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New data on wittichenite

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SUMMARY. The wittichenite (BM 1977, 172) discovered in the course of a reflected light study of polished sections from the Seathwaite deposit, Cumbria (described earlier in this journal by Stanley and Criddle), is the first authenticated occurrence of the species in Great Britain; for this reason it was examined in detail and compared with a specimen (BM 1437) from Wittichen, the type locality. Chemical analyses, cell dimensions, visible-spectrum reflectances, quantitative colour values, and VHN's are provided. They are in agreement with previously published data for the species.

Specimen preparation. Specimens from both localities were mounted in epoxy resin and ground by hand on water-lubricated glass plates with 600-grade and 800-grade carborundum and 1200-grade alumina. Grinding was continued with 14 μm, 6 μm, and 3 μm diamond on water-lubricated Hyprocel laps on Engis machines. A thick paste of MgO in distilled water was used on a stationary cloth lap for the final stage of polishing, which was by hand. This was found preferable to the finer grades of diamond in that a 'perfect' polish was achieved in less than 30 seconds, thus reducing polishing relief induced by the extended polishing times needed for finishing with diamond.

Measurement procedure. Six specimens labelled as wittichenite, from Wittichen, in the BM (NH) collection were examined, but only one was found suitable for measurement. In this, and in the Seathwaite specimens, the areas measured were examined for freedom from inclusions and surface imperfections with a $\times 40$ Nomarski objective. Three areas were selected for measurement on each of the Wittichen and Seathwaite mounts.

Measurements were made with a Zeiss Universal microscope equipped with $\times 16$ air and $\times 16$ oil objectives, immersion oil (Zeiss) $n_D = 1.5150$ at 23 °C and a SiC standard no. 232. This equipment is semi-automated. A step driven, wavelength scanning, line-interference filter and a digital voltmeter are 'on line' to a Hewlett Packard 9830 programmable calculator. An unpublished program written by G. S. Bearne was used to make measurements at 10 nm intervals from 400–700 nm and to derive from the measured reflectances the absorption coefficients, refractive indices, and quantitative colour values with respect to the CIE illuminants A, D_{65}, and C.

A modified Lanham stage was used to level and to interchange the specimens and the standard, which were focused in white light. As the precision of this apparatus was poor below 450 nm, at least two spectral scans were made for each grain measured and the results averaged. These data were plotted on a scale of 1 % R = 20 nm, and the curves smoothed graphically. The smoothed values (Tables I and II) differ from the measured values by no more than 0.2 % (absolute) at any wavelength. The quantitative colour values, Table III, were derived from these data by the weighted-ordinate method. The ordinates used were weighted for the wavelength range commonly employed in ore microscopy, that is, 400–700 nm, and not for the range generally used in colorimetry of 380–770 nm. The two-dimensional colour-space coordinates (polar) were derived mathematically from the rectangular chromaticity coordinates. Table III includes colour values with respect to the two illuminants recommended by the CIE, A, and D_{65} and for the C illuminant used in the IMA/COM Quant. Data File.

Optical characteristics. In plane-polarized light (colour temperature *c.* 3000 °K), wittichenite from Seathwaite is white to creamy-white; there is no change in its colour in oil. Under the same conditions of illumination the wittichenite from Wittichen appeared greyish-white and to have a lower reflectance. Neither reflectance-pleochroism nor bireflectance were discernible. However, all the grains examined were weakly anisotropic; between crossed polars the rotation tints are varying shades of dark brown.

The spectral reflectance curves for the species, from both localities, are similar and are weakly dispersed. For this reason individual curves have not been plotted; instead, the extreme R-values, in air and in oil, for each wavelength were selected, tabulated (Table IV), and plotted (fig. 1). It will be seen that the data for Seathwaite material are in good agreement with those obtained from the topotype specimen. Both are in excellent agreement with Caye and Pasdeloup's data quoted in the IMA/COM card 1.9760 (1977), for the species (from Butte, Montana, USA).

The complete reflectance data for each grain (Tables I and II) reveal that the R_2 curves for grain 1 from Seathwaite and grains 4 and 6 from Wittichen cross the corresponding R_1 curves at *c*.420 nm in air. In oil, R_2 crosses R_1 at *c*.400 nm for the Seathwaite grain 1 as it does for grain 6 from Wittichen. The trend of these curves is shown for the wavelength range 400–500 nm for both media (fig. 1). In the absence of oriented sections we cannot explain the consistent crossover at *c*.420 nm.

