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First finding of high miscibility in the system $CaMg(CO_3)_2$-$CaCo(CO_3)_2$ in nature

Jordanka Minčeva-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

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В образец от неизвестно находище е установен кобалтов доломит в ромбоедрични кристали с размери до 1 mm. Те са зонални с безцветно ядро и кобалтоносна периферия в наситено малиново-розов цвят. Периферията е финозонална в алтерниращи зони с по-високо (0,20 до 0,35 а.ч.) и по-ниско (0,03 до 0,18 а.ч.) съдържание на Со и широчина на зоните от 5 до 2 μm. Тоталното съдържание на Со се увеличава в посока към най-външните части на кристалите. Съдържанието на Са е винаги по-високо от 1 а.ч., поради наличие на финодиспергирани калцитови включения. При корекция за Са = 1 най-високото съдържание на Со е със стойност 0,46 а.ч., която е много близко до максималната за доломитовата част на системата $CaMg(CO_3)_2$ -$CaCo(CO_3)_2$. Най-високото съдържание на Со в доломити според данните в литературата до сега е 0,13 а.ч.

Представената зоналност е контролирана от ограничената смесимост в тази система, поради кристалохимичната неизгодност на фазата $CaCo(CO_3)_2$.В тази връзка е изказано становището, че всички природни кристали на кобалтовия доломит са зонално развити.

Смесимостта в системата $CaMg(CO_3)_2$-$CaCo(CO_3)_2$ не е свързана с разширение на обема на структурата, което означава, че тя е независима от *P*/*T* условията на кристализация. Изследваният кобалтов доломит е образуван в окислителна зона. Той е отложен върху гьотит.

Ключови думи: кобалтов доломит, смесимост в системата $CaMg(CO_3)_2$-$CaCo(CO_3)_2$

Адрес: Българска академия на науките, Геологически институт, 1113 София

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 cobaltoan 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 $\Sigma Me = 100\%$ (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 $\Sigma Me = 20\%$ 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 Cooper (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., *1*) forming spherulites. Inside the cavities on the goethite crust is deposited the investigated mineral as separate (Pl., *2*) or druse-like (Pl., *1*) small crystals. They are covered by calcite flat-rhombohedral crystals (Pl., *4*) (main form *e* $\{01\bar{1}2\}$ and slightly developed *m* $\{10\bar{1}0\}$) 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*$\{10\bar{1}1\}$. 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 zonality is revealed — raspberry-pink periphery 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 characterized 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 alternation 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.

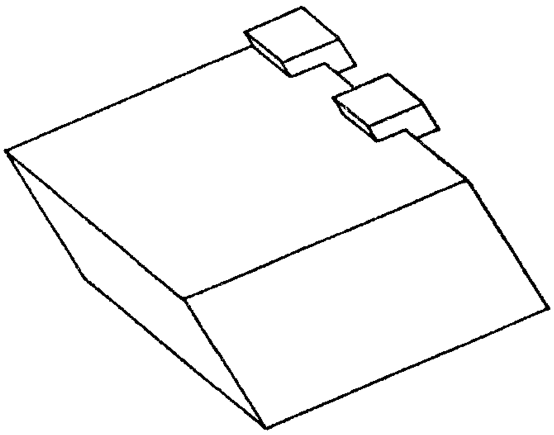


Fig. 1. Projection of a rhombohedral crystal of cobaltoan dolomite with overgrown in oriented position of two later nucleated rhombohedral microcrystals of cobaltoan dolomite too

Фиг. 1. Проекция на ромбоедричен кристал от кобалтов доломит с ориентирано нараснали две по-късно зародени ромбоедрични микрокристалчета също от кобалтов доломит

The X-ray diffractometry of the most intense coloured particles of the mineral established the entire identity of the *d*, Å 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 — $CaCO_3$; Mg — MgO; Co — CoAsS; Zn — Zn_2SiO_4; Fe — Fe_2O_3; Mn — MnO_2 and Cu — $CuSO_4$.

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).

