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Hydrated sulfates from Sydney Coalfield, Cape Breton Island, Nova Scotia, Canada: the copiapite group

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Abstract

Selected samples of copiapite from locations in the Sydney Coalfield are classified according to atomic proportions in the X position of the structural formula of copiapite. In particular, the metal content in the position is calculated by purely algebraic means, *i.e.*, by solutions of linear simultaneous equations. Proportions in the X and R positions of the structural formula are assumed 1:4 on the basis of substitution which at the same time serves as a check on obtained solutions. Identified species of the copiapite group include aluminocopiapite, copiapite, magnesiocopiapite, and even ferroan magnesiocopiapite. It appears that different parts in the coalfield represent different environments as judged by the chemical composition of the sampled copiapites.

Introduction

Over the last four years many hydrated sulfate specimens have been collected from the Sydney Coalfield, leading to several studies by Zodrow and McCandlish (1978a, b; 1979). Among these sulfates are certain minerals of the copiapite group, with aluminocopiapite being predominant. Minerals of this group have a wide geographical distribution in the coalfield; Figure 1 shows the locations of samples.

The copiapite group consists of hydrated sulfates with the general formula $XR_4(SO_4)_6(OH)_2 \cdot nH_2O$, where X is one oxygen equivalent (with a total charge of 2+). The X position contains one or more of Cu (cuprocopiapite), Fe (copiapite), Mn, Zn, Na, K, Co, Ca, Mg (magnesiocopiapite), Al, and others; R is mainly Fe^{3+} and some Al. The upper limit of n is 20 for fully hydrated minerals (Fanfani *et al.*, 1973); Berry (1947) proposed 21 on the basis of statistical averages. The substitutional possibilities are large and diversified in the X position; they are fully explainable by the weak bonding of the coordination polyhedra to the structural chain motif (Fanfani *et al.*, 1973). In aluminocopiapite (Berry, 1947, p. 25, 29), Al is the dominant metal in the X position.

The Al-rich nature of the sediments in the Sydney Coalfield is reflected in the composition of the hydrated sulfate minerals (Zodrow and McCandlish, 1978a, 1979), in the acid run-offs, and in shales and pyrite (Zodrow, in preparation); see Table 1. Copiapite group minerals occur on practically every outcrop of coal, on coal faces in the older mines, as precipitates from acid run-offs, and in shale in the proximity of coal.

Of all the hydrated sulfates observed in their natural environment, copiapite minerals are the most resistant to seasonal changes. For example, on the Emery seam in Glace Bay (Zodrow and McCandlish, 1978a, their Fig. 2) pickeringite [$MgAl_2(SO_4)_4 \cdot 22H_2O$], halotrichite [$FeAl_2(SO_4)_4 \cdot 22H_2O$], and other hydrated sulfates "bloom" only in the summer; a similar situation exists in the Point Aconi area (Fig. 1), where the predominant hydrated sulfate is sideronatrite [$Na_2Fe(SO_4)_2(OH) \cdot 3H_2O$]. These minerals vanished during winter but copiapite survived.

This paper, part of an environmental study of hydrated sulfates in the Sydney Coalfield, attempts to classify selected copiapite group minerals from the unit-cell content as calculated by Berry (1947, p. 30): ". . . an analysis is placed in one of the . . . five groups if the oxygen equivalent of the principal constituent of X exceeds 0.5." Berry's five groups are ferri-, alumino-, magnesio-, ferro-, and cuprocopiapites. In this study the number of atoms in the X and R positions are estimated by solutions of simultaneous linear equations based on the assumptions of substitutions in the general copiapite formula.

