The Ljubija geothermal field: A herald of the Pangea break-up (NW Bosnia and Herzegovina)

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ABSTRACT

The Ljubija ore deposits are the loci typici of siderite-barite-polysulphide deposits within the Inner Dinarides, Gemerides and Eastern Alps. Numerous sites of ore outcrops, smaller or larger ore bodies of mineralization, consisting of Fe carbonates, sulphides, barite and fluorite are scattered over an area of 150 square km. The half billion tons of iron ore resources occur as replacement in dolostones and limestones, and as open-space fillings (veins, veinlets) in phyllites and sandstones. The genesis of the Ljubija ore deposits has been explained as (i) syngenetic sedimentary-exhalative, (ii) hydrothermal-metasomatic in Middle Triassic time or (iii) hydrothermal replacement of sedimentary carbonates in Permian time. Basically two alternatives Variscan or Alpine metallogeny, frame the time of genesis from the Middle Carboniferous to the Middle Triassic. Genetic interpretation of the Ljubija ore deposits required convincing arguments based on recent achievements of plate tectonics. This contribution presents a set of new data on ore petrology, geochemistry, geology and time of formation. The Ljubija ore field could justifiably be termed the “Ljubija geothermal field”, due to its areal extent and the thermal characteristics of numerous ore deposits and occurrences within the Sana-Una Palaeozoic terrain. The Ljubija geothermal field marks the first signs of thermal instability of Pangea, revealing its breakdown along the deep fractures and heralding incipient intracontinental rifting, the first phase of the new Alpine Wilson cycle. The research reveals novel data on the P-T-X characteristics of ore forming fluids (microthermometry, ion chromatography, Raman spectrometry), sulphur isotopes, maturity of organic matter by vitrinite reflection, and age determination by 40Ar/39Ar and K-Ar methods. It adopts argumentatively all the estimated research parameters that constrain a justified genetic model.

1. INTRODUCTION

The Ljubija ore deposits are located in Northwest Bosnia and Herzegovina (44.55°N, 16.3°E; Fig. 1), at the margin of the Mesozoic carbonate platform, within the Sana-Una river Palaeozoic terrain, a part of the Inner Dinarides. Numerous sites of ore outcrops represent smaller or larger bodies of mineralization, consisting of Fe carbonate, sulphide minerals, barite and fluorite over an area of 150 square km. According to written documents, iron ore excavation in this area began in the years before Christ. The first miners were Phoenicians and Illyrians. Romans excavated and smelted iron ore for over 400 years in Ljubija and they transported iron bars by road and the Sana, Una, Sava, and Danube rivers to places for further processing. In the middle ages, iron ore was smelted by the Turks, as confirmed by the remains of primitive smelting plants in this area. In 1916, during World War I, modern mining of iron was started by the Austro-Hungarian monarchy and the production of iron ore has been ongoing for 99 years intermittently under the changing geopolitical divisions in this part of the Balkans. The potential reserves of iron ore have been estimated at 500 million tonnes with an average Fe content of 40-49 %. There are two types of iron ore, Fe-carbonates, siderites and ankerites, and secondary oxide ores with limonite, in proportions of approx. 1:1 (CVJIĆ, 2004).

Modern industrial mining in the Ljubija ore field (Adamuša ore deposit) began however, as a lead-zinc mine, and was temporarily aimed at mining barite and fluorite as well (CVJIĆ, 2001; CVJIĆ, 2004; GRUBIĆ & CVJIĆ, 2003). The Ljubija ore field includes four opencast mines (Adamuša, Tomašica, Omarska, and Vidrenjak) in an area of about 120 km². Besides iron, several other commodities such as zinc, lead, barite, and fluorite were also exploited.

The siderite occurs as a replacement in dolostones and limestones, and as open-space fillings (veins, veinlets) in phy-
llites and sandstones, with rare chalcopyrite and pyrite. The replacement ore has occasionally a zebra texture, with rhythmic banding of dark fine-grained and light sparry siderite, galena, sphalerite and quartz as open-space fillings. Large accumulation of limonite occurs as a secondary ore, named „brand“.

The genesis of the Ljubija ore deposits has been explained by a few streams of thinking, (i) as a syngenetic sedimentary-exhalative, or as washouts of lateritic crusts in the sedimentary basin from a dry land area in Carboniferous time (JURKOVIĆ, 1961; JURIĆ, 1971; ŠARAC, 1981), as (ii) of hydrothermal-metasomatic origin in Middle Triassic time (CISSARZ, 1951; JANKOVIĆ, 1977), or as (iii) a hydrothermal replacement of sedimentary carbonates in Permian time, recognized by KATZER (1925); and advocated by PALINKAŠ (1988; 1990), PALINKAŠ et al. (2003b) and co-workers BOROJEVIĆ ŠOŠTARIĆ (2004), STRMIĆ PALINKAŠ (2004), and STRMIĆ PALINKAŠ et al. (2009).

The Ljubija deposits are the loci typici of the siderite-barite-polysulfide deposits within the Inner Dinarides, Gemerides and Eastern Alps. Previous studies connected the formation of the deposits either to the Variscan or to the Alpine metallogeny and considered the Middle Carboniferous or Middle Triassic time of formation, respectively. However, the application of modern plate tectonic aspects of ore genesis is necessary for clarifying these controversial views on the origin of the mineralisation.

Variscan or Alpine metallogeny frame the time of genesis from the Middle Carboniferous to the Middle Triassic. Genetic interpretation of the Ljubija ore deposits required, however, convincing arguments based on the recent achievements of plate tectonics. A basic framework of Wilson cycles has been successfully established but difficulties have arisen from unresolved problems such as the time and space boundary between Variscan and Alpine tectogenesis. It was a source of ambiguity in the fundamental research of Ljubija ore genesis. A proper genetic model depends substantially on understanding of the geological evolution of the Dinarides. This contribution presents a set of new data on ore petrology, geochemistry and geology of the Ljubija ore field, or justifiably termed the „Ljubija geothermal field“ in this wider sense of meaning, due to its areal extent and thermal characteristics of numerous ore deposits and occurrences within it.

This paper presents new data on the P-T-X characteristics of ore forming fluids (microthermometry, ionic chromatography, laser Raman spectrometry), sulphur isotopes, maturity of organic matter by vitrinite reflection, and age determination by 40Ar/39Ar and K/Ar methods. It adopts argumentatively all the estimated research parameters which constrain a justified genetic model.
2. SUMMARY OF PREVIOUS STUDIES ON THE GEOLOGY AND ORIGIN OF THE LJUBIJA ORE DEPOSITS

The first description of the mineralization in the Ljubija basin came from KATZER (1910). He recognized the relationship between the Carboniferous limestone and siderite mineralization as a reaction contact, which was defined more precisely as a result of metasomatism, in his later work (KATZER, 1925). Thermal water enriched in iron bicarbonate, deposited siderite into the crevices of schists and limestones in the form of siderite veins with some sulphides and quartz. The solutions circulating through the networks of interconnected fractures within schists and limestone filled them with siderite. Simultaneously, solutions caused metasomatism of the limestones into siderite and more distant in fissures as ankerite. Later tectonics cut deposits into blocks and displaced them, into the present geological structure. The only exception, suggesting syngenic formation, was in Krivaja ore occurrences, in the Tomašica district. CISSARZ (1951) described the Ljubija mineral deposits as hydrothermal deposits of Palaeozoic age and related them to deep magmatism. All these descriptions are a short transposition of Katzer’s genuine observations and interpretations.

NÖTH (1952) supposed an intrusive-hydrothermal origin and Upper Palaeozoic age for the siderite veins and irregular ore bodies.

RAMOVIC (1957) distinguished three types of mineral deposits in the Ljubija area: (i) siderite veins hosted by Palaeozoic schists and related to metasomatism of limestones intercalated with smaller or larger quantities of clastic material, (ii) metasomatic ore bodies hosted by Palaeozoic limestones and (iii) secondary deposits formed by weathering.

JURKOVIC (1961) described Ljubija as marine sedimentary deposits of Upper Carboniferous age. The Fe carbonates, siderite and ankerite, were deposited as mud, together with some contributory clastic detritus, with irregular sedimentary proportions. Iron carbonates were cryptocrystalline and present-day textures were recrystallized through diagenetic processes.

JURIĆ (1971) supported a synsedimentary origin of the Ljubija mineral deposits.

JANKOVIĆ (1987) emphasized the importance of Permian-Triassic intracontinental rifting, with a magmatic paroxysm in the Middle Triassic. This is also the period when volcano-sedimentary deposits, skarns, massive sulphides, mercury deposits, bedded ferromanganese oxides, and MVT deposits were formed in the Dinarides. There is no distinction, however, between Permian early intracontinental rifting and Triassic advanced rifting stages, so the Ljubija deposits remain in the vast group of Triassic deposits. Their subterrestrial nature and lack of contemporaneous magmatism in the area did not attract attention as an argument for genetic modelling and discrimination from other Triassic deposits.

PALINKAŠ et al. (1985, 1988, 1990, 2010) applied a wide spectrum of analytical methods to the siderite-barite-sulphides mineral deposits hosted by Upper Palaeozoic sedimentary complexes of the Inner Dinarides. Special attention was paid to the Ljubija ore deposits. On the basis of fluid inclusion studies in quartz from three distinctive ore textures, e.g. dark massive siderite, zebra texture with dark and light siderite bands, and siderite veins in phylites and meta-sandstones, the deposits were unambiguously ascertained to be hydrothermal in nature. Boiling of ore forming fluids was recognised in the Žune-Dolina barite-fluorite ore body in the Ljubija ore field. It was used to reconstruct the depth of ore forming processes within one of numerous barite occurrences. Applied hydrostatic pressure determines variable depths of formation around 100-200 m. Based on the plumbotectonic modeling, PALINKAŠ (1985), suggested a new genetic model with a subterrestrial, hydrothermal convection cell and suggested the Permian as the formation time, related to the early intracontinental rifting. The model leaned on the contemporary plate tectonic reconstructions by CHANNEL et al. (1979), HORVATH & D’ARGENIO (1985), KOVACS (1984), and PAMIĆ (1984), which convincingly linked similar deposits along the present day edge of the carbonate platform, Trgovska Gora, Petrova Gora, Samoborska Gora (Croatia; PALINKAŠ et al., 2000, 2001, 2003a, 2010; BOROJEVIĆ ŠOŠTARIĆ et al. (2004, 2009), Rudabanya (Hungary; SZAKALL, 2001), Rudnyani (Slovakia, HURAI et al., 2002) and Erzberg (Austria, PROCHASKA et al., 1997) with an equivalent genesis in time and space.

