Metallogenic Model of the Trepča Pb-Zn-Ag Skarn Deposit, Kosovo: Evidence from Fluid Inclusions, Rare Earth Elements, and Stable Isotope Data

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Abstract

The Trepča Pb-Zn-Ag skarn deposit (29 Mt of ore at 3.45% Pb, 2.30% Zn, and 80 g/t Ag) is located in the Kopanik block of the western Vardar zone, Kosovo. The mineralization, hosted by recrystallized limestone of Upper Triassic age, was structurally and lithologically controlled. Ore deposition is spatially and temporally related with the postcollisional magmatism of Oligocene age (23–26 Ma). The deposit was formed during two distinct mineralization stages: an early prograde closed-system and a later retrograde open-system stage.

The prograde mineralization consisting mainly of pyroxenes (Hd54–100Jo0–45Di0–45) resulted from the interaction of magmatic fluids associated with Oligocene (23–26 Ma) postcollisional magmatism. Whereas there is no direct contact between magmatic rocks and the mineralization, the deposit is classified as a distal Pb-Zn-Ag skarn. Abundant pyroxene reflects low oxygen fugacity (<10−31 bar) and anhydrous environment. Fluid inclusion data and mineral assemblage limit the prograde stage within a temperature range between 390° and 475°C. Formation pressure is estimated below 900 bars. Isotopic composition of aqueous fluid inclusions hosted by hedenbergite (δD = −108 to −130‰; δ18O = 7.5–8.0‰), Mn-enriched mineralogy and high REE content of the host carbonates at the contact with the skarn mineralization suggest that a magmatic fluid was modified during its infiltration through the country rocks.

The retrograde mineral assemblage comprises ilvaite, magnetite, arsenopyrite, pyrrhotite, marcasite, pyrite, quartz, and various carbonates. Increases in oxygen and sulfur fugacities, as well as a hydrous character of mineralization, require an open-system model. The opening of the system is related to phreatomagmatic explosion and formation of the breccia. Arsenopyrite geothermometer limits the retrograde stage within the temperature range between 350° and 380°C and sulfur fugacity between 10−8.8 and 10−7.2 bars.

The principal ore minerals, galena, sphalerite, pyrite, and minor chalcopyrite, were deposited from a moderately saline Ca-Na chloride fluid at around 350°C. According to the isotopic composition of fluid inclusions hosted by sphalerite (δD = −55 to −74‰; δ18O = −9.6 to −13.6‰), the fluid responsible for ore deposition was dominantly meteoric in origin. The δ34S values of the sulfides spanning between −5.5 and +10‰ point to a magmatic origin of sulfur. Ore deposition appears to have been largely contemporaneous with the retrograde stage of the skarn development.

Postore stage accompanied the precipitation of significant amount of carbonates including the travertine deposits at the deposit surface. Mineralogical composition of travertine varies from calcite to siderite and all carbonates contain significant amounts of Mn. Decreased formation temperature and depletion in the REE content point to an influence of pH-neutralized cold ground water and dying magmatic system.

Introduction

The Trepča Pb-Zn-Ag skarn deposit (42.9° N, 20.9° E) is located near the town of Kosovska Mitrovica, about 40 km northwest from Priština, Kosovo (Fig. 1). The deposit is hosted by the Kopanik block of the western Vardar zone in the easternmost part of the Dinarides. In addition to the Trepča deposit, the Vardar zone comprises numerous economically significant deposits of lead-zinc-silver, antimony, bismuth, and molybdenum, as well as smaller copper, iron, tin, tungsten, and gold deposits. The Pb-Zn-Ag mineral deposits extend northward from Kosovo and southern Serbia (Trepča mineral belt) through western Serbia (Kićevak, Sastavci, Rudnik, and Veliki Majdan) to easternmost Bosnia (Srebrenica) (Fig. 1).

The Trepča mineral belt hosts several skarn, hydrothermal replacement, and vein-type Pb-Zn-Ag deposits (Janković, 1995). The most productive mines are Trepča (Stari Trg), Crnac, Belo Brdo, Kišnica, Avajlija, and Novo Brdo with total past production of 60.5 million metric tons (Mt) of ore at 8% Pb + Zn and more than 4,500 t of Ag. Their formation is related to Tertiary postcollisional magmatism in the western Vardar zone (Čvetković et al., 2004; Boroević Šoštarić et al., 2011).

Mining in the area began during the Middle Ages, while industrial production started with the formation of Trepča Mines Limited in 1927. Production was maintained during the Second World War, and then continued until 1999 under state ownership. Between 2000 and 2008 the Trepča deposit was administered by the United Nations Mission in Kosovo (UNMIK). The deposit exploitation started again in 2008.
under the administration of Privatisation Agency of Kosovo (PAK). With current reserves of 29 Mt of ore at 3.45% Pb, 2.30% Zn, and 80 g/t Ag (ITT/UNMIK 2001 report), together with the past production of approximately 34 Mt of ore, the deposit represents an important source of metals in the southeastern part of Europe.

Although the Trepcˇa deposit is described as a classic example of the Pb-Zn-Ag skarn mineralization (e.g., Schumacher, 1950, 1954; Smirnov, 1976; Guilbert and Park, 2007), neither geochemical nor stable isotope data from the deposit have been published. Recent papers on the deposit are represented by reviews (e.g., Féraud et al., 2007) or they are concerned with the metallogenic belt overall (e.g., Janković, 1995, 1997).

Studies of distal skarn deposits elsewhere have confirmed the magmatic origin of fluids involved in the early prograde anhydrous stage of skarn-forming metasomatism (e.g., Einaudi et al., 1981; Layne et al., 1991; Bowman, 1998; Meinert et al., 2003), whereas the source of fluids responsible for the later retrograde hydrous alterations is still under discussion. Several studies have found that formation of both anhydrous and hydrous assemblages involved only magmatic fluids (Meinert et al., 2003; Williams-Jones et al., 2010). By contrast, according to numerous authors (e.g., Einaudi et al., 1981; Bowman, 1998; Yücel Öztürk et al., 2008), meteoric water plays an increasing role toward the end of deposition history.

The present study documents the mineral chemistry, fluid inclusion and stable isotope data obtained on the skarn and hydrothermal mineral assemblages from the Trepcˇa deposit. The aims of the paper are to (1) constrain the physiochemical conditions during the prograde and retrograde (hydrothermal) stage of the mineralization; (2) determine the nature, origin, and evolution of the mineralizing fluids; and (3) establish the metallogenic model of the deposit.

**Samples and Analytical Methods**

A total of 62 handpicked rock samples were collected from existing underground exposures and from surface of the Trepcˇa deposit. Samples are subdivided into two major groups: (I) country rocks (limestone and schist), and (II) mineralized samples (skarn and hydrothermal mineralization). Paragenetic relationships were studied in thin sections by transmitted polarized light microscopy. Ore minerals were examined in polished thick sections by reflected light microscopy. X-ray powder diffraction (XRD) was conducted at the University of Zagreb on a Philips PW 3040/60 X’Pert PRO powder diffractometer (45 kV, 40 μA), with CuKα-monochromatized radiation (λ = 1.54056 Å) and θ-θ geometry. The area between 4 and 63° 2θ, with 0.02° steps, was measured with a 0.5° primary beam divergence. Compound identifications were based on a computer program X’Pert high score 1.0B and literature data. Elemental analyses of sulfides were obtained through electron microprobe at the Masarik University, Brno, by means of Camebax S100-type equipment. Natural mineral standards were used for calibration and the following operating conditions were applied: 3 to 40 μm beam, accelerating voltage 20 kV, current 10 nA, and counting time 200 s. Bulk chemical
compositions of 15 selected country rocks and gangue carbonate samples were prepared in an agate ball mill and analyzed at Acme Analytical Laboratories (Vancouver, Canada) after lithium metaborate or tetraborate fusion using inductively coupled plasma (ICP) for major elements and inductively coupled plasma-mass spectrometry (ICP-MS) for trace elements.

