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Lanthanide Geochemistry and Fluid Inclusion Peculiarities of the Fluorite from the Barite Deposits South of Kreševo (Bosnia and Herzegovina)

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Key words: Fluorite, Lanthanides, Fluid inclusions, Post-Variscan metallogeny, Bosnia

Ključne riječi: fluorit, lantanidi, fluidne inkluzije, postvariscijska metalogenija, Bosna

Abstract

"Strata-bound" barite deposits occur in Devonian dolomites, situated in the Mid-Bosnian Palaeozoic Schist Mountains. These contain barite as the main ore mineral (5.9 wt% $SrSO_4$ on average and $\delta^{34}S$= +8.3‰) which comprises 90-99 wt% of the bulk ores. The subordinate components are calcite, fluorite, Hg-Sb-tetrahedrite, pyrite and quartz.

Analysis of REE by INAA revealed an extremely low content of lanthanides (1.584 ppm), negative Eu anomalies (Eu^{3+}/Eu^{+} = 0.7398), and $(Tb)_N/(La)_N$ = 6.2 indicating late-stage mineralization.

Primary fluid inclusions show a uniform number of infilling phases (L+V+S), and persistent volume ratio. This indicates homogeneity of the hydrothermal ore-forming fluids and an absence of boiling phenomena at the time of fluorite formation. T_h is between 200° and 310°C, with a distinctive maximum at 250°C. T_{fm} -20.3°C predominates but careful examinations of the early melting behaviour of the inclusions warrants the existence of T_{fm} -51°C, and the presence of $CaCl_2$. High salinity between 25 and 26 wt% eq. NaCl was determined from the hydrohalite melting temperature (T_{mh}). Some additional daughter minerals are also present. Fluorite, barite and calcite formed from the high saline waters probably originated by mixing of heated hydrothermal fluids with the highly evolved post-Variscan Upper Permian formation waters. This is supported by the study of the isotopic composition of the carbon, oxygen and sulphur of the paragenetic carbonates and sulphides.

Sažetak

"Strata-bound" ležišta barita u devonskim dolomitima Srednjobosanskih škriljavih planina sadrže barit s prosječnih 5.9 % $SrSO_4$ i s izotopnim sastavom sumpora +8.3‰ $\delta^{34}S$ kao glavni mineral, što izgrađuje 90-99 tež. % rudne mase. Sporedni minerali su kalcit, fluorit, Hg-Sb-tetraedrit, pirit i kvarc.

Studij rijetkih zemalja (INAA) utvrdio je izvanredno niski sadržaj REE (1.584 ppm), negativne Eu anomalije (Eu^{3+}/Eu^{+} = 0.7398) te $(Tb)_N/(La)_N$ = 6.2, ukazujući na kasni stadij mineralizacije. Atomski odnosi Tb/Ca-Tb/La stavljaju fluorit u "sedimentno polje", što autori tumače posljedicom efekta asimilacije dolomitnog salbanda čime se umanjio odnos Tb/Ca i ukupni sadržaj lantanida.

Primarne fluidne inkluzije pokazuju uniforman broj faza (L+V+S) i stalan odnos volumena. To ukazuje na homogenost hidrotermalnih rudonosnih fluida kao i odsutnost fenomena ključanja u doba stvaranja fluorita. T_h je između 200° i 310°C, s jasnim maksimumom kod 250°C. T_{fm} -20.3°C je dominantna, ali se brižljivim ispitivanjem ranog ponašanja taljenja u inkluzijama sigurno utvrdila T_{fm} -51°C, što se podudara s visokim salinitetom između 25-26 tež. % eq. NaCl, utvrđeno na temelju temperature taljenja hidrohalita (T_{mh}). U toku kriometrijskih mjerenja, reekvilibriranjem, utvrđena je prisutnost nekih drugih soli, za sada neodređenih. Fluorit, barit i kalcit su se formirali iz vrlo slanih voda koje su vjerojatno nastale miješanjem vrlo zagrijanih fluida s postvariscijskim, formacijskim, gornjopermskim vodama. To shvaćanje je potkrijepljeno i studijom izotopa ugljika, kisika i sumpora minerala u barit-fluoritnoj paragenezi.

1. GEOLOGY, TECTONIC SETTING AND PARAGENESIS OF THE BARITE DEPOSITS

The fluorite-bearing barite deposits of the Mount Meduvršje (+1195 m) are part of the wider ore-bearing region represented by the Central Bosnian Schist Mountains. The region extends in the east from Toplica on the river Lepenica to Zečeva Glava and Smiljeva Kosa in the west. This belt runs ENE-WSW in its western part, and E-W in its eastern part. It is about 22 km long and 2 to 4 km wide (JURKOVIĆ, 1987) (Fig. 1).

According to JOVANOVIĆ et al. (1977) the Upper Silurian - Lower Devonian schists are represented in their lower horizons by chlorite and muscovite schists, as well as by phyllites and argillaceous schists, quartzites and lydites. These metamorphic rocks are locally covered by Devonian dolomites, dolomitic limestones and marbles. The age of these carbonate rocks has been determined as Devonian by analogy with the corresponding deposits on the neighbouring Prozor sheet (SOFILJ et al., 1980). Magmatic rocks are represented by porphyrites, quartz porphyries, and keratophyres. The former occur as sills in the chlorite and muscovite schists, while the latter (of Permian age) form extrusions on the verge of the carbonate complex of Devonian age. The youngest Palaeozoic sediments are conglomerates, sandstones and phyllites with Upper Permian flora and brecciated limestones.

The Devonian layered carbonate complex overlies the metamorphic complex, but their geological relationships is not clear. The carbonate complex is over 300 m thick and contains deposits of barite. The surrounding younger Permian and Triassic rocks, as well as the older Silurian strata are ore-barren; therefore, we consider the barite ore deposits as "strata-bound" barite deposits.

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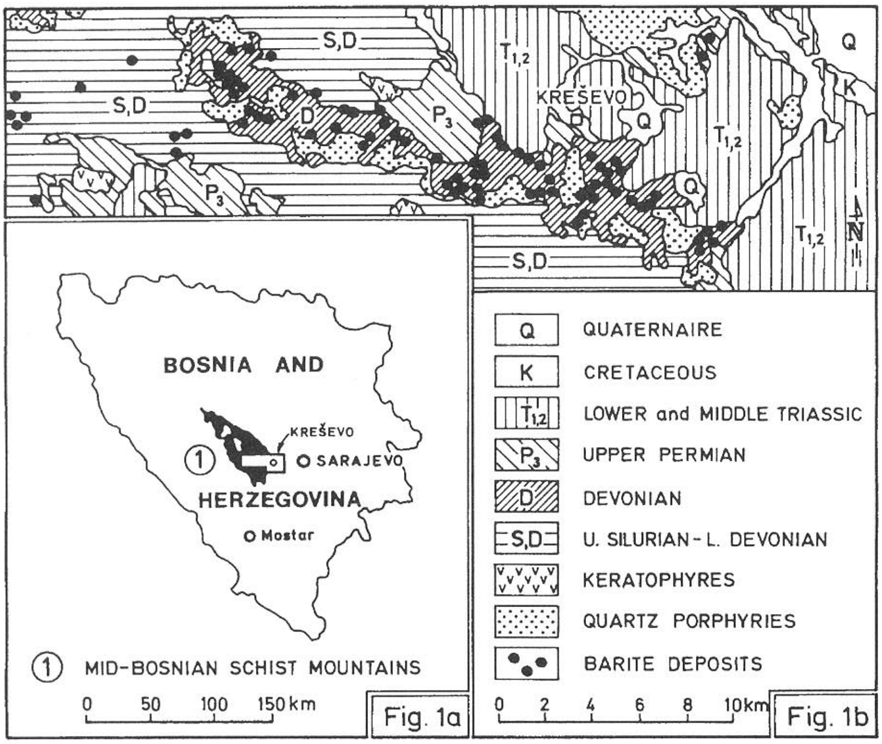

Fig. 1. Geological sketch map of the barite-bearing area east and west of the town of Kreševo, Bosnia.