BOROJEVIĆ ŠOŠTARIĆ (2004), on the basis of fluid inclusion studies, vitrinite reflection, 40Ar/39Ar and K-Ar dating supported a genetic model based on the subterrestrial hydrothermal convection cell and Permian time of mineralisation related to early intracontinental rifting events.

STRMIĆ PALINKAŠ et al. (2009) presented an extensive geochemical study of the ore and host rocks and made a significant breakthrough in the interpretation and confirmation of the previous studies. The study was focused on the stable isotope composition of barren and mineralized carbonates (δ13C and δ18O values), quartz (δ18O), and sulphur minerals (δ34S), the distribution of major and trace elements, including REE, in barren and mineralized carbonates and surrounding clastics, and organic geochemistry research (total organic carbon, hydrocarbons distribution, isotopic composition of individual alkanes (δ13C), and kerogen (δ13C, δ15N) of barren and mineralized samples.

3. GEOLOGICAL SETTING

3.1. REGIONAL GEOLOGICAL SETTING

The orogenic belt of the Dinarides stretches 700 km along the north-eastern margin of the Adriatic microplates (DERCOURT et al., 1993). In the north, this highly complex folded, thrusted and imbricated belt merges with the Southern Alps and in the southeast it extends into the Hellenides (PAMIĆ et al., 1998).The general strike of the folds, thrusts and knappes in the Central Dinarides is NW–SE, and the transport direction is towards the SW. The main tectonostatigraphic units of the Central Dinarides display a regular zonal pattern from stable Adria to Tisia. The historical division to “External” and “Internal” Dinarides, predates the plate tectonic concept, but it is still useful to discriminate tectonostratigraphic elements belonging to the passive and active Tethyan continental margins, respectively. The Dinaridic Palaeozoic complexes (PCs) occur in the Exter-
nal and Internal Dinarides. The PCs in the External Dinarides, close to or within the carbonate platform, acquired a comparatively autochthonous position relative to their Mesozoic cover. Within the Sava knappe, PCs are disrupted and allochthonous. They can be correlated tectonostratigraphically with those in the Southern Alps, and could be related to the passive continental margin of Gondwana.

The Palaeozoic formations with in a carbonate platform or adjacent to it, were not affected by high grade metamorphism. The PCs in the Sava knappe, including the Sana-Una PC, close to the ensialic Tisia block, however, underwent very low and low-grade metamorphism.

The Dinaridic metallogenic province developed as a result of opening of the Vardar and Dinaridic branches of the Neo-Tethyan Ocean and its closure by convergence of the African and Eurasian plates. The northern boundary of the Dinarides is related to the northern African margin (Adria–Apulia). The Dinarides embrace well-developed and preserved tectonostratigraphic units related to the Alpine Wilson cycle, in contrast to the neighbouring Alps where the indentation of Adria obliterated or blurred their regular distribution as a result of intensive tectono-metamorphic events (Fig. 1). The major stages of the cycle are: a) Permian early intra-continental rifting, b) Triassic advanced rifting, c) Jurassic oceanization, d) Cretaceous subduction, e) Palaeogene collision; and f) Late Palaeogene/Neogene post collision and extension followed by orogenic collapse.

The metallogeny of the Dinarides, based on the principles of plate tectonics, has been upgraded over recent decades. Each stage creates characteristic ore deposits related to specific geological environments. Thermal events in the stage of early intra-continental rifting were in response to the high heat flow caused by thermal doming and thinning of the continental crust. It generated numerous hydrothermal cells in the thick piles of the postVariscan overstep successions. In addition, the incipient magmatism penetrated the Variscan basement of Pan-Gaea (PALINKAŠ et al., 2001; PALINKAŠ et al., 2010; ROT-TURA et al., 1998). This stage produced numerous hydrothermal siderite-barite-poly sulphide deposits, including the Ljubija ore deposits. They are the *loci typici* among the other equivalent deposits within the Dinarides, Gemerides and Eastern Alps (Fig. 1), discriminated distinctly from the deposits of the advanced rifting stage occurring in the Middle Triassic (JANKOVIĆ, 1977, 1986; PETRASCHKE, 1977; PAMIĆ & JURKOVIĆ, 1997; HEINRICH & NEUBAUER, 2002; JURKOVIĆ, 2003).

### 3.2. THE SANA-UNA PALEOZOIC TERRANE

The Sana-Una PCs mostly consist of Carboniferous flysch sequences (*sensu* KARAMATA et al., 1997). The flysch is overlain by bedded limestones with conodonts of late Viséan age. A new (“post-Variscan”) sedimentary cycle started with the accumulation of shallow water limestones (Stara Rijeka formation) of Bashkirian age, which rarely yield marine shallow water fossils and fusulinids. The overlying Eljdište formation (sand and marly limestones) includes a rich brachiopod fauna. In the Una region, the Blagaj formation, covering the Carboniferous flysch, is an olistostromatic unit, termed “wild flysch” *sensu* GRUBIĆ et
al. (2000), with Devonian, Lower and Middle Carboniferous limestone clasts containing foraminifers, corals and conodonts, and is correlated with the “molasse” type Ivovik formation from the autochthonous Jadar Block Terrain. Disconformities between the Blagaj formation and the Carboniferous flysch have not been proven. These sequences are covered by Middle Permian clastic sediments (red breccias and conglomerates, sandstones, shales and evaporites) followed by Lower Triassic formations (Fig. 2) (PROTIĆ et al., 2000; GRUBIĆ & PROTIĆ, 2003; KRSTIĆ et al., 2005).

3.3. GEOLOGY OF THE ORE DEPOSITS
The Ljubija ore deposits are placed within the Javorik flysch formation, which is well exposed within the Adamuša and the Tomašica opencast mines (GRUBIĆ et al., 2000; GRUBIĆ & CVIJIĆ, 2003). At Adamuša, the upper part of the lower flysch horizon contains irregular limestone blocks (olistostromes).
Siderite with a zebra texture and sparry ankerite occur mostly within the siderite-metaclastics horizon. The Javorik flysch formation at the Tomašica opencast mine is represented by six horizons. The siderite-limonite horizon contains dark-grey massive to yellowish coarse-grained siderite and gossan composed of porous limonite. The olistostrome horizon comprises a wide variety of carbonates including dark massive limestones, dolomitic limestones, dolostones, Fe-enriched limestones, dark grey massive ankerite, and dark grey massive siderite locally weathered to porous limonite.

3.4. ORE MINERALIZATION

The Ljubija ore field comprises the large iron ore deposits of Adamuša, Tomašica, Omarska, and Vidrenjak, and a number of smaller ones. Important reserves occur in the secondary haematite-limonite ore, locally named “brand”, weathering products of carbonate ores. Beside iron ores important commodities are barite and fluorite occurrences, mined in the past, scattered over the whole Palaeozoic terrain.

PALINKAŠ (1988) recognized three major types of primary iron ore textures: (1) dark massive siderite and ankerite, (2) zebra siderite composed of dark massive and light sparry siderite bands, and (3) sparry siderite veins hosted by phylolithes and metasandstones (Figs. 3, 4, 5). A simplified stratigraphy for the paragenetic sequences of the Ljubija deposits is shown in (Fig. 6). Dark grey massive siderite and ankerite occur as replacements within limestone and dolostone blocks. The contacts between Fe carbonates and host carbonates are obscure. All carbonates mentioned above are dark grey in colour due to the presence of organic matter (STRMIĆ PALINKAŠ et al., 2009). A few millimetre thick white calcite veins, cross-cut dark grey limestones and are more abundant near Fe mineralisation. Similar, siderite, quartz and white calcite veins locally intersect the dark grey siderite. White sparry ankerite rarely occurs at the contact with dark massive siderite. Zebra siderite is characterized by the alternation of dark massive and light sparry siderite bands. Cavities infilled with white sparry ankerite, quartz, sulphides, and secondary phyllosilicates are common. Sparry yellowish to brownish-ochre siderite veins, thick a few decimetres, hosted by phylolithes and metasandstones, represent the latest phase of mineralization.

The contact between siderite and fine-grained clastics is marked by the presence of sulphides, mainly chalcopyrite. In the eastern part of the Ljubija ore field, economically important quantities of galena, tetrahedrite, chalcopyrite, and sphalerite have been exploited in the past.

Barite and fluorite ores are present mainly as E–W oriented veins that cross-cut the Palaeozoic dolostones. The Žune-Dolinac vein type deposit was the object of this study, and was described by JEREMIĆ, 1958; (Fig. 7). A barite vein is hosted by dolostone and phylolithes, close to the Scythian shales and sandstones. The vertical vein reaches 3-9 m in thickness. Barite incorporates coarse fragments of the host rocks and fluorite and quartz accumulations close to the walls. The structure and texture of the vein bears some elements of hydraulic fracturing, an important prerequisite for boiling of hydrothermal fluid, as recognized in the fluid inclusion studies.

4. ANALYTICAL METHODS

4.1. MICROTERMOMETRIC MEASUREMENTS

Microthermometric measurements were performed on double polished 0.3 to 0.5 mm thick quartz wafers and 0.05 to 0.1 mm thick fluorite wafers using a Leitz-Wetzlar microscope coupled with a Chaixmeca cooling and heating stage, operating between -180 and +600°C. Objective lenses P25/0.50 were used for
barite and (viii) 2 galena samples from vein-type siderite (Adamuša locality); (v) 3 quartz, (vi) 4 siderite, (vii) 2-
-60 and +10°C. Fluid inclusions were classified according to the criteria summarised by ROEDDER (1984) and SHEPHERD et al. (1985). The salinity of aqueous inclusions was calculated by temperatures of ice and hydrohalite melting using the FLUIDS computer program for NaCl-CaCl, bearing aqueous solutions at low temperatures (BAKKER, 1999). Calculations are based on purely empirical best-fits, with no fundamental thermodynamic modelling involved (NADEEN, 1996). Isochores were calculated by use of the computer program ISOC (BAKKER, 2003) using the equation of state by ZHANG & FRANTZ (1987) corrected for the volumetric properties of quartz (HOSIENI et al., 1985). The salinity of aqueous inclusions with the addition of CO₂ at the vapour phase is calculated according to COLLINS (1979).

