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GEOCHEMICAL AND MINERALOGICAL RESEARCH OF CARBONATE MINERALS AT NIŽNÁ SLANÁ - MANO DEPOSIT (GEMERICUM, WESTERN CARPATHIANS)

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Abstract: Fe-carbonates were formed as products of exchange reactions between the limestone and a fluid phase (open system) with Fe,Mg,Ca,CO_2. Carbonate, sulphide and stable isotope (C,O) analyses show two mineral associations: 1.calcite1 + pyrite1 + ?graphite 2.Mg-ankerite + Fe-ankerite + sideroplesite + siderite + pyrite2 + phengite + tetrahedrite + arsenopyrite + ?graphite + calcite + quartz. The second (metamorphic) association was formed on the relics of the first one. Pyrite1 is dispersed in carbonate. The younger pyrite2 grows on the cores of pyrite1, it is disseminated in carbonates, or forms clusters. The presence of Mn^{2+} in pyrite2 indicates its metamorphic origin with carbonates. Carbon derived from limestones played a decisive role in the formation of Fe-carbonates. Minor amounts of carbon may attributed also to the organic carbon, derived from the rocks surrounding the limestones. Isotopic values of the source fluid ($\delta^{13}C$ = -1 to -3 ‰, PDB; $\delta^{18}O$ = +10 to +14 ‰,SMOW) shows its metamorphic origin. Crystallization began in the sediments, calcite was altered to Mg-ankerite (T = 300 - 350°C) later to Fe-ankerite, finally terminated by the formation of sideroplesite and siderite (T= 200 °C), from the same fluid.

Previous work and mineralogical setting

The Nižná Slaná siderite ore deposit lies in the Early Paleozoic rocks of Gemericum. The Mano - Gabriela (Fig.1) depositional attitude is situated in the upper silurian sedimentary - volcanic complexes, in the central part of the Gelnica group, in Bystrý potok Formation (Bajaník et al. 1983), or in the Betliar Formation in the Gelnica group (Grecula et al. 1982). Geological position of the deposit consists of the following layers (upwards, Bajaník et al. 1983): 1.porphyroids 2.black and green phyllites 3.carbonate (limestone, ankerite, siderite) position in darkgrey and black phyllites, with thickness of 200 m and upper silurian - devonian age (Snopková and Snopko 1979, Planderová and Snopková 1979) 4.black and green phyllites 5.porphyroids (Bolaček and Mihok 1994).

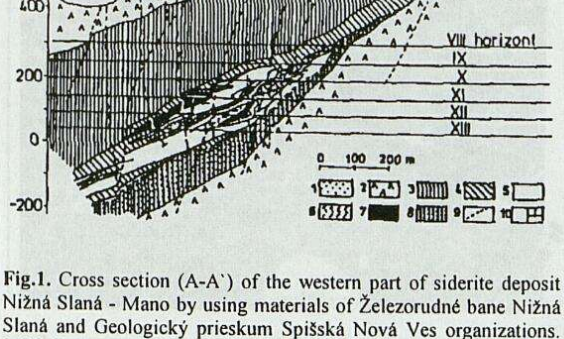


Fig.1. Cross section (A-A`) of the western part of siderite deposit Nižná Slaná - Mano by using materials of Železorudné bane Nižná Slaná and Geologický prieskum Spišská Nová Ves organizations. 1.debris 2.porphyroid 3.graphitic - sericitic and sericitic phyllite 4.black phyllites with enclosures of lydite intercalations 5.limestone 6.ankerite 7.siderite 8.underlying sericitic phyllite 9.fault 10.drill and mining work (Bolaček and Mihok 1994).

Despite the big amount of projects written about the Nižná Slaná deposit, the opinions of the genesis of carbonate mineralization differ. Generally, there are three opinions considered (Bolaček and Mihok 1994):

1. hydrothermal metasomatic, with magmatic source of solution
2. metamorphic metasomatic, with the source of solution from processess of regional metamorphosis
3. sedimentary.

Many scientists studied this deposit mineralogically and petrologically, either by the direct research of Nižná Slaná deposit (Hornáček and Varček 1963, Hanuš et al. 1963, Abonyi at al. 1963, Gubač 1973, 1977, Lorinz 1988, Turan and Turanová 1989, 1993, Turanová and Turan 1992, Bolaček and Mihok 1994, Radvanec and Iró 1994, Grecula et al. 1995, Grecula and Abonyi 1995), or in combination exploration of mineralization of whole Gemericum and the Western Carpathians (Ilavský 1957, 1959, 1962, 1974, Varček 1962, 1963, 1985, Grecula 1982, Grecula and Hovorka 1987, Rozložník 1989, 1990, Turanová et al. 1993, Grecula et al. 1994). There does not exist a state agreement in opinions of the genesis of the deposit and stratiform Fe-Mg-carbonate mineralization of Spis-Gemer Ore Mts. The opinion of the age of creation of siderite formation of Western Carpathians varies, too. Varček, Rozložník, and others say it is of Alpian, Grecula and others Variscan age. The source of siderite formation is discussed, as well. According to Rozložník* (1989, 1990), Slavkay and Petro

(1993) it is of magmatic, deeper, upper mantle source. Žák et al. (1991), Bartalský (1991) and others assume shallow (crustal) regional metamorphic source with majority of regional metamorphic effect over magmatic. Turan and Turanová (1989, 1993) emphasize also the big importance of sedimentary - diagenetic and metamorphic processes (besides the influence of tectonics processes) and they are against hydrothermal metasomatic theory of creation.

