CASTANITE, A BASIC FERRIC SULFATE FROM KNOXVILLE, CALIFORNIA*

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The status of castanite, a basic ferric sulfate with the formula $Fe_2O_3 \cdot 2SO_3 \cdot 8H_2O$, described from Sierra Gorda, Chile, by Darapsky[1] in 1890 is still in doubt. E. S. Dana[2] lists it as a distinct mineral, but Linck[3] states that castanite, along with paposite and hohmannite, is undoubtedly a synonym of amarantite ($Fe_2O_3 \cdot 2SO_3 \cdot 7H_2O$).

The study of some specimens recently collected at the old Redington or Boston quicksilver mine[4] at Knoxville, Napa County, California, furnishes data which indicate that castanite is a valid mineral species.

OCCURRENCE OF THE CASTANITE

My attention was called to the mineral here described, which was afterward identified as castanite, by Mr. George E. Gamble, owner and superintendent of the mine and one of my former students. Under Mr. Gamble's guidance I collected a number of castanite specimens from the footwall stope on the adit level in March 1930, and later Mr. Gamble kindly sent me additional material.

The castanite occurs in a brecciated impure opal replacement of serpentine which is known throughout the Quicksilver Region as "opaline."[5] In some of the specimens the castanite cements angular fragments of the opaline. A thin section of the opaline reveals opal as the principal constituent with some secondary chalcedony, disseminated pyrite and marcasite (metallic acicular crystals may be millerite), and relict grains of picotite from the peridotite stage.

Cinnabar and sulfur are directly associated with the castanite. All specimens contain minute well-formed sulfur crystals implanted on the castanite. A few of the specimens show cinnabar which occurs as a coating on the opaline fragments and seems to be earlier than the castanite.

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[1] *N. Jb. f. Min.*, **1890**, 2, pp. 267–9.

[2] *System of Mineralogy*, 6th ed., p. 964, 1892.

[3] Hintze's *Handbuch der Mineralogie*, I Band, 32 Lief., pp. 4426–7, 1929.

[4] Also called the Knoxville mine.

[5] See *Bull.* **27**, *California State Min. Bureau*, p. 20, 1908.

The following sulfate minerals, copiapite, coquimbite, botryogen (palacheite), redingtonite, and knoxvillite, have been found at this mine. The writer has identified a fibrous ferric sulfate mineral from the footwall stope but not directly associated with the castanite as fibroferrite. This famous mine also furnished the type specimens of metacinnabar.

The castanite consists of a massive aggregate of minute subhedral crystals out of which there have grown clusters and single crystals of prismatic habit. The massive castanite has a beautiful "burnt-orange" color (Ridgway 11*j*, between orange rufous and Sanford's brown); the crystals are dark brown (Ridgway 10 *l*).

GEOMETRICAL CRYSTALLOGRAPHY

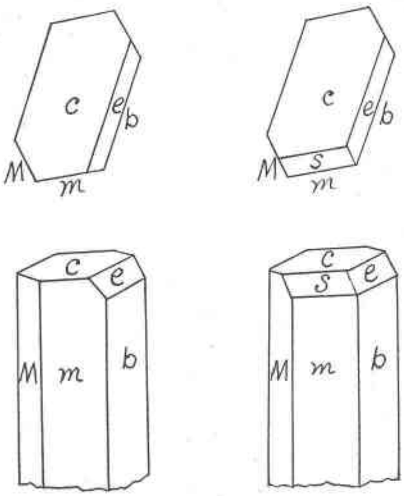

FIG. 1. FIG. 2.

FIGS. 1 and 2. Castanite crystals from Knoxville, California.
$b\{010\}$, $m\{110\}$,
$m\{1\bar{1}0\}$, $c\{001\}$,
$e\{011\}$, $s\{112\}$.

