First finding of high miscibility in the system CaMg(CO$_3$)$_2$-CaCo(CO$_3$)$_2$ in nature

Jordanka Mincheva-Stefanova

Abstract. In a specimen from an unknown deposit a cobaltoan dolomite is determined in rhombohedral crystals reaching up to 1 mm. They are zonal with colourless core and cobalt-bearing periphery in intense raspberry-pink colour. The periphery is fine zonal with alternating zones of higher (0.20 to 0.35 a.n.) and lower (0.03 to 0.18 a.n.) contents of Co, their width ranging from 5 to 2 µm. The total Co content increases towards the outermost crystal parts. The Ca content is always higher than 1 a.n. due to the presence of finely dispersed calcite inclusions. After correction for Ca = 1, the highest Co content is with a value of 0.46 a.n., very near to the maximum value for the dolomite part of the system CaMg(CO$_3$)$_2$-CaCo(CO$_3$)$_2$. The highest Co content reported up to now in the literature is 0.13 a.n.

The established zonality is controlled by the limited miscibility in this system because of the crystallochemical disadvantage of the phase CaCo(CO$_3$)$_2$. In this connection a statement is proposed that all natural crystals of cobaltoan dolomites are zonally developed.

The miscibility in the system CaMg(CO$_3$)$_2$-CaCo(CO$_3$)$_2$ is not connected with the structure volume expansion which indicates that it is independent on the P/T crystallization conditions. The investigated cobaltoan dolomite is formed in an oxidation zone. It is deposited on goethite.

Key words: cobaltoan dolomite, miscibility in the system CaMg(CO$_3$)$_2$-CaCo(CO$_3$)$_2$

Address: Bulgarian Academy of Sciences, Geological Institute, 1113 Sofia
Introduction

In accordance with the first data in the literature (Gibbs, 1897) for a presence of dolomite with cobalt content (CoO 5.17 wt. %) found at Pribram, Palache et al. (1957) admitted cobalt-aned variety of the mineral. That data remained the only in the literature up to 1992, when Douglass reported for cobaltoan dolomite from two deposits in Zaire—Kamoto mine and one unknown mine. Douglass (1992) has studied (in SEM conditions with EDX-system) the amount of Co in minerals labelled as cobaltoan calcite or spherocobaltite but with similar in intensity pink to pink-burgundy colour. The 13 point analyses on 8 specimens, as noted by Douglass, have revealed that all pink minerals are cobaltoan dolomites. According to the results from two to five analyses within the limits of two samples is concluded, that these minerals in their chemistry are quite heterogeneous. The contents of Co in atomic % at ΣMe = 100% (Douglass, 1992) are as follows: 5.7, 2.9, 2.7, 1.4, traces (4 times) and n.d. (4 times). The recalculation in the present paper of these quantitative data in atomic numbers at ΣMe = 20% gives (in the same order): 0.11, 0.06, 0.05 and 0.03 Co.

Douglass does not comment the genesis of the determined cobaltoan dolomites but the mentioned malachite is a fact for their formation at supergenous conditions.

Presenting different minerals from collections Copper (1992) includes a photo of specimen also from Kamoto mine, Zaire with cobaltoan dolomite with intense pink colour, deposited together with malachite over a supergeneous native copper.

Recently our attention was attracted by the intense raspberry-pink colour of one carbonate mineral, observed in a specimen unfortunately from unknown deposit. It was found that this mineral is also cobaltoan dolomite and forms only the periphery of rhombohedral crystals with core of colourless dolomite. The investigations on the chemical composition of these zonal crystals allowed to formulate some new conclusions about the crystal chemistry of the dolomite-structure type carbonates. These new conclusions are commented in the present paper.

Description of the specimen and the investigated mineral

The specimen is with dimensions 6×5×4 cm. It is a part of breccia with pieces of embedding rock and hydrothermal minerals — mainly coarse granular white calcite and coarse granular colourless dolomite. The latter mineral is locally coloured in pale pink resulting by the presence of fine zones containing CoO up to 2.49 wt. % or of small spots of infiltrated iron hydroxides (according to electron microprobe determinations).

