EDUARD MARTINY, IGOR ROJKOVIČ*

TRACE ELEMENTS IN MAGNESITES OF SLOVAKIA (CENTRAL WEST CARPATHIANS)

(Fig. 1-2)

A b s t r a c t: Comparative geochemical investigation of carbonate rocks, occurring at magnesite deposits of various genetic types in the West Carpathians region, was carried out. Studied were supergene carbonates on the ultrabasic body near Hodkovce and the magnesite deposits Bankov and Ochtiná in the Carboniferous of the Gemerides. The mentioned genetic types were compared with magnesites present in Triassic and Permian evaporites. The following associations of elements are typical for the studied genetic types of magnesites, beside Mg, for the Carboniferous type — Fe, Mn, Ti, B; for the supergene type — Ni, Co, Cu, Cr; for the studied genetic types of magnesites, besides Mg, for the Carbonihave been established by means of chemical analysis, derivatographically and by atomic absorption, the microcomponents by means of spectrochemical analysis and atomic absorption.

Резюме: Авторы статьи сравнивали геохимию карбонатовых пород находящихся в месторождениях магнезитов разного генезиса в области Западных Карпат. Наблюдались гипергенные карбонаты находящиеся на ультрабазическом теле у с. Годковце и на месторождениях магнезитов Банков и Охтина в карбоне гемерид. Описанные генетические типы авторы сравнивали с магнезитами выступающими в эвапоритах триаса и перми. Для изучаемых генетических типов магнезитов кроме магнезия типичны следующие элементы: карбонский тип — Fe, Mn, Ті В, гипергенный тип — Ni, Co, Cu, Cr, эвапоридный тип — Fe, Mn, Ti, B, Ba, Sr. Макроэлементы были определены химическим анализом, методом дериватографа и атомной абсорбцией, микроэлементы спектральным анализом и методом атомной абсорбции.

I. Supergene magnesites - Hodkovce

The ultrabasic body near Hodkovce is situated in a Lower Triassic sandstone - shaly complex (D. Hovorka et al. 1975) (Fig. 1). The body is not of a uniform petrographic character. In its composition take part (D. Hovorka

- a) Serpentinized dunites to dunite serpentinites.
- b) serpentinized peridotites to peridotite serpentinites,
- c) serpentinites.
- d) pyroxenites,
- e) supergeneously altered types of ultrabasics.

The above mentioned rock types gradually pass into one another in vertical and horizontal direction

In the time from the Paleogene to the end of the Miocene a weathering crust was forming at the surface of the ultrabasic body. According to the established zones in the profile of the weathering crust, the crust was designated as a real one with an ochreous-quartzy profile (J. Zlocha 1973).

^{*} Ing. E. Martiny, CSc., RNDr. I. Rojkovič, CSc., Geological Institute of Slovak Academy of Sciences, Dúbravská cesta, 886 25 Bratislava.

In vertical direction of the weathering crust of the mentioned body the following zones were distinguished toward the underlier (D. Hovorka — I. Rojkovič 1976):

- A. Ochreous zone
- B. Zone of silicified (decomposed) ultrabasics
- C. Zone of leached ultrabasics.

Thickness of weathering crust attains the maximum of 40 metres (J. Zlo-cha 1975).

Carbonates of supergene origin in the body near Hodkovce occur in the altered ultrabasic rocks in the zone of leaching and desintegration of ultrabasics. They form veins and nests of variable thickness (millimetres to decimetres).

The essential component of vein-filling are carbonates — magnesite and dolomite. Calcite and aragonite are subordinately represented. Besides carbonates also quartzy masses and minerals of the serpentine group haven been found (D. Hovorka et al. 1975).

Magnesite and dolomite form very fine-grained to submicroscopic crystalline aggregates. They are massive, forming also colloform botryoidal structures.

