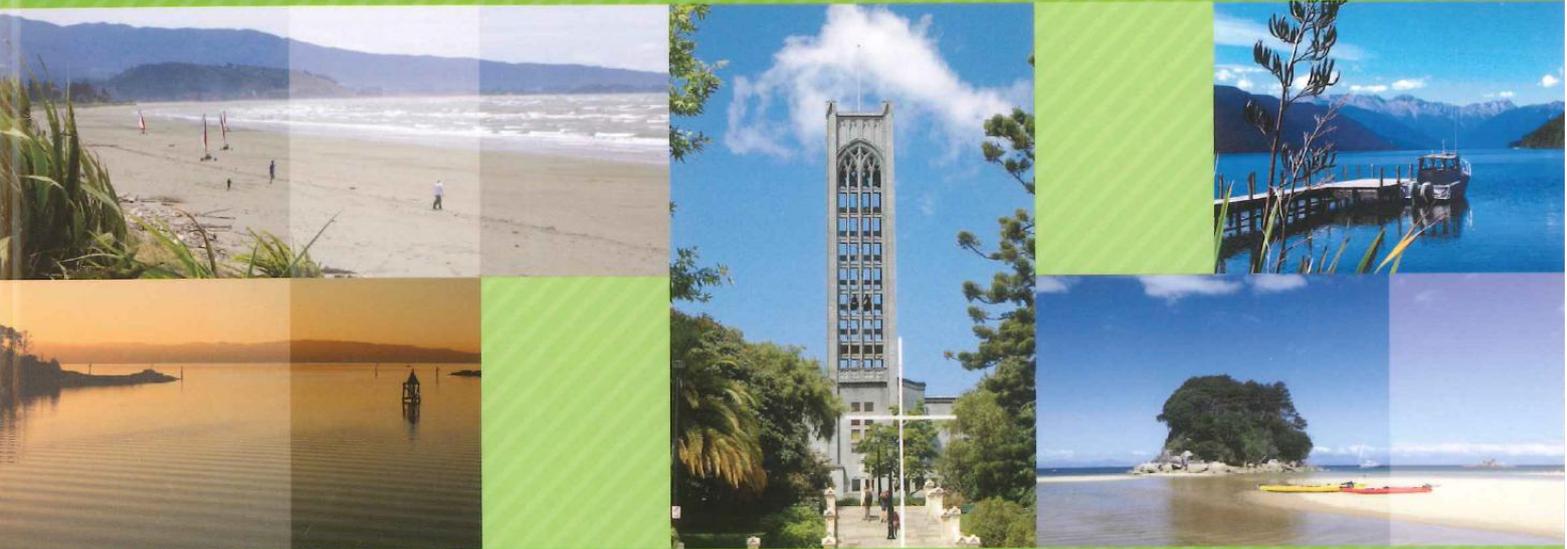


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Ore-fluid evolution at the Sasa Pb-Zn skarn deposit, Republic of Macedonia

S. Strmic Palinkas^{1*}, G. Tasev², T. Serafimovski², L. Palinkas¹, D. Smajgl¹
and Z. Peltekovski³

¹ Geological Department, Faculty of Science, The University of Zagreb, Horvatovac 95,
10000 Zagreb, Croatia, sabistrmic@geol.pmf.hr

² Institute of Geology, Faculty of Natural and Technical Sciences, University Goce Delcev,
2000 Stip, R. Macedonia, goran.tasev@ugd.edu.mk

³ Mine SASA DOO, Rudarska u. 28, 2304 Makedonska Kamenica, R. Macedonia,
z.peltekovski@sasa.com.mk

* Current address: School of Environment, The University of Auckland, Private Bag 92019,
Auckland Mail Centre, Auckland 1142, New Zealand, s.strmic-palinkas@auckland.ac.nz

Abstract

The Sasa Pb-Zn skarn deposit is located in the Serbo-Macedonian massif approximately 100 km east from Skopje, Republic of Macedonia. Ore reserves are estimated at 10 million metric tons with 7.5% lead and zinc. The deposit is hosted by the Lower Palaeozoic metamorphic complex composed of gneisses, marbles and quartz-graphite schists. The mineralisation is spatially and temporally related to Tertiary calc-alkaline magmatism. The volcanic rocks in the area are mostly quartz latite and andesite with K/Ar ages between 27 and 24 Ma.

