SULPHATE INCRUSTATIONS IN THE COPPER QUEEN MINE, BISBEE, ARIZONA

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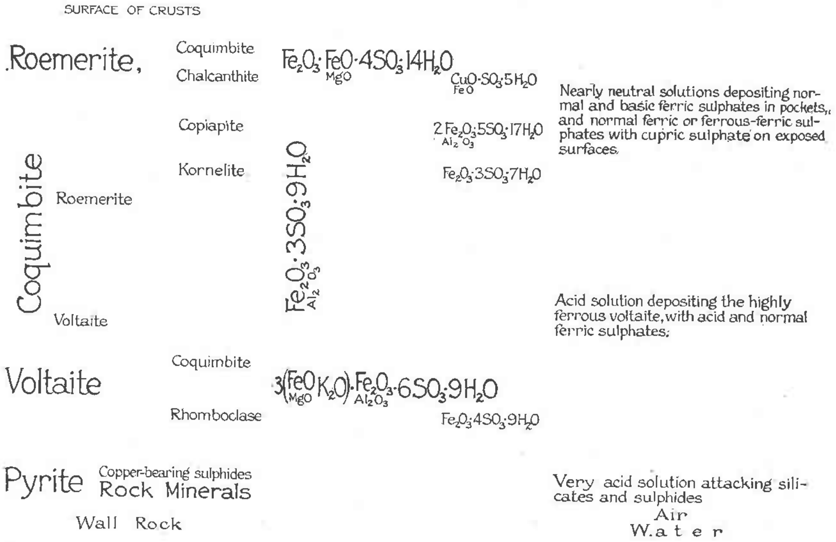
Through the courtesy of Dr. Augustus Locke the geologists of the Phelps Dodge Corporation sent us several incrustations from the walls of the Copper Queen Mine, Bisbee, Arizona. The crusts were described as usually moist but not dripping, and as formed at a temperature of about 32°C. (90°F.). The adherent wall rock is silicified porphyry and minutely impregnated with pyrite and small amounts of copper-bearing sulphides.

The crusts are irregular porous excrescences several inches thick with constituent minerals generally in a grading zonal order. The minerals are sulphates, and four of them typical ferric salts.



Theoretically, at ordinary temperatures in presence of water and oxygen, the complete oxidation of pyrite gives acid ferric sulphate which may crystallize completely to the mineral rhomboclase, $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. But in general oxidation of the iron lags behind oxidation of the sulphur, and a mixture is produced of ferrous and ferric sulphates and sulphuric acid. With mineralized wall rock present, the acid brings into solution other bases, which process lowers the acidity of the solutions. From the resulting complex solutions several minerals may form, as shown schematically for these incrustations in the accompanying chart.

Three general sets of minerals are recognized. In the set adjacent to the oxidizing pyrite and the wall rock the minerals are most acid and least oxidized and little ferric iron is present in the surrounding solution; in the set at the surface of the crusts the minerals are least acid (or even basic) and most oxidized and the solutions most concentrated; in the middle set acidity and oxidation are intermediate. Oxidation and acidity are directly related, for ferric iron combines with more sulphate ions than did the ferrous iron from which it was derived. The ferric sulphates here present are known to crystallize from solutions that are more acid than the crystals themselves. Thus the solutions that occasionally drip or flow from the porous crusts carry away some excess acid. A knowledge of the concentrations of acid and ferric oxide necessary for the growth of each of the four ferric minerals aids in an explanatory description of the formation of the other minerals.

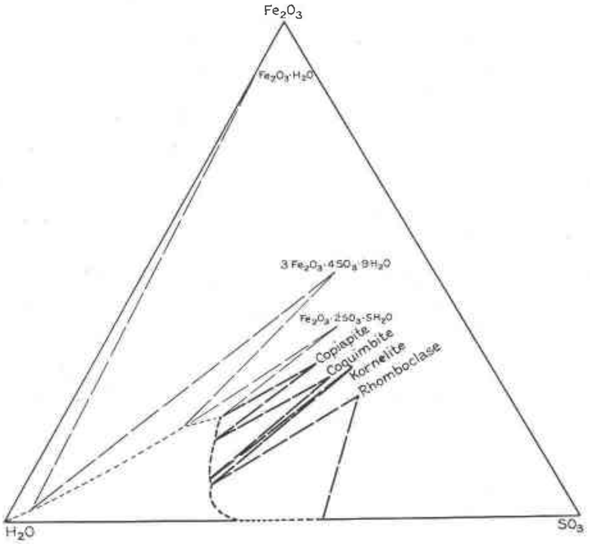


FIG. 1. The system, $Fe_2O_3-SO_3-H_2O$, between 30° and 40°. An extrapolation based on data by F. Wirth and B. Bakke (1914) at 25°, and those of E. Posnjak and H. E Merwin (1922).

