THE SULFUR HOLE, CALICO DISTRICT, SAN BERNARDINO COUNTY, CALIFORNIA

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Discovered by local borax miners in the 1880's as a possible source of agriculture sulfur, the Sulfur Hole has produced an attractive suite of well-crystallized, colorful hydrous sulfates including coquimbite, halotrichite, krausite, metavoltine, potassium alum, quenstedtite, römerite and voltaite. Associated minerals include botryogen, copiapite, anhydrite, gypsum, melanterite, marcasite, and sulfur.

INTRODUCTION

The Sulfur Hole has long been known by California collectors as a source of rare hydrous iron-potassium-aluminum sulfate minerals. These minerals occur in a columnar pipe that formed by ascending iron-bearing acidic hot fluids acting on the underlying volcanic rocks. Fine crystallized specimens of coquimbite, krausite, metavoltine, quenstedtite and voltaite have been collected here and the potassium iron sulfate krausite was first described as a new mineral from this locality. Potassium alum, also new to this locality, has been recently found as small brilliant octahedral crystals.

While the Sulfur Hole locality is well known to serious, older collectors, its remote location and lack of identifying landmarks have hindered the study of the locality. The site is located on the south wall of Mule Canyon in a shallow unobtrusive cleft against the wall with only a faint trail leading to it. The area is north

1

of the old borax claims near the old site of Borate in the Calico Hills and about 4 miles northeast of the town of Yermo, San
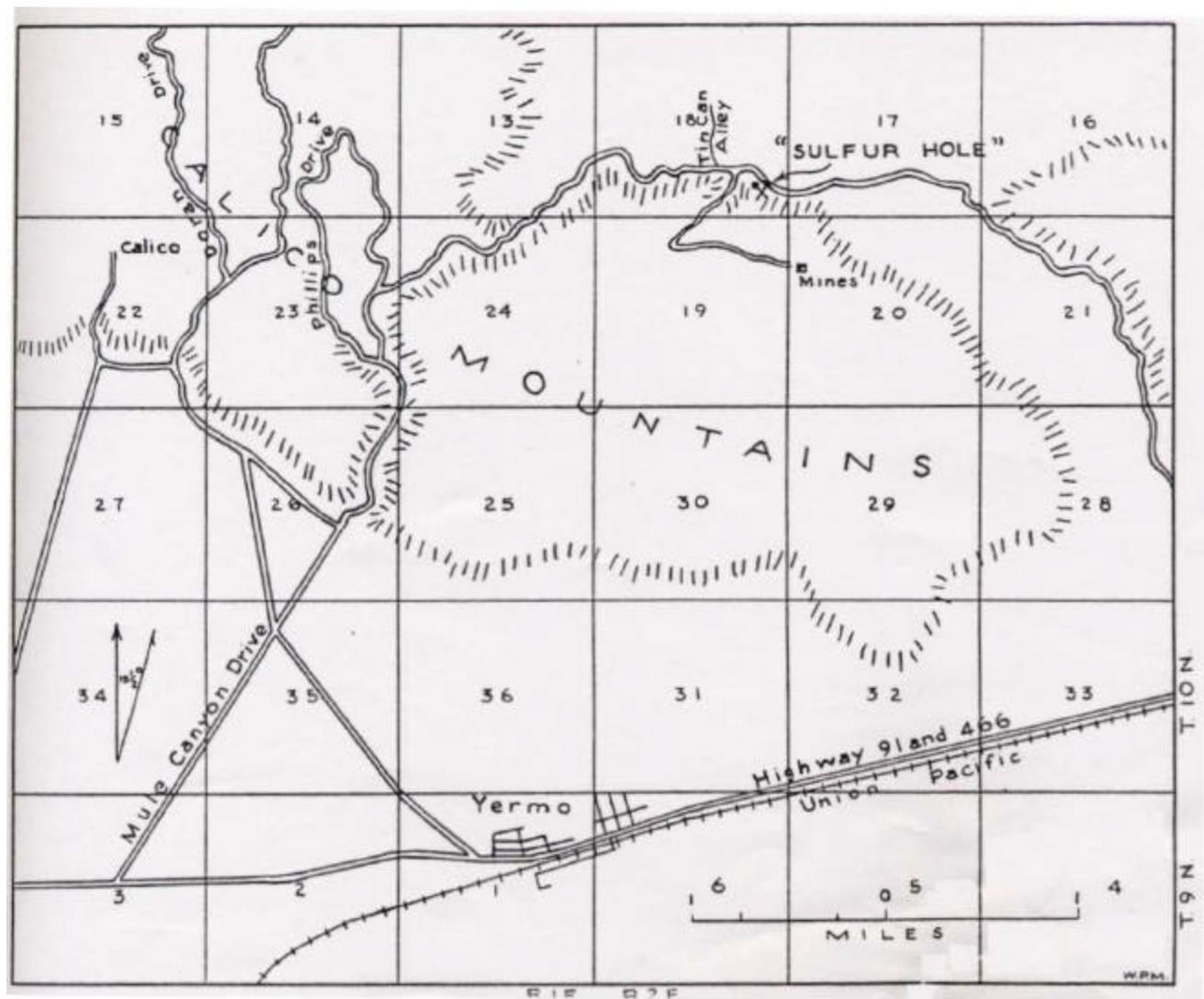

Figure 1. Map showing the location of the Sulfur Hole in the Calico Mountains, San Bernardino County, California. (After Moller, 1963a).

