

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

VOL. 15

MAY, 1930

No. 5

CURTISITE

A NEW ORGANIC MINERAL FROM SKAGGS SPRINGS,
SONOMA COUNTY, CALIFORNIA.

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In the hot spring area of the Franciscan formation at Skaggs Springs, inflammable gases are given off in small quantities at one of the surface vents in the sandstone. At this point specks of a greenish yellow mineral were observed by Mr. L. Curtis of Skaggs Springs; he in turn showed them to one of us (Allen) as something unusual. On examination we found its optical properties to be unlike those of any known mineral. Chemical tests showed it to be organic in nature. A detailed examination of its properties has proved the validity of the preliminary conclusions and demonstrated that the mineral is a hydrocarbon of high atomic weight and extremely high melting temperature.

The mineral occurs in small scattered particles, clusters and crystalline aggregates along cracks and porous parts in the pale gray and buff sandstone. It is associated with opaline silica, arsenic sulfide as realgar, and mercuric sulfide as metacinnabarite. The relations indicate that in this series of minerals deposition of the silica began first; that of the curtisite last. The periods of deposition overlapped considerably. Realgar occurs in the usual small prismatic, red to orange-red crystals, 1 to 3 mm. in length and with characteristic optical and other physical properties. The metacinnabarite occurs in small equant grains, 1 mm. or less in diameter and with indications of octahedral faces here and there, grayish black in color and of metallic luster. The metacinnabarite grains are found only sporadically and then in clusters. Both realgar and metacinnabarite are subordinate in amount to curtisite, which in turn is less abundant than the silica. The opaline silica is restricted to crack fillings whereas the other three minerals are in addition scattered through more porous portions of the sandstone itself.

The crystals of curtisite range in size from fine particles of irregular shape to square or six sided flakes, 1 mm. in diameter. Clusters of these flakes are common along cracks in the sandstone and are recognizable both by the color, yellow to pistachio green, and by the perfect basal cleavage which causes the minute cleavage faces to sparkle in the light after the manner of the micas. The luster is vitreous to adamantine. Fracture, conchoidal. Hardness less than 2. Specific gravity, as determined by heavy liquids (Klein's solution) is approximately 1.235 to 1.237.

No individual grains bounded by measurable crystal faces were observed. The crystal system is probably orthorhombic. Cleavage perfect after (001); poor after (100). In transmitted light the color is yellow to yellowish green; pleochroism noticeable, γ = yellow; β = yellow, α = pale yellow to nearly colorless; absorption, $\gamma \geq \beta > \alpha$. Refractive indices were determined by the immersion method and for sodium light are: $\alpha = 1.557 \pm .001$, $\beta = 1.734 \pm .001$, $\gamma = 2.07$. The optic axial angle, $2V = 83.5^\circ$, was measured directly with an oil immersion objective; the optical character is positive. The dispersion of the optic axes is slight, $2V_p > 2V_v$. The acute bisectrix emerges apparently normal to the cleavage plane (001); the plane of the optic axes is normal to (100). It is possible that the crystal system is monoclinic and that the acute bisectrix is slightly inclined to the cleavage plane; if so the inclination is so slight that it was not detected. Attempts to produce etch figures on (001) were not successful.

In order to obtain adequate amounts of the mineral for chemical analyses, a long series of separations, in part mechanical by heavy liquids, but chiefly chemical by solution in benzol and recrystallization, was made. After repeating the process of recrystallization in benzol 15 times we obtained a product nearly free from contamination by the small amounts of certain dark brown oils that are apparently associated with the mineral in the rock. For these recrystallization experiments, benzol was used in preference to other solvents because of its volatility and the ease with which it is removed. The mineral is only slightly soluble in hot acetone, amylacetate, butylalcohol, petroleum ether; less than one half per cent is dissolved in hot carbon bisulfide, carbon tetrachloride, chloroform, ether; in boiling benzol about one half per cent is dissolved; in boiling toluol, about 1.5 per cent; in xylol, about 2.5

per cent; in hot aniline over 10 per cent. It is also soluble to some extent in pyridine.

For the first chemical analyses made on the natural mineral and on samples that had been recrystallized only once or twice we are indebted to Dr. F. B. LaForge of the Bureau of Chemistry, U. S. Department of Agriculture. At the time the samples were given to Dr. LaForge we did not know of the organic impurities admixed or adsorbed by the curtisite and became aware of them only after he recommended that the curtisite be purified by recrystallization. The effect of the impurities was especially noticeable in the determinations of both melting point and molecular weight. The results of the combustion analyses made by Dr. LaForge are listed in Table 1.

