

DOLOMITE-GROUP FERROAN CARBONATES FROM KREMIKOVTSI DEPOSIT

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ABSTRACT

The dolomite-group ferroan carbonates (ferroan dolomite, ankerite) are the main non-metallic component in the primary ores of the Kremikovtsi deposit. They (1) formed carbonate assemblages in the transition zones between the siderite ore bodies and the host Middle Triassic dolomitic limestones, (2) accompanied all sulfide assemblages, (3) constituted alteration zones in the carbonate rocks hosting the Pb-Cu sulfide mineralization, and (4) deposited as post-ore rhombohedral crystals in cavities within the dolomitic limestones. In the *non-sulfide mineral assemblages* these minerals are represented by micro-grained aggregates of ferroan-manganooan dolomite in a coarse-grained ankerite matrix. Zonal manganooan ankerites with decreasing Fe contents toward the rims are characteristic for the *sulfide assemblages*. In *cavities* within the host carbonate rock linings from coarse-grained manganooan ankerite are formed with the highest FeCO₃ content (up to 23 mol%) in the deposit.

INTRODUCTION

The dolomite-group ferroan carbonates (ferroan dolomite, ankerite) are the main associated non-metallic components of the polymetallic sulfide mineralization in the Kremikovtsi deposit (Atanassov, 1977). They are also widespread in the transition zones between the siderite ore bodies and the host Middle Triassic dolomitic limestones (Damyanov, 1998). So far this type of ferroan carbonates has not been an object of detailed studies in view of their characteristics in the different mineral assemblages they form.

The purpose of this work is to study the chemical composition, structures and mineral associations of the dolomite-group ferroan carbonates from the Kremikovtsi deposit. Because there are no commonly adopted rules of nomenclature differentiation of the minerals in the CaMg(CO₃)₂-CaFe(CO₃)₂ limited solid solution (even a proposal of quite conventional sharing of type "low-Fe = ferroan dolomite, high-Fe = ankerite" has been made by Reeder, 1983), in this paper the nomenclature, proposed by Minceva-Stefanova and Gorova (1967) is used as follows: ferroan dolomite – 10÷30 mol% CaFe(CO₃)₂; ankerite - > 30 mol% CaFe(CO₃)₂.

MATERIALS AND METHODS

Representative samples of dolomite-group ferroan carbonates from different mineral assemblages (host Middle Triassic dolomitic limestones, siderite ore, polymetallic sulfide mineralization and pale- to dark-gray recrystallized dolomites) were examined by electron microprobe (58 an.), optical and scanning electron microscopy, XRD, DTA, Mössbauer and infrared spectroscopy. The micromorphology, size and chemical composition of different samples and minerals were

determined by a JSM-35-CF and a PHILIPS SEM-515 with an EDAX PV 9100 EDS system (with an operating voltage of 15 kV and electron beam diameter of 1µm). As the compositional variations in the distinct mineral assemblages and zonal grains are in the range of the experimental errors of the electron microprobe method and the apparatuses used, the data represented in Table 1 are summarized, as follows: № 14 – average of 11 analyses; № 1 – of 6 an.; № 2, 3, 5, 6 – of 5 an.; № 17, 4, 15 – of 3 an.; № 7, 8÷11, 16 – of 2 an.; the rest are single analyses. X-ray diffraction (XRD) patterns were obtained with a DRON-1 diffractometer (CuKα radiation, Ni filter, I = 24 mA, U = 34 kV) and a 57.3 mm Debye-Scherrer TUR-M-60 camera. DTA and TG curves were recorded with a Derivatograph apparatus in static air, DTA = 1/10, DTG = 1/15, G = 200, sample weight – 1 g, rate of heating – 10°/min, as well as with a Stanton Redcroft STA-780 series apparatus in the 18-1200°C temperature range (10°C/min). A Mössbauer study was carried out by using an UMS-3 spectrometer with a ⁵⁷Co (in Pd) source. Isomer shifts were always calculated vs. Fe metal. The infrared spectra were recorded in the 3800-400 cm⁻¹ range with a UR-10 i.r. spectrometer. The samples were prepared as KBr disks by standard methods. Used are prisms of LiF (3800-2000 cm⁻¹), NaCl (2000-700 cm⁻¹) and KBr (700-400 cm⁻¹).

