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CAUSE OF COLORS IN WAVELLITE FROM DUG HILL ARKANSAS[1]

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Abstract

Preliminary tests indicated that spherulites of wavellite found on Dug Hill, near Avant, Garland County, Arkansas contained vanadium. Samples were prepared from crushed spherulites restricting the fibers in each sample to one color as far as possible. Spectrographic analysis showed that the samples contained from 0.13–0.81 per cent vanadium, but that chromium, iron and other chromatic elements were present in only very small amounts or were absent. Analysis of the valence state of the vanadium present showed that none contained V_2O_3, some contained only V_2O_4, and others contained both V_2O_4 and V_2O_5. The correlation between the color of the sample fibers and the valence or valences of vanadium present was quite good.

Introduction

Wavellite found in Arkansas is known the world over for the varied colors of its spherulites—green, blue, blue-green, yellow and gray. This wavellite occurs on the top of a steep ridge, locally called Dug Hill[2] about 19 miles northwest of Hot Springs, and about one and one-half miles north of Avant, in Garland County. It occurs as fracture fillings and as replacement in the Bigfork Chert (Middle Ordovician) which is cut by numerous closely spaced joints.

Because he had found that the green color of variscite and metavariscite from Lucin, Utah, was caused by vanadium and chromium, it occurred to W. T. Schaller that perhaps these elements were also the cause of the colors of the spherulites of wavellite found on Dug Hill. Accordingly, he had preliminary tests for vanadium made on some samples which he, in company with H. D. Miser and C. S. Ross, had collected in 1937. The tests, which were made by J. M. Axelrod, using a semiquantitative method for vanadium which he had developed (Axelrod, 1946), indicated that vanadium was present in all the samples tested in amounts up to one or more per cent of vanadium oxide.

Preliminary optical examination showed that many specimens had an unusually strong pleochroism, yellow, pink, blue, that was distinctly different from the nonpleochroic green variscite and metavariscite from Utah. As the different states of valence of vanadium cause different colors, V^{3+} green, V^{4+} blue, and V^{5+} yellow, it seemed possible that vanadium present in different states of valence might be the cause of the

[1] Publication authorized by the Director, U. S. Geological Survey.

[2] According to Hugh D. Miser, U. S. Geological Survey, the ridge is so called because a road was dug through it to provide north and south passage across the country.

strong pleochroism of different colors, and of the variety of colors exhibited by the wavellite from Dug Hill. Accordingly, specimens restricted as far as possible to a single color were prepared for study.

Description of Samples

None of the wavellites from Dug Hill was absolutely colorless or pure white in mass effect; every specimen showed at least a tint of gray, blue or yellow. Some were very strongly colored—blue, blue-green, green, greenish yellow, or yellow.

Single spherulites appeared to change in color when broken down, and even single fibers showed such variation. Some spherulites appeared to have an inner dark-green zone with an outer yellow zone; others were the reverse. When broken down to single rather thick fibers, the apparently greenish fibers seemed much more bluish or bluish gray. For many fibers there was an abrupt intensification of color at the broadest width.

The samples analyzed were, therefore, not made up of fibers of a single color, but the color stated for each sample is believed to represent that of most of the fibers making up the sample. Seven samples of the colored wavellite, hand picked from selected and crushed spherulites, are described below, together with one pure white wavellite from Pennsylvania (no. 1) and several colored related aluminum phosphates, which were included for purposes of comparison.

No. 1. Lab. no. 50-1320. White friable spherulites about 2 cm. in diameter, from 3 miles east of Huntsdale, Cumberland County, Pa., contributed by J. C. Rabbitt. Not analyzed chemically as the spectrographic analysis showed neither vanadium nor chromium. Ground sample white.

No. 2. Lab. no. 50-1321. Spherulites, very light gray, slightly greenish on periphery, about 1 cm. in diameter; very compact, not separating into loose fibers readily. One specimen in sample. Ground sample light gray with yellowish tint. Crushed sample best matches Ridgway's color plate XXXI-27″, G-Y, but somewhat lighter.