According to Grecula (1982), besides the lithological environment (the source of metals), also the position of carbonates to metamorphic zones had a big influence on genesis of stratiform and vein siderite and magnesite. Magnesite is more closely to the zone of amphibolite facies, meanwhile siderite is close to the rocks of lower metamorphic facies (on the periphery) and it belongs to the lower temperature mineral association. Grecula (l.c.) also considers three possibilities of the Fe-Mg-carbonates genesis: 1.metamorphic 2.syngenetic (mainly siderites) and 3.epigenetic hydrothermal-metasomatic origin (mainly magnesite).

Ilavský and Sattran (1976) described so-called metasomatic type deposits, which lies in carbonates and graphitic shists with porphyroids. They connect them genetically, with basic volcanic rocks.

Methods

The rocks and vein material samples were obtained from the key mining horizons (Table1). Sampling was made between sections 43 and 44 (4 holes in metres 1099, below the 10-th horizon), in the section 37 (on the second level of horizon 10/11) samples were taken from two places. Next samples were taken from the second level of 11-th horizon, two samples (2097 and 2211 metres) from the 12-th horizon. Thin sections impregnated with epoxy were prepared for all the samples. They were polished in order to facilitate back-scaterred electron imaging of the specimen.

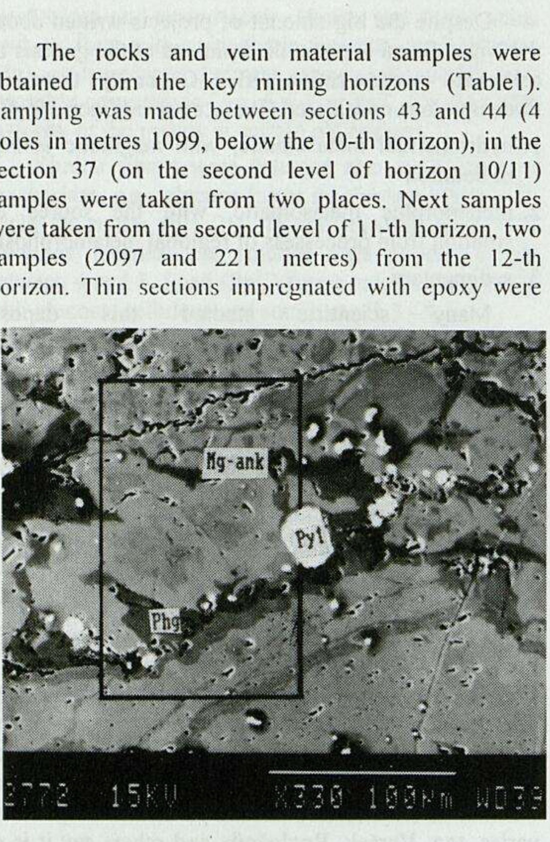
All thin sections were studied on a petrographic microscope. The elemental composition of some carbonate and sulphide (Table 2) minerals was determined on a electron microprobe machinery (JXA 840A, Comenius university, Faculty of Natural Sciences, Bratislava, analyst Krištín). Sample total (computed from major cations) of reported values were 100±2%. The back-scaterred electron imaging system on the microprobe was also used to detect zonation in siderite, and analyses were obtained for the individual zones (Table 2; 4). Carbon and oxygen isotopic analyses of carbonates were performed on samples hand ground from the mining samples (13 samples). Calcites and dolomites were identified from samples by colouring method (Geological Survey, Bratislava, analyst Repčok). After removing the organic matter, the carbonate were disintegrated in vacuum with 100% solution of phosphoric acid (calcite at 25 ^{o}C, dolomite at 100 ^{o}C). The carbon dioxide was measured on FINNIGAN MAT 250 mass spectrometer (measurement with accuracy ± 0,02%). Other samples of ankerite (MA, NS, Table 3) with content of Mn were meassured in laboratories of Czech Geological Institution (FINNIGAN MAT 251 spectrometr, analyst Žák, deviations ± 0,01%).

Data are reported in per mil ($^{o}/_{oo}$), deviations relative to the SMOW and PDB standards for oxygen and carbon, respectively.

Mineralogy and associations of minerals

By using of optical microscope the detailed contact of carbonates of various genetic types and chemistry were studied and more closely identified by electron microprobe (Fig.2).

Calcite. It occures as a main carbonate mineral in Mano deposit. It is abundant in limestones, together with graphitic phyllites and lydites is a part of Betliar Formation. These rocks together create the so-called