Calcite and aragonite have been found rarely only. Quartz, opal and chalcedony, particularly the last two are found in close paragenesis. They form veinlets or cavity-fillings in carbonates. Serpentine minerals are present in the carbonate veinfilling as shreds and relicts of serpentinites. Minerals of the serpentine group also form independent thin veinlets, which are older than hypergene carbonates. In the veinlets lizardite and chrysotile have been established.

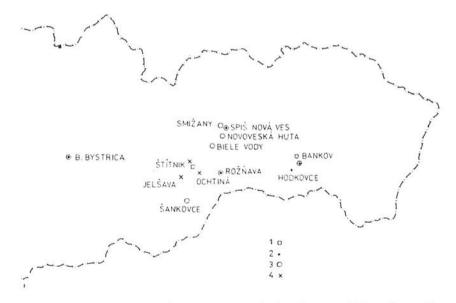


Fig. 1. Location of magnesite deposits in the Carboniferous of the Gemerides (1), supergene carbonates (2) magnesites bound to evaporites (3) and (4) Carboniferous limestones.

| | | | Τa | ble 1 | | | | |
|--------------|-----|-------------|--------|----------------------|----------|----|-----------|--------------|
| Arithmetical | and | geometrical | | element k o v c e | contents | of | carbonate | vein-filling |

| | $ \begin{array}{c} M \\ 90-100 {}^{0}/_{0} \\ n = 8 \end{array} $ | 50- | $M = 100^{0}/_{0} = 25$ | 50—100 ⁰ / ₀ n = 15 | | | |
|-------|--|-------|-------------------------|--|-------------|--|--|
| | ap | ар | gp ¹ | ap | gp | | |
| Mg | 26,82 | 23,46 | _ | 9,88 | _ | | |
| Ca | 0,39 | 1,20 | - | 15,82 | _ | | |
| Fe | 0,37 | 0,50 | 0,32 | 0,40 | 0,32 | | |
| l. r. | 2,78 | 6,73 | 4,31 | 15,60 | 11,28 | | |
| В | 1,5 | 6,2 | _ | 5,2 | - | | |
| Mn | 211 | 424 | 292 | 1204 | 1023 | | |
| Ti | 5 | 6,1 | _ | 17 | _ | | |
| Cu | 81 | 106 | 92 | 121 | 113 | | |
| Ni | 157 | 245 | 148 | 300 | 198 | | |
| Co | 23 | 22 | 21 | 23 | | | |
| Cr | 97 | 168 | 75 | 109 | 53 | | |
| Ba | 2 8 | 7,9 | | 33 | 18 | | |
| Sr | 8 | 44 | 20 | 505 | 424 | | |

M — magnesite, D — dolomite. Values of Mg, Ca, Fe, I. r. (insoluble residue) in %, other in ppm. n = number of samples, ap. — arithmetical mean, gp. — geometrical mean.

The chemical composition of the vein-filling was determined by chemical analysis, by means of derivatographic analysis and quantitative spectrochemical analysis of establishing trace elements (E. Martiny 1975). Chemical composition of the vein-filling reflects its mineral composition.

Essential components of the vein-filling are Mg, Ca and insoluble residue. In carbonate veins calcium is predominantly bound to dolomite and in several cases to calcite only. Magnesium is mainly represented in magnesite or dolomite, however, a small part is also bound to present heterogeneous admixtures of Mg-silicate rocks. The average content of CaO and MgO is in the ratio 1:3, approximately corresponding to an equal average representation of magnesite and dolomite. In vertical direction a relative increase of MgO with depth to the detriment of CaO has been found. The insoluble residue is mainly represented by opal, chalcedony, quartz and shreds of ultrabasic rocks.

