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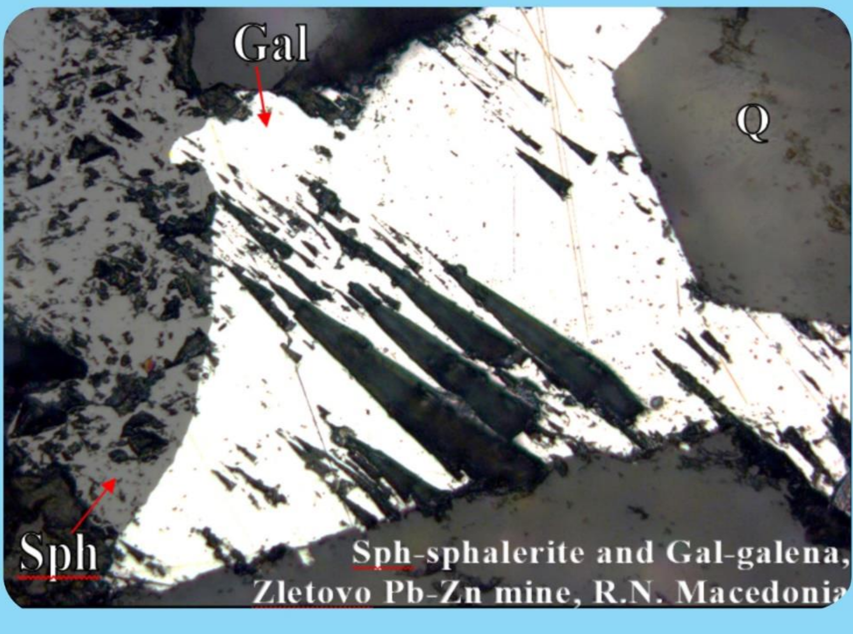

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CARBON AND OXYGEN ISOTOPE SIGNATURE OF HYDROTHERMAL MINERAL DEPOSITS IN A POST-COLLISIONAL MAGMATIC-HYDROTHERMAL SYSTEM: A REVIEW FROM NORTH MACEDONIA

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Abstract: The subaerial magmatic-hydrothermal system exposed on the territory of Republic of North Macedonia represents a natural laboratory for studies of ore-forming processes associated with post-collisional magmatism. In this part of the Balkan Peninsula, neotectonics uplifted and exposed Tertiary post-collisional mineral deposits formed at different crustal levels, including deeply sitting porphyry Cu deposits, proximal and distal skarn deposits, and Carlin-like deposits. Locally epithermal deposits are also preserved. This paper summarizes and discusses previously published carbon and oxygen isotope data obtained from gangue carbonates collected from the key deposits in North Macedonia.

Key words: carbon; oxygen; isotope; hydrothermal; North Macedonia

INTRODUCTION

Although classic examples of subaerial magmatic-hydrothermal systems have been associated with subduction-related magmatic arcs (Seltmann et al., 2014; Groves et al., 2021; Richards, 2022), several studies suggest that post-subduction magmatism associated with decompression melting during post-collisional extension may also result in formation of hydrothermal deposits, including those of porphyry Cu, skarn, Carlin-like, and epithermal types (e.g. Wang et al., 2018; Strmić Palinkaš et al., 2013; Borojević Šoštarić et al., 2012; Muntean et al., 2011).

The post-collisional magmatism occurred along the Balkan Peninsula in the period between ~30 and 1.8 Ma intruding pre-Tertiary terrains with abundant high-K calc-alkaline, shoshonitic and ultrapotassic lithologies (Figure 1; Cvetković et al., 2004; Prelević et al., 2005). The magmatism and associated hydrothermal deposits can be followed from the central Serbia in the north towards Greece in the south (Figure 1). The diversity of the post-collisional hydrothermal deposits is particularly well exposed on the territory of Republic of North Macedonia, where neotectonics uplifted post-collisional mineral deposits formed at different crustal levels, including deeply sitting porphyry Cu deposits (usually formed at depths of up to ~6 km; e.g., Kesler & Wilkinson, 2008), proximal and distal skarn deposits (mostly formed at depths between ~2 and 6 km; e.g., Meinert et al., 2003), Carlin-like deposits (with formation depths >2 km; e.g., Hofstra & Cline, 2000) and epithermal deposits (formed <500 m below the paleosurface; e.g., Henley, 1985).