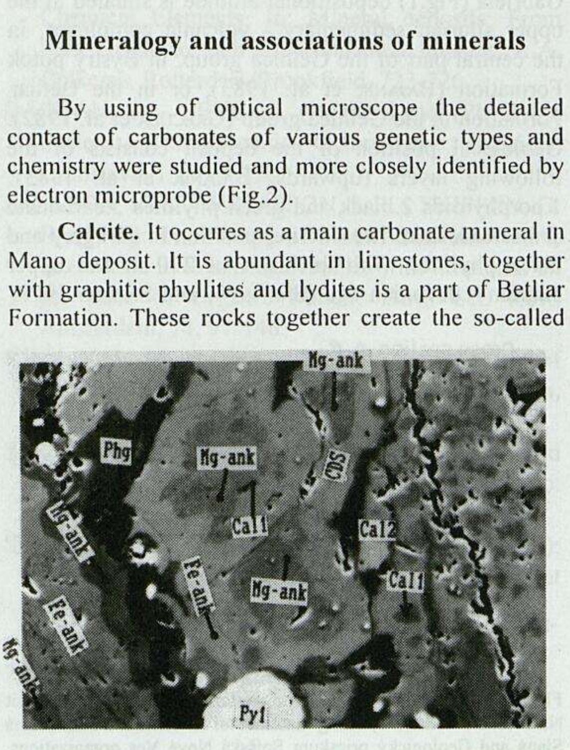


Fig.2 a,b. Fig.2b are details of fig.2a. Dark irregular cores of calcite (Cal1) and lighter cores of Mg-ankerite (Mg-Ank) are covered with light Fe-ankerite (Fe-Ank), which crystallized from metamorphic fluid and a CDS (cal-dol-sdr) phase. The light grain (Py1) is a pyrite from older generation, dark minerals in veins are created by phengite (Phg) and Mg-ankerite.

Tab. 1 Sample Localization, Macroscopic Description and Analytical Methods

Sample	Main horizon	Localization	Macroscopic description	Isotopes C, O	Chemical analysis
NŽ-1A	10	Under10.horiz,haulage level 43, cross cut1	limestone	+	
NŽ-1B	10	Under 10.horiz,haulage level 43,cross cut1	graphite ?		
NŽ-1C	10	Under 10.horiz,haulage level 43,cross cut1	Fe-carbonate		
NŽ-2A	10	Main gangway between 3-4 cross cut.	Fe-carbonate		
NŽ-3A	10	Main gangway-haulage level 43-cross cut 5	Fe-carbonate		
NŽ-4A	10	Main gangway-haulage level 43-cross cut 6 toN	Fe-carbonate	+	
NŽ-5B1	10	Main gangway-haulage level 43, between 8-9 cross cut	lydite	+	
NŽ-5B2	10	Main gangway-haulage level 43,between 8-9 cross cut	lydite + carbonate	+	+
NŽ-6A	10	Intermediate level-haulage level 43,at chute	Fe-carbonate		+
NŽ-7A	10-11	Intermediate level,10m from chute to N	limestone	+	+
NŽ-7B1	10-11	Intermediate level,10m from chute to N	limestone	+	+
NŽ-7B2	10-11	Intermediate level,10m from chute to N	Fe-carbonate	+	
NŽ-7C	10-11	Intermediate level,10m from chute to N	Fe-carbonate	+	
NŽ-7D	10-11	Intermediate level,10m from chute to N	calcite, Fe-carbonate		+
NŽ-8A	11	At the chute	Fe-carbonate		+
NŽ-9B1	11	2nd etage,cross cut12,10m from southern main face to N	Fe-carbonate	+	+
NŽ-9B2	11	2nd level,cross cut12,10m from southern main face to N	Fe-carbonate	+	
MA-5/1	11	haulage level 34	graphitic phyllite with lydite, limestone	+	+
MA-5/2	11	haulage level 34	graphitic phyllite with lydite,limestone	+	
MA-5/3	11	haulage level 34	graphitic phyllite with lydite, limestone	+	
MA-7	11	haulage level 34	graphitic phyllite with lydite, limestone	+	
NS-16	11	haulage level 34	graphitic phyllite with lydite, limestone	+	
MA-5/1	11	haulage level 34	graphitic phyllite with lydite, ?graphite	+	+
MA-5/2	11	haulage level 34	graphitic phyllite with lydite, ?graphite	+	
MA5/3	11	haulage level 34	graphitic phyllite with lydite, ?graphite	+	
MA-7	11	haulage level 34	graphitic phyllite with lydite, ?graphite	+	
NŽ-10A	11	cross cut 1 to N	Fe-carbonate		+
NŽ-11A	12	cross cut 32, begining	Fe-carbonate	+	
NŽ-11B	12	20 m from begining, cross cut 32	Fe-carbonate		
NŽ-12A	12	haulage level 40, main gangway	calcite	+	

Tab. 2 Mineral Composition of Samples of the Nižná Slaná - Mano Deposit

mineral / sample	NŽ - 1	NŽ - 5	NŽ - 6	NŽ - 7	NŽ - 8	NŽ - 10	MA, NS
calcite1	+			+			+
Mg-ankerite	+		+	+		+	
Fe-ankerite		+	+	+		+	
sideroplesite		+		+	+		
siderite		+			+		
pyrite	+	+	+	+	+	+	+
arsenopyrite							+
tetrahedrite	+						
graphite?	+	+	+	+	+	+	+
quartz	+	+	+	+	+	+	+
phengite	+			+	+		
chalcopyrite	+						

