

The Copiapite Problem: The Crystal Structure of a Ferrian Copiapite

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Abstract

Crystal structure, thermal and chemical data are reported for a ferrian copiapite from California, with a cell content $(\square_{0.31}\text{Fe}_{0.43}^{3+}\text{Al}_{0.23}^{3+}\text{Zn}_{0.03}^{2+})\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_{2.04} \cdot 18.78 \text{H}_2\text{O}$, lattice parameters: $a = 7.390(8)$, $b = 18.213(10)$, $c = 7.290(8)$ Å, $\alpha = 93^\circ 40'(15)'$, $\beta = 102^\circ 3'(25)'$, $\gamma = 99^\circ 16'(15)'$ and space group $P\bar{1}$; ρ calc = 2.123 g/cm³; ρ obs = 2.08-2.15. The crystal structure was solved with Patterson and Fourier methods and refined to an R value of 0.074 for 1435 independent observed reflections which were measured photometrically on integrated Weissenberg photographs. The main features of the atomic arrangement are: (1) chains formed by SO_4 tetrahedra and $\text{Fe}(\text{OH})(\text{H}_2\text{O})_2\text{O}_3$ octahedra, (2) isolated octahedra at the origin of the cell, and (3) water molecules not linked directly to cations and contributing to a complex system of hydrogen bonding.

The structure is somewhat different from that of a magnesiocopiapite from Alcaparrosa (Chile) reported by Süssé (1970). Lattice parameters of the material studied by this author seem to indicate that Alcaparrosa crystals are actually pseudocopiapite. The possibility that copiapite and pseudocopiapite are two stereoisomerically different mineralogical species is suggested.

Structural analysis accounts for the wide range of isomorphous replacement and large variability in water content of copiapite. When the X position is occupied by a trivalent cation, as is the case of copiapite under study, the occupancy is statistically 2/3, justifying the constant O/ X ratio with values near to 1, where O represents +2 (one oxygen equivalent) and $X = \Sigma$ (cationic charge \times occupancy of the cation) for all cations occupying the X site, as observed by Berry (1947).

Introduction

The present paper concerning the structure of a ferrian copiapite is a contribution to the crystal chemistry of iron sulfates. It follows two papers on the crystal structures of roemerite (Fanfani *et al.*, 1970) and butlerite (Fanfani *et al.*, 1971).

Several widely occurring basic hydrated iron sulfates, with variable chemical composition, are grouped under the name copiapite.

The mineral occurs frequently in association with other secondary minerals such as melanterite, alunogen, fibroferrite, halotrichite, botryogen, butlerite, amarantite and other sulfates. Generally it is a result of the oxidation of iron sulfides. Conditions for the formation of copiapite and other sulfates have been discussed by Bandy (1938) for the deposits of Alcaparrosa and Quetena (Northern Chile), where the mineral is one of the earliest basic minerals originating from the oxidation of pyrite ores.

Copiapite was first described and analyzed by Rose

(1833) and later named by Haidinger (1845). Melville and Lindgren (1890) proposed the following chemical formula for copiapite: $\text{Me}^{2+}\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 20 \text{H}_2\text{O}$. In 1938 Bandy proposed for some natural copiapites several chemical formulae of the type, $\text{Me}^{2+}\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$, to indicate a considerable range in water content. In 1947 Berry, on the basis of chemical analyses on 42 copiapite samples from different countries, derived the general formula, $X(\text{OH})_2\text{R}_4^{3+}(\text{SO}_4)_6 \cdot n\text{H}_2\text{O}$, where X is one oxygen equivalent (*i.e.*, a total charge of 2⁺ for the X site) of one or more of the elements Na, K, Cu, Fe²⁺, Mn, Mg, Zn, Al, Fe³⁺; R³⁺ is mainly Fe³⁺, sometimes Al³⁺, and the value of n is 20. The names ferriocopiapite, ferrocopiapite, magnesiocopiapite, aluminocopiapite, cuprocopiapite and zincocopiapite were proposed for varieties where X was mainly Fe³⁺, Fe²⁺, Mg, Al, Cu, and Zn respectively. This large variation in the chemical composition appears to cause changes in the physical properties of copiapite.

For example, as Berry pointed out, optically the varieties of copiapite fall into three distinct groups differing from one another in the values of the principal indices of refraction according to the chemistry of the X site: when $X = \text{Cu}$, the highest indices are exhibited; when $X = \text{Fe}^{2+}$ or Mg , the indices are at a minimum; copiapites with $X = \text{Fe}^{3+}$ or Al^{3+} have intermediate indices.

From a crystallographic point of view, the mineral was first considered orthorhombic, then monoclinic, until Ungemach (1935) and, about the same time, Palache (quoted in Palache, Peacock and Berry, 1946) discovered its triclinic symmetry; copiapite was assigned to the pinacoidal class on the basis of an examination of the very large number of forms observed. In 1939 Peacock (quoted also in Palache *et al.*, 1946) showed a close agreement between his morphological and X-ray data on Chuquicamata (Chile) crystals and the morphological data by Ungemach on Sierra Gorda (Chile) material referred to the standard setting:

(Peacock) $a:b:c = 0.4058:1:0.4039$,
 $\alpha = 93^\circ 50'$, $\beta = 102^\circ 10'$, $\gamma = 99^\circ 21\frac{1}{2}'$;
 $a = 7.34$, $b = 18.19$, $c = 7.28\text{\AA}$,
 $\alpha = 93^\circ 51'$, $\beta = 101^\circ 30'$, $\gamma = 99^\circ 23'$;

(Ungemach) $a:b:c = 0.4005:1:0.3971$,
 $\alpha = 93^\circ 58\frac{1}{2}'$, $\beta = 102^\circ 08'$, $\gamma = 98^\circ 50'$.