Carbonates, including calcite, ankerite and siderite, are common gangue minerals in subaerial magmatic-hydrothermal systems and their isotope composition ($\delta^{13}C$ vs. $\delta^{18}O$) can be utilized as indicators of ore-forming processes (e.g., Rabiee et al., 2003; Wang et al., 2007; Strmić Palinkaš et al., 2016).

In this paper we are summarizing previously published data on carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope compositions of gangue minerals from post-collision related hydrothermal mineral deposits in North Macedonia and discussing the significance of isotope data in understanding of magmatic-hydrothermal processes.

Geological setting

Republic of North Macedonia is located in the central part of the Balkan Peninsula and its geological setting is marked by five major geotectonic units: 1) Čukali-Krasta zone; 2) West-Macedonian zone; 3) Pelagonian massif; 4) Vardar zone; and 5) Serbo-Macedonian massif. The units exhibit a NNW-SSE orientation and their mutual contacts are marked by deep regional faults (Petrušev et al., 2021). The Čukali-Krasta zone, exposed in the westernmost part of North Macedonia, is predominantly composed of Upper Cretaceous sediments locally intercalated with evaporites (Robertson & Shallo, 2000). The West-Macedonian zone consists of a Paleozoic volcano-sedimentary complex subjected to greenschist facies metamorphism and Mesozoic sediments and volcanic rocks (Petrušev et al., 2021). The Pelagonian massif represents a fragment of the Precambrian continental crust made of ortho- and para-gneisses, micaschists and amphibolites that were intruded by granitoids during Upper Carboniferous and Late Permian – Early Triassic magmatic events (Dumurdžanov, 1985; Most, 2003). Locally the granitic to granodioritic intrusions are associated with granitic to intermediate pegmatites (e.g., Strmić Palinkaš et al., 2012; Boev & Bermanec, 2021; Boev et al., 2024). The Vardar zone, the main suture zone between the Adriatic/Apulian and the Euroasian plate, occupies the central part of the Balkan Peninsula (Figure 1). This geotectonic unit hosts lithologies of both continental and oceanic origin, including two parallel ophiolite belts formed as a part of the Tethyan ocean realm (Dimitrijević, 2001; Karamata, 2006; Zelić et al., 2010; Robertson et al., 2013). To the east, the Vardar zone is bordered by the Serbo-Macedonian massif (Figure 1; Dimitrijević, 2001; Karamata, 2006). The lower portion (Lower Unit) of the Serbo-Macedonian massif is composed of metamorphosed volcano-sedimentary sequences formed in the late Neoproterozoic to the earliest Cambrian along the active margin of north Gondwana and metamorphosed up to medium- to lower-amphibolite facies during the Variscan orogeny (Dimitrijević, 2001; Antić et al., 2016). The upper portion (Upper Unit) of the Serbo-Macedonian massif consists of the late Neoproterozoic ocean floor sediments and igneous rocks, overlain by a Lower Ordovician to Lower Carboniferous sedimentary sequence metamorphosed to greenschist facies (Dimitrijević, 2001; Petrušev et al., 2021).