Tab. 3 Stable Isotope Analyses of C,O from Carbonate Minerals

Sample	Main horizon	Analysed mineral	δ ^{13}C ‰ (PDB)	δ ^{18}O ‰ (PDB)
NŽ - 1A	10	dol. in sdr.	-6.874	-13.314
NŽ - 4A	10	dol. in sdr.	-4.941	-12.647
NŽ - 5B1	10	dol. in sdr.	-3.417	-12.710
NŽ - 5B2	10	dol. in sdr.	-5.745	-13.302
NŽ - 7A	10 - 11	calcite, Holec Beds	-0.694	-12.361
NŽ - 7B1	10 - 11	calcite, Holec Beds	-4.911	-13.302
NŽ - 7B2	10 - 11	dol. in sdr.	-5.420	-13.073
NŽ - 7C	10 - 11	dol. in sdr.	-3.231	-13.078
NŽ - 7D	10 - 11	Cal in sdr.	-5.426	-16.608
NŽ - 9B1	11	Dol-vein	-5.362	-13.037
NŽ - 9B2	11	Dol in sdr.	-4.769	-13.326
MA - 5/1	11	calcite, Holec Beds	-4.300	-12.000
MA - 5/2	11	calcite, Holec Beds	-4.200	-11.800
MA - 5/3	11	calcite, Holec Beds	-4.000	-11.900
MA - 7	11	calcite, Holec Beds	-5.200	-12.100
NS - 16	11	calcite, Holec Beds	-4.900	-14.000
MA - 5/1	11	graphite?,, Holec Beds	-22.900	-
MA - 5/2	11	graphite?,, Holec Beds	-22.900	-
MA - 5/3	11	graphite?,, Holec Beds	-23.300	-
MA - 7	11	graphite?,, Holec Beds	-25.500	-
NŽ - 11A	12	dol. in sdr.	-5.370	-
NŽ - 12A	12	dol. in sdr.	-4.345	-13.884

Tab. 4 Representative Analyses of Carbonates (a) and Sulphides (b) in Samples of the Nižná Slaná - Mano Deposit.
(Analyst Krištín, CLEOM PRIF UK, Bratislava)

4a) Carbonate (oxide content in weight%, content of elements in mol%)

Mineral	calcitel	Mg-ankerite	Fe-ankerite	sideroplesite	siderite
Place	matrix	matrix	matrix	fissures	matrix
Sample	NŽ-7-A	NŽ-10-B	NŽ-7-B	NŽ-8-A	NŽ-8-B
(a. No.)	(71b)	(93)	(74)	(115)	(131)
CaO	53.80	29.23	27.27	0.42	---
MgO	0.38	12.84	4.16	6.38	4.41
FeO	1.61	10.77	24.02	49.14	53.30
MnO	0.30	2.26	2.46	3.53	2.54
CO_2	43.81	44.95	42.19	39.59	39.04
Total	99.89	100.05	100.10	99.58	99.30
O=	3	6	6	3	3
n=	3	19	16	22	12
Ca	0.965	1.02	1.01	0.010	---
Mg	0.010	0.62	0.22	0.175	0.125
Fe	0.020	0.30	0.70	0.760	0.835
Mn	0.005	0.06	0.07	0.055	0.040
Total	1.000	2.00	2.00	1.000	1.000

4b) Sulphide (Content of Elements in Weight %)

Mineral	pyrite 1	pyrite 1	pyrite 2	pyrite 2	arsenopyrite	arsenopyrite	tetrahedrite
Place	core	rim	core	rim	core	core	core
Sample	NŽ-1-C	NŽ-1-C	NŽ-8-A	NŽ-8-A	12.hor.	12.hor.	NŽ-1-C
(a. No.)	(6)	(49)	(20)	(21)	(29)	(30)	(52)
Fe	43.52	48.75	45.83	46.96	32.68	33.72	7.19
As	2.38	-	-	-	45.54	47.57	0.04
Sb	0.08	0.09	-	0.07	2.86	0.27	28.25
Ag	0.01	0.02	-	-	-	-	0.43
Mn	-	-	-	0.01	-	-	-
S	54.04	51.53	53.71	53.17	19.39	18.37	26.80
Zn	-	-	-	-	-	-	1.39
Cu	-	-	-	-	-	-	34.91
Bi	-	-	-	-	-	-	0.13
Hg	-	-	-	-	-	-	0.63
Total	100.03	100.39	99.54	100.21	100.47	99.93	99.77

Holec Beds (according to the determination of old Paleozoic rocks - GRECULA 1982). The limestones are regionally metamorphosed (chlorite - biotite and biotite zones). Mineralogical associations (chlorite + phengite, locally biotite) in the porphyroids indicate the temperature of exchange around 400 - 500°C. The limestone with organic substance recrystallized under these conditions and changed to a sugar type shape. Calcite in the limestone is often in the association with the same sized (up to 3 mm) grains of quartz, also with dissemination of pyrite1. Calcite1 (sedimentary, older generation) contains Mg, Fe, Mn (Table 4). Another type of calcite with the same chemical composition occurs also in Fe-carbonates, creating the cores, which are covered by Mg-ankerite (Fig.2), and later by Fe-ankerite.

Mg-ankerite (according to the classification of WOODS and GARRELS 1992) is the second oldest carbonate. It covers calcite in the matrix (Fig.2), or locally creates short veins (thickness up to 0,5 cm).

Fe-ankerite. Opposite to Mg-ankerite, Fe-ankerite contains more Fe and less Mg (Table 4). As we can see on electron microprobe photos (Fig. 2b), Fe-ankerite pushes calcite and Mg-ankerite, i.e. Fe-ankerite crystallized after these minerals were formed. A part of Fe-ankerite crystallized with Mg-ankerite at the same time. Fe-ankerite is one of the most important part of matrix of the rocks (Fig.2), and creates also small younger veins.