The cement is of massive goethite (X-ray determined) which along the boundaries toward the numerous cavities is developed as colloform crust with cluster-like surface up to 2-3 mm thick. It is composed by densely packed radial acicular crystals (Pl., l) forming sphalerites. Inside the cavities on the goethite crust is deposited the investigated mineral as separate (Pl., 2) or druse-like (Pl., l) small crystals. They are covered by calcite flat-rhombohedral crystals (Pl., 4) (main form e {0112} and slightly developed m {1010}) with length along the a-axis up to 1.5 mm. The first mentioned crystals range from 200 to 700 μm or 1 mm and are bounded only by the unit rhombohedron r{1011}. Seldom on these crystals in oriented position are overgrown
microcrystals of the mineral as result of later nucleation. Their morphology and
colour are fully analogous to the basic crystals (Fig. 1). According to the electron
microprobe study the pink colour of the mineral depends on the Co content.

After breaking the crystals their zo-
nality is revealed — raspberry-pink pe-
riphery and colourless core. In SEM-
COMPO conditions is determined that the
periphery alone is fine zonal. According to
the different lightness degree and extent of
the alternating zones two “bands” are
distinguished. The inner one is charac-
terized by distinct differences in the lightness
degree of the neighbouring zones and by
bigger extent (5 to 3 μm) of the dark zones
(Pl., 4). The outer “band” is composed of
zones with most high lightness in alter-
nation with very fine zones of some lower
lightness (Pl., 4). The relation of the width
of the core and the two “bands” is approximately 1:1:1 up to 2:1:1.

The X-ray diffractometry of the most intense coloured particles of the mineral
established the entire identity of the d, A and I with those of pure dolomite (JCPDS — ICDD, 1994, 36-426).

The chemistry of the zonal dolomite - cobaltoan
dolomite crystals

The analyses are carried out in the Geological Institute of the Bulgarian Academy
of Sciences on a SEM JEOL SUPERPROBE 733 with a HNU ‘System 5000’ attachment
for energy dispersion microanalysis operating at 15 kV accelerating voltage and 1 nA
beam current. The following standards are used for Ca — CaCO₃; Mg — MgO; Co —
CoAsS; Zn — Zn₂SiO₄; Fe — Fe₂O₃; Mn — MnO₂ and Cu — CuSO₄.

The results are presented in the Tables 1 and 2. The order of the analyses is
correlated with the increase of the Co content. On the same basis is elaborated Fig. 2
too. The tendency of the real disposition of the zones according to their Co content
is schematically illustrated in Fig. 3. A photographic exactness of this illustration
could not be attained because of differences in zonal arrangements of the inner
“band” in the crystals (Pl., 1, 4) and extremely small width of many of the zones. The
latter peculiarity influences the information exactness of their chemistry.

Twenty-three quantitative electron microprobe analyses are carried out, from
which 18 are selected eliminating the doubling results. On the basis of the Co content
in atomic numbers the following nomenclature is adopted: up to 0.02 — dolomite; from
0.02 to 0.10 — Co-containing dolomite, and from 0.10 to 0.50 — cobaltoan
dolomite. The contents of the separate elements are determined as carbonate
components (in wt. %), whose values are recalculated in oxides (Table 1) and the
values of the atomic % — in atomic numbers (a.n.) for the crystallochemical formulae
(Table 2).
Fig. 2. Diagram of the variations in the contents of Co, Mg, Cu and Zn in the zonal dolomite-cobaltoan dolomite crystals, according to the electron microprobe analyses (Table 2), ordered in accordance with the increase of the Co content.