TABLE I
ANALYSES OF CURTISITE

No.	Amount taken, grams	Residue, grams	C	H
1	0.1073	None	92.48	5.42
2	0.1111	None	92.17	4.97
3	0.0917	.0004	92.39	5.53
4	0.1307	.0007	92.34	5.52
5	0.1560	.0025	91.87	5.32

Of these samples, Nos. 1 and 2 were crystallized once from pyridine before analysis; Nos. 3 and 4 were recrystallized several times from benzol. No. 5 was the original curtisite separated by heavy solutions from the sandstone and other matrix. This material on heating turned brown and showed no sharp melting point. We noted that with each recrystallization from benzol, the product became lighter in color and showed less tendency to turn brown on heating. It was thus evident that in order to obtain the mineral free from other organic material a series of repeated recrystallizations should be made. For this purpose additional material was kindly collected for us by Mr. Curtis. The samples were crushed and heated in boiling benzol, which dissolved the curtisite and also the impurities. The liquid was nearly colorless but noticeably fluorescent in pale blue tints. It was boiled down until precipitation of the curtisite began. After cooling, the fine flaky precipitate

was filtered. This process was then repeated; twelve to fifteen recrystallizations were thus carried through; with each operation an appreciable portion of the material was lost. The final yield was less than two grams of purified substance. With increase in purity the color of the mineral became pale lemon yellow and the benzol solution lost most of its fluorescence.

With this purified material combustion analyses were made by Wright in the laboratory of Dr. M. Phillips of the Color Laboratory of the Department of Agriculture. The results are given in Table 2.

TABLE 2
ANALYSES OF PURIFIED CURTISITE

No.	Amount taken, grams	Residue, grams	C	H
1	0.1238	0.0015	94.12	5.73
2	0.1548	0.0023	93.70	5.41

It is evident from these two analyses that the mineral is a hydrocarbon in which the ratio of the carbon atoms is to that of the hydrogen atoms as 4 to 3.

A series of molecular weight determinations was made by the depression of the boiling point method. For results on material recrystallized only once or twice from benzol, we are indebted to Dr. Phillips (see Table 3).

TABLE 3
MOLECULAR WEIGHT DETERMINATIONS ON CURTISITE

No.	Weight of mineral, grams	Weight of solvent, grams	Depression of Boiling point °C	Molecular weight
1	0.0877	19.6670	0.055	211.6
2	0.1128	21.2565	0.065	213.0

Determinations made by Wright with purer material, but with aniline as a solvent, yielded the results given in Table 4.

Of these determinations the first two are in good agreement; the last is much lower. Aniline is very hygroscopic and this may account for the lowering of the last value. Unfortunately there was

not sufficient material available to make a series of new determinations with xylol or toluol as solvents. The formula $C_{20}H_{15}$ has the molecular weight 255; the formula $C_{24}H_{18}$, the molecular weight 306. From the evidence available it is probable that $C_{24}H_{18}$ represents the composition of the mineral curtisite.

Comparative tests made with the aid of photographic plates showed no trace of radioactivity in this mineral.

The behavior on heating was first determined on the powdered natural mineral. The powder turned dark brown when held for a long time between 275° and $300^{\circ}C$; no definite melting temperature was observed. Heated over an open gas flame in a small glass tube

TABLE 4
MOLECULAR WEIGHT DETERMINATIONS ON CURTISITE (Purer Material)

No.	Weight of mineral, grams	Weight of solvent, grams	Depression of Boiling point $^{\circ}C$	Molecular weight
1	0.3894	23.7700	0.181	291.4
2	0.3569	22.5585	0.174	292.8
3	0.2085	22.5585	0.125	236.2

the mineral melts to a clear liquid, but discolors rapidly. Material that has been recrystallized 8 times also turns brown if held for a long time at $300^{\circ}C$. If it is immersed for one minute only, it begins to discolor at $345^{\circ}C$. At $350^{\circ}C$ it turns dark brown. At $358^{\circ}C$ it melts fairly sharply and discolors rapidly. A preparation of the highest purity (recrystallized 15 times) behaved as follows: At $360^{\circ}C$ the sample turned brown but failed to melt within one minute. At $370^{\circ}C$ it melted within one-half minute, at the same time turning very black.

Heated in a tube, open at both ends, the mineral sublims readily and is deposited on the cooler walls, away from the heated area, in very thin flakes that scintillate and show beautiful iridescent colors of interference.