Sulfur isotope analyses were carried out at the University of Lausanne. Measurements were performed by an on-line EAA-IRMS system consisting of a Carlo Erba 1108 elemental analyzer (EA) coupled with a continuous helium flow interface to the Thermoquest/Finnigan Mat Delta S IRMS. The EA oxidizes all sample compounds under a stream of helium and oxygen by flash combustion in a single oxidation-reduction quartz tube filled with oxidizing (tungsten trioxide) and reducing (elemental copper) agents at 1,030°C. The sulfur isotope values are reported in the typical δ notation relative to V-CDT standard. The reproducibility, assessed by replicate analyses of the laboratory standard (natural pyrite, 6.1‰; synthetic mercury sulfide, 15.5‰; barium sulfate, 12.5‰; δ34S) was better than 0.2‰. Oxygen isotope analyses of quartz and silicates were conducted with a Micromass-Isoprine, gas-source mass spectrometer at the Université Jean Monnet, Saint Etienne. A laser fluorination system, described by Harris et al. (2000) was used. Oxygen was produced by heating grains weighing regularly 2 to 4 mg with a 40W CO2 laser in an atmosphere of BrF5, which was then converted to CO2 by reaction with graphite, and was cryogenically purified. An internal standard (MONGT, δ18O = 5.55‰) was analyzed to adapt the data to the standard mean ocean water (SMOW) scale. Rapid heating by defocused beam (Spicuzza et al., 1998) was used to minimize sample loss of material during the reaction and yielding an average 92% of the expected amount for quartz. The missing material in all cases appeared to be ejected during the initial heating before reaction with BrF5.

Microthermometric measurements of fluid inclusions within transparent minerals were performed at the University of Zagreb. Double polished, ~0.5-mm-thick, transparent mineral wafers were used. Measurements were carried out on a Linkam THMS 600 stage mounted on an Olympus BX 51 microscope using 10× and 50× Olympus long-working distance objectives for visible light. Two synthetic fluid inclusion standards (SYN FLINC; pure H2O and mixed H2O-CO2) were used to calibrate the equipment. The precision of the system was ±4‰. Any CO2 present was removed cryogenically adapted from Coleman et al. (1982), and precision is estimated at ±4‰. Any CO2 present was removed cryogenically and the carbon isotope composition was determined.

**Geologic Setting**

The Vardar zone extends throughout the central part of the Balkan Peninsula. It is bounded by the Dinarides and the Hel- lenides on the west and the Serbo-Macedonian Massif on the east (Fig. 1). The Vardar zone is regarded as a main suture zone between the Adriatic and the Euroasian plate, which preserves tectonic units of both oceanic and continental origin (Dimitrijević, 1997, 2001; Karamata et al., 2000; Zelić et al., 2010). Dimitrijević (1995) divided the Vardar zone into three subzones: (1) the external Vardar subzone in the west comprises the Srem, the Jadar, and the Kopaonik blocks; (2) the central Vardar subzone; and (3) the internal Vardar subzone in the east.

The Kopaonik block is composed of metamorphosed rocks of Paleozoic and Triassic age covered by an ophiolite complex (Fig. 1). The ophiolitic mélangé represents a mixture of clasts and olistoliths of various sedimentary (limestone, chert, sandstone, well-developed turbidite blocks) and magmatic rocks (diabase, gabbro, ultramafites) within a sandy to silty-clay matrix. The weakly metamorphosed mélangé of Jurassic age, with predominantly basaltic fragments, is developed at the eastern margin of Kopaonik block. By contrast, the Jurassic-Cretaceous mélangé at the western margin of the block is characterized by a predominance of sandstones over other sedimentary and magmatic rocks (Sudar and Kovacs, 2006, and references therein). During the Oligocene-Miocene, the Kopaonik block was the location of considerable volcanic activity characterized by numerous lava flows and large masses of volcaniclastic rocks. The magmatic rocks are represented mostly by trachytes (with K/Ar and Ar/Ar ages of 23 to 26 Ma; Strmić Palinkaš, 2009), quartz-latites, andesites, and pyroclastic deposits (Janković, 1995). The volcanic activity was contemporaneous with the deposition of lacustrine sediments (e.g., Marović et al., 1999).

The structural and lithological control on mineralization processes is documented by the cross section through the Trepča deposit (Fig. 2A). The principal mineralized host rock is recrystallized Upper Triassic limestone with a developed karst system. The size of calcite grains varies from several millimeters at places spatially distal to the mineralization up to several centimeters at contact with the orebodies. The host limestone is placed within the core of an anticline and roofed by schists (Fig. 2A). The limestone-schist contact is marked by the presence of a phreatomagmatic breccia pipe (Schmacher, 1950, 1954; Féraud et al., 2007; Strmić Palinkaš et al., 2007; Strmić Palinkaš, 2009). The pipe consists of a hydrothermally altered trachyte core (with K/Ar and Ar/Ar ages of 23–24 Ma; Strmić Palinkaš, 2009), enveloped by a breccia mantle (Fig. 2). Although the breccia does not host the ore mineralization, we argue that its formation was a principal trigger for the ore deposition. The breccia is described in more detail in the following section.

Travertine deposits locally occur as a top layer capping the deposit and marking the preserved paleosurface. According to the scanning electron microscopy studies associated with EDX analyses travertine is composed of Ca-Fe carbonates (calcite, ankerite, siderite) significantly enriched in Mn. Fine-grained
galena scattered within carbonate matrix suggest that the deposition of travertine was associated with the ore-forming processes (Strmić Palinkaš, 2009).