Bernardino County in SE¼ of SE¼ of Section 18, T. 10N, R. 2E, San Bernardino Meridian or at 34° 57' N, 116° 49' W. The cleft containing the Sulfur Hole is not readily apparent and the sulfates are not normally exposed at the surface to mark the locality. To collect requires digging down to the sulfate body through the accumulated debris.

AREA HISTORY

The first mining interest in the area began in the 1860's with the discovery of rich silver ores in the hills above the small town of Calico. Calico quickly became a major silver producer and remained so for over

20 years. As the silver rush faded and the mines went into decline, prospectors searched the nearby lower hills for other profitable mineral deposits.

The colemanite deposits at Borate in the Calico Hills were discovered in 1883, and while these deposits were neither as large or as rich as the famed Death Valley borax deposits, they were able to successfully compete with them because of the primitive transportation system from Death Valley. Because of their proximity to the railroad shipping point at Dagget, the colemanite ores of Borate did not require the use of the famed "20 mule team" wagons that the Death Valley ores used and therefore, the small coyote hole diggings could be profitably worked. When the railroad reached Death Valley, the Borate colemanite ores became marginal and, as the easily mined ore had been removed, production at Borate declined until only a handful of miners still remained.

After the end of World War I, interest in the area was rekindled in the district and William F. Foshag of the U. S. National Museum examined the area as part of his study of the colemanite deposits of California. The borax deposits were still being worked in a desultory manner and local prospectors told Foshag of the unusual "Sulfur Hole" nearby. Foshag visited the locality and described the unusual mineralogy of the area including the new potassium iron sulfate, krausite (Foshag, 1931).

GEOLOGY

The geological features of the area have been described by Erwin and Gardner (1940) and are summarized here. The Calico Mountains are a rugged landscape of steep slopes supporting sparse vegetation with volcanic flows creating bold outcrops of hard, resistant material. They are composed of a series of Miocene sedimentary beds that are underlain by andesites and rhyolite tuffs. These sedimentary rocks have been entirely removed in the western portion of the area and the exposed multicolored volcanic rocks gave the district it's name, Calico, after the multicolored fabric. The eastern portion of the district is covered by remnants of the sediments that are composed of a series of sandstones, shales, marls and algal limestones that rest on the basement volcanic rocks. These sediments were originally deposited in a fresh water lake environment and concretionary nodules found in the area often contain fossil insects.

Hot springs have acted on the sedimentary rocks. In the upper limestone and marl beds, they formed the deposits containing nodules of colemanite associated with ulexite, celestite and strontianite. Lower in the series the sediments have been partially silicified and a series of chert and shale beds have been produced. The difference in metamorphism is apparently due to the porosity of the individual beds. Foshag (1922) found no apparent connection between the lower more silicic beds and the upper borate bearing limestones and marls. The relationship between the deposition of the sulfates in the shales and the colemanite bodies found in the marly limestones is not known.

According to Erwin and Gardner (1940), the rocks of the Calicos are predominantly middle Tertiary volcanics and lakebed deposits with remnants of a late Tertiary lava flow capping the numerous prominences.

Two major groups of volcanics have been recognized. These have been designated as the Tuff Series and the Lava Agglomerate Series, the latter being the younger. The former series are composed of red,

brown and gray rhyolitic and andesitic tuffs that exhibit both massive and bedded sections. They are especially well-exposed in the southern and western parts of the Calico Hills.

The Lava Agglomerate Series consists of red-brown to chocolate-brown lava flows and agglomerate beds which have been altered in part by hydrothermal activity to yield areas of greenish gray rock. A light purple vesicular dacite has also been included with this group, which is most conspicuous in the south central area of the Calicos. The uppermost 160 meters of the series is largely sedimentary, consisting of sandstone, highly fractured tuffs, agglomerate and conglomerate members, and reworked detrital gravels of Terteriary age.

Resting conformably upon the agglomerates are arkosic sand*stone*, argillaceous shales and tuffs along with two related igneous rocks and several members of hard, banded cherts that are designated Post-Volcanic Sedimentary Series. They are particularly apparent at the Sulfur Hole where the rocks surrounding the zone of sulfate deposition are chert members. Immediately above the chert are beds of dense arkosic sandstone and shale surmounted by light yellow tuff and a little thinly bedded shale.

With the exception of a thrust fault traceable about 1700 meters along the southern front of the range, normal faulting outlines the Calico Mountains. Their main orogeny appears to be post-Lower Pliocene, although evidence of tectonic movements has been found which antedates that time.

