The variation of optical properties with chemical composition in the rhodonite-bustamite series.

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A SPECIMEN of hardystonite from Franklin Furnace, New Jersey, U.S.A., purchased in 1899 from Mr. W. M. Foote of Philadelphia for the British Museum collection consists largely of an associated pale pink mineral which has at various times been thought to be rhodonite, fowlerite, wollastonite, or scapolite. This specimen has recently again attracted attention because of the remarkable fluorescent effects it shows in ultra-violet rays. The pink mineral displays a bright brick-red fluorescence, the hardystonite a violet; and some willemite present fluoresces a brilliant green. A description in the literature of such a mineral from Franklin Furnace being unknown to Dr. L. J. Spencer, he handed over to me the problem for investigation, and a detailed examination has proved the pink mineral to be bustamite.

This bustamite is evidently very different in appearance, as in its associated minerals, from the bustamite recently described from Franklin Furnace by J. V. Lewis and L. H. Bauer¹ or by E. S. Larsen and E. V. Shannon,² and indeed from any bustamite hitherto recorded from other localities. A more precise determination was therefore made of the optical constants, and the investigation has been extended to other members of the rhodonite-bustamite series, between the extreme members of which a continuous variation has been traced.

¹ J. V. Lewis and L. H. Bauer, Amer. Journ. Sci., 1922, ser. 5, vol. 4, p. 249 [Min. Abstr., 2-192].

² E. S. Larsen and E. V. Shannon, Amer. Min., 1922, vol. 7, pp. 95, 149 [Min. Abstr., **2**-362, 472].

Experimental.

The specimen (I) from Franklin Furnace (B.M. 84606) is a cleavage slab measuring 9 by 7 cm. of the pale pink mineral, which is veined with finely granular white hardystonite. It also shows spots of pale grey willemite, hardly distinguishable in ordinary light, but standing out magnificently under ultra-violet illumination, and a few minute specks of franklinite.

Two other specimens were chosen for examination; one was a specimen (III) from the Harstig Mine, Pajsberg, Sweden (B.M. 68037) showing small bright red crystals of the habit described by G. Flink ¹ for rhodonite from this locality (that is, acute wedges formed by large faces of $M(1\overline{10})$ and $k(\overline{221})$, with q(221), c(001), and $n(\overline{221})$ small) on massive iron-schefferite. This specimen was bought of Mr. Flink in 1892, and may fairly be assumed to be similar to the material that he had examined. The other (II) is a cleavage slab, 10 by 6 cm., of brownish-red rhodonite, with garnet, from Långban, Sweden (B.M. 43473). There was no difficulty in obtaining pure material for analysis from any of the specimens; with the first, from Franklin Furnace, a final selection was made under the ultra-violet lamp to ensure perfect freedom from hardystonite and willemite, but this aid could not be employed with the other specimens, as they showed little or no fluorescence under ultra-violet rays. Density determinations were made in carbon tetrachloride by the pyknometer, and are given below along with the analyses.

		Ι.	II.	III.
		Franklin	T 0 1	Harstig mine,
		Furnace.	Langban.	Pajsberg.
SiO ₂	•••	47.68 %	47.69%	46.33~%
Al ₂ O ₃	•••	0.25	0.43	0.26
Fe ₂ O ₃		0.061	0.05	0.831
FeO	•••	n.d.	1.93	n.d.
MnO		27.65	32.93	44 ·28
ZnO	•••	0.26	0.07	0.07
MgO		0.03	0.02	0.04
СаО	•••	24.86	15.24	8.02
Ignition	•••	0.06	0.29	0.22
		100.85	98.65 ²	100-05
Sp. gr.		$3 \cdot 302 \pm 0 \cdot 01$	$3.418 {\pm} 0.01$	3.615 ± 0.03

¹ Total iron as Fe₂O₃.

² Also some alkalis, not determined.

¹ G. Flink, Zeits. Kryst. Min., 1886, vol. 11, p. 518.