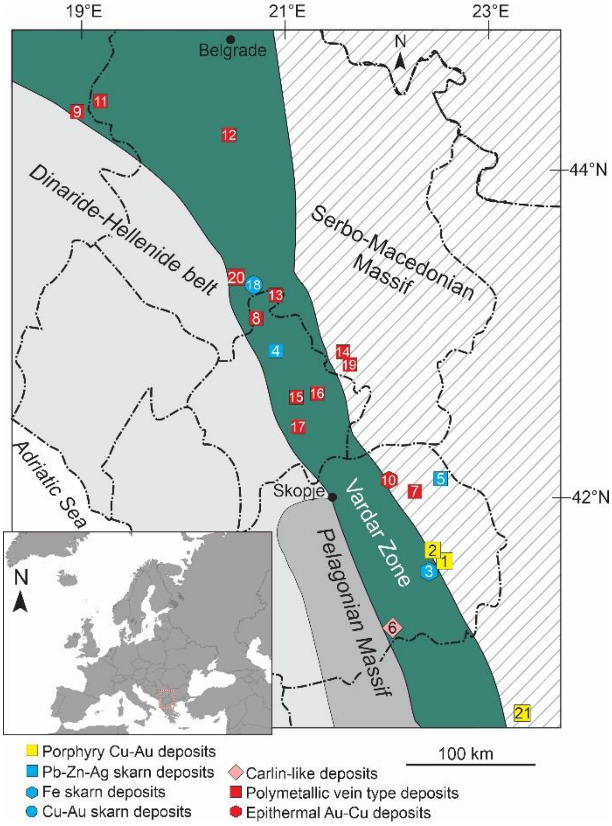

Fig. 1. Regional geologic setting of the most prominent Tertiary magmatic-hydrothermal mineral deposits within the Balkan Peninsula (modified after Dimitrijević (2001) and Karamata (2006)). 1) Borov Dol; 2) Bučim; 3) Damjan; 4) Trepča; 5) Sasa; 6) Allchar; 7) Zletovo; 8) Crnac; 9) Čumavići; 10) Plavica; 11) Boranja; 12) Rudnik; 13) Belo Brdo; 14) Leče; 15) Badovac' 16) Avajllija; 17) Kišnica; 18) Karavansalija; 19) Tulare; 20) Raška; 21) Skouries.

Since the middle Mesozoic the Balkan Peninsula has been subjected to subduction, collision and post-collisional extension (Karamata, 2006). In the Oligocene to Pliocene period (~30 to 1.8 Ma), the Serbo-Macedonian massif and the Vardar zone were affected by post-collisional collapse of the Alpine orogen, followed by extension and extensive magmatism of an intermediate, mostly andesitic to trachytic, composition. The post-collisional magmatism produces rocks with high-K calc-alkaline, shoshonitic and ultrapotassic character (e.g., Cvetković et al., 2004; Prelević et al., 2005; Melfos & Voudouris, 2017) and triggered formation of numerous hydrothermal deposits at crustal depths between ~6 km (porphyry Cu deposits, e.g. Bučim and Borov Dol; Serafimovski et al., 2010; Serafimovsski et al., 2016a; Gjorgjiev et al., 2020) and the paleosurface (epithermal deposits, e.g. Plavica; Alderton & Serafimovski, 2007; Melfos et al., 2019).

RESULTS AND DISCUSSION

Porphyry Cu deposits

The Bučim deposit is a porphyry Cu deposit situated in the westernmost part of the Serbo-Macedonian massif, along its contact with the Vardar zone (Serafimovski et al., 2016a; Figure 1). The deposit is hosted by Precambrian gneisses that are locally intercalated with Paleozoic amphibolites. The mineralization is temporally and spatially associated with post-collisional magmatic activity (Strmić Palinkaš et al., 2022) that resulted with emplacement of andesite and trachyandesite intrusions. The age of magmatic rocks in the Bučim area ranges between 24.04 ± 0.77 and 24.51 ± 0.89 Ma (U/Pb age; Lehmann et al., 2013).

The Cu-bearing mineralization occurs mostly disseminated or as veinlets both within Precambrian gneisses, especially along their contacts with porphyry intrusions, and within intrusions (Čifliganec, 1993; Lehmann et al., 2013; Serafimovski et al., 2016a). The main ore mineral is chalcopyrite. Chalcopyrite is accompanied by variable amounts of pyrite, magnetite, hematite, cubanite, valerite and bornite. The main gangue minerals are quartz and carbonates (Figure 2A). The supergene mineralization composed of azurite, malachite, chalcocite and minor amounts of native copper locally overprints the primary mineralization (Serafimovski et al., 2016).

