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Unexpected Fluid Inclusion Composition in Barite from the Lika Barite Deposits

Ladislav A. PALINKAŠ

Mining-Geology-Petroleum Engineering Faculty, University of Zagreb, Pierottijeva 6, 41000 Zagreb, Yugoslavia

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Ključne riječi: Fluidne inkluzije, Barit, Nekloridni kemijski sastav.

Barite minerals from the Lika ore deposits in the Upper Carbonitferous sedimentary rocks with »strata-bound« character and still puzzled origin were object of the fluid inclusion study. The results are not unequivocal, since fluid inclusions are suspected to be of secundary origin. Peculiar fluid inclusion composition (alkali sulfates, carbonates and bicarbonates) is not in contrary, however, to inclusion composition in barite from the Mississippi valley type deposits. Along with epigenetic origin, early and late diagenetic processess cannot be excluded. Less likely is engagement of hydrothermal convective cells, caused by disturbed thermal gradient during early intracontinental rifting in Dinaric realm.

U radu su prikazani rezultati istraživanja fluidnih inkluzija u baritu iz ličkih ležišta barita, s karakterističnim »strata-bound« načinom pojavljivanja i još uvijek neriješenom genezom. Rezultati nisu jednoznačni, pošto se sumnja u primarno porijeklo inkluzija. Međutim, neobični kemijski sastav inkluzija (alkalni sulfati, karbonati i bikarbonati) nije u suprotnosti sa sastavom inkluzija u baritu iz ležišta tipa Mississippi valley. Osim epigenetskih rudonosnih procesa u obzir dolazi i ranodijagenetsko i kasnodijagenetsko porijeklo mineralizacije. Manje vjerojatno je sudjelovanje hidrotermalnih konvektivnih ćelija, uzrokovanih poremećenim termalnim gradijentom u vezi s ranim intrakontinentalnim riftovanjem u Dinaridima.

INTRODUCTION

All appreciated ore deposits in Croatia are affiliated to the Upper Paleozoic terrains in Dinarides. They are situated along the borders of the stable Mesozoic platform. According to global-tectonic concept, it was a passive continental margin of the Adria microplate, an African promontory in the Mesozoic Mediterranean paleogeography (Channel et al. 1979).

Position of the ore deposits in Samoborska gora, Trgovska gora, Petrova gora and Ljubija in the Sana-Una river Paleozoic terrain is clearly related to the outer carbonate platform margin (eugeosyncline, Supradinaricum, sensu Herak, 1986). Lika and Gorski Kotar barite deposits are close, however, to the inner margin (between Adriatic foreland and miogeosyncline), but geotectonic relationship is rather complicated and Herak (1986) distinguishes a few allochthonous elements at the same place, Dinaricum, Epiadriaticum and Adriaticum, in vicinity of Fužinski Benkovac (Fig. 1).

While the siderite-barite deposits on the outer carbonate margin were probably formed in the Permian time by activity of hydrothermal convective cells in subterrestrial level, showing only locally exhalative phenomena (volcano-sedimentary), the deposits on the inner margin (possible failed rift) are detached of any pronounced thermal event at that time (Palinkaš, 1988), but not necessarily in the Middle Triassic (Tršće cinnabar deposit).

Gorski Kotar barite mineralization is early diagenetic formed in a tidal flat evaporitic facies (Sabkha, Palinkaš & Šinkovec, 1986, Palinkaš & Sremac, 1987). Lika barite deposits bear geological evidences of early-late diagenesis, but even epigenetic, hydrothermal ore forming processes cannot be excluded.

Fluid inclusion study of minerals in sediments and sedimentary ore deposits, in general, revealed valuable data on chemical composition of ore fluids and formation temperatures (Roedder, 1979). It provides another possibility for getting better insight into genetical problems. Difficulties arise in finding of proper fluid inclusions, regarding size and origin. While, searching for appropriate inclusions in minerals from the Gorski Kotar barite deposits failed due to cryptocrystalline and colloform texture of the ores, the barite minerals from the Lika deposits appeared to be sufficient transparent and fluid inclusion enough large to undertake cryometric measurements. Homogenization, however, was not performed for inconvenient mechanical properties of the barites.

