

SYNTHESIS AND X-RAY POWDER DIFFRACTION DATA FOR Mg-, Al- AND Ni- END-MEMBERS OF THE COPIAPITE GROUP

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ABSTRACT

This article describes the synthesis and X-ray powder diffraction data for magnesium, aluminum and nickel end-members of copiapite group.

X-ray powder diffraction patterns for the synthetic equivalents of magnesium copiapite, aluminum copiapite and the Ni-analogue were obtained and unit-cell parameters calculated.

Keywords: Copiapite group, Magnesium, Aluminum, Nickel, X-ray.

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INTRODUCTION

The general chemical formula of the copiapite-group minerals is $(A^{(II)}_{1-3x}A^{(III)}_{2x}Fe^{(III)})Fe^{(III)}_4(SO_4)_6(OH)_2 \cdot 20H_2O$, where the A sites are completely filled by divalent cations (Ca, Cu, Fe, Mg, Zn) for $x = 0$, or two-thirds filled by trivalent cations (Al, Fe) for $x = 1/3$. Up to now the only phase synthesized in laboratory is the equivalent of ferricopiapite. The natural minerals, on the other hand, represent intermediate members of solid solutions. Synthesis of end-members would be important, as stated by Kubisz [1], to establish the variation of the properties of

copiapite-group minerals, like unit-cell parameters and optical constants.

EXPERIMENTAL METHODS

Synthesis were carried out by the method developed by Scharizer [2], who obtained ferricopiapite from the treatment of synthetic rhomboclase, as show in Table 1.

Mixtures of *p.a.* salts were soaked in water and maintained in rest at room conditions. Total dissolution took place in a few hours except in the case of sample 1, in which not all the calcium sulfate was dissolved.

TABLE 1

Synthesis of copiapite group minerals: Initial products and final compounds

INITIAL PRODUCTS			FINAL PRODUCTS (expected and obtained)	
Sample number	Chemical formula	Mineralogical equivalence	Chemical formula	Mineralogical equivalence
1	CaSO ₄ ·2H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	gypsum kornelite	CaFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	calcicocopiapite(*)
2	CuSO ₄ ·5H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	chalcantite kornelite	CuFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	cuprocopiapite(*)
3	FeSO ₄ ·7H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	melanterite kornelite	FeFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	copiapite(*)
4	MgSO ₄ ·2H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	epsomite kornelite	MgFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	magnesiocopiapite
5	ZnSO ₄ ·7H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	goslarite kornelite	ZnFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	zincocopiapite
6	Al ₂ (SO ₄) ₃ ·17H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	alunogen kornelite	Al ₂₃ Fe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	aluminocopiapite
7	Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	kornelite	Fe ₂₃ Fe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	ferricocopiapite
8	NiSO ₄ ·6H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	retgersite kornelite	NiFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	the Ni-end-member(**)
9	MnSO ₄ ·H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	szmikite kornelite	MnFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	the Mn-end-member(**)
10	CoSO ₄ ·7H ₂ O Fe ₂ (SO ₄) ₃ ·7-8H ₂ O	bieberite kornelite	CoFe ₄ (OH) ₂ (SO ₄) ₆ ·20H ₂ O	the Co-end-member(**)

(*) obtained intermediate copiapite-group compounds having chemical composition similar to the expected ones.

(**) not yet recorded in natural occurrences.

RESULTS

The first precipitates appeared after 15 days and the last ones after 30 days. The crystallization of each sample took approximately 3 days. Sample number 8, corresponding to the Ni-end-member, displayed a light green color, while sample number 10, equivalent to the Co-end-member, exhibited yellowish rose color. The other samples presented yellow hues. The developed habit was, in most cases, botryoidal, otherwise it was massif.

All precipitated compounds belong to the copiapite group as determined by X-ray powder diffraction. Nevertheless, mixtures of synthetic analogues of gypsum, chalcantite and kornelite were detected in samples number 1, 2 and 3, respectively. Blue chalcantite crystals were macroscopically visible in sample 2. It was possible to verify, with chemical analyses, that the initial ratios of iron (II) and (III) were not modified in samples number 3 (copiapite) and 7 (ferricopiapite).