The mineralisation is represented by skarn and hydrothermal minerals as two end-member associations. The skarns occur in the form of replacement of marble, whereas the hydrothermal mineralisation appears as replacements and as open-space fillings. The skarn association has characteristic zonal structure and contains calc-silicate minerals (Fe-Mn-pyroxenes, Fe-Mn-pyroxenoids, garnets, ilvaite, epidote), magnetite, pyrite and pyrrhotite. The hydrothermal association, which is superimposed onto the skarn assemblages, contains argentiferous galena, sphalerite, pyrite and minor chalcopyrite. Carbonates and quartz are the most abundant gangue minerals.

Fluid inclusion studies recognised three major stages of mineralisation: (1) Metasomatic formation of skarn minerals during the prograde stage of mineralisation from saline and high-temperature fluid, probably of distal magmatic origin. The absence of mineralised contacts between the magmatic and the host rocks as well as the manganese rich mineralogy suggests metasomatism by infiltration of the mineralising fluids into the host rocks, rather than mineralisation by diffusion-driven contact metasomatism. (2) Hydrothermal alteration of skarn minerals (ilvaite, chlorite, magnetite, pyrrhotite, carbonates, quartz) followed by precipitation of ore and gangue minerals resulted from the mixing of magmatic and meteoric fluids during the retrograde stage. (3) Deposition of post-ore gangue minerals, mostly carbonates, from cooler and slightly diluted fluids.

Keywords: Pb-Zn deposit, distal skarn, fluid inclusions, pyroxene, carbonate, quartz, the Serbo-Macedonian massif.

Introduction

The Sasa Pb-Zn skarn deposit (42.0° N, 22.5° E) is located in the Serbo-Macedonian massif, approximately 100 km east from Skopje, Republic of Macedonia. The Serbo-Macedonian massif is a large, elongate basement complex situated in the eastern part of the Balkan Peninsula. It extends southward from Serbia through Kosovo, Republic of Macedonia and Bulgaria to the Chalkidiki Peninsula in northern Greece (Fig. 1) and comprises numerous economically important ore deposits of Cu, Au, Pb and Zn (e.g. Bor and Majdanpek, Serbia; Toronica, Sasa and Bucim, Republic of Macedonia; Osogovo, Bulgaria; Skouries, Greece).

The Sasa deposit is spatially and temporally related to Tertiary calc-alkaline magmatism (Serafimovski and Aleksandrov, 1995). It comprises prograde and retrograde mineral assemblages hosted by a sequence of Paleozoic marble intercalated with quartz-graphite schist (Peltekovski, 2012). The prograde mineralisation is represented by anhydrous Ca-Fe-Mn-silicate minerals (pyroxenes, pyroxenoids and garnets). A subsequent retrograde stage contains epidote, chlorite and ilvaite (Sijakova-Ivanova et al., 2012). The principal ore minerals are galena and sphalerite. With current reserves of 10 million metric tons of ore at 7.5% lead and zinc, the deposit represents an important source of metals in the southeastern part of Europe. Mining activities in the area date back to ancient times. The first geological investigations began in 19th century and industrial production started in 1966.

The aim of this ongoing study is to estimate the geochemical characteristics of the mineralising fluids and to constrain the physiochemical conditions during the skarn formation and ore deposition. The environment of the deposit formation was analysed through mineral equilibria, as well as mineralogical and paragenetic studies in order to interpret the $\log f_{O_2}$ - $\log f_{S_2}$ formation path.