GEOLOGICAL SETTING

The Upper Paleozoic sediments between Baške Oštarije and Gračac crop out in several isolated areas (Baške Oštarije, Počitelj, Raduša, Ričice), with characteristic Dinaric extension NW—SE. Northeastern margin of the Paleozoic terrain, in contact with the Liassic sediments, is tectonic, while in SW-direction Permocarboniferous rocks dip under the Lower Triassic sediments in normal succession.

According to Salopek (1949), the Upper Paleozoic sediments consist of different Upper Carboniferous, Auernig-beds, clayey shales, limestones, dolomites, quartz conglomerates and fusulinid sandstones. Permian Groeden sediments are preserved only at Poljane, lying transgressively over the Upper Carboniferous.

The barite ore occurrences are situated in NW—SE elongated Paleozoic terrain, 9 km long by 3 km wide, from Pilar to Štikada village. The barite ore bodies are strictly bound to the Upper Carboniferous limestones and dolomites, predominantly at the contact of carbonate rocks and underlying shales (Jurković, 1959, Šinkovec, 1979).

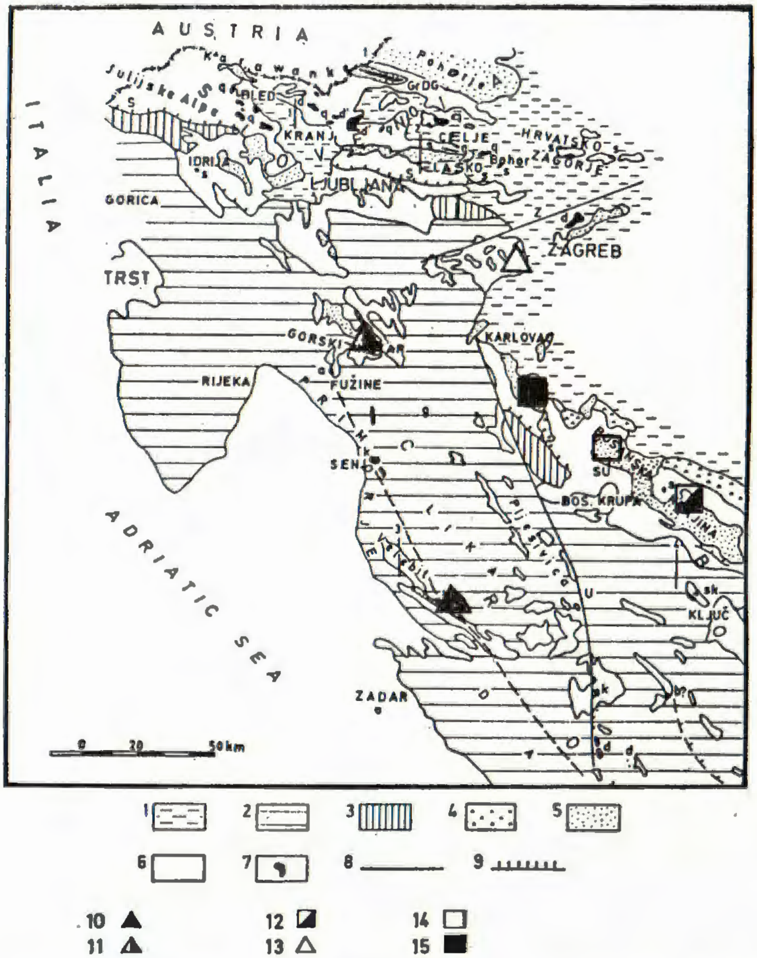

Fig. 1. Schematic geological map of NW Dinarides (after P a m i ć, 1983) with locations of the principle ore deposits along the border of the stable Mesozoic carbonat platform.

