TROILITE FROM THE LOW DIVIDE DISTRICT, DEL NORTE COUNTY, CALIFORNIA: PARAGENETIC CONSIDERATIONS

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The type terrestrial locality for troilite has always been assumed to be the Alta mine, Low Divide District, Del Norte County, California. Extensive field sampling coupled with optical and electron microscopy studies have shown that the original terrestrial source of troilite was the Union mine, located just northwest of the Alta mine. An apparent paragenetic sequence for the formation of troilite from the Low Divide District has been determined based on isotopic sulfur analysis, SEM/EDS analysis and ore microscopy observations of the sulfide veins.

INTRODUCTION

Troilite, stoichiometric iron sulfide (FeS), was named after Dominico Troili who first observed the mineral in a meteorite that had fallen at Albareto, in Modena, Italy in 1766 (Haidinger, 1863). Since that time, troilite has been recognized as a common but minor constituent of meteorites. In terrestrial environments, troilite in small amounts usually is associated with pyrrhotite and other sulfides and oxides, and has been identified from many world localities in igneous intrusion and alkali ophiolitic sulfide deposits.

In 1922 Dr. Arthur S. Eakle of the University of California, Berkeley, described the first terrestrial occurrence of troilite from samples submitted by Mr. Magnus Vonsen of Petaluma, California. Since the 1960's, the samples' unconfirmed source has been the Alta mine, because of the abundant troilite found there. During the 1990's, excellent samples of troilite matching Eakle's 1922 description were collected from mines along the headwaters of Copper Creek, which originates on the northwest side of the Low Divide. A study of these samples has revealed the source of Eakle's 1922 troilite description and has established a probable paragenesis of troilite from this locality.

LOCATION

The Low Divide copper mining district is located approximately 21 km northeast of Crescent City and 11 km east of the small town of Smith River, Del Norte County, California. The district can be reached by traveling east on Rowdy Creek road from Smith River to the divide between Hardscrabble and Copper Creeks, where the road crosses the Alta mine property.

The mines in the Low Divide mining district consist of the Alta, Union, Monument, and Occidental and are in Section 35, T18N, R1E, Humboldt Meridian (41° 24' 15" N, 124° 1' 49" W), in the Six Rivers National Forest. The underground workings are mostly caved, inaccessible, and extremely hazardous. Detailed descriptions of the mines, including underground workings and ore production, are given by Lowell (1914) and Laizure (1925).



Figure 1. Location map with a star marking the Low Divide mining district.

Topographical features of the area are typical of the northern California Coast Ranges and consist of steep, rugged mountains with deeply incised drainage systems. High areas have little relief and represent the remnants of a late Tertiary erosion surface known as the Klamath peneplane. Thin lateritic soils support a scrub forest. Landslides, some still active, have occurred on a large scale, particularly along streams that cut soft, easily eroded serpentinite.

Native American azalea shrubs, species *nudiflora*, abound throughout the area and exhibit beautiful pink flowers. Also, very rare pitcher plants (genus *Darlingtona*, species *Californica*, order *Sarraceniales*) occur along Hardscrabble Creek where cool natural springs occur. These are insect-eating plants native to many worldwide, moist environments.



Figure 2. View of abundant azalea shrubs that dominate the area.



Figure 3. Group of pitcher plants (genus *Darlington*, species *Californica*) along a small tributary near the headwaters of Hardscrabble Creek where cold water springs occur.



Figure 4. Close up of individual pitcher plants enjoying dinner and good conversation.

EARLY MINING HISTORY

Copper was discovered in the Low Divide district at the head of Copper Creek in 1853. In 1860, copper prices rose in response to the material needs of the Civil War, and the mining camp of Altaville came into being (Laizure, 1925; Maxon, 1933; O'Brien, 1952). In 1863, William H. Brewer, head of the Botanical Department of the Geological Survey of California, visited the Altaville camp that consisted of several hundred people and gives a colorful account of the life style during the heyday of mining activity in California (Brewer, 1865):

November 2 we footed it to Low Divide, or Altaville, about eighteen miles. The road was very crooked, running over high ridges and sometimes commanding grand views of the wide Pacific and of the surrounding rough landscape. The hills are covered with low brushes and here and there in the canyons heavy timber, as we approach the sea.

Low Divide is a little town on a sharp ridge-a "low divide," in truth, between higher hills. It is a regular mining town, of miners' cabins, a few stores, saloons, and a "hotel." At this last I stopped the entire week, and a filthier, dirtier, nastier, noisier place I have not struck in the state. The whole scene was truly Californian-everyone noisy. We found that the landlord had killed a pig that afternoon, and over sixty dollars had been lost or won in betting on its weight! You cannot differ with a Californian in the slightest matter without his backing his opinion with a bet...

Copper occurs here, scattered over quite an extent of country. A great number of claims are taken up and much work is being done on them. Only one of these mines, out of over thirty, had

paid expenses, and this has produced as yet scarcely over five hundred tons of ore, sold at perhaps \$50,000. But all hope to get rich. I trudged over the hills by day and sat in the dirty barroom or saloon during the evenings, and watched men lose their earnings at poker...