MINERAL ASSEMBLAGES

Host carbonate rocks and siderite ore

According to Kanurkov (1988), the earliest ankerite generation preceded the formation of primary Mn-siderite ore in the deposit. Its occurrence in the Kremikovtsi opencast workings may be established most often by indirect criteria based on the areal distribution of yellow to yellowish-brown low-Mn limonites.

In the transition zones between the siderite ore bodies and the host dolomitic limestones and rarely in the siderite ore, a *specific assemblage* of dolomite-group carbonates has been found. It forms massive, compact (porcelain-like), dark-gray aggregates, well differentiated visually on the background of the red Middle Triassic dolomitic limestones. Its textural features in the siderite ore are quite similar but the differentiation between the two mineral assemblages is very

complicated because of the identical coloring. The ferroan dolomite-ankerite assemblage is represented by veinlets and nest-shaped aggregates of a coarse-grained ankerite matrix with inclusions of rhombic ferroan dolomite grains (Fig. 1a). Its textural relationships with the host rock/ore suggest that the assemblage was probably formed during the stage of advanced diagenesis according to the criteria proposed by Leeder (1982).

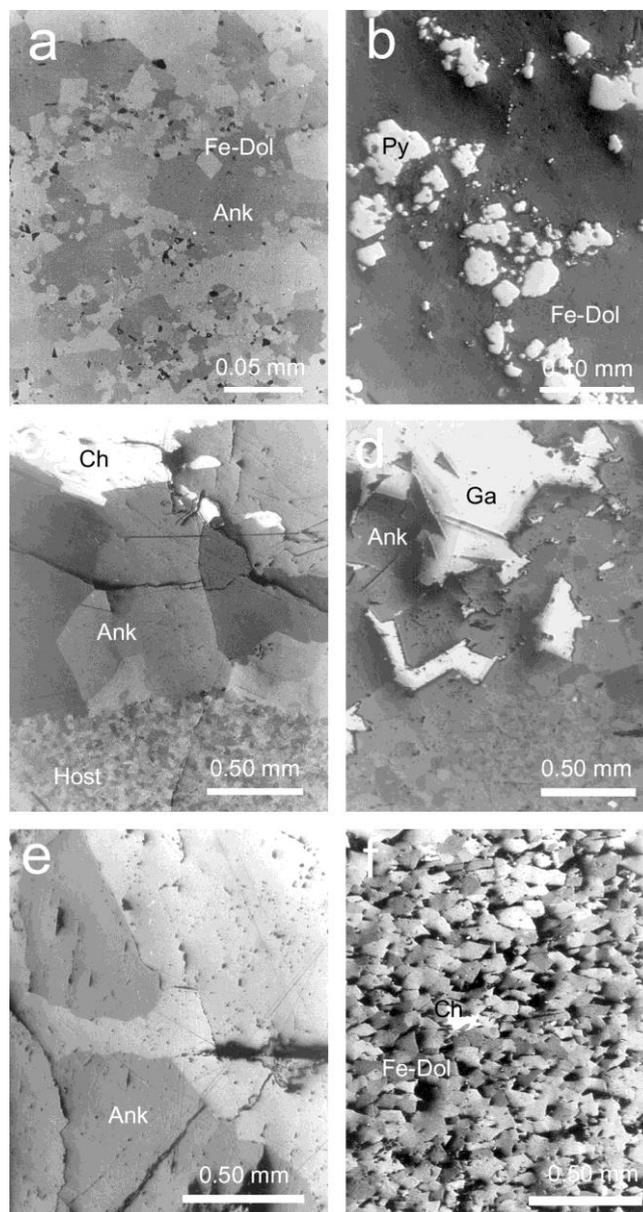


Figure 1. Textural features of dolomite-group ferroan carbonates from the Kremikovtsi deposit. a) fine-grained ferroan dolomite in an ankerite matrix; b) medium-grained ferroan dolomite impregnated interstitially by pyrite (recrystallized framboids); c) coarse-grained ankerite associated with chalcopyrite in a matrix of fine-grained dolomite (host dolomitic limestone); d) ankerite metacrystals in galena; e) coarse-grained ankerite lining solution cavities in dolomitic limestones; f) recrystallized ferroan dolomite from an alteration zone adjacent to the sulfide mineralization. Ank – ankerite; Ch – chalcopyrite; Fe-Dol – ferroan dolomite; Ga – galena; Host – host dolomitic limestone; Py – pyrite. Reflected light, II N.

Polymetallic sulfide mineralization

Several types of dolomite-group ferroan carbonates, accompanying the main sulfide assemblages (pyrite, chalcopyrite and galena) (Atanassov, 1977; Atanassov *et al.*, 1979, unpubl.

data¹), can be distinguished in the Kremikovtsi deposit. The first one is represented by ferroan dolomite, associated with

¹ Atanassov, V., Marinov, T., Sultanov, A., Vassileva, M., Petrov, I., Ganova, M. 1979. Mineral composition of the primary and secondary polymetallic mineralization in the Kremikovtsi deposit and petrographic characteristics of the host rocks. – Contract Report # 599/77, NIS MGU, 349 pp.