INTERFACIAL ANGLES OF CASTANITE

$(010)\wedge(110)=61°34'$ $(28', 33', 33', 38', 38')$
$(010)\wedge(110)=46\ 49$ $(42, 49, 50, 50, 56)$
$(001)\wedge(011)=42\ 32$ $(29, 31, 33, 34, 35)$
$(011)\wedge(010)=47\ 52$ $(46, 47, 54, 54, 60)$
$(001)\wedge(110)=89\ 10$ $(9, 10, 10, 11, 11)$

The crystals are prismatic in habit and on measurement prove to be triclinic. No doubly terminated crystals were found, but since positive and negative ends of different crystals have similar terminations the crystal class is probably pinakoidal. The crystals vary from about 2 mm. up to about 10 mm. in longest dimension. Six forms are present on the crystals examined. In order of prominence these are: $b\{010\}$, $M\{1\bar{1}0\}$, $m\{110\}$, $c\{001\}$, $e\{011\}$, and $s\{112\}$. Typical crystals are shown in Figs. 1 and 2. In habit the crystals are fairly constant. The only noteworthy variation is the relatively large size of the *e* faces on some crystals. The crystals are somewhat striated and etched and are not suitable for very accurate goniometric work. It was necessary to measure the three zones [001], [100], and $[1\bar{1}0]$ each on a different crystal. The measurements are given above (each the average of five). The (112) face was identified by the fact that it is common to the [001:110] and $[011:1\bar{1}0]$ zones. No good measurement could be obtained from this face.

From these five measured angles the following geometrical constants were calculated by spherical trigonometry:[6]

Geometrical constants of Castanite

$\alpha = 89°\ 50'$, $\beta = 91°10'$, $\gamma = 78°\ 46'$; $a{:}b{:}c = 0.726{:}1{:}\ 0.895$. The calculations also yield the interfacial angles $(100) \wedge (010) = 101°14'$; $(001) \wedge (010) = 90°\ 24'$; $(100) \wedge (001) = 88°\ 48'$; and the interzonal angles $[001] \wedge [010] = 90°10'$; $[001] \wedge [100] = 88°50'$; $[001] \wedge [1\bar{1}0] = 90°54'$; $[001] \wedge [0\bar{1}1] = 48°16'$. The stereographic projection of castanite drawn on one of the convenient Penfield sheets is shown in Fig. 3. In order to obtain the geometrical constants it was necessary to solve the spherical triangles *cmb*, *amc*, and *abe*, first finding the angle *am* by the harmonic modification of the cotangent formula.[7]

In order to check the axial ratio a gnomonic projection (Fig. 4) was constructed from the measured and calculated angles. Penfield sheets may also be used for gnomonic projections since scale No. 2 of these sheets gives gnomonic degrees.

The faces are plotted and the prominent zone-lines are drawn. The center of the projection is *z* and a line *zv* normal to the zone-

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[6] I am indebted to my assistant, Dr. J. D. H. Donnay, for a careful checking of the computations.

[7] T. V. Barker, *Graphical and Tabular Methods in Crystallography*, p. 63, **1922.**

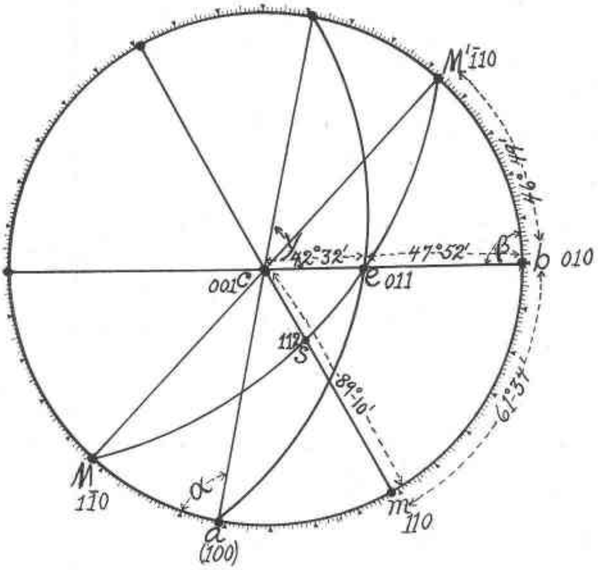

FIG. 3. Stereographic projection of castanite showing the five interfacial angles used in the calculations.

line [011:100] determines the point v. An arc with radius zv gives the point x on the line lp[8] (l being the intersection of zv with the zone-line [100:001] and p, the intersection of a line thru z parallel to the zone-line [100:001] with the circle of projection). A line through x parallel to lzv gives w. Then zw equals c in terms of the radius. A line zn through z normal to the zone-line [001:011] gives the point n on the zone-line [101:111]. An arc with the radius un gives the point y on the line uhy. Then yz is equal to c/a in terms of the radius. In order to determine a, the distance zr equal to zw is laid off on the line zy. Then draw any radius such as zt. Connect y and t and from the point r draw rq parallel to yt. Then zq equals a in terms of the radius of the circle. Graphically determined values for a and c are respectively 0.728 and 0.900 which check well with the calculated values.