The reflectance curves and tables show that the difference in colour and brightness between the Seathwaite and Wittichen wittichenites, noted

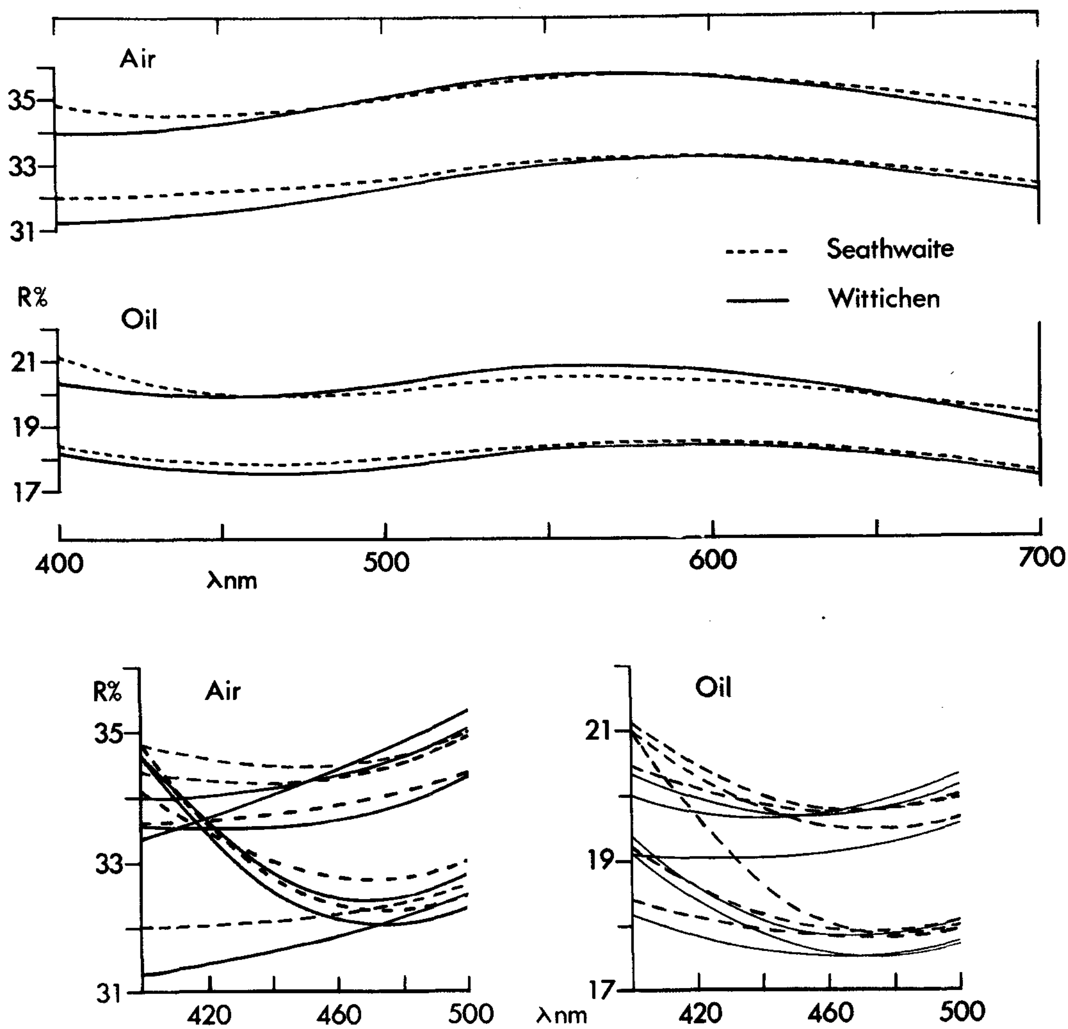

FIG. 1. Reflectance of wittichenite.

earlier, is not real. It is a result of the eyes' poor memory for brightness and colour, particularly where, as in this case, the associated minerals in the two mounts are different. In the Seathwaite specimens many of the associated minerals, including bornite, digenite, djurleïte, hematite, and covelline, are more strongly saturated, differ in hue and, in general, have lower brightness levels than has wittichenite. Hence, the wittichenite appears white to creamy-white, and to have a relatively high reflectance. In comparison, in the Wittichen mount, it appears greyish-white and not as highly reflecting. This is because it is associated with other copper bismuth and bismuth sulphides, which are similar in hue and saturation, but have higher reflectances. For these reasons, identification of the species from subjective optical criteria is difficult, but preliminary identification (as was the case with the topotype material in this study) may be made with some confidence from a few reflectance measurements.