**Phreatomagmatic Breccia**

The breccia at the TrepcŽa deposit displays features common to maar-diatreme breccias generated by phreatomagmatic processes (Féraud et al., 2007; Strmić Palinkaš et al., 2007; Strmić Palinkaš, 2009). An inverted cone shape, the vertical extension up to 800 m and up to 150-m diameter (Fig. 2B) correspond well to the shape and dimensions reported for phreatomagmatic breccias elsewhere (e.g., Sillitoe, 1985; Lorenz, 1987; Tamas and Milei, 2002; Lorenz and Kurszlaukis, 2007; Davies et al., 2008). The upper part of the diatreme (an underground segment of the phreatomagmatic breccia; Lorenz, 1973) is characterized by the presence of the hydrothermally altered trachyte dike emplaced within the pipe core (Figs. 2A, 3A). Despite the alteration processes the dike has a preserved porphyritic texture (Fig. 3B). According to the XRD data, the white fine-grained matrix comprises

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Fig. 2. A. Cross section along an approximately northwest-southeast transect, showing the geometry of the TrepcŽa Pb-Zn-Ag skarn deposit. B. Detail surface geologic map of the TrepcŽa deposit (after Schumacher, 1950).
Fig. 3. Photographs and photomicrographs showing distinctive features of the phreatomagmatic breccia at the Trepcˇa deposit. A. Altered trachyte composes core of the phreatomagmatic breccias. B. White fine-grained matrix incorporates bluish-colored remains of sanidine phenocrysts. C. Recrystallized limestone fragment with reaction rim composed of fine-grained Mn-enriched siderite and pyrite. D. Close view of dickite clusters within the breccia fragments. E. Fibroradial arsenopyrite aggregate accompanied with magnetite. F. Photomicrograph, plane-polarized light, represents polished thin section composed of magnetite replaced by arsenopyrite. Opaque minerals are surrounded by carbonate grains. G. Close view of the fragment composed of magnetite core and pyritic rim.
muscovite, quartz, and K-feldspars. The sanidine phenocrysts are partly altered to muscovite and quartz. The altered trachyte dikes, surrounded by the polymict breccia mantle, confirm the phreatomagmatic activity resulting from an interaction of magma with ground water.

Angular to well-rounded fragments ranging in size from a few centimeters to several meters occupy up to 90 vol % of the breccia. Fragments of the country rocks, limestones, and schist, together with magnetite- and sulfide-bearing fragments represent the principal types of clasts. Trachyte (juvenile) fragments occur as well.

Recrystallized limestone fragments usually have fresh white core and brownish reaction rim (Fig. 3C). The core consists of polysynthetically twinned calcite crystals ranging in size up to several centimeters. The reaction rim is composed of fine-grained Mn-enriched siderite and pyrite. Occasionally limestone fragments are intensively replaced by siderite enriched in Ca and Mn and impregnated by pyrite associated with microcrystalline quartz (Strmić Palinkaš et al., 2009a).

There are several types of magnetite- and sulfide-bearing fragments:

1. Fibroradial arsenopyrite aggregates accompanied with magnetite are found to be embedded within recrystallized
limestone fragments (Fig. 3E). As documented in Figure 3F, arsenopyrite postdates magnetite.

2. Fragments composed of magnetite core and pyrite rim (Fig. 3G) are frequent at the surface of the breccia pipe. Magnetite forms fibroradial to spherulitic aggregates. Small masses of pyrite are emplaced between magnetite grains (Fig. 3H). Usually pyrite is fractured, crushed, and altered by garnets (Fig. 3I). According to the microprobe data, garnets are andradite in composition. The fragment rim is characterized by predominance of fresh pyrite accompanied with carbonates and quartz (Fig. 3J).

3. The pyrite-pyrrhotite fragments predominantly comprise fractured pyrite and pyrrhotite (Fig. 3K). The space between grains is filled with fine-grained carbonates and quartz.

The breccia matrix comprises fine-grained rock flour. The contact between the breccia and the wall rocks is sharp but locally cut by lateral fractures (Fig. 3L) with rock flour infilling (“milled matrix fluidized breccia”) or with angular fragments (“jigsaw-puzzle breccia”). According to Corbett and Leach (1998) milled matrix fluidized breccia represents non-venting branches of the main phreatomagmatic body. The partly preserved maar structure (a surface expression of phreatomagmatic breccia; Lorenz, 1973) comprises tuffaceous (Schumacher, 1950) and pyroclastic deposits with common remnants of plant leaves and roots (Fig. 3M).

**Paragenesis of Skarn and Ore (Hydrothermal) Minerals**

The principal skarn minerals in the Trepcˇa deposit are Ca-Fe-Mn silicates, including pyroxenes, ilvaite, and minor garnets. Accessory minerals are Ca-Fe-Mn ± Mg carbonates and quartz. Paragenetic studies based on macro- and microtextures show that the skarn assemblage from the Trepcˇa deposit occurred in several stages, similar to other skarns (Meinert, 1992; Kwak, 1994; Newberry, 1998; Meinert et al., 2005; Yücel Öztürk and Helvaci, 2008).

Figure 4A displays the complete skarn sequence with a characteristic zonal mineral pattern. The prograde stage has an anhydrous character with hedenbergitic pyroxenes as the major mineral (Fig. 4B). Prismatic, 0.5 to several centimeters long, crystals usually form fibroradial to spherulitic aggregates. Ca-Fe garnets (andradite) occur rarely, exclusively in the uppermost levels of the deposit. The retrograde stage has a predominantly hydrous nature with ilvaite as an important product. Ilvaite occurs in the form of black prismatic, up to 10 cm long, crystals with a vitreous luster (Fig. 4C). The distinctly colored zones with fibroradial texture (Fig. 4A) comprise mixtures of carbonates and quartz (yellow and white zones), while gray zones contain pyrite as well.

The hydrothermal ore minerals commonly overprint the pyroxene-rich calcic skarn, although skarn mineralization free of the ore assemblage (Fig. 5A), as well as the ore mineralization without skarn precursor (Fig. 5B), is found. The ore paragenesis comprises oxide and sulfide minerals. Magnetite mostly occurs in the form of pseudomorphs after hedenbergite (Fig. 4B). Pyrrhotite clusters sporadically replace pyroxenes (Fig. 4A, C), and locally pyroxenes are completely converted into pyrrhotite and/or pyrite (Fig. 6). The primary fibroradial texture is preserved, and sulfides are accompanied by a mixture of carbonates and quartz.

Black-colored sphalerite, galena, and pyrite are the most abundant sulfide minerals (Fig. 7A). Pyrite is the earliest mineral with respect to galena and sphalerite (Fig. 7A) but minor pyrite occurs over the whole period of sulfide deposition (Fig. 7B). Galena precedes sphalerite (Fig. 7B, C). Locally pyrite is replaced by chalcopyrite (Fig. 7D). Sphalerite contains tiny chalcopyrite inclusions (Fig. 7E). Marcasite (Fig. 7F), arsenopyrite (Fig. 7G), pyrrhotite, and colloform pyrite have been found only in the ore assemblages with a skarn precursor (Fig. 7H). The paragenetic sequence of the Trepcˇa deposit is summarized in Figure 8.

**Compositions of Country Rocks and Gangue Carbonates**

**Major elements**

The bulk compositions of the country rocks (schist, barren recrystallized carbonates and host carbonates in contact with the mineralization) and gangue carbonates are given in Table 1. The barren recrystallized limestones are characterized with high CaCO3 content and negligible concentrations of other
divalent cations (Table 2). The host carbonates in contact with the mineralization, especially those in contact with the skarn-type mineralization, are enriched in Mn. Synore gangue carbonates, beside Ca and Mn, comprise Mg and Fe components as well. Concentration of Fe, Mn, and Mg decreased in the postore stage of mineralization. Consequently the postore gangue carbonates incorporate up to 95 mol % of CaCO₃.

Rare earth elements

The REE contents (Table 3) are normalized to post-Archean Australian shale (PAAS, values from Nance and Taylor, 1976). The schist is characterized by high REE contents and a flat REE pattern with a weak negative EuN anomaly (Fig. 9A).

The barren recrystallized limestones have low REE contents and show negative CeN anomaly (Fig. 9A) typical for marine carbonates (Elderfield and Greaves, 1982; Hu et al., 1988). The REE distribution patterns indicate that the recrystallization did not significantly affect the primary REE distribution of sedimentary precursor (Triassic marine limestone) and point to an isochemical character of the recrystallization processes.