The Međuvršje Mt., located in the immediate vicinity, S-SE of the town of Kreševo, is formed predominantly of the Devonian dolomites (Fig. 2). Barite ore bodies are emplaced in the hard, compact dolomite, which is light grey in colour. Its texture is microcrystalline, with grains 30-50 µm in size. Quantitative chemical analyses of fresh dolomites from Vidici and Glumac revealed that the ore-bearing rocks are dolomite rocks (JURKOVIĆ, 1986, 1987).

Barite occurrences are very irregular in form: impregnations, nests, variously sized veins and veinlets, irregular bodies, and brecciated ore bodies in the dolomite. The mineralization occurred for the most part in the open system of cracks, fissures and brecciated zones. The processes of replacement are less evident. The wall-rocks of ore occurrences are uneven, the walls are rarely smooth.

The paragenesis of the deposits is as follows: the main mineral is barite of the thin plate habit, type IVa, and allotriomorphic grain structured barite, type III. Neodolomite (ferrodolomite), calcite type II of rhombohedral habit, mercurian-antimonian tetrahedrite, quartz I, pyrite, fluorite, quartz II, gel-pyrite, calcite type III of scalenohedral habit are all visible without a microscope. The accessory minerals, visible only under the microscope, are chalcopyrite, sphalerite, enargite, famatinite, antimonite, "lautite", ascendent covellite and chalcocite, sericite, arsenopyrite, tourmaline, and rutile.

Barite is dominant throughout the Međuvršje area (the exception is at Rudna where silicification of the dolomite prevails) with 90 to 99 wt% $BaSO_4$. Barite contains from 2.8 to 8.5 wt% $SrSO_4$ (average is 5.9 wt% from 13 analyses). The isotopic composition of sulphur varies from +1.0 to +11.5 ‰ $\delta^{34}S$ (average is +8.3 ‰ $\delta^{34}S$ from 10 analyses) (ŠIFTAR, 1988).

Tetrahedrite is the most abundant mineral among the sulphides and sulphosalts in the Međuvršje region. It is Hg-Sb-tetrahedrite (JURKOVIĆ, 1986) containing 13.4 g/t Au and 382 g/t Ag. The isotopic composition of the sulphur is -8.20 ‰ (Vidici), -15.4 ‰ (Donji Martinovac), -5.5 ‰ (Trnjač), -6.96 and -11.43 ‰ (Duboki Vagan), -10.91‰ (Dubrave-Dugi Dol) (ŠIFTAR, 1988).

Fluorite is of octahedral habit (BARIĆ, 1942; JURKOVIĆ, 1956), violet or colorless, and transparent; its natural crystallographic planes are rough, probably formed by etching with acid fluids. Fluorite fills interstices within the plate-like barite crystals, and also occurs in the immediate dolomitic wall-rocks and in cavities together with short columnar quartz II. The octahedral habit indicates that the formation of fluorite has taken place under high temperatures.

Neodolomite forms through recrystallization of the pale-grey compact host dolomite rock. Some 10-15 wt % of the dolomite component was substituted by FeO from the hydrothermal solution (JURKOVIĆ, 1986). The grains were enlarged from 30 to 50 µm to 100-150 µm, in places up to 300 µm. Recrystallization is much stronger in the silicified zones.

The neodolomite in the wall-rock zones of the barite deposits is a very hard, compact rock, marble-like in appearance, white-grey in colour.

2. ANALYSIS

2.1. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) OF THE RARE EARTH ELEMENTS (REE) IN THE FLUORITE

Analyses by INAA were made at Institute for Petrography and Geochemistry, University Karlsruhe, Germany.

Techniques: For calibration, flux monitors and model spectra of the respective isotopes were used (ALFASSI, 1990). The international reference samples GSP-1, BHVO-1 and AGV-1 were run as unknowns. Samples and flux monitors were irradiated simultaneously in the reactor TRIGA II at the Cancer Investigation Center at Heidelberg under a thermal neu-

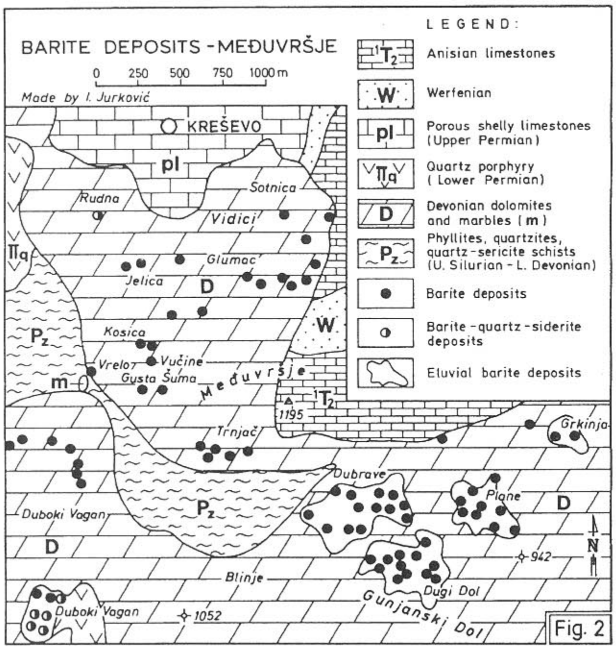

Fig. 2. Geological map of the barite-bearing area Međuvršje Mountain, south of the town of Kreševo, Bosnia.

tron flux of 8 x 10^{12} n $cm^{-2}sec^{-1}$ for 5 h. Two detector systems were used for measuring the gamma spectra: a coaxial HpGe detector with 1.85 keV FWHM at 1.332 MeV (^{60}Co) covering the energy range from 150 to 2000 keV and a planar HpGe detector with 540 eV FWHM at 122 keV for the energy range from 30 to 210 keV.

Two fluorite samples from the collection belonging to the Mineralogical and Petrographical Museum in Sarajevo under number 2811, were analysed by the INAA on the REE. Together these weighed 6.5 g and were sampled from the barite deposit Dubrave-Dugi Dol in the Međuvršje barite district. The fluorite was pure, transparent, glassy. The results of the analyses are presented in the Table 1.

Tables 2 and 3 represent the computation of the analyses, and Table 4 shows parameters of the fluorites A and B.