Other elements are present in lower concentrations. Iron does not display correlative relations to Mg, so its essential mode of occurrence in the form of hydroxides is probable. Manganese does not show correlative relations to other elements. By means of microscopic observation Mg-minerals, to which the prevailing part of manganese is bound, were found. An about three times higher Mn content in dolomites than in magnesite (Tab. 1) is caused by concentration of Mn minerals as a consequence of weathering processes in higher lying

¹ For evaluation of analytical data beside the arithmetical means also the geometrical means were calculated (E. Martiny 1975), which are more suitable for the description of lognormal distribution of elements than the arithmetical mean as the latter is much more influenced also only by one accidentally high result because its compensation by a negative is not possible. Special paper will deal with this problem.

carbonate rocks of joint fillings, a reflection of vertical distribution of magnesite and dolomite. Titanium is found in the majority of samples in concentrations lower than its detection limit and it may be only supposed that Ti is bound to Fe oxides. Strontium displays in relation to Ca a distinct degree of correlation in dolomite as well as magnesite samples (Ca/Sr + 0,544 and/ or 0,637), resulting in its binding to Ca component of carbonate minerals. Barium is probably bound to clay minerals as testified also by the values of correlation coefficients mainly in dolomites Ba (I. r. + 0,628). Vanadium, boron are found, beside Ba and Ti, in comparison with representation of other microelements essentially in the lowermost concentrations in the traced carbonates.

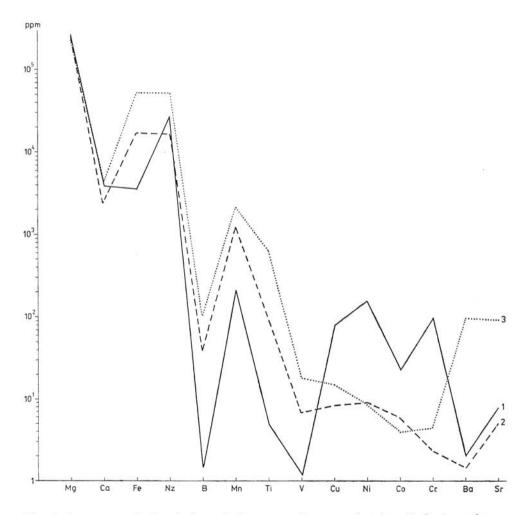


Fig. 2. Average contents of elements in magnesites occurring in ultrabasic rocks — Hodkovce (1), in the Carboniferous of the Gemerides — Bankov (2) and in evaporites (3).

From the values of correlation coefficients of B and V in relation to the insoluble residue (as well as to other elements bound to the mentioned component) their mutual linking may be supposed (l. r./B + 0,607, I. r./V + 0,585). Nickel, cobalt display increased contents (Tab. 1). The essential part of these elements is bound to serpentine minerals as also confirmed by medium to high values of Ni and Co correlation coefficients in relation to the insoluble residue (l. r./Ni + 0,679, I. r./Co + 0,511). In serpentine minerals Ni and Co display isomorphous substitution for Mg. Copper, chromium — whereas Cu is bound to chalcopyrite and Cr mostly to chromespinelides (I. Rojkovič — E. Martiny 1975), in Cr its linking with the insoluble residue is visible (I. r./Cr+0.618/Fe/Fe/Cr+0,614), V/Cr/V+0,686) and mainly Ni/Cr/Ni+0,810), as testified by its occurrence also in serpentine minerals.

For the predominantly carbonate filling of joints of ultrabasic rocks thus the following association of elements is typical: Mn, Ca, Si, Ni, Co, Cr and Cu (Fig. 2).

B. Deposits of magnesite in the Carboniferous of the Gemerides.

The investigation of magnesite deposits in the Carboniferous of the Gemerides, from the standpoint of their geological structure, deposit conditions, lithology, mineralogical and petrographical composition and mainly problems of genesis, has been considered by many authors. An essentially smaller number of works, however, are devoted to the geochemical investigation, dealt with by Z. Trdlička (1959), I. Varga (1965), A. Abonyi (1971), J. Turan — L. Vančová (1972), J. Gubač (1973), I. Rojkovič — E. Martiny (1975) a. o.