Fluid inclusions are measured in: (i) quartz from quartz veins within dark metasomatic siderite (Adamuša locality); (ii) quartz and siderite from metasomatic zebra siderite (Adamuša locality); (iii) quartz and siderite from vein-type siderite (Adamuša locality), and (iv) fluorite from fluorite-barite vein (Žune-Dolinac locality).

4.2. IONIC CHROMATOGRAPHY, BULK CRUSH-LEACH ANALYSIS

Bulk crush-leach analyses were performed by ion chromatography at Montanuniversität Leoben. Leachates were prepared according to the technique modified after BOTTRELL et al. (1988). A Dionex DX-500 system was used for halogen analyses. Cations were measured in the aliquots of the same solution using standard atomic absorption spectrometry. Bulk fluid inclusion composition is analysed in: (i) 3 quartz, (ii) 6 siderite, (iii) a single ankerite and (iv) galena sample from metasomatic zebra siderite (Adamuša locality); (v) 3 quartz, (vi) 4 siderite, (vii) 2 barite and (viii) 2 galena samples from vein-type siderite (Adamuša locality); (ix) 2 dark host limestone; (x) a single bladed calcite (Adamuša locality); (xi) 5 fluorite and (xii) 7 barite samples from fluorite-barite vein (Žune-Dolinac locality). Equilibration temperature between ore forming fluids and the host rocks was calculated using the equation of CAN (2002), GIGGENBACH (1988), FOURNIER & TRUESDELL (1973), and VERMA & SANTOYO (1997) for geothermometric pairs Na/K, K/Mg, Na/K/Ca and Na/Li. The evaporation trend of the sea water is taken from McCAFFERY et al. (1987), and Permian and recent water from HORITA et al. (1991).

4.3. RAMAN SPECTROSCOPY

The Dilor LabRAM instrument equipped with double Nd-YAG 100 nW (532 nm) and HeNe (613 nm) lasers was used at the Institute für Geowissenschaften, Mountanuniversität, Leoben. The instrument is connected to an Olympus BX-40 equipped with Linkam THMS 600 heating-freezing stage, operating between -180 and +600°C. Data were analysed using LABSPEC software. Laser Raman Spectroscopy was performed on fluorite samples from fluorite-barite vein (Žune-Dolinac locality).

4.4. VITRINITE REFLECTION

The analyses have been performed using a Leitz-MPV3 microscope-photometer, in oil, under magnification of 500× at the Organic geochemistry laboratory, INA Oil Company, Zagreb.

Samples are powdered, treated with HCl (3 days) and HF (3 days), washed and dried. Concentrated organic matter has been mixed with immersion oil and examined under the photometer. Synthetic spinel (R = 0.42 %) and garnets (R = 0.82 %; R = 1.76 %) are used for calibration. Mean random vitrinite reflectance (R.o in %) shows a strong correlation (r²=0.7, n=600) with maximum burial temperature (Tmax in °C). These data are modelled after BERKER & PAWLEWITZ (1994) by the linear regression equation T = (lnR.o + 1.68)/0.0124, R.o = degree of vitrinite reflectance. Vitrinite reflection is determined on (i) 6 host limestone samples; (ii) host siltstones (iii) host sediment containing sulphides, and (iv) siderite samples from a metasomatic ore (all samples from Tomašica locality).

4.5. SULPHUR ISOTOPES

Sulphur isotope analyses of sulphides and sulphates selected exclusively from the primary ore samples not from the sulfides in the host rocks, were performed at the University of Lausanne using a Carlo Erba 1108 elemental analyzer (EA) connected to a Thermo Fischer Delta S IRMS (EA/IRMS). The sulphur isotope values are reported relative to a Vienna-Cañon Diablo troilite standard (V-CDT). The reproducibility, assessed by replicate analyses of laboratory standards (pyrite, synthetic mercury sulphide, working; barium sulphate), was better than ±0.2‰ (STRMIĆ PALINKAŠ et al., 2009).

4.6. GEOCHRONOLOGY

K/Ar age dating

K/Ar age dating of the whole rock samples, 21 samples of metaclastic rocks and 7 samples of volcanic rocks, are performed at the Institute of nuclear physics, Debrecen, Hungary, after the procedure described by ODIN et al. (1982).
Figure 8. A) Dark and light bands in the Zebra texture (photomicrographs, crossed polars). The dark band consists of nonplanar, closely packed anhedral siderite crystals with curved, lobate and serrated boundaries. The light band is made of saddle siderite characterized by curved crystal faces or crystals with sectorial growth. The sweeping extinction indicates a warped crystal lattice. The saddle texture forms under hydrothermal conditions in the voids, between dark bands; B) The void-filling process starts with saddle siderite lining the walls and succeeded by minerals in the following order: ankerite, sulphides and quartz, not necessarily with the presence of all the successive members. The residual zones in microgeodes on the photomicrographs are lined with curved saddle siderite crystals and those with sectorial growth are filled with quartz, the object of fluid inclusion study; C) Ankerite (blue-green) replaces micritic dark limestones (pinkish red) as a sharp ferritization front (crossed polars, the colour hues come from alizarin red-S and Kferricyanide tests. Detailed description of the staining method of WARNE, 1962); D) Metasomatic replacement of late diagenetic dolomite by Fe-carbonate. The late diagenetic unimodal, planar-e dolomite, is mimically replaced by non-planar, unimodal ankerite, with curved and serrated intercrystalline boundaries. The crystal boundaries of ankerite grains gradually fade into a shapeless mass of siderite (plain-polarized light), E) Advancing sideritization front in the greywacke sandstone, with sparry siderite, develops an exotic aggregation of detrital grains. The virtual, quartz-like shape of the detrital aggregation is framed and constrained by sparry siderite crystal faces; F) An advancing sideritization front pervades greywacke sandstone forming fine grained sideritic cement. Texturally immature greywacke contains poorly sorted, angular grains of quartz and lithic fragments mostly metamorphics, slates, cherts and quartzites, set in a compact clay-fine matrix and detrital carbonaceous matter. The greywacke sandstone and black shales, a part of the „wild flysch“, originated as a product of strong turbidity currents at the edges of the continental shelves.
Figure 9. A) Siderite veins were formed in the late stage of mineralization in which ore bearing fluids, penetrated into the clastics, along brittle fractures and deposited sparry siderite in the open veins. While the quartz teeth grow inward from the vein walls, sulphides, pyrite, chalcopyrite and traces of galena and sphalerite fill open-spaces in the vein centre; B) Void filling processes in the light band zebra siderite proceeds with increased concentration of metasomatically released ions, Ca$^{2+}$, Mg$^{2+}$, and silica leached from incorporated clay particles in dark bands. Increased sulphur fugacity is marked by co-precipitation of finegrained pyrite and traces of galena as a veneer within sparry siderite, the major sulphide phase; C) and D) Void-filling paragenesis in the light bands of the zebra siderite; E) The host rocks underwent pervasive sideritization followed by silicification, recognized by strain fringes and strain shadows around the pyrite crystals; F) Hydraulic fracturing of galena by silica rich fluids is evidenced by jig-saw-fit texture with fragments stuck together by silica cement. Absence of grain boundary migration and rotation, evidenced by near parallel cleavage among the galena grains, which already past static recrystalization (triplet junction), is a sign of low temperature recrystallization in the following mineralization history; G) Penetrative fabrics might have been developed by crystallization pressure in veins, evidenced by stylolites between sparry siderite grains, or as low grade metamorphism in the presence of water when pressure solution was dominant (MERINO et al., 2006).
rather than by restricted diffusion sensu KORZHINSKII sustained by infiltration of an iron rich hydrothermal fluid, leaves open space for sparry siderite in the zebra texture. Replacement is lume of siderite and precursor limestone/dolomite, leaves open volume replacement of dolostones and limestones by Fe-saturated solution (Fig. 3). Metasomatizm is recongnized by the formation of plateau ages was carried out using ISOPLOT/EX software (LUDWIG, 2001, 2005).

5. RESULTS

5.1. PETROGRAPHY

Transmitted and reflected light microscopy supports the genetic interpretation of the ore textures (Figs. 8, 9). The three major type of textures are (i) dark grey massive siderite, (ii) zebra texture with dark and light siderite bands, and (iii) vein siderite.

(i) Dark massive siderite was formed by volume-per-volume replacement of dolostones and limestones by Fe-saturated solution (Fig. 3). Metasomatizm is recognized by the unimodal size of siderite grains, with nonplanar boundaries, non-mimical replacement of dolomite alloches, and traces of indigenous organic matter which still gives a dark colour to the bands. The nonplanar boundaries are characteristic of growth at elevated temperature and/or high supersaturation, as neomorphic of a precursor dolostone or limestone (Fig. 8D) (SIBLEY & GREGG, 1987).

(ii) Formation of the zebra texture is a combination of two different processes, replacement as simultaneous solution and deposition of siderite, in the manner of atom-per-atom, expressed by reactions 1) and 2).