We had rainy weather there a part of the time, which increased my discomforts-standing at night in a crowded barroom, with seats for half a dozen, while twenty or thirty wet, dirty men from the mines steamed around the hot stove. To go to bed was no relief. We slept on the floor upstairs, some twenty or twenty-five of us-they kept running in and out all night. The noise from below prevented sleep until late, and the last of the card players would be getting to bed in the morning after the first risers were up.

But all things must come to an end, and so must this. Saturday, November 7, I footed it four miles down the road to a little Dutch tavern, where I got the luxury of a clean bed and a clean table, yet had to sit with wet feet and listen to a drunken miner who was determined to enlighten me on the subject of geology.

Of all the district mines, the Alta, also known later as the Alta California, was the most prominent and produced the bulk of the ore shipped. Other mines in the district included the Occidental, Salt Lake-California (Union), and the Mammoth Group. Between 1860 and 1863, about 2,000 tons of ore were shipped from the district with a return of \$41 to \$102 a ton (Browne and Taylor, 1867). The first 42 tons of ore shipped from the Alta mine was composed chiefly of cuprite and came from a mass discovered near the surface that was nearly 1 meter wide and 17 meters long. It averaged 45 percent copper and was sold in San Francisco for \$7,000, with the cost of extraction and delivery not exceeding \$2,000 (Browne and Taylor, 1867).

Since copper smelters did not exist on the west coast of North America during that time, the Low Divide copper ore had to be shipped to Europe for smelting. The high-grade ores were packed in bags and transported by wagon down the steep slope to the coastal settlement of Crescent City, where they were carried by coastal schooner to San Francisco. Upon arriving at the San Francisco docks, the ore was transferred to sailing ships for the long voyage around Cape Horn and across the Atlantic Ocean to smelters in Wales and Germany (Lowell, 1914; Laizure, 1925).

When the end of the Civil War caused the price of copper to drop significantly, the mines shut down, although pockets of copper ore remained in most of them. Old records show most of the ore produced ran from 15 to 18 percent copper (Lowell, 1914).

The last recorded work in the district occurred in August 1951 when a partnership including John Noce, Joe Renarez, and Y. E. Yoder was engaged in cleaning out and re-timbering the old Alta shaft that had burned out above the adit. By the end of August the shaft had been re-timbered for 18 meters (O'Brien 1952). There is no record of any further work having been done on the property. When we visited the property in 1963, the site was found abandoned, the head frame and hoist had been removed, and remaining buildings were in a state of disrepair. Today nothing remains of Altaville except some stone foundations amongst the scrub brush and trees; only the mine dump and some crumbling foundations can be found at the Alta mine. The underground workings are caved, flooded and inaccessible.

The area also produced pockets of chrome ore in the serpentinite. The Copper Creek mine, located just northwest of the Monument mine above Copper Creek, produced magnesiochromite between 1914 and 1918 to support the war effort. We found it abandoned during our visit to the area in 1963.

COLLECTING HISTORY

The Troilite Locality Enigma

While in Crescent City in the early 1920's, Mr. Magnus Vonsen, an avid mineral collector from Petaluma, California, obtained several massive sulfide ore samples from a miner with no locality description other than "a copper claim northeast of Crescent City, in Del Norte County." After returning to the Bay Area, these samples were given to Dr. Arthur S. Eakle, who examined them and determined the massive ore to be a mixture of troilite with admixed magnetite and chalcopyrite. He subsequently described this find as the first terrestrial troilite occurrence after performing a series of tests on the samples. Dr. Eakle apparently never visited the Low Divide area but based his locality description solely on the data given by Magnus Vonsen who had obtained it from the miner.

In 1938, the late Charles W. Chesterman, a senior mining geologist with the California Division of Mines and Geology (CDMG), examined Mr. Vonsen's collection, became interested in troilite, and did considerable research on the samples' origin, since no specific locality had been given by Eakle (1922). However, Mr. Chesterman published nothing on his research. In the early 1960's, Salem J. Rice, also of the CDMG, visited the area and collected samples from various copper mines in the Low Divide area but found troilite only at the Alta mine.

Our interest in troilite began in 1963 when we learned of Eakle's work and the occurrence of troilite in Del Norte County. In July of that year we made a collecting trip to the Alta mine with the intent of examining the source of this unusual mineral. The mine dumps were found to contain moderate amounts of a massive, dark brown sulfide ore that we assumed to be troilite. Subsequent optical and chemical tests proved this material to be composed of a mixture of troilite, pyrrhotite, pentlandite, and other minor constituents. Contrary to Eakle's description, no magnetite was found in any of the sulfide samples examined from the extensive Alta mine dump.

In 1988, we re-examined the troilite samples from the Alta mine collected in 1963 and initiated a complete study that revealed major differences between the Alta mine troilite and that studied by Eakle. All the Alta mine troilite samples were very nearly identical, which heightened the mystery of the origin of Eakle's study samples provided by Magnus Vonsen.

Inquiries were made to the California Academy of Sciences, San Francisco (CASSF) and the University of California, Berkeley (UCB) to determine if samples of Vonsen's troilite were available for study. Through the courtesy of Dr. Jean DeMouthe of the Academy, several excellent samples of troilite from the Vonsen collection were made available for study. Dr. DeMouthe stated that all detailed locality information that Vonsen had on the samples had been destroyed after his death. Ms. Peggy Gennero of UCB made available a suite of five small troilite samples studied by Drs. Charles Meyer and Adolph Pabst. These samples had been provided by Mr. Vonsen and subsequently studied by Dr. Eakle. The only locality information for these samples was "Del Norte County."