1 — Cenozoic sediments, 2 — Outer Dinarides (karst region), 3 — Mesozoic flysch, 4 — Ophiolites with associated sediments, 5 — Paleozoic, 6 — Triassic, 7 — Triassic magmatism., 8 — Bigger faults, 9 — Nappes, 10 — Lika barite deposits, 11 — Gorski Kotar barite deposits, 12 — Ljubija siderit deposits, 13 — Rude deposit (Samoborska gora), 14 — Trgovska gora deposits, 15 — Petrova gora deposits, k — keratophyre, s — spilite, d — diabase, a — andesite, b — basalt, Bigger faults: I — Innsubrick, Z — Zagreb, U — Una, F — Sinj, Velebit, Fužine.

Sl. 1. Shematska geološka karta SZ Dinarida (prema P a m i ć u, 1983), s položajem glavnih rudnih ležišta uzduž rubova stabilne mezozojske karbonatne platforme.

1 — kenozojski sedimenti, 2 — Vanjski Dinaridi (kraško područje), 3 — mezozojski fliš, 4 — ofioliti s pridruženim sedimentima, 5 — paleozoik, 6 — trijas, 7 — trijaski magmatizam, 8 — veći rasjedi, 9 — navlake, 10 — lička ležišta barita, 11 — gorsko kotarska ležišta barita, 12 — Ljubija, 13 — Rude (Samoborska gora), 14 — rudišta u Trgovskoj gori, 15 — rudišta u Petrovoj gori, k — keratofiri, 5 — spiliti, a — andeziti, 6 — bazalti. Veći rasjedi: I — Innsubrik, Z — Zagreb, U — Una, F — Sinj, Velebit, Fužine.

MINERALIZATION

The Lika barite deposits have conspicuous »strata-bound« character, and are strictly in the Upper Carboniferous carbonates and clastics. The ore bodies are stratified lenses and beds but epigenetic appearance like veins and disseminated ores are present as well.

Ore deposit B r n i ć e v o deserves special attention, because of typical stratiform ore bodies in clastics (Fig. 5). The footwall and the hanging wall rocks are rich in pyritic cement, which at places becomes a massive pyrite. The style of mineralization suggests early diagenetic origin, in muddy environment. Anaerobic microbiological activity, followed by dissimilatory generation of H_2S remobilize disseminated $BaSO_4$ in sediments and at places of higher sulfate concentration, reprecipitation of barium sulfate may occur. This model requires intensive water circulation which could have provided enough sulfate ions for biological metabolic reduction and barite precipitation.

K r a v a r i c a is distinguished by expressive epigenetic style of mineralization. Well developed crystals of transparent barite fill out open spaces and pores in crinoidal limestone. Aragonitic joints of encrinites are often replaced by barite (Fig. 6). Metasomatic dolomitization may be observed in fissures around massive barite veins.

B a t is typical vein-like deposit. Barite occurs in veins like semitransparent euhedral crystals or white cryptocrystalline masses, convenient for fluid inclusion study.

P i l a r is the most remarkable among the Lika barite deposits. There are basicaly two types of ores, supposed early diagenetic one, with euhedral barite crystals in dark dolomite (Fig. 7), and epigenetic, mighty veins (Fig. 8), passing across light dolomites, which seems to play important role in the ore formation.

Secundary deposits are also frequent. There are accumulations of barite in dilluvial clays, on karstified carbonate substratum (Š i n k o v e c, 1979).

The main minerals in primary deposits are barite and dolomite. Much rearer is pyrite, galena and sphalerite and supergene goethite.

J u r k o v i ć (1959), stated that layered barite ore bodies are of submarine exhalative origin, while vein-like formations are secundary hydrothermal remobilization. Š i n k o v e c (1979) considers deposits to be sedimentary, but source of barite is unknown.