Фиг. 2. Диаграма на вариациите в съдържанието на Co, Mg, Cu и Zn в зоналните доломит-кобалтово доломитови кристали според електронно-микросондовите анализи (таблица 2), подредени съобразно повишаването на съдържанието на Co.
ПЛАТЭ

SEM photographs
1. A crust of druse-like zonal dolomite (in the core — dark gray) — cobaltan dolomite (gray to light gray) crystals, deposited on goethite spherulite (white). COMPO. Scale bar 100 µm
2. A separate rhombohedral \( (r\{1011\}) \) crystal of cobaltan dolomite. Scale bar 500 µm
3. Three rhombohedral crystals of cobaltan dolomite, including in calcite flat-rhombohedral crystal \( (c\{0112\}) \) with slightly developed \( m\{1010\} \). Scale bar 500 µm
4. Fine zonal dolomite — cobaltan dolomite crystals. COMPO. Scale bar 100 µm
   dark gray — dolomite core; gray — Co-containing dolomite zones; light to very light gray — zones of cobaltan dolomite with different Co content (direct correlation with the degree of lightness)

ТАБЛИЦА

SEM фотографии
1. Кора от друзовидни малки зонални доломит (в ядрото — тъмносиво) — кобалтово доломитови (сиво до светлосиво) кристи, отложени върху гьотитов сферолит (бяло), COMPO. Масшаб 100 µm
2. Отделен ромбоедричен \( (r\{1011\}) \) кристал от кобалтов доломит. Масшаб 500 µm
3. Три ромбоедрични кристи от кобалтов доломит, включени в калцитов плоскоромбоедричен кристал \( (c\{0112\}) \) със слабо развит \( m\{1010\} \). Масшаб 500 µm
4. Финозонални доломит — кобалтово доломитови кристи. COMPO. Масшаб 100 µm
   тъмносиво — доломитово ядро; сиво — Co-съдържащи доломитови зони; светло до много светлосиво — зони от кобалтов доломит с различно съдържание на Co (права корелация със степента на светлота)
Table 1

Chemical composition (only MO in wt. %) according to electron microprobe analyses of the zonal dolomite - cobaltoan dolomite crystals from an unknown mineral deposit. The order of the analyses is correlated with the increase of the Co content.

<table>
<thead>
<tr>
<th>Analyses No</th>
<th>CaO</th>
<th>MgO</th>
<th>CoO</th>
<th>CuO</th>
<th>ZnO</th>
<th>FeO</th>
<th>MnO</th>
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<td>18.91</td>
<td>0.53</td>
<td>1.27</td>
<td>0.08</td>
<td>0.09</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>31.12</td>
<td>20.40</td>
<td>0.61</td>
<td>0.18</td>
<td>0.22</td>
<td>n.d.</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
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<td>19.31</td>
<td>0.64</td>
<td>0.35</td>
<td>0.24</td>
<td>0.44</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>32.17</td>
<td>19.15</td>
<td>1.50</td>
<td>0.28</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
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<td>5.73</td>
<td>1.91</td>
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<tr>
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<td>34.04</td>
<td>13.00</td>
<td>6.32</td>
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<td>n.d.</td>
<td>n.d.</td>
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</tr>
<tr>
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<td>14.37</td>
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<td>n.d.</td>
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<td>11.99</td>
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<td>0.25</td>
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<td>1.94</td>
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<tr>
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<td>11.09</td>
<td>10.17</td>
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<td>0.14</td>
<td>n.d.</td>
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<td>9.32</td>
<td>12.12</td>
<td>2.44</td>
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<td>0.27</td>
<td>n.d.</td>
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<td>2.37</td>
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<td>n.d.</td>
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<td>2.39</td>
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<td>0.81</td>
</tr>
<tr>
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<td>33.34</td>
<td>7.09</td>
<td>12.86</td>
<td>2.74</td>
<td>0.62</td>
<td>n.d.</td>
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Table 2

Crystallochemical formulae calculated on the basis of 10 atoms (2 + 2(CO)J) according to the chemical analyses presented in Table 1.