Sofataric activity that produced the various sulfate minerals has been controlled largely by two fracture zones that produced numerous episodes of earth movement. The initial movement was along a fracture zone essentially perpendicular to the strike of the sediments and vertical to the bedding planes. The surface exposure of this fault is partially covered by a mantle of recently eroded rock that covers the surface, but it may be observed easily approximately 70 meters east of the Sulfur Hole, where the bedding changes abruptly from nearly perpendicular, as exhibited at the hole, to approximately horizontal with only a moderate dip southward. The second generation of deformation was a thrust fault parallel to the bedding planes that produced a vertical a displacement of unknown magnitude. Small fracture zones and drag folds may be observed in the vicinity of the Sulfur Hole.

The sulfates at the Sulfur Hole were formed as a result of low temperature aqueous acidic sulfate-bearing solutions that percolated through the hot volcanic rocks and attacked existing iron sulfides. These solutions were rich in ferrous and ferric iron and also contained leeched magnesium, potassium, sodium and aluminum from the underlying rock formations. The existing fault produced a fracture system that allowed the upward migration of these heated, highly acidic iron-rich solutions. Changes in temperature, pressure and pH allowed the formation of the various sulfate minerals.

DESCRIPTION OF THE SULFUR HOLE

The sulfates occur in pod-like masses up to several meters across in area of fractured shale that is cemented by white granular coquimbite. It is interesting to note that the sulfates in this deposit show a zoning pattern and that the material the authors found show a similar pattern to that mentioned by Foshag (1931) in his original paper.

Foshag estimated the original thickness of the exposed sulfates to be less than 3 meters and noted that the minerals were roughly zoned, with massive coquimbite occupying the footwall and grading into sugary granular coquimbite, while the hanging wall was composed of a mixed group of iron sulfates that became more acidic as the bottom edge of the deposit was neared.

The major portion of the sulfate mass is composed of granular white coquimbite and this may make up to half of the pod volume. The coquimbite varies in texture from a dense white fine-grained material near the footwall that grades into a more coarse grained sugary material near the center of the pod. The fine-grained coquimbite frequently shows shrinkage cracks and these are often lined with yellow-green to gray-green krausite crystals associated with occasional patches of golden yellow metavoltine.

The most interesting of these zones for the collector was the transition zone between the coquimbite and acid iron sulfate zone where colorful well-crystallized specimens typically occurred. This transition zone varied considerably in thickness and was entirely absent in some areas. Specimens commonly were contained in a base of granular sugary-white coquimbite that often contained large crystals of purple coquimbite, green krausite, reddish-brown römerite, golden yellow metavoltine and white fibrous halotrichite. Many of the rarer minerals were formed in this zone in cavities between the römerite and coquimbite crystals.
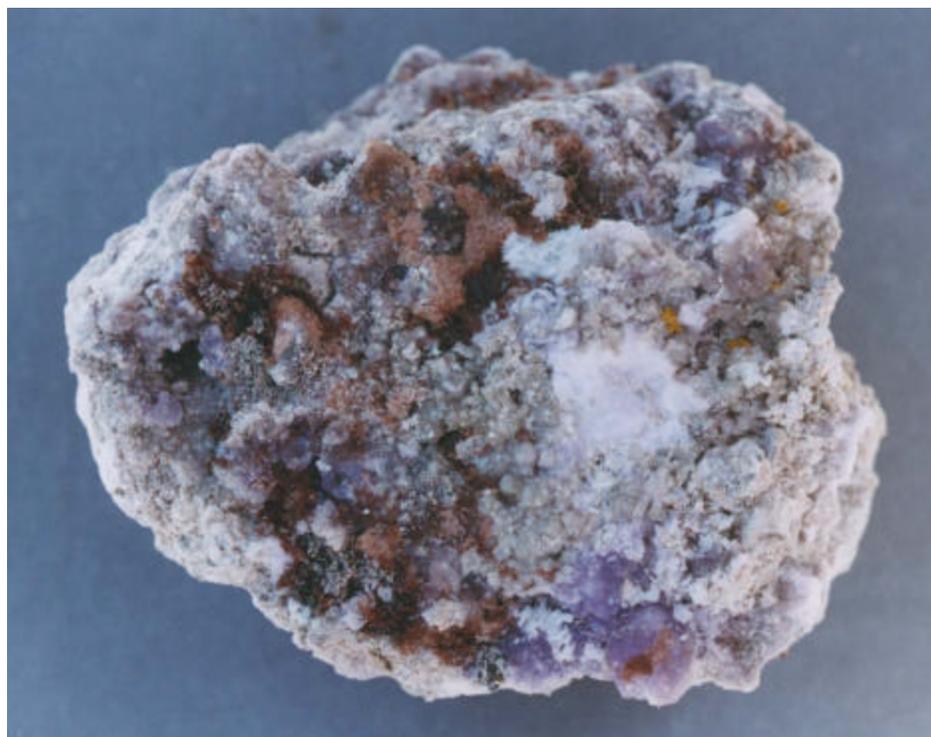

Figure 2. Hand sample, 5 x 7 cm, from the transition zone showing typical sulfate assemblage (purple coquimbite, brown römerite , gray-green krausite, and sugary-white coquimbite).