Comparable lattice parameters were reported for an aluminocopiapite (Jolly and Foster, 1967) and for a zincocopiapite (Kuang *et al.*, 1964).

In his study on morphology of copiapite crystals, Ungemach recognized an aberrant variety from Tierra Amarilla (Chile), which is visibly indistinguishable from copiapite, but gives different crystallographic elements, the most significant difference occurring in the value of angle α . Ungemach named this variety "pseudocopiapite." Berry (1938) studied Ungemach's crystals of this variety, confirming the morphological elements and measuring the cell constants. The elements of pseudocopiapite according to these authors are:

(Ungemach) $a:b:c = 0.3938:1:0.3951$,
 $\alpha = 91^\circ 18\frac{1}{2}'$, $\beta = 102^\circ 4'$, $\gamma = 98^\circ 59'$;

(Berry) $a:b:c = 0.4007:1:0.4005$,
 $\alpha = 91^\circ 22'$, $\beta = 102^\circ 22'$, $\gamma = 98^\circ 50'$;

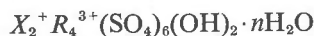
from morphological data; and:

(Berry) $a = 7.26$, $b = 18.67$, $c = 7.45\text{\AA}$,
 $\alpha = 90^\circ 58'$, $\beta = 104^\circ 35'$, $\gamma = 98^\circ 36'$,
 from X-ray data.

The difference in elements between copiapite and pseudocopiapite was ascribed presumably to variations in composition, but Berry could not carry out any chemical analysis on Ungemach's crystals of pseudocopiapite because of the minute amount of material at his disposal. In 1947, in the paper on composition and optics of copiapite, Berry measured the refractive indices of pseudocopiapite crystals and suggested on their basis that pseudocopiapite is in reality a ferro- or a magnesiocopiapite, rather than a ferricopiapite as assumed by Ungemach. Since the properties of pseudocopiapite lie within the observed or expected range of those of copiapite, the name "pseudocopiapite" was not considered useful as indicative of a mineralogical species by Berry.

Available crystallographic data for copiapites are reported in Table 9.

Since the space group of copiapite is $P\bar{1}$, it is interesting to note that from a structural point of view and assuming a fully ordered atomic arrangement, X must occupy a special position in the cell at an inversion center. Assuming then the O/ X ratio equal to one, as inferred by Berry (1947) and confirmed by Garavelli (1955) as the most probable one for copiapites, the X position is completely occupied only when X is represented by a divalent cation. When X is a trivalent cation, the corresponding position is required to have 2/3 occupancy, forming copiapites with lattice vacancies. A completely ordered structure can rule out the limiting chemical formula



proposed by Berry for some copiapites containing a certain amount of alkali metals. From a structural point of view O/ X ratios differing from the value of 1 can be explained, assuming that a change $\text{OH}^- \rightleftharpoons \text{H}_2\text{O}$ can occur in the structure without apparent changes in the atomic arrangement.

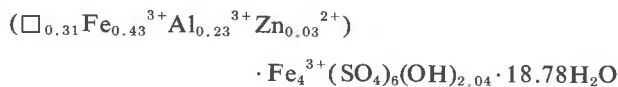
In 1970 Süssé published the preliminary results of the crystal structure of a copiapite from Alcaparrosa (Chile) with lattice parameters: $a = 7.37$, $b = 18.89$, $c = 7.42\text{\AA}$, $\alpha = 91^\circ 18'$, $\beta = 102^\circ 24'$, $\gamma = 98^\circ 59'$ and schematic cell content $\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$.

Therefore the structural study of a ferrian copiapite was undertaken in the attempt to contribute to a better knowledge of crystallochemical relationships in this widespread class of sulfate minerals.

Chemical Data

A chemical analysis on a sample from Coso Hot Spring, Inyo County, California, was carried out be-

fore undertaking the structural work. The material for the analysis was carefully selected from a specimen consisting of bunches and clusters of extremely tiny yellow crystals. The results are listed in Table 1, along with those kindly supplied by Professor Garavelli for material from the same locality. The chemical formula derived from the analytical data is:



corresponding to an intermediate term between a ferri- and an aluminocopiapite. The mineral has an O/X ratio very close to 1 and can be classified as a typical copiapite with lattice vacancies according to Berry (1947).

Thermal Data

Thermogravimetric (TG) differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves for Coso Hot Spring copiapite are shown in Figure 1. All endothermic peaks correspond with loss-in-weight steps. From the TG curve the mineral appears to lose water gradually. At 380°C dehydration is completed, in agreement with data reported by Scharizer (1927) on copiapite from Alcaparrosa and by Garavelli (1955) on material from Elba. The DTG curve shows four distinct peaks roughly centered at 135°, 185°, 225° and 360°C. The three lower temperature peaks are relatively sharp, while the higher temperature peak is quite broad. Assuming for our sample a total water content of 19.80 molecules according to the analysis, the water loss in the first three steps is 6.94, 6.37 and 4.45 molecules. The broad peak at 360°C corresponds to the loss of

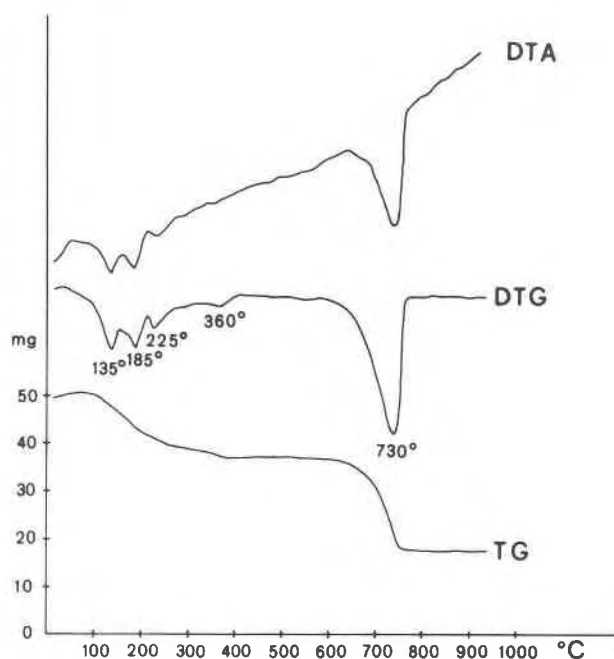


FIG. 1. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal (DTA) curves of copiapite. Rate of heating: 10°C/min.; thermocouple Pt/Pt + 10 percent Rh; reference material Al_2O_3 .