<table>
<thead>
<tr>
<th>Analyses No</th>
<th>Ca</th>
<th>Mg</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>Mn</th>
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<td>0.88</td>
<td>0.01</td>
<td>0.03</td>
<td>(0.002)</td>
<td>(0.002)</td>
<td>—</td>
</tr>
<tr>
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<td>1.03</td>
<td>0.94</td>
<td>0.02</td>
<td>(0.004)</td>
<td>0.01</td>
<td>—</td>
<td>(0.003)</td>
</tr>
<tr>
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<td>1.06</td>
<td>0.89</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
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<td>—</td>
</tr>
<tr>
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<td>1.07</td>
<td>0.88</td>
<td>0.04</td>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
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<td>0.67</td>
<td>0.15</td>
<td>0.05</td>
<td>0.01</td>
<td>(0.001)</td>
<td>—</td>
</tr>
<tr>
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<td>1.16</td>
<td>0.62</td>
<td>0.16</td>
<td>0.05</td>
<td>—</td>
<td>—</td>
<td>(0.005)</td>
</tr>
<tr>
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<td>1.06</td>
<td>0.69</td>
<td>0.18</td>
<td>0.05</td>
<td>0.02</td>
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<td>(0.001)</td>
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<tr>
<td>8</td>
<td>1.06</td>
<td>0.71</td>
<td>0.19</td>
<td>0.04</td>
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<td>1.06</td>
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<td>0.01</td>
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<td>(0.001)</td>
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<tr>
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<td>0.06</td>
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<td>—</td>
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<td>0.06</td>
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<td>0.01</td>
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<td>0.06</td>
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<td>(0.005)</td>
<td>—</td>
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<td>(0.005)</td>
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<tr>
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<td>0.38</td>
<td>0.34</td>
<td>0.06</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>18</td>
<td>1.21</td>
<td>0.36</td>
<td>0.35</td>
<td>0.07</td>
<td>0.01</td>
<td>—</td>
<td>(0.001)</td>
</tr>
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</table>
The crystal core is distinguished by homogeneous dolomite composition with low contents (in a.n.) of Co — up to 0.02; Cu — mean 0.02; Zn — up to 0.01 and traces of Fe and Mn (analyses 1-3, Table 2; Fig. 2).

In the zonal periphery the distribution of the different elements is in remarkable variations.

_Cobalt:_ the inner “band” starts with sharply outlined zone of cobaltoan dolomite, 2 μm wide and with high content of Co — 0.26 a.n. (anal. 12; Fig. 3) followed by Co-containing dolomite zone, comparatively most wide (up to 5 μm) and with Co content 0.03 a.n. (Pl., 4; Fig. 3). The next alternation includes zones of cobaltoan dolomites with variable Co content — 0.20 to 0.27 a.n. (anal. 9-13; Fig. 3) and width up to 2 μm, on one side and Co-containing dolomites with Co from 0.03 to 0.07 a.n. on the other side (representative analysis 4), which change gradually in cobaltoan dolomites with lower content of Co — 0.15 a.n. (anal. 5; Fig. 3). Their width diminishes from 5 to 2 μm. The outer “band” is distinguished by zones with the highest content of Co — 0.32 to 0.35 a.n. (anal. 14-18; Fig. 3) and width up to 2-3 μm. The fine zones between them are also of cobaltoan dolomites with content of Co mainly from 0.16 to 0.19 a.n. (anal. 6-8). It is of interest that the highest Co contents are characteristic also for the later nucleated little crystals (Fig. 1). The outermost zone of their basic crystals is however with some lower Co content — up to 0.32 a.n. which indicates that the later nucleation has been developed during the final episode of the growth of the zonal crystals, but only in separate places.

_Calcium:_ its content is always higher than 1 a.n. — from 1.03 to 1.21 (Table 2; Fig. 2).

In carbonates of dolomite-structure type content of Ca > 1 in direct correlation with the content of Fe and Mn is determined in ferromanganooan dolomites and
manganoan ankerites, deposited in well developed crystals at mesothermal conditions (Mīnčeva - Stefanova et al., 1967b; Mīnčeva - Stefanova, 1970). The distribution of Ca in part of the B sites is result of three formation conditions: increased temperature of the solutions favouring isomorphous relationships; high activity of Ca$^{2+}$ in the solutions (marbles as embedding rocks); content of Fe and Mn as elements influencing expansion of the structure.

