

THE AMERICAN MINERALOGIST

VOL. 3

AUGUST, 1918

No. 8

THE COLOR CHANGE IN VIVIANITE AND ITS EFFECT ON THE OPTICAL PROPERTIES

THOMAS L. WATSON

University of Virginia

VIVIANITE, the hydrous phosphate of ferrous iron, is generally described as colorless when pure and unaltered, but in most of its known occurrences it is green to blue, the latter color being probably the most common. The streak is at first colorless to faint bluish white, but rapidly changes to deep blue on exposure. Reduction of the mineral to powder by grinding likewise produces a rapid change in color, from colorless to deep blue. This change in color of vivianite has been ascribed to oxidation of a part of the iron to the ferric condition, since analyses of the strongly colored varieties of the mineral invariably show the presence of ferric oxide in quantity ranging up to 33 per cent. or more.

In a recent study¹ of vivianite in large crystals from a new locality near Plant City, Florida, it was found on microscopic examination that fragments broken from the pale green crystals, or coarse powder, immediately after grinding, were colorless and non-pleochroic. The powder, however, rapidly changed to deep blue and became strongly pleochroic. The microscopic aspect of the material suggested that the change might possibly be due to inversion from one form to another, and not to oxidation.

Chemical study of the mineral was undertaken to determine the cause of this change in color, which was observed to progress most rapidly on exposure, especially in sunlight. A lot of uniformly colored pale green crystals was selected and divided into two portions (*a*) and (*b*) in each of which ferrous iron was determined; (*a*) without grinding, and (*b*) after fine grinding. The

¹ Watson, T. L. and Gooch, S. D.: *Jour. Wash. Acad. Sci.*, 8, (4), 82-88. 1918; see abstract in this number, p. 163.

unground sample of vivianite crystals gave on analysis 42.88 per cent. FeO and no Fe₂O₃, as against 38.43 per cent. FeO in the finely ground sample. The figures clearly show that fine grinding resulted in the oxidation of 4.45 per cent. FeO to Fe₂O₃, equivalent to 4.94 per cent. Fe₂O₃. The results prove beyond reasonable doubt that the change of color in vivianite is due to oxidation and not to inversion. The rapidity with which oxidation takes place on fine grinding is noteworthy.

This rapid change of color in vivianite being thus shown to be due to oxidation and not to inversion, attention was directed to the effect of oxidation of a part of the ferrous iron upon the optical properties of the mineral. A search of the literature was without results, since the optical data given for the mineral from different localities were not accompanied by chemical analyses; this situation, which is met with in connection with many mineral descriptions, should certainly be remedied in future work.

TABLE 1. OPTICAL DATA FOR VIVIANITE

	Color.	Authority.	Char-acter.	Refractive Indices.				Pleochro-ism.
				α	β	γ	2V	
1	Pale green	Larsen ²	+	1.580	1.598	1.627	large	None
2	Deep blue	Larsen ³	+	1.579	1.603	1.633	85°	Strong
3	Blue	Rosicky ⁴	+	1.5809	1.6038	1.6361	73° 7-20'	Weak
4	Blue	Winchell ⁵	-	1.5766	1.6050	1.6267	73° 10'	Strong

² 1.5 miles southeast of Plant City, Florida. Watson and Gooch, *loc. cit.*

³ Mullica Hill, New Jersey. The writer is indebted to Dr. Larsen for permission to include these hitherto unpublished results.

⁴ Valdic, Bohemia. Quoted by Ford, *App. III, Dana's System of Mineralogy.*

⁵ *Optical Mineralogy*, p. 388, 1909.

The optical data determined by Dr. Larsen, for the Florida material, as given in the paper above cited, were obtained on pale green fragments, and undoubtedly represent true, unaltered, vivianite. The data given in the literature, on the other hand, appear to have been measured in most cases on blue material, in which part of the ferrous iron had been oxidized to the ferric state. The discrepancies between the various statements are probably explainable in this way, altho in the absence of analyses the exact relation of change in refractive indices and other properties to the ferric iron content can not be traced.

Nevertheless it may be of interest to compare the data on specimens from different localities; this is done in table 1.

The pleochroism of finely ground material from occurrence 1 is essentially identical with that shown by 2 and 4, namely: X deep blue, Y nearly colorless, Z colorless, pale olive green, or brownish. As in the first case the amount of ferric oxide is known to have increased from practically zero to nearly 5 per cent. it seems reasonable to conclude that the pleochroism is connected with this change in all cases, and that pure vivianite is an essentially non-pleochroic mineral.

With reference to the other optical properties, allowing for such variation as is likely to be shown from one specimen to another, coming from widely separated localities, and studied by different investigators, it seems clear that the oxidation of part of the iron is connected with a definite increase in the values of refractive indices β and γ , while α remains constant within the limits of accuracy of measurement. The relations in the case of the optic axial angles are less clear, for the data given appear to be inconsistent. Calculation of the angles for numbers 3 and 4 of table 1 by the usual formulas⁶ gave $82^{\circ}7'$ and $81^{\circ}46'$ respectively, whereas the values observed are decidedly less than these.

The general conclusions are justified, however, that the change of color shown by vivianite on exposure or grinding is connected with partial oxidation of the iron to the ferric condition, and that marked changes in pleochroism and refractive indices are connected with this alteration.

NOTE ON IRON AS A CAUSE OF BLUE COLORS IN MINERALS.

EDGAR T. WHERRY. *Washington, D. C.*—Since ferrous iron usually colors minerals green, and ferric iron yellow or brown, it may seem rather remarkable that the presence of both together should give rise to a blue color, as in the case described in the above paper. It may be pointed out, however, that this is by no means a unique instance of such an effect. Even apart from the artificial substances, "Prussian" and "Turnbull's" blues, which are complex cyanides containing both ferric and ferrous iron, there are several blue minerals in which the color seems explainable only on this basis. The most noteworthy of these are: crocidolite and related amphiboles; iolite; and blue tourmaline or indicolite. Other instances may perhaps be discovered, should this subject ever be investigated as it deserves to be.

⁶ See Johannsen, *Manual of petrographic methods*, p. 103, 1914.