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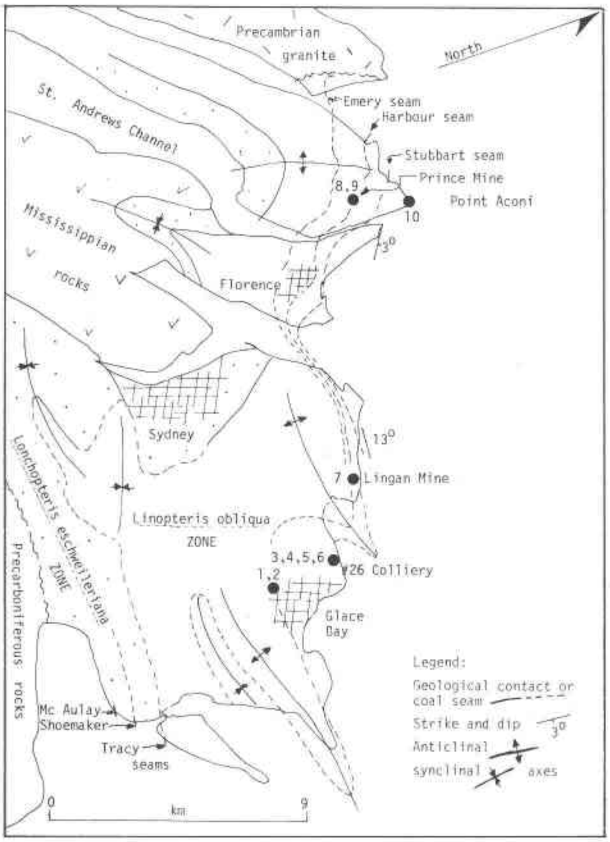


Fig. 1. Sample locations of copiapites ● 1,2 in Sydney Coalfield, Cape Breton Island, Nova Scotia, Canada

Analytical procedures

Samples for this study were hand-picked under a binocular microscope at 30× magnification. The purity of the samples is estimated to be in the range 96–100%. Standard chemical methods were employed for the quantitative analyses (Zodrow and McCandlish, 1979). In the X-ray identification of the specimens Fe-filtered Co*K* radiation was used. The samples were not ground, in order to avoid poor X-ray diffraction patterns owing to broadening of lines (Jolly and Foster, 1967, p. 1221). Portions of the samples [accession numbers 978GM-514(2), 977GF-682(2), 978GM-481, 366, 371, 346, 273, 282 and 524 of the Nova Scotia Museum in Halifax, Nova Scotia, numbered 1 to 10 in Table 2, respectively] are deposited with the National Museums of Canada in Ottawa, Ontario. Some of these samples are also deposited with the Smithsonian Institution, Washington, D. C., U.S.A., and the Musée de Minéralogie, Paris, France.

Experimental data

Table 2 indicates that minerals of the copiapite group vary greatly in composition; this is characteristic of the group. Sample #7 from Lingan has the lowest "Fe," but concomitantly the highest values of Al, Mg, Na, Mn, and Ni. A high Zn content reported for the Point Aconi sample (#10) is the second instance of high-Zn hydrated sulfates found in this general area. The other high Zn example was found in the aluminocopiapite from the Prince mine (Zodrow and McCandlish, 1979, p. 67). The lowest Al content is associated with #9 (collected from the coal face), whereas the other sample from this mine (#8) with an Al content of 2.46% was collected as a precipitate in the mine-drainage system close to the surface.

It is possible to predict the environment of formation of the copiapite group minerals, subsurface or surface, by color. Specimens of light lemon (canary) hue most likely crystallized on the surface, *e.g.*, on the Emery seam, the Point Aconi seam, and mine dumps, and in locations by the sea. Specimens of deep yellow hue are generally found underground, *e.g.*, in the Prince and 1-B mines. There is also a remarkable difference in reactivity of these minerals from the Prince mine as compared with copiapite samples from sample points 3, 4, 5, and 6 (Fig. 1), *i.e.*, the 1-B mine of #26 Colliery. The latter speci-

Table 1. Aluminum concentrations in the Sydney Coalfield, Cape Breton Island, Nova Scotia