The investigated zonal crystals, however, are deposited on goethite. They were developed at supergenous conditions — normal temperatures. On the other side the numerous calcite crystals deposited immediately after the zonal crystals are an indication for the high activity of Ca$^{2+}$ in the solutions still during their crystallization. As result a synchronous crystallization of calcite micro- to submicrocrystals had begun. They were included in the growing crystals as irregularly fine dispersed inclusions. In SEM-COMPO conditions are observed many calcite microcrystals in these zonal dolomite - cobaltoan dolomite crystals (Pl., 4). The values of $d$, Å of the coloured periphery, which are identical to those of the standard pure dolomite, are additional indication for the lack of Ca$^{2+}$ in the B sites.

In spite of the conclusions for content of Ca = 1 in the zonal crystals, recalculated values for Co content are not introduced in the text.

Magnesium: its content varies from 0.94 to 0.36 a.n. and is in inverse correlation with the content of Co as main elements in B sites. The symmetry of their both curves (Fig. 2) is interrupted by the content of Ca > 1. In the composition with the lowest content of Mg (0.36 a.n.) the content of Co is the highest (0.35 a.n.), but at Ca = 1.21 (anal. 18; Fig. 2). With the reasonable correction at Ca = 1 for the both elements are derived values 0.47 and 0.46 or 0.5 and 0.5 a.n. Therefore in the studied zonal crystals the relation between the two components of the system CaMg(CO$_3$)$_2$ - CaCo(CO$_3$)$_2$ reaches 1:1 with intermediate compositions only in the dolomite part.

Copper: in between all trace elements only the copper is in steady and comparatively enhanced contents — from 0.01 to 0.07 a.n. (Table 2) with tendency from 0.05 to 0.07 a.n. in the cobaltoan dolomites with Co > 0.15 a.n. (anal. 5-18; Fig. 2).

Zinc: this element is also of crystallochemical interest even though its contents are very low — from 0.01 to 0.02 a.n. after 8 analyses and < 0.01 to n.d. after the another 10 analyses.

Iron and manganese: these two elements are identified in quantities 0.01 a.n. only in 3 to 2 analyses (Table 2) and < 0.01 to n.d. in the all rest analyses. Also they are uncharacteristic elements for the chemistry of the studied zonal crystals.

Crystallochemical correlations and conclusions

There are three crystallochemical characteristics of the studied zonal dolomite - cobaltoan dolomite crystals:
— compositions with higher content of Co than the announced in the literature (up to now maximum 0.13 and 0.11 a.n. for the cobaltoan dolomites from the Pribram deposit and from the two deposits in Zaire). The derived Co content of 0.35 a.n. after correction to Ca = 1 reaches the limit for the dolomite part of the CaMg(CO$_3$)$_2$ - CaCo(CO$_3$)$_2$, system;
— development of two staged zonality: I — dolomite core practically without Co and cobalt-bearing periphery, and II — fine zonal development of the periphery. The generalized zonality in the total distribution of Mg and Co in the crystals along a profile from their centre is as follows: Mg→Mg>Co→Co≤Mg. The results from the
analyses display uninterrupted series with intermediate solid solution compounds in the dolomite part of the system (Table 2; Fig. 4);

— presence of Cu and Zn at Cu>Zn as characteristic trace-elements. The association Co - Cu - Zn is announced for the first time for natural carbonates of a dolomite-structure type.

The three crystallochemical characteristics of the studied zonal dolomite - cobaltooan dolomite crystals are the meaning of the main result of the present investigation — the first finding of high miscibility in the CaMg(CO<sub>3</sub>)<sub>2</sub>-CaCo(CO<sub>3</sub>)<sub>2</sub> system in nature.

