



Bogusław BĄK

Ferroan dolomites and ankerites from the Silesian-Cracow deposits of zinc and lead ores

Within the Silesian-Cracow deposits of zinc and lead ores occur dolomites, containing isomorphic admixtures of about several weight percent of bivalent iron and several weight percent of manganese. These rocks are regarded depending on the ratio Mg:Fe as ferroan dolomites or ankerites. Their occurrence is — as indicated the observations of the author and literature data — common and usually they are connected with mineralization, located both immediately nearby ores and on peripheries of mineralized zones.

INTRODUCTION

Dolomites in the Silesian-Cracow Zn-Pb ore deposits (particularly these one, being so-called ore-bearing dolomites), often contain in their crystalline lattice lower or higher admixture of Fe^{2+} (up to several weight percents) but subordinately also addition of Mn^{2+} and due to that they are often of ankerite type. These data are mentioned in works of F. Duwensee (1929), H. Gruszczyc and W. Wążewska-Riesenkampf (1960), S. Śliwiński (1966, 1969), I. Smolarska (1968), C. Harańczyk and L. Szostek (1969), C. Harańczyk (1981), S. Przeniosło (1974), K. Mochnacka and M. Sass-Gustkiewicz (1981), H. Kucha and K. Czajka (1984), A. Krzyczkowska-Everest (1990), B. Bąk (1986) and K. Czajka (1991).

The terminology of such dolomites is still open problem. According to W. A. Deer et al. (1962) the ferroan dolomites are such ones, for which the ratio Mg:Fe is higher than 4 but the ankerites are those, in which this ratio is lower than 4. The author favours this definition, adding for ferroan dolomites the term Fe-dolomites.

Table 1

The content of some metals and sulfur within ferroan dolomites and ankerites from the Silesian-Cracow deposits of zinc and lead ores (weight %)

Number of sample	Fe ³⁺	Fe ²⁺	Mn	Zn	Pb	S	Fe ²⁺ :Mn aver.= 7.2
T-7	0.20	3.04	0.36	0.16	0.05	0.28	8.4
T-8	0.32	3.28	0.37	0.03	0.05	0.22	8.9
T-26	-	4.80	0.58	1.96	0.12	0.94	8.3
T-27	-	4.90	0.56	1.64	0.15	0.95	8.6
T-27a	0.10	3.36	0.48	1.02	0.10	0.60	7.0
T-29	0.10	3.80	0.46	0.05	0.91	0.16	7.7
T-30	0.12	5.10	0.62	0.95	0.20	0.54	8.2
T-32	0.15	1.56	0.25	0.04	0.09	0.10	6.2
T-34	0.25	2.55	0.40	0.07	0.12	0.10	6.4
T-37	0.10	3.32	0.50	1.48	0.18	0.46	6.6
T-42	0.18	0.90	0.16	0.83	0.04	0.30	5.6
T-58	-	0.96	0.53	0.13	0.06	0.10	1.8
T-60	0.06	4.90	0.54	0.31	0.21	0.20	9.1
T-65	0.12	1.18	0.33	0.04	0.13	0.20	3.6
T-66	-	1.52	0.22	2.20	0.28	1.20	6.9
T-74	0.20	1.32	0.24	0.16	0.12	0.12	5.5
T-75	0.08	1.12	0.22	0.05	0.01	0.10	5.1
R-2a	-	6.80	0.80	0.05	-	1.85	8.5
R-2b	-	3.98	0.62	0.15	-	0.18	6.4
R-29	1.30	2.64	0.47	0.99	0.58	0.12	5.6
D-13	-	6.70	0.75	0.66	0.21	2.10	8.9
N-10	0.20	5.70	0.45	0.16	0.21	0.75	12.6
N-11	-	5.68	0.58	0.04	0.17	1.60	9.6

Samples from the mines: T— Trzebieńka, R — Orzeł Biały, D — Dąbrowka, N — Nowy Dwór

The aim of presented work is completing maximum amount of data, related to these minerals and modes of their occurrence within deposits.

RESULTS OF STUDIES

The index chemical analyses, obtained for dolomites from deposit of the Trzebieńka mine and from deposits in the Bytom Depression, are presented in Table 1. Fe²⁺ content changes there from 0.90 to 6.70 weight % but this iron occurs not completely in the dolomite lattice because it is partly joined with sulfur in form of finely dispersed pyrite, rarely — marcasite. Small amounts of Fe³⁺ are related with the admixtures of iron hydroxides.

Manganese is found from 0.16 to 0.80 weight %. Similar Mn content is noticed by S. Śliwiński (1966, 1969) for the ore-bearing dolomites and average value of calculated by him ratio Fe²⁺:Mn is 10:1. The average ratio, calculated by author (Tab. 1), is 7.2:1, slightly enlarged due to the fact that part of Fe²⁺ is included into sulfides.