Recrystallized limestone in contact with both skarn and ore mineralization, together with all analyzed syn- and postore carbonates has upward convex REE pattern with weak negative CeN and a marked positive EuN anomaly (Fig. 9A, B). The REE characteristics of hydrothermal carbonates are controlled by the composition of the mineralizing fluids and physicochemical conditions during precipitation (e.g., Bau and Möller, 1992). The positive Eu anomaly reflects the contribution of high-temperature acid fluids (T >230°C, pH <5; Michard, 1989). The major difference between different generations of the gangue carbonates appears to be their total REE abundance (Fig. 9B). The synore carbonates display a
clear increase in total REE content, whereas the postore carbonates are characterized by low REE concentrations.

**Compositions of Skarn and Ore Minerals**

The mean chemical composition of pyroxenes associated with the skarn mineralization has been analyzed by microprobe and summarized in Table 4. Figure 10 presents the ternary proportion of their diopside-johannsenite-hedenbergite components. Hedenbergite, with 54 to 100 mol %, represents the principal pyroxene constituent. Diopside and johannsenite contents vary up to 45 and 10 mol %, respectively. The manganese-rich mineralogy is typical for Pb-Zn skarn deposits distal from intrusions (e.g., Einaudi et al., 1981; Abrecht, 1985; Logan, 2000; Vassileva and Bonev, 2001; Vassileva et al., 2005; Canet et al., 2009).

The major ore minerals were analyzed on selected elements by microprobe (Table 5). Sphalerite is enriched in iron (up to 12 wt %), manganese (0.65 ± 0.19 wt %), and cadmium (0.23 ± 0.08 wt %). The analyses of galena revealed Bi and Ag as the most important minor elements. Pyrite carries up to 1.3 wt % arsenic. Pyrrhotite comprises 46.2 to 46.8 atom % iron. Arsenopyrite is slightly depleted in arsenic (27−31 atom %) and enriched in sulfur (36–40 atom %).

Arsenopyrite is the most refractory mineral among the common sulfides and its wide range of As/S content ratio makes it a potentially useful geochemical tool for determination of formation conditions (Kretschmar and Scott, 1976; Sharp et al., 1985; Koh et al., 1992; Choi and Youm, 2000). Considering that arsenopyrite accompanied by pyrite contains 30.8 atom % arsenic, its formation temperature is constrained between 350° and 380°C (Fig. 11A). Utilization of the log $f_{S2}$ versus temperature diagram published by Kretschmar and Scott (1976) and reexamined by Sharp et al. (1985) allows estimation of the sulfur fugacity in the range between $10^{-8.8}$ and $10^{-7.2}$ bars (Fig. 11B). Arsenopyrite with lower arsenic content (27.3 atom %) is recorded as well. Because arsenopyrite is a refractory mineral it is unlikely that changed conditions would modify composition of already deposited arsenopyrite. Rather, As-depleted arsenopyrite represents a lower temperature, younger generation of sulfides.

According to Hutchison and Scott (1981) the CuS content of sphalerite in the equilibrium with pyrite is a function of temperature. Whereas sphalerite from the Trepča deposit contains 0.015 to 0.035 mol % CuS, its formation temperature spans between 347° and 387°C and concurs to the temperature estimated by the arsenopyrite geothermometer.

**Fluid Inclusion Studies**

Fluid inclusion studies reveal several distinct temporal, compositional, and thermal populations in pre-, syn-, and postore minerals. Microthermometric investigations of skarn parageneses were focused on samples collected from Horizon X (75 m above mean sea level). Samples associated with the ore assemblages were gathered from different levels of the deposit (Horizon V, 375 m to Horizon XI, 15 m above mean sea level). Therefore it is possible to discuss temporal and spatial (horizontal and vertical) changes in physiochemical characteristics of the mineralizing fluids. Summarized microthermometric data are listed in Table 6.
Skarn paragenesis

Fluid inclusions hosted by hedenbergite reflect the physicochemical nature of the solutions involved in the prograde skarn-forming process. According to the criteria proposed by Roedder (1984) inclusions were classified as either primary or secondary in origin. Primary fluid inclusions are up to 15 μm in size, occur isolated, and have rounded shape. Secondary inclusions are usually arranged in clusters. Their size below 2 μm obstructed observation of phase transitions. At room temperature primary fluid inclusions consist of two (liquid and vapor, Fig. 12A) and seldom of three phases (liquid, vapor, and solid, Fig. 12B). The solid phase in the latter is halite. A eutectic temperature at about −52°C, for both types of primary inclusions, suggests that CaCl₂ and NaCl are dominant dissolved salts. The final ice melting temperature (T_{m(ice)}) in the two phase inclusions range from −11.0° to −17.5°C corresponding to salinities from 15.0 to 20.8 wt % NaCl equiv (Fig. 13). Homogenization temperatures (T_h) are recorded between 390° and 425°C (Fig. 13). Ice melting of rare multiphase (L + V + S) inclusions occurs in the temperature range between −10.5° and −11.7°C. Upon heating, halite dissolution is followed by disappearance of vapor bubble. T_h is recorded at 180°, 195°, and 220°C, and T_h in the interval from 380° to 390°C (Fig. 13). Combination of the ice melting and halite dissolution temperatures revealed a high bulk salinity between 31.1 and 32.9 wt % NaCl equiv (Fig. 13) and NaCl/(NaCl + CaCl₂) ratio in a narrow range between 0.47 and 0.54.

Ore paragenesis

Fluid inclusions were investigated in ore (sphalerite), synore (quartz, carbonates), and postore minerals (quartz, carbonates). Sphalerite, associated with both skarn and hydrothermal mineral assemblages, hosts moderate saline (7.6−13.8 wt % NaCl equiv; Fig. 13) two-phase, L + V , primary inclusions (Fig. 12C). The majority of inclusions homogenize in the temperature range between 238° and 315°C without significant differences between sphalerite from skarn and hydrothermal...
assemblages (Fig. 13). On the other hand, the homogenization recorded within sphalerite from the hydrothermal assemblage points to the temperature decrease associated with the depth decrease. Although several vapor-rich inclusions were recorded (Fig. 12D), due to poor optical quality, phase transitions were not observed.