2.2. DISCUSSION OF THE RESULTS

2.2.1. REE (Fluorite) / REE (Chondrite) ratios

Tables 2 and 3 reveal that the fluorite from Kreševo barite deposits has extremely low REE values, 0.42662 ppm (Fluorite A) and 0.40587 ppm (Fluorite B) respectively, for the seven analysed REE. It is only 0.56 (F_A) and 0.53 (F_B) of the chondrite abundances for the same REE. For all 14 REE normalized to chondrite (column 7 in the Tables 2 and 3) the Σ REE is 1.5227 (F_A) and 1.6453 (F_B) respectively. Σ REE(chondrite) = 0.46 (FA) and 0.50 (F_B). The values for 7 and 14 REE are very similar. Such low concentration of REE has been reported for marine carbonates (1.4 ppm in sea shells and 3.75 ppm in recent corals) by SCHOFIELD & HASKINS (1964), then for La in corals from Bermuda Islands (La= 0.2 to 0.8 ppm), for oolite sands from Bahamas (La= 0.42 ppm), as well as very low REE for limestone from Solnhofen (Germany) according to SCHNETZLER & PHILPOTT (1970). SCHNEIDER et al. (1975), investigating fluorites and carbonate sediments of the East-Alpine Middle Triassic sequences in the Northern Calcareous Alps, reported a mean value of 2.9 ppm for fluorites, below the chondrite abundances. Some single fluorite crystals belonging to generation III, were paradiagenetically remobilized, and show extremely low values: 0.17, 0.57, 0.72 ppm compared to their host rock limestone (0.87 ppm).

Carbonate rocks with REE concentration below chondrite abundances are reported by HEIN & SCHNEIDER (1983) and fluorites from limestones with REE concentration of about 0.5 of chondrite abundances by MÖLLER & MORTEANI (1983), EPPINGER & CLOOS (1990). MÖLLER & MORTEANI (1983) assert that fluorite, calcite and dolomite formed under hypersaline conditions can be extremely low in REE (i.e. they are submitted to very strong impoverishment of REE). SCHULTZ (1980) and MÖLLER & MORTEANI (1983) reported that the fluorite formed from evaporating brines in restricted basins are characterized by very low contents of REE.

	Fluorite A (F_A)			Fluorite B (F_B)		
La	22.96 ppb	±	8.86 ppb	29.32 ppb	±	5.33 ppb
Sm	0.12 ppm	±	0.01 ppm	0.15 ppm	±	0.00 ppm
Eu	23.73 ppb	±	2.10 ppb	24.70 ppb	±	3.76 ppb
Tb	22.98 ppb	±	7.93 ppb	25.88 ppb	±	8.52 ppb
Ho	8.19 ppm	±	0.08 ppm	0.11 ppm	±	0.03 ppm
Tm	22.78 ppb	±	12.49 ppb	44.97 ppb	±	13.17 ppb
Lu	24.17 ppb	±	6.03 ppb	21.00 ppb	±	5.89 ppb
Na_2O	92.91 ppm	±	2.75 ppm	22.76 ppm	±	1.16 ppm
Sc		±		1.27 ppb	±	1.40 ppb
Fe_2O_3	125.00 ppm	±	21.00 ppm	158.70 ppm	±	18.40 ppm
Co	11.04 ppb	±	9.44 ppb	4.39 ppb	±	7.51 ppb
Sb	0.79 ppb	±	0.05 ppm	0.18 ppm	±	0.03 ppm
W	895.00 ppm	±	0.90 ppm	140.00 ppm	±	0.30 ppm
Ta	60.29 ppb	±	2.37 ppb	9.09 ppb	±	1.88 ppb
U	0.13 ppm	±	0.07 ppm	19.69 ppb	±	25.57 ppb

Table 1. The results of the INAA analyses of two fluorite samples.

Table 2

Elements	1	2	3	4	5	6	7	8
La	0.02296	0.3100	0.0741	1.13	0.110	0.0920	0.0285	0.0920
Ce		0.8080		1.09	0.188	0.188	0.1519	0.188
Pr		0.1220		1.08	0.215	0.215	0.0262	0.215
Nd		0.6000		1.06	0.281	0.281	0.1686	0.281
Sm	0.12000	0.1950	0.6154	1.04	0.367	0.4912	0.0958	0.4912
Eu	0.02373	0.0735	0.3229	1.03	0.419	0.419	0.0380	0.3229
Gd		0.2590		1.02	0.479	0.479	0.1241	0.479
Tb	0.02298	0.0474	0.4848	1.	0.626	0.5554	0.0263	0.5554
Dy		0.3220		0.99	0.716	0.716	0.2306	0.716
Ho	0.19000	0.0718	2.6462	0.98	0.818	1.7321	0.1244	1.7321
Er		0.2100		0.97	0.936	0.936	0.1966	0.936
Tm	0.02278	0.0324	0.7031	0.96	1.069	0.8860	0.0287	0.8860
Yb		0.2090		0.95	1.223	1.223	0.2556	0.223
Lu	0.02417	0.0322	0.7506	0.94	1.398	1.0743	0.0346	1.0743
Σ La-Lu		3.2923					1.5227	

Table 3

Elements	1	2	3	4	5	6	7	8
La	0.02932	0.3100	0.0946	1.13	0.140	0.1173	0.0364	0.1173
Ce		0.8080		1.09	0.228	0.228	0.1842	0.228
Pr		0.1220		1.08	0.257	0.257	0.0314	0.257
Nd		0.6000		1.06	0.328	0.328	0.1968	0.328
Sm	0.15000	0.1950	0.7692	1.04	0.419	0.5941	0.1159	0.5941
Eu	0.02470	0.0735	0.3361	1.03	0.474	0.474	0.0348	0.3361
Gd		0.2590		1.02	0.535	0.535	0.1386	0.535
Tb	0.02588	0.0474	0.5460	1.	0.683	0.6145	0.0291	0.6145
Dy		0.3220		0.99	0.771	0.771	0.2483	0.771
Ho	0.11000	0.0718	1.5320	0.98	0.872	1.2020	0.0863	1.2020
Er		0.2100		0.97	0.985	0.985	0.2069	0.985
Tm	0.04497	0.0324	1.3880	0.96	1.112	1.2500	0.0405	1.2500
Yb		0.2090		0.95	1.257	1.257	0.2627	1.257
Lu	0.02100	0.0322	0.6522	0.94	1.420	1.0361	0.0334	1.0361
Σ La-Lu		3.2923					1.6453	

Tables 2 and 3. The computation of the INAA analyses of two fluorite samples. Table 2 - INAA of the fluorite A; Table 3 - INAA of the fluorite B. Legend: column 1 original analysis in ppm, column 2 REE values of chondrites; column 3 chondrite-normalized values of REE (col. 1/col. 2); column 4 ionic radii of REE; column 5 computed on the basis of $y=\exp(a+bx)$. Exponential curve computed from the values in column 3 (excepting value for Eu wich is anomalous); y=chondrite-normalized value on the smooth (even) curve, x=ionic radius, a and b are computed coefficients; column 6 corrected exponential curve (only for analysed REE) on the basis of the formula $k=(m + u)/2$, e.g. the mean value of the values in the columns 3 and 5 (Eu was not corrected); column 7 represents the corrected values in ppm, obtained by multiplication of values in column 6 and 2. The values in this column serve for the computation of the total sum for the LREE, MREE, HREE and total REE as well as for the computation of Eu anomaly; column 8 the same values as in the column 6, only the value for Eu is chondrite-normalized, serving for the design of the graphs.