The troilite samples from these two institutions were examined and found by optical and electron microscopy, Xray diffraction, and chemical analysis to be nearly identical and matched Eakle's 1922 description. To resolve this locality enigma, we again visited the Low Divide district in 1990 to collect additional samples from the Alta mine. In addition, we examined other workings south along the Hardscrabble Creek area but discovered no troilite samples. Next we visited the Union mine in the Copper Creek area just northwest of the Alta property, which revealed abundant troilite on the dumps. Further searching revealed a vein of *in situ* troilite containing veinlets of magnetite. All the Union mine workings produced abundant troilite containing chalcopyrite, the major copper ore mined. When we revisited the area in 1991, we examined the Copper Creek side of the Low Divide district in greater detail. We found that massive sulfide bodies rich in troilite were common in the area. This new material allowed us to compare troilite samples from the Alta mine, the Union min, and Vonsen's collection.

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GEOLOGICAL SETTING

Early geologic reconnaissances of this region were performed by Diller (1902), Hershey (1911), Maxson (1933), Wells et al. (1946), and Cater and Wells (1953). For the last two decades structural geologists, in addition to many other workers in closely related fields, have examined this region in increasing detail to better understand the complex tectonic events that have resulted in the present structural features, exposed and at depth.

This region of northwestern California and southwestern Oregon contains one of the largest intact ophiolites known, with an aerial extent of more than 800 square kilometers. This ophiolite, known as the Josephine Ophiolite, is a complex formation of igneous and metamorphic rocks that originated in a Late Jurassic back-arc sea basin adjacent to the then-existing coast. It is composed of a sequence of harzburgite tectonite, cumulative ultramafics, gabbro, high level gabbro and diorite, a sheeted dike complex, and upper layers of pillow lava and breccia (Harper, 1980, 1984; Harper et al. 1988).

The Josephine Ophiolite and the overlying Galice Formation are part of the Western Jurassic Belt of the Klamath Mountains geomorphic province. In general, the Klamath Mountains consist of arcuate, fault-bounded belts of diverse eugeosynclinal terranes. These belts display a general age progression with rocks ranging from early Paleozoic in the east to primarily Upper Jurassic in the west (Irwin, 1960, 1966, 1972, 1981)

Rocks in the Low Divide district consist of Josephine peridotite and a harzburgite composed of olivine and enstatite. Along the joints and fractures, typically more than half the olivine and enstatite are replaced by serpentinite. The weathered harzburgite has a pyroxene-studded, tan to reddish-brown surface and weathers to a red lateritic soil.

The Copper Creek shear zone formed late in the sequence as indicated by cross-cutting relationships. This large north-striking shear zone appears to dip 50 to 75 degrees to the east and is bounded by the Alta Fault on the west and the Wimar Fault on the east. Locally, the Alta Fault dips steeply to the west and the Wimar Fault dips steeply to the east.



Figure 5. Map showing the Copper Creek shear zone with associated fault zones. Rocks of the district are mainly harzburgite and serpentinized harzburgite. District mines are shown along the slope east of Copper Creek and along the slope west of Hardscrabble Creek. Geology from Gregory D. Harper, State University of New York, Albany, written communication, 1983. Topographic map base from U.S. geological Survey (High Divide, California-Oregon, 7-1/2', 1966).



Figure 6. View to the west across Hardscrabble Creek showing the extensive Alta mine dump. The reddish-brown area near the Alta shaft is composed of oxidized troilite and secondary copper minerals.



Figure 7. View of the Alta vein above the shaft area. The original vein is fully oxidized and the harzburgite margins are weakly serpentinized. This area is suspected of being the source for a moderate mass of cuprite and native copper discovered in the early 1860s.



Figure 8. View of the adit connecting with the Alta mine shaft at the head of Hardscrabble Creek. The adit is mostly caved and contains abundant melanterite, malachite and goethite stalagmites.

Detailed mapping of the Low Divide district by Dr. Gregory D. Harper (State University of New York, Albany, written communication, 1983) has shown that sulfide mineralization is restricted to the Copper Creek shear zone. This shear zone is bounded on the west by relatively unaltered peridotite and on the east by a fault-generated peridotite-serpentinite complex.

MINERALOGY

Sulfide-bearing samples for this study were collected from the Alta, Union, and Monument mines, the major mines along the Copper Creek shear zone. No sulfide-bearing rocks were noted in the several workings of the Occidental mine just south of the Alta mine, although oxidized material was abundant. All field samples were carefully catalogued to maintain locality integrity among the several mines.

Using standard ore preparation methods, more that 100 polished sections were prepared for optical and SEM/EDS examination from the field samples. The data obtained from these polished samples constituted the sulfide vein mineralogy and textural relationships for this report. Sulfur isotopic analyses were performed by Dr. Robert A. Zierenberg, U.S. Geological Survey, Menlo Park, California; this data would be critical in determining the paragenesis of the sulfides identified in the Low Divide district.

Eakle's 1922 Troilite

Before Dr. Eakle had described the first terrestrial occurrence of troilite, the physical and chemical properties of troilite had not been determined sufficiently to differentiate it from pyrrhotite. Because of the abundance of troilite in Del Norte County, it offered Dr. Eakle an opportunity to compare properties to the well-known occurrence in meteoric iron.

