THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

VOL. 5 OCTOBER, 1920 No. 10

FLAGSTAFFITE, A NEW MINERAL FROM ARIZONA

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In the investigation of tree rings and their relation to cyclic changes in weather and to certain astronomical features,[1] Dr. A. E. Douglass, Professor of Astronomy at the University of Arizona, found in the radial cracks of certain buried tree trunks a pure, transparent, crystalline substance. The investigation of this material is made the subject of this paper. The logs, evidently of some species of pine, were found buried in the debris washed down from the San Francisco Mountains, a few miles north of Flagstaff, Arizona. They became exposed by a later deep cut, resulting from the flood waters of these mountains. From a study of the trees of the immediate district it is estimated that the logs have been buried not less than five hundred years. This conclusion is arrived at from an investigation of the rings in the trees and stumps still standing and rooted in the debris. Dr. Douglass also states that the ring cycles are entirely different from those found in trees at present living in the district, and that, furthermore, the buried logs vary greatly among themselves. The figure given above, 500 years, is accordingly a minimum value, and many of the logs must have been much older.

The filling in the radial cracks resembles on a small scale typical vein structure, as the walls appear to be covered with the crystalline material, which frequently projects towards the center, leaving many drusy cavities. In these cavities the most perfect crystallizations are found. In places the cracks are filled with more compact and less well crystallized material. The

[1] A. E. Douglass. Climatic Cycles and Tree-growth, A Study of Annual Rings of Trees in Relation to Climatic and Solar Activity. *Publ. Carnegie Inst. Wash., Bull.* 289.

cracks from which most of the material was secured averaged about two millimeters across. It was first thought by the writer that the material was simply some common resinous substance, but on examination with a hand lens beautiful transparent ice-like crystals were observed, with sharp faces, and it was thought worth while to investigate as far as possible the limited amount of material available. Thus far only about three grams of the purified material have been obtained.

The crystals are very soft, being easily crushed between paper. They are colorless and transparent like ice, with a melting point of 99–100.5° C. Sublimation takes place at the temperature of melting, sharp hair-like needles being formed in the tubes in which the melting point was determined. On platinum foil the crystals melt and burn with a smoky flame like a drop of oil. No residue is left on the foil. The crystals are very soluble in warm alcohol, depositing in short needles by rapid evaporation, and in stouter crystals on slower cooling. In heated benzene they are also very soluble, depositing on cooling in thin needles sometimes nearly 2 cm. in length. They are less soluble in ether, and insoluble in water. The average index of refraction as found by the immersion method, using mixtures of clove and almond oils, is 1.510 ± 0.003. An Abbe refractometer was used to determine the value of the oils. The density is 1.092.

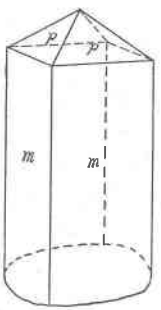

FIG. 1.

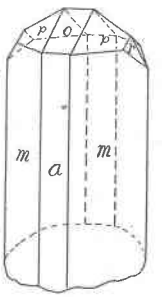

FIG. 2.

Several of the best crystals were selected for measurement, the largest being about one millimeter in length, and one half millimeter in diameter. These were mounted on the end of a needle by means of sticky shellac (shellac and alcohol) and after the material had hardened the crystals were measured on a

Goldschmidt two-circle goniometer. The crystallization was found to be orthorhombic, the simplest and most common combination being represented in Fig. 1. Fig. 2 is somewhat idealized and shows a combination of all of the forms observed; one crystal measured contained representatives of all of these forms in approximately the relationship shown in this figure. The domes and pyramids are very frequently unsymmetrically developed in such a manner as to give the crystal a monoclinic aspect.

The crystallographic data obtained are given in the following table.

TABLE 1

CRYSTALLOGRAPHY OF FLAGSTAFFITE

$p_0 = 0.4813$, $q_0 = 0.5951$. $a : b : c = 1.2366 : 1 : 0.5951$.

Letter	φ	ρ	Symbol	No. of Faces Measured
p.....	38° 58′	37° 26′	111	12
o.....	90 00	25 40	101	6
r.....	15 40	61 32	131	4
m.....	38 58	90 00	110	4
a.....	90 00	90 00	100	2

In order to obtain a sufficient amount of the material for a chemical analysis it was found necessary to devise a method for its purification. This was successfully accomplished by first treating the material with ether to dissolve as much as possible of the yellow resin, with which the crystals were mixed, and then recrystallizing from alcohol. During the process of recrystallization, when the crystals became yellowish due to resinous material, they were washed rapidly with ether. The next crop of crystals from alcohol would be nearly colorless. Some of the pure crystals from alcohol were measured and found to be identical with those from the wood. They were therefore of the same chemical composition and no reaction with the solvent had taken place. The average of the best results from five analyses is given in the table below. The results checked among themselves as well as is usually the case in elementary organic analysis.

	Per cent.	Ratio	Simplified ratio
Carbon.....	66.21	5.52	3.97
Hydrogen.....	11.55	11.45	8.31
Oxygen.....	22.24	1.39	1.00

As seen from the last column, the empirical formula for the substance is C_4H_8O.

In order to determine the molecular formula a molecular weight determination is necessary. This was accomplished successfully by the boiling point method, using benzene (C_6H_6) as a solvent. The crystals from benzene were also measured on the goniometer and found to be identical with the original ones, showing that no combination took place between the solvent and the substance. The molecular weight was found to be 210 ± 7, this being the result from six determinations. This shows conclusively that the empirical formula is to be taken three times, giving $C_{12}H_{24}O_3$ as the molecular formula, with a theoretical molecular weight of 216.

No results have been obtained as yet regarding the molecular structure of the substance. Work in this direction is in progress but the small amount of material available makes a successful outcome exceedingly doubtful.

The occurrence of this mineral in buried logs and its association with resinous material would seem to show conclusively that it has been derived, thru some process of oxidation or hydration perhaps, from the natural resins of the wood. A search among the terpenes and their derivatives, however, fails to bring to light any substance corresponding to flagstaffite. The nearest approach, perhaps, is colophonin, $C_{10}H_{22}O_3$, a crystalline product mentioned by Beilstein.[2] The monohydrate of this is described as subliming easily and melting at 106°. It is easily soluble in water. Tschirsch has published a large number of analyses of resinous substances.[3] Many of these are non-crystalline and may be mixtures, and none correspond very closely to flagstaffite.

A number of other organic minerals of occurrence similar to flagstaffite have been described from time to time. Many of these are amorphous or at best poorly crystallized, but a few are well crystallized. One of the best known, perhaps, is fichtelite. In its mode of occurrence it resembles flagstaffite very closely, but in composition it differs, since it is without oxygen. Many other organic compounds have been described as minerals, but do not resemble flagstaffite in any respect except that they are of organic origin.[4]

The name *flagstaffite* is given to the new mineral from the town, Flagstaff, Arizona, near which it was found.

[2] Handbuch der Organischen Chemie, (3), 563, 1897.

[3] Die Harze und die Harzbehälter, Leipzig, 1906.

[4] See Dana, System of Mineralogy.