1) \[ \text{CaCO}_3 + \text{Fe}^{2+} = \text{FeCO}_3^- + \text{Ca}^{2+} \]
\[ \Delta V_{\text{reac}} = -22\% , \Delta G_{\text{reac 500}} = -27.95 \text{kJ} \]
\[ \log K_{\text{reac 500}} = 2.91 , T = 500 \text{ K} \]
\[ \Delta G_{\text{reac 500}} = -27.95 + 9.59 \log a_{\text{CO}_3}^- - 9.59 \log a_{\text{Fe}^{2+}} \]

2) \[ (\text{Ca,Mg})\text{CO}_3 + 2\text{Fe}^{2+} = 2\text{FeCO}_3^- + \text{Ca}^{2+} + \text{Mg}^{2+} \]
\[ \Delta V_{\text{reac}} = -11\% , \Delta G_{\text{reac 500}} = -43.7 \text{kJ} \]
\[ \log K_{\text{reac 500}} = 4.5 , T = 500 \text{ K} \]
\[ \Delta G_{\text{reac 500}} = -43.7 + 9.59 \log a_{\text{CO}_3}^- + 9.59 \log a_{\text{Mg}^{2+}} - 19.18 \log a_{\text{Fe}^{2+}} \]

It is accompanied by a significant change of volume, \( \Delta V_{\text{reac 500}} = -22\% \) and -11%. A difference between the molar volume of siderite and precursor limestone/dolomite, leaves open space for sparry siderite in the zebra texture. Replacement is sustained by infiltration of an iron rich hydrothermal fluid, rather than by restricted diffusion sensu KORZHINSKII (1968).

The succeeding step was the crystallization of saddle style siderite in open voids from Fe-impoverished and Ca/Mg2+-enriched fluids. This highly variable concentration and composition of the fluid is a cause for the growth of curved crystal faces and sweeping extinction of saddle siderite (Fig. 4A, 8B; 9D) (SAERL, 1989):

3) \[ \text{Fe}^{2+} + \text{CO}_3^2- = \text{FeCO}_3^- \]
\[ \Delta G_{\text{reac 500}} = -12.26 \text{kJ} \]
\[ \log K_{\text{reac 500}} = 1.27 , T = 500 \text{ K} \]
\[ \Delta G_{\text{reac 500}} = -12.26 - 9.59 \log a_{\text{Fe}^{2+}} - 9.59 \log a_{\text{CO}_3}^- \]

This is a typical of open space filling processes identified by many vugs and cavities, coarsening of minerals from the walls of the voids to their centre, comb structure or interdigitated vuggy zone, and symmetrical banding. The void-filling process starts with saddle siderite, lining the walls and proceeds in the following sequential mineral order: ankerite, quartz and sulphides, not necessarily with the presence of all the successive members (Fig. 9B, 9D).

Some thermodynamic consideration of the free energy change (\( \Delta G_{\text{reac 500}} \)) at 500 K (227°C) confirms the preference of reactions (1) and (2) during the early metasomatic phase, and the formation of dark bands. The increase of Ca2+/Mg2+ concentration increases \( \Delta G_{\text{reac 500}} \) and supports the tendency of reaction (3) to dominate during crystallization of light sparry siderite bands. The presence of CO2 (recognized at the trace level by Raman spectroscopy) is an irrelevant variable in the reactions (1) and (2) and equilibria is controlled by the Fe2+/Ca2+ ratio. Reaction (3) proceeds under neutral and slightly alkaline conditions, buffered by carbonate host rocks and the dominant species are HCO3- and CO32-, and fugacity of CO2 is negligible. It is not the case in the siliciclastic host rocks, during development of barite vein deposits, whereas liquid CO2 also participated in the control of pressure and boiling (BOROJEVIĆ ŠOSTARIĆ et al., 2009).

(iii) Siderite veins, another structural facet of the ores, were formed by mineralizing fluids, enriched in Fe-bicarbonate ions by widespread collateral metasomatic reactions (Fig.5). They penetrated into the shales, silt and sandstones, along planar discontinuities caused by fault slip events under brittle conditions and deposited sparry siderite in open veins with fuzzy boundaries (Fig. 9E). The host rocks underwent pervasive sideritization during the mineralization phase followed by silicification, recognized by antitaxial strain fringes and strain shadows around the rigid pyrite porphyroblasts. Characteristic dilatation sites were formed by silica rich fluids at low-temperature (200-300°C) and high fluid pressure (OLIVER & BONS, 2001). Enrichment of the silica component in the fluids came from the alteration of phyllosilicates and residual clay particles in the carbonate precursor. The best conduits of the fluids were dark seams, composed of organic detritus, phyllosilicates, and insoluble material, deformed around a rigid object, e.g. a corroded detrital quartz grain (Fig. 9E). Hydraulical fracturing of galena is another aspect of the high fluid pressure (Fig. 9F). The galena triple-junction system, forms a hexagonal network of recrystallized grains, which underwent fracturing, sustaining a jig-saw-fit texture with fragments stuck together with silica cement (lower corner of Fig. 9F).
The quartz grain shows clear signs of dynamic recrystallization by development of subgrains and gradual bulging (STIPP et al., 2002). Beside fluid inclusion data, deformation lamellae in siderite crystals could be used as an approximate temperature gauge of vein formation. Narrow straight twins (Fig. 9E, type I, BURKHARD, 1993) indicate temperatures below 170°C. The tabular thick twins, which can be optically resolved (Fig. 8C, type II, >1µm, FERRIL et al., 2004), dominate above 200°C and up to 300°C. Penetrative fabrics which might be related to the crystallization pressure in veins, are evident by stylolites between sparry siderite grains (Fig. 9G, MERINO et al., 2006). The siderite walls of the vein include quartz-comb textures grown inward, accompanied by pyrite, chalcopyrite, traces of galena and sphalerite (Fig. 9A). Chert and schist fragments in the greywacke are inherited porphyroclasts from the Variscan high-grade metamorphic provenance, incorporated during the turbidite phase (Fig. 8F).

5.2 FLUID INCLUSION STUDY

Fluid inclusion studies in quartz from quartz veins within the dark metasomatic siderite (Adamuša locality)

Quartz veins are several mm to 10 cm thick containing milky white quartz. At several places open space cavities are found containing half-transparent idiomorphic quartz, several millimetres in size. Fluid inclusion petrography shows the presence of primary and pseudosecondary liquid-rich inclusions of a uniform degree of fill. Eutectic melting occurs at temperature ranges from -39.4 to -21.0°C. Ice melting in the temperature range from -23.9 to 1.5°C shows salinities from 23.4 to 2.1 wt.% NaCl equiv. Homogenization by vapour disappearance occurs in a temperature range from 80 to 160°C.

Fluid inclusion study in quartz from cavities within metasomatic zebra siderite (Adamuša locality)

The investigated quartz follows precipitation of light zebra siderite, and precedes the precipitation of sulphides (galena, sphalerite, chalcopyrite, pyrite) within the cavities. Quartz crystals are idiomorphic, transparent up to 1 cm in size. They contain numerous fluid inclusions which are located within growth zones and classified as primary according to the criteria outlined by ROEDDER (1982): Type I; Liquid-rich four phase, aqueous inclusions containing a halite daughter mineral, also sometimes contain an unknown anisotropic daughter mineral, \((L+V+S_{hal}±S_{A})\); Type II; Liquid-rich three phase aqueous inclusions, containing an unknown anisotropic daughter mineral \((L+V±S_{hal})\), high salinity; Type III; Inclusions contain immiscible liquids \((L_1±L_2)\). Type IV; Monophase liquid

Figure 10. Fluid inclusions in quartz from void-fillings in the zebra siderite, and mesothermal siderite-quartz veins in the greywacke (Ljubija/Adamuša). a) „Zebra siderite”: primary \((L+V+S_{hal}), (L+V+SA)\) and \((L+V)\) inclusions, Type I and II; b) Array of primary inclusions \((L+V)\), Type II with the same degree of filling; c) Array of primary \((L+V+S_{hal})\) inclusions; d) Primary \((L+V)\) and \((L+V+SA)\) inclusions, Type II; e) Primary inclusions with immiscible fluids \((L_1±L_2)\), Type III; f) Primary inclusions \((L+V+S_{hal})\), Type I. Mesothermal siderite-quartz veins: g) Quartz with marked primary \((P)\), pseudosecondary \((PS)\) and secondary \((S)\) inclusions; h) Array of liquid inclusions, Type IV; j) Primary \((L+V)\) and \((L+V+SA)\) inclusions, Type III (see text).
inclusions, liquid inclusions containing a halite daughter mineral (L±V±S_{hal}) and (V); Monophase gas inclusions (Fig. 10). The study was focused on a primary assemblage of aqueous inclusions. Within halite bearing inclusions eutectic melting occurs in a temperature range from -65.7ºC to -51.0ºC, followed by ice melting in the temperature range from -44.2ºC to -21.6ºC, and hydrohalite melting (transformation to halite) at a temperature range of -40.9ºC to +0.1 ºC. Under metastable conditions, hydrohalite exists up to 22ºC in a few inclusions. In addition, several inclusions show melting of an unknown, optically isotropic phase at a temperature range from -35.0ºC to 36.1ºC. Total homogenization occurs in the temperature range from 201ºC to 259ºC, showing salinities from 35 to 39 wt.% NaCl equiv. During homogenization, inclusions show different behaviours: (i) the disappearance of vapour follows the disappearance of halite; (ii) the disappearance of halite follows the disappearance of vapour, or (iii) halite and vapour disappear simultaneously.

The case of simultaneous disappearance of vapour and halite occurs at temperature ranging from 220º to 259ºC. The existence of three and the disappearance of two phases (L+V+S_{hal}→L) in the NaCl-H₂O system (T_h total), is univariant equilibria which enables determination of fluid pressure and salinity (32.9-35.3 wt.% NaCl equiv.). Thermochemical properties of the H₂O-NaCl saturated solutions (HAAS, 1976) constrain the pressure at 16.5 bars or 32.7 bars, respectively. Halite undersaturated inclusions show eutectic melting at temperatures ranging from -60º to 51ºC, followed by hydrohalite melting at temperatures ranging from -27.5º to -20.8ºC. Ice melting in a range from -23º to -20.8ºC. Ice melting in a range from -23º (undercooling below 21.2 ºC) to -2.5ºC, indicate salinities from 22.5 to 3.5 wt. % NaCl equiv. They all homogenized by vapour disappearance, in the temperature range of 11º - 210ºC.