The following statements are recorded by Dr. Eakle (1922) in his description of the troilite samples submitted to him. "Optical tests determined that troilite to be distinct from pyrrhotite in several respects, namely color, lack of magnetism, and solubility in sulfuric acid. The color of untarnished troilite (freshly broken) was observed to be light grayish-brown with no bronze-colored tinge but oxidation darkened exposed surfaces. He found the sulfide had inclusions of a bluish-black serpentinite containing much iron. The inclusions, however, did not affect the analysis because of their insolubility in sulfuric acid. A small amount of copper was detected but no nickel or chromium (chromium in the form of magnesiochromite is abundant in the district). A magnetic phase in the sulfide was attributed to included magnetite, which was easily separated by a magnet. Further observations of troilite showed thin rims of magnetite grading into the troilite. The magnetite appears to be residual material from a conversion of a larger mass into troilite."

"The owner of the copper claim reported that the chalcopyrite bodies occur in a shear zone of serpentinite along an extensive fault zone. This shear zone consists of fractured and altered rock with slickensides, which has evidently been invaded by sulfide solutions that deposited the chalcopyrite. The owner stated that the massive iron sulfide (later determined by Eakle to be troilite) was found in one of the tunnels, in rounded masses with slickensides." Eakle (1922) concluded that "these masses were probably magnetite in the original serpentinite, and solutions rich in hydrogen sulfide transposed them into troilite. The large amount of iron in the form of magnetite appears to have conditioned the formation of the monosulfide instead of the more common pyrrhotite with its excess sulfur over iron."

The Alta Mine Troilite

Massive troilite samples recovered from the Alta mine dump are characteristically covered by a brown iron oxide crust and can be distinguished from the harzburgite by their high specific gravity and blocky fracture. Freshly BAM Journal, Vol. 9, No. 2 11 www.baymin.org

broken troilite is silver-white to gray with a granular texture, unlike pyrrhotite or pyrite. Upon exposure to air the surface rapidly develops an iridescent tarnish that turns a dull bronze color in a few hours. All troilite specimens from the Alta mine are weakly magnetic due to admixed pyrrhotite.



Figure 9. Typical hand samples of massive troilite recovered from the Alta mine dump.



Figure 10. Freshly fractured troilite sample from the Alta mine dump showing a silvery bronze color before becoming tarnished.



Figure 11. Fen Cooper relaxing at our Alta mine base camp in 1991.



Figure 12. Gail Dunning reviewing site descriptions at the Alta mine during 1991 trip.



Figure 13. Field observations being recorded at the Alta mine by Fen Cooper during 1991 trip.

In polished section, the troilite-rich sulfide matrix consists of a heterogeneous mixture of troilite, lowtemperature pyrrhotite and pentlandite. The grains of this mixture, as viewed under polarized light, show preferred orientation with respect to the flow direction during emplacement and movement along the fracture system. Troilite generally makes up the larger fraction of the mixture with pyrrhotite second, followed by pentlandite. Troilite may be easily distinguished from low-temperature pyrrhotite and pentlandite optically in polished section. The troilite exhibits polarization colors ranging from deep gray to deep brown whereas pyrrhotite has polarization colors ranging from dark blue to gray to brown. Pentlandite shows no color change due to its isometric symmetry.

Inclusions of cobaltite, often showing a cubic form, are dispersed throughout the sulfide matrix. These crystals sections, some of which contain a core of a gold-silver alloy, are usually fractured and surrounded by troilite. Much of the pentlandite surrounding these cobaltite cubes is cobalt-rich and has been determined to be nickel-bearing cobalt-pentlandite.

Tochilinite and valleriite have formed as a direct replacement of troilite along individual grain boundaries and appear to be an alteration of the troilite during low-temperature hydrothermal serpentinization at depth.

No magnetite was observed in any of the polished sections from the Alta mine troilite, even though the surrounding harzburgite contains small grains of magnetite and nickel sulfides.

CASSF and UCB Troilite Samples

A macroscopic examination of the troilite samples from the Vonsen collection at CASSF and UCB indicates these closely agree with Eakle's 1922 description of troilite. Two excellent hand samples of troilite from CASSF, labeled V95 and V2227, were examined in detail for texture and mineralogy. The first, V95, is a mass of dark bronze-brown troilite, (11 x 6 x 2.5 cm) weighing about 475 grams. This sample shows distinct parting planes and

extensive cracks. On one end is a thin slickenside composed of magnetite that extends into the troilite along the fractures.

The second sample, V2227, is a larger mass of troilite, measuring $10 \ge 7 \ge 6.5$ cm, and weighing about 1000 grams. The color is quite similar to specimen V95 but somewhat brighter. The smaller end is a sawed surface that shows a number of magnetite veins penetrating the troilite to 4 cm. One surface, presumably the one in contact with the serpentinite, is a slickenside composed of a bluish-black iron and chromium-rich chlorite.

Five of Vonsen's Del Norte County troilite samples labeled #1337, #1338, #1339, M3219 and #21327 were identified in the UCB collection. A macroscopic examination showed they were very similar to those obtained from CASSF.