Background concentrations	
Groundwater: well holes[1]	
Lonchopteris eschweileriana zone	Linopteris obliqua zone
0.05 ppm and less	0.05 ppm and less
Mc Askill Brook[2]	
water column	stream sediments
0.16 to 0.30 ppm	1,300 ppm
Shales	
argillaceous	carbonaceous
11.14 to 14.83 per cent	15.37 per cent
Coal and Pyrite	
Phalen seam: 465 ppm	pyrite (Mc Aulay seam): 475 ppm
Acid Run-Offs	
Lingan mine, coal storage:	4,350 (2,000)[3] ppm
Lingan mine, coal storage:	90 ppm, recent accumulation
Prince mine, coal storage:	680 (1,090) ppm

1 uncontaminated wells scattered about the coalfield.
2 sampled over a range of discharges and over all four seasons; leached from -60 mesh grain size of sediments. This stream is regarded as a standard because of its uncontaminated water. 3 resampled after four weeks with the last week having heavy rains.

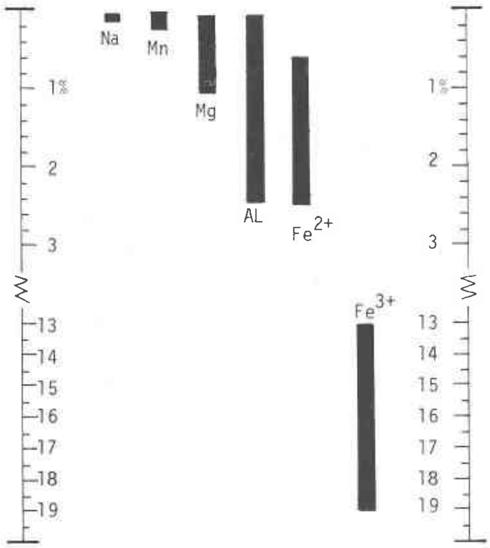
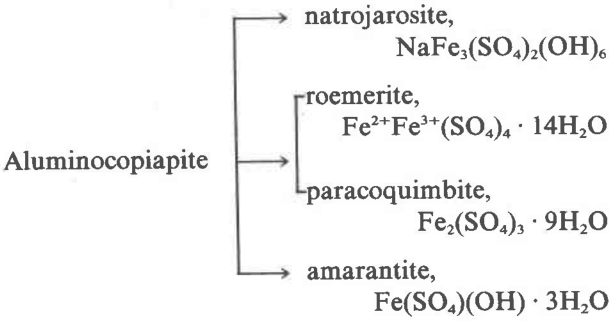


Fig. 2. Range of chemical elements in copiapite samples studied over which Model 1 in Table 4 applies.

mens show no alteration reactions after two years of storage under ambient conditions, whereas some specimens from the Prince mine show these reactions *in vitro* while stored under the same conditions as the 1-B mine samples:



The reactions leading to natrojarosite and amarantite need confirmation.

A linear substitution model

On the assumption that Na, Ca, Mg, Mn, Fe^{2+}, and Al substitute in the X position and some Al for Fe^{3+} in the R position of the structural formula, a model of substitution in copiapite, ignoring Zn in sample #10 and K for all of the samples, can be proposed:

$$[Na_V Ca_W Mg_X Mn_Y Fe^{2+}_Z Al_{1-(V+W+X+Y+Z)}]$$
$$[Fe^{3+}_G Al_{1-G}]_4(SO_4)_6(OH)_2 \cdot nH_2O$$

The molecular weight (= MW), correct to two decimal places, is given by $MW = a - bV - cX + dY + hZ + fG + jW$, where $a = 1105.59$, $b = 3.99$, $c = 2.66$, $d = 27.95$, $h = 28.86$, $f = 115.46$ and $j = 13.09$. V, W, X, Y, Z, and G are stoichiometric coefficients that are numerically evaluated by the solution of a set of simultaneous linear equations. Table 3 shows a generalized form of the linear equations in matrix format. There are no numerical restrictions on the coefficients, but the proportions of X to R or 1:4 in the structural formula of the copiapite group require that each coefficient lie between zero and unity, that G be between zero and unity, and that the sum of the coefficients be less than unity:

$$(0 < V, W, X, Y, Z < 1); (0 \leq G \leq 1)$$
$$(V + W + X + Y + Z) < 1 \qquad (1)$$

