\text{C}$  range of the CMWs and hydrothermal deposits (Fig. 3) and the elevated F concentrations in the majority of the CMWs, it is safe to conclude that there is a connection between the CMW CO<sub>2</sub> and hydrothermal processes. Considering the elevated concentrations of radioactive elements, there is a link between the CMWs and the granitoid intrusions. The oxidizable forms of carbon in the hydrothermal fluids (CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>) may be traced to magmatic sources and leaching of sedimentary carbonates (OMOTO & RYE 1982). It follows from all the above that the CO<sub>2</sub> gas in Serbia's lithosphere can be generated by temperature-induced transformation, from carbonates of Tertiary hydrothermal processes, magmatic rocks, and Proterozoic, Paleozoic and Mesozoic sedimentary and metamorphic rocks. However, given that the carbonates from the Tertiary hydrothermal processes are actually leached carbonates from sedimentary and metamorphic rocks and/or magmatic rocks, and that carbon is assimilated by magmatites from the same rocks, it

follows that the Proterozoic, Paleozoic and Mesozoic sedimentary and metamorphic rocks in the lithosphere up to a depth of some 10 km can be considered as the parent substrates of the CO<sub>2</sub>.

If the registered minimum temperatures (150 and 320 °C) are taken into account, at which dolomite and calcite are transformed and CO<sub>2</sub> released (PATRICK & WHITE 1968), as well as the geotemperature conditions in Serbia's lithosphere (MILIVOJEVIĆ 1989) and the results of regional geological investigations of the make-up of Serbia's lithosphere (Fig. 4), it follows that temperature-induced transformations of carbonates in the VZ may be expected below a depth of 3–8 km. As apparent in Fig. 4, this is the transition zone between the "granitoid metamorphic layer" and the Prote-

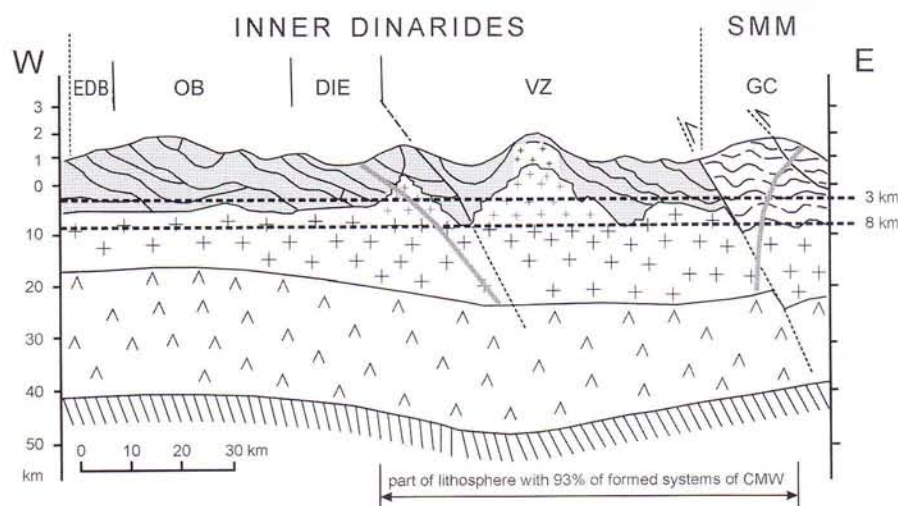


Fig. 4. Geological cross section of Serbia's lithosphere, part of the Inner Dinarides geological tectonic unit (ANDELKOVIĆ 1988, modified). Legend: 1, Pz-Mz sedimentary and metamorphic rock complex with magmatic intrusions; 2, Ptz metamorphic rocks; 3, granite-metamorphic layer; 4, basalt layer; 5, minimum depths for optimal geological and temperature conditions for geochemical processes of CO<sub>2</sub> production from dolomite (3 km) and calcite (8 km). Geological-structural units: CB, Carpathian-Balkan Region; SMM, Serbian-Macedonian Massif; GnC, Gneiss Complex; GC, Greenrock Complex; VZ, Vardar Zone; DIE, Drina-Ivanjica Element; OB, Ophiolite Belt; EDB, East-Durmitor Block.

rozoic, Paleozoic and Mesozoic complex of sedimentary and metamorphic rocks, interspersed with vulcanite and granitoid intrusions.

With regard to the previously-identified potential connection between the CMWs and hydrothermal processes, the CMW CO<sub>2</sub> could be traced to carbonates from completed hydrothermal processes and/or contemporary hydrothermal processes in the final stages of "quenching" of volcanic activity. In hydrothermal solutions, CO<sub>2</sub> from carbonates may be generated as a result of dissolving reactions (e.g., CaCO<sub>3</sub> + 2H<sup>+</sup> → H<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O) and decarbonization reactions (e.g., 3 dolomites + 4 quartzites + H<sub>2</sub>O → talc + 3 calcites + 3CO<sub>2</sub>) (OMOTO & RYE 1982). The first reaction is dominant under surface conditions, while at high temperature, both reactions play significant roles. The carbonate dissolution reaction leads to the formation of HCO<sub>3</sub><sup>-</sup> under surface conditions and CO<sub>2</sub> at high temperatures.