Polished sections were prepared from thin slabs cut from CASSF V95 and V2227. Also, small fragments from UCB samples 1337, 1338 and 1339 were mounted without cutting. Optical examination of these polished sections showed the general texture relationships between CASSF and UCB samples to be identical.

Union Mine and Monument Mine Troilite

The troilite samples collected from the *in situ* vein and the scattered dumps of the Union mine closely resemble those from the Alta mine but display certain textural and physical differences. When broken, the Union mine troilite displays a definite set of parting planes that the Alta material lacks. Although the Union mine material has the same silver–white to gray color on fresh surfaces, tarnishes to a vivid blue within minutes of exposure to air. This color further darkens with time to a bronze color similar to the Alta mine troilite. Magnetite occurs as small octahedrons in the cavities of the ore and as thin veins cutting it. In polished section, troilite samples from the Union and Monument mines were found to be identical to those of CASSF and UCB.



Figure 14. Vein of *in situ* troilite at the Union mine containing abundant magnetite and extending about 10 meters in a northerly direction.



Figure 15. Same exposed troilite vein at the Union mine showing melanterite coating after a rain.



Figure 16. Closer example of troilite surface oxidation after a rain.



Figure 17. California Academy of Sciences troilite sample #V95 showing parting plane and light yellow oxidation. Sample measures 11 x 6 x 2.5 cm and is from the Magnus Vonsen collection.



Figure 18. Fen Cooper collecting troilite samples from the Union mine.



Figure 19. Fen Cooper examining a troilite vein at the Union mine.



Figure 20. Fen Cooper at entrance to one of the Union mine adits.



Figure 21. Example of hand-hewn mine timbers at the Union mine.



Figure 22. View of the old ore-loading shoot from the Union mine to ore truck loading along Copper Creek.



Figure 23. View of the Grand Union mine adit, now collapsed.



Figure 24. View of an open adit at the Union mine.



Figure 25. California Academy of Sciences troilite sample #V2227 showing light yellow oxidation. Sample measures 10 x 7 x 6.5 cm and is from the Magnus Vonsen collection.



Figure 26. Hand sample of troilite from the Vonsen collection, #V95, showing a thin surface of magnetite and thin penetrating veins of magnetite into the troilite.



Figure 27. Polished end section of sample #V95 showing the magnetite filling fractures in the troilite. Field of view 114 x 88 microns.



Figure 28. Polished section of a troilite-pyrrhotite-pentlandite sample from the Alta mine showing a cubic cross section of a cobaltite crystal with a reaction rim rich in cobalt pentlandite. Field of view 28.6 x 22 microns.



Figure 29. Polished section of a troilite-pyrrhotite-pentlandite sample from the Alta mine showing replacement by tochilinite and valleriite. Field of view 28.6 x 22 microns.



Figure 30. Polished section of troilite-pyrrhotite-pentlandite from the Alta mine showing residual magnesiochromite grains surrounded by troilite. Field of view 57 x 44 microns.



Figure 31. Polished section of troilite-pyrrhotite-pentlandite from the Alta mine showing replacement veins of tochilinite and valleriite with light grains of maucherite. Field of view 28.6 x 22 microns.

Associated Minerals

The mineralogy of the Low Divide copper deposit is related to the deposition of massive sulfide bodies that are composed of a heterogeneous mixture of troilite, pyrrhotite and pentlandite. Troilite generally composes 40 to 70 percent of the sulfide mass with pyrrhotite and pentlandite making up the difference. Associated minerals within the massive sulfide occur as minute grains or segregations in the sulfide mass. Only rarely are the grains large enough to identify with the naked eye. Cobaltite, magnetite, chalcopyrite, and the tochilinite-valleriite group are notable exceptions.

Minerals associated with the troilite-pyrrhotite-pentlandite sulfide veins include bismuth, chalcopyrite, magnesiochromite, cobaltite, copper, cuprite, cobalt-pentlandite, gold-silver, magnetite, maucherite, sphalerite tenorite, tochilinite and valleriite. Minerals that have resulted from the oxidation of the sulfide veins include chalcanthite, chalcocite, erythrite, goethite, malachite, melanterite, starkeyite. Small amounts of calcite and aragonite also have been noted in the oxidized surface rocks.

Minerals identified within the sulfide veins and masses.

Cobaltite CoAsS

Cubes of cobaltite occur as individual or multiple groups in the dark harzburgite rock and in the troilite at the Alta mine. Polished sections of troilite have shown the cobaltite cores composed of a gold-silver alloy. These cubes show the effects of surface solutioning by the sulfide before solidification.

Cobalt pentlandite (Co,Fe,Ni)₉S₈

Cobalt pentlandite was identified in the sulfide phases surrounding partially solutioned cobaltite cubes in the sulfide phases.

Copper Cu

Native copper was reported as part of the large mass of cuprite discovered during early years of mining. No copper was noted in any of the polished sections of troilite examined.

Cuprite CuO

Cuprite formed the majority of the large, elongated mass of copper ore discovered near the surface where the Alta shaft is now located. It is presumed that the cuprite was the product of supergene enrichment.

Chalcocite Cu₂S

Massive chalcocite was a part of the massive cuprite discovered during early mining near the surface associated with native copper and cuprite.