the earliest deposited sulfides (pyrite, marcasite, chalcopyrite) from the *pyrite assemblage*. Pyrite is one of the most widespread sulfide minerals in the deposit, but it is concentrated mainly in an ore body located at the 520 and 532 m levels in the opencast. Major components of this ore body are ferroan dolomite and fine-grained pyrite (recrystallized framboids) that are interstitially distributed in the carbonate matrix (Fig. 1b).

The next type is of ankerite, accompanying the deposition of copper mineralization in the deposit (*chalcopyrite assemblage*). It forms small veins and veinlets with nests of chalcopyrite in the host carbonate rock (Fig. 1c). The ankerite is coarse-grained (up to 1-2 mm crystals), dominantly idiomorphic with well-pronounced cleavage in two directions. Interstitially of the carbonate grains are located sulfide inclusions (mainly pyrite) and organic matter. The main ore mineral in this assemblage, chalcopyrite, is coarse-grained, monomineralic or associated with tennantite. Galena and sphalerite are rarely observed.

Later type of ferroan dolomite-ankerites deposited in the *galena assemblage* which is the main sulfide assemblage in the deposit. The ferroan dolomite-ankerites form veins with nests of coarse-grained galena (up to 10 cm) within the carbonate host. Main ore mineral in this assemblage is galena, associated with tetrahedrite, chalcopyrite and rarely sphalerite.

The last type of ferroan carbonates is occasionally established as small *veinlets or cavity linings* in the dolomitic limestones. The ankerite is coarse-grained, white to translucent with up to 1-1.5 cm limpid sparry crystals (Fig. 1e) and associated with tabular barite, needle-like quartz and cube-octahedral galena.

The latest type of ferroan carbonate in the Kremikovtsi deposit is represented by post-ore ferroan dolomite. It is rarely established as fine rhombohedral crystals in solution cavities, associated with barite crystals and authigenic phyllosilicates (Damyanov and Vassileva, 2001).

The dolomite-group ferroan carbonates are not only associated minerals of sulfide mineralization, but also a *component of host rock alteration*. The sulfide ore-formation in the Kremikovtsi deposit is accompanied by local recrystallization (Fig. 1f) and ferroan dolomitization-ankeritization of the carbonate host. The recrystallized carbonate rocks are gray to dark-gray due to the impregnation with sulfides and organic matter.

Processes of ferroan dolomitization of the host carbonate rocks, preceding and accompanying the sulfide mineralization, have been established also in the Sedmochislenitsi-type polymetallic deposits from the Western Balkan (Minceva-Stefanova, 1988, 1989). These deposits are very similar mineralogically and petrographically to the sulfide mineralization in the Kremikovtsi deposit. In contrast to them however, the galena assemblage in the Kremikovtsi deposit is subsequent to the chalcopyrite one.