## Conclusions

CMW systems in Serbia's lithosphere were formed in dependence on complex interactions between geochemical, geotemperature, magmatic and structural-neotectonic factors. The parent CO<sub>2</sub> substrates in Serbia's lithosphere are carbonates from Proterozoic, Paleozoic and Mesozoic sedimentary and metamorphic rocks, up to a depth of some 10 km. The depth of CO<sub>2</sub> generation of about 3 km is characterized by favorable geotemperature conditions for carbonate transformation. From a geotectonic perspective, more than 93 % of the CMW systems were formed within the Vardar Zone and on the fringes of nearby units, or in the part of the lithosphere which features Tertiary magmatite intrusions and eruptions. The linear distribution of the CMWs, the fact that the CMWs are by necessity associated with deep tectonic structures, and the faults in the mobile (and particularly stretching) parts of the Earth's crust featuring the highest permeability clearly indicate that the CMW systems are predisposed by neotectonic structures.

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## Резиме

### Фактори формирања система угљокиселих минералних вода Србије

Највећи број регистрованих појава угљокиселих минералних вода (УМВ) распрострањен је у подручју централног јужног дела територије Србије. Ван тог централног дела регистрован је мањи број усамљених појава, а у северном, источном и југоисточном делу Србије нису регистроване. На територији Србије појаве УМВ су груписане тако да маркирају различите регионалне геолошке структуре (антиклинале, разломне зоне и др.). Систем УМВ подразумева целину повезаних порозних водоносних геолошко-структурних елемената у простору литосфере између области храњења, зоне мешања инфилтрационих вода и CO<sub>2</sub> и зоне дренажа УМВ. За системе УМВ Србије утврђена је њихова просторна веза са геоструктурном јединицом Вардарске зоне (ВЗ), те магматизмом и регионалним неотектонским структурама. Затим је утврђено, да је порекло угљеника примарно везано за оксидационе форме карбоната у Ptz, Pz и Mz седиментним и метаморфним стенама и да се CO<sub>2</sub> генерише у домену ВЗ на дубини испод 3 km. Односно, на дубинама где владају повољни геотемпературни услови за геохемијске процесе температурне метаморфозе карбоната и ослобађање CO<sub>2</sub>. Постигнути резултати су омогућили да се закључи да су основни фактори формирања система УМВ у литосфери Србије геохемијски, геотемпературни, магматски и структурно-неотектонски.

Са доста поузданости се може закључити да се у домену ВЗ, која се карактерише сложенем геолошко-тектонском грађом и Тс магматизмом, налазе главни генератори  $\text{CO}_2$  и да се дистрибуција  $\text{CO}_2$  и инфилтрација вода са површине врши регионалним неотектонским дисконтинуитетима који се издвајају добром пропусношћу. Системи УМВ Србије залежу сагласно залегању ВЗ. У том делу литосфере терцијарни магматити прожимају цео комплекс седиментних и метаморфних стена богатих карбонатима. Према томе, веза система УМВ са ВЗ сасвим је логична, с обзиром да кроз њу воде главни доводни канали Тс вулканита и грантоидних интрузива, из дубоких делова литосфере Србије до површине. Повишени садржаји F, As Pb, и других тешких метала, указују на њихову везу са вулканским процесима. По подацима Папић и Стојковић (2012) и Протић (1995) у УМВ Србије садржај F је 0,1–14,25 mg/l (око 60 % изнад садржаја 1,0 mg/l), садржај U у границама 0,1–8,0  $\mu\text{g/l}$ , Ra 0,06–1,4 Bq/l и Rn 7,4–2035 Bq/l. Готово у више од 75 % УМВ утврђен је повишен садржај U, Ra или Rn. На основу доброг поклапања опсега вредности

изотопа  $\delta^{13}\text{C}$  у УМВ у хидротермалним лежиштима, и повишеног садржаја F у већем броју УМВ, може се са доста поузданости закључити да постоји веза  $\text{CO}_2$  УМВ са хидротермалним процесима. На основу повишених садржаја радиоактивних елемената постоји веза УМВ са гранитоидним интрузивима, па произилази да се као матични супстрати  $\text{CO}_2$  могу сматрати Ptz, Pz и Mz седиментне и метаморфне стене у литосфери, до дубине око 10 km. Дубина генерисања  $\text{CO}_2$  од око 3 km, дефинисана је повољним геотемпературним условима за трансформацију карбоната. У геотектонском погледу више од 93 % система УМВ је формирано у домену Вардарске зоне и на маргинама суседних јединица, односно у делу литосфере који се карактерише пробојима и изливима терцијарних магматита. Линијски распоред појава УМВ, чињеница да УМВ морају бити везане за дубоке тектонске структуре и да су највеће водопрпусности разломи у мобилним деловима Земљине коре и посебно у деловима њеног растезања, јасно намећу закључак да су системи УМВ предиспонирани неотектонским структурама.