The compound CaCo(CO<sub>3</sub>)<sub>2</sub> does not occur as mineral nor has it been synthetized. The miscibility in that system as part of the system CaCO<sub>3</sub>-MgCO<sub>3</sub>-CaCO<sub>3</sub> has been considered until now only according to the results obtained by experimental investigations (Goldsmith, 1983). The experiments have been carried out however at 600, 650, 700 and 750°C and a confining pressure of 15 kbar. Along the direction CaMg(CO<sub>3</sub>)<sub>2</sub>-CaCo(CO<sub>3</sub>)<sub>2</sub> (the latter defined as a hypothetical end member) a very narrow field of cobaltooan dolomite extends at 600°C approximately 22% and at 750°C — 52%.

The conditions of these syntheses are discrepant with P/T condition in an oxidation zone.

The explanation of the established crystallochemical dependences in the chemistry of the studied zonal dolomite - cobaltooan dolomite crystals is possible only in comparison with the miscibility of the dolomite-structure type carbonates (R<sup>3</sup>) including the calcite-structure type carbonates (R<sup>3c</sup>) too. As it is known the degree of these miscibilities is in dependence on the difference in ionic radii of the metals — conditions controlling the volume of the structure. These dependences are clearly illustrated on the example of R<sup>3c</sup> carbonates by Reede (1983), but the diagram is demonstrative also for the possible carbonates of dolomite type as well for the degree of isomorphic relationships in their B sites. Lacking is only projection of Cu; the participation of Cd will be not included in the following consideration.

About the R<sup>3c</sup> carbonates it is of interest here the following relations connected with the calcite, but in dependence only on their formation conditions in nature:

— a miscibility in the join calcite-sphero-cobaltite is impossible, due to the distinctly large difference in the ionic radii of Ca and Co<sup>2+</sup> — 0.26 Å, which is very near to the same value for Ca and Mg — 0.28 Å. This means that cobaltooan calcites or calcian sphero-cobaltite could not be formed in nature. A revision of the minerals labelled in various collections as cobaltooan calcites could reveal that they are related to the cobaltooan dolomites as the results communicated by Douglass (1992) show or eventually to sphero-cobaltite;

— a miscibility in the system calcite-rhodochrosite is possible at favourable temperatures above 200°C (mainly in mesothermal conditions) since the significant difference in the ionic radii of Ca and Mn<sup>2+</sup> — 0.17 Å. Simultaneously this difference
is valid for the ordered carbonates \( R^3 \) too and especially for the ordered phase 
\( \text{CaMn(CO}_3)_2 \).

Concerning the carbonates of the dolomite-structure type only the dolomite is distinguished with most favourable and stable in crystallochemical aspect structure, which determines not only its wide distribution in nature but also its role as basic composition in the miscibility of this structure type carbonates.

On the diagram presented by Reed (1983) (Fig. 4) estimating the projection of Mg as a starting point two groups of \( M^2+ \) as mutual partners of Mg in B sites in the structure can be differentiated:

— the first one includes \( \text{Fe}^{2+} \) and \( \text{Mn}^{2+} \) whose ionic radii are distinctly larger than that of Mg with differences 0.06 and 0.11 Å respectively. In connection with previous investigations the author (Mînêeva-Sтеfano\( \mathit{v} \)a et al., 1967 a, b; Mînêeva-Sтеfano\( \mathit{v} \)a, 1970) of the present paper formulated a conclusions for the miscibility dependences in the system \( \text{CaMg(CO}_3)_2 \)-\( \text{CaFe(CO}_3)_2 \)-\( \text{CaMn(CO}_3)_2 \) from the \( P/T \) mineral formation conditions. The increase of the Fe content in the system \( \text{CaMg(CO}_3)_2 \)-\( \text{CaFe(CO}_3)_2 \) (up to 80 mol % \( \text{CaFe(CO}_3)_2 \)) is expressed with volume expansion of the structure of the intermediate compounds on account of which the miscibility is in direct correlation with the temperature. The miscibility in the system \( \text{CaMg(CO}_3)_2 \)-\( \text{CaMn(CO}_3)_2 \) is definitely favoured by simultaneous participation in the solid solutions compounds of the phase \( \text{CaFe(CO}_3)_2 \), the isomorphous \( \text{Fe}^{2+} \) of which caused an expansion of the structure. With the increase of the Mn content at the indispensably favoured temperatures the miscibility would tend toward disordered phases, including (\( \text{CaMn})\text{CO}_3 \) with \( \text{Ca: Mn} = 1:1 \). For growing of ordered phase with very high content of \( \text{CaMn(CO}_3)_2 \) a mutual influence of higher pressure is necessary;