Microthermometric data obtained for synore quartz (Fig. 12E) and carbonates (Fig. 12F) partly overlap with these recorded in sphalerite (7.2−14.0 wt % NaCl equiv; Th = 295°−365°C; Fig. 13). Eutectic temperature suggests a CaCl2-NaCl-H2O system. Hydrohalite melting temperature (Tm(hydrohalite)) between −22.3° and −23.5°C reveals the predominance of NaCl over CaCl2 in quartz samples. Contrary, decreased values of Tm(hydrohalite) in carbonates (−26° to −28.5°C) suggest increased influence of CaCl2 in the solution. Several CO2-enriched inclusions were recorded in carbonates. According to final melting temperature of clathrates (Tm(clathrate) = 4.7°−5.9°C) salinity spans from 7.6 to 9.5 wt % NaCl equiv. Homogenization was not recorded due to decrepitation of CO2 inclusions at about ~275°C. Inclusions observed within synore carbonates from Horizon VII (255 m

### Table 3. REE Composition (in ppm) and REE Ratios of Samples at the Trepcˇa Pb-Zn-Ag Skarn Deposit

<table>
<thead>
<tr>
<th>Sample type</th>
<th>PAAS</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>ΣREE</th>
<th>La/Sm</th>
<th>Tb/Yb</th>
<th>La/Lu</th>
<th>Ce/Ce*</th>
<th>Eu/Eu*</th>
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<td>Schist T-1</td>
<td>78.8</td>
<td>185.2</td>
<td>19.62</td>
<td>69.4</td>
<td>9.4</td>
<td>0.84</td>
<td>4.27</td>
<td>0.61</td>
<td>2.37</td>
<td>0.44</td>
<td>1.24</td>
<td>0.25</td>
<td>1.75</td>
<td>0.32</td>
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Note: n.d. = not detected
1 PAAS-normalizing (N) values from Nance and Taylor (1976)
2 (La/Lu)N = fractionation of LREE from the HREE; Ce and Eu anomalies are given as (Ce/Ce*)N = CeN/[LaN*PrN]0.5 and (Eu/Eu*)N = EuN/[SmN*GdN]0.5, where values >1 for positive anomaly, <1 for negative anomaly, =1 no anomaly

![Diagram](https://pubs.geoscienceworld.org/segweb/economicgeology/article-pdf/108/1/135/3468503/135-162.pdf)

![Another Diagram](https://pubs.geoscienceworld.org/segweb/economicgeology/article-pdf/108/1/135/3468503/135-162.pdf)

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**Figure 9.** The post-Archean Australian shale (PAAS) normalized plots of REE concentrations of (A) country rocks (barren recrystallized limestone and shale) and the host recrystallized limestone at contact with skarn and hydrothermal mineralization, and (B) syn- and post-ore gangue carbonates associated with the skarn and hydrothermal mineral assemblages.
above mean sea level) show a boiling effect (Fig. 12G). Homogenization of coexisting liquid- and vapor-rich inclusions is
recorded in the interval between 295° and 315°C. Salinity of liquid-rich inclusions estimated from the final ice melting
temperature lies in a relatively narrow range between 8.0 and 9.9 wt % NaCl equiv (Tm(ice) = −5.1° to −6.5°C). Laser Raman
spectroscopy has shown that vapor-rich inclusions occasionally comprise CO2.

Postore gangue minerals were precipitated from cooler fluids (Th = 245°−325°C) with variable salinity (0.9−14.0 wt %
NaCl equiv; Fig. 13). Eutectic temperature indicates CaCl2
and NaCl as the dominant dissolved salts.

**Stable Isotope Data**

**Isotope composition of fluid inclusions (δD, δ18O)**

The oxygen and hydrogen isotope data of the fluid inclusions hosted by the skarn and ore mineralization are summa-
rized in Table 7 and depicted in Figure 14. For calculation of the δ18O signature of fluids in equilibrium with hedenbergite,
the hedenbergite-water fractionation equation of Zheng (1993) has been used. Sphalerite allows direct measuring of
δ18O values of enclosed fluids.

Isotope composition of water hosted by hedenbergite (δD = −108 to −130‰; δ18O = 8.7−9.4‰) suggests a magmatic
origin of mineralizing fluids (Fig. 14). Decreased δD values
indicate that primary magmatic water has been slightly mod-
ified on its pathway from the solidifying magma toward the
mineralization site. Low δD values may reflect extensive
magma degassing as well (Giggenbach, 2003; Seghedi et al.,
2007; De Hoog et al., 2009).

Fluid inclusions within sphalerite are enriched in deu-
terium (δD = −55 to −74‰) and depleted in 18O (δ18O = −9.6
to −13.6‰). The δ18O versus δD values of water hosted by
sphalerite are slightly higher than the present-day global me-
teoric line (Fig. 14).

**Sulfur isotope composition of sulfides**

Sulfur isotope ratios of sulfides separated from skarn and
hydrothermal mineral assemblages are reported in Table 8.
The $\delta^{34}S$ values of the sulfides generally increase in the order galena (0.9 ± 2.3) ≤ chalcopyrite (2.9) ≤ pyrrhotite (3.1 ± 0.8) ≤ sphalerite (3.7 ± 1.6) ≤ pyrite (4.2 ± 2.8). The variation in isotope composition of sulfide is presented in Figure 15. The significant variations in the vertical distribution as
### Table 6. Summary of Fluid Inclusion Data for the Trepcˇa Pb-Zn-Ag Skarn Deposit

<table>
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<tr>
<th>Sample Type</th>
<th>Host</th>
<th>Level (masl)</th>
<th>Phases</th>
<th>P/S</th>
<th>V (vol %)</th>
<th>n</th>
<th>Composition (wt % NaCl equiv)</th>
<th>T&lt;sub&gt;b&lt;/sub&gt; (°C)</th>
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<td>Skarn mineral assemblage</td>
<td>Hdl</td>
<td>75</td>
<td>L + V</td>
<td>P</td>
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<td>75</td>
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<td>P</td>
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<td>P</td>
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<td>P</td>
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<td>L + V</td>
<td>P</td>
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<td></td>
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<td>Qtz</td>
<td>255</td>
<td>L + V</td>
<td>P</td>
<td>10-30</td>
<td>10</td>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;-NaCl-H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.9−4.2</td>
</tr>
</tbody>
</table>

Cal = calcite, Hdl = hedenbergite, Qtz = quartz, Sph = sphalerite
well as the differences between sulfides associated with the skarn and hydrothermal mineral associations are not observed. Contrary, the variations in isotope composition of co-genetic sulfides can be prominent (e.g., the $\delta^{34}S$ values of galena and sphalerite associated with the skarn mineralization range up to 9.9 and 7.2‰, respectively).

**Discussion**

The Pb-Zn-Ag Trepča deposit exhibits all principal distinctive features of the calcic Pb-Zn skarn deposits worldwide (e.g., Meinert et al., 2005). The proposed metallogenic model is summarized in Figure 16.

The mineralization is spatially and temporally related with the postcollisional magnetism of Oligocene age (23–26 Ma). Because there is no visible contact between the mineralization and magmatic rocks, the deposit should be considered as a result of interaction of the mineralizing fluids and the host carbonate rocks. The mineralizing fluids have been derived, not only from small-scale dike emplaced within the breccia pipe, but probably also from the parent magma chamber.
below the ore deposit, similar to skarn deposits elsewhere (Einaudi et al., 1981; Yun and Einaudi, 1982; Meinert et al., 2003; Williams-Jones et al., 2010).

The Trepcˇa deposit is located within a slightly metamorphosed terrane. The metamorphism could be, at least partly, attributed to the thrusting of the ophiolite complex over the Triassic limestone. Furthermore, Oligocene magmatic activity contributes to metamorphism as well. The barren recrystallized limestone displays high CaCO₃ content (98.9–99.7 wt % CaCO₃). Its REE pattern with negative CeN and no EuN anomaly, typical for the marine carbonates, indicates that the original geochemical features of sedimentary precursor were not disturbed by metamorphism and support isochemical characteristics of the process.