No. 3. Lab. no. 50-1322. Pale canary-yellow spherulites about 2 cm. in diameter. Prominent concentric banding in shades of yellow. One specimen in sample. Ground sample more yellow than no. 5 below. Crushed sample pale green yellow, Ridgway's color Pl. V.-27, G-Y.

No. 4. Lab. no. 50-1323. Dark bluish-green outside portion of three similar bicolored spherulites 2 to 3 cm. in diameter. A sharp separation on the basis of color was not possible. Ground sample pale green; greener and darker than no. 2. Crushed sample yellowish-glaucous, Ridgway's Pl. XLI-25‴, YG-Y.

No. 5. Lab. no. 50-1324. Yellow inner portions of same bicolored spherulites used for no. 4 above. No sharp separation on the basis of color was possible, but contains more greenish material than no. 4 contains yellow. Crushed sample pale glass green, Ridgway's Pl. XXXI-29″, GG-Y.

No. 6. Lab. no. 50-1325. Whole bicolored spherulites similar to those used for samples nos. 4 and 5, bluish-green on outside with yellow core, thus representing a composite of nos. 4 and 5. Spherulites 2 to 3 cm. in diameter. Ground sample pale greenish-gray. Crushed sample yellow glaucous, Ridgway's Pl. XLI-25‴, YG-Y, like no. 2.

TABLE 1. SPECTROGRAPHIC ANALYSES OF MINOR ELEMENTS IN WAVELLITE FROM DUG HILL, ARKANSAS, AND IN RELATED ALUMINUM PHOSPHATES

Sample number	V	Cr	Fe	Cu	Mn	Ni	Zn	Ga	Be	Ti	Ba	Sr	B
						Wavellites							
1	—	—	0.02	0.005	—	—	—	—	0.019	—	—	—	0.00x
2	0.18	0.002	.05	—	—	—	—	—	.003	—	0.003	0.05	.00x
3	.81	.004	.2	—	—	—	0.04	—	.004	—	.001	.05	.00x
4	.81	.002	.06	.0007	—	—	—	—	.008	—	.001	.006	.00x
5	.74	.002	.07	.0004	—	—	.03	—	.007	—	—	.004	.00x
6	.61	.001	.07	.0003	—	—	—	—	.007	—	—	.004	.00x
7	.42	.003	.04	—	—	—	—	—	.007	—	—	.006	.006
8	.14	.040	.02	.015	—	—	—	—	.0002	—	.002	.006	.00x
					Other aluminum phosphates								
9	.21	.19	.06	.0007	—	—	—	0.025	—	0.08	—	—	.00x
11	.53	.069	.03	.0006	—	—	—	.025	—	.03	—	.01	.00x
12	.37	.067	.3	.0005	0.007	0.0007	.15	.019	.0003	.03	.01	>1.0	.00x
13	.13	.094	.06	.0003	—	—	—	.006	—	.08	.001	—	.00x

Looked for but not found: Co, Cd, Ge, In, Tl, Bi, Ag, Mo, W, Pb, Sn, As, Sb, Y, La, Nb, U, Th.
K. J. Murata, analyst.

No. 7. Lab. no. 50-1326. Spherulites 1 to 2 cm. in diameter, more blue-gray, less green, than no. 4, with paler, almost colorless, core. Sample is deepest blue of blue-gray material. Ground sample pale bluish gray. Crushed sample pale glaucous green, but lighter than Ridgway's Pl. XXXIII-39″, B-G.

No. 8. Lab. no. 50-1329. Small nearly white crystals similar to no. 2 in color. Ground sample light gray, but lighter than Ridgway's Pl. XLVII-25‴, YG-Y.

No. 9. Lab. no. 50-1328. Metavariscite, green tabular crystals described by Schaller (1912, 1916), as variscite, from Lucin, Utah. Chemical data given in Schaller (1912, 63–65). Ground sample variscite green, Ridgeway's Pl. XIX-37′, GB-G.

No. 11. Lab. no. 50-1330. Variscite, massive, green, from Fairfield, Utah. Ground sample deep greenish glaucous, Ridgway's Pl. XLI-33″, GY-G.