Microhardness. The Vickers hardness number was measured on twelve grains from both Seathwaite and Wittichen material. Wittichenite from Seathwaite had VHN_{100} 180 (standard error of the mean ± 2.04) with a range of 170 to 187. Topotype material had VHN_{100} 186 (standard error of the mean ± 1.58) and range 178 to 197.

The indentations were slightly fractured at their corners, had concave sides, and were almost square in outline. For each measurement the final value was calculated by using the averages of the two diagonals of the quadrilaterals. Results from both Seathwaite and Wittichen wittichenite are in agreement with previously published data by Pärnamaa (1963), Young and Millman (1964), and Nordrum (1972).

Structure. 11.483 cm diameter powder patterns (Cu-$K\alpha$ radiation, Ni filter) were obtained with material removed from polished mounts from Seathwaite and topotype wittichenite. The *d*-values are in excellent agreement with Berry and Thompson's (1962) data for wittichenite from the type locality. Cell parameters were calculated from the first 28 lines using an unpublished computer program for the orthorhombic system:

	Wittichen BM 1437	Seathwaite BM 1977, 172
a	7.677 ± 0.010 Å	7.657 ± 0.015
b	10.349 ± 0.015	10.308 ± 0.022
c	6.706 ± 0.009	6.707 ± 0.013

Chemistry. Six areas of wittichenite on the Seathwaite sections and seven on the Wittichen section were analysed by electron probe. In both cases three of the analyses were on scribed areas previously used for reflectance measurements. A Cambridge Microscan 5 operated at 20 kV was used, the radiations measured being Bi-$L\alpha$, Cu-$K\alpha$, S-$K\alpha$ and using standards Bi_2S_3, Cu, and FeS_2. The results (Table VI) were corrected using a computer program devised by Duncumb and Jones (1969).

The average compositions Cu 38.0; Bi 42.8; S 18.3% for Seathwaite and Cu 37.7; Bi 43.4; S 18.7% for Wittichen material compare well with published data (Sugaki *et al.* 1974; Kocman and Nuffield, 1973) and the stoichiometric composition. Wittichenite from both localities is chemically homogeneous. Solid solution with silver, which has been previously reported (Oen and Kieft, 1976, and Sugaki *et al.*), was not found.

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REFERENCES

Berry (J.) and Thompson (R.), 1962. *Geol. Soc. Am. Mem.* **85.**

Caye (R.) and Pasdeloup (J.), 1977. In *IMA/COM Quantitative Data File*, ed. N. F. M. Henry.

Duncumb (P.) and Jones (E. M.), 1969. *Tube Investments Research Labs., Report no. 260.*

Kocman (V.) and Nuffield (E. W.), 1973. *Acta crystallogr.* **B29,** 2528–35.

Nordrum (F. S.), 1972. *Norsk. Geol. Tidsskr.* **52,** 257–71.

Oen (I. S.) and Kieft (C.), 1976. *Can. Mineral.* **14,** 185–93.

Pärnamaa (E.), 1963. *Lunds. Univ. Årsskrift,* **59.**

Sugaki (A.), Shima (H.), and Kitakaze (A.), 1974. *J. Japan Assoc. Mineral. Petr. Econ. Geol.* **69,** 32–43.

Young (B. R.) and Millman (A. P.), 1964. *Bull. Inst. Min. Metall. Trans.* **73,** 437–66.

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Table I Reflectance data (Air)