From deposits in the Carboniferous of the Gemerides were traced Bankov and Ochtiná.

The deposit Bankov is situated in the eastern part of the southern magnesite strip of the Gemeride Carboniferous. It is formed by a complex of magnesite bodies. In the underlier are found graphite schists and phyllites with layers of banked limestone, beneath which diabase tuffs and tuffites occur (J. Guľa 1959). The overlier is formed by graphite schists, gradually passing into finegrained dolomites, dolomitic limestones and limestones. The deposit proper is lying in rocks of Upper Carboniferous age and formed by three layers lying above one another (M. Ťapák 1967). The layers of magnesite contain thin beds of graphitic phyllites and sandstones.

The deposit Ochtiná occurs in the middle part of the southern magnesite strip at the western margin of the community Ochtiná.

The geological situation was studied in detail by A. Abonyi — M. Abonyi ová (1962), A. Abonyi (1971) and others. The underlier of magnesite is formed by graphite schists, which are gradually passing into carbonates with pelitic shales. The latter are passing into dolomitic shales, schistose dolomites to grey compact dolomites.

Mineralogical conditions of magnesite deposits in the Upper Carboniferous of the Gemerides were studied mainly by Z. Trdlička (1959). According to A. Abonyi (1971), from mineralogical and geochemical view magnesite deposits are very similar to one another and some differences are shown in quantitative representation of some minerals. Z. Trdlička (1959) ordered

the minerals of magnesite deposits according to the decreasing representation as follows: magnesite (three types), dolomite (5 types), talc (2 types), quartz, calcite, chlorite, pyrite, ankerite, rutile, zircon, apatite, sericite, chalcopyrite and others. Present are also goethite and haematite. Beside the mentioned carbonate minerals J. Turan — L. Vančová (1972) proved the presence of breunerite.

Calcium and magnesium, the content of which was calculated from derivatographic analyses, are due to this fact exclusively bound to carbonate minerals: magnesite, dolomite and calcite. Beside that a small part of Ca and Mg is bound also to the present heterogeneous admixtures, mainly of silicate rocks. The content of magnesite at the deposit Ochtiná is around $30\,^0/_0$ and at the deposit Bankov $68\,^0/_0$ (A. Abonyi, 1971). The insoluble residue in the investigated carbonates is mainly represented by quartz, chlorite minerals and sericite, which occur independently or in the form of rock fragments (chloritic and graphitic schists).

Iron is present as Fe⁺² as well as Fe⁺³. Fe⁺³ is essentially bound to ochres and Fe+2 to the carbonate component of magnesite and dolomite, in which it isomorphously substitutes Mg. A small part of Fe+2 is also bound to sulphides and chlorites. Manganese displays, similarly as iron, the highest average contents in magnesites at the deposit Ochtiná (Tab. 2). In relation to Fe a distinct correlation of manganese is evident (Fe/Mn + 0.778). In connection with isomorphous substitution Mn/Mg a good correlation between these elements was shown in magnesites at the locality Ochtiná (Mg/Min + 0.571), which, as mentioned, contain the highest average contents of manganese. From the mentioned correlation relations results that although manganese preferably substitutes in the lattice of Fe minerals, it may also, however, to a much lesser degree, substitute with Mg in magnesites. Beside isomorphous replacement in carbonate minerals. Mn may be also bound to minerals of the insoluble residue as also testified by the relatively high value of correlation coefficient in limestones at the locality Bankov (Mn/I. r. + 0,723). Strontium is bound to Ca-component of carbonate minerals (calcite, dolomite), as also confirmed by its higher contents in dolomite and limestone in contrast to magnesite. The high degree of correlations is shown best in the total set of carbonates (Ca/Sr + 0.835) whereas in limestones the low degree of correlation is caused by the low variability of Sr with regard to the contents of Ca. Boron displays in the sets of magnesite and dolomite samples at the locality Bankov approximately an equal average content (around 40 ppm). Magnesites and dolomites display in general an enrichment in boron in contrast to limestones. In samples with a higher content of B this is mainly bound to tourmaline. Titanium in all observed carbonates displays a mean value of the correlation coefficient in relation to the insoluble residue (I, r./Ti + 0.690) as well as to other elements bound to the insoluble residue. Titanium is present in rutile, which is accessorically represented in the insoluble residue. It can also isomorphously substitute in Fe-minerals or enter the lattice of alumosilicates. The lowest contents of Ti are found in closer sets of carbonates (monomineral). which have also the lowest contents of the insoluble residue. Low values of correlation coefficients Ti/Fe are due to the fact that the established Fe represents contents in the carbonate proportion and in HCl of soluble parts of carbonate rocks. Vanadium displays average contents in magnesite samples at both localities essentially similar (7-10 ppm). In general an increase in