MICROSCOPIC DESCRIPTION OF FLUID INCLUSIONS IN BARITE FROM KRAVARICA, BRNIĆEVO, BAT AND PILAR

Barite minerals contain following observed type of inclusions:

(a) monophase inclusions (L), secundary origin (Fig. 9)
(b) two-phase inclusions (L+V), secundary origin (Fig. 9)
(c) two-phase inclusions (L+V), with possible presence of CO_2.
(d) monophase inclusions (S), with hematite, supergene pseudomorphs after pyrite (Fig. 10)
(e) monophase inclusions (S), with well developed dolomite crystals (Fig. 13A, B)

The most often kind of inclusions is type (a). Partial decrepitation of monophase (L) inclusions (leakage), with appearance of vapor bubble, was observed even at temperature close to 100 °C, during preparation of polished wafers by use of heated balsam. Preparation of wafers at ambient temperatures proved that supposition, but also presence of natural (L+V) inclusion as well (Fig. 9).

Natural (L+V) inclusions could have been formed, however, by mechanical splitting along cleavage planes, what causes leakage, and change in fluid density by appearance of two phases. Homogenization measurements were given up after suspecting in natural origin of (L+V) inclusions and for wide span of homogenezation temperature between 160 °C and over 300 °C.

CRYOSCOPIC STUDY

Microthermometric measurements have been performed by the Chaixmeca stage; mounted on a standard Zeiss Amplival photomicroscop in the Department for mineralogy of the Lorand Eötvös University, Budapest. Electronics attached to the stage enables control of temperature between —190 °C (liquid nitrogen) to 600 °C and precision of 0.1 °C (Poty et al., 1976).

Wafers of barite thick about 1 mm, have been prepared by standard grinding material and polished with chromium oxide. All samples have been slightly preheated to develope a bubble and avoid difficulties with monophase inclusions during cryometric measurements.

Rate of heating, during cryometry was 1—2 °C/min and close to temperature of phase transition (S → L) was lowered to 0.2 °C/min.

MEASUREMENTS

Cryometric measurements of monophase inclusions (L) have faced »overexpended liquid« problem that causes high negative pressure and increase of the ice melting point. Newly formed vapor phase eliminated that effect and enabled better observation of the first melting point (Tfm) or eutectic temperature, what was otherwise a serious problem during measurements.

In the course of cooling, two-phase inclusions behaved metastably and freezing could be recognized only by collaps of a vapor bubble. Completely transparent, white appearance of ice excluded $CaCl_2$-NaCl-$MgGl_2$ type of solutions, as well as very high eutectic temperature. The first hardly observable melting sign was rounding of a bubble at —6.0 oC (Fig. 3). The first melting point in some inclusions was reaching 0 °C. This unexpected fluid inclusion composition should be referred to alkali sulfates, carbonates and bicarbonates since K_2SO_4-Na_2SO_4-$MgSO_4$-Na_2CO_3-$NaHCO_3$ in different combinations have eutectic temperatures between —6.0 °C and —.1.2 °C (Borisenko, 1977). In some very tiny inclusions one may observe a rapid bubble movement, sometimes related to presence of CO_2, not strange in the mentioned chemical composition.

Complete melting proceeded very soon after obtaining eutectic temperature in an interval of a few degrees, sometimes in only 0.1 oC (Fig. 2),