Sideroplesite. Sideroplesite is one of the youngest and most important carbonates in the deposit. It crystallized in the matrix after Fe-ankerite. Its most important accumulations are in the voluminous fissures of the matrix. It pushes the Fe-carbonates of the matrix - so it is difficult to recognise the original fissure. Sideroplesite is well crystallized (grains up to 2 cm).

Siderite. Siderite with sideroplesite together belong to the youngest minerals in the deposit. Its chemical composition (with content of MgO = 4,41w%, MnO = 2,54w%, Table 4) is closed to sideroplesite. Siderite and sideroplesite fill in the fissure and also pushe the Fe-carbonates in matrix. Calcite, dolomite and siderite create also the (CDS) mixture, with chemical composition similar to ankerite (Fig. 4,2b).

Pyrite creates isolated idiomorphous granes or clusters in carbonates, lydites (Holec Beds, Grecula 1982) and graphitic shists. It locally creates also massive ores (up to 0,5 cm) on the contact of carbonate with graphitic shist. There are two generations of pyrite: pyrite1 and pyrite2 (Table 4). The older Py1 is chemically zoned (often with content of As= 0,4-2,3 w%, Sb=0,2-0,14 w% in core), on the rim without admixtures, or it contains hundreds % of Sb, As, Cu, Ag etc. (Table 4). The younger Py2 overgrowths the core of Py1, or Py2 is independently disseminated in carbonates. Py2 more often creates clusters with insignificant amount of Py1 up to massive ores. Py2 is locally chemically zoned, or is also homogenous. It contains hundreds % of Mn, As, Sb, Ag. The presence of Mn in structure of Py2 indicates its crystallization together with carbonates. All Fe-carbonates contains Mn.

Py2 with ratio Fe : S = O,95 : O,86 (according to weight %) respects to Py1, more closely to ideal crystallochemical composition and, it contains an oversupply of Fe. Py1 crystallized in the time of the limestone sedimentation. In graphitic phyllite and lydite in the body of the deposit, the Py1 has the same characteristic features as the stratiform submarine exhalaceonus pyrite in the lower ore horizon of Smolník type (BARTALSKÝ and RADVANEC 1993). The presence of the lower ore horizon in Mano deposit is proved in Mano deposit on the border between the Holec Beds (graphitic phyllite) and Smolník layers of chloritic shists (GRECULA 1982). Py2 crystallized in younger age, which is connected with crystallization of Fe-carbonates in the deposit. According to the similar time and stratigraphic position, Py2 has the same textural, structural and crystallochemical characterization as the metamorphic pyrite in the biotite zone of regional metamorphosis of the lower horizon in the locality Turecká (BARTALSKÝ and RADVANEC 1993).

Arsenopyrite occures on the contact between carbonates and graphitic phyllites creating clusters and very often massive ores. Arsenopyrite crystallized in younger age, with Py2, tetrahedrite and Fe-carbonates. It contained Sb (0,30-2,86 w%) in each analyzed sample, partially also Ni (0,9%) and Cu (0,4%). The rate between Fe and As in arsenopyrite is close to its ideal crystallochemical composition.

The crystallochemical composition of arsenopyrite is generally used for temperature determination of crystallization of coexisting minerals, however, using the geothermometer is limited by concentration of trace elements (KRETSCHMAR and SCOTT 1976, SUNDBLAD et al. 1981). Their content in our analyses overstepped the limit, therefore we couldn´t exactly use this geothermometer. Arsenopyrite crystallized at a higher temperature, with value from 350 to 400 °C. This temperature is in connection with the temperature of the regional metamorphosis in the region of the deposit, and also with calculated temperature (350 - 400°C) of the 1-st phase of coexisting carbonates (calcite 1 - Mg ankerite). The temperature was calculated according to POWELL et al. (1984, Fig.7).

Associations of minerals

Two mineral associations were identified in the analysed samples, that crystallized in the following time advance:

1. calcite1 + pyrite1 + ? graphite

2. Mg-ankerite + Fe-ankerite + sideroplesite + siderite + quartz + pyrite2 + phengite + tetrahedrite + arsenopyrite + ? graphite + calcite2 + quartz.

Stratiform carbonates were created by reaction changes between the previous limestones (marble) and fluid phase, with content of Fe, Mg, Ca, CO_2 in open system for fluid phase in variscan regional metamorphosis. The 1-st association (older) is connected with sedimentation of limestone, with creation of volcanosedimentary sequence in Holec Beds and it is premetamorphosed. The second, (younger) mineral association crystallized on the relic of the 1-st one (Fig.2). From the structural and textural point the second association has got all the marks of crystallization of reaction changes.

Interpretation of $\delta^{13}C$ and $\delta^{18}O$ values in carbonates

The carbon isotopic composition in carbonate minerals depends on the isotopic composition in primary solution, but also on the temperature and the form of carbon presence in the source solution, e.g. like HCO_3^-, H_2CO_3, or free CO_2. The oxygen isotopic composition depends on the temperature and oxygen isotopic composition in hydrothermal solution, from where it precipitated. The temperature of carbonate crystallization reached from 350 to 400 °C. We determined it from the values of the calcite - dolomite geothermometer (POWELL et al. 1984, Fig.7). The same temperature was also determined from the regional metamorphosis and informative measurements of the arsenopyrite geothermometer. Our assement shows, that the youngest sideroplesite and siderite crystallized at 200°C.