Figure 11. Histograms of microthermometric measurement for the inclusions from quartz in zebra siderite and quartz from mesothermal siderite veins. The histograms present frequency of A) Eutectic temperature (T_e); B) Hydrohalite melting temperature (T_m hyd); C) Final ice melting temperature (T_m ice); D) Salinity; and E) Total homogenization temperature (T_h).
The extremely low eutectic temperature ($T_e$) observed in some quartz samples could be interpreted as a metastable eutecticum in CaCl$_2$-NaCl-H$_2$O or MgCl$_2$-NaCl-H$_2$O systems (DAVIES et al. 1990), but can also be explained by the presence of Li$^+$ ions in ore-bearing fluids as well.

**Fluid inclusion study in siderite from metasomatic zebra siderite (Adamuša locality)**

Fluid inclusions have been studied in siderite crystals separated from light bands within metasomatic zebra ore. Most inclusions in siderite crystals are two-phase (L+V) and can be defined as primary. They acquire negative crystal, or irregular, three-dimensional shapes and are distributed irregularly within the crystals. Primary inclusions show consistent liquid–vapour (L/V) volume ratios, which indicate entrapment of a homogeneous fluid. The eutectic temperature spans the range between -53$^\circ$C and -49.9$^\circ$C, suggesting a CaCl$_2$-NaCl-H$_2$O system. Hydrohalite melting occurs in the narrow range between -31.1$^\circ$C and -29.0$^\circ$C. Ice melting temperatures recorded in an interval from -12.0$^\circ$C to -10.1$^\circ$C corresponds to a salinity between 14.1 and 16.0 wt.% NaCl equiv. Total homogenization, always into the liquid phase, ranges between 147 and 164$^\circ$C. Secondary two-phase (L-V) inclusions are recorded as well, but they have not been measured due to their small size.

**Fluid inclusion study in quartz from hydrothermal quartz-siderite veins (Adamuša locality)**

Vein-type siderite contains two types of quartz crystals: irregular, milky white quartz which does not contain measurable FIs, and semi-transparent quartz-siderite intergrowth, containing Type III; Primary liquid-rich inclusions, with or without an anisotropic daughter mineral, (L+V±S$_A$); Type IV; Pseudosecondary liquid-rich inclusions (sometimes with an anisotropic daughter mineral), (L±V±S$_{hal}$) generating vapour bubbles after the freezing run. This is either a sign that our fluid inclusions were stretched during the freezing run or just metastability is affecting the re-appearance of the vapour phase after freezing.

Primary inclusions show eutectic melting at temperatures ranging from -63$^\circ$C to -43$^\circ$C, followed by hydrohalite melting at temperatures from -31.0$^\circ$C to -21$^\circ$C. Salinities calculated from the ice melting temperatures (-17.7$^\circ$ to -7.1$^\circ$C) ranged from 20 to 11.5 wt.% (in those inclusions with the presence of a vapour phase at room temperature) NaCl equiv. Several inclusions show eutectic melting at -4.7$^\circ$C and gas hydrate melting at +10$^\circ$C, suggesting the presence of bicarbonates and CO$_2$ hydrates. Homogenization was in the range from 97$^\circ$ to 250$^\circ$C. Pseudosecondary liquid-rich inclusions show eutectic melting at temperatures between -60$^\circ$ to -44$^\circ$C, followed by hydrohalite melting between -34$^\circ$ to 22$^\circ$C and ice melting between -7.1$^\circ$ to -1.4$^\circ$C. Calculated salinities ranged from 2.0 to 9.0 wt.% NaCl equiv., whereas homogenization temperatures (by vapour disappearance) range from 90$^\circ$ to 133$^\circ$C.

**Fluid inclusion study in siderite from hydrothermal quartz-siderite veins (Adamuša locality)**

Several primary fluid inclusions have been recorded in sparry siderite crystals from siderite veins hosted by the Carboniferous shale. A eutectic temperature around -52$^\circ$C suggests a CaCl$_2$NaCl-H$_2$O system. Hydrohalite melting spans an interval between -29.5$^\circ$ and -21.0$^\circ$C. Ice melting temperature recorded between -4.2$^\circ$ and -3.5$^\circ$C points to a salinity between 5.7 and 6.7 wt.% NaCl equiv. Homogenization into the liquid phase occurs in the range from 120$^\circ$ to 127$^\circ$C.

Results of microthermometric measurements on quartz from the three principal types of the Fe mineralisation in Ljubija/Adamuša are presented in Fig. 11.
A ternary diagram NaCl-CaCl$_2$-H$_2$O (Fig. 12) for all types of FIs in the Ljubija/Adamuša deposit shows a shift of data points from the NaCl-H$_2$O line toward the CaCl$_2$-H$_2$O according to the dominant metasomatic process. The diagram also emphasizes the wide distribution of salinity from very low to very high. An explanation is suggested by the diagram $T_m$ vs. salinity (Fig. 13). The diagram shows a wide range of high to low salinity, and a narrow but declining trend of $T_m$, from high to low, which suggests the mixing of the two types of contrasting fluids. The high temperature, high salinity, Type I, true evaporitic brine, and the low temperature, low salinity Type II, indicating that the sea water not only evolved by evaporation. Mixing happened a few hundred metres close to the topographic surface. A P-T diagram with isochores calculated by the ISOC computer program is presented in Figure 14.

Fluid inclusion study in fluorite from a fluorite-barite vein (Žune-Dolinac locality)

Purple fluorite crystals with well developed growth zones were selected for the fluid inclusion analysis. The petrography revealed the presence of various inclusion types, classified as primary: type I; Liquid-rich aqueous inclusions containing a halite daughter mineral and an unknown anisotropic daughter mineral, high salinity (L+V+Shal±SA) (Fig. 15B), Type II; Liquid-rich aqueous inclusions containing an anisotropic daughter mineral, high salinity (L+V±SA), (Fig. 15B), Type III; Liquid-rich aqueous inclusions (L+V), low to moderate salinity, (Fig.15D), Type IV; Vapour rich aqueous inclusion (V+L±SA), low to moderate salinity, possibility of leaking (Fig. 15), Type V; Vapour rich with halite daughter mineral (V±L+Shal) (Figs. 15E,F), Type VI; Two immiscible liquids (L$_1$+L$_2$), no sign of fluorescence, neither freezing, Type VII; Vapour inclusions (V) (Fig. 15F), Type VIII; Solid inclusions (S$_A$) (Fig. 15C), anisotropic mineral present in the Types I, II, and IV. Type IX; Liquid inclusions (L), (important note that all numbered types coexist within one single grain, Fig. 16).

Fluid inclusion study was performed on liquid rich and vapour rich inclusions with or without daughter minerals. Halite saturated aqueous inclusions (+ unknown anisotropic daughter mineral) Type I and II show first melting at temperatures from -66.4º to 49.0ºC, followed by ice melting in the tem-
temperature range from -41.2 to -21.6°C and hydrohalite melting/ transformation between -35.5º to -1.2ºC. During heating, within the majority of the inclusions, the vapour phase disappeared first, followed by halite dissolution in the temperature range between 125º to 275ºC. Type IV, vapour rich aqueous inclusions show eutectic melting in a temperature range from -56º to -48ºC, followed by hydrohalite melting (T_{hyd} = -44º to -21ºC) or ice melting (T_{ice} = -38º to -3.1ºC). Salinities range from 33.4 to 5.1 wt% NaCl equiv, whereas homogenization to a vapour phase occurred in the range from 125º to 245ºC. Several inclusions decrepitated during heating procedure (Fig. 17).

The co-existence of liquid rich inclusions Type II, (L+V+S_{hal}), of high salinity from 25 to 42 wt% NaCl equiv, and Type IV, vapour rich (V+L) with very low salinity between 0.4 to 5 wt% NaCl equiv, homogenizing in the same temperature interval between 125 and 245 ºC, corroborate the indication of boiling.

The inclusions with halite as the last homogenization phase after (L+V+S_{hal})→(L+S_{hal})→(L) at 300ºC, and vapour rich inclusions with halite crystals (V+S_{hal}) and those with solid halite inclusions (S_{hal}) are the product of a distillation (boiling evaporation) process in a semiclosed system with variable pressure, communicating with the open space on the earth surface followed by heterogeneous trapping. However, the behaviour of these high salinity and low salinity FI-s, especially the type (V+S_{hal}), and solid inclusion (S_{hal}) cannot be explained by one single episode of boiling. This impressive collection of fluid inclusion types, (more than 9 in one single crystal) requires multistage episodes of boiling producing a mixture of liquid water and bubbles, suspension of crystals, halite, sylvite, and unknown solids, trapped into one single crystal. It represents repeated boiling episodes under changeable pressure, due to a change in hydraulic head, water table, pressure of gases (suspected hydrocarbon liquids in inclusions), breakage of sealing, or maybe the intrusion of hot superheated water or steam from below into low salinity meteoric water, causing the rise of vapour and boiling, etc. The ternary diagram NaCl-CaCl$_2$-H$_2$O (Fig. 18), also indicates the boiling process. The T$_{hyd}$ vs. salinity diagram also confirms boiling and the separation of high salinity liquids from low salinity vapour (Fig. 19). In this plethora of FI-s types and disequilibrium conditions, there was an attempt to determine the pressure of boiling by coexisting inclusions in one crystal, 33.4 wt% NaCl equiv. (L+V), and 0.4 wt% NaCl equiv. (V+L), and homogenization at the same temperature, (Th), at 245ºC which yields 36.1 bars. Applying hydrostatic pressure, the depth of boiling would be 361 m (HAAS, 1976, 1971).

Figure 16. Selection of fluid inclusion types in one single crystal of fluorite, Žune-Dolmac locality (PALINKAŠ, 1988).
5.3. LASER RAMAN SPECTROSCOPY

Laser Raman spectroscopy was performed on fluid inclusions from fluorite (fluorite-barite vein, Žune-Dolinac locality) on the four-phase, \((L+V+S_{\text{hal}}+S_{\text{Sa}})\) Type I; the three-phase, \((L+V+S_{\text{hal}})\) Type II; two-phase \((L+V)\) Type III. Liquid-rich aqueous inclusions containing halite daughter minerals, with high salinity. At room temperature they are composed of aqueous liquid (broad shoulder at around 3400 cm\(^{-1}\)) and aqueous gas and/or traces of \(\text{CO}_2\) (peaks at 1278 and 1383 cm\(^{-1}\)). Other volatiles were not detected. At -21ºC fluid inclusions contain ice (a broad peak at 3100 cm\(^{-1}\)) and hydrohalite (a doublet around 3418 cm\(^{-1}\) and a sharp peak at 3543 cm\(^{-1}\)).