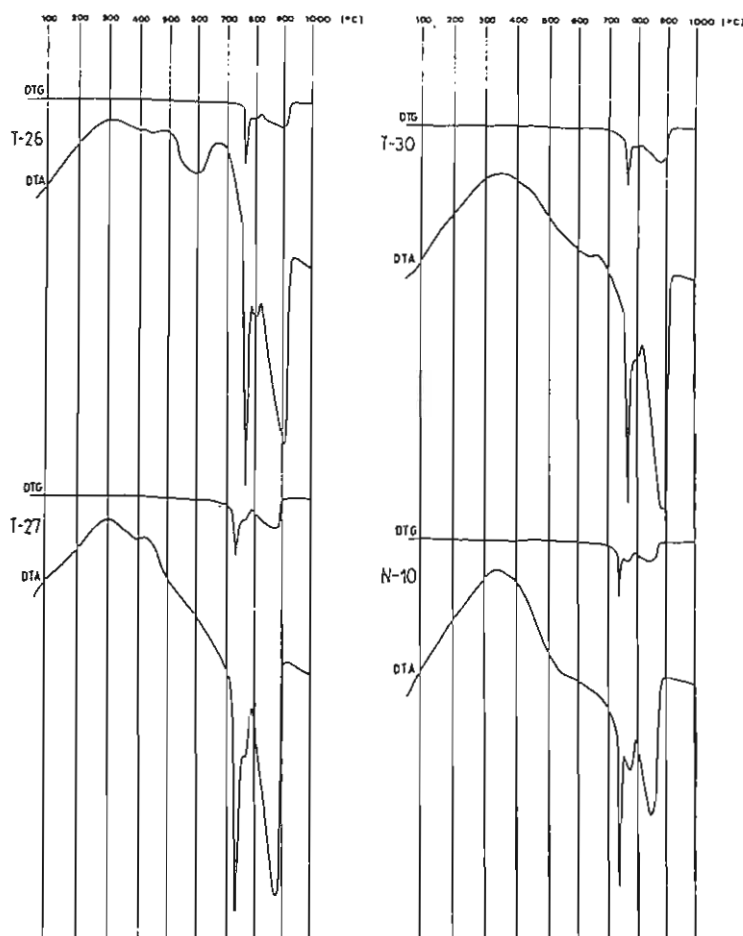


Fig. 1. DTA and DTG curves for ferroan dolomites and ankerites

Samples from the mines: T — Trzebieńka, N — Nowy Dwór

Krzywe DTA i DTG dolomitów żelazistych i ankerytów

Próbki z kopalń: T — Trzebieńka, N — Nowy Dwór

Zinc and lead contents are connected with additions of ore minerals (sphalerite and galena that is confirmed by microscopic studies in reflected light) but part of Zn occurs probably together with Fe^{2+} in dolomite lattice (B. Witek, 1976; B. Bąk, 1986).

The ankerite character of studied dolomites is indicated by thermal studies (Fig. 1). Three endothermic effects, typical for ankerite, generally located within the range 670–930°C, are marked distinctly both on the DTG and DTA curves. Exothermic peak, resulted from an oxidation of Fe^{2+} to Fe^{3+} and characteristic for ankerites with high iron content (J. L. Kulp et al., 1951), has been found by the author in none of

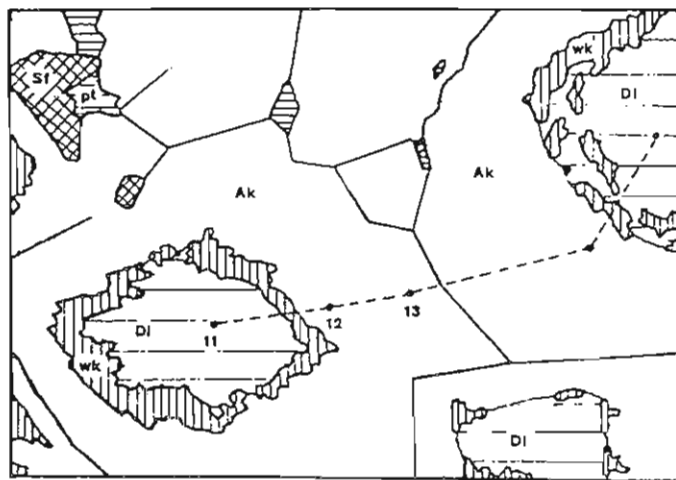


Fig. 2. Schematic and simplified microscopic image (magn. about $\times 200$) of fragment of sample T-26 from the deposit from the Trzebieńka mine, with marked analyzed points, studied with microprobe
 Dashed line — diagram of concentration of elements (see Fig. 3); 11, 12, 13 — quantitative analyses (see Tab. 2); Dl — dolomite; Ak — ankerite; Sf — sphalerite; wk — „crumblings”; pt — voids
 Schematyczny i uproszczony obraz mikroskopowy (pow. około 200 \times) fragmentu próbki T-26 ze złoża kopalni Trzebieńka, z zaznaczonymi miejscami analiz wykonanych za pomocą mikroskopy elektronowej
 Linia przerywana — wykres koncentracji pierwiastków (patrz fig. 3); 11, 12, 13 — analizy ilościowe (patrz tab. 2); Dl — dolomit; Ak — ankeryt; Sf — sfaleryt; wk — wykruszenia; pt — pustki

studied samples. The application of thermal methods for the identification of Fe-dolomites and ankerites is described by W. Riesenkauf (1990).