CHEMICAL COMPOSITION

Summarized microprobe data for the dolomite-group ferroan carbonates from the Kremikovtsi deposit are represented in

Table 1. The results obtained show a pronounced tendency of compositional variations of the carbonate studied. The earliest formed sulfides (pyrite) are accompanied by ferroan dolomite.

Table 1. Representative microprobe analyses (mol%) and structural formulae of dolomite-group ferroan carbonates from Kremikovtsi deposit – summarized data.

No	Description	CaCO ₃	MgCO ₃	FeCO ₃	MnCO ₃
<u>Non-sulfide mineralization</u>					
<i>Host carbonate rock</i>					
1.	Medium-grained Fe-dolomite	52.22 (1.04)	38.48 (0.77)	6.04 (0.12)	3.26 (0.07)
<i>Siderite ore</i>					
2.	Fine-grained Fe-dolomite	49.90 (1.00)	42.70 (0.85)	5.40 (0.11)	2.00 (0.04)
3.	Coarse-grained ankerite matrix	49.30 (0.99)	28.60 (0.57)	17.90 (0.36)	4.20 (0.08)
<u>Sulfide mineralization</u>					
<i>Pyrite assemblage</i>					
4.	Medium-grained Fe-dolomite	51.03 (1.02)	27.71 (0.55)	13.34 (0.27)	7.92 (0.16)
<i>Chalcopyrite assemblage</i>					
5.	Zonal meta-crystals	c 49.60 (0.99)	29.57 (0.59)	15.83 (0.32)	5.00 (0.10)
6.		r 49.92 (1.00)	32.85 (0.65)	12.37 (0.25)	4.86 (0.10)
7.	Veinlets with chalcopyrite nests	50.84 (1.01)	21.39 (0.43)	21.87 (0.44)	5.90 (0.12)
<i>Galena assemblage</i>					
8.	Zonal metacrystals	c 52.47 (1.05)	39.45 (0.79)	5.92 (0.12)	2.16 (0.04)
9.	with early PbS, host rock	r 52.46 (1.05)	36.93 (0.74)	10.03 (0.20)	0.58 (0.01)
10.		c 49.29 (0.99)	29.51 (0.59)	18.26 (0.36)	2.94 (0.06)
11.		r 49.75 (0.99)	31.43 (0.63)	16.51 (0.33)	2.31 (0.05)
12.	Veinlets with galena nests	c 52.43 (1.05)	23.33 (0.47)	18.09 (0.36)	6.15 (0.12)
13.		r 51.21 (1.02)	26.35 (0.53)	16.42 (0.33)	6.02 (0.12)
14.	Coarse-grained ankerite in solution cavities	50.10 (1.00)	35.00 (0.70)	10.85 (0.22)	4.05 (0.08)
15.		49.85 (1.00)	24.05 (0.48)	19.71 (0.39)	6.39 (0.13)
16.		52.20 (1.04)	18.11 (0.36)	22.74 (0.46)	6.95 (0.14)
<i>Post-ore mineralization</i>					
17.	Fe-dolomite rhombohedr. crystals	52.19 (1.04)	33.32 (0.67)	10.29 (0.21)	4.20 (0.08)

c – core, r – rim of zonal crystals

The later ones (chalcopyrite, tennantite, galena) are associated with high-ferroan dolomites to typical ankerites. During the final stage of sulfide mineral-formation once again deposited ferroan dolomite. The composition of late post-ore ferroan dolomite is distinguished from that of the earlier pyrite assemblage with higher Mg and lower Mn and Fe contents.

