CRYPTOCRYSTALLINE PYRITE FROM ALPINE COUNTY, CALIFORNIA

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Introduction

A few months ago the writer enjoyed the opportunity of visiting the Leviathan mine with a party from the California State Division of Mines. This mine is located on the eastern, right, bank of Leviathan Creek at an elevation of about 7,200 feet, seven miles east of Markleeville, the county seat of Alpine County (Fig. 1). The mine is owned by the Leviathan Sulphur Co., and is leased at present by the Calpine Corporation, a subsidiary of the Texas Gulf Sulphur Co.

Shipments of sulphur have been reported[1] from Alpine County only during 1933 and 1934, but the amount produced has not been made public. Though the reserves of the Leviathan mine are large, production so far may not have been more than a few hundred tons.

At the entrances to the mine there is no sulphur in evidence, but seams of sulphur are said to reach the surface at higher levels. The deposit was discovered through workings of a small copper mine located just above it, and long since abandoned.

The Sulphur Deposit

The main body of the sulphur occurs as an impregnation of a completely opalized, fine grained, andesite tuff. The sulphur content of this material is 35% or more, but the mixture of sulphur with other materials is such that economical separation has proved most difficult. The opalized tuff is a nearly horizontal sheet about 100 feet thick between other volcanic rocks, mostly andesitic mud-flows and breccias. No detailed geologic map of the region has been published, but the new Geologic Map of California (1938) shows only tertiary volcanic rocks for miles in all directions (Fig. 1).

Access to the deposit is gained by tunnels run in at the top and bottom of the sulphur-impregnated tuff and by numerous crosscuts and raises. Both tunnels enter the deposit through the so-called footwall, a fault that dips east under the ore and makes its western boundary. The lateral walls of the deposit are also determined by faults, but these have been touched by the mine workings in only a few spots.

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[1] *Bulletins* **110** and **111,** *California State Division of Mines.*

The sulphur appears to have been introduced through fault fissures and trapped in the opalized tuff. The western part of the deposit, adjoining the footwall fault, is greatly fractured and traversed by veins of almost pure sulphur, some of them several yards thick. This is the high grade ore. Smaller amounts of high grade ore occur at various points in the mine. Breccias of opalized and sulphur-impregnated tuff fragments in pure sulphur are also common in the western part of the deposit.

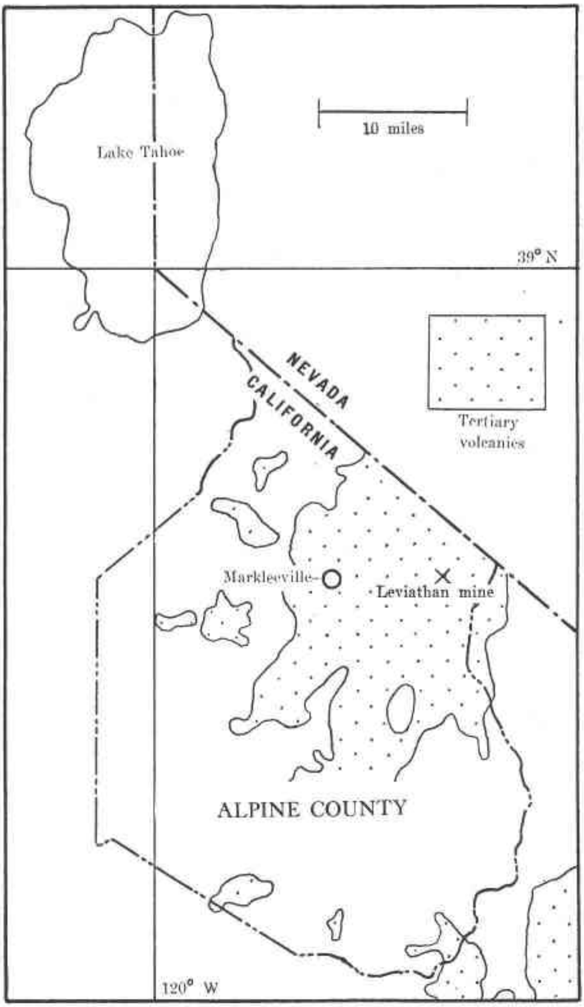

Fig. 1. Distribution of tertiary volcanic rocks in Alpine County, from Geologic Map of California, 1938.