The X-ray studies have indicated that the lattice parameters of described dolomites (B. Bąk, 1986), containing about 4-5 weight % of Fe^{2+} , had values medial between data of D. L. Graff (1961) for dolomite and assumed element $\text{Ca}_{50}\text{Fe}_{50}(\text{CO}_3)_2$ (nearer in general to dolomite) but they are approximate to values obtained by R. A. Howie and F. M. Broadhurst (1958) for ankerite with 9.38 weight % of Fe^{2+} .

The ferroan dolomites and ankerites have been found (B. Bąk, 1986) in several types of dolomitic rocks; most often within recrystallized, hipidiomorphic, porous, medium and various crystalline dolomites; rarely within recrystallized, massive, fine crystalline dolomites and in dolomites of micritic structure (early diagenetic ones?). They have been noticed in similar dolomite types from the Zn and Pb ore deposits from the Olkusz region by A. Krzyżkowska-Everest (1990).

The microscopic studies of samples, coloured with the potassium ferricyanide, have indicated that the Fe-dolomites and ankerites are best developed on the crystal margins, around rock voids and in the zones of microfractures. It suggests that the solutions with Fe^{2+} have penetrated into dolomites along pores, fracture systems and twin planes of crystals. In such way the crystals with zonal structure could originate with external parts of variable thickness from several to over 100 μm

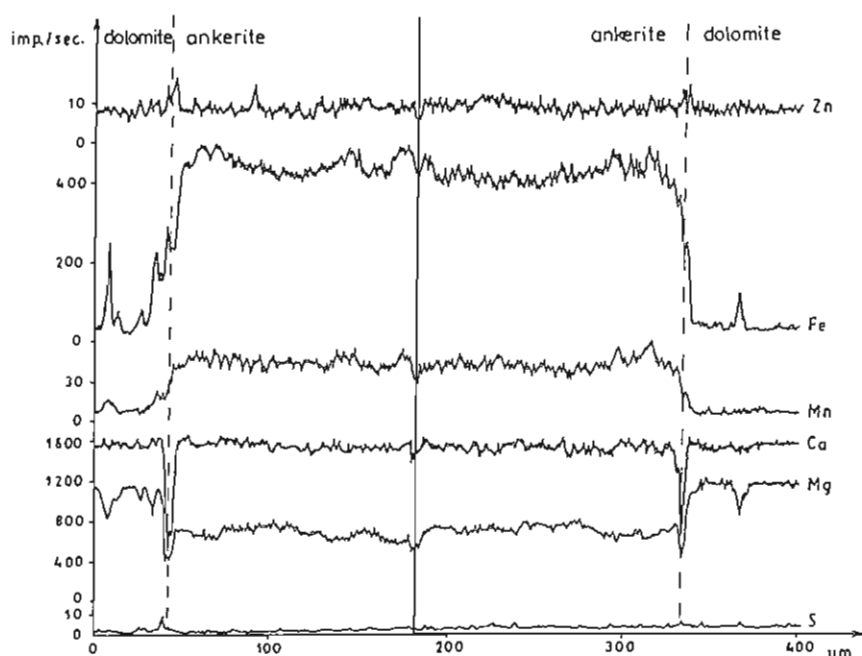


Fig. 3. The diagram of concentration of Zn, Fe, Mn, Ca, Mg, S in dolomitic-ankeritic crystals with zonal structure (sample T-26, see Fig. 2), obtained with the microprobe

Dashed line — „rumblings” occurring within crystal at boundary of internal, dolomitic part, and external, ankeritic one; continuous line — boundary between two crystals

Wykres koncentracji Zn, Fe, Mn, Ca, Mg, S w kryształach dolomitowo-ankerytowych o budowie strefowej (próbka T-26, patrz fig. 2), uzyskany za pomocą mikroskopy elektronowej

Linia przerywana — wykruszenia występujące w kryształach na granicy między częścią wewnętrzną — dolomitową — a zewnętrzną — ankerytową; linia ciągła — granica między dwoma kryształami

composed of Fe-dolomite or ankerite, but their interiors contain pure dolomite. The analyses of microareas (Figs. 2, 3, Tab. 2 — sample T-26) document that iron in external parts of crystals is uniform and often its content is similar in adjoining crystals. Boundary between internal part, poor in iron and external one, enriched in it, is sharp although slightly deformed by often occurring there „crumblings”. They attain thickness up to several tens of μm (Figs. 2, 3). Their origin could be related to volume change of external part of crystal due to ankeritization or due to occurrence of stresses within lattice of rhombohedrons, resulted from differences of chemical composition of crystal at boundary: dolomite — ankerite. Often, especially in the zones of microfractures where the crystals with zonal structure are unknown, the ferroan dolomites are irregularly developed and iron content changes sometimes within one crystal. It is indicated by varied intensity of tinge and confirmed with the studies of microareas (Tab. 2, sample N-11). Similar ankeritized dolomitic rocks are noticed more rarely.