The highest Fe/Mg ratio is characteristic of ankerite from the chalcopyrite assemblage and the later galena assemblage (coarse-grained and cavity lining ankerites) (Fig. 2). In contrast to the Chiprovtsi carbonates (Dragov and Neykov, 1991), the Kremikovtsi ones are characterized by higher Mn contents

(MnCO_3 up to 8 mol%). They are mostly represented by Ca-rich varieties ($\text{CaCO}_3 > 50$ mol%). Many authors noted variations as compared to stoichiometric composition and negligible excess of Ca in the dolomite-group carbonates (Deer *et al.*, 1966; Minceva-Stefanova and Gorova, 1967; De Grave and Vochten, 1985; Reeder and Dollase, 1989; Reksten, 1990). The higher Fe and Mn concentrations are considered to be a favorable prerequisite for formation of Ca varieties. Some authors (Deer *et al.*, 1966; Minceva-Stefanova and Gorova, 1967; Reeder and Dollase, 1989) supposed an isomorphic substitution of a part of Mg^{2+} -cations by Ca^{2+} instead of the differences in their cationic radii.

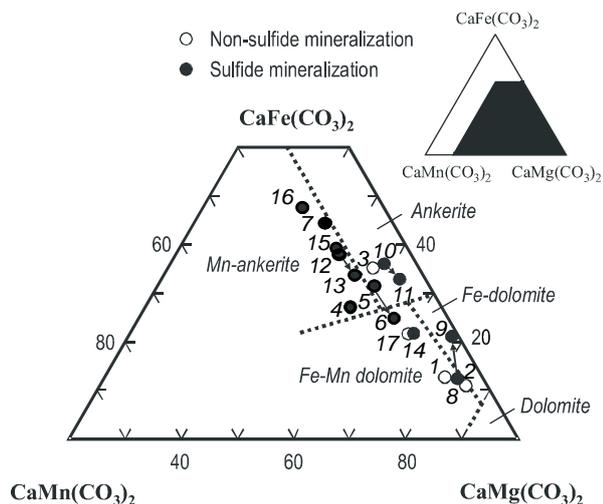


Figure 2. Compositional variations of the dolomite-group ferroan carbonates from the Kremikovtzi deposit in the $\text{CaMn}(\text{CO}_3)_2$ - $\text{CaMg}(\text{CO}_3)_2$ - $\text{CaFe}(\text{CO}_3)_2$ system. Zonal trends of type "core-rim" are marked by arrows. The numbers of analyses are as in Table 1. The fields of nomenclature differentiation are after Minceva-Stefanova and Gorova (1967)

According to Kucha and Wieczorek (1984), non-stoichiometric Ca-ankerites are characterized by a heterogeneous domain structure. Reksten (1990) considered the non-stoichiometric composition of some low-temperature Ca-ankerites as provoked by the microstructure features of the mineral and the presence of impurities. In contrast to the Ca-rich varieties, the stoichiometric ankerites, containing up to 66 mol% $\text{CaFe}(\text{CO}_3)_2$, are practically homogeneous (Reeder and Dollase, 1989). The splitting of some peaks in a part of diffractograms, obtained by the dolomite-group ferroan carbonates (Fig. 3), gives us a reason to propose a possible microheterogeneity in them.

Very often during the SEM studies of carbonate minerals, a compositional zoning is established, which provokes terminological difficulties. In the ankerites from the chalcopyrite assemblage e.g., pale-gray microlamellae with higher Fe contents have been observed. Heterogeneous zonality, represented by repeatedly alternating darker (ferroan dolomite) and lighter (ankerite) zones, has been established in some coarse-grained carbonates from solution cavities.

The XRD studies of dolomite-group ferroan carbonates from the different mineral assemblages show a distinct increase of the d-values in accordance with the increase of the Fe contents in the minerals examined. In comparison with the standard data of ferroan dolomite (PDF # 340517), these of the Kremikovtzi ankerite have higher d-values probably because of the higher Fe and Mn contents (Fig. 3). The positive correlation between the cell parameters a_0 and c_0 and the Fe contents in the dolomite-ankerite series has been discussed by many authors (Reeder, 1983; Reeder and Dollase, 1989; Gil *et al.*, 1992). The weak reflections with d-values (Å) at 3.03, 1.909-1.914 and 1.620-1.623 on the typical diffractograms shown in Fig. 3, are due to the presence of small quantities of calcite.