The mathematical existence of the V, ... , G coefficients is dependent on a non-zero determinant of the matrix shown in Table 3. Al and SO_4 percentages may be predicted and compared with experimentally obtained values of Table 2. To predict Fe and SO_4 percentages, interchange subscripts of Al and Fe; a new matrix must now be formed (that in Table 3 must be rearranged).

Table 2. Chemical analyses of copiapite samples from the Sydney Coalfield, Cape Breton Island

No.[1]	1	2	3	4	5	6	7	8	9	10
Total Fe%	18.64	18.72	13.28	18.72	16.24	18.88	8.00	14.24	21.60	17.60
Fe^{3+}	18.02	17.83	13.01	17.92	15.62	18.68	3.18	13.26	19.06	16.53
Fe^{2+}	0.62	0.89	0.27	0.80	0.62	0.20	4.82	0.98	2.54	1.07
SO_4	52.74	47.78	45.97	48.70	45.77	46.68	47.07	48.40	47.84	49.61
Al	1.10	1.87	1.66	1.63	1.40	0.98	3.62	2.46	0.10	1.45
Mg	0.64	0.57	2.36	0.17	1.58	1.54	2.76	1.08	0.10	0.56
Ca	0.06	0.07	0.02	0.02	0.02	0.02	0.09	0.03	0.04	0.19
Na	0.10	0.12	0.96	0.11	0.92	0.16	2.12	0.16	0.14	0.19
Mn	0.26	0.16	0.38	0.06	0.29	0.20	0.92	0.22	0.07	0.04
K	0.02	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
ppm										
Cu	176	160	82	82	64	22	274	269	85	80
Ni	376	416	328	136	240	120	520	400	128	408
Zn	84	84	428	124	204	48	640	560	92	3300
Insol.*	0.10	0.50	nil	nil	nil	nil	0.16	nil	0.08	0.08
Total (less H_2O and OH)	73.56	69.33	64.63	69.42	66.23	68.47	64.59	66.60	59.91	59.66

*Coal

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[1] For locations of samples see Fig. 1.
Samples No. 1 and 2 are from the exposed coalface of the Emery seam in Glace Bay; No. 3,4,5 and 6 from various locations in 1-B mine, #26 Colliery; No. 7 is a mine water precipitate from open air storage of coal at Lingan mine; No. 8 and 9 were collected from the Prince mine: 9 is a direct alteration product of pyrite in situ (in coal), while 8 is a precipitate from an underground drainage ditch; No. 10 originated from an outcrop of the Point Aconi seam.