 $\begin{array}{c} & \text{Table 2} \\ \text{Arithmetical and geometrical means of element contents in carbonate rocks} \\ & \text{Bankov} \end{array}$

| | 90-1 | $100^{0}/_{0} = 45$ | 50—1 | VI 100 ⁰ / ₀ = 86 | $ \begin{array}{c} D \\ 00-100 {}^{0}/_{0} \\ n = 45 \end{array} $ | D 50—100 ⁰ / ₀ n = 18 | 90—1 n = | 00 % | 50—1 n = | 00 % |
|----|-------|---------------------|-------|---|---|---|-------------|-------|-------------|------|
| | ap | gp | ap | gp | ap | ap | gp | ap | ap | gp |
| Mg | 26,89 | _ | 25,62 | _ | 12,79 | 12,97 | | 0,20 | 0.99 | - |
| Ca | 0,24 | _ | 1,05 | _ | 20,83 | 17,93 | | 32,67 | 32,93 | |
| Fe | 1,75 | 1,70 | 1,83 | 1,78 | 0,96 | 1,26 | 1,18 | 0,38 | 0,81 | 0,61 |
| Nz | 1,67 | 1,34 | 3,82 | 2,67 | 0,55 | 6,01 | 2,45 | 2,37 | 5,77 | 3,57 |
| В | 39,— | | 34,— | | 40,— | 40,— | | 2 | 5,9 | _ |
| Mn | 1243 | 1212 | 1262 | 1224 | 1027 | 1216 | 1148 | 269 | 353 | 320 |
| Ti | 93 | 76 | 214 | 107 | 75 | 409 | 312 | 357 | 747 | 520 |
| V | 6,9 | 6,3 | 10 | 7,8 | 15 | 23 | 19 | 27 | 39 | 33 |
| Cu | 8,4 | 4,9 | 7,5 | 4,5 | 24 | 17 | 13 | 4,3 | 11 | 8,9 |
| Ni | 9,3 | 7,2 | 11 | - | 3,7 | 9 | - | 5,3 | 11 | 7,1 |
| Co | 6,— | 5,— | 6,2 | 4,5 | 2,5 | 3,8 | | 1,5 | 3,6 | |
| Cr | 2,3 | _ | 5,5 | 1,3 | 2,5 | 6,7 | _ | 5,— | 7,7 | - |
| Ba | 1,4 | - | 1,8 | - | 4,3 | 23,— | 9,5 | 20 | 38 | 32 |
| Sr | 5 | _ | 26 | - | 420 | 391 | 329 | 410 | 374 | 359 |

M- magnesite, D- dolomites — limestones Values of Mg, Ca, I. r. in %, other in ppm n = number of samples, I. r. insoluble residue ap. — arithmetical mean, gp. — geometrical mean