Geological setting

The Serbo-Macedonian massif is the N-S zone between the Vardar ophiolite zone in the west and the Rhodope massif in the east (Fig. 1). It comprises an Upper (low-grade) and a Lower (medium to high-grade) unit (Dimitrijevic, 1995). The protoliths of both units are reported as volcanic to sedimentary rocks of Precambrian to Paleozoic age, metamorphosed up to greenschist and amphibolite facies, respectively. The Serbo-Macedonian massif was penetrated by andesitic to trachytic volcanic rocks during Cretaceous and Tertiary time. The age of magmatism decreases from approximately 84 Ma in the north (Clark and Ullrich, 2004) to 19 Ma in the southernmost part of the Serbo-Macedonian massif (Frei, 1995). Associated ore deposits are subdivided into two distinct groups: 1) Porphyry Cu-Mo-Au and subordinate epithermal gold deposits, and 2) Pb-Zn(-Ag) hydrothermal deposits (Neubauer, 2002).

The Sasa deposit is hosted by Paleozoic marble intercalated with quartz-graphite schist and surrounded by Precambrian gneiss (Fig. 2). Although a direct contact between magmatic rocks and the mineralisation has not been found the mineralisation is considered as a product of the Tertiary magmatic activity. The volcanic rocks in the area are mostly quartz latite and andesite with K/Ar ages between 27 and 24 Ma (Tasev et al., 2005).

The mineralisation is represented by skarn and hydrothermal minerals as two end-member associations. The skarns occur in the form of replacement of marble, whereas the hydrothermal mineralisation appears as replacements and as open-space fillings. The skarn association has characteristic zonation and contains Mn-enriched calc-silicate minerals (pyroxenes, pyroxenoids, garnets, epidote, chlorites and ilvaite), magnetite, pyrite and pyrrhotite. The hydrothermal association, which is superimposed onto the skarn assemblages, contains galena, sphalerite, pyrite and minor chalcopyrite. Carbonates and quartz are the most abundant gangue minerals. The paragenetic sequence of the Sasa deposit is summarised in Figure 3.

Sample and analytical methods

A total of 26 handpicked rock samples were collected from existing underground workings at the Sasa deposit. Samples are subdivided into two major groups: 1) country rocks (marble and quartz-graphite schist), and 2) mineralised samples (skarn and hydrothermal mineralisation).

Paragenetic relationships were studied in thin sections by transmitted polarised light microscopy. Ore minerals were examined in polished thick sections by reflected light microscopy. X-ray powder diffraction (XRD) was conducted on a Philips PW 3040/60 X'Pert PRO powder diffractometer (45 kV, 40 uA), with CuK α -monochromatised radiation ($\lambda = 1.54056 \text{ \AA}$) and 0-9 geometry. The area between 4 and $63^\circ 2\theta$, 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.

Microthermometric measurements of fluid inclusions were performed on doubly polished, $\sim 0.3\text{-mm}$ -thick, transparent mineral wafers of quartz, carbonates and pyroxenes. Measurements were carried out on a Linkam THMS 600 stage mounted on an Olympus BX 51 microscope using 10x and 50x Olympus long-working distance objectives for visible light. Two synthetic fluid inclusion standards (SYN FLINC; pure H $_2$ O and mixed H $_2$ O-CO $_2$) were used to calibrate the equipment. The precision of the system was $\pm 2.0^\circ\text{C}$ for homogenisation temperatures, and $\pm 0.2^\circ\text{C}$ in the temperature range between -60° and $+10^\circ\text{C}$. Apparent salinity was calculated from final ice melting temperatures using the equation of Bodnar (1993). The computer package FLUIDS (Bakker 2003; Bakker and Brown, 2003) was used to calculate fluid properties, including isochores. The fluid inclusions bulk density and isochores were calculated according to the equation of state published by Zhang and Frantz (1987).