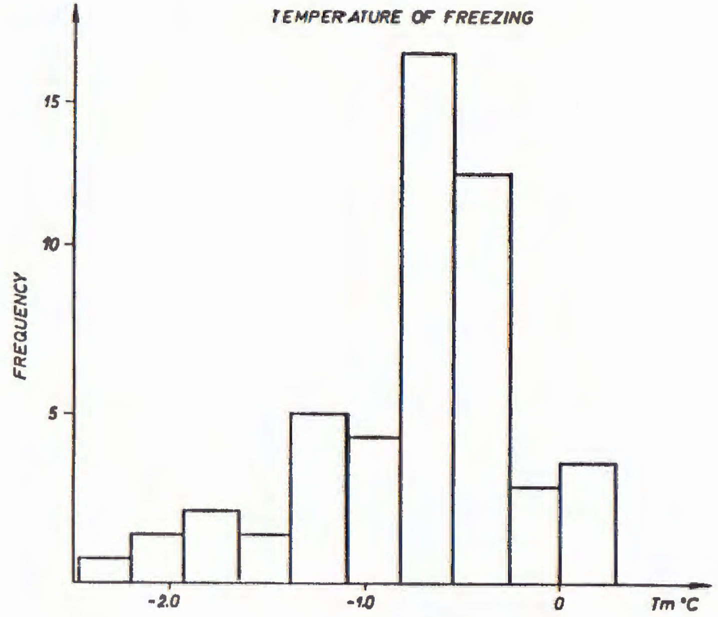
TEMPERATURE OF FREEZING
FREQUENCY
15
10
5
-2.0
-1.0
0
Tm °C

Fig.2

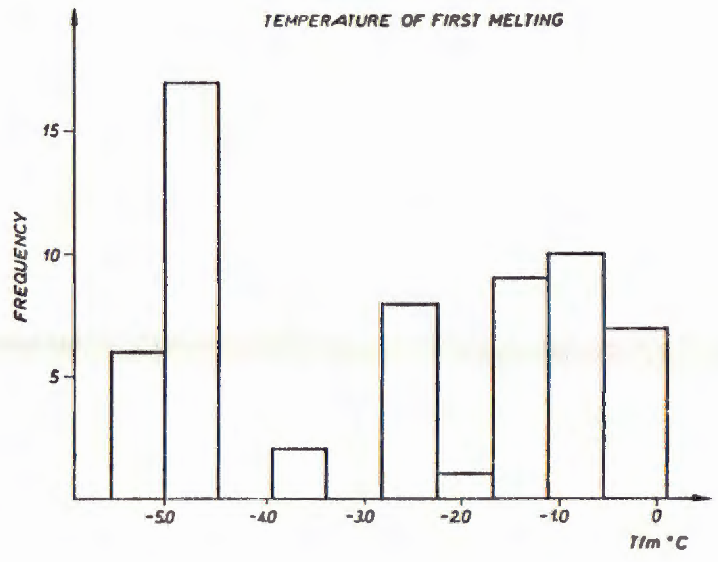
TEMPERATURE OF FIRST MELTING
FREQUENCY
15
10
5
-5.0
-4.0
-3.0
-2.0
-1.0
0
Tfm °C

Fig.3

with ice as the last solid phase (B o r i s e n k o, 1974). Salinity expressed in wt. % NaCl equ. is between 0 and 4 wt.% and is not constituted by sodium or any other chloride definitely (Fig. 4).

The data for the first and last melting point at all investigated localities are very similar, however, Brnićevo and Kravarica might have more sulfate in composition and higher concentration of solutions.

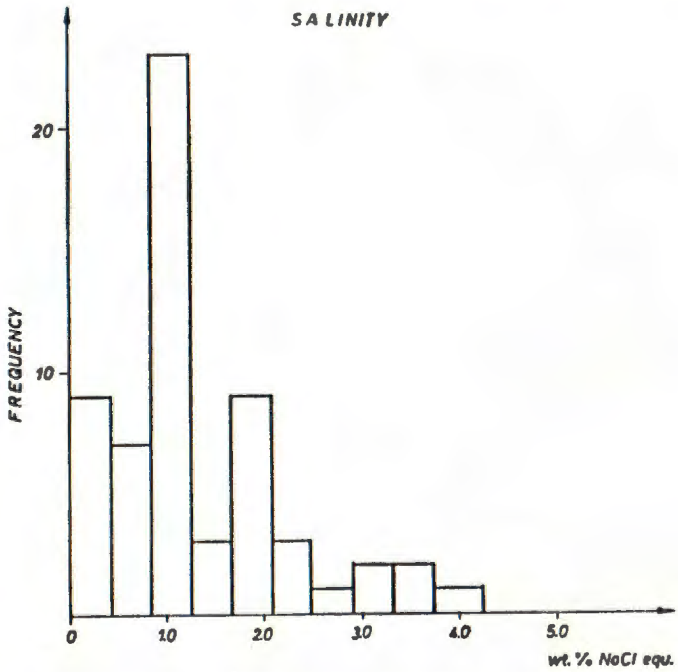

Fig. 4

Quartz crystals found in dilluvial clays do not have particular importance for presented survey, but may be a motto in searching for quartz crystals in original position, connected with mineralization. Their thermometric characteristics are as follows :Th between 100 °C and 180 °C, eutectic point might be assigned to KCl-H_2O system, and salinity is 4 wt. % NaCl equ.