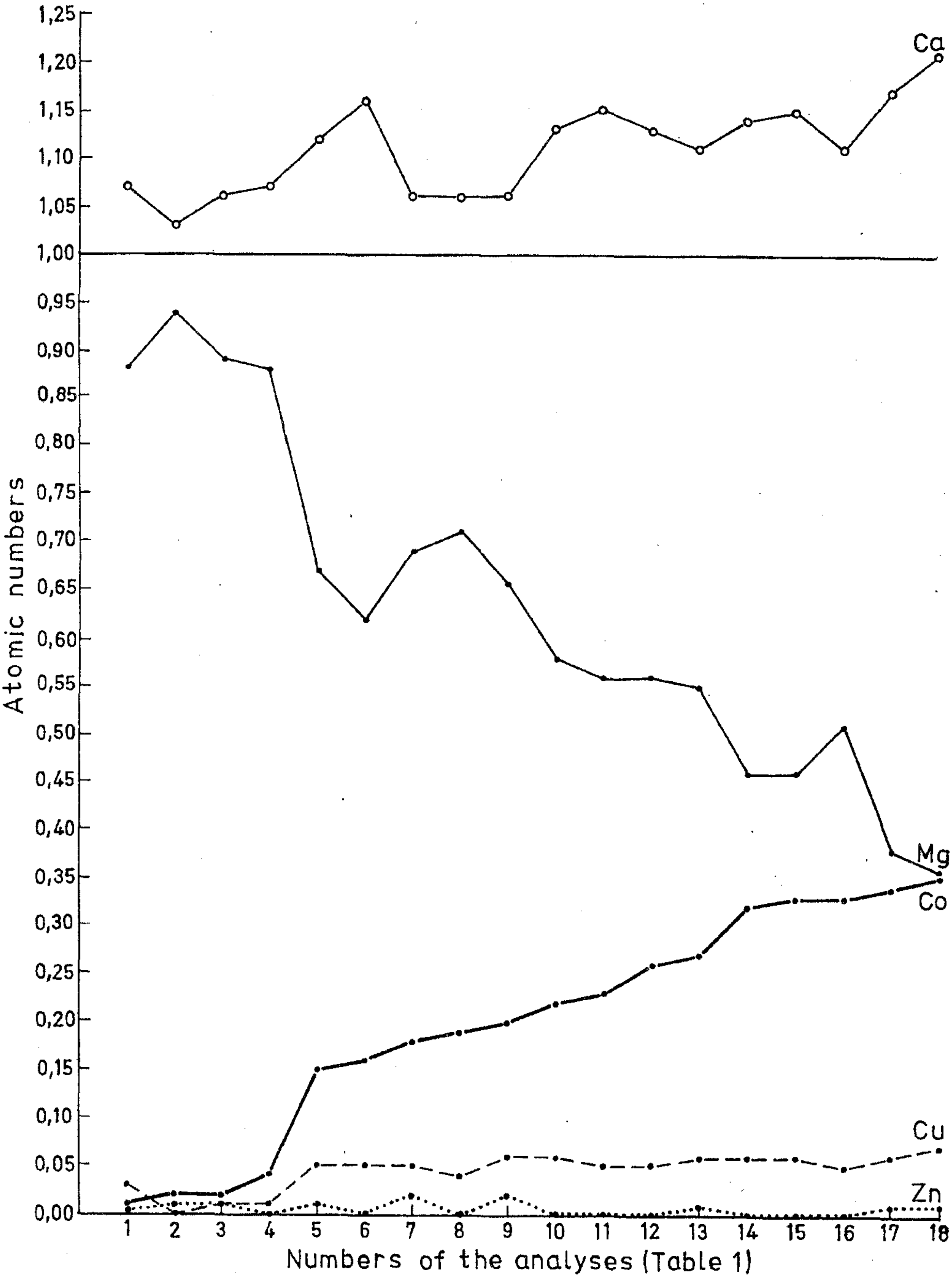
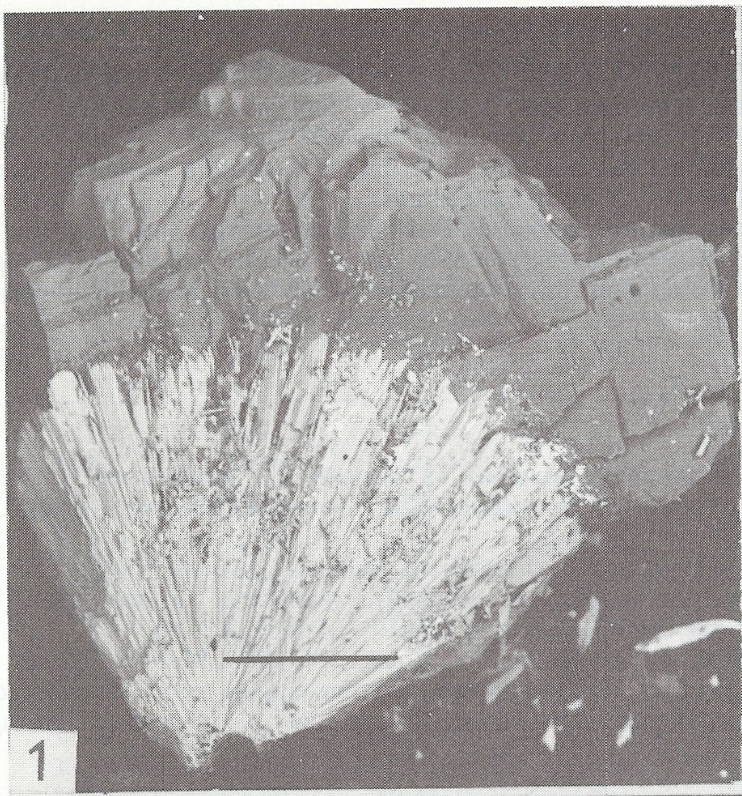
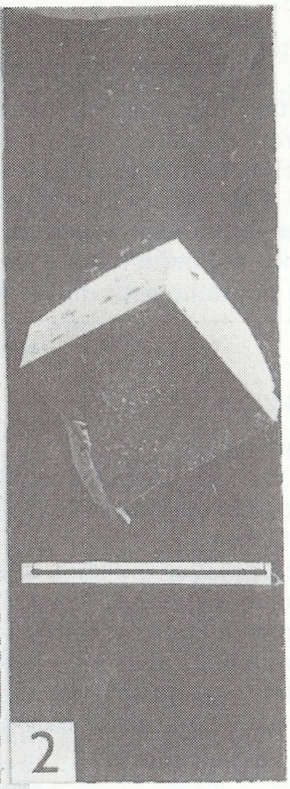