The skarn mineralization, defined by the presence of Ca-Fe-Mg-Mn silicates, shows evidence of prograde and retrograde stages. The principal prograde mineral is hedenbergite enriched in Mn. The Mn-rich mineralogy is characteristic of the Pb-Zn skarn deposits placed distal from a magmatic source (e.g., Einaudi et al., 1981; Abrecht, 1985; Logan, 2000; Vassileva and Bonev, 2001; Vassileva et al., 2005; Meinert et al., 2005; Canet et al., 2009) and reflects remobilization of Mn from the country rocks. In the Dinarides the principal source of manganese is represented by the Middle Triassic, rifting-related, sediments (Palinkaš et al., 2008). So we assume that magmatic fluids released from a solidifying magmatic body, prior to their interaction with the Upper Triassic limestones, infiltrate the country rocks along fissures and lithologic contacts and leach mobile elements, including Mn²⁺, Fe²⁺, Pb²⁺, Zn²⁺, and Ag⁺. According to Korzhinskii (1970) fluid transport is controlled by pressure gradient (infiltration) and by chemical potential (diffusion). Although a pure diffusion model can be applied successfully to thin reaction zones, it is unlikely that diffusion can result in metasomatic zones of metric size observed within the Trepcˇa deposit, as well as within other skarn deposits (e.g., Einaudi et al., 1981; Nicolescu and Cornell, 1999; Ciobanu and Cook, 2004; Pinto-Linares et al., 2008, Bertelli et al., 2009; Williams-Jones et al., 2010).

### Table 7. Hydrogen and Oxygen Isotope Composition of Fluid Inclusions Hosted by Skarn and Ore Minerals from the Trepcˇa Pb-Zn-Ag Skarn Deposit

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogy</th>
<th>δD (H₂O) (‰ V-SMOW)</th>
<th>δ¹⁸O (H₂O) (‰ V-SMOW)</th>
<th>δ¹⁸O (mineral) (‰ V-SMOW)</th>
<th>δ¹⁸O (H₂O) (‰ V-SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T9-2b</td>
<td>Hedenbergite</td>
<td>-121</td>
<td>7.3</td>
<td>8.7</td>
<td>7.3</td>
</tr>
<tr>
<td>T6</td>
<td>Hedenbergite</td>
<td>-108</td>
<td>8.0</td>
<td>9.4</td>
<td>8.0</td>
</tr>
<tr>
<td>T6-1</td>
<td>Hedenbergite</td>
<td>-116</td>
<td>7.5</td>
<td>8.9</td>
<td>7.5</td>
</tr>
<tr>
<td>T6</td>
<td>Hedenbergite</td>
<td>-112</td>
<td>5.0</td>
<td>9.4</td>
<td>5.0</td>
</tr>
<tr>
<td>T6-1</td>
<td>Hedenbergite</td>
<td>-130</td>
<td>7.5</td>
<td>8.9</td>
<td>7.5</td>
</tr>
<tr>
<td>T9-2</td>
<td>Hedenbergite</td>
<td>-127</td>
<td>7.3</td>
<td>8.7</td>
<td>7.3</td>
</tr>
<tr>
<td>T8-2</td>
<td>Sphalerite</td>
<td>-55</td>
<td>-9.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T7-1</td>
<td>Sphalerite</td>
<td>-73</td>
<td>-13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T9-4</td>
<td>Sphalerite</td>
<td>-74</td>
<td>-11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T6</td>
<td>Sphalerite</td>
<td>-62</td>
<td>-12.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Calculated according to the hedenbergite-water oxygen-isotope fractionation equation of Zheng (1993) for 400°C.

**Fig. 14.** Plot of δ¹⁸O vs. δD values of water hosted by prograde (hedenbergite) and retrograde minerals (sphalerite) suggests two distinct sources of fluids involved in the prograde and retrograde mineralization events at the Trepcˇa Pb-Zn.Ag skarn deposit. The magmatic water box is drawn after Criss and Taylor (1986). GMWL = global meteoric water line, SMOW = standard mean ocean water composition.
Concentration gradients, the driving force for diffusive mass transport, decrease as the thickness of reaction zones increase and the metasomatic process stops. A long distance transport must result, therefore, from the fluid flow induced by pressure and temperature gradients.

Recrystallized limestone was replaced by hedenbergite according to the following metasomatic reaction:

\[
\text{CaCO}_3 + 2\text{H}_2\text{SiO}_4 + \text{Fe}^{2+} \rightarrow \text{CaFe}_2\text{Si}_2\text{O}_6 + \text{CO}_2 + 3\text{H}_2\text{O} + 2\text{H}^+. \tag{1}
\]

Predomination of hedenbergite over andradite reflects a high ferrous/ferric ratio as a consequence of reductive environment (Gustafson, 1974). According to the fluid inclusion data, hedenbergite was formed by moderate saline Ca-Na chloride fluids at temperatures above 390°C. Isotope composition (δ18O vs. δD) of fluid inclusions supports the magmatic origin of fluids involved in the prograde stage of mineralization. Decreased δD values could be attributed to the influence of organic matter due to infiltration of the mineralizing fluids along the sedimentary complex (e.g., Sheppard, 1986; Charef and Sheppard, 1987). Furthermore, organic matter would maintain reductive conditions essential for achievement of high ferrous/ferric ratio. Because the lack of organic matter content and stable isotope data related to the sedimentary complex in the Trepcˇa area, it is difficult to estimate quantitatively the contribution of organic matter.

The clear increase in REE content from less than 5 ppm (ΣREE) in the barren carbonates to 180 ppm (ΣREE) in the carbonates on the contact with the skarn mineralization points to an input of these elements during the skarn formation process. A magmatic origin of the REE is plausible, but remobilization from the sedimentary complex should be considered as well. Namely, according to experimental data, fluids released from the solidifying magma generally display low REE content, LREE enrichment, HREE depletion, and variable positive Eu anomaly (Flynn and Burnham, 1978; Ayers and Eggler, 1995; Reed et al., 2000; Gaspar et al., 2008). On the other hand, the reducing, acidic, high-temperature mineralizing fluids have a capability for the remobilization of numerous elements, including iron, manganese, and REE, from the country rocks (e.g., Bau and Möller, 1992; Strmić Palinkaš et al., 2009). Consequently, the REE content of mineralizing fluids depends on the redox potential, pH, temperature, water/rock ratio, and moreover on the distance between the magmatic source and the deposition site. In addition, increased REE content in the host limestone on the contact with the skarn mineralization, the manganese-rich mineralogy likewise reflects the distal position of the Trepcˇa deposit.

The prograde stage has an anhydrous character, with Ca-Fe-Mg-Mn pyroxenes as the principal minerals. According to Fournier (1992) at temperatures above 400°C the country rocks behave in a ductile fashion, sealing the system from significant infiltration of connate and meteoric waters. Consequently, the prograde mineralization occurred under a lithostatic regime. The formation pressure could be constrained by a combination of fluid inclusion data and an independent geothermometer. For example, the lack of wollastonite from the paragenesis could be utilized as an indicator of temperature under known CO2 pressure (Greenwood, 1967). The absence of a liquid CO2 phase in fluid inclusions in hedenbergite suggests H2O-rich fluids and a X CO2 < 0.1 during the prograde stage (e.g., Kerrick, 1971; Logan, 2000; Canet et al., 2011). H2O-rich metasomatic fluids (X CO2 = 0.01−0.1) have been documented in other Pb-Zn skarn deposit as well (e.g., Taylor and O’Neil, 1977; Vázquez et al., 1998; Logan, 2000). Concentration gradients, the driving force for diffusive mass transport, decrease as the thickness of reaction zones increase and the metasomatic process stops. A long distance transport must result, therefore, from the fluid flow induced by pressure and temperature gradients.