— the second group of elements includes Co, Zn, Cu and Ni, the ionic radii of which are very near between themselves and to that of Mg (Fig. 4). Consequently \( V (\text{Å}^3) \) of the unit cell of their ordered phases will be with very near dimensions and the miscibility between these phases must be independent from the \( P/T \) conditions and could be achieved at lower to normal temperatures and normal pressure. Actually at low temperature hydrothermal or supergene conditions of mineral formation the solid solubility of elements in a main mineral phase is controlled by the impossibility for volume expansion of the structure. This conclusion is formulated on the example of the chemical composition of the cobaltoan smithsonite from Sedmochislenitsi deposit (Mînêeva-Sтеfano\( \mathit{v} \)a, Nêyko\( \mathit{v} \), 1991).

Although the crystallostructural and crystallogmetrical analogy the miscibility of the ordered phases of the second group elements is strongly limited due to the crystallochemical disadvantage for formation of their crystal structures. Only the phase \( \text{CaZn(CO}_3)_2 \) is found as mineral named minrecordite (Gæ\( \mathit{r} \)æ\( \mathit{v} \)æ\( \mathit{l} \)i et al., 1982), but it contains (after two analyses) always some Mg — 0.07 and 0.13 a.n. Kæ\( \mathit{l} \)æ\( \mathit{r} \) (1984) recorded for Tsumeb (up to now a single occurrence of minrecordite) too the presence of zincian dolomite with different to highest content of Zn, partly pink coloured by isomorphous Co.

The question why the another three ordered carbonates \( \text{CaCo(CO}_3)_2 \), \( \text{CaCu(CO}_3)_2 \) and \( \text{CaNi(CO}_3)_2 \) are crystallochemically “forbidden” is discussed but not explained in the literature. This problem includes also the pure ordered phase \( \text{CaFe(CO}_3)_2 \) which is not found as mineral nor has it been synthetized despite of the numerous experiments for syntheses. Reed (1983) concluded that the cation pairs in the carbonate of the dolomite-structure type may be divided into two categories (Table 3) — “stable” and “unstable”. Discussing the relationship in the system \( \text{CaMg(CO}_3)_2 \)-\( \text{CaFe(CO}_3)_2 \)-\( \text{CaMn(CO}_3)_2 \) a comparison with the difference in
Table 3
Some crystallochemical data for $M^{2+}$ in the structure of dolomite type carbonates

<table>
<thead>
<tr>
<th>Stable pairs</th>
<th>$\Delta^\text{VI} r$ (Å)</th>
<th>Values of electronegativity (EN) of the same cations according to Pauling (1932)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca - Mg</td>
<td>0.28</td>
<td>Ca 1.0</td>
</tr>
<tr>
<td>Ca - Mn</td>
<td>0.17</td>
<td>Mg 1.2</td>
</tr>
<tr>
<td>Ca - Zn</td>
<td>0.26</td>
<td>Mn 1.4</td>
</tr>
<tr>
<td></td>
<td>$\Delta^\text{VI} r$ (Å)</td>
<td>Zn 1.5</td>
</tr>
<tr>
<td>Unstable pairs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca - Fe</td>
<td>0.22</td>
<td>Fe 1.7</td>
</tr>
<tr>
<td>Ca - Co</td>
<td>0.26</td>
<td>Co 1.7</td>
</tr>
<tr>
<td>Ca - Ni</td>
<td>0.31</td>
<td>Ni 1.8</td>
</tr>
<tr>
<td>Ca - Cu</td>
<td>0.27</td>
<td>Cu 2.0</td>
</tr>
</tbody>
</table>

the electronegativity (EN) of Ca and the metal in B sites was given (Mišceva-Stefanova, Gorova, 1967), which is extended here for the pairs Ca-Co, Ca-Zn, Ca-Cu and Ca-Ni (Table 3). Very good concordance is received with the indicated differences by Reeder (1983). For the “stable” pairs of cations $\Delta$EN is with lower values in comparison with the values of $\Delta$EN for the “unstable” pairs. The $\Delta$EN of Ca and Mg is very low.