Carbonates from the Central ore body are characterized by $\delta^{13}C$ values between –10.8 and –3.8‰ VPDB, while their $\delta^{18}O$ values range from 14.0 to 22.7‰ VSMOW (Table 1; Serafimovski et al., 1996; Tasev, 2003). The $\delta^{13}C$ values suggest a magmatic source of CO_2 (Figure 3). The $\delta^{18}O$ values point to a significant contribution of the meteoric water (e.g., Cerling, 1984). The isotope data from the Vršnik ore body (Table 1; Strmić Palinkaš et al., 2022) revealed that different alteration zones were formed under variable magmatic water/meteoric water ratios (Figure 3). The phyllic alteration zone host carbonates with $\delta^{13}C$ and $\delta^{18}O$ values between –1.6 and –1.3‰ VPDB and between 9.1 and 12.9‰ VSMOW, respectively. The argillic alteration zone is characterized with a wider range of both $\delta^{13}C$ and $\delta^{18}O$ values, with $\delta^{13}C$ varying between –7.2 and 2.0‰ VPDB, and the $\delta^{18}O$ values in the range between 9.1 and 24.2‰ VSMOW. Carbonates from the chlorite alteration zone show a relatively limited variation in their $^{13}C/^{12}C$ ratios but a significant change in the $^{18}O/^{16}O$ ratios (Figure 3).

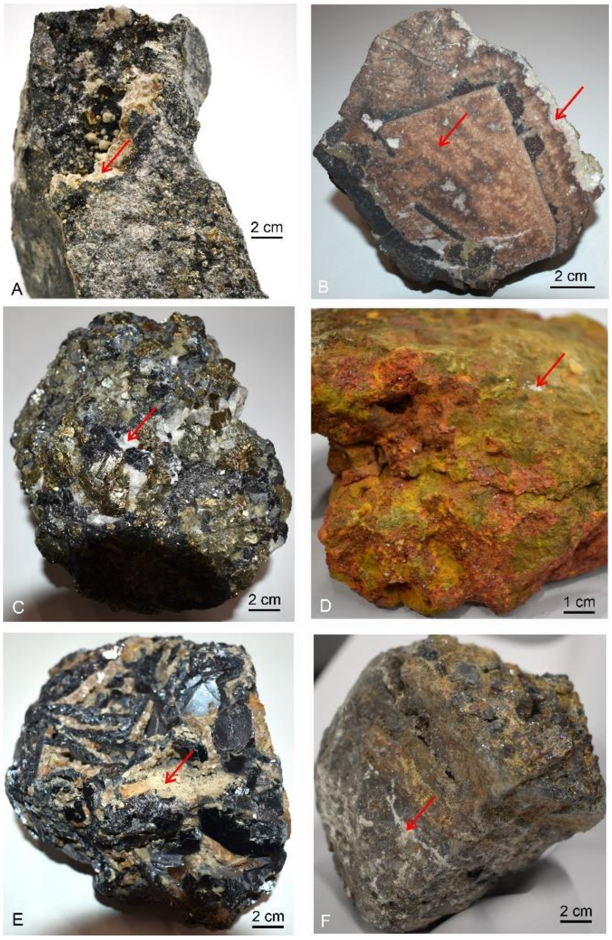

Fig. 2. A) Typical porphyry Cu mineralization from the Bučim deposit; **B)** Multiple generations of hydrothermal carbonates from the Damjan Fe proximal skarn deposit; **C)** Hydrothermal mineralization from the Sasa Pb-Zn-Ag distal skarn deposit; D) The Tl-As bearing mineralization from the Allchar Carlin-like deposit; **E)** The lead rich mineralization from the Zletovo Pb-Zn-Ag epithermal deposit; **F)** The zinc rich mineralization from the Zletovo Pb-Zn-Ag epithermal deposit.
In all images carbonates are marked with red arrows.

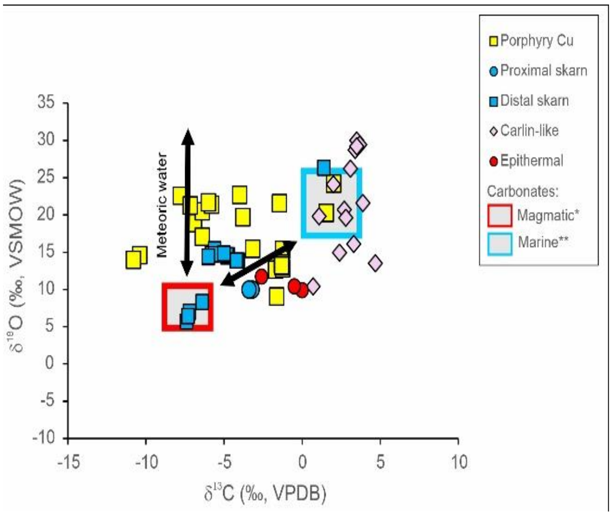

Fig. 3. A $\delta^{13}C$ vs. $\delta^{18}O$ plot illustrating the isotope signature of carbonates from the Tertiary post-collisional hydrothermal deposits in Republic of North Macedonia. Reference values for magmatic carbonates (*) and marine carbonates (**) are from Taylor et al. (1967) amd Veizer & Hoefs (1976), respectively.