Table 3. Model of substitution of copiapite in matrix format

$$\begin{array}{lclclclclclcl}
(Na + \underline{Na}\cdot b)V & + & \underline{Na}\cdot c\cdot X & - & \underline{Na}\cdot d\cdot Y & - & \underline{Na}\cdot h\cdot Z & - & \underline{Na}\cdot f\cdot G & - & \underline{Na}\cdot j\cdot W & = & a\underline{Na} \\
\underline{Mg}\cdot b\cdot V & + & (Mg + \underline{Mg}\cdot c)X & - & \underline{Mg}\cdot d\cdot Y & - & \underline{Mg}\cdot h\cdot Z & - & \underline{Mg}\cdot f\cdot G & - & \underline{Mg}\cdot j\cdot W & = & a\underline{Mg} \\
\underline{Mn}\cdot b\cdot V & + & \underline{Mn}\cdot c\cdot X & + & (Mn - \underline{Mn}\cdot d)Y & - & \underline{Mn}\cdot h\cdot Z & - & \underline{Mn}\cdot f\cdot G & - & \underline{Mn}\cdot j\cdot W & = & a\underline{Mn} \\
\underline{Fe^{2+}}\cdot b\cdot V & + & \underline{Fe^{2+}}\cdot c\cdot X & - & \underline{Fe^{2+}}\cdot d\cdot Y & + & (Fe^{2+} - \underline{Fe^{2+}}\cdot h)Z & - & \underline{Fe^{2+}}\cdot f\cdot G & - & \underline{Fe^{2+}}\cdot j\cdot W & = & a\underline{Fe^{2+}} \\
\underline{Fe^{3+}}\cdot b\cdot V & + & \underline{Fe^{3+}}\cdot c\cdot X & - & \underline{Fe^{3+}}\cdot d\cdot Y & - & \underline{Fe^{3+}}\cdot h\cdot Z & + & (4Fe - \underline{Fe^{3+}}\cdot f)G & - & \underline{Fe^{3+}}\cdot j\cdot W & = & a\underline{Fe^{3+}} \\
\underline{Ca}\cdot b\cdot V & + & \underline{Ca}\cdot c\cdot X & - & \underline{Ca}\cdot d\cdot Y & - & \underline{Ca}\cdot h\cdot Z & - & \underline{Ca}\cdot f\cdot G & + & (Ca - \underline{Ca}\cdot j)W & = & a\underline{Ca}
\end{array}$$

Where Na, Mg, Mn, Fe and Ca are atomic weights; $\underline{Na}$, $\underline{Mg}$, $\underline{Mn}$, $\underline{Fe^{2+}}$, $\underline{Fe^{3+}}$ and $\underline{Ca}$ are analytical values (TABLE 2) of sodium, magnesium, manganese, iron and calcium, respectively. The coefficients from the molecular-weight formula (MW) are b, c, d, h, f, j and a. The stoichiometric coefficients to be computed are V, X, Y, Z, G *and* W. ($a\underline{Na}$, $a\underline{Mg}$, $a\underline{Mn}$, $a\underline{Fe^{2+}}$, $a\underline{Fe^{3+}}$, $a\underline{Ca}$) is the constant matrix vector.

NOTE: divide the MW coefficients by 100 because of percentage calculations before solving for the stoichiometric coefficients.

Other substitutional schemes may be derived by adding (subtracting) metals to the model. This necessitates a new MW and subsequently a new matrix. The latter is formed from that in Table 3 by adding (subtracting) appropriate rows (columns), manipulating the coefficients and their signs consistently; see the appended derivation.

Values in Table 4 were obtained by computing V to G on the basis of the chemical data in Table 2, then calculating weight percentages shown. Not all solved systems satisfy the conditions in (1), but all numerical solutions satisfying the algebraic equations are valid. Model 1 in Table 4 is a direct mathematical realization of the expanded structural formula; in Model 2 calcium is deleted, and Model 3 is characterized not only by deleting calcium but also by assuming that all Al is in the X site. The Fe% values are reproduced from solutions of the systems of simultaneous linear equations and thus afford an evaluation of the mathematical efficiency (numerical accuracy).

Table 5 summarizes those formulae, according to Model 1, in which (1) is satisfied. The water content for each representation was obtained from a deterministic simulation process under the assumption of constant $(OH)_2$ content. Decreasing $n = 20$ by 0.1, that number of water molecules was selected subjectively when calculated metal totals plus sulfate compared well with those in Table 2. As the copiapite group minerals may readily lose several "free" molecules of water without significant damage to the framework (Fanfani *et al.,* 1973, p. 321), the range of simulated values of *n* is theoretically defensible.