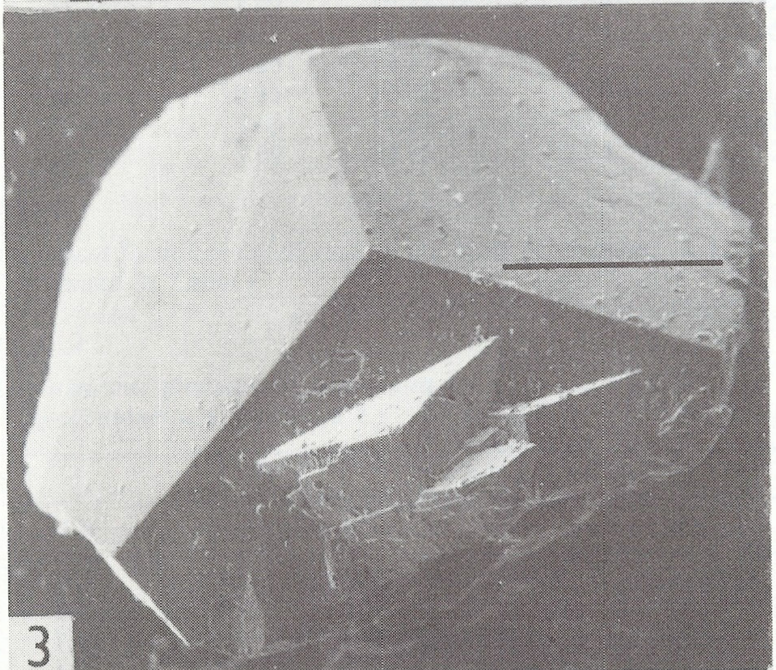
Fig. 2. Diagram of the variations in the contents of Co, Mg, Cu and Zn in the zonal dolomite - cobaltoan dolomite crystals, according to the electron microprobe analyses (Table 2), ordered in accordance with the increase of the Co content