Ochtiná

| | M 50—100 % n = 12 | | $\begin{array}{c} D \\ 90 - 100 {}^{0}/_{0} \\ n = 5 \end{array}$ | 50—1 n = | 00 % | $00-100^{0}/0$ $n=12$ | |
|----|-------------------------|------|--|-------------|------|-----------------------|------|
| | ap | gp | ap | ap | gp | ap | gp |
| Mg | 22,68 | _ | 12,52 | 19,10 | _ | 0.22 | 1 |
| Ca | 4,64 | 10-0 | 20,55 | 17,30 | _ | 38,44 | |
| Fe | 2,65 | 2,61 | 0,75 | 1,7 | 1,1 | 0,07 | 0,06 |
| JR | 3,84 | 3,39 | 3,77 | 14,04 | 7,86 | 1,25 | 0,81 |
| В | 6,1 | | 1,8 | 7,3 | | | |
| Mn | 2408 | 2355 | 1012 | 1211 | 1116 | 34 | 30 |
| Ti | 83 | _ | 54 | 310 | 230 | 71 | 42 |
| V | 7,2 | - | 14 | 23 | 14 | 13 | 12 |
| Cu | 21 | | 26 | 18 | 12 | 2,3 | |
| Ni | 2,9 | | 5,8 | 11 | 7 | 2,3 | _ |
| Co | 2,3 | _ | 2,8 | 4,3 | | 4,3 | _ |
| Cr | 1,6 | _ | 1,8 | 4,3 | | 2,4 | - |
| Ba | 17 | | 3,2 | 23 | 11 | 10 | - |
| Sr | 53 | 20 | 79 | 74 | 52 | 191 | 189 |

M — magnesites, D — dolomites, V — limestones, V* — limestones N of Ochtiná. Values of Mg, Ca, Fe.

n = number of samples

I. r. (insoluble residue) in 0/0, other in ppm

ap. - arithmetical mean, gp. - geometrical mean

V content depending on the insoluble residue may be observed. This relation is expressed-also by the values of correlation coefficient, on the basis of which a moderate to high degree of V correlation to the insoluble residua was evident (V/I. $\rm r.+0.718$). In the insoluble residue vanadium is partly bound to Feminerals, in the form of isomorphous admixture and partly may be adsorbed to organic substance and alumosilicates (chlorite and sericite). Copper, nickel, cobalt and chromium are found in carbonate rocks in low concentrations.

The maximum content of Co and Cr exceeds the value 10 ppm only in sporadical cases and thus their average values essentially vary at the detection limit. The low to medium values of correlation coefficients regarding to the insoluble residue testify to their presence in minerals included in the insoluble residue, chiefly in sulphides (pyrite, chalcopyrite). Barium displays directly proportional increasing concentrations depending on the contents of the insoluble residue. This relation is expressed also by the value of correlation coefficients in dolomites (I. r./Ba \div 0,753) and limestones (I. r. \div 0,928), corresponding to its presence in alumosilicates, mainly sericite.

Closing it may be said that for magnesites and dolomites in the Carboniferous of the Gemerides the association of these elements is typical: Mg, Ca, Fe, Mn, Ti, B, V. This association of elements is also typical of limestones in the close underlier of magnesites at the locality Bankov. The Carboniferous limestones near Ochtiná and Jeľšava do not display this association.

The views of the origin of magnesite deposits in the Gemeride Carboniferous as well as of the Mg source are different, also in spite of that many authors paid attention to this problem. In essential there are two opinions: 1) hydrothermal-metasomatic and 2) sedimentary-diagenetic. In our opinion the genesis of magnesites can be solved only after termination of the complex investigation of magnesites in full extent and beside hydrothermal processes also the processes of metamorphism and diagenesis should be more taken into consideration.

C. Magnesites bound to evaporites. localities: Biele Vody, Novoveská Huta, Smižany, Šankovce.

Evaporite deposits are relatively largely extended in the West Carpathians. In the past, however, no more attention was paid to mineralogical and geochemical problems of the mentioned evaporites. With the detailed investigation of evaporite deposits with regard to the occurrence of magnesite have recently been dealing J. Turan - L. Vančová (1974).