Results

Country rocks

The principal host rock is medium to coarse grained white saccharoidal marble, banded with quartz-graphite schist. Microthermometric studies were carried out on selected quartz grains from the quartz bands. All measurable inclusions have secondary origin. They comprise two phases (L+V) with a degree of fill (F) between 0.6 and 0.7. Moderate salinity (5.0 to 6.9 wt. % NaCl equiv.) is determined from the ice melting temperature ($T_{m\text{ice}}$) in the interval between -3.0° and -4.3°C . Homogenisation to the liquid phase occurs in a wide temperature range between 229° and 400°C with a median value of 349°C .

Skarn mineral association

The prograde stage is characterised by metasomatic replacement of the host marble with anhydrous Ca-Fe-Mn silicates, mostly pyroxenes, pyroxenoids and minor garnets. According to the microscopic investigations and the XRD analyses pyroxenes range from hedenbergite (CaFeSi $_2$ O $_6$) to johannsenite (CaMnSi $_2$ O $_6$). The principal pyroxenoids are bustamite ((Mn,Ca) $_3$ Si $_3$ O $_9$) and rhodonite ((Mn $^{2+}$,Fe $^{2+}$,Mg,Ca)SiO $_3$). Garnets are represented mostly by andradite (Ca $_3$ Fe $_2$ (SiO $_4$) $_3$).

Fluid inclusions hosted by pyroxenes reflect the physicochemical nature of the solutions involved into 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 $10 \mu\text{m}$ in size, are isolated, and have rounded shapes. Secondary

inclusions are commonly arranged in clusters. Their small size, which is typically less than 2 μm , obstructed observation of phase transitions. At room temperature primary fluid inclusions consist of two phases (L+V) and exhibit a degree of fill of 0.75. Eutectic temperatures between -50° and -54°C suggest that CaCl_2 and NaCl are the dominant dissolved salts. Ice melting temperatures between -10.5° and -12.5°C correspond to salinities from 14.5 to 16.4 wt % NaCl equiv. Homogenisation temperatures (T_H) are recorded between 400° and 420°C . Fluid density is estimated in the range between 0.692 and 0.763 g/cm^3 .

The retrograde stage resulted with a partial alteration of prograde minerals. Prograde minerals are commonly overprinted by a mixture of hydrous silicates (ilvaite ($\text{CaFe}^{2+}_2\text{Fe}^{3+}\text{Si}_2\text{O}_8(\text{OH})$), epidote ($\text{Ca}_2\text{Al}_2(\text{Fe}^{3+},\text{Al})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$), and chlorite), magnetite, carbonates (mostly Mn-enriched calcite, ankerite and siderite) and quartz. Pyrrhotite and pyrite occur as well.

Ore (hydrothermal) mineral association

Pyrite formed earlier than galena and sphalerite, but minor pyrite occurs over the whole period of sulphide deposition. Pyrite is locally replaced by chalcopyrite. Argentiferous galena precedes sphalerite. Sphalerite is black due to its high Fe content and it commonly contains tiny chalcopyrite inclusions. Carbonates and quartz are the most abundant gangue minerals.

Primary fluid inclusions trapped by syn-ore gangue minerals represent the remains of the ore-bearing fluids. Quartz contains primary and secondary two-phase (L+V) inclusions. Primary inclusions occur in growth zones or isolated, and commonly have irregular shapes. Their size varies between 5 and 25 μm . The degree of fill is estimated around 0.75. Secondary inclusions occur along healed fractures. They are mostly irregular to elongated and exhibit a degree of fill around 0.85. Carbonates have entrapped primary and secondary two-phase (L+V) inclusions as well. Primary inclusions commonly occur in isolated clusters and show negative crystal shapes. Their size ranges from 5 to 50 μm . The degree of fill is estimated around 0.75. Secondary inclusions are rare, smaller (up to 10 μm) and have a degree of fill between 0.85 and 0.9. Microthermometric data obtained for primary fluid inclusions in syn-ore quartz and carbonates overlap (6.3-7.9 wt % NaCl equiv; $T_H = 270^\circ\text{-}300^\circ\text{C}$). Eutectic temperature suggests a $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ system. Estimated fluid density spans between 0.800 and 0.834 g/cm^3 .