2.04 water molecules and can be partially attributed to the loss of OH groups.

The behavior in dehydration in our sample is not in complete agreement with that found by Garavelli (1955). The DTA curve, too, is slightly different from that reported by Cocco (1952) for an elban copiapite. These discrepancies in thermal behavior are not surprising considering the wide range in compositional limits and crystallographic properties.

Single Crystal X-Ray Study

Experimental. A well-formed tabular crystal with dimensions $0.18 \times 0.19 \times 0.04$ mm, parallel respectively to the c , a , and b axes, was employed for X-ray data collection with $\text{CuK}\alpha$ radiation. Cell dimensions were measured from oscillation and basal Weissenberg photographs, rotating the crystal around the a and c axes. Photographs were calibrated with Ag powder, and the following values were obtained by least-squares refinement, starting from 2θ values of high angle reflexions:

$$\begin{aligned} a &= 7.390 \pm 0.008 \text{ \AA}, \alpha = 93^\circ 40' \pm 15' \\ b &= 18.213 \pm 0.010 \text{ \AA}, \beta = 102^\circ 3' \pm 25' \\ c &= 7.290 \pm 0.008 \text{ \AA}, \gamma = 99^\circ 16' \pm 15' \end{aligned}$$

TABLE 1. Analysis of Coso Hot Spring Copiapite

| | % in oxides | | | Cell content | | |
|-------------------------|-------------|-------|----------------------|------------------|-------|------|
| | (a) | (b) | | (a) | (b) | |
| Fe_2O_3 | 29.33 | 29.01 | X | Fe^{3+} | 0.43 | 0.38 |
| Al_2O_3 | 0.99 | 1.23 | | Al | 0.23 | 0.29 |
| ZnO | 0.20 | -- | | Zn | 0.03 | -- |
| FeO | -- | 0.34 | | Fe^{2+} | -- | 0.06 |
| CuO | -- | 0.01 | | Cu | -- | 0.00 |
| SO_3 | 39.62 | 39.85 | | \square | 0.31 | 0.27 |
| H_2O | 29.57 | 29.33 | Fe^{3+} | 4.00 | 4.00 | |
| | | | SO_4 | 6.00 | 6.00 | |
| | | | OH | 2.04 | 2.13 | |
| | | | H_2O | 18.78 | 18.55 | |
| Total | 99.71 | 99.77 | | | | |

(a) - Present work.

(b) - Garavelli (private communication).

These results are in good agreement with the values reported by Palache *et al.* (1946). The theoretical density for the cell content determined by the chemical analysis is 2.123 g/cm³; experimental density for copiapites is in the range 2.08–2.15 g/cm³, Palache *et al.* (1963).

For the structural study intensity data from *hk0* to *hk5* and from *0kl* reciprocal lattice layers were collected and photometrically measured on integrated Weissenberg photographs. 1435 independent reflections with intensity above the limit of observation were measured on a total of 2950 collected reflections. Data were corrected for the usual geometrical factors. Transmission factors for the absorption correction ($\mu = 179.8 \text{ cm}^{-1}$, for CuK α) were computed by a direct analytical procedure using a program written by De Meulenaer and Tompa (1965). Squared structure factors were then put on the same relative scale by comparison of the common reflections occurring on the *0kl* photograph.

Structure Determination and Refinement

The structure proposed by Süsse (1970) for a magnesian copiapite from Alcaparrosa was used as the starting point of our investigation. The calculated values of the structure factors were not in agreement (conventional *R* index equal to 0.65). The differences in chemical composition and lattice parameters between Alcaparrosa copiapite and Coso Hot Spring copiapite led us to suppose that large differences have to occur in the atomic arrangement.

A three-dimensional Patterson function was then computed to determine the positions of iron ions in the cell. By successive Fourier maps, three sulfur atoms and twenty-three oxygen atoms were located in the asymmetric unit. The *X* site at the inversion center 0, 0, 0 was considered occupied by a hypothetical ion with scattering factor $1/3 f_{\text{Al}^{3+}} + 2/3 f_{\text{Fe}^{3+}}$ and a total occupancy of 0.69, in agreement with the chemical analysis. The scattering factors for Al³⁺, Fe³⁺, S and O were taken from *International Tables for X-ray Crystallography* (1962).

A first refinement of the structure was carried out by electron-density maps to an *R* value of 0.22. The refinement was then continued by least-squares method, employing a block-diagonal program written by Shiono for the IBM 1130. During the first five cycles, positional parameters and individual isotropic thermal parameters were varied, and the conventional *R* value was reduced to 0.10. Further reduction in *R* was achieved in two cycles of anisotropic

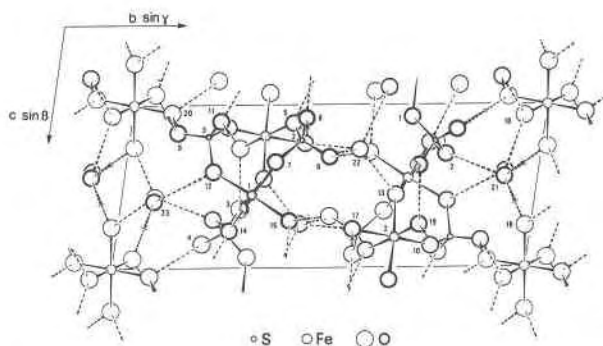


FIG. 2. The crystal structure of copiapite viewed along [100].