According to isotope analyses (Table 3) and mineral parageneses in graph of $\delta^{13}C$ versus $\delta^{18}O$ (Fig.3) three groups of carbonate samples can be determined:

1. Calcite from metamorphic limestone from Holec Beds, intermediate horizon 10-11, with value of $\delta^{13}C$ from -0,5 to -4 ‰, PDB
2. Dolomite (Mg-ankerite), which crystallized on the core of calcite ($\delta^{13}C$ = from -3 to -7 ‰, PDB). The dolomite has a homogenous isotopic composition not dependent on the horizons of the mine
3. Calcite from the stratiform position of metamorphic limestone on the 11-th and 12-th horizon ($\delta^{13}C$ = from -4 to -5,5 ‰, PDB). This group partially covers the field of the dolomite.

The oxygen isotopic composition of majority of analyses of all 3 groups is in range $\delta^{18}O$ = from +16 to +18,5 ‰, SMOW.

From the comparison of both groups of calcite in Fig.3 and the vertical position of the samples in competent horizons there is clearly seen the vertical zonation in calcite of the Holec Beds. Lower values of $\delta^{13}C$ in the deeper horizons are either reflection of higher temperature of the source solution of carbonates, or (if we assume the same temperature of carbonate crystallization) they have higher influence on the carbon of the organic origin, which was mobilised in the same process as the carbon from limestone (calcite). In the process of the regional metamorphosis, the mixing of carbon appeared in two sources:

1. the limestone
2. kerogen of the Holec Beds, in which the carbonate body lies. The carbon of mobilization of carbonate rocks had the dominant role in the limestone (calcite). On the 11-th and 12-th horizon, there was also the mild influence of carbon mobilised in direct surroundings of the limestone of organic material ($\delta^{13}C$ = from -23 to -25,5 ‰, PDB).

There are extrapolated isotopic values of carbonates represented in Fig.3 at temperature T=350°C. Characteristic feature for the source solution show higher values of $\delta^{13}C$, in the field outside of area of typically deep, mantle carbon ($\delta^{13}C$ = from -5 +2 ‰, PDB, KYSER 1986). The origin of carbon of carbonate source solution is mainly of two sources:

1. decomposition or maturation of organic matter of the Holec Beds (graphitic phyllites), and
2. mobilization or metamorphic decarbonatization of limestones.

By mixing of carbon of these two sources, it is possible to obtain the carbon source with the value

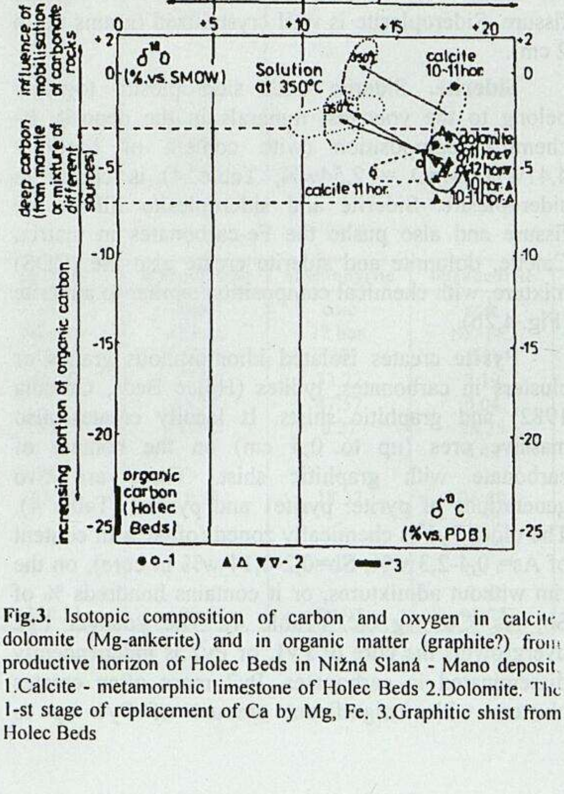


Fig.3. Isotopic composition of carbon and oxygen in calcite dolomite (Mg-ankerite) and in organic matter (graphite?) from productive horizon of Holec Beds in Nižná Slaná - Mano deposit. 1.Calcite - metamorphic limestone of Holec Beds 2.Dolomite. The 1-st stage of replacement of Ca by Mg, Fe. 3.Graphitic shist from Holec Beds

$\delta^{13}C$ = from +2 up to -3 °/$_{oo}$. Carbon in fluid originated predominantly from mobilization of carbonate rocks (Fig.3). So there is a change going of the limestone, reaction change, in the body of the limestone, and its recrystallization to the crystalline calcite caused the source fluid generated in itself ($\delta^{13}C$ of solution = from -1 to -3 °/$_{oo}$, PDB). This fluid fully worked in the 1-st phase of the change of limestone to dolomite (Mg-ankerite), which crystallized on the core of calcite (Fig.2).

The crystallization of Mg-ankerite - dolomite on the core of calcite from the same source of carbon, which caused the recrystallization of the limestone, is the main argument and proof, that the Mano deposit originated gradually, by chemical reaction change between fluid phase (with content of Fe, Mg) and the limestone.

The isotopic composition of oxygen from the carbonate source solution of temperature T=350°C falls in the region of metamorphic fluids (Fig.3.), that means the change of crystallization reactions between the solid and liquid phase that went off under the influence of fluid and arised in time of regional metamorphosis.