Magnetite Fe₃O₄

Magnetite is common in the troilite from the Union and Monument mines along Copper Creek but not at the Alta mine. It occurs as thin veins and coatings on the massive troilite.

Maucherite Ni₁₁As₈

Maucherite has been identified in polished section as individual grains within the troilite at the Alta mine.

Bismuth Bi

Grains of native bismuth have been observed in polished sections of troilite from the Alta mine.

Chalcopyrite CuFeS₂

Massive chalcopyrite was the major copper ore mined in the district and occurs in all the mines as veins and pods along the margins of the troilite.

Pentlandite (Fe,Ni)₉S₈

Massive pentlandite is one of the three constituents identified in the troilite at the Alta, Union and Monument mines.

Sphalerite ZnS

Rare massive sphalerite associated with chalcopyrite has been identified in polished section from the Alta mine.

Tenorite CuO

Massive tenorite was one of the minerals identified from the large cuprite mass near the surface where the Alta shaft is.

Tochilinite $6(FeS) \cdot 5[Mg(OH)_2]$

Tochilinite occurs as an alteration product of troilite from the Alta and Union mines. It manifests itself along the grain boundaries of the troilite associated with vallerite.

Valleriite 4(Fe,Cu)S 3[(Mg,Al)(OH)₂]

Valleriite, associated with tochilinite, occurs as an alteration product of troilite and chalcopyrite along grain boundaries from ore samples of the Alta and Union mines.

Minerals identified as post-mine minerals

Aragonite CaCO₃

Fracture surfaces of troilite from the Alta mine dump contain small, elongated crystals and masses of aragonite as a post-mine mineral.

Calcite CaCO₃

Calcite has been identified along fractures in the rocks from the Alta mine.

Chalcanthite CuSO₄ [·] 7H₂O

Chalcanthite is common in the Alta adit where concentrations of chalcopyrite have weathered.

Erythrite Co₃(AsO₄)₂ 8H₂O

Thin, light pink coatings of erythrite have been discovered on the Alta dump associated with weathering cobaltite crystals embedded in black harzburgite. Only a few samples have been recovered.

Goethite α -Fe³⁺O(OH)

Stalagtites of goethite are abundant in the Alta adit near where it intersects the caved shaft. The ground in this region is saturated with water.

Malachite Cu₂(CO₃)(OH)₂

Stalagtites of malachite occur in the Alta adit near where it intersects with the caved shaft.

Melanterite FeSO₄ [·] 7H₂O

Melanterite is a common alternation product of troilite in both the Alta and Union mines. It occurs as finegrained white masses.

Starkeyite (Mg,Fe)SO₄ [·] 4H₂O

Ferroan starkeyite, as white, fine-grained coatings, occurs along the fracture surfaces of troilite at the Alta mine.

ORIGINS OF THE LOW DIVIDE SULFIDE DEPOSIT

The origin of the Low divide massive sulfide deposit is directly related to the formation of the Copper Creek shear zone, its intrusion by iron-rich sulfide solutions in a sub-oceanic environment, and subsequent serpentinization and uplift to its present position. The geochemical conditions required for the formation of natural troilite are not typical of normal sulfide deposition (Gronvold and Haraldsen, 1952; Konev et al. 1970; Nambu et al. 1976; Karup-Møller, 1978).

Possible sources for the sulfur composing the massive sulfide bodies include (1) immiscible fluids derived from mafic magmas, which have been remobilized under geochemical conditions different from their origin, or (2) hydrothermal solutions derived from downwelling seawater containing sulfate ions that penetrated the upper mantle along fracture zones and reacted with metal-rich solutions. Isotopic sulfur analysis allows the differentiation of the sulfur source.

Troilite samples from the Alta and Union mines, and chalcopyrite from the Union mine were subjected to isotopic sulfur analyses and represent material from the extremes of the mineralized shear zones. The results of the isotopic sulfur analyses on these samples show that the source of the sulfur was an immiscible melt rather than downwelled seawater (Zierenberg, USGS, Menlo Park, written communication, 1993, 1995). These results show that troilite from the Union mine has a δ^{34} S value of -2.6% and the Alta mine sample has a value of -3.7%, relative to a value of 0‰ for the Canyon Diablo troilite standard. The chalcopyrite from the Union has a δ^{34} S of -3.9%, strongly suggesting that the chalcopyrite and the troilite from both the Union and Alta mines derive their sulfur from the same source. Peterson, *et al.* (2003) presents a discussion of sulfur isotope analysis and its interpretation.

The massive nature of the ore, troilite geochemistry, copper enriched stringers, and the control of mineralization by the shear zones indicate the sulfide bodies did not result from simple magmatic segregation. There has clearly been remobilization and concentration of the massive sulfide melt into fractures along the shear zones, as well as geochemical changes in the original monosulfide solid solution (MSS) that may have separated from the melt at high temperature. In order for troilite to form, a high iron-to-sulfur ratio has to be present. Low temperatures required for troilite formation by hydrothermal remobilization of the MSS are compatible with the sulfur isotopic data (R. Zierenberg, USGS, written communication, 1993, 1995).

Mineral	Early		Late
Magnesiochromite			
Cobaltite			
Gold-Silver			
Bismuth			
Troilite			
Pyrrhotite			
Pentlandite			
Cobalt pentlandite			
Chalcopyrite			
Sphalerite			
Magnetite			
Cuprite			
Copper			
Chalcocite			
Tochilinite			
Valleriite			

Figure 32. Paragenetic flow chart for the sulfide vein mineralogy of the Low Divide mining district.