The graphic method just outlined was described by the writer.[9]

Since the closely related mineral amarantite is also triclinic, the question arises as to whether the Knoxville crystals are not amar-

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[8] To avoid confusion lp is not drawn.

[9] *School of Mines Quarterly*, vol. **29**, pp. 28–29, 1907.

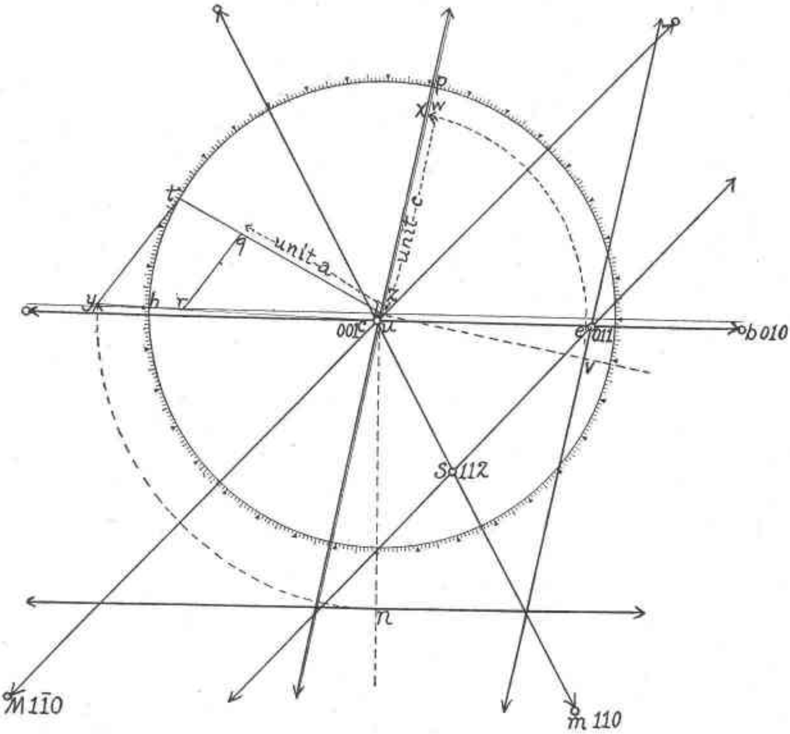

FIG. 4. Gnomonic projection of castanite showing graphic determination of the axial ratio $a:b:c$.

antite with a different orientation than that given by Penfield.[10] Although two of the interfacial angles for amarantite (100∧001 = 88° 53′ and 001∧111 = 42° 46′) are close to two for castanite (100∧001 = 88° 48′ and 001∧011 = 42° 32′) the other angles do not check. As far as I can judge from the geometrical crystallography, castanite and amarantite are different minerals. It is fortunate that the one-circle measurements of Penfield are available, for with the data given in Goldschmidt's WINKELTABELLEN it would be difficult to prove that castanite is a distinctive mineral. Two-circle measurements have some serious limitations.

In case more complex crystals of castanite are found in the future it may be convenient to have a list of coördinate angles available. And so coördinate angles for the known forms of castanite have

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[10] *Am. Jour. Sci.*, [3], vol. **40**, p. 199, 1890.

been calculated by the formulae for transforming interfacial angles to coördinate angles given by Moses and Rogers.[11] The following are the angles obtained:

COÖRDINATE ANGLES FOR CASTANITE

	ϕ	ρ
(001)	108°55′	1°14′
(011)	1 17	42 9
(112)	62 56	33 8
(010)	0 0	90 0
(100)	101 14	90 0
(110)	61 34	90 0
$(1\bar{1}0)$	133 11	90 0

For the three first forms good graphic checks were obtained as follows: ϕ^{001}(109° 10′), ρ^{001}(1° 15′), ϕ^{011}(1° 30′), ρ^{011}(42° 12′), ϕ^{112}(63° 40′) ρ^{112}(35° 30′). The polar elements and symbols of Goldschmidt are not used, for in the opinion of the writer they serve no useful purpose.