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Hedenbergite occasionally hosts highly saline fluid inclusions (31.1−32.9 wt % NaCl equiv) with slightly decreased homogenization temperatures (380°−390°C). Increased salinity could be attributed to the decompression and the transition from lithostatic to hydrostatic pressure. An initially one-phase moderate saline fluid (15.0−20.8 wt % NaCl equiv) will intersect the two-phase (L + V) boundary on the liquid side of the critical curve, leading to the boiling and the separation of a high saline liquid phase and a low saline vapor phase (Fournier, 1999; Heinrich, 2007; Becker et al., 2008). A liquid phase with salinity around 32 wt % NaCl equiv will be produced in the temperature interval between 380° and 390°C under pressure around 200 bars (Fig. 18).

Hedenbergite is commonly overprinted by ilvaite, magnetite, pyrrhotite, arsenopyrite, pyrite, and a mixture of carbonates and quartz. The possible reactions leading to hedenbergite breakdown into retrograde minerals are the following:

\[
6\text{CaFe}_2\text{Si}_2\text{O}_6 + H^+ + O_2 + 5\text{CO}_2 \rightarrow \text{CaFe}_2\text{Fe}_3\text{Si}_3\text{O}_8(\text{OH}) + \text{Fe}_2\text{Fe}_3\text{O}_4 + 5\text{CaCO}_3 + 10\text{SiO}_2, \tag{2}
\]

\[
3\text{CaFe}_2\text{Si}_2\text{O}_6 + 3\text{CO}_2 + \frac{1}{2} O_2 \rightarrow \text{Fe}_2\text{Fe}_3\text{O}_4 + 3\text{CaCO}_3 + 6\text{SiO}_2, \tag{3}
\]

\[
\text{CaFe}_2\text{Si}_2\text{O}_6 + 2\text{CO}_2 \rightarrow \text{CaCO}_3 + \text{FeCO}_3 + 2\text{SiO}_2, \tag{4}
\]

\[
\text{CaFe}_2\text{Si}_2\text{O}_6 + \frac{1}{2}\text{S}_2 + \text{CO}_2 + 2\text{H}^+ \rightarrow \text{FeS} + \text{CaCO}_3 + 2\text{SiO}_2 + \text{H}_2\text{O}, \tag{5}
\]

and

\[
\text{CaFe}_2\text{Si}_2\text{O}_6 + \text{S}_2 + \text{CO}_2 + 2\text{H}^+ \rightarrow \text{FeS}_2 + \text{CaCO}_3 + 2\text{SiO}_2 + \text{H}_2\text{O}. \tag{6}
\]

Genesis of arsenopyrite in skarn assemblages could be related to retrograde alteration of hedenbergite as well:

\[
\text{CaFe}_2\text{Si}_2\text{O}_6 + \frac{1}{2}\text{S}_2 + \text{As(OH)}_3 + \text{CO}_2 + 5\text{H}^+ \rightarrow \text{FeAsS} + \text{CaCO}_3 + 2\text{SiO}_2 + 4\text{H}_2\text{O}. \tag{7}
\]

According to the geothermometer proposed by Kretschmar and Scott (1976) and modified by Sharp et al. (1985) arsenopyrite was deposited in the temperature interval between 350° and 380°C under a sulfur fugacity between 10^{-7.2} and 10^{-8.8} bars.

Figure 19 displays stability fields for various species involved in the retrograde reactions within log f_{S_2} versus log f_{O_2} space. The diagram is constructed for a temperature of 350°C.
and a pressure of 300 bars employing the SUPCRT92 database (Johnson et al., 1992) and thermodynamic data published by Helgeson and Kirkham (1974), Helgeson et al. (1978), and Moecher and Chou (1990). The retrograde mineral assemblage reflects an increase in both oxygen and sulfur fugacities.

The oxygen and sulfur fugacities increase points to the opening of the system, probably during the phreatomagmatic explosion and formation of the breccia. Although the breccia does not host the hedenbergite mineralization, there are several types of fragments which represent, according to their textural and mineralogical features, the altered hedenbergite remains. Namely, fibroradial arsenopyrite-magnetite fragments, magnetite-pyrite fragments and pyrite-pyrrhotite fragments might be formed by the same reactions proposed for the retrograde mineral assemblage (see equations (3), (5), (6), and (7)).

The trachyte body placed within the breccia core may represent a component of the deeply sourced intrusion. The trachytic magma penetrated toward the surface along the contact between limestone and the overlying impermeable schist, which represented a fluid barrier. Interaction of the

![Fig. 16. Schematic diagram depicting the formation of the Trepcă Pb-Zn-Ag skarn deposit.](https://pubs.geoscienceworld.org/segweb/economicgeology/article-pdf/108/1/135/3468503/135-162.pdf)
Fig. 17. Pressure-temperature diagram showing the ranges of fluid inclusion isochores for the prograde (hedenbergite, solid lines) and retrograde/hydrothermal (sphalerite, dashed lines; calcite, dash-dot line) stage. The trapping conditions for the prograde stage are limited by P-T stability of wollastonite and the homogenization into the liquid phase recorded for moderate saline inclusions. Formation temperature for sphalerite is estimated assuming the hydrostatic regime during the retrograde stage.

Fig. 18. NaCl-H2O P-T-X phase diagram (after Driesner and Heinrich, 2007), explaining increased salinity and decreased homogenization temperature for rare three-phase inclusions hosted by hedenbergite as a consequence of sudden decompression due to the opening of the system during the phreatomagmatic explosions.
hot magmatic body with cold ground water resulted in phreatomagmatic explosions and formation of the phreatomagmatic breccia. The orientation of intrusive emplacement and phreatomagmatic brecciation was probably influenced by the permeability contrast between the schist and the underlying limestone. The breccia comprises country-rock fragments, juvenile fragments, and altered fragments of previously formed skarn. The milled matrix is the result of hydraulic fracturing of the country rocks. Magma reinvaded the breccia pipe and initiated another cycle of activity. This is supported by the well-milled, reworked character of fragments, as well as a mixture of plant and organic material-rich sedimentary rock clasts derived from the maar lake/floor environment. Presence of an altered trachyte body implies that the trachytic magma intruded into the breccia prior to the termination of hydrothermal activity.

Once formed, the phreatomagmatic breccia served as a sink for invasion of groundwater into the system. Increased thermal gradient in the area allowed formation of a hydrothermal convection cell and enhanced the leaching of metals from the country rocks. Additionally, opening of the skarn system to the surface, by formation of the breccia, allowed escape of CO₂ from depth and consequently contributed to the advanced replacement of host limestone by hydrothermal mineralization. Increased sulfur fugacity is mostly a consequence of sulfur degassing from the magma body. Solubility of sulfur in silicate magma is a function of temperature, pressure, FeO content of melt, fO₂, and sulfur speciation in the gas phase. Since solubility of sulfur under reducing condition decreases with decreasing temperature, cooling of magma will cause degassing of sulfur (Carroll and Webster, 1994). Furthermore, opening of the system by phreatomagmatic explosion decreased the pressure and additionally favored sulfur release. Increased sulfur fugacity diminished the metal-bearing capacity of the mineralizing fluids and enabled the sulfide deposition.