2.2.2. Chondrite-normalized REE_N diagrams and $(\text{La})_N/(\text{Yb})_N$ ratios

The chondrite-normalized REE_N diagrams for the data presented in Tables 2 and Table 3 are shown in Fig. 3. Enrichment factors for fluorite increase systematically from La to Yb, but with raised values for Sm and especially for Ho. Both curves are very similar, the differences are only in Sm, Ho and Tm.

The ratio of $(\text{La})_N$ to $(\text{Yb})_N$, indicating the overal slope of the curve, is 0.1115 for the fluorite A and 0.1386 for the fluorite B reflecting a very distinct enrichment in HREE. According to EKAMBARAN et al. (1986) and EPPINGER & CLOOS (1990) such slope of the curve indicates late-stage fluorite formation. The analysed fluorite from Kreševo belongs to the last phase of the mineralization.

2.2.3. Tm_N/Sm_N ratios

Tm_N/Sm_N ratios are 1.1425 for the fluorite A and 1.8045 for the fluorite B. Increased values for Sm and decreased values for Tm have been interpreted by BOWERS & HELGESON (1983) and WENDLANT & HARRISON (1979) for the fluids supersaturated with respect to CO_2 and halides. In such cases LREE are preferentially fractioned into a vapour phase that separates from the liquid. The liquid will suffer depletions

	Σ REE	Σ(La-Nd)	Σ(Sm-Ho)	Σ(Er-Lu)	ΣLREE	ΣHREE	$\frac{\Sigma LREE}{\Sigma HREE}$	$\frac{\Sigma REE\ fl}{\Sigma REE\ chon}$
F_A	1.5227	0.3752	0.6320	0.5155	0.4710	1.0209	0.4614	0.46
F_B	1.6453	0.4488	0.6530	0.5435	0.5646	1.0459	0.5398	0.50

	$(La)_N/(Yb)_N$	Eu^{3+}/Eu^{2+}	$(Tb/La)_N$	$(Tm)_N/(Sm)_N$	Tb/Ca ppm	Tb/La ppm
F_A	0.1115	0.7706	6.5425	1.1425	$1.129\ 10^{-8}$	$8.748\ 10^{-1}$
F_B	0.1386	0.7091	5.7717	1.8045	$1.271\ 10^{-8}$	$7.717\ 10^{-1}$

Table 4. Parameters of the fluorites A and B.

of both Ce and Tm with respect to Sm. The CO_2 vapor phase should be depleted in Sm. It is uncertain whether at the temperatures of 250°-350°C and pressure of 1.0 kbar conditions vapour could have separated from an aqueous phase.

2.2.4. The values for the Eu anomalies

Fluorite A shows $Eu^{3+}/Eu^{+} = 0.7706$; fluorite B shows $Eu^{3+}/Eu^{+} = 0.7090$. Both fluorites have distinctly negative Eu values which are in agreement with the presence of sulphides and sulphosalts in the barite deposits. JARVIS et al. (1975) suggested that metamorphism or metasomatism may cause Eu^{3+} to be reduced to Eu^{2+}.

2.2.5. Sigma values (σ)

Figure 4 shows the relative abundance distribution patterns of REE normalized to chondritic composition and further to La (La = 1.0), σ values. The plot reflects an enrichment of Ho and its neighbouring lanthanides, more pronounced in fluorite A than in fluorite B, as well as an enrichment in Sm. The different values for Tm and Lu in the two fluorites are also characteristic.

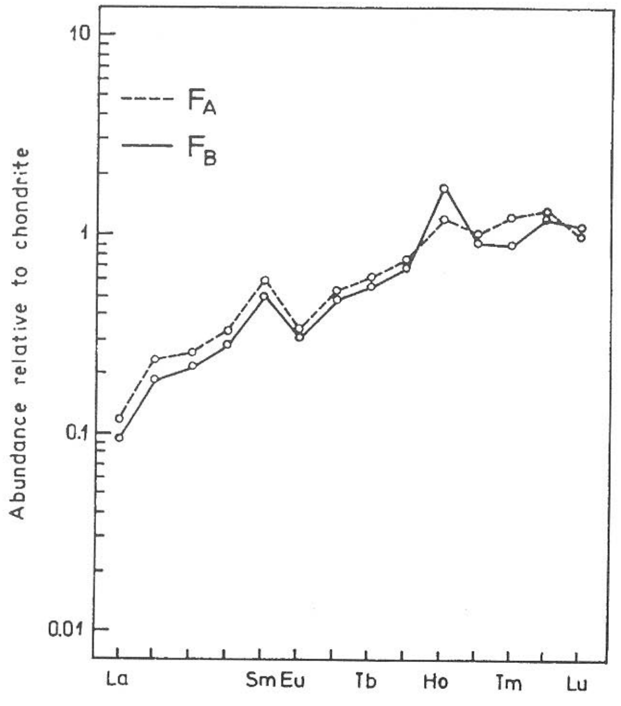

Fig. 3. Chondrite-normalized REE in fluorites A and B.

2.2.6. Tb/La - Tb/Ca ratios; fractionation and genetic indexes

BRÄTTER et al. (1972) have clearly indicated that the REE distribution could well represent a geochemical indicator for the genesis of fluorite. JACOB (1974) (cited in SCHNEIDER et al., 1975) demonstrated that the magnitude of the Tb/Ca wt. ratio relative to that of Tb/La ratio in fluorite could be used as a criterion for the genesis of the fluorite. He established two demarcated fields (defining the above two parameters): pneumatolytic + hydrothermal and sedimentary fields for the fluorite from Central and South Europe. SCHNEIDER et al. (1975, 1977) and MÖLLER et al. (1976) have used the Tb/Ca ratio as a genetic index, and the Tb/La ratio as a fractionation index. MÖLLER & MORTEANI (1983) stress that only both ratios (Tb/Ca and Tb/La) taken together turn out to be a useful set of geochemical indicators for solving the genesis of fluorite. They consider the Tb/La ratio as an environmental index.

The fractionation indexes (Tb/La atom ratios) versus the genetic indexes (Tb/Ca ratios) for the fluorites from Kreševo presented in Table 4 plot in the "sedimentary field" according to SCHNEIDER et al. (1975, 1977). This is not in accordance with the geological observations and with the results of the fluid inclusion study of the fluorite and other paragenetic minerals (Fig. 5).

The assimilation of calcium-rich dolomitic host rocks by the ore forming fluids could very likely diminish the Tb/Ca atom ratios so much that the fluorite generated by this way exhibits a Tb/Ca ratio characteristic of a sedimentary instead of a hydrothermal fluorite. Interaction of hydrothermal solutions with limestones or other Ca-rich-sediments results in an uptake or exchange of Ca^{2+} ions together with other trace elements. Similar opinions are expressed by SCHNEIDER et al. (1975), JARVIS et al. (1975), MÖLLER et al. (1976), BELLANCA et al. (1981), and MÖLLER & MORTEANI (1983). The process of ferrodolomitization ranging from 5 to 15 wt % FeO in the immediate dolomitic wall rocks (JURKOVIĆ, 1986), releasing adequate amounts of MgO, might also change the REE distribution patterns.