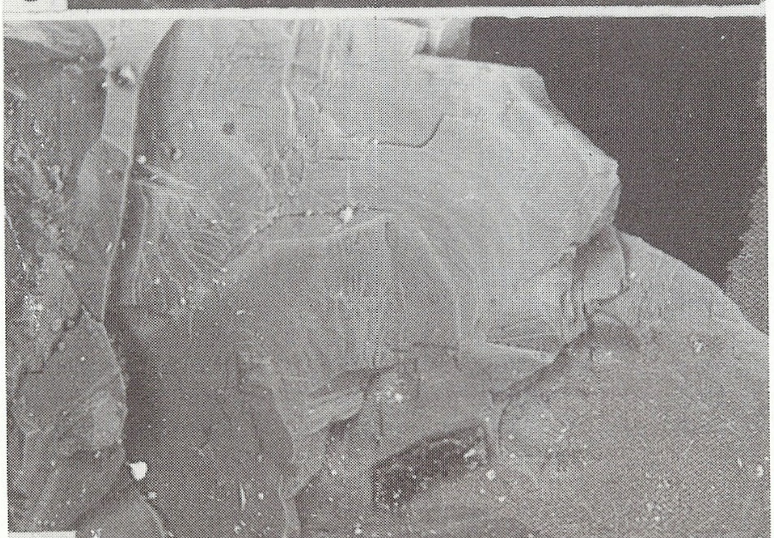
Фиг. 2. Диаграма на вариациите в съдържанието на Co, Mg, Cu и Zn в зоналните доломит-кобалтово доломитови кристали според електронно-микросондовите анализи (таблица 2), подредени съобразно повишаването на съдържанието на Co

PLATE ТАБЛИЦА









PLATE

SEM photographs

1. A crust of druse-like zonal dolomite (in the core — dark gray) — cobaltoan dolomite (gray to light gray) crystals, deposited on goethite spherulite (white). COMPO. Scale bar 100 μm

2. A separate rhombohedral (*r* $\{10\bar{1}1\}$) crystal of cobaltoan dolomite. Scale bar 500 μm

3. Three rhombohedral crystals of cobaltoan dolomite, including in calcite flat-rhombohedral crystal (*e* $\{01\bar{1}2\}$ with slightly developed *m* $\{10\bar{1}0\}$). Scale bar 500 μm

4. Fine zonal dolomite — cobaltoan dolomite crystals. COMPO. Scale bar 100 μm

dark gray — dolomite core; gray — Co-containing dolomite zones; light to very light gray — zones of cobaltoan dolomite with different Co content (direct correlation with the degree of lightness)

ТАБЛИЦА

СЕМ фотографии

1. Кора от друзовидни малки зонални доломит (в ядрото — тъмносиво) — кобалтово доломитови (сиво до светлосиво) кристали, отложени върху гьотитов сферолит (бяло), COMPO. Мащаб 100 μm

2. Отделен ромбоедричен (*r* $\{10\bar{1}1\}$) кристал от кобалтов доломит. Мащаб 500 μm

*3.*Три ромбоедрични кристали от кобалтов доломит, включени в калцитов плоско-ромбоедричен кристал (*e*$\{01\bar{1}2\}$ със слабо развита *m* $\{10\bar{1}0\}$). Мащаб 500 μm

4. Финозонални доломит — кобалтово доломитови кристали. COMPO. Мащаб 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 светлост)

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

Таблица 1

Химичен състав (само MO в тегл. %) според електронно-микросондови анализи на зоналните доломит - кобалтово доломитови кристали от неизвестно находище. Редът на анализите е съобразен с повишаването на съдържанието на Co