Table 2

The chemical composition of ferroan dolomites and ankerites from the Silesian-Cracow deposits of Zn and Pb ores, determined with the microprobe (weight %)

Compo- sition	Number of sample							
	T-26			N-10			N-11	
	points							
	11	12	13	1	2	3	1	2
Fe	0.20	5.12	5.15	6.37	4.14	6.95	5.82	1.83
FeO	0.26	6.58	6.62	8.19	5.32	8.94	7.48	2.35
Mn		0.62	0.75	0.83	0.53	0.46	0.30	0.14
MnO	≤ 0.02	0.80	0.97	1.07	0.68	0.59	0.39	0.18
Zn	0.04	0.07	0.04	0.03		0.03	0.03	
ZnO	0.05	0.09	0.05	0.04	≤ 0.02	0.04	0.04	≤ 0.02
Pb								
PbO	≤ 0.04	≤ 0.04	≤ 0.04	≤ 0.04	≤ 0.04	≤ 0.04	≤ 0.04	≤ 0.04
Ca	22.55	22.05	21.60	21.20	21.60	21.80	20.90	21.10
CaO	31.60	30.85	30.20	29.65	30.20	30.50	29.25	29.50
Mg	12.00	9.30	9.40	8.95	9.95	8.65	9.30	11.65
MgO	19.90	15.40	15.80	14.85	16.50	14.35	15.40	19.30
S	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02
CO ₂	46.54	45.63	45.40	45.19	45.43	45.44	44.64	45.84
Sum	98.35	99.35	98.85	98.99	98.13	99.86	97.20	97.17
Mg:Fe (weight)	60.00	1.82	1.82	1.40	2.40	1.24	1.60	6.36
Mg:Fe (mole)	137.05	4.17	4.19	3.23	5.52	2.86	3.67	14.60
Fe:Mn (weight)	-	8.26	6.87	7.67	7.81	15.11	19.40	13.07
Fe:Mn (mole)	-	8.12	6.78	7.55	7.72	14.99	18.95	13.12

≤ detection limit by microprobe

Part of pores and voids as well as of fractures and joints within ankeritized dolomites is infilled with sphalerite, which sometimes also replaces them, that suggests it has originated slightly later than Fe-dolomite and ankerite. It corresponds with sphalerite of III generation, distinguished by A. Krzyczkowska-Everest (1990). In ankeritized

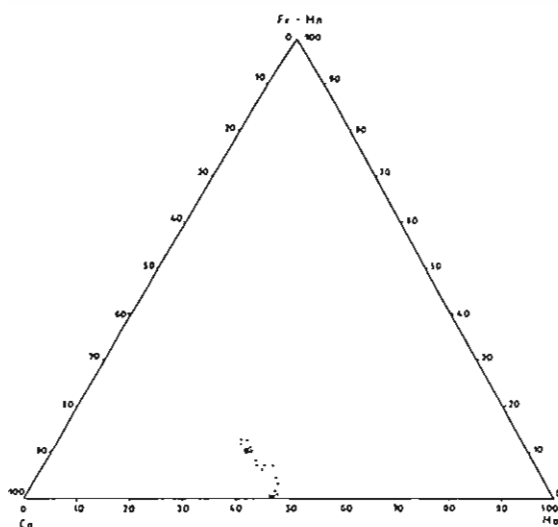


Fig. 4. The chemical composition (data from microareas) of studied ferroan dolomites and ankerites, in triangle Ca - Mg - Fe+Mn (mole %), from the deposit in the Trzebieńka mine and from the deposits in the Bytom Depression (after B. Bąk, 1986)

Skład chemiczny (oznaczenia w mikroobszarach) dolomitów żelazistych i ankerytów, w układzie Ca - Mg - Fe+Mn (% mol), pochodzących ze złoża kopalni Trzebieńka i złóż niecki bytomskiej (według B. Bąka, 1986)

dolomites: some amount of chalcedony, fine dispersed pyrite, iron hydroxides, clay minerals (mainly illite), sporadically galena and often calcite within the dedolomitization zones are also noticed.

Increased iron content (Tab. 1, samples T-7 and T-8) were observed also in micritic dolomites (early diagenetic ones?), occurring nearby contact with ankeritized ore-bearing dolomites within the deposit from the Trzebieńka mine. There are visible initial stages of recrystallization and clay laminae and fine dispersed pyrite occur.