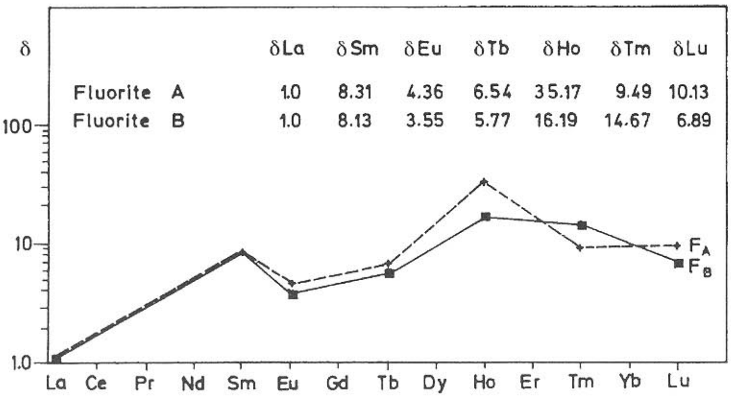

Fig. 4. σ sigma values, fluorites from Kreševo barite deposits

$$\sigma = \frac{\text{ppm La-Lu (fluorite)}}{\text{ppm La-Lu (chondrite)}} \Big/ \frac{\text{ppm La (fluorite)}}{\text{ppm La (chondrite)}}$$

2.2.7. Depletion of LREE

Complex formation and distribution of the REE are responsible for their fractionation during mineralization (WHITAKER & MUNTUS, 1970; BILAL el al., 1979; BILAL & BECKER, 1979).

Fluorite bearing settings containing NaCl (of 0.5 to 1.0-3.0 M) and pH 3-5 may have, besides the main ligand for complexing the REEF$^-$, also the anions Cl$^-$, SO_4^{2-}, OH$^-$, HCO_3^-, and CO_3^{2-} which may form together with F$^-$ ion REE mixed ligand complexes. At pH >5, we have to regard only F$^-$, Cl$^-$ (neglected by PEPPARD et al., 1962) and SO_4^{2-} (only of importance at higher sulphate levels according to BILAL & KOSS, 1980).

Complexing with carbonates in highly alkaline solutions is described by ALEKSANDROV et al. (1969) and DUMONCEAU et al. (1978). MARCHAND et al. (1976) stress the important role of the carbonate complexes concerning the fractionation of the REE in the natural conditions. BROOKINS (1983) recorded that the field of $(REE)_2CO_3$ stability decreases from Eu to Dy and carbonate complexes of Ho to Lu are metastable.

The F$^-$ ion is the main ligand in the fluorite bearing setting, which may form with HCO_3^- and CO_3^{2-} REE mixed ligand complexes at pH <5, and with Cl$^-$ and SO_4^{2-} at pH >5 (BILAL et al., 1979).

The stability constants of the monofluoride complexes gradually increase from La to Lu (WALKER & CHOPPIN, 1967). BILAL et al. (1979) studied in detail the stability constants of the monofluore complexes (β_1) proving the maximum at Tb and a slight decrease to Lu rather than to La. The different ionic strenght (I) may cause a variation in the complex stability and also the fractionation tendency along the REE series.

La^{3+} forms the least stable fluoride complexes in solution (HERMANN, 1970). It is removed from solution early, causing a progressive increase in the Tb/La ratio of the fluid and its crystalline products. Fluorites that crystallize late from a mineralization solution would have $(Tb/La)_N$ >1.0 and hence an increasing pattern from La to Tb when normalized to chondritic REE abundances, as is the case for the Kreševo fluorite. The enrichment of MREE and HREE relative to LREE may have been due to the formation of more stable MREE and HREE complexes with F$^-$ and CO_3^{2-} relative to their LREE complexes.

Another mode of fractionation of REE during mineralization is observed during remobilization which leads to a conspicuous impoverishment of La during mobilization while Tb remains virtually constant (MÖLLER et al., 1976). During its migration through the rock La becomes relatively depleted in the mobile phase because of the lower stability constants of La-F complexes than of the corresponding Tb-F complexes. Tb remains relatively stable in the mobile phase and keeps reprecipitating along with the subsequent fluorite generations.

In the Kreševo district the hydrothermal solution underwent a relatively long period of remobilization and metasomatism from

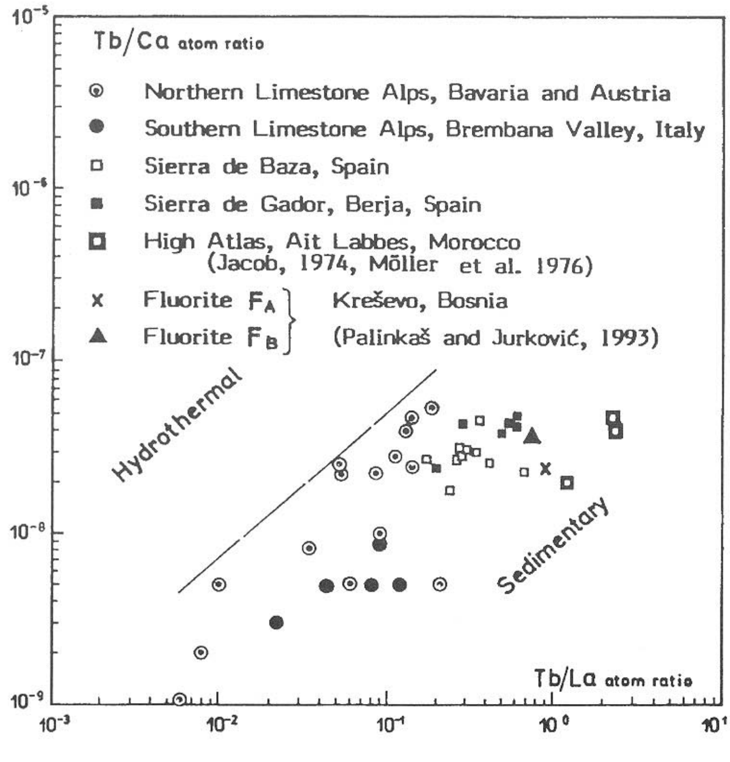

Fig. 5. Tb/Ca - Tb/La atom ratios

the first phase (silicification, local potassic alteration, pyritization), through second phase (baritization, calcitization), into third phase (sulphides and sulphosalts), ending with the formation of fluorites. During this time La^{3+} ions have been partially removed from solutions causing a progressive increase in HREE/LREE ratio of the fluid and its products.

Some selective REE distribution patterns of the "so called" remobilized and late-stage fluorites (calcites), cited in the literature, in comparison with the Kreševo fluorites, indicate that the latter ones belong to the same genetic group (Fig. 6).

3. FLUID INCLUSION STUDY

Microthermometry has been performed on the CHAIXMECA microthermometry apparatus type MTM 85 (Department of Geology, Faculty of Mining and Geology, Zagreb). Techniques: Temperature range: -180°C (with liquid nitrogen) to +600°C; Digital read out with ±0.1° resolution; Small vertical gradient (e.g. 0.8°C for one millimeter in the center of the field, at 400°C; Reproducibility of measurements: 0.1°C between -60°C and +400°C; Built in silica condenser for better illumination of sample; Infrared filter to decrease heating of the sample by the light of the microscope.