The first to call attention to the occurrence of magnesite at the sulphate deposit Novoveská Huta was F. Němec (1953) and at the deposit Biele Vody M. Mišík (1962). The presence of dolomite in layers of anhydrites and gypsum in borehole VŠ-1 Šankovce is mentioned by G. Andrusovová — Halahyjová — K. Borza — E. Martiny (1968). At other mentioned localities magnesite was identified by J. Turan — L. Vančová (1974).

Magnesite is present mainly in Permian-Triassic evaporite, gypsum and andhydrite deposits at the periphery of the North-Gemeride geosyncline whereas in evaporites of the South Gemerides magnesite is less abundant (J. Turan – L. Vančová 1974). According to the mentioned authors magnesites at evaporite deposits attain contents around $5-80_0$, more rarely around 100_0 in the

| | | | Та | b I | e 3 | | | | |
|--------------|-----|-------------|----------|-----|----------|----------|----|------------|------|
| Arithmetical | and | geometrical | means | of | element | contents | in | magnesites | from |
| | | evapori | tes (sep | ara | ted magn | nesites) | | | |

| | M | |
|----|--------|------|
| | n = 15 | |
| | ap | gp |
| Mg | 22,84 | |
| Ca | 0,43 | |
| Fe | 5,47 | 4,84 |
| JR | 5,45 | 4,19 |
| В | 103 | 89 |
| Mn | 2234 | 2027 |
| Ti | 630 | 441 |
| V | 18 | 17 |
| Cu | 15 | 7,5 |
| Ni | 8,5 | 7,4 |
| Co | 3,9 | _ |
| Cr | 4,5 | |
| Ba | 93 | 70 |
| Sr | 93 | 52 |

M — magnesites from evaporites, values of Mg, Ca, Fe, I. r. in ⁰/₀, other in ppm, n = number of samples, I. r. — insoluble residue
 ap. — arithmetical mean, gp — geometrical mean

sulphate, predominantly anhydrite groundmass. From other carbonate minerals the authors quote at the individual observed deposits representation of variable admixtures of dolomite and calcite, from noncarbonate minerals are present anhydrite, gypsum, quartz, pyrite, chlorites, feldspars, halite and others.

For comparison of the geochemical investigation of magnesites of the observed genetic types J. Turan and L. Vančová provided 15 samples of separated magnesites from evaporite deposits of the above mentioned localities.

Calcite displays highest representation from the traced macrocomponents in the studied rocks. Ca is particularly bound to the groundmass of sulphate deposits-anhydrite and to a lesser extent occurs in the form of gypsum, dolomite and calcite. In separated magnesites Ca is present (up to 1.5%) mainly in imperfectly separated sulphates or heterogeneous dolomite. Magnesium is in the majority of cases bound to magnesite and dolomite. Iron shows a very variable representation in separated magnesites and its average content in the investigated rocks is higher (4.8% of -Tab. 3) when compared with other studied types. Fe is bound mainly in the lattice of magnesite as also shown in the shift of reflexes (e. g. 1014 - and 0006) towards higher values in contrast to magnesite, resulting from X-ray-diffraction analysis, depending on Fe content. The high value of negative correlation coefficient confirms also the inverse proportionality of mutual quantitative relations Fe - Mg (Fe/Mg - 0.792). The observed samples are a typical example of isomorphous replacement Fe - Mg in the order MgCO3 - FeCO3. A small part of Fe may be also bound to independent Fe-minerals (e. g. pyrite). The insoluble residue is particularly represented by fragments of rocks and quartz, then by clay minerals, feldspars,