The acid iron sulfate zone near the footwall was also variable in thickness and was composed mainly of a mixture of melanterite, halotrichite, voltaite and römerite. The most abundant mineral in this zone is

römerite and granular friable masses of rough römerite crystals over 10 cm thick were found. Melanterite and halotrichite veinlets commonly cut these römerite masses and occurred as white to pale green fibrous veinlets. Pockets were not common in this zone but voids occurred in the coarsely crystalline römerite. They often contained other acid sulfates and voltaite occurred in this area both as massive material and well-crystallized masses of black cubic crystals.

At the base of the acid sulfate zone a thin discontinuous layer of loose friable sandy shale fragments was found. It was impossible to determine the extent of this layer but its absence of fines indicated that it was extremely porous. Sulfates were rare in this layer and composed mainly of minute feathery crystalline aggregates of melanterite and gypsum. Embedded in this layer were small masses of potash alum. Much of this material was massive but occasional pockets showed well-formed brilliant octahedral crystals.

MINERALS

Alunite(?) $K_2Al_6(SO_4)_4(OH)_{12}$

Alunite was reported by Foshag (1922) as being relatively abundant at the Sulfur Hole, occurring as white granular masses near the hanging wall. Material resembling that described by Foshag was collected by the senior authors and was found to contain only iron and sulfate. A microscopic examination revealed only granular aggregates composed of minute bipyramidal crystals of coquimbite. Alunite was not found during the present study. XRD of samples previously reported to be alunite by Moller (1963a,b) proved to be coquimbite. To date no alunite has been identified from any samples collected at the Sulfur Hole.

Anhydrite $CaSO_4$

Foshag (1931) reported anhydrite associated with gypsum in the upper section of the Sulfur Hole. It probably formed as a dehydration product of gypsum.

Botryogen $MgFe^{3+}(SO_4)_2(OH) \cdot 7H_2O$

Rare brick-red minute botryoidal groups of botryogen occur on top of sugary coquimbite. Only a few samples were found to contain botryogen and it is probably the least abundant mineral present. It was identified by its color, radiating structure and EDS spectrum.

Copiapite $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$

Copiapite occurs in the aureole surrounding the sulfate body and is locally abundant within the sulfate mass. It is a yellowish-green to yellow brown color and occurs as small patches in cavities of the coquimbite in the transition zone and is often associated with römerite. Copiapite is commonly associated with seams of gypsum and occurs as thin yellow coatings on it.

Coquimbite $Fe^{2+}Fe^{3+}_4(SO_4)_3 \cdot 9H_2O$

Coquimbite is the most abundant mineral present in the Sulfur Hole and probably makes up almost eighty percent of the sulfates present. It forms the major portion of the vein filling material and occurs as colorless to pale lilac granular masses up to a foot thick. Microscopic examination of this granular material reveals it is composed principally of minute colorless bipyramidal crystals associated with scattered small anhedral masses of coquimbite. The most common crystal forms present are the pyramidal form {1011}

6

associated with a secondary prism {1010} face. The crystals occasionally show the development of (0001) and {1120} faces but these are not common.

Near the transition zone larger coquimbite crystals start to occur and purple masses of equant crystals up to 2 cm across are relatively common. Most of the larger crystals are blocky in outline but occasional crystals that show the typical hexagonal bipyramid are also found. Although the larger crystals often show a blocky form and resemble overgrowths, paracoquimbite has not been identified from the site. Specimens of sulfate rock from the transition zone can be quite attractive and colorful with the large purple coquimbite crystals, bright yellow metavoltine, green krausite crystals and red brown römerite crystals embedded in a white granular coquimbite groundmass.
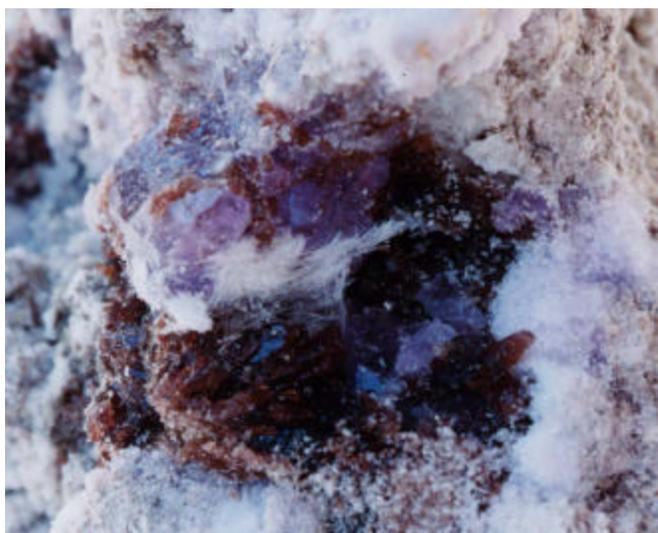