Proximal skarn deposits

The Damjan Fe deposit represents an example of proximal skarn mineralization. The deposit is located in a close vicinity of the Bučim porphyry Cu deposit (Figure 1) and has been considered as a product of the same magmatic event (Lehmann et al., 2013). The mineralization is hosted by a Paleogene flysch sequence that has been penetrated by at least two generations of andesites. The older generation of andesites is characterized by a coarse-grain texture and has been subjected to extensive hydrothermal alterations. In contrast, the younger generation appears more fresh and shows a fine-grain porphyritic texture (Serafimovski, 1982; Serafimovski et al., 1997).

The mineralization has mostly an exoskarn character, with endoskarns present only locally. Magnetite and hematite are the main ore minerals and they are associated with traces of pyrite and chalcopyrite. The gangue mineral assemblage is complex and consist of silicate minerals, such as garnets, pyroxenes, chlorites, epidote, accompanied by quartz and abundant carbonates (Figure 2B; Serafimovski, 1982).

The $\delta^{13}C$ values of the gangue carbonates from the Damjan skarn deposit ranges between –3.4 and 0.4‰ VPDB, while the $\delta^{18}O$ values spans from 10.0 to 20.3‰ VSMOW (Table 1; Dolenec et al., 2015; Kiš, 2015). The $\delta^{13}C$ vs. $\delta^{18}O$ correlation shows a mixing trend between magmatically sourced CO_2 and marine carbonates (Figure 3). This type of isotope signature in gangue carbonates has been documented in skarn deposits globally (e.g., Chiaradia, 2003; Strmić Palinkaš et al.; 2016; Zahedi et al.; 2023).

Distal skarn deposits

The Sasa Pb-Zn-Ag skarn deposit, located within the Serbo-Macedonian massif (Figure 1), is a classic example of distal skarn mineralization. The deposit is hosted by a metamorphosed volcano-sedimentary complex composed of a Paleozoic marbles and quartz–graphite schists. The mineralization shows spatial and temporal relationships with the Tertiary calc-alkaline magmatism (Janković et al., 1995) mostly of a trachytic to trachydacitic composition and the K/Ar age is between 31 Ma and 24 Ma (Tasev et al., 2005).

The main ore minerals are Ag-bearing galena and sphalerite, and they are accompanied with variable amounts of pyrite, pyrrhotite and chalcopyrite. The gangue mineralogy is represented by prograde and retrograde assemblages. The prograde assemblages predominantly consist of anhydrous Ca-Fe-Mn-silicate minerals such as pyroxenes and pyroxenoids. The retrograde assemblages contain amphiboles, epidote, chlorites, ilvaite, quartz, and carbonates (Figure 2C; Peltekovski, 2012; Šijakova-Ivanova et al., 2012).

The isotope composition of different generations of carbonates from the Sasa deposit are published by Strmić Palinkaš et al. (2018a) and listed in Table 1. The $\delta^{13}C$ and $\delta^{18}O$ values obtained from the barren host marble ($\delta^{13}C$ = 1.4‰ VPDB; $\delta^{18}O$ = 26.3‰ VSMOW) reflect a marine origin of its protolith (Figure 3). Calcite isolated from the retrograde skarn mineral assemblages exhibits $\delta^{13}C$ values in a narrow range between –7.4‰ and –7.2‰ VPDB, and their $\delta^{18}O$ values span from 5.7‰ to 7.0‰ VSMOW (Table 1). Such stable signature points to a significant contribution of magmatic CO_2 during the retrograde stage of the Sasa deposit (Strmić Palinkaš et al., 2018a). In contrast, syn-ore and post-ore hydrothermal calcite has mostly overlapping $\delta^{13}C$ and $\delta^{18}O$ values in the range between –6.4‰ and –4.1‰ VPDB and 13.9‰ and 15.4‰ VSMOW, respectively, revealing a diminishing influence of magmatic CO_2 and more significant contribution of the host cipollino marble during the syn-ore and the post-ore stages of this deposit (Figure 3; Strmić Palinkaš et al., 2018a).