5.4. BULK CRUSH-LEACH ANALYSES

Bulk crush-leach analysis by ionic chromatography was performed on quartz, siderite, ankerite and galena from metasomatic zebra-type siderite; quartz, siderite, barite and galena samples from vein-type siderite, dark host limestone; bladed calcite (Adamuša locality) and fluorite and barite samples from a fluorite-barite vein (Žune-Dolinac locality, Table 1).

Recalculated bromine contents from leachates in quartz from metasomatic zebra siderite are elevated and vary between 535 and 685 ppm, whereas within vein-type siderite varies between 165 and 256 ppm (according to the procedure outlined by CHANNER et al. (1999). The recalculated bromine concentration in fluorite from the Žune-Dolinac locality is similar to the quartz from the metasomatic zebra-type siderite, ranging from 430 ppm to 605 ppm. A high concentration of bromide is registered in the dark limestone and barite as well.

\(\text{Na}^+\), \(\text{Ca}^{2+}\), \(\text{K}^+\), and \(\text{Mg}^{2+}\) are major cations, while the dominant anion is \(\text{Cl}^-\) followed by \(\text{SO}_4^{2-}\). These data correspond to the observed low eutectic temperature and depression of hydrohalite melting, both indicating the presence of divalent cations within the fluids, with the exception of \(\text{Mg}^{2+}\) which is
below the detection limit within quartz zebra siderite. It explains the precipitation of ankerite in the middle of the light bands, and the formation of saddle siderite crystals. High Ca$^{2+}$ and Mg$^{2+}$ concentrations are the direct results of intensive metasomatic ankeritization and sideritization.

Concentration of sulphate is between 0.1 wt % and 0.3 wt % within quartz from the zebra type mineralisation and between 0.3 wt % and 0.7 wt % within vein type quartz, whereas within fluorite samples (Žune-Dolinac locality) it is between 0.4 and 0.5 wt %. Maximum SO$_4^{2-}$ values up to 30,000 ppm (3 wt%), were observed within a single fluorite sample. This very high concentration level, not confirmed by presence of gypsum or anhydrite in the fluid inclusions, (due to high Ca concentration), is most likely attributed to contamination (e.g., solid inclusions of barite) since barite is frequently found in the paragenesis. However, it also points to a significant change in the fluid chemistry responsible for the genesis of barite deposits, decreased depth of formation, and the increased contribution of sea water. A deficit of cations is observed in the vein-type quartz. This can be attributed to the presence of Fe$^{2+}$ within the fluids, which was not measured during the procedure or to the absorption of divalent cations to the quartz powder during the crushing procedure.

The lithium content is highly elevated within zebra-type quartz and varies between 366 ppm and 2300 ppm, whereas for the vein type quartz it is in the range between 60 ppm and 150 ppm. Fluorite samples have uniform lithium concentrations varying between 325 ppm and 405 ppm. The presence of Li in the ore fluids was suspected by the extremely low eutectic temperature in quartz fluid inclusions from the zebra siderite down to -90 °C.

High Li concentration in the leachates and the presence of dio-triocatachedral chlorites from the donbassite-tosudite-cookeite solid solution and (LiAl$_4$(Si$_4$A$_1$)O$_9$(OH)$_2$), (Fig. 4C, SLOVENEC & PALINKAŠ, 2003) in the same cavity, confirms the high Li concentration in evaporitic bitter brines taking part in siderite genesis. This is one piece of evidence which connects evolved sea water from Permian evaporitic basins or lagoons with the ore forming process. High Li and B concentrations are common components in evaporitic bitter brines elsewhere (STEVEN & ZVI, 2011; 209 ppm, LIPPMANN et al.,1999). An additional contribution of Li may come from leaching of the surrounding host rocks, shales and sandstones. (McCAFFREY et al., 1987). CÉCILE et. al. (2002) consider high-salinity fluids, derived from sedimentary basins, responsible for the Li enrichment in FI-s in the barren quartz from the Spanish Central System (Sierra de Guadarrama). According to KRAUSKOPF (1982), the average shale contains 60 ppm of Li, twice that of the average granite.

Diagram Na/Cl vs. Cl/Br follows the sea water evaporation line. The measured ratios are the result of sea water evaporation rate between 12 and 36 % (Fig. 20A). It confirms the evaporation trend on all samples of zebra siderite, vein siderite, ankerite, quartz in siderite veins, vein barite and dark limestone. Galena exhibits very variable ratios. Galena associated with zebra siderite has Na$^+$ around the sea water composition, and in the vein siderite, above sea water on the evaporation line. It means a possible contribution of halite dissolution from evaporites. It should be mentioned that sulphide paragenesis in the cavities within zebra siderite is the last phase in the succession of dark siderite-light siderite-quartz-sphalerite-galena which suggests a prolonged time-span of ore formation.

The Ca$_{excess}$/Na$_{deficiency}$ diagram (Fig. 20B) shows a wide spectrum of contemporaneous ore forming processes which follow concurrently the metasomatism of Carboniferous limestones and dolostones by hydrotherms. The major trends are: (i) Ca$_{excess}$ increases by metasomatism of carbonates, ankeritization and sideritization, and (ii) albitionization of plagioclases (1 mole of Na for 1 mole of Ca).

The temperature of fluids was also calculated on the basis of geothermometric pairs: Na/K = 210-258 °C (mean 184°C); K/Mg = 261-443 °C (mean 355°C); Na/K/Ca = 280-441 °C (mean 328°C); and Na/Li = 124-589 °C (mean 329°C). The use of traditional geothermometric pairs which includes Ca and Mg, obtains unreliably high values. Their use is provided for water/ fluid equilibria in the common aquifer rocks, while in the Ljubija geothermal field metasomatism excessively predominates other equilibrium processes. In contrast, the Na/K geothermometer gives reasonable temperature, although in geothermal and epithermal environments this geothermometer reflects the deep reservoir fluid/rock equilibration rather than the fluid inclusion entrapment temperature (SIMPSON et al., 2015).

5.5. VITRINITE REFLECTANCE

Nine of seventeen samples from the Tomasića locality are selected for vitrinite reflection: (i) 6 host limestones; (ii) phyllite (aleurolite, frequently used in the literature on Sana-Unca, Paleozoic lithology); (iii) siderite, and (iv) sulphide rich sediment, which all contained >0.5% of organic carbon. According to petrography, most of the samples are composed of amorphous organic matter (99-100%) with traces of vitrinite and rarely pyrobitumen. The exception is the sample composed of 70% amorphous organic matter and 30 % vitrinite. All samples show a high thermal alteration index (TAI ~ 4). The degree of vitrinite...
reflection within the limestones is represented by R_0 of 4.0 – 4.6%. Using the diagram T - T_R (time of effective heating, maximum temperature, vitrinite reflectance) gives a temperature of 200-210 °C (BOSTICK et al., 1979) and 247-258 °C after (BERKER & PAWLECZIT, 1994); The sample of limestone by two methods. Sediments with sulphides, where R_0 gives T of 215-258 °C and Na/K, where T is 210-258 °C.

5.6. SULPHUR ISOTOPOES

Sulphur isotope compositions were determined on sulphides and sulfates. Sulfur isotopic data are presented in Table 2 (STRMČIĆ PALINKAŠ, 2004). The δ^{34}S values of the sulphides increases in order to 3.0 ‰ ≤ chalcopyrite ≤ (-0.8 to +2.3 ‰) ≤ sphalerite (+0.4 to +4.4 ‰) < pyrite (+5.4 to +8.5 ‰). There was no distinction perceived between sulphides separated from dark siderite and zebra ore. The δ^{34}S values of barite samples (+9.2 to ± 0.2 ‰ V-CDT) fall within the range of the latest Permian marine evaporites (HOLSER & KAPLAN, 1966). The temperature of coenogenetic geothermometric pairs was calculated by the constants given by OHMOTO & RYE (1979). The calculated temperature suggests the absence of isotopic equilibria. The reasonable temperature of 245°C was
<table>
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<th>Cl (mol/l)</th>
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<th>NaBr (mol/l)</th>
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<th>Clb (mol)</th>
<th>evapor. (%)</th>
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<th>GeOT: Na/K: K2Mg (oc)</th>
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Table 1. Ljubija/Adamuša

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<th>Palinkaš et al.: The Ljubija geothermal field: A herald of the Pangea break-up (NW Bosnia and Herzegovina)</th>
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obtained by galena-sphalerite pair from cavities in the zebra siderite calculated by the equation of KIYOSU (1973) and FRIEDMAN & O'NEIL (1977). The Δ34S_vesicles-vesicles vs. Δ34S_liquid diagram enabled determination of the δ34S_Saul = X_{Saul}/X_{Saul} by the equation after OHMOTO (1986). A determined value of +9.2 % V-CDT supports the evolution of Permian sea water by evaporation as the main sulphur source. Sulphur isotope values of sulphates were not affected by thermochemical reduction, it explains a low fugacity of sulfur and small quantity of sulfides including pyrite in the overall area. Some contribution from the decomposition of organically-bound sulphur and oxidation of pyrite from the sedimentary host rocks, dark colored clastics, are not excluded (Fig. 21).

5.7. GEOCHRONOLOGY

K/Ar dating

K/Ar dating was performed on the following samples: (i) 5 phylmites from the Trnava locality; (ii) 6 phylmites from the Blagaj locality; (iii) 6 phylmites from the Adamuša locality, 4 of them are fragments associated within vein-type siderite mineralization; (iv) a single phylite sample from the Tomasića locality; (v) single phylite sample from Jezero locality; (vi) limestone undisolved residuum from the Adamuša locality, and (vii) 9 samples of rhyolite rocks from the Trnava locality.