The post-ore stage of the mineralisation is characterised by deposition of a significant amount of carbonates, predominantly calcite, and minor amount of quartz. Measurable primary fluid inclusions in post-ore minerals are rare; they occur isolated and mostly show negative crystal forms. According to microthermometric data (5.5-6.2 wt % NaCl equiv; $T_H = 125^\circ\text{-}233^\circ\text{C}$) post-ore minerals were deposited from cooler and slightly diluted fluids.

Discussion

The Pb-Zn Sasa deposit exhibits all principal distinctive features of the calcic Pb-Zn skarn deposits worldwide (e.g. Einaudi et al., 1981; Meinert et al., 2005; Williams-Jones et al., 2010). The mineralisation is spatially and temporally related with the calc-alkaline magmatism of Oligocene age (24-27 Ma).

The Sasa deposit is located within a metamorphosed terrain. The metamorphism could be, at least partly, attributed to Oligocene magmatic activity. Fluid inclusions hosted by quartz

bands within quartz-graphite schist suggest that metamorphism occurred under the influence of moderate saline hot fluids.

The skarn mineralisation, defined by the presence of Ca-Fe-Mg-Mn silicates, shows evidence of prograde and retrograde stages. Because there is no visible contact between the mineralisation and magmatic rocks, the deposit should be considered as a result of interaction of the mineralising fluids and the host carbonate rocks. The Mn-rich mineralogy is characteristic of the Pb-Zn skarn deposits emplaced distal from a magmatic source (e.g. Logan, 2000; Canet et al, 2009; Strmic Palinkas et al., 2013) and reflects remobilisation of Mn from the country rocks. The prograde minerals have an anhydrous character. According to the fluid inclusion data the prograde mineralisation was deposited from saline fluids at temperatures hotter than 400°C. At such temperatures the country rocks behave in a ductile fashion, sealing the system from significant infiltration of connate and meteoric waters (Fournier, 1992). Consequently, the prograde mineralisation occurred under a lithostatic regime. Predomination of pyroxenes and pyroxenoids over garnets suggests low oxygen fugacity (Gustafson, 1974) and the absence of Fe-sulphide minerals reflects low sulphur fugacity (Fig. 4).

The prograde mineral assemblage is overprinted by the retrograde silicates and hydrothermal (ore) mineralisation. Fluid inclusion data indicate that ore deposition occurred at lower temperature from moderately saline fluids. Cooling of the country rocks below 400°C may have moved the system from the ductile to the brittle regime, and allowed infiltration of cold ground water that would contribute to the increase in oxygen fugacity. Consequently prograde minerals are altered by a mixture of hydrous silicates and magnetite (Fig. 4). At the same time, the pressure drop from lithostatic to hydrostatic values would favour sulphur degassing from the cooling magmatic body. Increased sulphur fugacity promoted sulphide deposition (Fig. 4).

The post-ore stage of the mineralisation is characterised by deposition of a significant amount of carbonates. Lower homogenisation temperature and salinity suggest that post-ore fluids had decreased metal transport capability.

Ongoing geochemical investigations, including stable isotopes studies ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$), determinations of the REE content in pre-ore, syn-ore and post-ore carbonates, as well as microprobe data on skarn and ore minerals, will provide better insight into the genesis of the Sasa deposit.

Conclusions

Fluid inclusion studies recognised three major stages of mineralisation: (1) Metasomatic formation of skarn minerals during the prograde stage of mineralisation from saline and high-temperature fluid, probably of distal magmatic origin. The absence of mineralised contacts between the magmatic and the host rocks as well as the manganese-rich mineralogy reflects metasomatism by infiltration of the mineralising fluids into the host rocks, rather than mineralisation by diffusion-driven contact metasomatism. Formation temperatures hotter than 400°C, together with the anhydrous character of mineralisation, suggest a ductile lithostatic system; (2) Hydrothermal alteration of skarn minerals (ilvaite, magnetite, pyrrhotite, carbonates, quartz) followed by precipitation of ore and gangue minerals resulted from the mixing of magmatic and meteoric fluids during the retrograde stage as well as increase in both

oxygen and sulfur fugacity; (3) Deposition of post-ore gangue minerals, mostly carbonates, from cooler and slightly diluted fluids.