Table 1

Isotope composition of carbonate minerals from post-collision related hydrothermal deposits in North Macedonia

Locality	Sample	Mineralogy	δ13C (‰, VPDB)[1]	δ18O (‰, VSMOW)[2]	Note	Reference
Porphyry Cu deposits						
Bučim , Central ore body	B1	Calcite	–10.4	14.6		Serafimovski et al., 1996
Bučim , Central ore body	B2	Calcite	–7.8	22.6		Serafimovski et al., 1996
Bučim , Central ore body	B3	Calcite	–6.9	18.9		Serafimovski et al., 1996
Bučim , Central ore body	B4	Calcite	–6.4	20.5		Serafimovski et al., 1996
Bučim , Central ore body	B5	Calcite	–5.8	21.4		Serafimovski et al., 1996
Bučim , Central ore body	B6	Calcite	–3.8	19.7		Serafimovski et al., 1996
Bučim , Central ore body	B7	Calcite	–4.0	22.7		Serafimovski et al., 1996
Bučim , Central ore body	B8	Calcite	–6.4	17.1		Serafimovski et al., 1996
Bučim , Central ore body	B9	Calcite	–10.8	14.0		Serafimovski et al., 1996
Bučim , Central ore body	B10	Calcite	–6.0	21.7		Tasev, 2003
Bučim , Vršnik ore body	VS7	Calcite	–1.7	12.7	potassic→chlorite	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS14	Siderite	–1.5	21.6	potassic→chlorite	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS19	Siderite	2.0	24.2	potassic→argillic	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS12	Calcite	–1.3	15.3	potassic→chlorite	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS6	Calcite	–1.6	9.1	phyllic	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS7	Calcite	–1.3	13.5	potassic→chlorite	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS1	Calcite	–1.3	12.9	phyllic	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS19	Siderite	–1.3	13.2	potassic→argillic	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS19	Siderite	1.5	20.3	potassic→argillic	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS14	Siderite	–7.2	21.3	potassic→chlorite	Strmić Palinkaš et al., 2022
Bučim , Vršnik ore body	VS12	Siderite	–3.2	15.5	potassic→chlorite	Strmić Palinkaš et al., 2022
Proximal skarn deposits						
Damjan Fe skarn	D-7	Calcite	–3.2	10.0		Kiš, 2015
Damjan Fe skarn	D-30b	Calcite	–3.4	10.0		Kiš, 2015
Distal skarn deposits						
Sasa Pb-Zn-Ag skarn	Sa-1-C	Calcite	1.4	26.3	Cippolino marble	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-101	Calcite	–7.4	5.7	Altered skarn	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-101-1	Calcite	–7.3	6.4	Altered skarn	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-102	Calcite	–7.2	7.0	Altered skarn	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-103	Calcite	–7.3	6.4	Altered skarn	Strmić Palinkaš et al., 2018a