DISCUSSION

Present solutions in investigated fluid inclusions are surprising to some extent, particularly absence of chlorides. It might mean that early diagenetic barite mobilization (Brnićevo deposit and barite in dark dolomite in Pilar deposit) as well as late diagenetic remobilization (Kravarica, Bat, vein occurrences in Pilar) happened in freshwater, swampy (or mildly brackish) environment, i.e. after marine sedimentary conditions (thin layers of coal in the Upper Paleozoic sediments).

Dolomitization, which might have preceded baritization or was contemporaneous with it (Fig. 13A, B), could be a Dorag type, diagenetic process in the zone of salt and fresh water mixing (Sellwood, 1986, Badiozamani, 1973). Dolomitization plays important role, and serves as a useful prospecting criterion in Mississippi valley type ore deposits. High concentration brines were discovered in almost all the minerals but not in barite, where freezing temperature reached —0.47 °C and —0.32 °C (Nuns Cove, Tennessee), and —0.15 °C in Click Creek, what appropriates to almost pure water. Roedder (1976), explains it by physical properties of barite and its incapability for preservation of fluid inclusion content.

Hematite inclusions, pseudomorphs after pyrite, in solid barite crystals, point out on supergene oxidation. It might have happened since Carboniferous to the present time, due to fissibility of barite crystals for breaking along cleavage plains and ability for healing of fractures by recrystallization. Fig. 12 A, B shows development of a large fluid inclusion, which disperses into hundreds of tiny monophase (L) incusions.

Thermometric investigation of fluid inclusions in barite from the Lika barite deposits did not show unequivocal origin of ore forming fluids. There is wide possibility from early to late diagenesis, connected with Dorag type dolomitization or even Mississippi valley epigenetic processes, caused by upwelling, deeply seated connate brines from thick package of sediments into marginal zone, between a sedimentary basin and a stable platform. Hydrothermal convective cells, observed along the outer border of the passive continental margin and caused by magmatic activity during early intracontinental rifting, are not very likely encountered here.

Inclusion in barite from a hydrothermal deposit Gejkovac (Petrova gora mountain, Fig. 11) in negative crystal forms and with normally developed liquid and vapor phase prove that barite at some circumstances may preserve its original fluid inclusion content.

Further investigation should pay more attention to fluid inclusions in other kinds of transparent minerals. Study of dolomitization by oxygen isotopes, as well as other stable and unstable isotope methods would be also useful.

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Neočekivani sastav fluidnih inkluzija u baritu iz Ličkih ležišta barita

L. A. Palinkaš

Termometrijska istraživanja fluidnih inkluzija u baritu iz ličkih ležišta barita nisu jednoznačno ukazala na porijeklo rudonosnih fluida. Prisutne otopljene soli (alkalni sulfati, karbonati i bikarbonati) su u izvjesnom smislu neočekivane s obzirom na pretpostavljeno marinsko vulkanogeno-sedimentno ili sedimentno porijeklo. Na taj način bi ranodijagenetska baritna mineralizacija (ležište Brnićevo, i baritna mineralizacija u tamnom dolomitu na Pilaru), kao i kasnodijagenetska remobilizirana rudna tijela (Kravarica, Bat, žilne tvorevine) bile stvarane u slatkoj ili slabo bočatoj vodi, tj. nakon marinskih uvjeta sedimentacije (tanki proslojci ugljena u gornjopaleozojskim sedimentima).