Discussion of results

Although Table 2 shows diversity of composition of the copiapite samples studied, they may be classified in the copiapite group with ease, as shown in Table 5: #8 is a magnesiocopiapite, #9 is a copiapite, #10, 2, and 1 are magnesian aluminocopiapite, and #4 is an aluminocopiapite. Thus the only aluminocopiapite identified so far originated from the 1-B mine, followed closely by #1 from the Emery seam in Glace Bay. It is amazing to observe that the coal face and its mine-drainage ditch represent such different environments as to produce copiapite and magnesiocopiapite, samples #9 and 8, respectively. It appears that the copiapite minerals precipitated from acid mine-waters are relatively enriched in Al, Mg, Mn, Ni, Zn and Cu, but relatively depleted in "Fe," *e.g.,* samples #7 and 8.

Table 4 shows that if all Al is assumed to be in the X position of the copiapite structure and Ca is deleted as a substituting metal, Model 3 gives the relative worst-predicted values of Al and SO_4, the relative worst-reproduced Fe%, and three instances of negative Al content. Definite improvements are offered by Models 1 and 2 in these respects. Solutions by simultaneous linear equations satisfying proportions in the general formula X to R as 1:4, according to the preferred Model 1, are observed only over particular ranges of analytical values (Fig. 2). This ratio

Table 4. Comparison between predicted and observed values of Al and SO_4 according to different assumptions in the substitutional model of copiapite

Sample No.	1	2	3	4	5	6	7	8	9	10
MODEL 1: $(Na_VCa_WMg_XMn_YFe^{2+}_ZAl_{1-(V+W+X+Y+Z)})(Fe^{3+}_GAl_{1-G})_4(SO_4)_6(OH)_2\cdot 20.0H_2O$										
Al% Predicted Value	1.04	1.10	0.95+	1.62	0.30+	-0.09+	3.33+	2.91	0.08	1.71
Al% Observed, TABLE 2	1.10	1.87	1.66	1.63	1.40	0.98	3.62	2.46	0.10	1.45
SO_4% Predicted Value	47.07	47.07	48.64	47.08	47.82	47.10	49.96	48.30	46.30	47.30
SO_4% Observed, TABLE 2	52.74	47.78	45.97	48.70	45.77	46.68	47.07	48.40	47.84	49.61
Fe% Reproduced Value*	18.67	18.75	13.39	18.73	16.35	18.85	8.08	14.28	21.62	17.63
Fe% Observed, TABLE 2	18.64	18.72	13.28	18.72	16.24	18.88	8.00	14.24	21.60	17.60
MODEL 2: $(Na_VMg_XMn_YFe^{2+}_ZAl_{1-(V+X+Y+Z)})(Fe^{3+}_GAl_{1-G})_4(SO_4)_6(OH)_2\cdot 20.0H_2O$										
Al% (Predicted Value	1.04	1.11	0.95+	1.62	0.30	0.15+	3.34+	2.91	0.09+	1.71
SO_4%(Predicted Value	47.08	47.08	48.64	47.09	47.82	47.22	49.98	48.30	46.31	47.42
Fe% (Reproduced Value*	18.67	18.75	13.39	18.73	16.35	18.40	8.08	14.28	21.60	17.63
MODEL 3: $(Na_VMg_XMn_YFe^{2+}_ZAl_{1-(V+X+Y+Z)})\ Fe^{3+}_4\cdot(SO_4)_6(OH)_2\cdot 20.0H_2O$										
Al% (Predicted Value	0.94	0.92	-1.89+	1.47	-1.09+	0.16	-6.29+	0.23	0.64	0.84
SO_4%(Predicted Value	47.08	46.99	47.25	47.01	47.14	47.22	46.11	46.98	46.58	46.98
Fe% (Reproduced Value*	18.45	19.10	18.58	19.02	18.89	18.40	22.76	19.19	20.60	19.28

*Total Fe computed from corresponding molecular weight formula. +Stoichiometric requirements not satisfied.

is not satisfied for any value that falls outside its range. The possibility that certain pure end-members in the group, *e.g.*, Mn or Mg, are mathematically not feasible is thus implied.