refinement. At this stage a difference Fourier map was computed to try to confirm the likely positions of hydrogen atoms from geometrical and electrostatic considerations. The poor resolution of the synthesis did not allow assignment of a physical meaning. Therefore hydrogen atoms were not included in calculations. The refinement was then continued to a final *R* value of 0.074. The weighting scheme used was as follows: $w^{1/2} = 1$ for $|F_o| \leq 4|F_{\text{min}}|$; $w^{1/2} = |4|F_{\text{min}}|/|F_o|$ for $|F_o| > 4|F_{\text{min}}|$. Unobserved reflections were excluded from calculations. Observed and calculated structure factors are listed in Table 2.¹

Discussion of the Structure

The structure of copiapite projected along the *a* axis is shown in Figure 2. Table 3 gives the atomic coordinates and Table 4 shows the anisotropic thermal parameters and the isotropic equivalents calculated according to Hamilton (1959). The distinction between oxygen atoms, hydroxyl groups, and water molecules is made on the basis of electrostatic valence rule. For sake of comparison, the labelling of atoms is maintained equal to that reported by Süsse (1970).

Interatomic distances and angles are listed in Tables 5 and 6.

The two crystallographically non-equivalent Fe³⁺ ions (both in general positions) lie in distorted oxygen octahedra of the same configuration and share one vertex. In both octahedra the ligands are:

¹ To obtain a copy of Table 2, listing observed and calculated structure factors of copiapite, order NAPS Document Number 02061. The present address is Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N.Y. 10017. Please remit in advance \$1.50 for microfiche or \$5.00 for photocopies. Please check the most recent issue of this journal for the current address and prices.

TABLE 3. Final Atomic Coordinates with Their Standard Deviations in Parentheses*

| | x | y | z |
|-----------------------|------------|------------|------------|
| X | O | O | O |
| Fe (1) | .7848 (3) | .3135 (1) | .5524 (4) |
| Fe (2) | .5990 (3) | .6718 (1) | .8058 (4) |
| S (1) | .8325 (5) | .7398 (2) | .2195 (6) |
| S (2) | .8170 (5) | .4175 (2) | .2188 (6) |
| S (3) | .6402 (5) | .1927 (2) | .1953 (6) |
| O (1) | .7367 (15) | .6750 (6) | .0714 (16) |
| O (2) | .6930 (14) | .7698 (7) | .2963 (17) |
| O (3) | .0483 (14) | .2921 (7) | .6322 (17) |
| O (4) | .0527 (16) | .2022 (7) | .8547 (18) |
| O (5) | .6201 (14) | .3910 (6) | .1085 (15) |
| O (6) | .8296 (14) | .4886 (6) | .3208 (16) |
| O (7) | .8774 (13) | .3626 (6) | .3474 (15) |
| O (8) | .9350 (14) | .4228 (7) | .0842 (16) |
| O (9) | .5655 (18) | .1159 (7) | .1687 (17) |
| O (10) | .5099 (14) | .7637 (6) | .8635 (16) |
| O (11) | .7921 (14) | .2131 (7) | .0980 (16) |
| O (12) | .7185 (14) | .2128 (6) | .4053 (16) |
| OH (13) | .4626 (14) | .6604 (6) | .5454 (16) |
| H ₂ O (14) | .6859 (15) | .2699 (7) | .7673 (16) |
| (15) | .8686 (16) | .4142 (7) | .7138 (18) |
| (16) | .2076 (27) | .9474 (11) | .0665 (28) |
| (17) | .6933 (15) | .5740 (6) | .7598 (17) |
| (18) | .0158 (28) | .9866 (12) | .7338 (28) |
| H ₂ O (19) | .8301 (15) | .7282 (6) | .7309 (16) |
| (20) | .1713 (26) | .0926 (11) | .0473 (29) |
| (21) | .7660 (23) | .9196 (9) | .4381 (24) |
| (22) | .5280 (14) | .5608 (6) | .2767 (16) |
| (23) | .6356 (31) | .0743 (12) | .5949 (31) |

* Occupancy factors are equal to 1 for all atoms except for the X ion, for which it is 0.69.

three oxygen atoms belonging to three SO₄ groups, two water molecules, and one hydroxyl group which represents the common vertex. Average distances are 1.95 Å for Fe-OH, 2.00 Å for Fe-O and 2.04 Å for Fe-H₂O.

The site $\bar{1}$ at the origin of the cell is surrounded octahedrally by six water molecules at a mean distance of 1.93 Å. This site is occupied randomly by Al³⁺ and Fe³⁺ (the atomic ratio Al/Fe is 1/2) to a total occupancy of 0.69.

It is interesting to note that all the Al present is in the X position, a result analogous to that found in coquimbite (Fang and Robinson, 1970; Giacobazzi *et al.*, 1970), where the Al present in the cell preferentially fills a site surrounded octahedrally by six water molecules.

SO₄ groups are tetrahedral with S-O distances ranging from 1.40 to 1.52 Å. Each SO₄ tetrahedron shares two corners with two Fe octahedra, the other two vertices being unshared. As already pointed out in roemerite (Fanfani *et al.*, 1970) this fact affects sulfur-oxygen distances; thus, the average

bond length between sulfur and oxygen bonded to iron (1.49 Å) is significantly longer than the average distance between sulfur and unshared oxygen atoms (1.44 Å).

The pair of Fe octahedra sharing the hydroxyl group is also linked by S(2) and S(3) tetrahedra to form a cluster of two octahedra and two tetrahedra. The S(1) tetrahedron connects two adjacent clusters to produce a chain which runs in the [101] direction. The chain is shown schematically in Figure 3, the chain composition being [Fe₂(OH)(H₂O)₄(O₂SO₂)₂(OSO₃)_n⁻ⁿ.