The chemical composition (data from microareas) of studied Fe-dolomites and ankerites in triangle Ca - Mg - Fe+Mn (mole %) is presented on Fig. 4 (selected analyses, Tab. 2). The iron content in analyzed samples changes in range 0.20-6.95 weight % and sometimes varies in adjoining microareas. Manganese (lower than 0.02-0.83 weight %) seems to be related to iron because the lowest value is observed in samples with lowest iron content. It is visible also on the diagram of elements concentrations (Fig. 3). The ratio Fe:Mn, calculated from analyses done on microareas, is 9:1 and is similar to one with value 10:1, estimated by S. Śliwiński (1969) for ore-bearing dolomites. Iron together with manganese form probably isomorphic replacements of magnesium in the dolomite lattice. The magnesium content changes from 8.65 to 12.80 weight % and is antipathetic to iron and manganese (Tab. 2, Fig. 3). It is one of important proofs for isomorphic replacement of Mg^{2+} by Fe^{2+} and Mn^{2+} in dolomite lattice. According to the definition of ankerite after W. A. Deer et

al. (1962) it seems that in many cases on studied microareas are noticed the ankerites (ratio Mg:Fe is lower than 4 — Tab. 2).

The calcium content is similar in all studied samples (20.90–22.55 weight %). The characteristic feature of studied Fe-dolomites and ankerites is an excess of Ca over the sum of Mg+Fe+Mn (Fig. 4), similiary as in the zinc-bearing dolomites such excess over the sum of Mg+Zn (B. Bąk, 1986). This excess of calcium over magnesium in the ore-bearing dolomites is according to S. Śliwiński (1966, 1969) common phenomenon, also confirms that A. Krzyczkowska-Everest (1990). After W. A. Deer et al. (1962) this excess of Ca over Mg+Fe is a feature of most of Fe-dolomites and ankerites. The zinc, lead and sulfur admixtures on studied microarcs occur in insignificant volumes although sometimes are noticed larger zinc amounts, probably within lattices of Fe-dolomites and ankerites (F. Duwensee, 1929; B. Witek, 1976; B. Bąk, 1986).

The microscopic observations and studies of microareas have indicated that described samples consist of dolomite, Fe-dolomite and ankerite. Often all these three phases, structurally identical, occur in the same crystal. Such composition and development of studied samples cause that the chemical, thermal, spectroscopic in infrared or X-ray analyses offer average results, depended on quantitative relations between individual components.

The studies of chemical composition of dolomites, containing Fe^{2+} , suggest an occurrence of solid solution of dolomite up to 70 mole % of $\text{CaFe}(\text{CO}_3)_2$ but ions Fe^{2+} replace only positions of Mg^{2+} . Ferroan analogue of dolomite $\text{CaFe}(\text{CO}_3)_2$ is unknown in nature, is unstable and has not been synthesised up till now in numerous experiments. Ankerites and Fe-dolomites, both natural and synthetic ones, contain normally an excess of CaCO_3 (P. E. Rosenberg, 1968; P. E. Rosenberg, F. F. Foit, 1979). Some doubts, referred to internal structure of Fe-dolomites and ankerites, had caused that the diffraction investigations of them have been initiated in an electron microscope (H. Kueha et al., 1984). Material for diffraction were taken under microscopic control from places, for which the sample composition has been determined with the microprobe. The results of electron diffraction suggest that analyzed Fe-dolomites have domain, periodic antiphase structure. The whole unit of periodic antiphase structure of Fe-dolomite could consist of three elements — $\text{CaMg}(\text{CO}_3)_2$ as basal host lattice, $\text{CaFe}(\text{CO}_3)_2$ and CaCO_3 . According to this idea Fe^{2+} and an excess of Ca^{2+} seem to be included into the host lattice of $\text{CaMg}(\text{CO}_3)_2$ in form of domains $\text{CaFe}(\text{CO}_3)_2$ and CaCO_3 , uniformly located but not simply on places of the Mg^{2+} with a regular period, controlled by an average content of Fe^{2+} within dolomite, as it is assumed for classic continuous stable solution. The data from electron diffraction have indicated that size of domains $\text{CaFe}(\text{CO}_3)_2$ were too small (lower 10 nm) to be detected with X-ray method or with microprobe. Due to that they are not contradictory with results of earlier studies and become only their new interpretation.

The results of electron diffraction of Fe-dolomites presented here are quantitatively the same as of ankerite (H. Kucha, A. Wieczorek, 1984) and of zinc dolomite (H. Kucha et al., 1983; M. R. Khan, D. J. Barber, 1990) that allows to assume the other double rhombohedral carbonates have also the domain structure.