	Seathwaite						Wittichen					
Grains -	1		2		3		4		5		6	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
400	33.62	34.77	34.83	34.10	34.38	32.02	33.36	34.65	34.02	31.31	33.58	34.58
410	33.65	34.22	34.73	33.80	34.34	32.04	33.51	34.15	34.03	31.37	33.54	34.03
420	33.68	33.68	34.64	33.54	34.30	32.09	33.67	33.68	34.05	31.45	33.52	33.53
430	33.71	33.22	34.57	33.27	34.30	32.11	33.85	33.23	34.08	31.55	33.51	33.00
440	33.75	32.82	34.53	33.03	34.30	32.16	34.03	32.86	34.14	31.67	33.51	32.57
450	33.81	32.51	34.50	32.87	34.31	32.23	34.25	32.60	34.22	31.78	33.53	32.28
460	33.88	32.33	34.53	32.76	34.37	32.30	34.50	32.46	34.35	31.91	33.60	32.12
470	33.98	32.26	34.58	32.75	34.45	32.39	34.73	32.45	34.50	32.04	33.72	32.06
480	34.10	32.27	34.67	32.79	34.61	32.41	34.92	32.50	34.67	32.18	33.88	32.05
490	34.23	32.35	34.82	32.88	34.73	32.50	35.12	32.62	34.88	32.36	34.08	32.12
500	34.37	32.46	34.98	33.01	34.90	32.67	35.31	32.77	35.06	32.55	34.27	32.24
510	34.50	32.57	35.17	33.14	35.09	32.80	35.47	32.92	35.23	32.73	34.44	32.42
520	34.60	32.69	35.31	33.26	35.24	33.00	35.60	33.06	35.38	32.91	34.58	32.59
530	34.69	32.80	35.40	33.37	35.40	33.12	35.70	33.22	35.49	33.06	34.69	32.76
540	34.80	32.91	35.47	33.47	35.49	33.28	35.77	33.38	35.56	33.19	34.77	32.92
550	34.88	33.00	35.55	33.55	35.51	33.32	35.83	33.50	35.59	33.34	34.82	33.04
560	34.95	33.09	35.58	33.61	35.59	33.40	35.82	33.60	35.62	33.44	34.86	33.14
570	34.99	33.17	35.60	33.66	35.58	33.46	35.78	33.67	35.62	33.52	34.87	33.21
580	35.01	33.22	35.61	33.71	35.54	33.47	35.74	33.70	35.59	33.56	34.87	33.25
590	35.01	33.24	35.58	33.72	35.50	33.46	35.65	33.70	35.55	33.56	34.84	33.27
600	35.00	33.24	35.55	33.71	35.50	33.41	35.56	33.66	35.46	33.53	34.80	33.26
610	34.96	33.20	35.50	33.64	35.42	33.38	35.44	33.58	35.37	33.47	34.73	33.22
620	34.90	33.14	35.43	33.56	35.33	33.30	35.33	33.48	35.24	33.40	34.64	33.14
630	34.85	33.07	35.34	33.48	35.13	33.20	35.20	33.36	35.11	33.31	34.54	33.06
640	34.79	33.02	35.25	33.37	35.01	33.13	35.17	33.22	34.98	33.19	34.42	32.94
650	34.73	32.94	35.16	33.26	34.98	33.00	34.93	33.06	34.84	33.06	34.30	32.82
660	34.65	32.86	35.05	33.14	34.88	32.82	34.77	32.91	34.72	32.92	34.18	32.68
670	34.56	32.77	34.94	33.02	34.80	32.71	34.63	32.73	34.58	32.75	34.04	32.56
680	34.47	32.66	34.83	32.90	34.72	32.61	34.47	32.59	34.44	32.58	33.92	32.43
690	34.37	32.57	34.78	32.79	34.64	32.49	34.32	32.42	34.30	32.43	33.79	32.27
700	34.25	32.47	34.63	32.68	34.53	32.38	34.14	32.24	34.18	32.27	33.67	32.13

Table II Reflectance data (Oil)