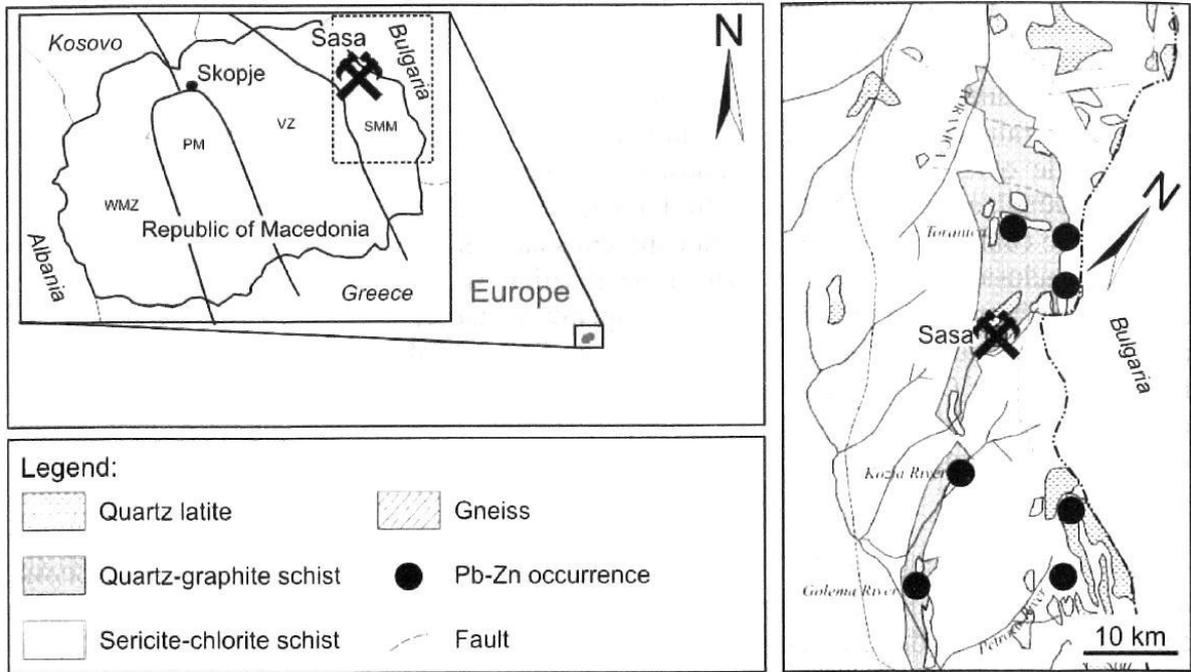


Figure 1. Regional geologic setting of the Sasa Pb-Zn skarn deposit within the Serbo-macedonian massif (simplified after Dimitrijevic, 1995, and Serafimovski and Aleksandrov, 1995). WMZ - Western Macedonian zone; PM - Pelagonian massif; VZ - Vardar zone; SMM - Serbo-Macedonian massif.