The main body of sulphur-impregnated tuff is pale grayish yellow in hand specimen, still showing faintly the original banding. Joints or cracks are lined by a thin coating of sulphur in which small crystals are recognizable. The density of this mixed material is 1.98–2.03, but since this is very close to the density of either sulphur or opal one can draw no conclusions from this figure as to the proportions of the constituents. In thin section the sulphur appears mostly in irregular, rather coarse-grained, patches in the interstices of almost wholly opalized tuff. No replacement of structures by the sulphur was observed.

The mine waters are highly acid and secondary sulphates are found in many parts of the mine. So far chalcanthite, iron-copper chalcanthite, römerite, melanterite and halotrichite have been identified.[2] The blue and red brown coatings of chalcanthite and römerite on masses of solid sulphur make as colorful a mine wall as anyone could wish.

CRYPTOCRYSTALLINE PYRITE

Some peculiar varieties of pyrite occur with the sulphur. They are found for the most part on the fringes of the deposit, especially at the lower level. The pyrite is all cryptocrystalline and mostly black or gray, only the most compact specimens showing a brownish color. The luster is earthy or dull, in a few cases submetallic. Some of the material is quite friable, but in part it reaches the normal hardness of pyrite. In a few places this pyrite occurs with sulphur, in one specimen forming selvages of hard pyrite around clean coarse fragments of sulphur embedded in friable black pyrite.

Since the nature of this peculiar pyrite was at first in doubt it was examined in detail. Microscopic examination of thin sections and polished surfaces showed that the very fine grained pyrite has replaced the opalized tuff (Figs. 2 and 3). Some phenocrysts have been perfectly pseudomorphed by the replacing pyrite. Such material was collected at several points in the mine at the base of the sulphur deposit. Close examination of this replaced material also shows a few minute veinlets of cryptocrystalline pyrite.

Satisfactory polished surfaces can be obtained only from the more compact specimens which develop the typical pyrite luster and color on polishing. The softer, friable, pieces show only specks here and there that assume the common appearance of pyrite. No trace of any other metallic mineral was found in the polished surfaces. Thin sections showed only voids and chalcedony or opal in addition to pyrite. It seems probable that the tuff suffered a double replacement in some parts, being first

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[2] Gary, Geo. L., Sulphate minerals at the Leviathan sulphur mine, Alpine County, California: *Calif. Jour. Mines and Geology,* **35,** no. 4 (Oct. 1939).

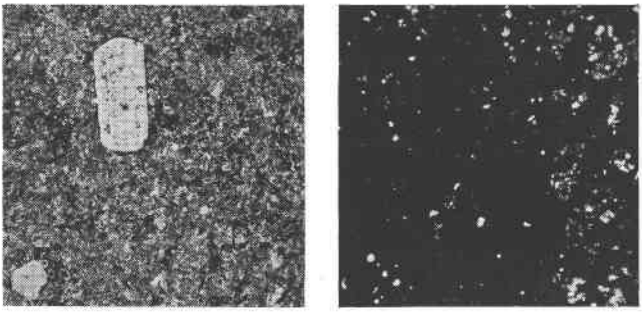

FIG. 2 (left). Phenocryst and groundmass replaced by pyrite in reflected light. Magnification 12.5×.
FIG. 3 (right). The same as Fig. 2 by transmitted light. Same magnification.

opalized and then almost completely pyritized. In places where the pyrite is soft and friable, or mixed with sulphur, replacement is not readily apparent.