Analyses No	CaO	MgO	CoO	CuO	ZnO	FeO	MnO
1	32.13	18.91	0.53	1.27	0.08	0.09	n.d.
2	31.12	20.40	0.61	0.18	0.22	n.d.	0.11
3	31.91	19.31	0.64	0.35	0.24	0.44	n.d.
4	32.17	19.15	1.50	0.28	n.d.	n.d.	n.d.
5	32.38	13.93	5.73	1.91	0.61	0.02	n.d.
6	34.04	13.00	6.32	2.08	n.d.	n.d.	0.19
7	30.67	14.37	6.96	2.12	0.72	n.d.	0.05
8	30.55	14.71	7.31	1.82	0.16	0.02	n.d.
9	30.31	13.57	7.64	2.45	0.04	n.d.	n.d.
10	32.37	11.99	8.22	2.23	n.d.	0.14	0.25
11	32.89	11.47	8.95	1.94	n.d.	0.04	n.d.
12	32.12	11.47	9.85	1.85	n.d.	n.d.	0.10
13	31.38	11.09	10.17	2.50	0.52	0.14	n.d.
14	31.91	9.32	12.12	2.44	0.05	0.27	n.d.
15	32.01	9.26	12.27	2.37	n.d.	0.21	n.d.
16	31.15	10.35	12.33	1.83	n.d.	n.d.	0.22
17	32.48	7.63	12.57	2.39	0.41	0.27	0.81
18	33.34	7.09	12.86	2.74	0.62	n.d	0.02

Table 2

Crystallochemical formulae calculated on the basis of 10 atoms ($2 + 2[CO_3]$) according to the chemical analyses presented in Table 1

Таблица 2

Кристалохимични формули, изчислени на база 10 атома ($2 + 2[CO_3]$) според химичните анализи, представени в таблица 1

Analyses	Atomic numbers						
No	Ca	Mg	Co	Cu	Zn	Fe	Mn
1	1.07	0.88	0.01	0.03	(0.002)	(0.002)	—
2	1.03	0.94	0.02	(0.004)	0.01	—	(0.003)
3	1.06	0.89	0.02	0.01	0.01	0.01	—
4	1.07	0.88	0.04	0.01	—	—	—
5	1.12	0.67	0.15	0.05	0.01	(0.001)	—
6	1.16	0.62	0.16	0.05	—	—	(0.005)
7	1.06	0.69	0.18	0.05	0.02	—	(0.001)
8	1.06	0.71	0.19	0.04	(0.004)	(0.001)	—
9	1.06	0.66	0.20	0.06	0.02	—	—
10	1.13	0.58	0.22	0.06	—	(0.004)	0.01
11	1.15	0.56	0.23	0.05	—	(0.001)	—
12	1.13	0.56	0.26	0.05	—	—	(0.003)
13	1.11	0.55	0.27	0.06	0.01	(0.004)	—
14	1.14	0.46	0.32	0.06	(0.001)	0.01	—
15	1.15	0.46	0.33	0.06	—	(0.005)	—
16	1.11	0.51	0.33	0.05	—	—	(0.005)
17	1.17	0.38	0.34	0.06	0.01	0.01	0.02
18	1.21	0.36	0.35	0.07	0.01	—	(0.001)