Fe-hydroxides, sulphates. The separated magnesites, in contrast to other genetic types, are characterized by a variable content of the insoluble residue $(4.2)^{\circ}$ on an average). Manganese displays a high degree of correlation in relation to Fe (Mn/Fe + 0,8435), isomorphously replacing it in the carbonate proportion as well as in own Fe-minerals. Boron, barium, vanadium, on the basis of their adsorption properties, are mostly bound to clay-minerals. Linking of B and especially V and Ba with the insoluble residue is also expressed by the values of correlation coefficients (V/I. r. + 0,736, Ba/I. r. + 0,603). Besides clay minerals B may be also bound to the established accessory tourmaline whilst a part of Ba can occur as an isomorphous admixture in Ca-sulphates or in the form of barite. The average contents of B and Ba (90, and/or 70 ppm) are essentially higher when compared with other above mentioned types of the traced magnesites. Titanium displays distinct correlative relations to the insoluble residue (I. r./Ti + 0.796) and a moderate degree of correlation to Fe(Fe/Ti + 0.316). The mentioned makes clear that the prevailing part of Ti is represented in clay minerals and only a small part is bound isomorphously to Fe. The average representation of Ti (630 ppm) in the sedimentary type of magnesites is about 6 times higher than in other genetic types. Strontium, according to data by J. Turan — L. Vančová (1974), displays a marked decrease in separated magnesites in contrast to the contents in original evaporite rocks, in which it isomorphously replaces Ca. It is bound to the heterogeneous admixture of sulphates and dolomite. The average content of Sr in magnesites is around 90 ppm and nearly twice higher than in magnesites at the locality Bankov. The following traced elements as Cu. Ni. Co and Cr are probably bound chiefly to sulphides or can be isomorphously replacing with Fe. The contents of the mentioned elements are very low, varying at the detection limit in the majority of samples.

Typical of magnesites occurring in evaporites is so the following association of elements: Mg, Ca, Fe, Mn, Ti, Sr, Ba, B and V.

Besides distribution of the mentioned elements in a part of samples, also distribution of mercury has been studied in genetic types of carbonates. According to observations of Z. Maksimović - A. Dangić (1974) Hg may be an indicator element regarding to the genesis of various types of magnesite deposits. Mercury was established by the method of atomic absorption. In samples from the deposits Bankov and Ochtiná it has been found that carbonates contain in general equal amounts of Hg (30 ppm) whilst in supergene carbonates some variability of contents was evident (30-60 ppm Hg). For determination of Hg in magnesite of evaporite type the necessary amounts of samples have not been available. The established contents of Hg have not confirmed the conclusions of Z. Maksimović - A. Dangić (1974), according to which magnesite deposits of the type Veitsch contain 27-70 ppm Hg and magnesites on ultrabasic rocks (Yugoslavia) around 30 ppm Hg. The purpose of tracing distribution of Hg in the investigated genetic types of carbonates, however, was to point to one of the further possibilities of application of geochemical investigation in solution of genetic questions. The presented results are only of informative character because of the small number of identifications.

Representation of the traced elements in carbonates at magnesite deposits of various genetic type shows that the magnesites in the Carboniferous of the

Gemerides display essentially higher contents of Ti, V, Mn and Fe when compared with supergene magnesites, characterized by increased contents of B, Cu, Ni, Co and Cr. An analogous situation may be observed also in dolomites. The limestones underlying the magnesites at the deposit Bankov also display higher contents of B, Ti, V and Ni when compared with limestones from the surroundings of the deposit area. Magnesites of evaporite type, in contrast to the above mentioned types, show a distinct increase in Fe, Mn, Ti, Sr. Ba, B and V contents.

On the basis of the obtained data, besides Mg, the following typical elements may be recognized for the individual associations of genetic magnesite types: supergene magnesites - Ni, Co, Cu, Cr, Carboniferous magnesites - Fe, Mn, Ti, B, V, magnesites in evaporites - Fe, Ti, Sr, Ba, B and V.

Translated by J. PEVNÝ.

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Review by B. CAMBEL.