The failure of the model in certain instances, as for example if (Na + Mg) > 1.70 or when Fe^{2+} is rather low, and an apparent excess of sulfate (average observed are larger than average predicted values), are problems demanding attention. The excess sulfate is marginally decreased but the spread between predicted and observed Al values widens considerably when residual positive charges of the X position of the stoichiometric formulae in Table 5 are algebraically eliminated; this may be seen from Table 6, in which the average of 47.30 percent of predicted sulfate is marginally higher than the 47.19 percent average of predicted values from stoichiometric formulae in Table 4, as compared with the observed average value of 49.18 percent (Table 2). Aluminum predictions in Table 6 are definitely inferior to those in Table 4.

Whether the excess of sulfate is a characterizing

Table 5. Stoichiometric formulae of minerals from the copiapite group, Sydney Coalfield, Cape Breton Island

$(Na_{0.083}\ Ca_{0.009}\ Mg_{\underline{0.531}}\ Mn_{0.048}\ Fe^{2+}_{0.210}\ Al_{0.119})$	$(Fe^{3+}_{0.710}\ Al_{0.290})_4$	$(SO_4)_6$	$(OH)_2\cdot \approx 20.0H_2O$	Sample No. 8
$(Na_{0.076}\ Ca_{0.012}\ Mg_{0.051}\ Mn_{0.016}\ Fe^{2+}_{\underline{0.566}}\ Al_{0.280})$	Fe^{3+}_4	$(SO_4)_6$	$(OH)_2\cdot \approx 18.5H_2O$	Sample No. 9
$(Na_{0.100}\ Ca_{0.058}\ Mg_{\underline{0.280}}\ Mn_{0.009}\ Fe^{2+}_{0.233}\ Al_{\underline{0.320}})$	$(Fe^{3+}_{0.902}\ Al_{0.098})_4$	$(SO_4)_6$	$(OH)_2\cdot \approx 18.0H_2O$	Sample No. 10
$(Na_{0.064}\ Ca_{0.021}\ Mg_{\underline{0.287}}\ Mn_{0.035}\ Fe^{2+}_{0.195}\ Al_{\underline{0.398}})$	$(Fe^{3+}_{0.979}\ Al_{0.021})_4$	$(SO_4)_6$	$(OH)_2\cdot \approx 18.5H_2O$	Sample No. 2
$(Na_{0.053}\ Ca_{0.018}\ Mg_{\underline{0.323}}\ Mn_{0.058}\ Fe^{2+}_{0.136}\ Al_{\underline{0.412}})$	$(Fe^{3+}_{0.989}\ Al_{0.011})_4$	$(SO_4)_6$	$(OH)_2\cdot \approx 16.0H_2O$	Sample No. 1
$(Na_{0.058}\ Ca_{0.006}\ Mg_{0.085}\ Mn_{0.013}\ Fe^{2+}_{0.175}\ Al_{\underline{0.663}})$	$(Fe^{3+}_{0.983}\ Al_{0.017})_4$	$(SO_4)_6$	$(OH)_2\cdot \approx 18.4H_2O$	Sample No. 4

Note: charge-balanced formulae have these Al coefficients, by $(2 - V - 2(W + X + Y + Z))/3$:
0.107, 0.211, 0.246, 0.286, 0.292, and 0.461, respectively.

Sample No. 8 is a magnesiocopiapite; No. 9 the species' name, copiapite; Nos. 10, 2, and 1 are magnesian aluminocopiapite, and No. 4 is aluminocopiapite.