Dolomitizacija, koja je mogla prethoditi ili biti sinhrona s baritizacijom logično bi se vezala za Dorag tip, karakterističan za zonu miješanja slatke i slane morske vode. Dolomitizacija inače igra važnu ulogu u genezi Mississippi valley-tipu rudnih ležišta, gdje služi kao dobar prospekcioni kriterij. Slani rasoli s visokom koncentracijom soli su otkriveni u svim mineralima osim u baritu, što Roedder objašnjava njihovim fizičkim svojstvima, odnosno mehaničkom nesposobnošću da sačuvaju primarni sastav fluidnih inkluzija.

Hematitne krute inkluzije, nastale pseudomorfozom pirita u supergenim uvjetima, ukazuju na moguće utjecaje meteorskih voda na inače, po izgledu, intaktne kristale barita. To se je moglo dogoditi u širokom vremenskom rasponu od karbona do danas. Inkluzije u baritu iz Gejkovca (Petrova gora) dokazuju da u određenim uvjetima i barit može sačuvati savršene primarne inkluzije.

Geneza ležišta zasada još uvijek nije riješena. Postoje široke mogućnosti od rane do kasne dijageneze, povezane s Dorag dolomitizacijom, ili čak epigenetski procesi Mississippi tipa, karakteristični za rubne dijelove stabilne platforme i labilnog sedimentacijskog prostora. Hidrotermalne konvektivne ćelije, uzrokovane magmatskom aktivnošću u toku ranog intrakontinentalnog riftovanja, kakve možemo očekivati u eugeosinklinalnom prostoru su manje vjerojatne.

Fig. 5 A barite bed in the Upper Carboniferous shales and sandstones at the Brničevo locality. The hangingwall and footwall layers are rich in pyritic cement which at places becomes massive pyrite, and most of it has been oxidized into limonite in supergene conditions. Deterioration of vegetion is due to highly acid conditions caused by oxidation of pyritic sediments.

Fig. 6 Reef limestones, a host rock of epigenetic barite veins with coarse euhedral barite crystals, provide good material for fluid inclusion study. The arrow points to joints of encrinites, metasomaticaly replaced by barite. Kravarica locality.

Fig. 7 Big euhedral barite crystals in dark dolomites suggest early diagenetic origin of mineralization. Pilar locality.

Fig. 8 Mighty epigenetic barite veins in light dolomites at Pilar ore deposit.

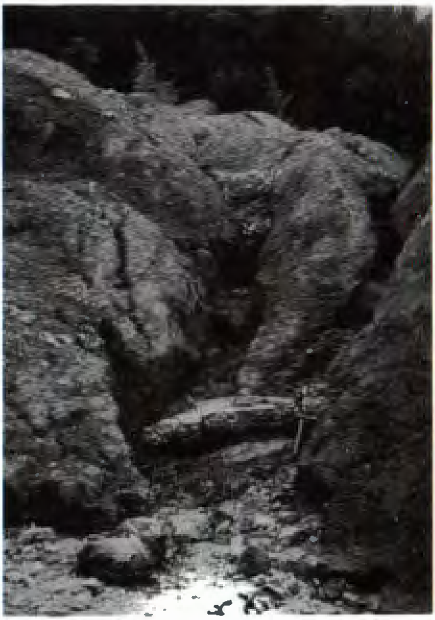

Fig. 5

Fig. 6

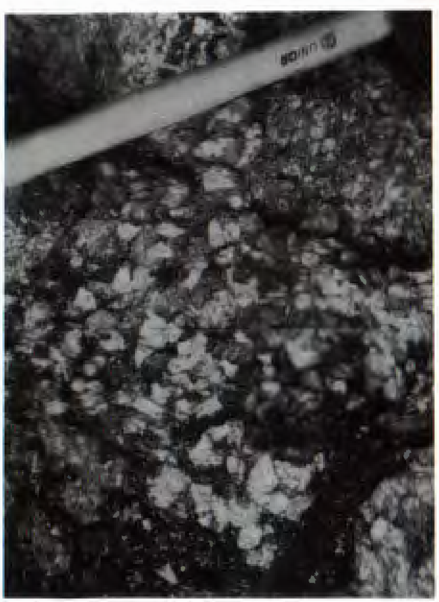

Fig. 7

Fig. 8

Fig. 9 Secundary monophase (L) and two-phase (L+V) inclusions in barite from Kravarica ore deposit. Secundary origin is suspected by irregular shape of inclusions and different degree of filling.

