

HYDROUS IRON SULPHIDE IN CALIFORNIA CRYSTALLINE LIMESTONE*

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Hydrous iron sulphide, called hydrotroilite, has been reported by Russian and perhaps by other workers as a constituent of unconsolidated or poorly consolidated continental and marine sediments, from Russian and other localities (1). A similar black, easily soluble, hydrous iron sulphide occurs in the crystalline limestone at two southern California localities.

On the northwest slope of Ontario Peak, in the eastern San Gabriel mountains, there is a steeply dipping series of crystalline limestones and quartzites, intruded by plutonic rocks. In addition to carbonates, a varied assemblage of metamorphic minerals has developed chiefly in the limestone. Within a distance of three quarters of a mile, garnet, malacolite, corundum, tremolite, forsterite, soda amphiboles, lazurite, fuchsite, and other minerals occur in some abundance (2). Near the mouth of Cascade Canyon, in the SW $\frac{1}{4}$ of sec. 31, T2N, R7W, San Bernardino Base and Meridian, the limestone is colored a very dark bluish gray, or nearly black, by the iron sulphide. Boulders of the same material as well as a black, partly serpentinized, impure dolomite are to be found scattered down stream. The surfaces of the boulders are nearly always very light colored, or only slightly iron stained and commonly much corroded. The black color of the unweathered rock is only to be seen on breaking through the white outer layers.

At a second locality, 30 miles southeast, in the "New City Quarry" near Victoria Avenue, Riverside, a bed of similar crystalline limestone with garnet and forsterite, perhaps 50 feet thick and a few hundred feet long, stands nearly vertical in quartz diorite. The white limestone contains thin dark bands and patches, some of which are composed of graphite flakes, others of yellow-bronze pyrrhotite grains, coated by black material, and still others entirely of a finely granular black iron sulphide.

At neither locality does the limestone have a fetid odor. The forsterite found at these localities appears to be the first recognized in California, as this mineral is not listed by Pabst (3).

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CASCADE CANYON OCCURRENCE

The fresh rock has a deep bluish black color, corresponding to the quaker blue shown at 5-E, Plate 40, of Maerz and Paul's dictionary of color (4). A lens shows the presence of scattered, minute, brassy grains of pyrite (harder than steel, insoluble in HCl). The rock is soft and easily scratched by the knife; its powder is non-magnetic.

The material studied in thin sections is a calcite-forsterite rock in which the forsterite has mostly altered to serpentine. The serpentine is intricately penetrated by the opaque sulphides, some secondary calcite, and a brown translucent mineral which is probably an iron oxide. Minor original minerals are pale garnet, colorless mica, and rutile.

Upon treatment with dilute hydrochloric acid the black pigmenting material as well as the calcite and some of the other constituents of the rock pass readily into solution with evolution of hydrogen sulphide. The remaining residue is almost entirely white, and usually shows no undissolved black minerals under the lens. Hot dilute sulphuric acid also completely dissolves the black material with evolution of hydrogen sulphide.

The attack is somewhat slower with cold dilute sulphuric acid due to the protective action of precipitated calcium sulphate, but after the lapse of half an hour the black mineral is completely dissolved. Even dilute acetic, oxalic or citric acids dissolve the black material with the evolution of hydrogen sulphide.

When ignited in a closed tube, fumes of hydrogen sulphide are evolved along with a small amount of water which shows a slight but definite acid reaction to litmus. No sublimate of sulphur was observed. The strongly ignited material shows a white or faintly pinkish color on cooling.

Chemical analysis. A spectrographic analysis of the material by Dr. T. G. Kennard showed the following constituents to be present in the proportions indicated.

Large	Mg
Medium	Al, Fe
Small	Si, Ca
Very small	Na, K, Ti
Traces	Li, Ba, B, Cu, Mn
Extreme traces	Ga, V

Quantitative analysis, after treatment with hot dilute hydrochloric acid, gave the following results:

H ₂ O	11.90%	
SiO ₂	13.65	
Al ₂ O ₃	3.40	
Fe ₂ O ₃	2.26	
CaO	8.27	
MgO	9.14	
S	1.57	(aqua regia solution)
CO ₂	5.97	
Insoluble	44.98	
	101.14%	
Less O, equivalent to S and S ₂73	
	<hr/> 100.41%	

Since it was highly probable that some of the iron and sulphur shown in the above analysis was derived from other sources than the iron sulphide dissolved by the weak acids, a second determination for the iron and sulphur obtained from a hot, four per cent solution of oxalic acid was made with the following results:

Fe ₂ O ₃	(dissolved in 4% oxalic)	2.20% of rock
S	(dissolved in 4% oxalic)	0.37% of rock

From the iron and sulphur percentages in the oxalic acid extract, and the sulphur extracted by aqua regia, it was calculated that the rock contains about 2% FeS₂, pyrite, and 1% FeS, probably as hydrotroilite.