No. 12. Lab. no. 50-1331. Crandallite (pseudowavellite), yellowish, associated with green variscite (no. 11), from Fairfield, Utah. Ground sample cream color, Ridgway's Pl. XVI-19′, YO-Y.

No. 13. Lab. no. 50-1332. Metavariscite, massive, compact, deep-green nodule collected by J. J. Fahey and K. J. Murata, 1946, near Lucin, Utah. Contains admixed chert. Ground sample variscite green, Ridgway's Pl. XIX-37′, GB-G.

Kind and Amount of Chromatic Elements Present

Spectrographic analyses, made by K. J. Murata, for minor elements in the wavellites, and in several related aluminum phosphates, are given in Table 1. These analyses show that vanadium is the dominant chromatic element present in the Dug Hill wavellites. The next most dominant chromatic element present is Fe, but this amounts to less than 0.08 per cent, except in no. 3, which contains 0.2 per cent. Cr is present in amounts of less than 0.005 per cent, except in no. 8, which contains 0.04 per cent. This sample contains the least V, only 0.14 per cent, and no. 2 contains only 0.18 per cent. All the other samples contain more than 0.4 per cent of V. The highest amount of V was found in nos. 3 and 4, both of which contained 0.81 per cent.

The different states of valence in which V was present were determined by digesting weighed portions of the samples in (1+2) H_2SO_4 in small stoppered Erlenmeyer flasks (50 ml) on the steam bath for 7 to 10 days, the air in the flasks having previously been displayed by CO_2. When solution appeared to be complete, the contents of each flask were transferred to a 500 ml Erlenmeyer flask, the solution diluted to 250 ml with distilled water, heated to 80° C., and titrated to the first permanent pink with 0.05 N $KMnO_4$ solution. This titration represents the amounts of V present in valences less than 5. The flask was then placed on an electric heater and SO_2 gas was passed through the solution for 10 minutes, reducing all the V present to the V^{4+} state. A rapid stream of CO_2 was then passed through the solution, still kept hot, until it was free of SO_2 (about 1 hour). After adjusting the temperature of the solution to 80° C. again, it was titrated a second time with $KMnO_4$ to the first permanent pink. From the relations between the first and second titrations, after deducting the $KMnO_4$ equivalent of the iron present, the amounts of V_2O_3, V_2O_4, and V_2O_5 present can be calculated. If the first titration was the same as the second, all the V was present in the original solution as V^{4+} and all the Fe as Fe^{2+}. If the second titration was greater than the first, some or all of the V and Fe were present in the original solution as V^{5+} and Fe^{3+}, depending on the relations between the 1st, 2nd, and Fe titrations. If, on the other hand, the second titration is less than the first

TABLE 2. ANALYSES OF CHROMATIC CONSTITUENTS IN WAVELLITES FROM DUG HILL, ARKANSAS, AND IN RELATED PHOSPHATES

		Wavellites		
Sample No.	V_2O_4	V_2O_5	Cr_2O_3	Fe_2O_3
2	0.33	0.07	—	0.03
3	.58	.71	—	.16
4	1.26	.00	—	.03
5	.91	.28	—	—
6	.95	.07	—	.05
7	.70	.00	—	.02
8	.31	.00	.19	—
		Other aluminum phosphates		
9	.43	.00	0.25	.02
11	1.05	.00	.13	.01
12	.55	.72	.14	.03
13	.33	.04	.12	.02

Margaret D. Foster, analyst

titration, some or all of the V was present in the original solutions as V^{3+}, and all the Fe was present as Fe^{2+}.

The titrations indicated that none of the wavellite samples contained V^{3+}, three (nos. 4, 7, and 8) contained V^{4+} only, and four (nos. 2, 3, 5, and 6) contained both V_2O_4 and V_2O_5. The percentages of V_2O_4 and V_2O_5 found in the Dug Hill wavellites are shown in Table 2.