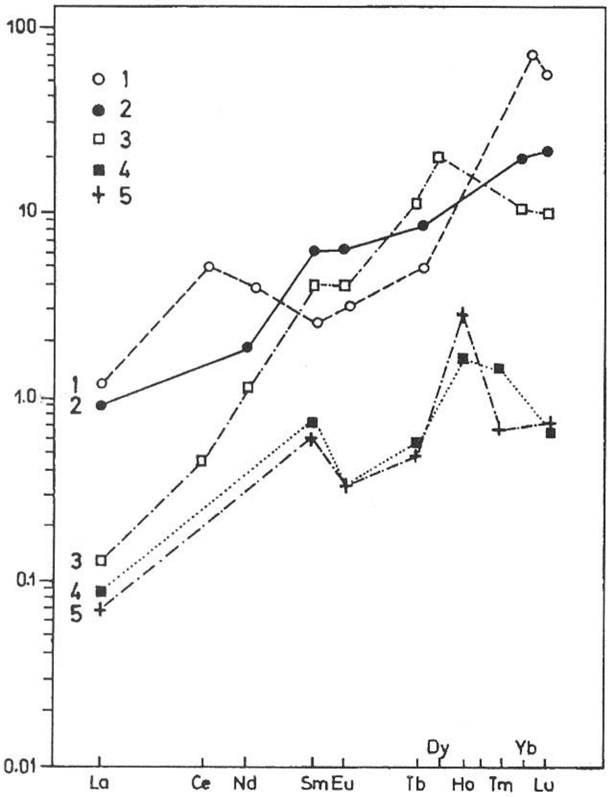

Fig. 6. REE distribution patterns in fluorites. Legend: 1 - remobilized fluorites, Ait Labbes, high Atlas, Morocco (JACOB, 1974; MÖLLER & MORTEANI, 1983); 2 - remobilized calcite from alpine fissures, Zillertaler Alpen, Austria (MÖLLER & MORTEANI, 1983); 3 - fluorite SP-1, Spar deposit, Western Montana, USA (EKAMBARAN et al. 1986); 4 - (F_A) and 5 - (F_B) late stage fluorites, barite deposits, Kreševo, Bosnia and Herzegovina (PALINKAŠ & JURKOVIĆ, 1993).

3.1. INCLUSION MORPHOLOGY

The inclusions are irregular, usually not mimicking the cleavage direction of the host, but spheroidal and oblate shapes are also common. The size of the inclusions is between 50-500μ. A large part of the inclusions may be termed primary or pseudosecondary according to ROEDDER's (1984) criteria (Fig. 7). Inclusions occur in a threedimensional random distribution and are often separated one from another, by distances greater than 5x the inclusion diameter, although planar groups are present too, which terminate at the growth zones.

The degree of fill ($F=V_L/(V_L+V_V+V_S)$) has been determined on multiphase solid inclusions (3S+L+V), by measuring areas of appropriate phases on the inclusion photographs. The measured inclusions were preferentially flat, in order to approach the area=volume. The average degree of fill F=0.92 (±1%) as determined on 8 inclusions, with a very narrow dispersion of F values (less than 1%) points to a homogeneous parent fluid. Since the solid phases occupy less than 1% of the total volume, they have not been taken into consideration. The shape of the inclusions is oblate and disk-like, so one may expect certain differences between the real degree of fill and the one obtained by measuring phase areas on the photos.

The inclusions contain three recognised solid phases (Figs. 7. a, b, c, e). The first, with rhombohedral habit, marked relief change on rotation in polarized light, and expressed anisotropy, might be a carbonate. The second (according to size), has moderate relief and birefringence and could also be a carbonate. The third, with exceptionally high relief (which obstructed normal observation of anisotropic colour effects) is the smallest one. It is almost opaque in appearance (Fig. 7d). The permanent number and kind of daughter crystals and their proportional size versus inclusion size are demonstrable additional signs of parent fluid homogeneity.

3.2. MICROTHERMOMETRIC RESULTS

Homogenization temperatures (T_h) in the range between 200-310°C, with a distinctive maximum at 250°C, have been determined on 38 inclusions (Fig. 8c). All inclusions homogenize into the liquid state and no boiling effects were observed. Partial decrepitation commenced in some inclusions at temperatures as low as 114°C, but massive decrepitation with complete discharge of fluid content started above 330°C. Determination of Th on the larger inclusions (>250 μm) has not been perfomed owing to unpredictable decrepitation.

The daughter minerals failed to dissolve or change their shape during heating.

The large size of the inclusions enabled the precise determination of the first melting temperatures T_{fm}. A

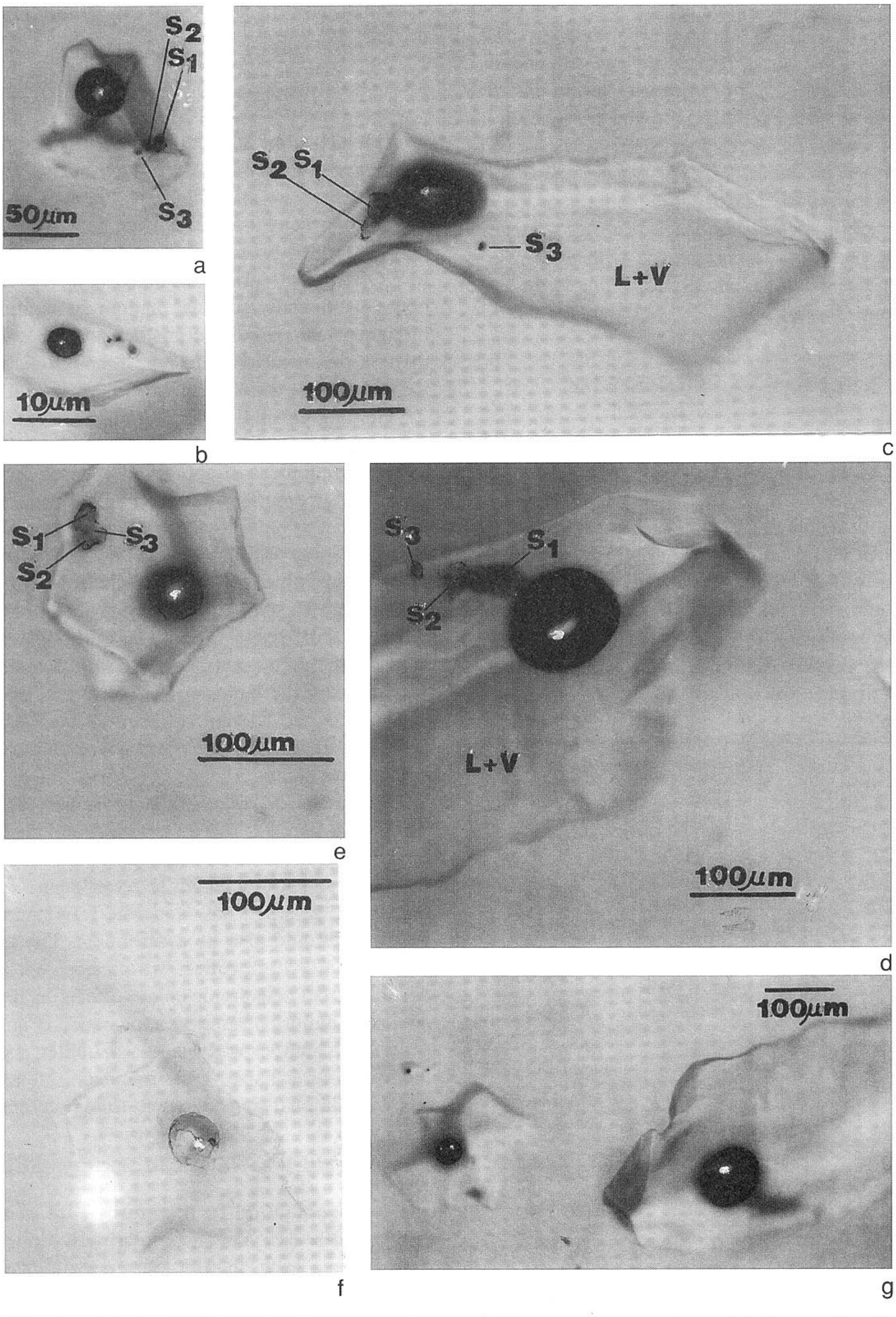

Fig. 7a, b, c. Five phase inclusions (S_1+S_2+S_3+L+V), with the same degree of filling (F) and the same number and kind of solid phases.