Whole rock phylbite samples (4 samples) from the Trnava locality contain between 1.3 and 3.6 % of potassium and gave an age between 171.3+6.6 and 195.4±7.5 Ma, whereas a single
mica concentrate (4.2 % of potassium) gave an age of 212.0±8.0 Ma. Whole rock phyllite samples (4 samples) from the Blagaj locality (1.2 to 3.6 % of potassium) gave an age between 214.2±8.3 and 233.1±9.4 Ma, whereas two mica concentrates (4.2 % of potassium) gave an age of 188.7±7.1 and 193.7±7.3 Ma. Two whole rock phyllite samples (1.2 and 4.0 % of potassium) gave ages of 290.0±11.0 Ma and 283.4±10.6 Ma, respectively. Additional 4 whole rock phyllites associated with vein-type siderite mineralization (0.7 to 3.6 % of K) yielded ages between 200.0±9.0 and 236.0±9.0 Ma. A whole rock phyllite sample from the Tomašica locality contains 1.5 % of K and gave an age of 238.7±9.2 Ma, whereas a whole rock phyllite sample from the Jezero locality (3.9 % of K) yielded an age of 132.9±5.1 Ma. Whole rock analysis of the undissolved residuum of the limestone of the Adamuša locality (2.1 % of K) gave an age of 220±10.0 Ma.

Whole rock rhyolite samples (9 samples) of the Trnava locality contain from 0.1 to 2.0 % potassium with an age range from 56.6±4.3 to 237.0±9.5 Ma.

Wide spectrum of data from 56 Ma to 290 Ma on phyllites and volcanics shows different degrees of loss of radiogenic Ar, due to long-term tectonism and associated thermal events in the polyphase metamorphic evolution of the Dinarides (PALINKAŠ & PECSKAY, 1996, unpublished, Fig. 22).

The first group (i), (283-290 Ma), belongs to the post-Variscan thermal event in Lower Permian time, connected with an incipient intra-continental rifting stage. It corresponds to the post-Variscan ages determined in the Mid-Bosnian Schists Mts. (PAMIČ et al., 2004). The group (ii) varies widely (175-238 Ma) and represents disturbed ages by the later tectono-thermal events, as indicated by the 40Ar/39Ar dating. The third group (iii) with a Lower Cretaceous overprint (98-132 Ma) is most likely a result of later resetting in a tectonically active zone. It has a regional significance and marks obduction related tectonism and metamorphism, traditionally named the Eoalpine, which started 130 Ma ago (HSÜ, 1989). This Lower Cretaceous overprint is recognized on the Silurian-Devonian metamorphic complex on the Medvednica Mts. (110-122 Ma), (BELAK et al., 1996), on the Drina-Ivanjica Palaeozoic block in Serbia (129-139), (MILOVANOVIC, 1984), and in the metarhyolites in the Mid-Bosnian Schist Mts. (92-121), (PAMIČ et al., 2004).

The group (iv), younger Palaeocene overprint (56-64 Ma) determined on volcanics, corresponds to the Palaeocene early collision stage between Africa (Adria) and Euroasia (Tisia-Moesia), the cause of the Dinaride uplift in the Eocene. PAMIČ & PÉCSKAY (1996) reported Late Cretaceous K/Ar ages of 94.3 and 85.4 Ma from basalt and diabase from the northwestern side of the Medvednica Mts.

40Ar/39Ar analysis

40Ar/39Ar analysis is performed on the low potassium white mica concentrate (paragonitic white mica), from phyllite fragments associated with the vein type of mineralization. The white mica concentrate yields a strongly disturbed pattern. The low-energy steps of the age spectrum show significant excess argon and an age of 340 Ma, whereas high energy steps gave a plateau-type of age at 275 Ma constituting together 96.7 percent of 39Ar (steps 2-4, Fig. 23; BOROJEVIĆ ŠOŠTARIĆ, 2009). 40Ar/39Ar released spectra could be interpreted in another way. The plateau age of 340 Ma might be an inherited Variscan age (Lower Carboniferous) of the sedi-
A white mica concentrate from the phyllite, sample LJUB 1, from the Palaeozoic Sana-Una Unit yielded a plateau age of 335.1 ± 23.1 Ma comprising 96.8 percent of 39Ar released. The inverse isochrone plots show a slightly disturbed initial 40Ar/36Ar ratio of 322± 27 Ma, and an age of 327±30 Ma, together constituting 100 percent of 39Ar released (BOROJEVIĆ ŠOŠTARIĆ, 2012).

6. ORE GENESIS

Genesis of the Ljubija ore deposits was a subject of controversy. The basic interpretation models have two approaches (i) a syn-sedimentary stratiform type with an obscure origin of iron, and the alternative (II) hydrothermal replacement and epigenetic vein type. To solve the dilemma, in the past decades a number of analytical procedures and methodologies have been applied in building a convincing genetic model. There was a number of ambiguities which obscured the solution, and paved the ground for unsupported genetic hypotheses. The objective approach requires resolution of the following particularities: textural-structural characteristics, time of formation, source of metal, pressure, temperature and chemistry of the ore forming fluids, alterations, and not least, the metallogenic affiliation to the equivalent deposits in the frame of plate tectonic divisions and reconstruction of the Dinarides, and the wider area within the Neotethyan domain.

6.1. TEXTURAL-STRUCTURAL CHARACTERISTICS

The Fe mineralisation in the Ljubija ore field comprises strata-bound siderite and ankerite bodies hosted by Carboniferous limestones, and siderite-sulphide veins placed within organic rich shales. PALINKAŠ (1988) recognized three major types of primary iron ore textures: (1) dark massive siderite and ankerite, and (2) zebra siderite composed of dark massive and light sparry siderite bands, and (3) sparry siderite veins hosted clastics (Figs. 3, 4, 5).

Ore microscopy and transmitted light microscopy offer a visual observation of metasomatic processes (Figs. 8, 9). The textural type (1) was formed by the metasomatic replacement of dark massive limestone by dark massive siderite. The differences between massive siderite (1) and zebra siderite texture (2) were the result of chemical kinetics controlled by temperature, acidity buffered by the host rocks, and salinity. All these parameters have been reasserted by the research data (PALINKAŠ et al., 2003b; STRMIĆ PALINKAŠ, 2004, 2009; BOROJEVIĆ ŠOŠTARIĆ, 2004).

When the dissolution volumetric rate of calcite was equal to the precipitation volumetric rate of siderite, the primary texture was retained, i.e. dark metasomatic Fe-carbonate was precipitated. In contrast, when the volumetric rate of dissolution was higher than the rate of precipitation, cavities are formed and the primary texture is lost. Further supply of mineralizing fluid caused crystallization of light sparry siderite directly from solution (STRMIĆ PALINKAŠ, 2004).

The genesis of three textural types has been ascertained by the chemistry of metasomatic processes, (STRMIĆ PALINKAŠ, 2004; STRMIĆ PALINKAŠ et al., 2009) through the following contributions: (i) Variations in δ13C values of the barren and mineralized carbonates suggest the progressive replacement, and depositional character of vein siderite; (ii) The δ18O values of siderite and the calcite vein from dark massive siderite give a value of isotope equilibrium temperature, T\text{isotope} = 224 \, ^\circ\text{C}; (ii) The δ18O values of siderite and the calcite vein from dark massive siderite give a value of isotope equilibrium temperature, T\text{isotope} = 224 \, ^\circ\text{C}; (ii) The δ18O values of siderite and the calcite vein from dark massive siderite give a value of isotope equilibrium temperature, T\text{isotope} = 224 \, ^\circ\text{C}; (iii) The δ18O values of siderite and quartz pairs from siderite veins give T\text{isotope} = 168 \, ^\circ\text{C}; (iv) The δ34S values of sphalerite and galena pairs from zeba ore give T\text{isotope} = 245 \, ^\circ\text{C}; (v) The δ34S value of barite falls within the range of contemporaneous Permain sea water; (vi) The pristine/phitane ratio higher than 1

Figure 20. A) Diagram showing Na/Cl/Br variation of fluids extracted as leachates from the ore and host minerals. Most of data follow the evaporation trend, and only a few the trend of halite dissolution, the Ljubija/Adamuša ore deposit; B) Diagram Ca access vs. Na deficiency with theoretical trends of fluid evolution. Legend: HDL halite dissolution line; BLF line of basinal fluids; zebra siderite, banded texture; vein mesothermal siderite; dark limestones, footwall of the ore mineralization.
in the barren and mineralized samples points to an oxic depositional environment for the host rock carbonates, an inconvenient condition for the synsedimentary deposition of siderite ore. A reducing environment during diagenesis, controlled by indigenous organic matter, however, is a prerequisite for epigenetic metasomatic sideritization.

6.2. TEMPERATURE AND CHEMISTRY OF FLUIDS

Study of fluid inclusions in quartz from three textural siderite types and within the siderite itself from the ore deposit Adamuša/Ljubija, and fluorite from the fluorite-barite deposit Žune-Dolinac supported by crush-leach analysis and vitrinite reflectance, paved the way to substantial information on ore forming fluids, their temperature and composition.

The ore forming fluids with highly variable salinities (2-39 wt% NaCl equiv., Adamuša/Ljubija; 5-33.4 wt% NaCl equiv., Žune-Dolinac), are essentially modified sea water derived through different degrees of evaporation in lagoons, up to the point of halite precipitation (the evaporation line on the diagram Na/Cl vs Cl/Br). Boiling phenomena, observed and determined on fluid inclusions, contributed to the variable salinity of fluids, which underwent distillation (boiling evaporation), at the topmost position of the cell, near the land surface. The boiling temperature was controlled by hydrostatic pressure at depths of 100-200 m below the land surface.

The hydrothermal solution in fluid inclusions is primarily represented by NaCl-H$_2$O and NaCl-CaCl$_2$±MgCl$_2$-H$_2$O systems. Ca$^{2+}$ and Mg$^{2+}$ ions are evidence of the widespread metasomatic replacement of limestones and dolomites by Fe$^{2+}$ (Ca$_{\text{excess}}$ vs. Na$_{\text{deficiency}}$ diagram).