The main features of copiapite structure are: (1) chains of SO₄ tetrahedra and Fe(OH)(H₂O)₂O₃ octahedra (2) isolated octahedra at the origin and (3) six water molecules per cell not linked directly to cations and contributing to the complex system of hydrogen bonding present in the structure.

Features (2) and (3) are common to other iron sulfates. For example, isolated octahedra and free water molecules were found in roemerite (Fanfani *et al.*, 1970), and in coquimbite and para-coquimbite (Robinson and Fang, 1971).

The system of hydrogen bonding has been derived by optimizing the criteria reported by Baur (1972); hydrogen bond lengths are listed in Table 5. The resulting oxygen electrostatic balance is reported in Table 8, on the assumption that the donor atom receives 0.83 *v.u.* (5/6) of the bond strength donated by the hydrogen atom, while the acceptor receives 0.17 *v.u.* (1/6). The results in the case of copiapite are of course over-simplified and approximate, because the system of hydrogen bonds is somewhat disordered, especially in the zone around the origin. For example, when the X position is empty, the water molecules surrounding it probably rearrange, setting up H-bonds along the edges of X octahedron. Furthermore, these water molecules, as well as the "free" molecules H₂O(21) and H₂O(23), which participate in the same H-bond system, seem to be only statistically present, as shown by the abnormally high value of their thermal parameters and by the water content revealed by chemical analysis.

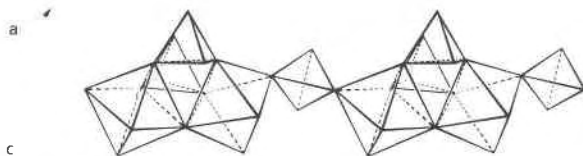


FIG. 3. Arrangement of octahedra and tetrahedra in copiapite chains.

TABLE 4. Anisotropic Thermal Parameters, with Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors after Hamilton*

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} | B (\AA^2) |
|-----------------------|--------------|--------------|--------------|--------------|--------------|--------------|----------------------|
| X | .0158 (12) | .0032 (2) | .0166 (17) | .0012 (5) | .0038 (11) | .0006 (5) | 3.54 |
| Fe (1) | .0090 (4) | .0025 (1) | .0102 (6) | .0007 (2) | .0008 (4) | .0005 (2) | 2.40 |
| Fe (2) | .0091 (4) | .0026 (1) | .0097 (6) | .0009 (1) | .0011 (4) | .0004 (2) | 2.42 |
| S (1) | .0072 (6) | .0024 (1) | .0068 (10) | .0009 (2) | .0009 (6) | .0006 (3) | 1.96 |
| S (2) | .0076 (6) | .0020 (1) | .0086 (10) | .0006 (2) | .0021 (6) | .0009 (3) | 1.95 |
| S (3) | .0090 (6) | .0019 (1) | .0079 (10) | .0011 (2) | .0007 (6) | .0003 (3) | 1.97 |
| O (1) | .0141 (21) | .0021 (4) | .0099 (27) | .0006 (8) | -.0019 (19) | .0004 (8) | 2.65 |
| O (2) | .0095 (19) | .0035 (4) | .0155 (30) | .0013 (8) | .0044 (19) | .0004 (9) | 3.10 |
| O (3) | .0079 (18) | .0037 (4) | .0142 (29) | .0015 (8) | -.0006 (18) | .0014 (9) | 3.11 |
| O (4) | .0149 (24) | .0029 (4) | .0154 (31) | .0003 (9) | .0014 (22) | .0012 (10) | 3.36 |
| O (5) | .0095 (18) | .0033 (4) | .0052 (25) | -.0000 (7) | .0021 (16) | .0001 (8) | 2.45 |
| O (6) | .0102 (19) | .0018 (4) | .0150 (29) | .0015 (7) | .0013 (19) | .0016 (9) | 2.46 |
| O (7) | .0085 (18) | .0026 (4) | .0084 (26) | .0014 (7) | .0011 (17) | .0014 (8) | 2.23 |
| O (8) | .0083 (18) | .0033 (4) | .0095 (28) | .0013 (7) | .0030 (17) | .0009 (9) | 2.55 |
| O (9) | .0261 (28) | .0027 (4) | .0094 (30) | .0023 (9) | -.0001 (23) | -.0002 (9) | 3.64 |
| O (10) | .0086 (19) | .0029 (4) | .0100 (28) | .0012 (7) | -.0001 (18) | .0001 (9) | 2.55 |
| O (11) | .0094 (19) | .0040 (5) | .0093 (28) | .0009 (8) | .0039 (18) | .0011 (9) | 2.92 |
| O (12) | .0119 (20) | .0020 (3) | .0109 (27) | .0017 (7) | .0009 (18) | .0011 (8) | 2.36 |
| OH (13) | .0083 (18) | .0030 (4) | .0118 (28) | .0017 (7) | .0003 (18) | .0016 (9) | 2.63 |
| H ₂ O (14) | .0112 (21) | .0028 (4) | .0091 (30) | -.0003 (8) | .0016 (19) | .0005 (9) | 2.66 |
| (15) | .0139 (21) | .0031 (4) | .0150 (31) | .0022 (8) | .0030 (20) | .0012 (10) | 3.19 |
| (16) | .0373 (49) | .0066 (8) | .0389 (56) | .0023 (18) | -.0009 (42) | -.0026 (18) | 8.33 |
| (17) | .0114 (20) | .0025 (4) | .0136 (29) | .0018 (7) | .0010 (19) | .0009 (9) | 2.73 |
| (18) | .0500 (60) | .0071 (9) | .0369 (57) | .0009 (21) | .0116 (44) | .0003 (19) | 8.99 |
| H ₂ O (19) | .0127 (20) | .0027 (4) | .0115 (28) | .0003 (8) | .0045 (18) | -.0006 (9) | 2.77 |
| (20) | .0302 (43) | .0053 (8) | .0507 (62) | .0012 (16) | -.0022 (43) | .0015 (18) | 8.11 |
| (21) | .0315 (39) | .0049 (7) | .0321 (45) | .0013 (14) | .0051 (33) | -.0016 (14) | 6.56 |
| (22) | .0139 (20) | .0028 (4) | .0144 (29) | .0022 (7) | .0072 (19) | -.0000 (9) | 2.94 |
| (23) | .0524 (61) | .0061 (9) | .0430 (61) | .0040 (20) | .0086 (50) | .0043 (19) | 8.97 |