Fig. 7d. The same (3S+L+V) inclusion. The first solid (S_1), high relief, expressed anisotropy, probably carbonate, the second (S_2), moderate relief and anisotropy; the third (S_3), extremely high relief obstructing observation of anisotropic colours, and making its appearance almost opaque.

Fig. 7e, f. (3S+L+V) inclusion in parallel and crossed Nicols showing expressed anisotropy of the daughter minerals.

Fig. 7g. The series of 4 primary inclusions (3S+L+V). Solid phases out of focus. Degree of filling F= 0.92 shows a very small variation (less than ± 1%). Obscure images of the inclusion boundaries confirm high salinity of the fluid, as determined by the cryometric measurements.

pale brown colouration of the frozen inclusion content, after metastable cooling, suggested the presence of $NaCl-CaCl_2(\pm MgCl_2)$ (SHEPHERD et al., 1985). Darkening and coarsening started as early as -57°C, but the measurements on the hardly noticeable dissolutions had three maxima at -51°C, -30°C, and -21°C. This does not neccessarily mean, however, three different aqueous systems, but rather a small quantity of eutectics, as proved by careful reequilibration and breeding of the particular crystal phases using a heat/freeze technique (inclusion on Fig. 7a).

The experiment revealed 5 solid phases as well as their melting temperatures. The true eutectic temperature, T_e= -51°C, has been observed clearly on the residual eutectic liquid, frozen in the interstitial space between the fully grown crystal phases. The second phase to dissolve is slightly anisotropic, T_{m2} = -28.0°C; the third, with very low relief and rounded isotropic crystals, T_{m3} = -11.8°C, the fourth, with clear anisotropy and prismatic and pyramidal habit, T_{m4} = -8.0°C, and the fifth prismatic, anisotropic, reluctant to coalesce, Tm_5 = -1.5°C; might be a hydrate. Distribution of T_{fm}'s (first melting) with the three ambiguous maxima shows a complex dissolution process within a multi-component aqueous system. Accurate determination of T_e= -51°C, points towards the presence of $CaCl_2$ (supported by limited microthermometric measurements on a paragenetic barite). It contains conspicuous evidence of boiling and presence of $CaCl_2$-$NaCl$-H_2O inclusions, some of them very close to the eutectic composition (T_e = -51°C, T_m = -49°C, CROWFORD, 1981).

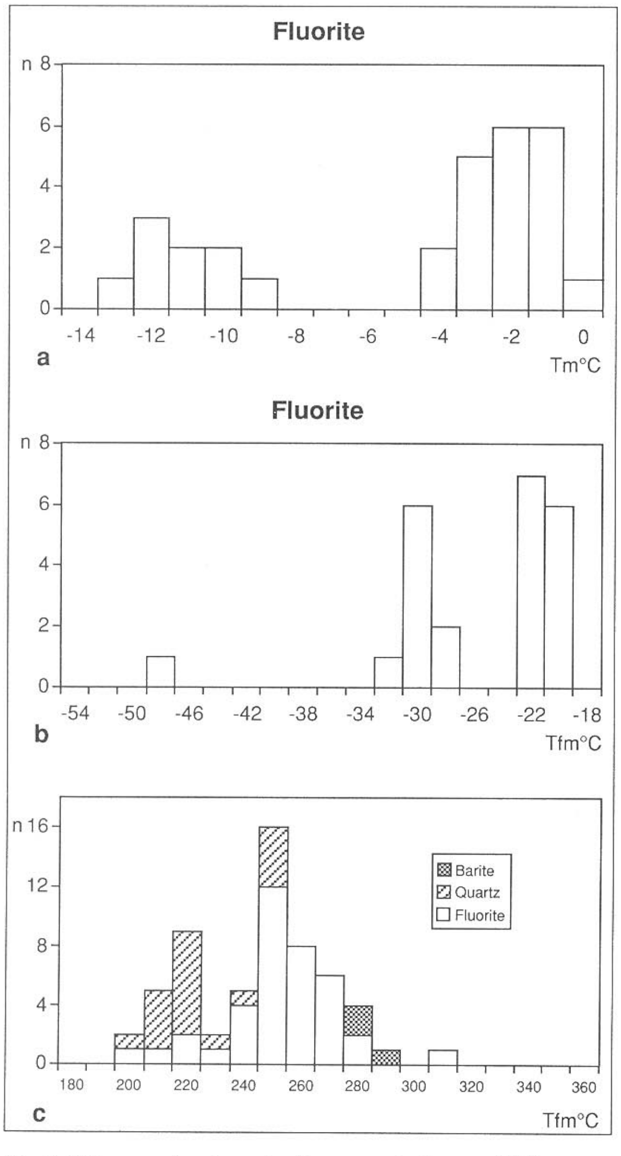

Fig. 8. Histogram showing microthermometric data. a - Melting temperature(T_m); b - Temperature of first melting (T_{fm}); c - Temperature of homogenization (T_h).

The complex character of the fluid inclusion composition in the fluorite might be suggested by the daughter minerals, not affected during homogenization runs.

Using the binary tie line on the hydrohalite side of the H_2O-$NaCl$ system for the inclusions whose T_{fm} are between -30°C and -20°C, the gross salinity is in the range of 24.2-26.3 wt% NaCl eq. assuming that the last melting hydrate is hydrohalite. The pitfall of this presumption is in the uncertain determination of T_m-ice since any of T_{m2}, T_{m3} and T_{m4} might be ascribed to ice (presence or absence of anisotropy does not warrant determination, due to variability in thickness, of the inclusion). If T_{m4} = -8.0°C or $T_{m\ 3}$= -11.8°C belonged to ice, some additional anions had to be added, e.g. HCO_3^-, CO_3^{2-} or/and SO_4^{2-} (BORISENKO, 1975).

Combined measurements T_h vs. salinity are presented on Fig. 9 in addition to data for a fluorite from the Žune ore body in the Ljubija ore district, NW Bosnia (PALINKAŠ, 1988), with clear boiling phenomena. Homogenization temperatures and salinity data gave way to the overall densities at the temperature of filling (T_h= 250°C; HAAS, 1976) of 1.00-1.05 kgm^{-3}, which appropriaties to a degree of fill (F=0.87), since ρTOT= ρLF = 1.03 kgm-3 (ρTOT=overall density, rL= density of saline water phase, 25 wt% NaCl, 25°C). The discrepancy between F=0.92, obtained by integrating the phase areas on the photos, and F=0.87 is probably due to differences between the real chemical composition of the inclusions compared to that expressed in wt% NaCl eq.