	Seathwaite						Wittichen					
Grains -	1		2		3		4		5		6	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
400	21.00	21.04	21.15	19.25	20.52	18.42	20.08	19.38	20.36	18.20	19.16	19.14
410	20.70	20.45	20.78	18.95	20.37	18.38	19.89	18.98	20.18	18.04	19.14	18.81
420	20.37	19.85	20.47	18.67	20.19	18.28	19.77	18.61	20.03	17.89	19.11	18.48
430	20.08	19.23	20.20	18.40	20.00	18.12	19.70	18.32	19.90	17.76	19.10	18.18
440	19.85	18.68	20.00	18.22	19.90	18.03	19.70	18.10	19.80	17.66	19.12	17.94
450	19.67	18.27	19.89	18.07	19.87	17.94	19.75	17.95	19.73	17.60	19.15	17.74
460	19.56	18.05	19.84	18.00	19.81	17.88	19.86	17.85	19.70	17.56	19.21	17.62
470	19.49	17.92	19.83	17.97	19.78	17.81	19.95	17.88	19.75	17.54	19.24	17.55
480	19.49	17.90	19.86	17.97	19.80	17.83	20.10	17.93	19.84	17.56	19.32	17.55
490	19.55	17.94	19.92	18.04	19.91	17.88	20.23	18.01	19.97	17.64	19.43	17.61
500	19.66	18.00	20.04	18.15	20.03	17.98	20.38	18.11	20.10	17.77	19.58	17.71
510	19.77	18.08	20.14	18.28	20.12	18.10	20.50	18.24	20.24	17.93	19.73	17.83
520	19.87	18.17	20.25	18.38	20.21	18.23	20.65	18.38	20.34	18.08	19.88	17.96
530	19.96	18.25	20.32	18.47	20.21	18.39	20.70	18.51	20.38	18.23	19.97	18.08
540	20.04	18.33	20.35	18.53	20.23	18.50	20.75	18.62	20.42	18.35	20.02	18.17
550	20.08	18.39	20.36	18.57	20.29	18.50	20.75	18.70	20.44	18.43	20.04	18.25
560	20.13	18.44	20.36	18.61	20.31	18.54	20.75	18.74	20.44	18.50	20.05	18.34
570	20.14	18.47	20.36	18.64	20.32	18.62	20.70	18.74	20.43	18.52	20.05	18.39
580	20.16	18.49	20.35	18.65	20.31	18.63	20.63	18.73	20.38	18.53	20.04	18.42
590	20.15	18.48	20.31	18.63	20.30	18.60	20.53	18.70	20.33	18.52	20.00	18.40
600	20.13	18.47	20.25	18.57	20.22	18.55	20.40	18.63	20.25	18.50	19.93	18.38
610	20.08	18.43	20.17	18.50	20.12	18.48	20.27	18.54	20.16	18.44	19.84	18.33
620	20.03	18.38	20.08	18.41	20.01	18.39	20.12	18.44	20.06	18.36	19.74	18.25
630	19.95	18.31	20.00	18.33	19.90	18.31	19.99	18.33	19.95	18.28	19.65	18.18
640	19.87	18.23	19.91	18.23	19.81	18.19	19.85	18.21	19.83	18.18	19.56	18.09
650	19.80	18.14	19.81	18.14	19.72	18.11	19.72	18.08	19.69	18.08	19.45	17.98
660	19.73	18.05	19.73	18.05	19.60	18.02	19.58	17.93	19.56	17.97	19.35	17.88
670	19.63	17.97	19.63	17.97	19.50	17.91	19.46	17.80	19.44	17.84	19.24	17.77
680	19.54	17.87	19.54	17.87	19.38	17.82	19.32	17.68	19.31	17.72	19.13	17.64
690	19.44	17.79	19.44	17.79	19.30	17.70	19.20	17.52	19.17	17.56	19.02	17.54
700	19.35	17.69	19.35	17.69	19.21	17.61	19.03	17.37	19.05	17.43	18.92	17.44

Table III Quantitative Colour Values

		AIR					OIL				
		x	y	λ_D	P_e%	Y	x	y	λ_D	P_e%	Y
SEATHWAITE											
A	R_1	0.4483-0.4489	0.4094-0.4098	576-579	1.9-2.2	34.5-35.4	0.4470-0.4481	0.4088-0.4094	560-576	0.8-1.3	20.0-20.2
	R_2	0.4484-0.4489	0.4082-0.4096	578-582	1.1-2.3	33.0-33.5	0.4475-0.4485	0.4076-0.4096	518-577	0.0-2.1	18.4-18.5
D_{65}	R_1	0.3146-0.3151	0.3323-0.3329	569-572	1.4-1.7	34.8-35.4	0.3132-0.3141	0.3307-0.3314	561-575	0.7-0.9	20.0-20.2
	R_2	0.3142-0.3152	0.3330-0.3310	574-582	0.7-1.8	33.0-33.5	0.3130-0.3149	0.3279-0.3322	-534-572	0.5-1.5	18.3-18.5
C	R_1	0.3120-0.3125	0.3194-0.3201	570-573	1.4-1.6	34.8-35.4	0.3106-0.3115	0.3178-0.3185	562-576	0.7-0.8	20.0-20.2
	R_2	0.3116-0.3127	0.3172-0.3201	572-585	0.6-1.7	33.0-33.5	0.3103-0.3123	0.3150-0.3194	-542-573	0.6-1.4	18.3-18.5
WITTICHEN											
A	R_1	0.4480-0.4485	0.4099-0.4106	573-576	2.1-2.4	34.7-35.6	0.4463-0.4480	0.4102-0.4113	561-573	1.4-2.5	19.9-20.5
	R_2	0.4486-0.4499	0.4086-0.4101	579-582	1.7-3.4	33.0-33.4	0.4480-0.4491	0.4090-0.4101	574-581	2.1-3.2	18.2-18.6
D_{65}	R_1	0.3146-0.3149	0.3332-0.3343	565-569	1.8-2.1	34.7-35.6	0.3135-0.3149	0.3327-0.3344	558-567	1.3-2.0	19.9-20.5
	R_2	0.3147-0.3165	0.3308-0.3344	572-579	1.1-2.6	32.9-33.4	0.3147-0.3162	0.3313-0.3336	570-578	1.4-2.3	18.2-18.5
C	R_1	0.3121-0.3124	0.3204-0.3215	566-570	1.7-2.0	34.7-35.6	0.3110-0.3123	0.3198-0.3215	559-567	1.2-1.9	19.9-20.5
	R_2	0.3121-0.3139	0.3179-0.3216	573-581	1.0-2.5	32.9-33.4	0.3121-0.3136	0.3185-0.3209	571-580	1.3-2.2	18.2-18.5