* The anisotropic temperature factors are in the form :

$$T = \exp \left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \right].$$

The complex formed by X octahedra and H₂O(21) and H₂O(23) molecules bridges two iron-sulfur chains through hydrogen bonds. Furthermore adjacent chains are interlinked by hydrogen bonds, both directly and through the H₂O(22) molecules.

The structure accounts for the perfect {010} cleavage.

Comparison With Alcaparrosa Copiapite and Conclusions

The crystal structure analysis of Coso Hot Spring copiapite show analogies and differences with respect to that reported by Süssé (1970) for Alcaparrosa copiapite. Configuration of ligands about iron and X octahedra is equal for both structures. The general atomic arrangement is similar, the structure proposed by Süssé consisting of chains of sulfur and iron coordination polyhedra, isolated magnesium octahedra, and free water molecules building up a complex system of hydrogen bonds. However, a comparison of atomic coordinates reveals significant changes in the positions of all atoms: deviations mainly concern the x and z coordinates, while y coordinates are approximately in agreement. These

deviations produce a different reciprocal orientation of octahedra and tetrahedra, even if the packing of polyhedra is not greatly affected. In the atomic arrangement the main change concerns the orientation of the X octahedron and the location of water molecules H₂O(22) between the chains. Of course these displacements affect the system of hydrogen bonding, which differs noticeably between the two structures.

These structural differences could be expected on the basis of the different chemical cell content and lattice parameters. Since crystal elements found by Süssé closely agree with those for pseudocopiapite by Ungemach and by Berry, the magnesiocopiapite investigated by Süssé may be a pseudocopiapite. This agrees with the suggestions of Berry—based on optics—that pseudocopiapite is probably a magnesio- or a ferro-copiapite. On this assumption copiapite and pseudocopiapite can be considered two stereoisomerically distinct mineralogical species. In confirmation of this hypothesis, we observe that, despite the large range in composition of copiapites, a continuous variation in lattice parameters between the limits found for copiapite and pseudocopiapite is

TABLE 5. Bond Lengths, with Standard Deviations

| Atoms bonded* | Bond lengths (Å) |
|---------------------------------|------------------|
| X(I)-H ₂ O(16) (III) | 1.93 (2) ** |
| -H ₂ O(18) (II) | 1.97 (2) ** |
| -H ₂ O(20) (I) | 1.90 (2) ** |
| Fe(1) (I)-O(3) (IV) | 2.02 (1) |
| -O(7) (I) | 1.98 (1) |
| -O(12) (I) | 2.00 (1) |
| -OH(13) (V) | 1.96 (1) |
| -H ₂ O(14) (I) | 2.02 (1) |
| -H ₂ O(15) (I) | 2.05 (1) |
| Fe(2) (I)-O(1) (VI) | 1.98 (1) |
| -O(5) (V) | 2.06 (1) |
| -O(10) (I) | 1.95 (1) |
| -OH(13) (I) | 1.94 (1) |
| -H ₂ O(17) (I) | 2.05 (1) |
| -H ₂ O(19) (I) | 2.04 (1) |
| S(1) (I)-O(1) (I) | 1.52 (1) |
| -O(2) (I) | 1.43 (1) |
| -O(3) (V) | 1.46 (1) |
| -O(4) (V) | 1.45 (1) |
| S(2) (I)-O(5) (I) | 1.49 (1) |
| -O(6) (I) | 1.43 (1) |
| -O(7) (I) | 1.47 (1) |
| -O(8) (I) | 1.44 (1) |
| S(3) (I)-O(9) (I) | 1.40 (1) |
| -O(10) (V) | 1.47 (1) |
| -O(11) (I) | 1.46 (1) |
| -O(12) (I) | 1.52 (1) |

* The Roman numerals designate coordinates for the atoms as follows:

| | |
|-------------------|---------------------|
| (I) x, y, z | (VII) 2-x, 1-y, 1-z |
| (II) x, y-1, z-1 | (VIII) 1-x, 1-y, -z |
| (III) x, y-1, z | (IX) x-1, y, z |
| (IV) 1+x, y, z | (X) 1-x, 2-y, 1-z |
| (V) 1-x, 1-y, 1-z | (XI) x, y, -1+z |
| (VI) x, y, 1+z | |

** Two such symmetrically equivalent bonds are present.

not reported in literature. This can be seen in Table 9, where crystal data for several copiapites are listed. Moreover, this table shows the impossibility, until now, of relating chemical data with the two different sets of lattice parameters.

However, in our opinion, the problem of the relationships between chemical data and atomic arrangement still remains open. It would be interesting to verify with new data whether the copiapite and pseudocopiapite structures are typical of certain compositions or whether they merely represent two polymorphic forms.

The following crystal chemical considerations can be derived from the results of the structural analysis of Coso Hot Spring copiapite:

1) the possibility of a wide range of substitution, mainly in the X position, where the coordination polyhedron is only weakly connected to the

structural chain motif, is fully explained. This confirms the observations on other iron sulphates, that Al-Fe substitution occurs preferentially in X(H₂O)₆ isolated octahedra.