The DTA curve of ankerite (Fig. 4a) is characteristic for the mineral and has no visible differences in comparison with the standard one (Ivanova *et al.*, 1974). It is characterized by the presence of 3 endothermic peaks at 740°, 790° and 890°C. The first one reflects the ankerite decomposition and its dissociation of FeCO_3 and MgCO_3 and simultaneous oxidation of FeO toward Fe_2O_3 . The second peak at 790°C is considered to be a result of interaction between Fe_2O_3 and CaCO_3 and formation of Ca-ferrite. The third endothermic peak corresponds to the dissociation of the rest CaCO_3 quantity (Ivanova *et al.*, 1974).

The Mössbauer spectrum of ankerite from the Kremikovtzi deposit consists of one quadrupole doublet with an isomer shift near 1.19 mm/s and quadrupole splitting - 1.49 mm/s (Fig. 4b). The results obtained conform to the data published in the literature (De Grave and Vochten, 1985; Reeder and Dollase, 1989). The experimental studies of ankerites with different Fe contents (17-66 mol% $\text{CaFe}(\text{CO}_3)_2$) showed that the quadrupole splitting values decrease inversely proportional to the Fe contents. The Mössbauer data obtained testify to the octahedral position of the Fe^{2+} -cations and weak trigonal distortion of the (Mg, Fe) O_6 octahedrons. In comparison with the spectra of other ferroan carbonates (e.g. siderite), that of ankerite is characterized by a considerable decrease of the quadrupole splitting values while the isomer shifts amounts are very close. The distinctions in the Mössbauer spectra of ferroan carbonates with different structures (ankerite, siderite) can be used to distinguish them qualitatively and quantitatively in mixed aggregates.

The infrared spectra of Kremikovtzi ankerites are characterized by 3 main bands at 1445, 880 and 729 cm^{-1} indicating respectively the 3 normal vibrations (Y_3 , Y_2 and Y_4) of CO_3^{2-} -group in the ankerite (Plyusnina, 1977). According to Dubrawski *et al.* (1989) and Gil *et al.* (1992) in parallel with the increase of the Fe content in the dolomite-ankerite series occurs an increase of the absorption bands frequencies of Y_4 and Y_2 vibrations of the CO_3^{2-} -group.