RIVERSIDE OCCURRENCE

The sulphide-bearing rock at the Riverside "New City Quarry" near Victoria Avenue is a coarsely crystalline white limestone, containing calcite crystals more than 1 cm. across. Dark streaks and patches are in most cases pyrrhotite and probably hydrotroilite, more rarely graphite in flakes up to 2 mm. diameter. The sulphide grains commonly have cores of bronze-yellow pyrrhotite, which is magnetic and fairly easily scratched by a needle; other grains are entirely black and very soft. Part of the black material appears to be magnetic; it may be melnikovite, the magnetic form of FeS₂ (1). A few $\frac{1}{4}$ mm., wholly unaltered, hexagonal, short pyramidal crystals of pyrrhotite are present. The best crystal was exceptional, in that it was not visibly attracted by a $1\frac{1}{2}$ inch alnico horse-shoe magnet. On this crystal Mr. Edgar Bailey identified the forms *c*, *m*, *s*, *z*, with *i*(10 $\bar{1}$ 2) listed as doubtful.

Thin sections prepared from the darkest portions of the rock, showed that the black sulphide occurred as stringers of exceedingly fine particles filling cracks and surrounding individual grains of calcite, serpentine, and other minerals. When treated with citric or stronger acids, the rapid solution of the black mineral was observed. In most cases a skeleton of undissolved white material remained which maintained the shape of the

section. Microchemical tests carried out on the section at the time of solution showed the presence of much hydrogen sulphide. When oxalic acid was used, only parts of the black areas were attacked with the formation of yellow ferrous oxalate and the liberation of hydrogen sulphide.

Petrographically the rock is similar to that from Cascade Canyon, a calcite-forsterite rock with pale and deep-red garnet, idocrase, uniaxial white mica, and opaque sulphides. Some of the forsterite is clear and colorless, with rounded outlines which reveal only suggestions of crystal

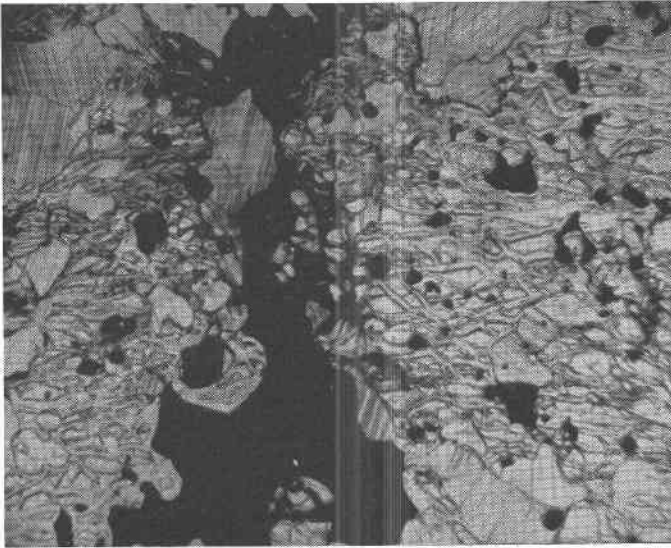


FIG. 1. Sulphides in crystalline limestone, New City Quarry, Riverside, Calif. Striated areas: calcite; meshed areas: forsterite veined by serpentine; black: sulphides and a few rutile grains. The veinlike black material is mostly pyrrhotite, the thin black veinlets mostly hydrotroilite. $\times 22$. Photomicrograph by David Howell.

faces. It shows little or no cleavage, optically probably positive, with $\alpha = 1.635$, and $\gamma = 1.671$, both $\pm .003$. The serpentine often enmeshes residual forsterite areas (Fig. 1). The indices of at least part of the serpentine are approximately $\alpha = 1.545$ and $\gamma = 1.550$. The mica is optically identical with a coarser grained pale green mica from North Hill, Riverside, which is an Mg-Al silicate with Cr, Fe, Na, and K; it appears uniaxial or has a barely perceptible (2° - 3°) 2V; γ is somewhat variable, 1.580 - $1.584 \pm .002$; $\gamma - \alpha = .035$ -. 040 ; apparently the mineral is a chrome eastonite (5). The principal garnet is nearly colorless, pinkish or pale lilac-gray; crystals are minute malformed octahedrons modified by the

rhombic dodecahedron; n is approximately 1.72, and hence the mineral is grossularite, or possibly pyrope. A very few even smaller, deep red, iron garnets appear to be rhombic dodecahedrons. Deep brown, nearly opaque grains with high relief and very low double refraction are considered to be an iron oxide. A substance occurring as numerous minute black, submetallic crystals and found by spectrographic analysis to be a Mg-Ti compound with some Mn, is not a manganiferous geikielite, for thin slivers are deep brown in color and isotropic. It may be a new mineral. A single octahedron, one millimeter in size, of magnetite or magnesioferrite was also found. A few very dark sky-blue grains, with no apparent cleavage, slight pleochroism, low double refraction and high indices may be serendibite (6). The opaque sulphides cut the other constituents, as shown in Fig. 1.