Locality	Sample	Mineralogy	$\delta^{13}C$ (‰, VPDB)[1]	$\delta^{18}O$ (‰, VSMOW)[2]	Note	Reference
Sasa Pb-Zn-Ag skarn	Sa-15	Calcite	–4.7	14.6	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-15-2	Calcite	–4.8	14.4	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-15-3	Calcite	–4.8	14.6	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-16-C	Calcite	–5.1	14.7	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-17	Calcite	–6.0	14.3	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-17-0	Calcite	–5.6	15.4	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-17-1	Calcite	–5.8	14.7	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-17-M1	Calcite	–4.1	13.9	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-17-M2	Calcite	–4.2	13.9	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-17-C	Calcite	–5.6	14.7	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-18-O	Calcite	–6.4	8.3	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-19	Calcite	–6.0	14.4	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Sasa Pb-Zn-Ag skarn	Sa-19-C	Calcite	–5.0	14.8	Hydrothermal ore	Strmić Palinkaš et al., 2018a
Carlin-like type deposits						
Allchar	1	Calcite	2.4	14.9		Volkov et al., 2006
Allchar	2	Calcite	3.4	28.7		Volkov et al., 2006
Allchar	3	Calcite	2.7	20.7		Volkov et al., 2006
Allchar	4	Calcite	3.1	26.2		Volkov et al., 2006
Allchar	5	Calcite	3.9	21.6		Volkov et al., 2006
Allchar	6	Calcite	2.0	24.1		Volkov et al., 2006
Allchar	ADP-232	Dolomite	3.5	30.0	Tertiary dolomite, barren	Strmić Palinkaš et al., 2018b
Allchar	100	Dolomite	3.7	29.4	Tertiary dolomite, barren	Strmić Palinkaš et al., 2018b
Allchar	Ad-823	Dolomite	3.5	29.2	Tertiary dolomite, barren	Strmić Palinkaš et al., 2018b
Allchar	Tl-Adit	Dolomite	1.1	19.8	Mineralized Tertiary dolomite	Strmić Palinkaš et al., 2018b
Allchar	TR-ADP-49	Calcite	2.8	19.6	Triassic marble, barren	Strmić Palinkaš et al., 2018b
Allchar	Adit I	Calcite	3.3	16.1	Mineralized Triassic marble	Strmić Palinkaš et al., 2018b
Allchar	Adit River	Calcite	4.7	13.5	Late hydrothermal calcite	Strmić Palinkaš et al., 2018b
Allchar	S2	Calcite	0.7	10.4	Late hydrothermal calcite	Strmić Palinkaš et al., 2018b
Epithermal deposits						
Zletovo Pb-Zn-Ag deposit	13 M-73	Siderite	0.0	9.9	Vein 12a	Mudrinić & Serafimovski, 1992
Zletovo Pb-Zn-Ag deposit	M-73	Siderite	–0.5	10.4	Vein 12	Mudrinić & Serafimovski, 1992
Zletovo Pb-Zn-Ag deposit	M-21	Calcite	–2.6	11.7	Vein d	Mudrinić & Serafimovski, 1992

[1]VPDB – Vienna Pee Dee Belemnite, [2]VSMOW – Vienna Standard Mean Ocean Water

Carlin-like deposits

The Allchar Au-As-Sb-Tl deposit is located in the Vardar zone in the southernmost part of North Macedonia. Based on its geological and geochemical features, this deposit has been classified as a Carlin-like type of mineralization (Figure 1; Strmić Palinkaš et al., 2018b). The deposit is hosted by a Mesozoic metasedimentary complex and unconformable Tertiary volcanic and carbonate rocks. The metasedimentary complex consists of Triassic marble, dolomite, and schists, and has been subjected to the regional greenschist facies metamorphism (Percival & Radtke, 1994). The K/Ar, $^{40}Ar/^{39}Ar$, and fission track ages suggest that hydrothermal activity was contemporaneous with Pliocene calc-alkaline to shoshonitic volcanism (~5 Ma; Kolios et al., 1980; Jakupi et al., 1982; Boev et al., 1988; Troesh & Frantz,1992; Strmić Palinkaš et al., 2010).

The Allchar mineralization and associated hydrothermal alterations show a spatial zonation. The southernmost portion of the deposit shows a significant enrichment in gold accompanied by deposition of amorphous silica. The central part of the deposit is marked by abundant stibnite-bearing jasperoids. The northernmost part of the deposit is characterized by As- and Tl-bearing sulfide mineralization associated by carbonates and barite (Figure 2D). Pyrite is a common mineral throughout the entire deposit (Boev, 1988; Percival & Radtke, 1994; Strmić Palinkaš et al., 2010; Strmić Palinkaš et al., 2018b; Vaněk et al., 2024).

The isotope composition of barren Triassic marble reflects the $^{13}C/^{12}C$ ratios typical for Phanerozoic marine carbonates (Veizer and Hoefs, 1976), and their $^{18}O/^{16}O$ ratios are consistent with values published for Triassic marine carbonates globally (Claypool et al., 1980). These data indicate that the original marine carbonate isotope signature has not been affected during the regional metamorphic event. The $\delta^{13}C$ values of barren Tertiary dolomite overlap with those recorded for Triassic marble lithologies in the Allchar area, but their $\delta^{18}O$ values are higher (Table 1). The isotope composition of hydrothermal carbonates reveals a magmatic CO_2 input as well as a significant contribution of host carbonate lithologies during the carbonate rocks/hydrothermal fluids interaction (Figure 3).