All samples were sensible to atmospheric humidity, and partially deliquesced a few days after the end of crystallization. Brownish rose aggregates of r merite were formed in sample 3 (copiapite) several days after the precipitation. The stability of the samples was also tested at temperature of approximately 60°C. The partially deliquesced materials were submitted to this temperature and recuperated in a few hours. Very intense color variations were not then observed, as for example, the orange color developed in sample 9 (the Mn-end-member). A longer treatment, of several days, at 60°C altered sample 3 to a mixture of rhomboclase and $(\text{H}_3\text{O})\text{Fe}(\text{SO}_4)_2$.

X-ray powder diffraction

X-ray powder diffraction patterns for the synthetic equivalents of magnesiocopiapite and aluminocopiapite and the Ni-analogue (not known from natural occurrences) were obtained for the first time (Tables 2, 3 and 4). These data were obtained in a Veb Carl Zeiss Jena diffractometer, mod. URD6, using graphite monochromatized $\text{Cu K}\alpha$ radiation from 3 to 120° (2 θ) with a step of 0,02° (2 θ) and a detector time counter of 5s.

TABLE 2

X-ray powder diffraction for synthetic magnesiocopiapite

h	k	l	$d_{\text{obs.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I_{\text{obs.}}(\%)$	$I_{\text{calc.}}$
0	1	0	18.402	18.524	59	281
0	2	0	9.246	9.262	100	21
0	1	-1	6.823	6.852	<1	81
0	3	0	6.178	6.175	63	11
0	2	1	5.525	5.536	<1	32
0	4	0	4.632	4.631	<1	11
0	3	1	4.558	4.561	1	40
1	3	0	4.318	4.326	1	28
1	1	1	4.318	4.310	<1	11
1	-4	0	4.203	4.205	5	73
1	3	-1	4.026	4.031	1	87
1	2	1	3.884	3.895	<1	22
0	4	1	3.795	3.798	2	14
1	-4	-1	3.759	3.761	<1	22
0	5	0	3.703	3.705	1	1
2	-2	0	3.526	3.514	<1	113

TABLE 2

X-ray powder diffraction for synthetic magnesiocopiapite. Cont...

h	k	l	d _{obs.} (Å)	d _{calc.} (Å)	I _{obs.} (%)	I _{calc.}
1	3	1	3.458	3.454	2	22
1	4	-1	3.458	3.460	2	11
1	-5	-1	3.242	3.239	1	39
0	5	1	3.223	3.220	3	58
0	6	0	3.089	3.087	3	3
1	5	0	3.088	3.086	3	2
1	-6	0	3.016	3.016	2	8
1	4	-2	2.780	2.781	1	8
0	6	1	2.780	2.781	1	7
1	-6	1	2.746	2.747	<1	9
1	-7	0	2.624	2.623	4	2
1	-7	-1	2.483	2.484	4	17
1	0	-3	2.447	2.444	<1	12
0	8	0	2.315	2.316	1	8
1	-8	-1	2.213	2.213	2	5
0	7	-2	2.194	2.194	<1	3
2	-8	0	2.101	2.102	<1	4
3	3	0	2.101	2.101	<1	4
1	8	0	2.101	2.103	<1	4
0	9	0	2.059	2.058	7	7
3	3	-2	2.011	2.012	<1	8
1	9	0	1.897	1.896	<1	3
1	9	-1	1.887	1.886	1	4
0	10	0	1.852	1.852	<1	4
0	10	-1	1.821	1.820	2	3
3	-8	-1	1.808	1.808	1	3
0	9	2	1.744	1.745	1	9