Brucite, nontronite, pyroxenes and wollastonite are abundant in the City Quarry, but were not found in association with the sulphide bands. Many other minerals have also been found in this limestone mass.

Chemical analysis. In the analysis of the Riverside rock recourse was made to the use of citric acid as the solvent. Attempts to make separations of the black sulphide by means of heavy liquids proved unsuccessful due to the fact that it existed in such fine division and in such close association with calcite and serpentine that all three were floated in the liquids. Therefore, an average sample of the whole sulphide-bearing rock was taken for the analysis.

Quantitative determinations were made with the results which follow, one gram samples being used for the analyses. Four per cent citric acid was used as the solvent.

Insolubles	36.34%
Soluble (by difference)	63.66
Total water in original rock	4.68%
Water recovered from oven-dried insolubles	1.88
Difference, or water assigned to soluble portions	2.80
Summary of constituents found in portion soluble in citric acid:	
H ₂ O (see above)	2.80%
SiO ₂	1.57
Al ₂ O ₃	0.74
FeO	1.37
CaO	28.12
MgO	6.71
S* (evolved as H ₂ S with citric acid)	0.14
CO ₂	21.20
	<hr/>
	62.65%
Less O, equivalent to S11
	<hr/>
	62.54%

*Equivalent to 0.38% FeS.

Alkalies were not determined.

Examination of the insoluble fraction showed the presence of colorless mica, precipitated finely granular silica, quartz, unattacked pyrrhotite, and a few crystals of garnet.

A study was made of the effect of citric acid on serpentines which showed that the iron sulphide must be freed from serpentine before its water content could be estimated. This was accomplished by repeated centrifuging with methylene iodide. Microscopic examination of the heavy separate showed it to consist of garnet and pyrrhotite as well as the amorphous black mineral, but to be free from limonite and serpentine.

When the heavy separate is treated with 4% citric acid, H_2S is evolved and some iron passes into solution. The reaction takes place either upon heating or in the cold.

When five hundred milligrams of the heavy separate had been collected, washed with benzene, and dried at 110° for 4 hours, a Penfield determination for water was made using previously fused PbO as a retainer for S. Under these conditions 1.28% of H_2O was recovered from the separate, indicating about 3% H_2O (above 110°) for the black sulphide.

Control experiments using pyrite, pyrrhotite, and marcasite gave negative results for H_2O .

DISCUSSION

Microscopic examination and qualitative reactions indicate that a black metallic sulphide is present as the pigmenting material of the limestones. Spectrographic and chemical analyses show that, aside from iron, no element capable of forming dark colored sulphides is present in sufficient abundance to account for the color of the rock. Microscopic and microchemical study showed two sulphides to be present in each case. Only one of these was soluble when boiled with dilute oxalic or citric acid.

For the Cascade Canyon material, amounts of iron and sulphur in the entire rock and in the fraction soluble in oxalic acid can only be satisfied by two iron sulphide minerals. The monosulphide, dissolved in dilute oxalic acid, makes up about one per cent of the total rock, and pyrite, which is not dissolved in the oxalic acid, is present to about two per cent.

In the case of the Victoria Avenue material, the sulphur recovered from the treatment of a typical sample of the black rock with citric acid is small, 0.14 per cent. When calculated as the monosulphide only 0.38 per cent is shown. Analysis of a concentrate showed that the black sulphide must be hydrous. The black iron sulphide is probably $FeS \cdot nH_2O$. It might be a polysulphide from our quantitative data, but qualitative data suggest hydrotroilite in every respect but one. The California mineral does not oxidize as readily as the hydrotroilite described by Doss (1).

It should be noted that Tarr (7) found a non-magnetic black iron sulphide, which he compared to melnikovite, with pyrite and marcasite in Missouri limestones. His published description does not exclude the possibility that he was dealing with hydrotroilite. Ehrenberg (8) has described a dark yellow gel-formed pyrite with a composition between FeS and FeS₂.

ORIGIN OF THE HYDROUS IRON SULPHIDE

Hydrotroilite and serpentine are among the youngest minerals present at either locality. They may both belong to a very late hydrothermal stage, later than most of the minerals listed as "late hydrothermal" by Richmond (6), or the hydrotroilite may represent a first stage in the weathering of the other iron sulphides. We think that the hydrotroilite is probably hydrothermal, though convincing evidence is lacking.

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