Rise of Fe-carbonate mineralization in the Mano deposit

From results of mineral, chemical and isotopic analyses were derived the progression of creation of Fe-carbonate mineralization on the Mano deposit.

In the first stage of changes (Fig.2.) Mg-ankerite (dolomite) crystallized on relics of calcite of the premetamorphic stage. In the second stage Fe-ankerite crystallized. In the third stage sideroplesite crystallized and at the end of this stage the process finished by crystallization of siderite (Fig.4).

The reaction change started in the sediment (limestone) by diffusion and evolution of crystalline calcite with Mg-ankerite and Fe-ankerite. Crystallization of Fe-carbonates ended with evolution of siderite and sideroplesite veins mainly in the upper parts of the deposit (10-horizon). The mode of crystallization of Mg-ankerite and Fe-ankerite is typical in the initial stages of crystallization, when vein form of carbonate pushes the same phase in the matrix of the metasediment (Fig.2). The dependance of form and progression crystallization of Fe-carbonates on the depth in the main body is visible in diagram Mn^{2+} : Fe^{2+} (Fig.5). The content of Mn^{2+} in the same compared minerals is highest in the deepest horizon (11/12 horizon). On the highest horizon (10/11) Fe-ankerite prevails to Mg-angerite with lower content of Mn^{2+}. Sideroplesite with the high content of Mn^{2+} occures in the 11-th horizon and siderite with low content of Mn^{2+} is only present in the 10-th horizon, whereas the transient form of sideroplesite to siderite with content of Mn^{2+} was identified between the 10-th and 1-1th horizon. The presence of Mn^{2+} in Fe-carbonates and Py2 of Nižná Slaná deposit indicates, the similarity in other deposits of Gemericum (Turecká, Rudňany - Bartalský and Radvanec 1993, Radvanec 1994) - the process of regional metamorphosis with mobilization of elements and creation of vein mineralization, as well as a great signification of regional metamorphic processes for generation of Fe,Mn carbonate ores with stratiform position (Nižná Slaná - Volovec - Holec belt).

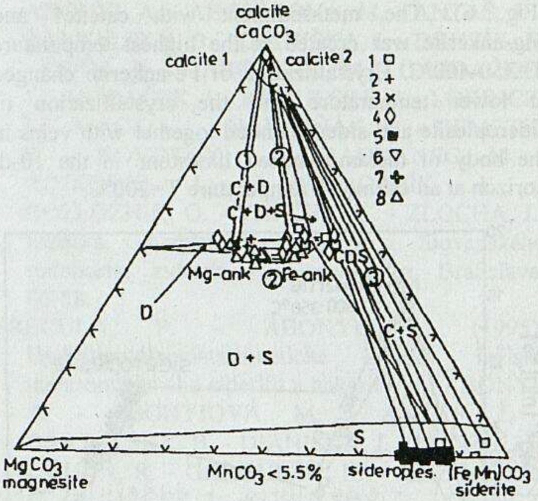


Fig.4. Phase triangular diagram of gradual crystallization of calcite1 (Cal1), Mg-ankerite (Mg-Ank) - dolomite, calcite2 (Cal2), Fe-ankerite (Fe-Ank), sideroplesite (sideroples), CDS (cal - dol - sdr) phase and the youngest siderite (sdr) on the Nižná Slaná - Mano deposit. Numbers in the triangle represents the reaction changes gradually from calcite1, over Mg-ankerite up to the siderite. Samples: 1.NŽ5A 2.NŽ6B 3.NŽ7A 4.NŽ7B 5.NŽ7D 6.NŽ8A 7.NŽ8B 8.NŽ10B. Borders of solid solution phases in triangular diagram (D - dolomite, C - calcite, S - siderite) are according to Rosenberg (1967).

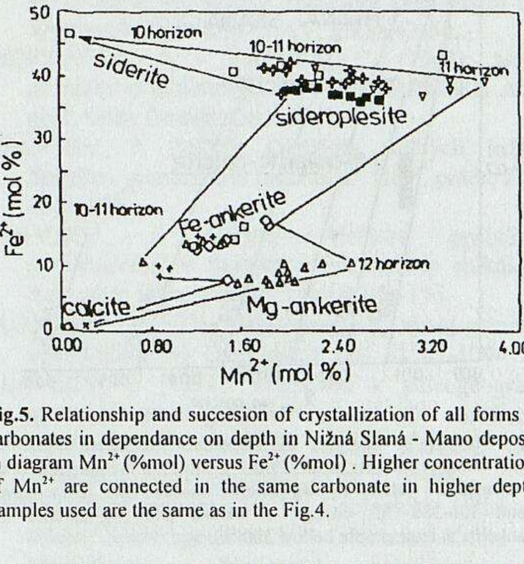


Fig.5. Relationship and succesion of crystallization of all forms of carbonates in dependance on depth in Nižná Slaná - Mano deposit, in diagram Mn^{2+} (%mol) versus Fe^{2+} (%mol) . Higher concentrations of Mn^{2+} are connected in the same carbonate in higher depth. Samples used are the same as in the Fig.4.

There is a crystallization of Fe-Mg-carbonates (from reaction change) in dependance on temperature changes at the time of the crystallization of Fe-carbonates is shown on the diagram Mg^{2+} : Fe^{2+}

(Fig. 6). The metasediment with calcite1 and Mg-ankerite was created at the highest temperature T=350-400°C. Crystallization of Fe-ankerite changed at lower temperature and the crystallization of sideroplesite and siderite ended together with veins in the body of metamorphosed limestone in the 10-th horizon at an estimeted temperature T=200°C.