2) The ratio O/X = 1, regarded as the most probable one for copiapites on the basis of a large number of chemical analyses, is struc-

TABLE 6. Bond Angles, with their Standard Deviations

| Atom trio forming angle* | Angle(degrees) |
|---|----------------|
| H ₂ O(16) (III)-X(I)-H ₂ O(18) (II) | 89.3 (9) |
| -H ₂ O(20) (I) | 90.0 (9) |
| H ₂ O(18) (II)-X(I)-H ₂ O(20) (I) | 93.0 (9) |
| O(3) (IV)-Fe(1) (I)-O(7) (I) | 85.2 (5) |
| -O(12) (I) | 86.9 (5) |
| -OH(13) (V) | 174.2 (5) |
| -H ₂ O(14) (I) | 96.7 (5) |
| -H ₂ O(15) (I) | 89.3 (5) |
| O(7) (I)-Fe(1) (I)-O(12) (I) | 93.1 (5) |
| -OH(13) (V) | 89.0 (5) |
| -H ₂ O(14) (I) | 176.2 (5) |
| -H ₂ O(15) (I) | 87.9 (5) |
| O(12) (I)-Fe(1) (I)-OH(13) (V) | 93.6 (5) |
| -H ₂ O(14) (I) | 90.3 (5) |
| -H ₂ O(15) (I) | 176.0 (5) |
| OH(13) (V)-Fe(1) (I)-H ₂ O(14) (I) | 89.0 (5) |
| -H ₂ O(15) (I) | 90.3 (5) |
| H ₂ O(14) (I)-Fe(1) (I)-H ₂ O(15) (I) | 88.9 (5) |
| O(1) (VI)-Fe(2) (I)-O(5) (V) | 85.0 (5) |
| -O(10) (I) | 90.9 (5) |
| -OH(13) (I) | 175.6 (5) |
| -H ₂ O(17) (I) | 86.4 (5) |
| -H ₂ O(19) (I) | 92.0 (5) |
| O(5) (V)-Fe(2) (I)-O(10) (I) | 91.1 (5) |
| -OH(13) (I) | 92.8 (5) |
| -H ₂ O(17) (I) | 87.2 (5) |
| -H ₂ O(19) (I) | 175.2 (5) |
| O(10) (I)-Fe(2) (I)-OH(13) (I) | 93.0 (5) |
| -H ₂ O(17) (I) | 176.9 (5) |
| -H ₂ O(19) (I) | 92.6 (5) |
| OH(13) (I)-Fe(2) (I)-H ₂ O(17) (I) | 89.7 (5) |
| -H ₂ O(19) (I) | 89.9 (5) |
| H ₂ O(17) (I)-Fe(2) (I)-H ₂ O(19) (I) | 88.9 (5) |
| O(1) (I)-S(1) (I)-O(2) (I) | 109.4 (7) |
| -O(3) (V) | 105.8 (7) |
| -O(4) (V) | 112.4 (7) |
| O(2) (I)-S(1) (I)-O(3) (V) | 109.0 (7) |
| -O(4) (V) | 110.7 (7) |
| O(3) (V)-S(1) (I)-O(4) (V) | 109.5 (7) |
| O(5) (I)-S(2) (I)-O(6) (I) | 109.6 (7) |
| -O(7) (I) | 110.9 (7) |
| -O(8) (I) | 106.5 (7) |
| O(6) (I)-S(2) (I)-O(7) (I) | 110.9 (7) |
| -O(8) (I) | 111.2 (7) |
| O(7) (I)-S(2) (I)-O(8) (I) | 107.6 (7) |
| O(9) (I)-S(3) (I)-O(10) (V) | 110.3 (7) |
| -O(11) (I) | 113.3 (7) |
| -O(12) (I) | 107.0 (7) |
| O(10) (V)-S(3) (I)-O(11) (I) | 110.1 (7) |
| -O(12) (I) | 107.6 (7) |
| O(11) (I)-S(3) (I)-O(12) (I) | 108.2 (7) |

* See footnote to Table 5.

TABLE 7. Supposed Hydrogen Bond Lengths

| Presumed hydrogen bond* | | | Length |
|---------------------------|-----|---------------------------------|--------|
| OH(13) (I) | - H | H ₂ O (22) (I) | 2.76 Å |
| H ₂ O (14) (I) | - H | O (2) (V) | 2.71 |
| | - H | O (11) (VI) | 2.70 |
| H ₂ O (15) (I) | - H | O (6) (VII) | 2.68 |
| | - H | O (8) (VI) | 2.63 |
| H ₂ O (16) (I) | - H | O (9) (VIII) | 2.94 |
| | - H | H ₂ O (23) (V) | 2.58 |
| H ₂ O (17) (I) | - H | H ₂ O (8) (VII) | 2.73 |
| | - H | H ₂ O (22) (V) | 2.69 |
| H ₂ O (18) (I) | - H | H ₂ O (21) (IX) | 2.61 |
| | - H | H ₂ O (21) (X) | 2.71 |
| H ₂ O (19) (I) | - H | O (3) (V) | 2.99 |
| | - H | O (11) (VII) | 2.81 |
| H ₂ O (20) (I) | - H | O (4) (XI) | 2.67 |
| | - H | O (9) (I) | 2.82 |
| H ₂ O (21) (I) | - H | O (2) (I) | 2.78 |
| | - H | H ₂ O (23) (V) | 2.95 |
| H ₂ O (22) (I) | - H | O (5) (VIII) | 3.03 |
| | - H | O (6) (I) | 2.74 |
| H ₂ O (23) (I) | - H | O (12) (I) | 2.99 |

* See footnote to Table 5.

turally confirmed; when X is a trivalent cation, lattice vacancies are observed to maintain the total positive charge in the X position at approximately 2.