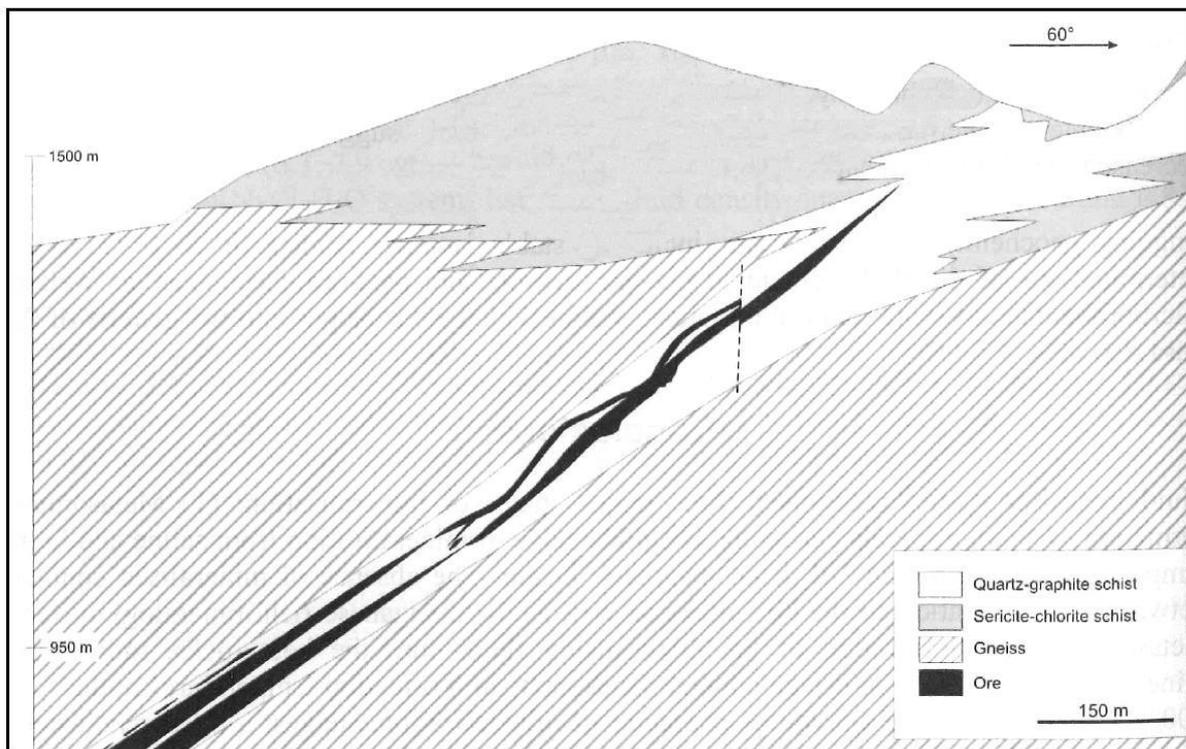


Figure 2. Cross section along an approximately northwest-southeast transect, showing the geometry of the Sasa Pb-Zn skarn deposit (simplified after Peltekovski, 2012)