Table 6. Comparison between predicted and observed values of Al and SO_4 according to Model 1: residual positive charge of stoichiometric formulae in Table 5 is eliminated

Sample No.	1	2	3	4	5	6	7	8	9	10
Al%[1]	0.74	0.82	1.91+	1.17	1.00+	-.08+	5.49+	2.86	-.09	1.42
TABLE 4	1.04	1.10	0.95+	1.62	0.30+	-.09+	3.33+	2.91	0.08	1.71
Observed TABLE 2	1.10	1.87	1.66	1.63	1.40	0.98	3.62	2.46	0.10	1.45
SO_4%	47.19	47.18	48.16	47.29	47.48	47.09	48.82	48.31	46.37	47.46
TABLE 4	47.07	47.07	48.64	47.08	47.82	47.10	49.96	48.30	46.30	47.30
Observed TABLE 2	52.74	47.78	45.97	48.70	45.77	46.68	47.07	48.40	47.84	49.61

AVERAGES

	This TABLE	TABLE 4	Observed (TABLE 2)
Al%[2]	1.153	1.410	1.435
SO_4%[2]	47.300	47.187	49.178
SO_4%[3]	47.535	47.664	48.056

[+] Stoichiometric requirements not satisfied.

[1] Let the coefficient of Al in TABLE 4 be: (2 - V - 2(W+X+Y+Z))/3 and also substitute this expression in the molecular weight formula (MW) to obtain a new formula weight and hence the values; see TABLE 5.

[2] Average of 6 samples, or samples of +Stoichiometric requirements not satisfied are excluded.

[3] Average of all 10 samples.

feature of copiapite samples from the Sydney Coalfield, or a problem of mathematical manipulation in the prediction process, is not known at this juncture without further investigation. Fanfani *et al.* (1973), however, show well the problem between the relationship of chemical data and atomic arrangements in some copiapite samples.

Continuing research is concentrated on possible (OH) substitutions and recognition of additional anions, and sulfate content. Unit-cell refinements are in progress.

Appendix

Derivation of a system of simultaneous linear equations

The MW is obtained directly from Model 1, Table 4, by expanding: $\mathrm{Na_V + Ca_W + Mg_X + Mn_Y + Fe_Z + 4Fe_G + [4Al - 4Al_G + Al - Al(V + W + X + Y + Z)] + 6(SO_4) + 2(OH) + 20H_2O}$ which upon evaluation in terms of atomic weights of the components leads directly to $(a - bV - cX + dY + hZ + fG + jW) = MW$. To reproduce $\underline{\mathrm{Ca}}$% from Table 2 we consider that $\underline{\mathrm{Ca}}\% = \mathrm{Ca_w}/MW$ which when rearranged becomes the last equation (row) in Table 3.

$$\underline{\mathrm{Ca}} = \mathrm{Ca_w}/(a - bV - cX + dY + hZ + fG + jW)$$

Exchange the constant term a $\underline{\mathrm{Ca}}$ with $\mathrm{Ca_w}$, collect terms to obtain

$$-\underline{\mathrm{Ca}}bV - \underline{\mathrm{Ca}}cX + \underline{\mathrm{Ca}}dY + \underline{\mathrm{Ca}}hZ + \underline{\mathrm{Ca}}fG - (\mathrm{Ca} - \underline{\mathrm{Ca}j})W = -a\underline{\mathrm{Ca}}$$

when multiplied by −1 the last row of the matrix in Table 3 is realized. This procedure is systematically followed for the remaining elements.

To add a metal, say Cu, to the substitutional model would necessitate (a) augmenting the number of subscripts and calculating a new MW, and (b) forming a new Table 3 according to the above developments. The sign of the Cu component in MW is "+" as Cu has a larger atomic weight than Al, *the metal value to be predicted.* However, in the matrix format the "+" changes to a "−". To delete a metal component, put zero in the appropriate term of MW (and delete the corresponding row and column in the matrix).

Note added in proof

Aluminocopiapite, according to X-ray analysis, collected from a coal seam in Smithers, B.C., Canada, by Keith McCandlish in 1979 with composition 11.92% Fe^{3+}, 2.23% Fe^{2+}, 42.75% SO_4, 1.54% Al, 1.05% Mg, 0.13% Ca, 0.02% Na, and 0.04% Mn does not satisfy the stoichiometric conditions, *i.e.*, Fe^{3+} and Na contents appear to be too low according to the empirical criteria in Figure 2.

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