The values are relative to the CIE illuminants A, D_{65} and C, having colour temperatures of 3300°K, 6500°K and 6750°K respectively. The rectangular coordinates are x and y from which were derived the polar coordinates λ_D, the dominant wavelength, and P_e%, the excitation purity. Y is the 'luminance'. As the colour values were so similar for all the grains measured the range of values is shown rather than individual grain values.

Table IV Reflectance Data

	Seathwaite				Wittichen			
	AIR		OIL		AIR		OIL	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
400	34.8	32.0	21.2	18.4	34.0	31.3	20.4	18.2
420	34.6	32.1	20.5	18.3	34.1	31.5	20.0	17.9
440	34.5	32.2	20.0	18.0	34.1	31.7	19.8	17.7
460	34.5	32.3	19.8	17.9	34.5	31.9	19.9	17.6
470	*34.6*	*32.3*	*19.9*	*17.9*	*34.7*	*32.0*	*20.0*	*17.6*
480	34.7	32.3	19.9	17.8	34.9	32.1	20.1	17.6
500	35.0	32.5	20.0	18.0	35.3	32.3	20.4	17.7
520	35.3	32.7	20.3	18.2	35.6	32.6	20.7	18.0
540	35.5	32.9	20.4	18.3	35.8	32.9	20.8	18.2
546	*35.6*	*33.0*	*20.4*	*18.3*	*35.8*	*33.0*	*20.8*	*18.2*
560	35.6	33.1	20.4	18.4	35.8	33.1	20.8	18.3
580	35.6	33.2	20.4	18.5	35.7	33.3	20.6	18.4
589	*35.6*	*33.2*	*20.4*	*18.5*	*35.7*	*33.3*	*20.5*	*18.4*
600	35.6	33.2	20.3	18.5	35.6	33.3	20.3	18.4
620	35.4	33.1	20.1	18.4	35.3	33.1	20.1	18.3
640	35.3	33.0	19.9	18.2	35.1	32.9	19.9	18.1
650	*35.2*	*32.9*	*19.8*	*18.1*	*35.0*	*32.8*	*19.7*	*18.0*
660	35.1	32.8	19.7	18.0	34.8	32.7	19.6	17.9
680	34.8	32.6	19.5	17.8	34.5	32.4	19.3	17.7
700	34.6	32.4	19.4	17.6	34.2	32.1	19.0	17.4

These values are the R maxima and minima from the three groups of measurements made on specimens from both localities. (Tables I and II). They include graphically interpolated values for the 4 COM wavelengths *470*, *546*, *589* and *650* nm.

Table VI Chemical analyses

	Seathwaite						Wittichen						
				1	2	3	4	5	6				
Cu	37.80	38.11	37.37	38.26	38.18	38.32	37.77	37.58	37.83	37.41	37.48	37.71	37.85
Bi	43.17	42.90	43.16	42.01	42.70	42.93	43.06	43.76	43.46	43.47	43.38	43.24	43.73
S	18.49	18.37	18.50	18.06	17.96	17.94	19.06	19.07	19.02	18.16	18.23	18.51	19.11
TOTAL	99.46	99.38	99.03	98.33	98.84	99.19	99.89	100.41	100.31	99.04	99.09	99.46	100.69

Numbers 1-6 correspond to the areas measured in the reflectance study.