The high structure stability of the dolomite and the crystallochemical “forbiddance” for the structure of the ordered phases of the second group elements controlled the limitation of the miscibility in the corresponding binary joins in the part of the dolomite component (a little exception for the CaZn(CO$_3$)$_2$-part).

Natural compounds of dolomite with Cu and Ni content are not found unless as trace elements. With the present interpretation is confirmed the validity of the formulation only for the system CaMg(CO$_3$)$_2$-CaCo(CO$_3$)$_2$.

The deduced three crystallochemical characteristics of the studied zonal dolomite - cobaltan dolomite crystals are in connection with the presented main features of the dolomite type crystal chemistry. The established miscibility in the given system is developed only in the dolomite part and is not connected with a volume expansion of the structure. Characteristic trace elements are only Cu and Zn. The contents of Ca higher then 1 a.n. are caused by calcite microcrystals inclusions. The zonal crystals were deposited at supergene conditions.

The proper zonality, represented by a core of homogeneous almost pure dolomite composition and zonal Co-bearing periphery with expressed tendency for changing in the total content of Mg and Co, is highly informative for the crystallochemical control during the crystal growth. Together with the influence of the physico-chemical formation conditions the most important dependences of this control are as follows:

— the crystallization start with core of dolomite is result not so much of the stronger advantage for growing of the most stable structure than of the impossibility for deposition of rich in Co dolomite from solution with insufficient activity of Co$^{2+}$;

— after the enclosing of considerable part of the Mg$^{2+}$ in the growing crystals and the realized in connection with that abrupt increase of Co$^{2+}$ activity in the solution was possible the crystallization of cobaltan dolomite with comparatively high content of Co — 0.26 a.n. (Pl., 4). As it could be reasoned by the small width (1 to 3 µm) of
this zone the growth of the crystals with such Co content has been quickly interrupted. The cause for this blocking might be only the unfavourable influence of Co$^{2+}$ incorporated in the dolomite structure. On account of the crystallochemical disadvantage of the phase CaCo(CO$_3$)$_2$, these Co$^{2+}$ play a role of adsorbed impurities. The crystal growth has been restored by the oriented overgrowth of dolomite with low Co content at longer episode of crystallization (the width of this zone is 2 to 3 times bigger). The following alternation of dolomite zones with higher or respectively lower Co content (Fig. 3) is a manifestation of the control of the activity changes of Co$^{2+}$ and Mg$^{2+}$ in the solution and as well as the permanent blocking of the growth of the zones with higher Co content. In other words the further growth of the crystals was supported by the poorer in Co dolomite zones. Just after the considerable diminution of the Mg$^{2+}$ activity in the solution had possible development of the zones with the highest Co content (up to 0.5 a.n.). An indication for dropping role of the Mg$^{2+}$ in the solution is also the growth stopping of the crystals and followed individual crystallization of calcite.

On the grounds of the studied zonal dolomite - cobaltooan dolomite crystals is taken out the statement that all natural crystals of cobaltooan dolomite are in zonal development. From this position are understandable and the published by D o u g l a s s (1992) variations of the Co content for the cobaltooan dolomites from Zaire.

The presented zonality is a new important example supporting the published attitude for the significance of the chemical zoning in crystals as an indicator for the limitations on isomorphous miscibility in minerals (M i n ĝ e v a - S t e f a n o v a, 1986).

The necessity of high activity of Co$^{2+}$ in the supergeneous solution for the crystallization of cobaltooan dolomite determines the significance of this mineral as a typomorphic one for ore deposits with high content of Co.

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