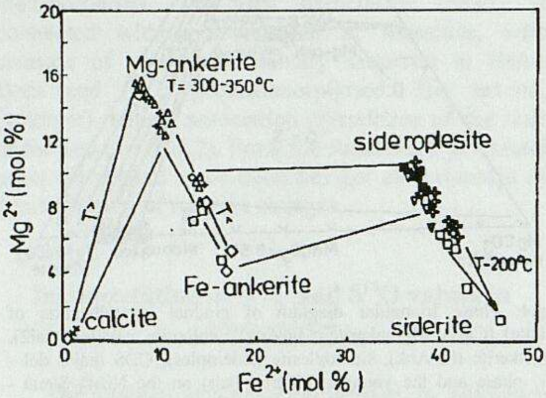


Fig.6. Relationship between the temperature of carbonate crystallization on the Nižná Slaná - Mano deposit in diagram Fe^{2+} versus Mg^{2+}. Samples are the same as in the Fig.4.

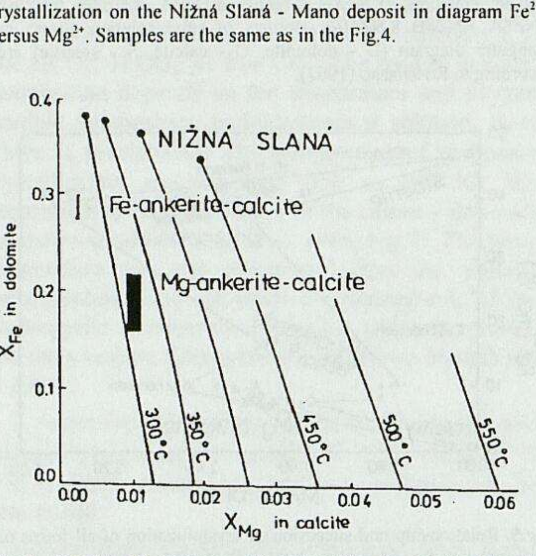


Fig.7. Results of analyses of carbonates in calcite-dolomite geothermometer (Powell et all. 1984). It shows in the diagram, that the change of calcite to Mg-ankerite reached the temperature around 300-350 °C, change of calcite and Mg-ankerite to Fe-ankerite at temperature bellow 300 °C.

In the 1-st stage of gradual change of carbonates, calcite in the limestone reacted with fluid phase from prograde metamorphosis. Stable isotope (C, O) data confirmed a metamorphic origin of source solution (fluid phase) in this reaction (Fig.3). Generation and separation of fluid phase with content of Fe, Mn, Mg, Ca together with CO_2 and H_2O was proved by Radvanec (1992) exact petrological study of old Paleozoic rocks of Gemericum. Bartalský and Radvanec (1993) found out in the Turecká region the influence of the same fluid phase to the relic of older disseminated mineralization as counted in the 1-st stage of crystallization: creation of Mg-ankerite. The crystallization of Fe-carbonates continued in the following procedures reaction changes in the interaction of fluid phase with content of Fe and solid phase until the creation of siderite.

Conclusion

The stratiform Fe-carbonates in the Mano deposit originated by crystallization by the reaction changes between the fluid phase with content of Fe, Mg, Mn, Ca, CO_2 and the solid phase (limestone, calcite - relic of the sedimentary stage). From observations in the explorated areas of the deposit, microanalyses of carbonates, sulphides and analyses of stable isotopes (C, O) in carbonates were determined two mineral associations, which crystallized in this time succesion: 1.calcite1 + pyrite1 + ?graphite 2.Mg-ankerite (dolomite) + Fe-ankerite + sideroplesite + siderite + quartz + pyrite2 + tetrahedrite + arsenopyrite + ?graphite + calcite2. The first association crystallized before the second one and it is a relic of the premetamorphic stage. It is connected with the process of the sedimentation with origin of volcanosedimentary sequences in the Holec Beds. The second association crystallized on the relics of the first one and also by pushing up of its minerals. From the structural and textural point of view the second association shows that it has the marks of crystallization of the interaction between fluid phase (with content of Fe^{2+}, Mg^{2+}, CO_2, H_2O) with solid phase (limestone).

There are two generations of pyrite. The older one Py1 is chemically zoned (it contains often As, Sb in core). It is disseminated in carbonates. The younger Py2 grow over the Py1, it is disseminated in carbonates and creates also clusters or massive ores. Py2 is only slightly zoned. The presence of Mn in Py2 indicates its synchronous crystallization with Fe-carbonates and metamorphic origin.

Carbon generated by mobilization of carbonate rocks played a dominant role for crystallization of carbonates, carbon from organic materials around limestone (Holec Beds) had a minor influence.

The carbonate source solution with values $\delta^{13}C=$ from -1 to -3 ‰ (PDB) and composition of oxygen with temperature T=350°C is $\delta^{18}O=$ from +10 to +14 ‰ (SMOW) shows the metamorphic origin of the source solution.

The crystallization of carbonates started in sediment on the relic of calcite by creation of Mg-ankerite (temperature T=350-400°C), later by Fe-ankerite. The crystallization ended with evolution of sideroplesite and siderite mainly in the upper parts of the deposit (estimated development temperature T=200°C) from one fluid solution.

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