Fig. 10 Hematite solid inclusions, pseudomorphs after pyrite in seemingly fresh barite crystals.

Fig. 11 Primary two-phase inclusions (L+V) in barite from Gejkovac, Petrova gora in cavities with well developed negative crystal forms, show capability of barite to preserve primary fluid content.

Fig. 12A,B Secundary monophase (L) inclusion developed by healing along cleavage planes.

Fig. 13A,B Solid monophase inclusions (S) of dolomite in barite from Kravarica, point out on important connection between dolomitization and ore formation (one and crossed Nichols).

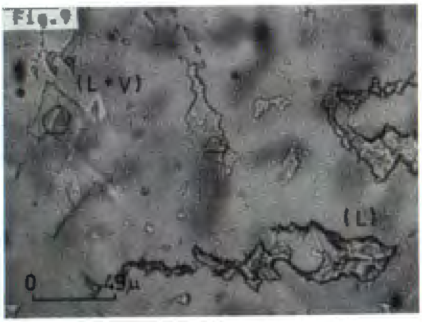

Fig.9

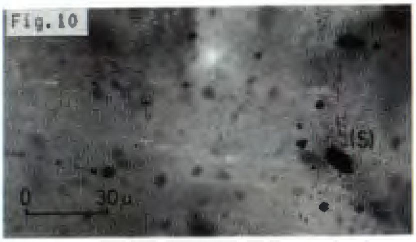

Fig.10

Fig.11

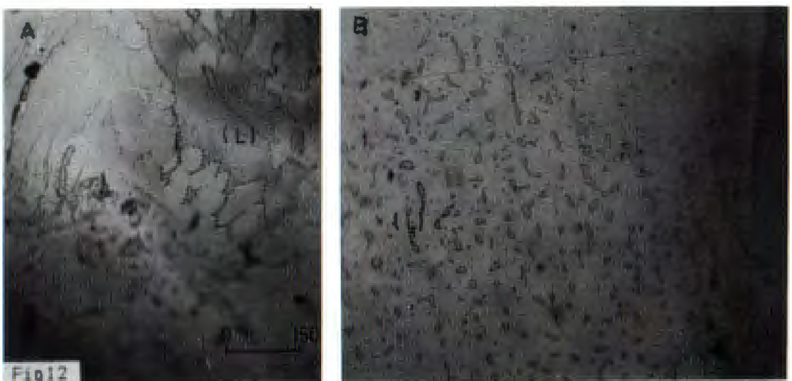

Fig12

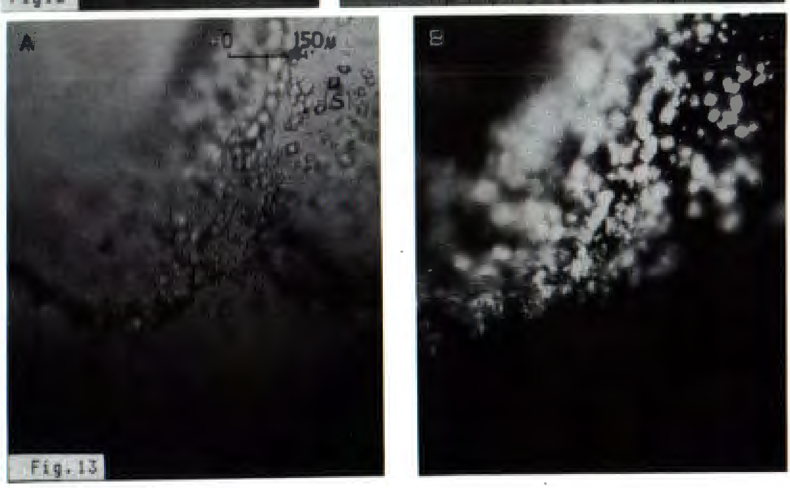

Fig.13