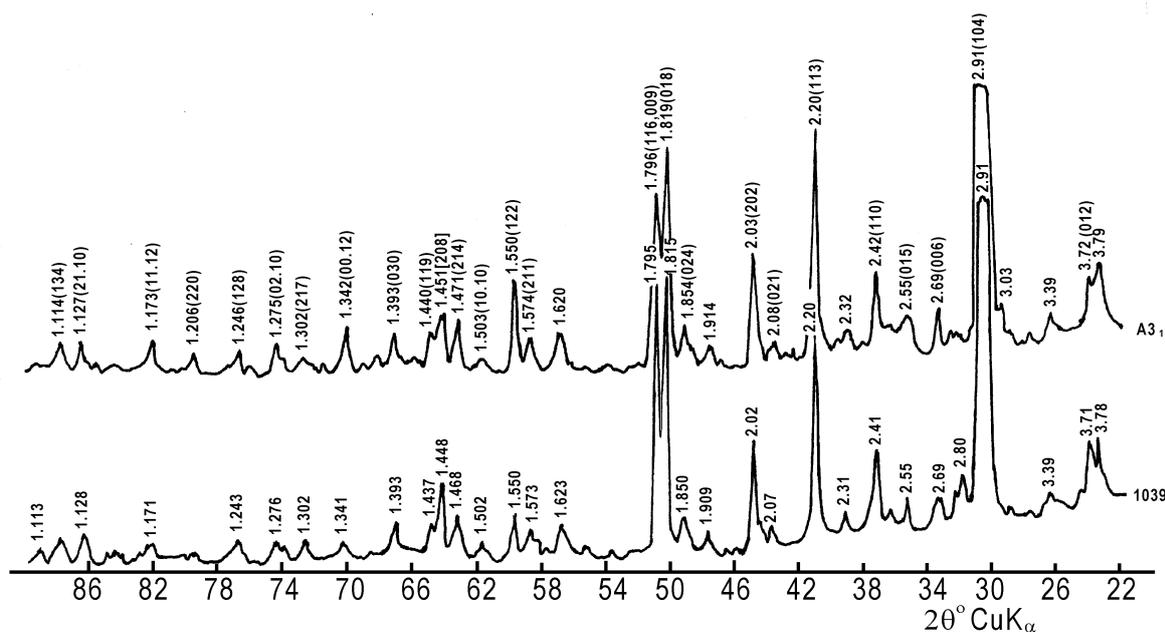


Figure 3. Diffractograms of coarse-grained manganiferous ankerite from cavity linings in the dolomitic limestones (a) and from veinlets with chalcopyrite nests (b).

SUMMARY AND CONCLUSIONS

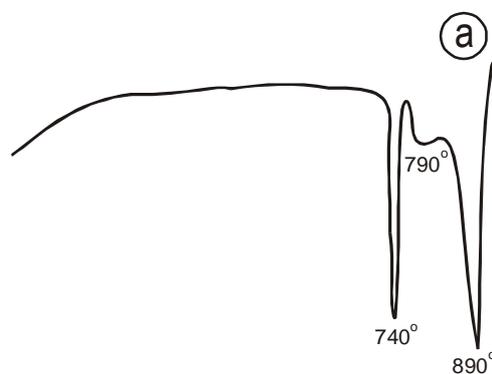
The dolomite-group ferroan carbonates are the main non-metallic component in the primary ores of the Kremikovtsi deposit. They (1) formed carbonate assemblages in the transition zones between the siderite ore bodies and the host Middle Triassic dolomitic limestones – the result of dolomitization of the host rock in the presence of Fe and Mn, (2) accompanied all sulfide assemblages, (3) constituted alteration zones in the carbonate rocks hosting the Pb-Cu sulfide mineralization, and (4) deposited as post-ore rhombohedral crystals in cavities within the dolomitic limestones.

In the *non-sulfide mineral assemblages* the dolomite-group ferroan carbonates formed micro-grained to medium-grained mosaic aggregates with massive, nest-like and veinlet textures. They are represented mainly by ferroan dolomite but within the siderite ore ankerite, as a coarse-grained mass with rhombic inclusions of ferroan dolomite is established as well.

In the *sulfide assemblages* predominate zonal ankerite metacrystals with decreasing Fe contents toward the rims – an indication of drop in temperature of the mineral-forming solution and exhaustion of its metal load in the process of crystallization (Minceva-Stefanova and Gorova, 1967).

Typical for the dolomite-group ferroan carbonates is the stable presence of Mn – a characteristic element for the deposit, the contents of which increase from the non-sulfide (2÷4 mol% MnCO_3 in the ferroan dolomite) to the sulfide (4÷8 mol% MnCO_3 in the ankerite) mineral assemblages. Thus, from a nomenclature point of view (Minceva-Stefanova and Gorova, 1967) the main part of the minerals studied should be referred

to the varieties *ferroan-manganiferous dolomite* and *manganiferous ankerite*.



(b)

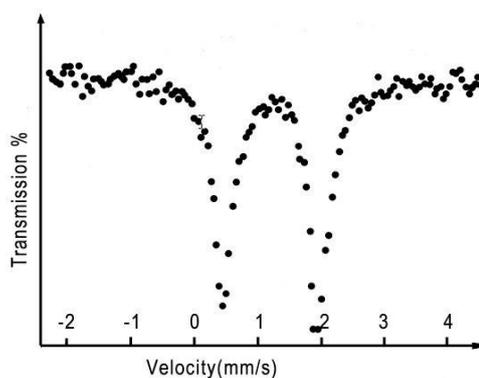


Figure 4. Representative DTA curve (a) and Mössbauer spectrum (b) of coarse-grained cavity lining ankerite.

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