Well within the main body of sulphur ore there occurs a mass of rather pure glistening yellow sulphur. Associated with this is a considerable amount of sulphur that has the typical fracture and luster, but is dark brown or black. Microscopic examination shows that this peculiar color is due to finely disseminated pyrite in rather coarse grained massive sulphur. In part the pyrite shows faint banding and is gathered into clusters (Fig. 4). The maximum density determined on this material was 2.35, as against 2.04 for the adjoining pure sulphur. From these figures and the known density of pyrite it can be calculated that the dark sulphur contains nearly 10 per cent pyrite by volume or over 20 per cent by weight, in agreement with estimates from the microscopic observations, though the pyrite cannot be seen at all in the hand specimen.

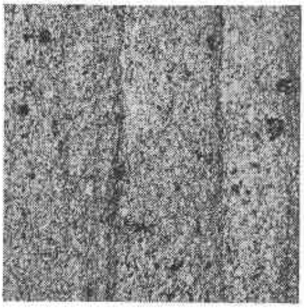

FIG. 4. Thin section of pyrite in coarse sulphur. Transmitted, ordinary, light. Magnification 4.2×.

Two portions of the cryptocrystalline pyrite were selected for further study:

A—The hardest and most compact, and
B—The soft, black, friable, pyrite.

X-ray powder patterns of the two varieties were kindly prepared by Mr. W. H. Dore of the Division of Plant Nutrition, College of Agriculture, University of California. The patterns show only the lines of pyrite and are identical except that the one from the soft material is a little stronger. The lattice constant, calculated from 21 measured and indexed lines is 5.396±0.010Å for both varieties. This differs less than 1/500 from the accepted value, 5.405Å, (*SB.* I).

The density of the friable material is not readily obtainable because the powder behaves badly in a pycnometer. The same is true of the more compact material when powdered. The highest value of the density obtained by using a Jolly balance on selected fragments of the compact variety, without visible inclusions or holes, was 4.3. This is far below the theoretical value, 4.97, for pyrite. From the microscopic examination and the analysis it is certain that this discrepancy is due to impurities and voids in the specimen.

Spectrographic examination by Dr. T. G. Kennard of Claremont, California, yielded the following results:

	A	B
	Dark compact pyrite	Black friable pyrite
Large amount	Fe	Fe
Medium to small	—	Ni, Ti
Small, X%	Ti	Si
Very small, 0.X%	As, Ni, Si	As, Cr
Traces, 0.0X% or 0.00X%	Na, Ca, Mg, Al, Cr, Cu, Mn, V	Na, Ca, Mg, Al, Cu, Mn, V

suggesting that the most important chemical difference may be a slightly higher concentration of nickel, titanium and chromium in the friable variety.

Somewhat incomplete quantitative analyses of both varieties were made by Mr. W. H. Herdsman of Glasgow, and are recorded below.

	A	B
	Dark compact pyrite	Black friable pyrite
Fe	40.26%	34.40%
S (total)	48.80	41.24
SO_3	2.60	7.37
H_2O	2.56	5.33
Insoluble residue	5.22	7.25
Total	99.44	95.59
Correction for S	−1.07	−3.03
Corrected total	98.37	92.56

In addition the analysis of the black friable pyrite showed several tenths per cent of nickel. The correction to the totals of the analyses is for S reckoned both in the total S and in the SO_3. The ratio of S not in SO_3 to Fe is 2.021 for Sample A and 1.935 for Sample B, which must be considered satisfactory for analyses of this character. The SO_3 shown in the analyses is partly from free sulphuric acid. Most specimens of the cryptocrystalline pyrite develop crusts of melanterite or other secondary minerals even though they may at first appear quite clean. Some have grown several "crops" within a few months.