OCCURRENCE AND ORIGIN OF FERROAN DOLOMITES AND ANKERITES IN THE SILESIA-CRACOW DEPOSITS OF ZINC AND LEAD ORES

The ferroan dolomites and ankerites, found in the deposits of the Bytom Depression and in the deposits of the Trzebieńka mine, occur both in the immediate vicinity of mineralized zones and in farther distance from them, from several tens, locally up to 200 m (B. Bąk, 1986). They are noticed — as was mentioned earlier — mainly in recrystallized dolomites, medium, fine and various crystalline, with hipidiomorphic structure, often porous. Their origin could be related to an influence of solutions containing Fe^{2+} on dolomite, which solutions have penetrated into rock along systems of fractures and microfractures, pores and caverns and along twin planes of crystals. Due to that the Fe-dolomites and ankerites form zones (rims) around dolomite crystals (crystals with zonal structure), they occur in voids and caverns, along joints and in zones of microfractures. The solutions could also carry zinc ions, reflecting in form of sometimes found in Fe-dolomites and ankerites probably isomorphic admixture of zinc. Sphalerite, infilling voids within dolomites and Fe-dolomites and overgrowing on its crystals in caverns, forms a little later than Fe-dolomite. It could origin due to sulfidization of zinc, introduced into lattice of Fe-dolomites and ankerites. After G. Kullerud (1967) iron is not sulfidized as long as zinc is not combined with sulfur. Removing of zinc from lattice of Fe-dolomites and ankerites should cause decrease of crystals volume. It is possible that it is a reason of origin of described earlier „crumbings” within crystals with zonal structure at boundary: Fe-dolomite (ankerite) dolomite.

The generation of Fe-dolomites and ankerites in forms observed recently could result due to dolomitization and recrystallization of early diagenetic dolomites as well as of primary carbonate sediment, containing a small amount of Fe^{2+} , placed uniformly in form of isomorphic admixture. Inserting of iron and manganese into carbonate sediment takes place mainly in form of Fe and Mn oxides but also introducing of an iron in form of replacement within clay minerals, transported in suspension. It is a source for calcite, forming in that stage. But before Fe and Mn are introduced into lattice of calcite they should be reduced, probably at the cost of organic matter. In that reaction the organic matter is consumed and Fe-calcite is formed, containing also Mn and other metals, clay minerals and quartz, that is observed in the Navan deposit of zinc ore (H. Kucha, 1987).

The Fe-dolomites and ankerites, occurring in the Silesian-Cracow deposits of Zn and Pb ores, form probably halos around mineralized zones, similar as in the Réocin deposit of Zn and Pb ores in Spain (L. Barbanson et al., 1983). The Fe-dolomites, found there, form similar as our ones the crystals with zonal structure within reery-

stallized dolomites. Small amount of samples and point method of sampling allows the author only to suppose that the halos of this type also exist in our deposits. If it is true it will be an additional criterion for searching for sulfide ores of Zn and Pb in the Silesian-Cracow area.

The origin of Fe-dolomites and ankerites in the Silesian-Cracow deposits of Zn and Pb could be referred with various stages of development of dolomites of the Lower Muschelkalk but are possible also several other processes, involving their generation. Farther studies are necessary to define which of them were dominant.

CONCLUSIONS

The dolomites from the Silesian-Cracow zinc and lead ore deposits contain the isomorphic admixtures of Fe^{2+} of several weight percent and magnesium of several weight percent. These rocks, depending on the ratio $\text{Mg}:\text{Fe}^{2+}$, should be regarded as ferroan dolomites (Fe-dolomites) or ankerites.

The bivalent iron forms in the dolomite lattice isomorphic replacements of magnesium, with a regular period controlled by average content of Fe^{2+} in dolomite (classical stable solution) or, as it is suggested by the results of electron diffraction, Fe^{2+} and excess of Ca^{2+} are introduced into the host lattice of $\text{CaMg}(\text{CO}_3)_2$ in form of domains: $\text{CaFe}(\text{CO}_3)_2$ and CaCO_3 , uniformly located (so-called domain, periodic antiphase structure).

The ferroan dolomites and ankerites occur mainly within recrystallized medium, fine and various crystalline dolomites, often porous. They are connected with the mineralization, placed both in proximity of ores and on some distance, in peripheries of mineralized zones. Probably they could form the aureoles around these zones, with thickness up to several tens of meters.

Acknowledgments. Author thanks the scientists from Instytut Geologii i Surowców Mineralnych AGH, particularly Prof. dr W. Żabiński for help in carried investigations. MSc. ing. M. Szuwarzyński from the Trzcibionka mine and MSc. ing. J. Żeglicki from the Orzeł Biały mine are kindly thanked for discussions and help in sampling. Special regards are to MSc. ing. P. Bolechala from Instytut Technologii Odlewnictwa AGH for X-ray microanalyses.