CLEAVAGE

There is perfect cleavage parallel to (010) and less perfect parallel to (110) and $(1\bar{1}0)$.

OPTICAL CRYSTALLOGRAPHY

Cleavage flakes parallel to (010) give a brownish-red color for vibrations parallel to the slower ray and a medium yellow for vibrations parallel to the faster ray. The faster ray makes an angle of about 22° with the trace of the *c*-axis. The sketch of Fig. 5 gives an idea of the behavior of the cleavage fragments in polarized light. With convergent light a somewhat eccentric biaxial interference figure with moderate 2V and high dispersion is obtained. Besides being eccentric the axial plane is somewhat inclined to (010) as shown in Fig. 6. The optical character is negative.

The principal indices of refraction are: $n_\alpha = 1.553 \pm .003$, $n_\beta = 1.643 \pm .003$, $n_\gamma = 1.657 \pm .003$; $n_\gamma - n_\alpha = 0.104 \pm .006$. These values were found by the immersion method.

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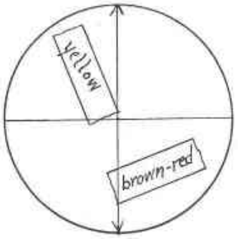
[11] *School of Mines Quarterly*, vol. **24,** p. 36, 1902; also *Zeit. f. Kryst. u. Min.*, vol. **38,** p. 226, 1903.



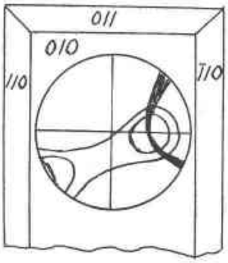


FIG. 5. FIG. 6.

FIG. 5. Cleavage flakes of castanite in polarized light.

FIG. 6. Interference figure of castanite on (010).

SPECIFIC GRAVITY

The specific gravity of the castanite is about 2.2 as judged by its behavior in a mixture of methylene iodide and benzol.

PYROGNOSTIC TESTS

Heated in the closed tube the castanite turns dark and gives water which has an acid reaction.

Carefully heated before the blowpipe in platinum forceps, a fragment of the mineral turns first pale orange, then grayish brown, next dark red, and finally black, and becomes rounded on the edges (fusibility about 5). If a long splinter is heated at the extreme tip the various colors mentioned may be observed on the splinter as shown in the sketch of Fig. 7 with the original brown at the lower unheated end.

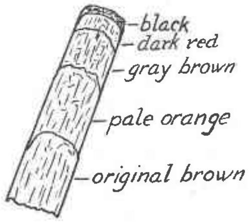


FIG. 7. Heated splinter of castanite (×10).

CHEMICAL PROPERTIES

The castanite is practically insoluble in cold water, but it is decomposed by hot water. It is easily soluble in hydrochloric acid and the solution gives tests for ferric iron and the sulfate radical. All the iron is in the ferric condition and no aluminum and only a trace of magnesium is present.

A chemical analysis made by my colleague, Mr. O. C. Shepard, furnished the following results:

ANALYSIS OF CASTANITE BY O. C. SHEPARD

		Mol. Ratios		Theory
Fe_2O_3	34.47	0.215	1	34.58
SO_3	35.11	0.438	2.03	34.58
$H_2O+110°C=14.58$ $H_2O-110°C=15.73$	30.31	1.685	7.83	30.84
Insol.	0.22			
Total	100.21			

The molecular ratios are 1:2.03:7.83, which is very close to the empirical formula $Fe_2O_3\cdot 2SO_3\cdot 8H_2O$ assigned to castanite by Darapsky.

Castanite is stable at ordinary room temperature, but specimens on a window sill exposed to the sun changed from burnt orange to pale orange and gradually fell to a powder. Several specimens were spoiled in this way.

Dehydration tests were carried out by Mr. Shepard at varying temperatures. The only prominent break is at 27°C. Heated for nine days at this temperature the loss in weight is 14.91 per cent (average of 14.83 and 14.98 for two samples of different weights).