The following statements summarize the apparent paragenetic history for this unique troilite-bearing deposit:

1. The ultramafic rocks that hosted the initial sulfide-rich fluids formed deep below the ocean floor as a result of cooling of a mafic magma. As the mass cooled, magmatic segregation began, forming magnesiochromite and cobaltite (containing gold and silver), which were incorporated in the peridotite body.

2. Tectonic stresses on this peridotite body created faults and shear zones, channels for later fluid migration.

3. The immiscible fluids derived from magmatic segregation of the ultramafic magma formed an iron-nickel sulfide solid solution but the copper remained more mobile.

4. This solid solution was remobilized and redeposited as troilite, pyrrhotite, and pentlandite in fractures in the Copper Creek shear zone during the early stages of serpentization. Serpentinization, which produced an uplift of the entire area, subjected the rocks hosting the sulfides to minor alteration.

5. The geochemical conditions favoring the formation of troilite and low temperature pyrrhotite remained fairly constant as demonstrated by the uniform vein mineralogy.

6. Copper and zinc were enriched along the margins of the troilite veins as localized pods and stringers of chalcopyrite and sphalerite. Minor replacement of troilite by chalcopyrite took place in the Union mine ore body but was not widespread.

7. During the final stages of serpentinization magnetite penetrated along fractures in the troilite, and fibrous veins of tochilinite-valleriite formed.

8. Weathering of the copper-rich portions of the Alta mine sulfide body produced a supergene enrichment zone rich in cuprite, native copper and chalcocite.

DUSCUSSION AND CONCLUSIONS

Even though troilite occurs worldwide, it remains a very rare mineral. In at least three deposits noted in the literature, it has formed as exsolution lamellae within hexagonal pyrrhotite (Vorma, 1970; Nambu et al., 1985). In other occurrences it formed as the result of magmatic segregation in ultramafic rocks (Corlett, 1977).

Troilite from the Troodos Ophiolite near Pafkos, Cyprus, that is very similar to the Low Divide troilite occurrence, has been described by Panayiotou (1977). In this deposit, the primary sulfide-arsenide assemblage includes troilite, valleriite, maucherite, oregonite, chalcopyrite, pentlandite, gersdorffite, chromite, magnetite, graphite, molybdenite, and sphalerite.

Panayiotou (1977) suggests the formation of the Pafkos deposit is associated with the evolution of the Troodos Ophiolite during fractional crystallization of a basaltic magma thought to have been derived from the partial melting of a portion of the upper mantle. During this period immiscible fluids were segregated in the early ultramafic dunites and harzburgite. Subsequent pervasive serpentinization and tectonic movement of the dunites and harzburgite caused remobilization of the original sulfides with formation of troilite and minor changes in the mineralogy of the original sulfide assemblage.

The following conclusions have been drawn from geological field studies in the Low Divide district and by a detailed optical and electron microscopic examination of the massive sulfide ore.

1. The troilite samples provided by M. Vonsen, upon which Eakle (1922) based his description, were most probably obtained from one of the tunnels of the Union mine, not the Alta mine as previously assumed, as the Alta mine has only one adit about 50 meters below the shaft entrance.

2. The massive troilite-bearing sulfides originated below the sea floor as a result of magmatic segregation of immiscible fluids with subsequent remobilization during favorable geochemical conditions (high Fe/S ratios, low temperatures).

3. Isotopic sulfur analysis data suggest the massive sulfide was most likely of magmatic origin deep in the earth's crust and not from the reduction of seawater sulfate in downwelling oceanic waters.

4. The copper mineralization at the Alta mine was concentrated along the upper margins of the massive iron sulfide veins and pods and was subjected to supergene enrichment forming native copper, cuprite, and chalcocite.

5. The copper mineralization in the Union and Monument mines consists only of chalcopyrite with no evidence of post-depositional enrichment.

6. The paragenetic sequence derived from the ore microscopy studies suggests the following order of sulfide/oxide formation: 1) cobaltite, gold-silver, magnesiochromite, native bismuth; 2) troilite, pyrrhotite, pentlandite, cobalt-pentlandite, maucherite; 3) chalcopyrite, sphalerite; 4) chalcocite, native copper, cuprite; 5) magnetite, tochilinite, valleriite.

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We hope our efforts in bringing this project to completion have fulfilled the goals of Mr. Chesterman and Dr. Pabst in understanding the paragenesis and location of the troilite samples from northern California. Charles was always a friend and mentor to professional and amateur mineral enthusiasts and his knowledge of California geology and mineralogy was invaluable during our early years in the mineralogy field.