Translated by Grzegorz Czapowski

Oddział Karpacki
Państwowego Instytutu Geologicznego
Kraków, ul. Skrzatów 1

Received: 15.12.1992

REFERENCES

- BARBANSON L., TOURAY J. C., SAULAS D., VADALA P. (1983) — Auréole ferrifère et minéralisation Zn-Pb du type Réocin. *Chron. Rech. Min.*, 473, p. 39-47.
- BAK B. (1986) — Węglanowa mineralizacja Zn, Pb i Fe w śląsko-krakowskich złożach rud cynku i ołowiu. *Arch. AGH. Kraków*.
- CZAJKA K. (1991) — Geochemia złóż rud Zn-Pb w niecce bytomskiej. *Rudy Metale*, 36, p. 107-112, nr 3.
- DEER W. A., HOWIE R. A., ZUSSMAN J. (1962) — Rock-forming minerals, non silicates. Longmans.
- DUWENSEE F. (1929) — Die oberschlesische Bleizinkerzlagertstätte auf Grund der Ergebnisse der geologischen Untersuchung der Deutsch-Bleischarley-Grube. *Mettal. u. Erz*, 26, p. 481-492.
- GRAFF D. L. (1961) — Crystallographic tables for the rhombohedral carbonates. *Amer. Miner.*, 46, p. 1283-1613.
- GRUSZCZYK H., WAŻEWSKA-RIESENKAMPF W. (1960) — Carbonates in Silesian-Cracovian deposits of zinc and lead ores. *Bull. Acad. Pol. Sci. Sér. Sci. Géol. Géogr.*, 8, p. 299-304, nr 4.
- HARAŃCZYK C. (1981) — Ontogeneza dolomitów kruszczoonych. *Prz. Geol.*, 29, p. 513-518, nr 10.
- HARAŃCZYK C., SZOSTEK L. (1969) — Uwagi o niektórych poglądach na budowę złoża rud cynku i ołowiu kopalni „Trzebionka” i genezę dolomitów kruszczoonych. *Rudy Metale*, 14, p. 218-225, nr 4.
- HOWIE R. A., BROADHURST F. M. (1958) — X-ray data for dolomite and ankerite. *Amer. Miner.*, 43, p. 1210-1216.
- KHAN M. R., BARBER D. J. (1990) — Composition related microstructures in zinc-bearing carbonate assemblages from Broken Hill, New South Wales. *Miner. Petrol.*, 41, p. 229-245, nr 2-4.
- KRZYCZKOWSKA-EVEREST A. (1990) — Petrographic characteristics of the ore-bearing dolomites of the Górażdża Beds, from Olkusz — Bolesław region (South Poland). *Pr. Miner. Komis. Nauk Miner. PAN Oddz. w Krakowie*, nr 81.
- KUCHA H. (1987) — Carbonate and silicate precursors of the sulphide mineralization in the Navan Zn-Pb deposits, Ireland. *Tschermaks Miner. Petrogr. Mitt.*, 37, p. 51-77.
- KUCHA H., BAK B., WIECZOREK A. (1983) — Preliminary report on superstructures in zinc-dolomite. *Miner. Pol.*, 14, p. 19-27, nr 1-2.
- KUCHA H., BAK B., WIECZOREK A., FITTA G. (1984) — Preliminary report on superstructures in iron-dolomite with CaCO₃ excess. *Miner. Pol.*, 15, p. 21-27, nr 1-2.
- KUCHA H., CZAJKA K. (1984) — Sulphide-carbonate relationships in Upper Silesian Zn-Pb deposits (Mississippi Valley type), Poland, and their genesis. *Trans. Inst. Mining and Met. Sect. B*, 93, p. 12-22.
- KUCHA H., WIECZOREK A. (1984) — Evidence for superstructuring in ankerite. *Tschermaks Miner. Petrogr. Mitt.*, 32, p. 208-216.
- KULLERUD G. (1967) — Sulphide studies. *Researches in geochemistry*, 2, p. 49-67. John Wiley and Sons. New York.
- KULP J. L., KENT P., KERR P. F. (1951) — Thermal study of the Ca-Mg-Fe carbonate minerals. *Amer. Miner.*, 36, p. 643-670.
- MOCHNACKA K., SASS-GUSTKIEWICZ M. (1981) — The metasomatic zinc deposits of the Pomorzany mine (Craow-Silesian ore district, Poland). *Ann. Soc. Geol. Pol.*, 51, p. 133-151, nr 1-2.
- PRZENIOSŁO S. (1974) — Cynk i ołów w utworach węglanowych triasu zawierciańskiego. *Biul. Inst. Geol.*, 278, p. 115-186.
- RIESENKAMPF W. (1990) — Identyfikacja termiczna ankerytów i dolomitów żelazistych. *Rudy Metale*, 35, p. 317-322, nr 12.
- ROSENBERG P. E. (1968) — Subsolidus relations on the dolomite join CaMg(CO₃)₂-CaFe(CO₃)₂-CaMn(CO₃)₂. *Amer. Miner.*, 53, p. 880-889.
- ROSENBERG P.E., FOIT F. F. (1979) — The stability of transition metal dolomites in carbonates systems: a discussion. *Geochim. Cosmochim. Acta*, 43, p. 951-955.
- SMOLARSKA I. (1968) — Charakterystyka mineralogiczna dolomitów kruszczoonych wschodniej części śląsko-krakowskiego zagłębia kruszcowego. *Pr. Miner. Kom. Nauk Miner. PAN Oddz. w Krakowie*, nr 13.
- ŚLIWIŃSKI S. (1966) — Dolomitizacja morskich utworów triasu krakowsko-śląskiego. *Rudy Metale*, 11, p. 122-132, nr 3.