The latest of several studies of the synthetic formation of ferric sulphates at ordinary temperatures (25°C.) was made by Baskerville and Cameron (1935)—who give a bibliography—but usually the characteristics of the crystals produced are entirely confined to chemical formulas arrived at indirectly. For temperatures of 50 to 200°C. the crystalline phases are better known—see Posnjak and Merwin (1922). By interpolation, approximate solubility relationships of the various crystalline ferric compounds near the temperatures at which the minerals formed in the mine, are shown in Fig. 1. The clear cuspate area in the lower left represents solutions that are unsaturated. At its dotted boundaries crystals appear, and become more abundant outward. In each wedge-shaped area one crystalline phase, with composition represented by the point of the wedge, is stable in contact with the solutions at the head of the wedge. Only that part of the diagram is now considered that is in bold outline.

Rhomboclase is the least soluble of these sulphates and forms from the most acid solutions. Doubtless this mineral in the incrustations crystallized from solutions near the upper limit of its solubility. Similar ratios of acid to ferric oxide must apply to the accompanying highly ferrous voltaite, for the ferrous and potassium sulphates in solution could affect this condition but little.

Coquimbite is the most abundant mineral of the crusts. Synthetically it was not found at 50°C., but at lower temperatures Scharizer (1906) prepared crystals of normal ferric sulphate, for which an analysis indicated a 9-hydrate, having crystallographic and optical properties characteristic of natural coquimbite. Applebey and Wilkes (1922) considered that their crystals, which T. V. Barker found to be like coquimbite crystallographically, were a 7-hydrate. Analyses of the natural mineral are in poor agreement as to 9 mols. of water. Roemerite, which contains much less ferrous iron than voltaite, is abundant, and forms chiefly under the same conditions as coquimbite: (1) in solution the ratio of acid to ferric oxide is less than for voltaite and rhomboclase; (2) likewise the amount of ferric oxide in solution is greater. Both of these conditions result from oxidation of ferrous sulphate, and from occasional washing away of interstitial acid solution, especially during the early stages of crust formation.

The mineral designated as kornelite is a lower hydrate of normal ferric sulphate than coquimbite. In synthetic experiments it was found to occupy a considerable field at 50°C., and two indirect analyses indicated a 7-hydrate. Identity of the crystals in the crusts with those prepared at 50°C. was established in detail microscopically.[1] At 25°C. Baskerville and Cameron (1935) by indirect analyses of synthetic products having unknown physical properties have inferred an 8-hydrate. The original kornelite of Krenner (1888) was supposed to be orthorhombic and contain $7\frac{1}{2}$ mols. of water. Schaller (1931) has reported a new occurrence of the mineral but has not yet published the details. Larsen and Berman's

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[1] Delicate, very pale violet-colored tufts of laths with twin lamellae parallel to the long thin edges, symmetrical extinctions of 18°; elongation α; γ normal to plane of flattening; cleavage nearly normal to α; α 1.572, β 1.548, γ 1.639.

(1934) tables list the properties of the mineral essentially like those of the 7-hydrate but give the composition as 8-hydrate. Kornelite is a very minor constituent of the Bisbee incrustations. Solutions only rarely maintain the proper concentrations for its growth, as indicated by a narrow field in Fig. 1.

Copiapite is a basic ferric sulphate, but it also crystalizes from solutions containing more acid with respect to ferric oxide than do the crystals. However, at 50°C., the ratio of acid to ferric oxide in the solution may be either greater or less than the "normal" ratio, $SO_3:Fe_2O_3=3:1$, which may be considered as the neutrality ratio. Copiapites, so called, differ in habit, optical properties, and composition. The causes of the variations have been little studied, but the name should not be applied to a mineral that is not bright yellow in powder unless modification of such yellow by chromophoric substitution can be established.

Chalcanthite occurs in the outer parts of the crusts. It is but a small proportion of the total incrustation, and its presence is due to concentration of copper in the solutions as they approach the evaporation surface.

These processes of crust formation may now be contrasted with processes of leaching near the surface of the ground of oxidizing pyritic ore bodies. As solutions such as those already described begin to accumulate around pyrite which is oxidizing in a rock matrix, two other processes are active; one is the lowering of acidity by reaction with bases of the rock, and the other is intermittent dilution. These processes lead to the formation of jarosites which are analogues of the basic salt $3Fe_2O_3\cdot 4SO_3\cdot 9H_2O$ of Fig. 1[2] and through them—or directly—to the usual ultimate product, a limonitic form of goethite, in the "iron hat" overlying the pyritic ore body.

In measuring indices of refraction of immersed grains, the matching for the apparent principal indices was checked by using a very narrow beam of light incident at all the angles in the chief plane of extinction that the objective would admit. Use was made of a sliding diaphram with a single aperture about 0.5 mm diameter as close as possible to the open condenser iris.

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[2] Baskerville and Cameron (1935) state that solutions containing 26.4 per cent SO_3 deposit at 25°C. one continuous series of solid solutions between ferric oxide probably somewhat hydrated and the other probably approaching in composition the basic salt $Fe_2O_3\cdot 2.5SO_3\cdot 7H_2O$. According to the model for the system, $Fe_2O_3-SO_3-H_2O$, between 200 and 50°C., Posnjak and Merwin (1922), it seems more than improbable that the fields of stability of the more basic salts, would almost suddenly—over a 25°C. interval—be transformed into a single field for a single series of solid solutions. The interpretation of Baskerville and Cameron does not appear to follow necessarily from their data.

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