Comparison with Related Materials

Black, cryptocrystalline or amorphous FeS_2 has been described by Doss[3] occurring as small granules in miocene clay encountered in a bore hole in Russia. His accounts are extremely diffuse, but, at least it is certain that he wished to apply the name melnikovite to what he considered to be a new mineral of the composition FeS_2, which is black, magnetic, has a hardness of 2 or 3, and a density of 4.2–4.3. He expressly stated that he considered this material to be distinct from marcasite or pyrite and that it is an "iron bisulphide gel become crystalloid." He also described the alteration of melnikovite to pyrite.

The name melnikovite has not been widely adopted and, indeed, material of this character is not common. Niggli[4] has used the term in his textbook in two senses. In one place he uses it to designate "$FeS_2 . nH_2O$" of colloidal character from which dense marcasite has formed. In another place he lists it as a "metacolloid" equivalent to pyrite or pyrrhotite, with the name "Melnikowitgel" for a "Gelmineral" of the composition "$FeS \cdot nH_2O$, possibly bisulfide or oxysulfide."

Tarr[5] used the name melnikovite for "amorphous black iron disulphide." He applied it "tentatively" to a "soft black powder" occurring with marcasite and pyrite. The only reason for his uncertainty in applying the name melnikovite appears to have been that the black powder was not magnetic, as was the material for which the name was first used.

Ehrenberg[6] has described cryptocrystalline iron sulphides, having an

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[3] Doss, B., Über die Natur und Zusammensetzung des in miocänen Tonen des Gouvernements Samara auftretenden Schwefeleisens; *Neues Jahrb. Min.*, etc., *BB.* **33,** 662–713 (1912); and Melnikowit, ein neues Eisenbisulfid, und seine Bedeutung für die Genesis der Kieslagerstätten: *Zeits. prakt. Geol.*, **20,** 453–483 (1912).

[4] Niggli, P. *Lehrbuch der Mineralogie*, 2nd. Ed., **2,** pp. 490, 678 (1926).

[5] Tarr, W. A., Alternating deposition of pyrite, marcasite and possibly melnikovite: *Am. Mineral.*, **12,** 417–421 (1927).

[6] Ehrenberg, H., Das Auftreten und die Eigenschaften ehemaliger FeS_2-Gele insbesondere auf metasomatischen Blei-Zinkerzlägerstatten: *Neues Jahrb. Min.*, etc., *BB.* **57,** 2 (1928).

S/Fe ratio slightly less than 2, which yield x-ray patterns showing only pyrite lines. The sulphur deficiency he ascribes to the presence of pyrrhotite which can be made visible by annealing. The original manner of distribution of the pyrrhotite is left in doubt. The very fine grained parts of this material are designated by Ehrenberg as "the gel form of the compound FeS_2, which Doss called melnikovite."

Schneiderhöhn and Ramdohr discuss " 'Melnikovit-Pyrit' Kristallin gewordenes FeS_2-Gel" as mineral number 37 in their textbook on the microscopy of ores.[7] Following Ehrenberg, they consider that the finely banded and colloform habit of the material indicates that it formed from a gel, a view of the origin of colloform pyrite also held by Smitheringale.[8] The material referred to by Ramdohr and Schneiderhöhn and the authors they cite differ from the melnikovite of Doss in various respects, particularly in being harder and not black.

CONCLUSIONS

1. The name melnikovite and various derivatives have been applied to cryptocrystalline forms of pyrite by several writers. It is not certain that any of them dealt with material closely resembling the original melnikovite.
2. A gel condition or origin has been ascribed to material called melnikovite by the originator, and by later users of the name. Not one of these writers has shown that solid FeS_2 occurs in a non-crystalline state. In the only two cases, known to the writer, in which the x-ray diffraction method has been used, the German occurrences described by Ehrenberg and the material from Alpine County described here, the material in question has been shown to be pyrite.

ACKNOWLEDGMENT

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[7] Schneiderhöhn, H., and Ramdohr, P., *Lehrbuch der Erzmicroskopie*, **2**, 170–173 (1931).

[8] Smitheringale, W. V., Mineral association at the George gold-copper mine, Stewart, B. C.: *Econ. Geol.*, **23**, 193–208 (1928).