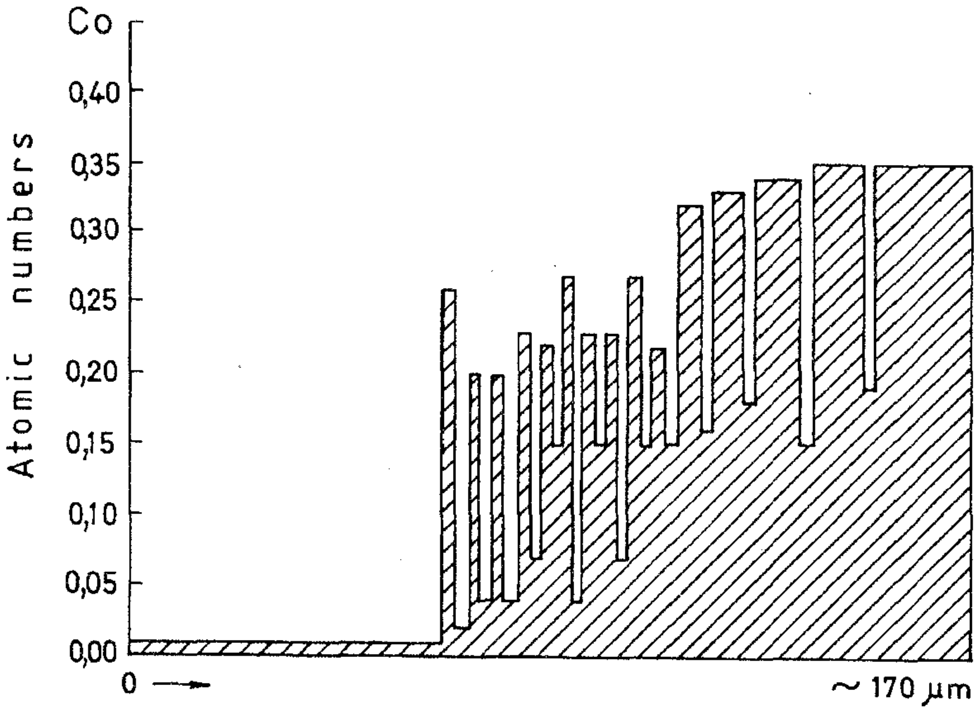


Fig. 3. Schematic illustration of the tendency in the real distribution of the zones according to their Co content in the zonal dolomite - cobaltoan dolomite crystals

Фиг. 3. Схематично представяне на тенденцията в реалното разпределение на зоните според тяхното съдържание на Co в зоналните доломит - кобалтово доломитови кристали

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, comparativelly 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 ferromanganoan dolomites and manganoan ankerites, deposited in well developed crystals at mesothermal conditions (Minčeva-Stefanova et al., 1967b; Minčeva-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 crystallyzation. As result a synchronous crystallyzation 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: $Mg \rightarrow Mg > Co \rightarrow Co \leq Mg$. 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 - cobaltoan dolomite crystals are the meaning of the main result of the present investigation — the first finding of high miscibility in the $CaMg(CO_3)_2$-$CaCo(CO_3)_2$ system in nature.

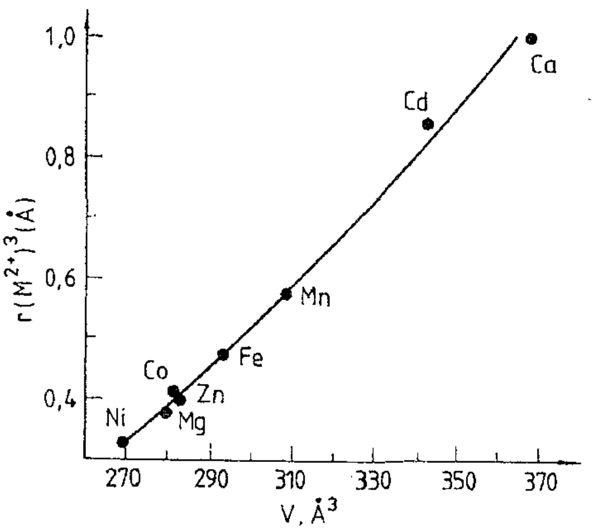


Fig. 4. Comparison of the $[M^{2+}]^3$ ionic radius with the unit cell volume for calcite-structure carbonate (MCO_3) according to Reeder (1983)

Фиг. 4. Сравнение на $[M^{2+}]^3$ -йонни радиуси с обема на елементарната клетка на съответните карбонати (MCO_3) с калцитов тип структура, според Reeder (1983)