4. GENETIC REMARKS

The deposition of fluorite requires conditions whereby a concentrated acid brine decreases in T, P, or salinity, or increases in pH or in Ca^{2+} ion activity (RICHARDSON & HOLLAND, 1979; PLIMMER, 1984). The solubility of fluorite is increased with increased $NaCl$, $CaCl_2$, $MgCl_2$ concentration, as a result of the formation of the NaF° species and CaF^+ and MgF^+ complexes. In NaCl solutions, fluorite solubility decreases rapidly beneath 150°C. In concentrated $CaCl_2$ solutions the solubility of fluorite decreases rapidly well above 150°C.

Fluorite precipitation may also be induced by the increase in pH of an initially acid hydrothermal fluid caused by hydrothermal alteration reaction or by mixing of Ca^{2+} solutions with F^- solutions (BONI et al., 1990). If a hydrothermal fluid entering a limestone terrain dissolves $CaCO_3$ (±$MgCO_3$) the Ca^{2+}(±Mg^{2+}) concentration of the fluid is increased. Such an increase in the Ca^{2+} concentration can lead to the precipitation of

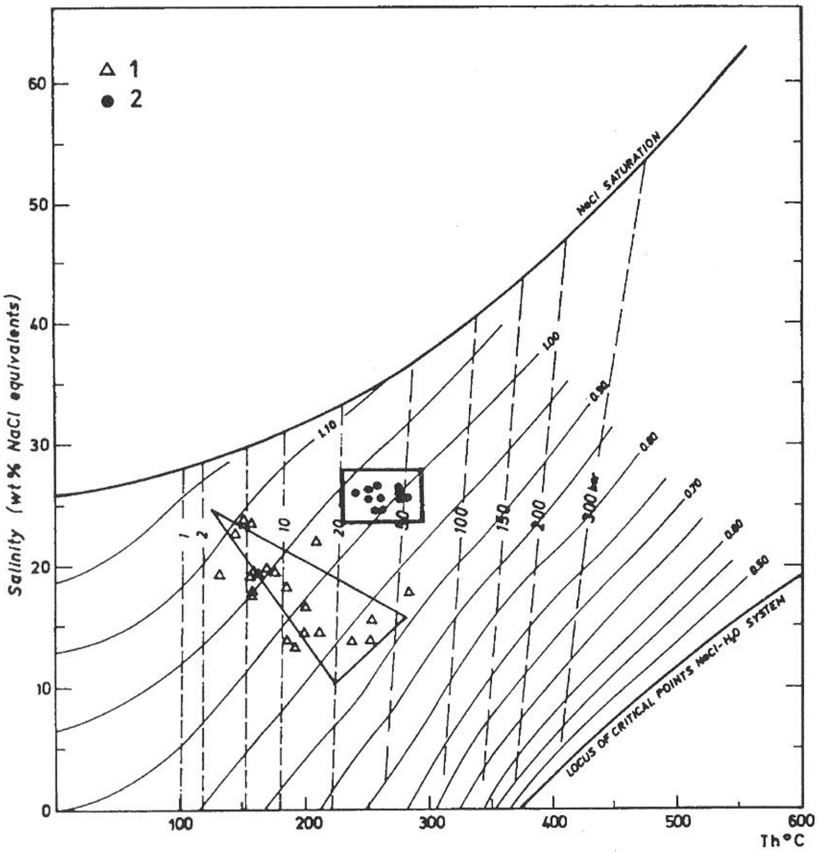

Fig. 9. Salinity versus homogenization temperature (T_h) of fluid inclusions in the fluorite from: 1 - Žune vein deposit (Ljubija, NW Bosnia); 2 - Kreševo deposit (Central Bosnia).

fluorite. A decrease in the Ca^{2+} or in the Mg^{2+} concentration by precipitation of minerals (calcite) may lead to fluorite precipitation. Dolomitization of limestone may also lead to fluorite precipitation.

Fluorite deposition in the Kreševo district has been constrained: (a) by the increase in pH of the initially acid hydrothermal fluid caused by hydrothermal alteration reaction with the host dolomite rock; (b) by the simultaneous dissolving of $CaCO_3$ and $MgCO_3$ whereby the Ca^{2+} and Mg^{2+} concentration of the fluid increases; (c) by the ankeritization (ferrodolomitization) of the host rock; (d) by a decrease in the Ca^{2+} concentration owing to the precipitation of the significant amount of rhombohedral calcite.

5. CONCLUSION

The barite deposits in the Kreševo area display a simple and uniform paragenesis comprising barite (dominant mineral), Hg-tetrahedrite, locally quartz, calcite, fluorite, pyrite and minor sulphosalts.

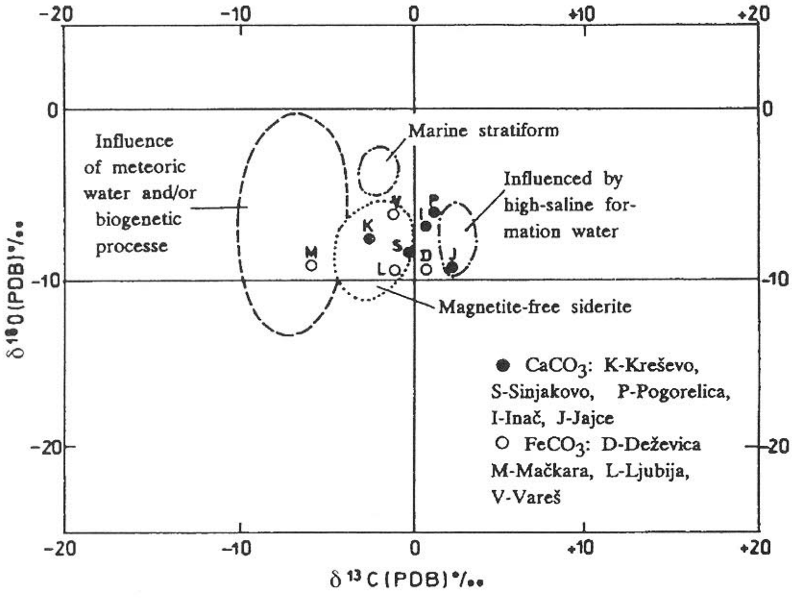

Fig. 10. $\delta^{13}C/\delta^{18}O$ diagram of the calcites and siderites from Bosnian deposits. Fields are given after SCHROLL et al. (1986).

The REE study revealed that the fluorite belongs to the late-stage mineralization. It is characterized by extremely low contents in REE and Tb/La ratio >1.0.

The fluid inclusion study proved that the fluorite, barite, calcite and quartz formed from the high saline waters that probably originated by mixing of the magmatic hydrothermally heated fluids with the highly evolved Upper Permian formation waters, as reported for the European fluorite deposits (BEHR et al., 1985; HEIN et al., 1990; BONI et al., 1990).

This assumption is supported by the study of the isotopic composition of carbon and oxygen in calcite and siderite (Fig. 10), as well as by the sulphur isotopic composition in barite, pyrite and tetrahedrite.

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