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REFERENCES

- BREWER, W.H. (1865) *Up and down California in 1860-1864; The Journal of William H. Brewer*: 3rd edition, 1966, Frances P. Farquhar, editor: University of California Press, Berkeley, California, 486-489.
- BROWN, J.R. and TAYLOR, J.W. (1867) Reports upon the mineral resources of the United States: Government Printing Office, Washington, D.C., 153-155.
- CATER, F.W., JR. and WELLS, F.G. (1953) Geology and mineral resources of the Gasquet quadrangle, California-Oregon: U.S. Geological Survey Bulletin 995-C, 79-133.
- CORIETT, M., (1977), Iron oxides and pyrrhotites from Igdlukungauq, Disko Island, Greenland: *Canadian Mineralogist*, **55**, 55.
- CRAIG, J. R., and SCOTT, S. D. (1974) *Sulfide phase equilibria. Sulfide Mineralogy,* P. H. Ribbe, editor, Mineralogical Society of America Short Course Notes, 1, CS-1–CS-20.
- DILLER, J. S., (1902) Topography development of the Klamath Mountains: U.S. Geological Survey Bulletin 196, 69.
- DING, K.S. and WU, F., (1985) The discovery and significance of troilite in basic igneous rock of Panzhihua-Xichang district: *Scientia Geologica Sinica*, **3**, 243-250.
- EAKLE, A.S., (1922) Massive troilite from Del Norte County, California. American Mineralogist, 7, 77-80.
- GRONVOLD, F. and HARALDSEN, H. (1952) On the phase relations of synthetic and natural pyrrhotites. *Acta Chemistry Scandinavia*, **6**, 1452-1469.
- HAIDINGER, W. (1863) Meteorit von Albareto im k. k. Hof-Mineralienkabinet vom Jahre 1766, un der troilit: K. Academie der Willenschaften, Vienna (Wien), Mathematisch-naturwissen-schaftiche Klasse, Sitzumsberichte, 47, 283-298.
- HARPER, G.D. (1980) The Josephine Opiolite-remains of a Late Jurassic marginal basin in northwestern California. *Geology*, **8**, 333-337.
- HARPER, G.D. (1984) The Josephine Ophiolite, northwestern California. *Geological Society of America Bulletin*, **95**, 1009-1026.
- HARPER, G.D., BOWMAN, J.R., and KUHNS, R. (1988) A field, chemical and stable isotope study of subseafloor metamorphism of the Josephine Ophiolite, California-Oregon. *Journal of Geophysical Research*, 93, 4625-4656.
- HERSHEY, O.H. (1911) Del Norte County Geology. Mining and Scientific Press, 102, 468p.
- IRWIN, W.P. (1960) Geologic reconnaissance of the northern Coast Ranges and Klamath Mountains, California, with a summary of the mineral resources. *California Division of Mines Bulletin* **179**, 80p.
- IRWIN, W.P. (1966) Geology of the Klamath Mountains Province, in Bailey, E.H., editor, Geology of northern California. *California Division of Mines and Geology Bulletin* **190**, 19-38.
- IRWIN, W.P. (1972) Terranes of the western Paleozoic and Triassic belts in the southern Klamath Mountains, California. U.S. Geological Survey Bulletin **800-C**, 103-111.
- IRON, W.P. (1981) Tectonic accretion of the Klamath Mountains, in Ernst, W.G., editor, The geotectonic development of California, Rubey V. I. Prentice-Hall, Englewood Cliffs, New Jersey, 29-49.
- KARUP-MØLLER, S. (1978) The ore minerals of the Ilimaussaq intrusion: their mode of occurrence and their condition of formation. *Bulletin of Gronlands Geologiska Undersoglse*, **127**, 52p.
- KONEV, A.A., USHCHAPOVSKAYA, Z.F., and LEBEDEVA, V.S. (1970) Troilite from skarn of the Tazheran alkalic intrusion. *Doklady Academy of Science, USSR, Earth Science Section*, **191**, 114-116.
- LAIZURE, C. McK (1925) San Francisco field division, Del Norte County in Mining in California. California State Mining Bureau, *Report XXI of the State Mineralogist*, **2**1, 281-294.
- LOWELL, F.L. (1914) Del Norte County, in Mines and mineral resources of portions of California. California State Mining Bureau, *Report XIV of the State Mineralogist*, **14**, 373-390.

- MAXSON, J.H. (1933) Economic geology of portions of Del Norte and Siskiyou counties, northwestermost California. *California Journal of Mines and Geology*, **29**, 123-160.
- NAMBU, M., KANO, S., and MURAMATSU, Y. (1976) Troilite from the Akagane and Kamaishi mines, Iwate Prefecture, Japan. Journal of Japanese Association of Mineralogists, Petrologists and Economic Geologists, 71, 18-26.
- O'BRIEN, J.C. (1952) Mines and mineral resources of Del Norte County, California. *California Journal of Mines* and Geology, **48**, 261-309.
- PANAYIOTOU, A. (1977) Geology and geochemistry of the Limassol Forest Plutonic Complex and the associated Cu-Ni-Co-Fe sulfide and chromite deposits, Cyprus. Ph.D. dissertation, University of New Brunswick, Canada.
- PETERSON, R. C., KYSER, K., PAGANO, R. and KLASSEN, K. (2003) Sulfur isotope analysis for the identification of sulfur sources. *Mineralogical Record*, **34**, 171-175.
- VORMA, A. (1970) Pyrrhotite-troilite intergrowth from Luikoniahti copper deposit, eastern Finland. *Geological* Society of Finland Bulletin 134, 76p.
- WELLS, F.G., CATER, F.W. and PYNEARSON, G.A. (1946) Chromite deposits of Del Norte County, California. *California Division of Mines Bulletin* **134**, 76p.