This indicates that the composition for the compound formed is $Fe_2O_3\cdot 2SO_3\cdot 4H_2O$. On changing from $Fe_2O_3\cdot 2SO_3\cdot 8H_2O$ to $Fe_2O_3\cdot 2SO_3\cdot 4H_2O$ the loss in weight should be 15.57 per cent. A mineral with the composition $Fe_2O_3\cdot 2SO_3\cdot 4H_2O$ from Chile was analyzed by Mackintosh[12] but the mineral was not named or adequately described although it was stated that it was perhaps an alteration of amarantite. At 100°C the loss in weight is only 15.62 per cent. Had sufficient time been given, the loss would probably have been attained at 27°C. Heated at intervals of 20°C the loss in weight is gradual until a temperature of 360°C is reached, when the loss is 30.97 per cent which is the total water content (theoretical amount =30.84 per cent).

COMPOUNDS OF THE $Fe_2O_3\cdot 2SO_3\cdot nH_2O$ SERIES

In addition to castanite there are a number of other compounds of the $Fe_2O_3\cdot 2SO_3\cdot nH_2O$ series with the variations in the value of n. The following have come under my notice:

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[12] *Am. Jour. Sci.* [3], vol. **38**, p. 243–5, 1889.

$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$	( )	Orthorhombic.	Maus, 1827.
$Fe_2O_3 \cdot 2SO_3 \cdot 3H_2O$	(Rubrite)	?	Darapsky, 1890.
$Fe_2O_3 \cdot 2SO_3 \cdot 4H_2O$	( )	?	Mackintosh, 1889.
$Fe_2O_3 \cdot 2SO_3 \cdot 5H_2O$	(Butlerite?)	Monoclinic.	Posnjak and Merwin, 1922.
$Fe_2O_3 \cdot 2SO_3 \cdot 7H_2O$	(Amarantite)	Triclinic.	Frenzel, 1887.
$Fe_2O_3 \cdot 2SO_3 \cdot 8H_2O$	(Castanite)	Triclinic.	Darapsky, 1890.
$Fe_2O_3 \cdot 2SO_3 \cdot 10H_2O$	(Fibroferrite)	Monoclinic?	Rose, 1833.

This is a remarkable series of hydrates, but they are not all well-established. Posnjak and Merwin[13] in a rather elaborate study of the Fe_2O_3-SO_3-H_2O system produced $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ and $Fe_2O_3 \cdot 2SO_3 \cdot 5H_2O$ within the temperature range of 50°–200°C. What is possibly a dimorphous form of $Fe_2O_3 \cdot 2SO_3 \cdot 5H_2O$ was described under the name "butlerite" by Lausen.[14] They failed to obtain $Fe_2O_3 \cdot 2SO_3 \cdot 3H_2O$, the rubrite of Darapsky,[15] for which there is no adequate mineralogical description. As a consequence it has not been accepted as a mineral. They also failed to produce $Fe_2O_3 \cdot 2SO_3 \cdot 4H_2O$, which was assigned to an unnamed mineral from Chile by Mackintosh. There is no adequate description of this compound and its status is doubtful.

The amarantite, castanite, and fibroferrite are now well-established minerals and the failure of Posnjak and Merwin to obtain these minerals is due to the fact that they worked above 50°C.

ORIGIN OF THE CASTANITE

That castanite is a low-temperature mineral seems certain because it is unstable above 27°C and because Posnjak and Merwin failed to produce it at temperatures above 50°C. In view of its close association with sulfur and cinnabar it seems likely that castanite is a low-temperature solfataric mineral. Its ultimate source is in all probability the marcasite and pyrite which are prominent in some parts of the mine.

VALIDITY OF CASTANITE

The crystallographic study combined with the chemical analysis indicates that castanite is a definite mineral with the formula $Fe_2O_3 \cdot 2SO_3 \cdot 8H_2O$.

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[13] *Jour. Am. Chem. Soc.*, vol. **44,** pp. 1965–94, 1922.

[14] This journal, vol. **13,** p. 211, 1928.

[15] *N. Jb. f. Min.*, **1890,** 1, p. 65.