Fluid inclusion data obtained on sphalerite and synore gangue minerals suggest precipitation from moderate saline fluids with predominantly Ca-Na chloride composition. Since homogenization temperatures represent the minimum trapping conditions, the formation conditions were estimated from isochores intersected by temperatures calculated from sphalerite CuS geothermometer proposed by Hutchison and Scott (1981). The CuS content of sphalerite in equilibrium with pyrite suggests the formation temperature in the range between 347°C and 387°C for the samples from the horizon X (75 m above mean sea level). Calculated temperature corresponds well to temperature of the retrograde stage deduced from the arsenopyrite geothermometer (T = 350°C–380°C; Fig. 20). A combination of the fluid inclusion data and sulfide geothermometers revealed the formation pressure in the wide range between 400 and 1,100 bars (40 and 110 MPa, Fig. 17).

Travertine deposits preserved at the present-day surface suggest absence of erosion and allow determination of the formation depth. Therefore, fluids present in inclusions on the 75-m mine level were trapped approximately 780 m below the surface. If the system was completely open, a 780-m depth corresponds to a hydrostatic pressure of 78 bars (7.8 MPa). Significant variations in determined fluid pressure indicate a partially sealed system. Local boiling effects point to
unsealing of the system, probably by extending of the paleokarst due to intensive dissolution of the carbonate host rock by acid ore-bearing fluids. The boiling effect recorded in fluid inclusions from synore carbonates (horizon VII; 255 m above mean sea level; approximately 600 m below the surface) suggests precipitation temperature between 295° and 315°C and fluid pressure in the range between 50 and 70 bars (Fig. 17).

The isotope composition (δ¹⁸O vs. δD) of fluid inclusions hosted by sphalerite suggests that the main stage of sulfide deposition incorporated meteoric water into the system (Fig. 14). A discrepancy between the sphalerite data and the global meteoric water line may be the result of the alteration processes during the retrograde stage (e.g., Criss and Taylor, 1986). According to the reactions (2) through (7), significant alteration products are minerals with a strong tendency to concentrate ¹⁸O, such as quartz and magnetite. The precipitation of minerals with increased δ¹⁸O values could deplete the mineralizing water and shift its ¹⁸O value to the left of the meteoric water line. There are two plausible mechanisms which could affect the δD values of the mineralizing water. The first one is the alteration of K-feldspar (sanidine) into muscovite. Whereas muscovite prefers the isotopically light hydrogen, its precipitation leads to enrichment in D in the mineralizing water. The second mechanism is the precipitation of minerals with increased δ¹⁸O values.

H₂O + HDS ⇌ HDO + H₂S.  (8)

Isotope composition of sulfides points to a magmatic origin of sulfur. The isotope fractionation temperature of coexisting sulfide pairs, calculated from the equations given by Li and Liu (2006) for a temperature interval between 0 and 1,000°C, generally suggests the absence of sulfur isotope equilibrium in which the isotopic fractionation factors between the dominant sulfur species in aqueous solution and the precipitating minerals were controlled by kinetic rather than by equilibrium isotope effects. Considering the textural features there is a weak temporal shift in the deposition of the principal sulfide minerals. The pyrrhotite and arsenopyrite were precipitated during the early retrograde stage of mineralization and represent the earliest sulfides in the deposit. Galena followed by sphalerite deposition and pyrite occurs during the whole period of the hydrothermal stage. The isotope disequilibrium, interpreted mainly as a result of the multistage depositional process, is frequent in the Pb-Zn skarn deposits (e.g., Corsini et al., 1980).

According to Ohmoto and Rye (1979), for a fluid pressure ranging from 500 to 3,000 bars (50−300 MPa) and a mole fraction of water in the fluid of between 0.8 to 1.0, which are acceptable conditions for the hydrothermal stage, at 350°C, the pyrrhotite + pyrite + magnetite equilibrium assemblage is restricted within an fO₂ range where H₂S is the prevailing sulfur species in the fluids. Isotope composition of sulfur in the fluid at the beginning of sulfide deposition could be estimated assuming the local equilibrium between pyrrhotite, as the earliest sulfide in the deposit, and H₂S. Isotope equilibrium fractionations of Li and Liu (2006) reveal δ³⁴S(pyrrhotite-H₂S) of 0.6 at a temperature of 380°C and refers the δ³⁴SH₂S value between 2.0 and 3.5‰. A slight shift toward positive values could be attributed to (1) a loss of isotopically lighter sulfur through vapor phase, (2) a marine sulfate input, (3) a pH increase of the mineralizing fluids, or more probably to (4) a transition...
from oxidizing to reduced conditions (e.g., Rye and Ohmoto, 1974; Lieben et al., 2000).

Synore carbonates associated with the skarn and hydrothermal mineral assemblages show similar roof-shaped patterns typical for the hydrothermal and metasomatic carbonates (e.g., Bau and Möller, 1992; Hecht et al., 1999; Strmić Palinkaš et al., 2009b). The principal difference between synore carbonates from the skarn and hydrothermal mineral assemblages are their total REE concentrations (81.4 and 26.2 ppm, respectively). The alteration of the prograde skarn minerals (e.g., hedenbergite) should be considered as the potential source of the high REE content in synore carbonates associated with the skarn mineral assemblage. Contrary, the synore carbonates from the hydrothermal mineralization, characterized by the low REE content, reflect the chemical composition of the mineralizing fluids.

The fluid inclusion data obtained on the postore minerals suggest precipitation from slightly diluted fluids. Decreased temperature and the lower REE content of postore carbonates are attributed to the influence of ground water and dying magmatic system. Precipitation of the large masses of carbonates and travertine deposition require a pH-neutralized environment.

Conclusions

The geological, mineralogical, and geochemical characteristics of the Trepcă deposit, including the mineralization hosted by limestone, the presence of the prograde and the retrograde mineral assemblages, the spatial and temporal link between the mineralization and the magmatic activity and Mn-enriched mineralogy, are common for distal Pb-Zn-Ag skarn deposits worldwide.

The structurally and lithologically controlled mineralization was formed during two distinct mineralization stages: an early prograde closed-system and a later retrograde open-system stage. The transition from the prograde to the retrograde stage was initiated by the phreatomagmatic explosions and formation of the breccia. Phreatomagmatic breccia unsealed the system, decreased the pressure, enhanced sulfur release from the magmatic body, and consequently increased the sulfur fugacity. The breccia pipe served as the sink for the ground water which contributed to an oxygen fugacity and a water/rock ratio increase.

Prograde skarnification resulted from the action of magmatic fluids with the recrystallized carbonate rocks. The absence of mineralized contacts between the magmatic and the host rocks suggests the metasomatism by infiltration of the mineralizing fluids into the host rocks, rather than mineralization by the diffusion-driven contact metasomatism. The predomination of pyroxene reflects low oxygen fugacity. Fluid inclusion data and mineral assemblage set the prograde stage that deposition of a significant amount of carbonates. Decreased formation temperature and depletion in the REE content point to an influence of pH-neutralized cold ground water and a dying magmatic system.

Acknowledgments

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