Figure 3. Purple coquimbite crystals associated with halotrichite (acicular white), römerite (dark brown) embedded in sugary-white coquimbite. 2 cm.
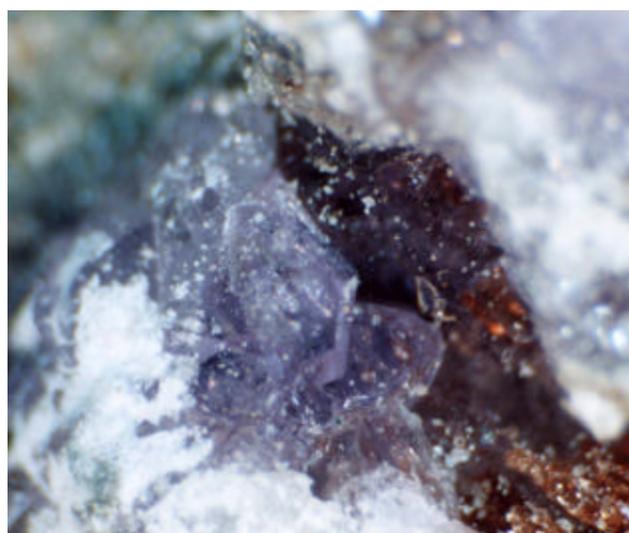

Figure 4. Typical blocky purple coquimbite crystals, to 6.8 mm, associated with brown römerite in fine-grained coquimbite.

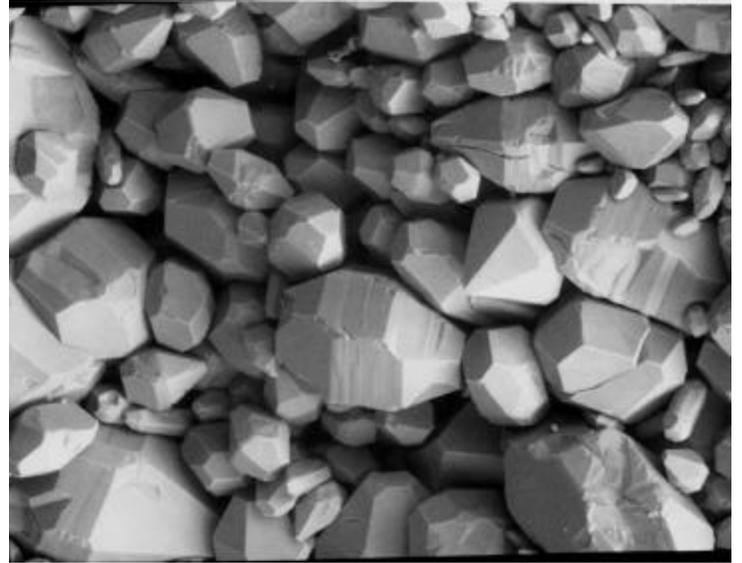**Figure 5. Bipyramidal coquimbite crystal associated with krausite on massive coquimbite. 1.7 mm.**

Figure 6. SEM photo of sugary-white coquimbite showing the bipyramidal habit of the individual crystals. 10 – 100 microns.

Fibroferrite(?) $Fe^{3+}(SO_4)(OH)^{..}5H_2O$

Fibroferrite was reported as occurring at the locality by Foshag (1922). The fibroferrite reported by Moller (1963a) was re-examined by XRD and found to be halotrichite admixed with copiapite. To date no fibroferrite has been identified from the samples collected at the Sulfur Hole.

Gypsum $CaSO_4^.2H_2O$

Gypsum occurs as isolated masses and veins of satin spar gypsum in the edge of the high iron sulfate zone near the footwall associated with copiapite. The gypsum is colorless to white, fibrous and can be up to 3 cm thick. They are often encrusted by massive yellow copiapite and fracture faces are often corroded. The gypsum shows a pale yellow fluorescence and often shows a yellow phosphorescence under short wave ultraviolet light.

Halotrichite $Fe^{2+}Al_2(SO_4)_4^.22H_2O$

Halotrichite is relatively common in the more acid rock near the footwall where it forms white fibrous veins associated with melanterite. The veins cut coarsely crystalline granular masses of römerite and are commonly intergrown with melanterite. Occasionally it is found as delicate tufts of acicular crystals in cavities associated with römerite and voltaite crystals. Halotrichite veins often grade into massive apple green melanterite and intergrowths of fibrous halotrichite and melanterite are occasionally found.

Figure 7. Sample of sulfates to 5 cm showing fibrous halotrichite vein with brown römerite .

Jarosite(?) $K_2Fe_6(SO_4)_4(OH)_{12}$

   Jarosite was reported by Foshag (1922) at the Sulfur Hole occurring as yellow coatings of minute crystals. Material resembling that described by Foshag was collected by the authors and was found to contain iron, potassium and sulfate and a microscopic examination revealed minute yellow crystals of metavoltine. To date no jarosite has been identified from the samples collected at the Sulfur Hole.