TABLE 3

X-ray powder diffraction for synthetic aluminocopiapite

h	k	l	d _{obs.} (Å)	d _{calc.} (Å)	I _{obs.} (%)	I _{calc.}
0	1	0	18.600	18.509	34	467
0	2	0	9.135	9.254	100	291
1	-2	0	6.048	6.096	55	40
0	3	1	4.524	4.532	8	54
1	-4	0	4.166	4.189	4	57
0	1	-2	3.543	3.546	<1	75
2	-2	0	3.479	3.481	1	94
1	4	-1	3.451	3.451	2	30
2	2	0	3.137	3.127	6	14
1	-5	1	3.090	3.094	11	20
0	6	0	3.090	3.084	11	6
1	-6	0	3.002	3.009	3	12
2	-4	-1	2.961	2.967	4	21
1	-6	1	2.743	2.741	1	13
2	-4	1	2.667	2.664	2	14
2	4	-1	2.616	2.620	<1	15
2	4	0	2.605	2.606	1	1
2	3	-2	2.501	2.501	<1	33
3	-2	-1	2.398	2.398	4	1
1	-1	-3	2.398	2.398	4	3
2	-1	2	2.291	2.293	3	5
3	-4	0	2.248	2.244	5	2
1	-7	-2	2.135	2.132	3	5
3	3	0	2.081	2.084	2	3
3	2	-2	2.081	2.082	2	3
2	3	2	2.038	2.038	>1	6
3	-6	-1	2.038	2.036	<1	11
3	3	-2	1.997	1.997	3	6
3	5	0	1.852	1.851	1	3
0	10	0	1.852	1.851	1	3
1	-6	3	1.839	1.837	3	1
3	-8	-1	1.796	1.796	1	4
2	-9	-2	1.733	1.733	2	13
0	7	3	1.717	1.717	<1	3
3	-5	2	1.717	1.718	<1	1
2	2	-4	1.717	1.717	<1	1

TABLE 4

X-ray powder diffraction for synthetic Ni-end-member

h	k	l	d _{obs.} (Å)	d _{calc.} (Å)	I _{obs.} (%)	I _{calc.}
0	1	0	18.776	18.513	48	280
0	2	0	9.236	9.256	100	215
0	3	0	6.124	6.171	87	113
1	-2	0	6.124	6.143	87	62
0	3	1	4.580	4.564	4	40
1	0	1	4.580	4.584	4	26
1	-3	1	3.990	3.966	1	11
1	2	1	3.872	3.890	<1	22
1	-4	-1	3.761	3.766	<1	22
0	0	2	3.619	3.618	<1	28
1	-2	-2	3.343	3.347	1	22
2	-3	0	3.319	3.322	1	8
0	2	2	3.315	3.304	1	10
1	-3	-2	3.116	3.114	<1	9
1	5	0	3.082	3.078	2	3
1	3	-2	3.044	3.047	<1	9
2	0	-2	2.872	2.867	1	1
2	3	0	2.872	2.874	1	12
1	-6	1	2.752	2.752	<1	9
2	3	-2	2.521	2.517	1	28
3	-3	0	2.340	2.341	<1	6
1	3	-3	2.279	2.283	1	1
0	6	2	2.279	2.282	1	6
2	1	2	2.238	2.236	1	1
2	0	-3	2.238	2.236	1	2
2	5	-2	2.174	2.176	<1	3
0	4	3	2.086	2.089	<1	7
1	6	2	2.025	2.023	3	1
1	-4	3	2.025	2.027	3	1
0	10	-1	1.821	1.820	1	3
4	-1	0	1.792	1.792	1	1

Unit-cell parameters calculated using the programs LCLSQ, version 8.4 [3] and DBWS, version 9006PC [4] are listed in Table 5. The data are in good agreement with those of the natural magnesiocopiapite and aluminocopiapite [5], while the data of the Ni-analogue are similar to those of the

copiapite-group compounds. XRD studies on Zn-, Fe³⁺-, Mn- and Co- end-members, synthesized by us, are in progress. More precise X-ray data are also been collected in order to refine the crystal structure of the end-member synthetic compounds of the copiapite group.

TABLE 5

Cell parameters for synthetic copiapite-group end-members.

	Mg	Al	Ni
<i>a</i> (Å)	7.371(3)	7.298(4)	7.359(8)
<i>b</i> (Å)	18.778(3)	18.76(1)	18.78(2)
<i>c</i> (Å)	7.389(4)	7.320(5)	7.420(8)
α (°)	91.31(3)	91.57(5)	91.35(8)
β (°)	102.29(6)	102.24(5)	102.33(8)
γ (°)	98.85(3)	98.72(4)	99.06(9)

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