- ŚLIWIŃSKI S. (1969) — Rozwój dolomitów kruszczośnych w obszarze krakowsko-śląskim. Pr. Geol. Kom. Nauk Geol. PAN Oddz. w Krakowie, nr 57.
- WITEK B. (1976) — Zmienność litologiczna dolomitów triasowych złoża Żelatowa i jej wpływ na ich przydatność przemysłową. Arch. PWr. Wrocław.

Bogusław BĄK

DOLOMITY ŻELAZISTE I ANKERYTY W ŚLĄSKO-KRAKOWSKICH ZŁOŻACH RUD CYNKU I OŁOWIU

S t r e s z c z e n i e

Badania mineralogiczne wykazały, że w śląsko-krakowskich złożach rud cynku i ołowiu występują dolomity zawierające izomorficzne domieszki Fe^{2+} , a także prawdopodobnie manganu (tab. 1 i 2). W zależności od stosunku Mg:Fe (patrz W. A. Deer i in., 1962) są to dolomity żelaziste (Fe-dolomity) lub ankeryty. Potwierdzają to krzywe DTA i DTG (fig. 1) badanych próbek, wykazujące typowe dla ankerytu trzy efekty endotermiczne ogólnie w zakresie 670-930°C. Obserwacje mikroskopowe i analizy w mikroobszarach (tab. 2, fig. 2, 3-4) wykazały, że próbki składają się z dolomitu, Fe-dolomitu i ankerytu. Często wymienione fazy występują w jednym kryształcie. Taki ich skład i wykształcenie powodują, że analizy chemiczne, termiczne, spektroskopowe w podczerwieni czy rentgenowskie dają wyniki uśrednione uzależnione od proporcji ilościowych między poszczególnymi składnikami.

Żelazo dwuwartościowe podstawia izotermicznie magnez z regularną okresowością kontrolowaną przez średnią zawartość Fe^{2+} w dolomicie (klasyczny roztwór stały) lub, jak sugerują wyniki dyfrakcji elektronowych Fe^{2+} i nadmiar Ca^{2+} , są wprowadzone do sieci goszczącej $CaMg(CO_3)_2$ w postaci domen $CaFe(CO_3)_2$ i $CaCO_3$ jednolicie rozmieszczonych (tzw. domenowa, uporządkowana struktura antyfazowa). Dane z dyfrakcji wykazały, że rozmiary domen są zbyt małe, aby mogły być wykryte za pomocą metody rentgenowskiej lub mikros sondy elektronowej.

Dolomity żelaziste i ankeryty stwierdził autor głównie w zrekrystalizowanych dolomitach średnio-, różno- i drobnokrystalicznych, często porowatych, oraz w dolomitach mikrytowych (wczesnodiaogenetycznych). Najlepiej rozwinięte są w zewnętrznych częściach kryształów, w strefach mikrospęknięć, wokół pustek, wzdłuż szczelin i w kawernach. Często można obserwować kryształy o budowie strefowej (część wewnętrzna — dolomit, zewnętrzna — Fe-dolomit lub ankeryt). Powstanie Fe-dolomitów i ankerytów można więc wiązać z penetrującymi dolomit roztworami zawierającymi jony Fe^{2+} . Możliwe jest też, że utworzyły się one w wyniku dolomityzacji i rekrystalizacji dolomitów wczesnodiaogenetycznych zawierających niewielkie ilości Fe^{2+} , rozmieszczonego dość równomiernie w postaci domieszki izomorficznej.

Występowanie Fe-dolomitów i ankerytów w śląsko-krakowskich złożach rud Zn i Pb, jak wskazują obserwacje autora i dane z literatury, jest powszechne i związane z okruszcwanicm. Spotykane są one zarówno w bezpośrednim sąsiedztwie kruszców, jak i w pewnym oddaleniu na peryferiach stref okruszczowanych. Zbyt mała ilość i punktowy sposób pobierania próbek nie pozwalają autorowi na stwierdzenie czy wokół stref okruszczowanych występują aureole z Fe-dolomitami i ankerytami. Gdyby tak było, to stanowiłoby to dodatkowe kryterium poszukiwawcze siarczkowych rud Zn i Pb w obszarze śląsko-krakowskim.