Krausite $KFe^{3+}(SO_4)_2 \cdot H_2O$

   Krausite is relatively abundant in the transition zone and in the granular coquimbite near it. It occurs as groups of pale green to yellow green short equant crystals in shrinkage cracks and discrete masses embayed by coquimbite. It often covers areas as much as several cm across and almost always occurs as small monoclinic crystals with the terminating faces showing giving it an almost octagonal shape. In the transition zone crystals may be associated with lilac coquimbite and reddish brown römerite. The largest crystals of this mineral occur in the transition zone and single crystals of krausite up to 7 mm across have been found embedded in granular white coquimbite. The larger crystal faces are not brilliant as the smaller crystals and often appear to have been etched. This is the type locality for krausite described by Foshag (1931).

Figure 8. Sample showing dark green krausite crystals to 4 cm (center) surrounded by purple coquimbite, golden metavoltine, white acicular halotrichite on fine-grained coquimbite.

Figure 9. Blocky krausite crystals to 8.4 mm associated with golden metavoltine.

Marcasite FeS_2

Marcasite has been noted as small patches and grains on the rock that encloses the sulfate mass near the footwall. It generally shows a greenish-yellow color and a botryoidal surface. No marcasite has been noted in the sulfate mass and only a few specimens were found.

Melanterite $FeSO_4 \cdot 7H_2O$

Melanterite is only found in the mass of acidic iron sulfates that formed near the footwall. Melanterite occurs as small irregular grains and as veins of fibrous crystals that range in color from light green to white and is commonly intergrown with halotrichite. The green color disappears as the specimens dehydrate. Veins of fibrous melanterite up to 1 cm thick and a meter long have been found cutting the römerite and voltaite and were presumably among the last minerals to form.

Metavoltine $K_2Na_6Fe^{2+}Fe^{3+}_6(SO_4)_{12}O_2 \cdot 18H_2O$

Metavoltine is locally abundant at the Sulfur Hole and has been found as areas of scale-like bright golden yellow crystals that have the (010) form dominant. This material is most abundant in thin shrinkage cracks in the granular coquimbite and is most abundant near the upper portion of the coquimbite body in the more fine-grained material. While krausite is often closely associated with the metavoltine, the shrinkage cracks containing metavoltine generally show only this mineral and it is presumed to have been one of the last minerals to form.

Figure 10. Hand sample, 7 x 9 cm, showing golden metavoltine vein in fine-grained coquimbite.

Figure 11. Metavoltine crystals showing hexagonal outline. Field of view 1.5 mm.

Figure 12. SEM photo of metavoltine crystals to 50 microns showing the stacked hexagonal plates.

Potassium Alum $KAl(SO_4)_2 \cdot 12H_2O$

Potassium alum was noted as occurring in a thin black, extremely porous friable layer at the base of the footwall of the Sulfur Hole. A few small rounded nodules that contained small cavities lined with brilliant octahedral crystals were found. This material proved to be a potassium aluminum sulfate with only minute amounts of iron present. Potassium alum has not been previously reported from this locality.

Figure 13. Clear octahedrons of potassium alum. Field of view 4 mm.

Quenstadtite $Fe^{3+}_2(SO_4)_3 \cdot 10H_2O$

Quenstadtite was first identified from the Sulfur Hole by Weber and Graal (1975) and must be considered one of the rarest of the minerals found here. It has been found only on the acid sulfates deposited near the footwall. Quenstadtite occurs as jackstraw groups of minute colorless to pale pink triclinic crystals and usually occurs as monomineralic groups of crystals in cavities of römerite.
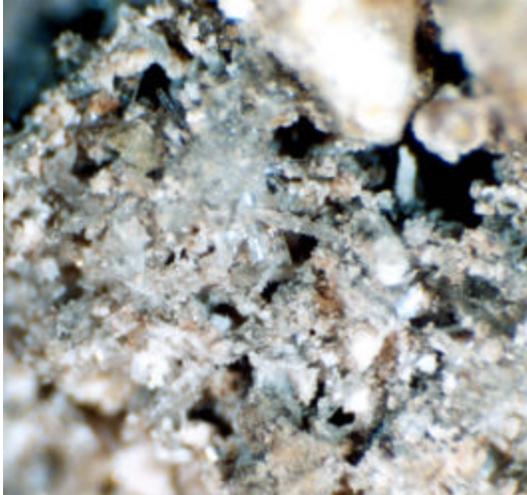

Figure 14. Typical surface showing clear to light pink, jack-straw crystals of quenstedtite. Width 4 mm.

Figure 15. Enlargement of Figure 14 showing the acicular habit of quenstedtite associated with golden metavoltine and clear, blocky krausite. Crystal length 0.5 mm.