TABLE 8. Balance of Electrostatic Valences for Oxygen Atoms*

| | S | X | Fe | -H | -H... | ...H- | Total |
|----------------------|-----|-----|--------|----|--------|--------|-------|
| O(1) | 3/2 | | 1/2 | | | | 2 |
| O(2) | 3/2 | | | | | 1/6 x2 | 2-1/6 |
| O(3) | 3/2 | | 1/2 | | | 1/6 | 2+1/6 |
| O(4) | 3/2 | | | | | 1/6 | 2-1/3 |
| O(5) | 3/2 | | 1/2 | | | 1/6 | 2+1/6 |
| O(6) | 3/2 | | | | | 1/6 x2 | 2-1/6 |
| O(7) | 3/2 | | 1/2 | | | | 2 |
| O(8) | 3/2 | | | | | 1/6 x2 | 2-1/6 |
| O(9) | 3/2 | | | | | 1/6 x2 | 2-1/6 |
| O(10) | 3/2 | | 1/2 | | | | 2 |
| O(11) | 3/2 | | | | | 1/6 x2 | 2-1/6 |
| O(12) | 3/2 | | 1/2 | | | 1/6 | 2+1/6 |
| OH(13) | | | 1/2 x2 | | 5/6 | | 2-1/6 |
| H ₂ O(14) | | | 1/2 | | 5/6 x2 | | 2+1/6 |
| (15) | | | 1/2 | | 5/6 x2 | | 2+1/6 |
| (16) | | 1/3 | | | 5/6 x2 | | 2 |
| (17) | | | 1/2 | | 5/6 x2 | | 2+1/6 |
| (18) | | 1/3 | | | 5/6 x2 | | 2 |
| H ₂ O(19) | | | 1/2 | | 5/6 x2 | | 2+1/6 |
| (20) | | 1/3 | | | 5/6 x2 | | 2 |
| (21) | | | | | 5/6 x2 | 1/6 x2 | 2 |
| (22) | | | | | 5/6 x2 | 1/6 x2 | 2 |
| (23) | | | | I | 5/6 | 1/6 x2 | 2+1/6 |

* X was assumed to be one oxygen equivalent.

3) The water content limit of copiapite is 20 molecules per cell. The occurrence of "free" water molecules justifies the possibility of partial dehydration, as suggested by chemical analyses, without significant damage in the framework.

TABLE 9. Crystallographic Data for Copiapites

| Morphological data | | | | X-ray data | | | Ref.* | |
|--------------------|---------|---------|---------|--|--------|-------|-----------------------|-----|
| a:b:c | α | β | γ | a(Å) | b(Å) | c(Å) | | |
| 0.4005:1:0.3971 | 93°58½' | 102°08' | 98°50' | Fe _{0.90} Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ ·20.0 H ₂ O | | | (1) | |
| 0.4058:1:0.4039 | 93°50' | 102°10' | 99°21½' | 7.34 | 18.19 | 7.28 | 93°51' 101°30' 99°23' | (2) |
| | | | | (Zn _{0.75} Fe _{0.07} Mn _{0.06} Ca _{0.04} K _{0.04} Na _{0.02})Fe _{3.70} (SO ₄) ₆ (OH) _{1.10} ·17.30 H ₂ O | | | (3) | |
| | | | | 7.35 | 18.16 | 7.28 | 93°50' 101°30' 99°22' | |
| | | | | (Mg _{0.59} Co _{0.03} Fe _{0.03} Cu _{0.02} Al _{0.30}) (Fe _{0.89} Al _{0.11}) ₄ (SO ₄) ₆ (OH) _{2.24} ·19.46 H ₂ O | | | (4) | |
| | | | | 7.251 | 18.161 | 7.267 | 94°00' 102°17' 97°58' | |
| | | | | (Fe _{0.43} Al _{0.23} Zn _{0.03})Fe ₄ ³⁺ (SO ₄) ₆ (OH) _{2.04} ·18.78 H ₂ O | | | (5) | |
| | | | | 7.390 | 18.213 | 7.290 | 93°40' 102°03' 99°16' | |
| 0.3938:1:0.3951 | 91°18½' | 102°04' | 98°59' | pseudocopiapite | | | (6) | |
| 0.4007:1:0.4005 | 91 22' | 102°22' | 98°50' | pseudocopiapite | | | (7) | |
| | | | | MgFe ₄ (OH) ₂ (SO ₄) ₆ ·20 H ₂ O | | | (8) | |
| | | | | 7.37 | 18.89 | 7.42 | 91°18' 102°24' 98°59' | |
| | | | | (Fe _{0.06} Al _{0.41})(Fe _{0.98} Al _{0.02}) ₄ (SO ₄) ₆ (OH) _{1.35} ·18.66 H ₂ O | | | (9) | |
| | | | | 7.312 | 18.650 | 7.337 | 91°12' 102°06' 98°49' | |

* Reference: (1) From Sierra Gorda, Chile (Ungemach,1935). (2) From Chuquicamata, Chile (Palache et al.,1946).Analyst Gonyer. (3) From Tsaidam Basin, China (Kuang et al.,1964).Chemical formula recalculated assuming 6 SO₄ groups in the unit cell. (4) From Mosquito Fork, Alaska (Jolly and Foster, 1967). (5) From Coso Hot Spring, California (present study). (6) From Tierra Amarilla, Chile (Ungemach,1935).No analysis available. (7) From Tierra Amarilla, Chile (Berry,1938). No analysis available. (8) From Alcaparrosa, Chile (Sasse,1970).No detailed analysis available. The cell content is probably idealized. (9) From Ritorto, Italy (Garavelli, private communication).

Temperature factors seem to indicate that the more movable of them are H₂O(21) and H₂O(23), and the three molecules bonded to the X cation. This result agrees with the data by Süsse for Alcaparrosa crystals.

Note Added in Proof. In 1972 Süsse published the final results of his study on copiapite (*Z. Kristallogr.* **135**, 34–55). Since no significant differences from the preliminary study occur, considerations developed in the present paper are still valid.

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