The compound $CaCo(CO_3)_2$ does not occur as mineral nor has it been synthetized. The miscibility in that system as part of the system $CaCO_3$-$MgCO_3$-$CaCO_3$ 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 $CaMg(CO_3)_2$-$CaCo(CO_3)_2$ (the latter defined as a hypothetical end member) a very narrow field of cobaltoan 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 - cobaltoan dolomite crystals is possible only in comparison with the miscibility of the dolomite-structure type carbonates ($R\bar{3}$) including the calcite-structure type carbonates ($R\bar{3}c$) 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 $R\bar{3}c$ carbonates by Reeder (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 $R\bar{3}c$ 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-spherocobaltite is impossible, due to the distinctly large difference in the ionic radii of Ca and Co^{2+} — 0.26 Å, which is very near to the same value for Ca and Mg — 0.28 Å. This means that cobaltoan calcites or calcian spherocobaltite could not be formed in nature. A revision of the minerals labelled in various collections as cobaltoan calcites could reveal that they are related to the cobaltoan dolomites as the results communicated by Douglass (1992) show or eventually to spherocobaltite;

— 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^{2+} — 0.17 Å. Simultaneously this difference is valid for the ordered carbonates $R\bar{3}$ too and especially for the ordered phase $CaMn(CO_3)_2$.

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 Reeder (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 Fe^{2+} and 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 (Minčeva-Stefanova et al., 1967 a, b; Minčeva-Stefanova, 1970) of the present paper formulated a conclusions for the miscibility dependences in the system $CaMg(CO_3)_2$-$CaFe(Co_3)_2$-$CaMn(CO_3)_2$ from the P/T mineral formation conditions. The increase of the Fe content in the system $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ (up to 80 mol % $CaFe(CO_3)_2$) 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 $CaMg(CO_3)_2$-$CaMn(CO_3)_2$ is definitely favoured by simultaneous participitation in the solid solutions compounds of the phase $CaFe(CO_3)_2$, the isomorphous 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 $(Ca,Mn)CO_3$ with Ca:Mn = 1:1. For growing of ordered phase with very high content of $CaMn(CO_3)_2$ 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 ($Å^3$) 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 supergeneous 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 (Minčeva-Stefanova, Neykov, 1991).

Although the crystallostructural and crystallometrical 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 $CaZn(CO_3)_2$ is found as mineral named minrecordite (Garavelli et al., 1982), but it contains (after two analyses) always some Mg — 0.07 and 0.13 a.n. Keller (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 $CaCo(CO_3)_2$, $CaCu(CO_3)_2$ and $CaNi(CO_3)_2$ are crystallochemically "forbidden" is discussed but not explained in the literature. This problem includes also the pure ordered phase $CaFe(CO_3)_2$ which is not found as mineral nor has it been synthetized despite of the numerous experiments for syntheses. Reeder (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 $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-$CaMn(CO_3)_2$ a comparison with the difference in

Table 3

Some crystallochemical data for M^{2+} in the structure of dolomite type carbonates

Таблица 3

Отделни кристалохимични данни за M^{2+} в структурата на доломитовия тип карбонати

Ionic radius differences of the M^{2+} pairs (in A and B positions) according to Reeder (1983)		Values of electronegativity (EN) of the same cations according to Pauling (1932)	
Stable pairs	$\Delta^{VI} r$ (Å)		
		Ca	1.0
Ca - Mg	0.28	Mg	1.2
Ca - Mn	0.17	Mn	1.4
Ca - Zn	0.26	Zn	1.5
Unstable pairs	$\Delta^{VI} r$ (Å)		
Ca - Fe	0.22	Fe	1.7
Ca - Co	0.26	Co	1.7
Ca - Ni	0.31	Ni	1.8
Ca - Cu	0.27	Cu	2.0

the electronegativity (EN) of Ca and the metal in B sites was given (Minčeva-Stefanova, Gorova, 1967), which is extended here for the pairs Ca-Co, Ca-Zn, Ca-Cu and Ca-Ni (Table 3). Very good considerence is received with the indicated differences by Reeder (1983). For the "stable" pairs of cations ΔEN is with lower values in comparison with the values of ΔEN for the "unstable" pairs. The ΔEN 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 - cobaltoan 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 cobaltoan 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 - cobaltoan dolomite crystals is taken out the statement that all natural crystals of cobaltoan dolomite are in zonal development. From this position are understandable and the published by Douglass (1992) variations of the Co content for the cobaltoan 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 (Minčeva - Stefanova, 1986).

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

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