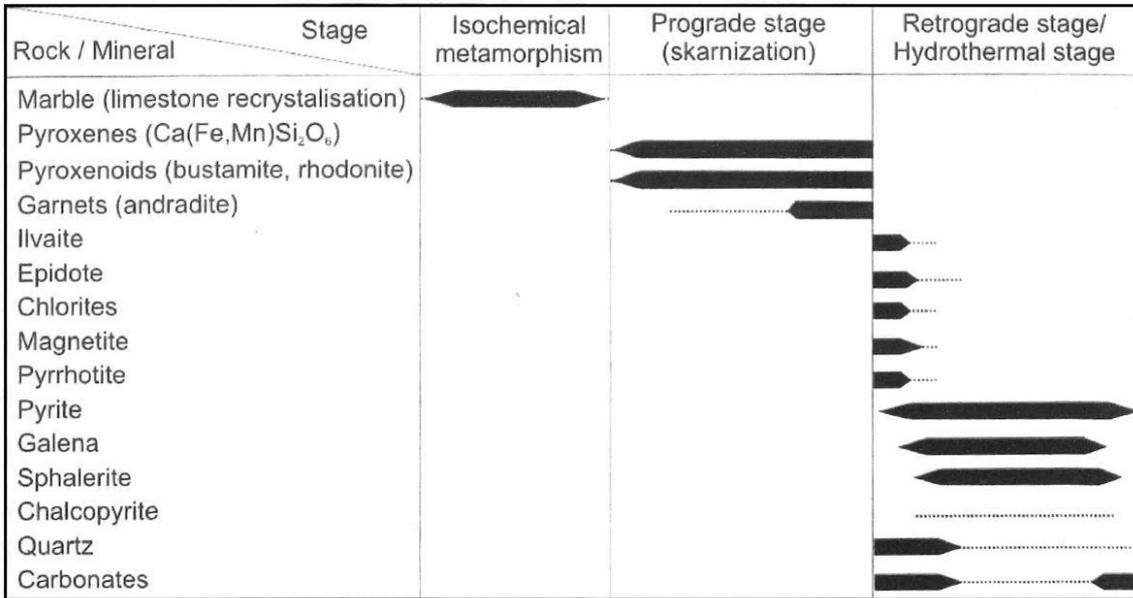


Figure 3. Paragenetic sequence of the Sasa Pb-Zn skarn deposit

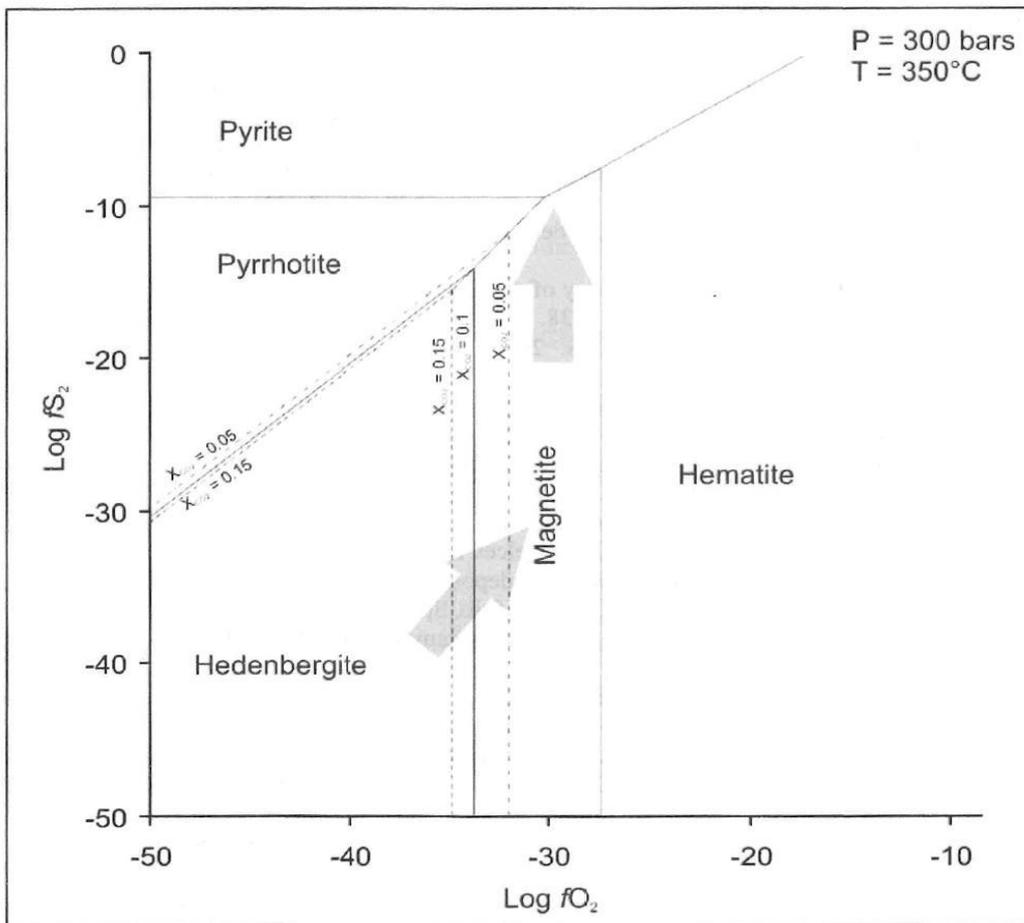


Figure 4. Log fO_2 vs. log fS_2 diagram for the system Ca-Fe-Si-S-OH, showing a proposed environment for the prograde and retrograde stages and sulphide deposition at the Sasa Pb-Zn skarn deposit.

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