Epithermal deposits

The Zletovo Pb-Zn-Ag deposit is located within the Tertiary Kratovo–Zletovo volcanic terrain that covers the contact between the Vardar zone and Serbo-Macedonian massif (Figure 1). The volcanic terrain is composed of andesites, dacites, dacitic ignimbrites, and volcanic tuffs (Serafimovski, 1990; Serafmovski, 1999; Tasev, 2003).

The mineralization occurs in form of steeply dipping veins, locally associated with minor amounts of mineralized stockworks and disseminated mineralization. The main ore minerals are sphalerite and Ag-bearing galena, while quartz and carbonates represent the prevailing gangue minerals (Figures 2E and 2F). The Zletovo deposit represents a deeper portion of an epithermal system, and its upper extension can be traced towards the Plavica Au-Cu epithermal deposit (Alderton & Serafimovski, 2007; Serafimovski et al., 2016b; Serafimovski et al., 2022).

The $\delta^{13}C$ values of obtained on hydrothermal carbonates range between –2.6 and 0.0 ‰ VPDB, with siderite being slightly isotopically heavier than calcite. The $\delta^{18}O$ values span between 9.9 and 11.7 ‰ VSMOW (Mudrinić & Serafimovski, 1992; Table 1). This isotopic signature suggests that ore-forming fluids at the Zletovo deposit experienced a strong contribution of magmatic CO_2 (Figure 3).

CONCLUSIONS

The subaerial magmatic-hydrothermal system exposed on the territory of Republic of North Macedonia represents a natural laboratory for studies of ore-forming processes associated with post-collisional magmatism. The isotope signature obtained from the studied magmatic-hydrothermal deposits reflects that an interplay of magmatic volatiles, sediment (marine) carbonates and meteoric water controls $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in gangue carbonates phases (Figure 3).

The porphyry Cu mineralization shows that alteration zones typical for this type of mineralization were formed under variable magmatic water/meteoric water ratios. The proximal skarn mineralization reveals a mixing trend between magmatically sourced CO_2 and marine carbonates. This similar trend has been documented for the distal skarns, but carbonates spatially associated with the retrograde skarn minerals point to a significant contribution of magmatic CO_2. In contrast, syn-ore and post-ore hydrothermal calcite reflects a diminishing influence of magmatic CO_2 and more significant contribution of host lithologies, sourced from the marine carbonate protoliths. Similar to the skarn deposits, the Carlin-like mineralization is characterized by a mixing trend between magmatic CO_2 and CO_2 sourced from the host carbonate lithologies. The Pb-Zn-Ag mineralization found in the deep portion of the epithermal system records a strong contribution of magmatic CO_2 (Figure 3).

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Р е з и м е

ЈАГЛЕРОДНИ И КИСЛОРОДНИ ИЗОТОПНИ ПОТПИСИ НА ХИДРОТЕРМАЛНИТЕ РУДНИ ЛЕЖИШТА ВО ПОСТ-КОЛИЗИОНИТЕ МАГМАТСКОХИДРОТЕРМАЛНИ СИСТЕМИ: ПРЕГЛЕД ОД СЕВЕРНА МАКЕДОНИЈА

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Откриениот субаерски магматскохидротермален систем на територијата на Република Северна Македонија претставува природна лабораторија за проучување на процесите на формирање руди поврзани со постколизиониот магматизам. Во овој дел од Балканскиот Полуостров неотектониката ги издигнала и ги изложила терцијарните постколизиони рудни наоѓалишта формирани на различни нивоа во Земјината кора, вклучувајќи ги длабоките порфирски наоѓалишта на бакар, проксималните и дистални скарновски наоаѓалишта и наоѓалиштата од Карлински тип. Локално се зачувани и епитермалните наоѓалишта. Овој труд ги сумира и дискутира претходно објавените податоци за изотопи на јаглерод и кислород, добиени од јаловите карбонати од главните рудни наоѓалишта во Северна Македонија.