Römerite $Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14H_2O$

Römerite is relatively abundant in the area of the footwall and large masses of friable reddish brown crystals can be found. The römerite is often cut by veins of green melanterite and white fibrous halotrichite that contains

small cubic crystals of black voltaite. Römerite rarely forms good crystals but is most often found as granular masses of elongate anhedral crystals.
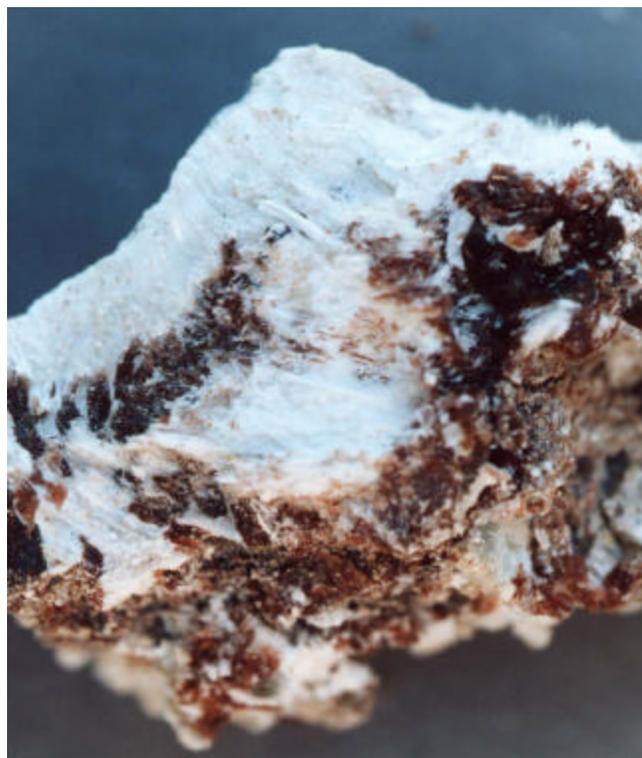

Figure 16. Sample of dark brown römerite associated with white fibrous halotrichite. Width 3 cm.

Figure 17. Typical sample, 2 x 5 cm, of dark brown römerite with white fibrous halotrichite.

Sulfur   S

Sulfur is not common in the mineral assemblage at the Sulfur Hole and occurs as thin pale yellow crusts associated with white granular coquimbite and krausite. It appears to have been one of the last minerals formed and is known from a few specimens. It occurs as pale yellow granular masses coating other sulfate minerals.

Voltaite $K_2Fe^{2+}_5Fe^{3+}_4(SO_4)_{12} \cdot 18H_2O$

Voltaite is relatively common close to the footwall of the Sulfur Hole where more acidic conditions exist. It often occurs in association with römerite and melanterite as black patches and well-formed cubic crystals. These crystals may reach 5 mm across and normally are brilliant cubes with no modifying faces. The römerite–melanterite-voltaite sulfate complex is the least stable of the sulfate assemblages and often forms a crumbly mass. It is interesting to note that the cube is the dominant form at this locality while the octahedron often forms in acid sulfate assemblages from post mine sulfate deposition.
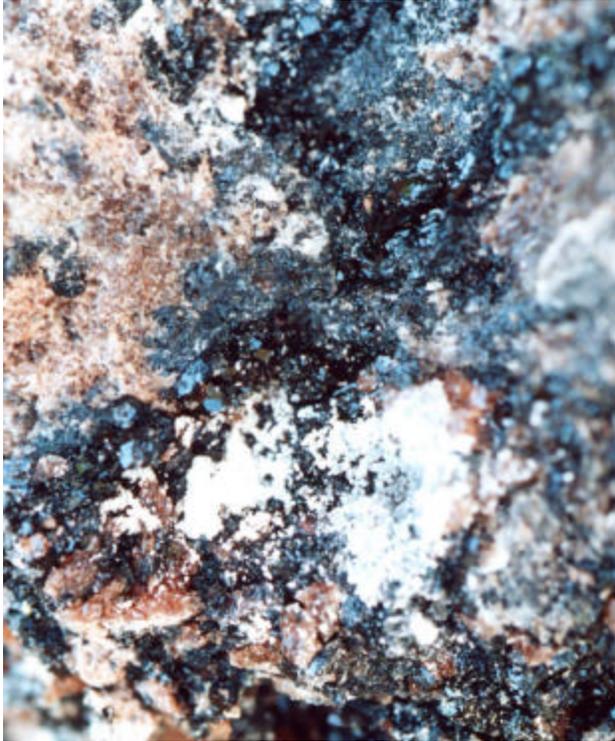
Figure 18. Typical specimen of voltaite showing black cubic outline associated with brown römerite and halotrichite. Width 1 cm.

Figure 19. Voltaite specimen showing 2 mm cubic crystal outline (center top) associated with brown römerite (left).

Collecting

At present no restrictions are placed on entry to the area and it appears to be under the control of the Bureau of Land Management. Collecting at the Sulfur Hole is mainly a question of finding the locality and digging out the accumulated debris. This will produce a hole several feet deep and often requires removing slabs of the shale beds that have fallen into the sulfate body over the years. At best it is dry and dusty work but if you are lucky enough to find a pocket of sulfates the work is definitely worth the effort.

Figure 20. Camp scene at the Sulfur Hole on November 25, 1961, showing the collecting locality at the dark area in the center of the photo.