As expected, the palest colored of the samples, nos. 2 and 8, contained the least V, 0.18 and 0.14, respectively, which was present almost entirely as V^{4+}. The two samples, nos. 3 and 4, that contained the most V, 0.81 per cent in each, differed in color and in the respective amounts of V^{4+} and V^{5+} present. No. 3, which is pale yellow, contained 0.58 per cent V_2O_4 and 0.71 per cent V_2O_5, and no. 4, which was made up of the blue-green outer parts of bicolored spherulites, contained 1.26 per cent V_2O_4 and no V_2O_5. Thus the colors of these samples agree very well with the respective amounts of V_2O_4 and V_2O_5 present. However, sample no. 5, which was made up of the inner yellow cores of the bicolored spherulites whose outer portions form no. 4, contains more than three times as much V_2O_4 as V_2O_5, rather than the reverse. In the description of this sample it is noted that it contains more greenish material than no. 4 contains yellow. The relation of V_2O_4 to V_2O_5 suggests that more green material was present than was thought. No. 6, which is made up of bicolored spherulites similar to those used in preparing nos. 4 and 5, contains less V than either 4 or 5, almost entirely present as V_2O_4. In no. 7, blue-gray in color, all the V is present as V_2O_4, but the amount of V present is only about half of that in no. 4.

Indices of Refraction

The indices of refraction for the seven samples of wavellite from Dug Hill are:

Sample	α	β	γ
No. 2	1.522	—	1.548
No. 3	1.526	—	1.553
No. 4	1.525	1.534	1.553
No. 5	—	—	1.552
No. 6	1.523	1.533	1.552
No. 7	1.523	1.533	1.552
No. 8	1.527	—	1.553
Average	1.524	1.533	1.552

Determined by Schaller.

These values are very close to the indices of refraction for non-colored wavellite reported in the literature.

The distribution of colors in the Dug Hill wavellites observed under the microscope in polarized light is variable. In some fragments very little pleochroism is seen, the fibers appear almost colorless; in others, the colors are very intense. Parallel to the *c*-axis, the fragments may be pale to deep yellow or pale to deep pink, commonly with alternating streaks of yellow or pink having no sharp boundary. Normal to the *c*-axis the fragments appear colorless or pale to deep sky blue. Sections cut normal to the elongation of the fibers of the spherulites, and hence tangential to the round spherulites, are nearly colorless or faintly colored parallel to the *a*-axis and sky blue parallel to the *b*-axis. Yellow fibers on end stay yellow or in some cases show a pale blue area in one direction.

Chromatic Elements in Related Aluminum Phosphates

For comparative purposes spectrographic and chemical analyses were made of several related aluminum phosphates (nos. 9, 11, 12, and 13). The spectrographic analyses of these samples are included in Table 1 with the spectrographic analyses of the wavellites. Chemical determinations of the chromatic elements are given in Table 2.

All these samples contain significant amounts of both vanadium and chromium, but variscite and crandallite contain considerably more vanadium than the metavariscites. The green color of the variscite and the two metasvariscites may thus be attributed to the presence of Cr and of V^{4+}. V^{5+} is absent in one of the metavariscites (no. 9) and in the variscite. The other metavariscite (no. 13) contains only 0.04 per cent V_2O_5.

Discussion

Variously colored wavellites have been reported from numerous localities. Hintze (1931) reports wavellites colored yellow green, yellow, blue, green, reddish white (hematite), reddish yellow, brown, and ashy green. Orlov (1931) gives deep blue, deep green, grass green, greenish yellow, pale yellow, and white, as colors found in wavellites. The deep blue variety referred to by Orlov from Cernovic was reported by him to contain the following chromatic elements: CuO, 0.06 per cent; FeO 2.63; Fe_2O_3 3.18; and Cr_2O_3 0.52. The dominance of FeO and Fe_2O_3 suggests a ferro-ferri complex as the cause of the blue color. Vanadium is not mentioned by Orlov, nor is vanadium or chromium listed by Hintze in any of his analyses. On the other hand, the only chromatic element present in significant amounts in the wavellite at Dug Hill is vanadium, and it is the amount and the state of valence, or combinations of states of valence of the vanadium, that is the cause of the varied colors displayed by the wavellite at this locality.

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