The high concentration of Li$^+$ ions in leachates, and the presence of cookeite, (LiAl$_4$(Si$_3$Al)$_{10}$(OH)$_8$) as an alteration mineral, confirm the engagement of chloride rich evaporitic sea water, responsible for the mobilization of metasomatic Fe$^{2+}$ from shale, but some proportion comes from leaching of Li-rich mica. The SO$_4^{2-}$ ion, recorded in leachates, was essential for deposition of the ubiquitous barite deposits. In spite of a slight variation, the $\delta^{34}$S values of barite around +9.2‰ V-CDT, the $\delta^{34}$S$_{\text{barite}}$ value bears witness to Permian sea water as a dominant water supplier in the circulation cell. The minor thermochemical reduction of sulphate was the source of HS$^{-}$ for sulphide deposition.

Thermal characteristics of the ore forming fluids are confirmed by the study of fluid inclusions (Th, 100-275°C), Na/K ratio in leachates (141-281°C), vitrinite reflectance (210-260°C) and stable isotope geothermometers (164-224°C). This overall range of temperatures could be more specific in a sketch presen-
tation of thermal distribution in the hydrothermal circulation cell (Fig. 24).

The shape of the circulation cells, formed over the foci of high heat flow, at the Adamuša/Ljubija deposit, is defined by the position of isotherms reconstructed by the temperature of mineral formation. The chemical zonation is accompanied by thermal zonation. The highest trapping temperature and salinities are registered at the lower position of the cell, in the quartz of the zebra metasomatic siderite (salinity 35-39 wt% NaCl equiv., Th 215-275°C). The lowest temperature and salinity are measured in the quartz in siderite veins in the uppermost part of the cell (salinity 2-9 wt% NaCl equiv., Th 100-250°C). The plume of heat controls the shape and the character of fluids from high salinity bitter brines at deeper parts of the cell, to the diluted aliquots, with lower salinity, supplied by normal sea or meteoric water. The wide range of temperatures suggest mixing of hot-high salinity water FLUID 1 and cold-low salinity waters FLUID 2 (Fig. 13, diagram T vs. salinity).

The Žune-Dolinac barite-fluorite deposit (like the other numerous barite deposits in the Ljubija geothermal field) experienced intensive boiling due to their near-surface setting.

6.3. TIME OF MINERALIZATION

Age determination relied on indirect methods, available during research, (i) 39K/40Ar, (ii) 40Ar/39Ar, and (iii) origin of sulphur in the ore mineralization implied through its isotope signature.

The K/Ar blocking temperatures, determined on phyllites, indicate four significant thermal events. The group (i), (283-290 Ma), belongs to the post-Variscan thermal event in Lower Permian time, connected with the incipient intra-continental rifting stage. The group varies widely (175-238 Ma). The lowest temperature and salinity are measured in the quartz in siderite veins in the uppermost part of the cell (salinity 2-9 wt% NaCl equiv., Th 100-250°C). The plume of heat controls the shape and the character of fluids from high salinity bitter brines at deeper parts of the cell, to the diluted aliquots, with lower salinity, supplied by normal sea or meteoric water. The wide range of temperatures suggest mixing of hot-high salinity water FLUID 1 and cold-low salinity waters FLUID 2 (Fig. 13, diagram T vs. salinity).

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6.4. LJUBIJA GEOTHERMAL FIELD

The Ljubija ore deposits were formed within the Ljubija geothermal field which extends into the Trgovska gora and Petrova gora Paleozoic terrains. The Ljubija geothermal field deserves the term “geothermal field” because of the areal extension of its ore deposits of several hundred square kilometres over the Sana-Una Paleozoic. The Ljubija geothermal field incorporates a huge accumulation of Fe-carbonate, sulphide, barite and fluorite.
mineralisation, with almost half a billion tonnes of Fe ore, at the Adamuša/Ljubija, Tomašica, and Omarska ore districts. The chemistry, pressure and temperature of the thermal waters enriched in Ca, Mg, Na, chloride and bromine, are common in rifting-related fluids elsewhere (e.g., HARDI, 1990; ROWLAND & SIBSON, 2004; SIMPSON et al., 2015). The general characteristics of the Ljubija geothermal field corresponds in many aspects to the Salton sea geothermal field, an active rifting environment, regarding composition and temperature of Ca rich brines, metaliferous sediments, etc. (CRAIG, 1966; SKINNER et al., 1967).

Due to the initial phase of rifting, the crust in the passive margin was thinner than adjacent crust, and geothermal systems developed at high heat flow foci along an elongated rifting zone and fractures controlled convection circulation systems. Here the geothermal water had been circulating to considerable depth (> 1 km), through mostly vertical fractures, to extract the heat from the rocks.

SAEMUNDSSON (2009) classified geothermal systems on the basis of geological setting, reservoir temperature and enthalpy: (i) Low-temperature systems with reservoir temperatures at 1 km depth below 150°C; (ii) Medium-temperature systems with reservoir temperature at 1 km depth between 150-200°C; (iii) High-temperature systems with reservoir temperature at 1 km depth above 200°C, with reservoir fluid enthalpies greater than 800 kJkg⁻¹.

The pressure-temperature characteristics of the Ljubija geothermal field are closer to the (iii) High temperature system. The Ljubija geothermal field was water dominated, and at places, to varying degrees, vapour dominated. The enthalpy content in the two-phase boiling system in Žune-Dolinac was close to 982 kJkg⁻¹ for the liquid phase and 2877 kJkg⁻¹ for the developing vapour phase (data for the temperature of 245°C and salinity of 33 wt. % NaCl).

Carboniferous and Permian formations were cap rocks (total thickness of 600-800 m), a blanketing seal of the geothermal system and their rock formation were the object of metamorphic sideritization. The rifting fault zones provided conduits for fluid flow and heat flow, and hydraulic pressure forces fluids to the surface forming hot springs, fumaroles, etc., in the boiling zone, at places the temperature and pressure followed the boiling point curve and where steam and water coexisted.

The barite-fluorite vein deposit of Žune/Dolinac is a feeder zone of one of the many hot springs. Thermal gradients calculated on the basis of high hydrothermal water, issuing on the surface, and colder Permo-carboniferous host rocks are not a convenient place to calculate a regional geothermal gradient. A proper geothermal gradient, providing the thermal water, is in the aquifer reservoir below the Carboniferous and Permian formations.

As initial rifting proceeded, listric fault systems formed and further subsidence resulted in the creation of a Red sea type basin, developed by the formation of the Neo-Tethyan ocean crust. Equivalent types of huge siderite-barite-polysulfide mineralisations are situated within the similar geotectonic environment, however, with a much more complex tectono-thermal history in the course of the Alpine orogeny. The siderite mineralisation with similar characteristics, in low to medium grade metamorphic Variscan basement units, has been studied in the Western Carpathians and Eastern Alps (GRECULA et al., 1995; HURAI et al., 2002, 2008a; RADVANEČ et al., 2004; URBAN et al., 2006; HURAI et al., 2008b, b; POHL, 1986; LAUBE et al., 1995; PROCHASKA & HAFFELLNER, 1994), EBNER et al. (1999). The origin and age of this mineralisation is still under discussion. As a corollary, the Ljubija geothermal field is a herald for the birth of the Tethyan Ocean and the onset of the new Alpine Wilson cycle.
Reconstruction of the opening scenario which loosely defines space, time and related geotectonic events is depicted on the palinspastic sketch of the North Hungarian Triassic units, with special reference to Ladinian palaeogeography (not to scale!), (Fig. 25, KOVÁCS, 1984). The sketch portrays advanced rifting in progress toward the northwest (present geographical orientation) dissecting Pangea into the Gondwana and Eurasian continental blocks. Early rifting formations and Permo-Carboniferous geothermal fields, were covered by newly growing Dinaridic and Moesian carbonate platforms on the opposite sides of divergent, drifting continental margins (PALINKAŠ et al., 2016, this publication). Tectonic evolution, uplift, napping, thrusting and erosion uncovered their mineral load to the present exposed situation.

7. SUMMARY
The Ljubija ore deposits are situated within the thick Upper Palaeozoic sequence of the allochthonous Sana-Una Palaeozoic complex of the Inner Dinarides. The primary ore occurs as stratabound metasomatic bodies of iron carbonates within Carboniferous limestones and dolostones, and siderite veins within the Carboniferous phyllites and metasandstones.

Primary mineralization consists of siderite-ankerite-barite-polysulphides with three textural types, dark massive siderite, zebra siderite, alternation of dark and light siderite bends with sulphide cavities, and open space fillings in the veins. The shape of the cell is defined by isotherms based on mineral formation temperature, tentatively. The most influential processes in the formation of chemical components of fluids are metasomatic sideritization and ankeritization. The ore forming fluids are dominantly NaCl-CaCl$_2$-H$_2$O, with highly variable salinity (0.4 to 39 wt% NaCl equiv.) and $T_h$ between 100 and 310°C.

The hydrothermal fluids are a mixture of high-temperature-high-salinity Permian evaporitic sea water, diluted by low-temperature-low-salinity sea or meteoric waters. Boiling of near-surface hydrothermal reservoirs contributed to the high variability of temperature and salinity of the fluids. Sulphur isotopes confirm Permian sea water as the major source of sulphates ($\delta^{34}S$ +9.2 ‰ V-CDT) for barite formation. Thermal reduction of marine sulphates supplies HS- for the precipitation of sulphides, which were deposited out of equilibria, with the exception of the cogenetic pair galena-sphalerite, formed at 245°C. The temperature of formation determined by oxygen isotopes on calcite-siderite-quartz cogenetic mineral pairs is in the range between 164° to 224°C. Temperatures of the cation geothermometer (Na/K) matches those obtained from fluid inclusion, vitrinite reflectance and isotope thermometry.

The age determination recorded two prominent tectono-thermal events, Variscan (332.8±3.1 Ma and 342.9±3.3 Ma), overprinted by a thermal post-Variscan event at ca. 265.6±6.2 to 274.2±3.1 Ma, and interpreted as the maximum age of hydrothermal activity in the Middle Permian.

The ages and thermal features coincide well with those in the neighbouring deposits in the Palaeozoic of Trgovska gora and the Petrova gora Mts., its counterparts in space and time, announcing the future break-up of Pangea and the birth of Tethys (Fig. 26).

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