Figure 21. Gail Dunning (left) and Dwight Weber examining specimens of sulfate minerals collected at the Sulfur Hole, December 20, 1959.

The Sulfur Hole does strange things to people. On our second visit (JFC & GED) we had driven for over 400 miles that day, arrived at dusk and had a hasty dinner after setting up camp. After dark we walked up to the locality, ostensibly to leave our tools for tomorrow. We started digging and shortly found a thin vein of massive coquimbite that we followed down to a good pocket of mixed sulfates, which produced many fine transition zone specimens of coquimbite, krausite römerite and the other sulfates the locality is famous for. We finished up about 4 A.M., covered with sulfate dust and in possession of some of the nicest coquimbite and krausite specimens we had ever seen from the locality.

Preservation of Specimens

The sulfates at this locality appear to be relatively stable with the exception of the acid sulfate mineral assemblage that occurs near the footwall. Specimens collected by (JFC) almost forty years ago and stored in plastic boxes show little deterioration. While this may be true of most specimens from the Sulfur Hole, some of the minerals are sensitive to humidity and will hydrate and deteriorate unless care is taken to store them carefully. Exposure to either low or high humidity will allow the minerals found in the more acid footwall zone (römerite, voltaite, melanterite) to literally dissolve in their own water of crystallization or crumble into a fine grained powder.

16

In extreme cases storing the specimens with desiccants has proved successful and coating the surface with acrylic resins has also proved successful, although doing so will change the luster of the crystal faces. Under normal conditions, storage in a sealed plastic box will suffice but the survivability of the acid footwall minerals are best guaranteed in a sealed jar.

Associated minerals in the area

The old borax mines in the area contain several minerals of interest. Colemanite formed friable masses and crystal lined geodes were relatively common. The geodes reached several feet in diameter and often were lined with well-formed colemanite crystals up to several inches across. The colemanite is often associated with colorless to pale blue celestite prisms and occurs on a groundmass of pale yellow strontianite and makes attractive specimens. The prospects also produce well-crystallized gypsum specimens that show a characteristic flattened form. These specimens frequently show a pale yellow fluorescence under short wave ultraviolet light and often phosphoresce white. Bassanite forms small rounded masses in the mudstones in the area. Specimens of this material often show a radiating structure and are highly prized, as the nucleating agent for the concretion was often a fossil insect.

PARAGENESIS

While no direct paragenesis of the sulfates present is possible, the zoned nature, associations and chemistry of the deposit allows an apparent paragenetic relationship to be suggested. Examination of specimens has supported this hypothesis, however there is considerable species overlap. The more acid species were among the earlier sulfates to form while the less acid coquimbite assemblage formed later in the system's history. The apparent relationship of the minerals to each other is shown in Figure 21.

DISCUSSION

Foshag's original description of the Sulfur Hole included alunite, fibroferrite and jarosite as the minerals occurring at the locality. Alunite was considered to be abundant and fibroferrite and jarosite were an important part of the mineral suite as described by him. The authors were unable to find specimens of these minerals in the material collected by them although many of the samples resembled the descriptions of these minerals given by Foshag. Botryogen, copiapite, gypsum, haliotrichite, krausite, marcasite, melanterite, metavoltine, potassium alum, quenstadtite, römerite, sulfur and voltaite were verified by either XRD (WPM) or EDS (GED) methods and their occurrence at the Sulfur Hole has been confirmed. Material previously identified as alunite, fibroferrite and jarosite were restudied and found to be fine grained coquimbite, halotrichite stained by copiapite and the yellow crystals of jarosite are metavoltine respectively. Foshag (1931), in his original description of the locality, does not describe the methods used to identify these minerals and merely mentions them as being present. No authentic samples of these three minerals from the Sulfur Hole are known to exist. In light of the present investigation, the existence of alunite, fibroferrite and jarosite at the Sulfur Hole must be considered questionable.

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Table 1. Minerals from the Sulfur Hole, San Bernardino County, California

Mineral	Formula
Anhydrite	$CaSO_4$
Botryogen	$MgFe(SO_4)_2(OH) \cdot 7H_2O$
Copiapite	$FeFe_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Halotrichite	$FeAl_{12}(SO_4)_4 \cdot 22H_2O$
Krausite	$KFe(SO_4)_2 \cdot H_2O$
Marcasite	FeS_2
Melanterite	$FeSO_4 \cdot 7H_2O$
Metavoltine	$K_2Na_6FeFe_6(SO_4)_{12}O_2 \cdot 18H_2O$
Potassium Alum	$KAl(SO_4) \cdot 12H_2O$
Quenstadtite	$Fe_2(SO_4)_3 \cdot 10H_2O$
Römerite	$FeFe_2(SO_4)_4 \cdot 14H_2O$
Sulfur	S
Voltaite	$K_2Fe_3Fe_4(SO_4)_{12} \cdot 18H_2O$

Figure 22. Paragenetic timeline for the formation of the sulfate minerals at the Sulfur Hole.