Or, in molecular proportions, expressed so that the sum of the monoxides (MnO, FeO, ZnO, CaO, MgO) is 100:

			I.	II.	III.
SiO ₂	•••		94.15	103.88	100.25
FeO	•••		n.d. ¹	3.51	n.d.
MnO	•••	•••	46.55	60.74	81.15
ZnO	•••		0.38	0.11	0.12
MgO	•••	•••	0.09	0.07	0.14
CaO	•••		52.98	35.57	18.59

¹ Less than 0.08 as calculated from the total iron.

For optical examination, a cleavage flake from each specimen was mounted in Canada balsam after being definitely oriented by measurement on the goniometer. The flakes were of different orientations, and for comparative purposes the results of measurement on the Fedorov universal stage were plotted directly on a stereographic net, and then projected on b(010), with $a'(\bar{1}00)$ at $\phi = 0^{\circ}$; so plotted, the poles of the three principal planes lie at the following positions for red and for green light:

			I.]	I.	III.	
		Red.	Green.	Red.	Green.	Red and Green.	
-	١φ	354°	353 ‡°	357°	357°	350°	
a	lρ	83	83	80	80	83	
ρ	\φ	252	247	244	246	249	
μ	<i>λρ</i>	29	21	24	25	30	
•••	ιφ	88	86 1	91	91	86	
γ	lø	62	70	69	67	61	

The migration-paths of the three poles for the increase in manganese content from I to III are very peculiar, and quite different for different wave-lengths. They are plotted in fig. 1. The great dispersion of the bisectrices is very striking in the Franklin Furnace material (I), and has vanished within the accuracy of measurement in the Harstig material (III).

The refractive indices of all three specimens for sodium-light were determined by the immersion method, with the following results $(all \pm 0.003)$:

		I.	II.	III.
a		 1.664	1.695	1.720
β	•••	 1.675	1.703	1.725
γ	•••	 1.679	1.710	1.733
$(\beta-1)$)/d	 0.2044	0.2057	0.2005

Approximate values for the optic axial angles of I and III were obtained on the Fedorov stage, the former by extinction trials in known directions, the latter by direct location of one of the optic axes; for II, an optic axial angle could not be obtained by this method, but when the section, parallel to $M(1\overline{1}0)$, used for the Fedorov stage measurements was examined in convergent light, using an oil-immersion objective, an optic axis was observed on the border of the field, and the position approximately measured, so that it could be plotted. The values obtained agree well with those obtained from the measured refractive indices. The optical sign of all three specimens was carefully tested, and it was found that the Harstig material with a lime content about 8%, an ordinary rhodonite (pajsbergite), is optically positive. This is in agreement with the results of A. Des Cloizeaux,¹ and not with the usually accepted conclusions of G. Flink. On the other hand I and II are negative. The extinctions were also measured on several faces, and agree well with the values obtained graphically from the other optical data.

			Ι.	II.	III.
2V	•••	•••	50–55°	84° approx.	75° approx.
Optical sign	·		Negative.	Negative.	Positive.
Extinction	on :				
m to edge	e [m : b]	•••	$10 - 15^{\circ}$	20°	24°
M to edge	e [M: b]	•••	± 0	—	15
b to edge	e[b :M]	•••	3	0 - 3	
a to edge	e [a : b]		—		30

The Franklin Furnace material shows three good cleavages, b(010), m(110), and $M(1\overline{1}0)$, and a poor one, a(100), all in one zone; the Långban material shows good cleavages parallel to m and M, less perfect to b, and possibly an imperfect cleavage c(001); the Harstig material, finally, shows good cleavages m and M and less perfect c. Clearly, with a fall in calcium content, the c-cleavage develops and the b-cleavage drops out.

The goniometric measurements made for the purpose of orienting the fragments used for optical study revealed a quite appreciable variation in the angles with the lime content; while the angles on the Harstig material agreed closely (as was to be expected) with Flink's figures, those for the Franklin Furnace mineral differed by as

¹ A. Des Cloizeaux, Bull. Soc. Min. France, 1884, vol. 7, p. 72.

much as a degree; accurate measurements were not obtained on the Långban material.

Harstig.—Mc 86° 36' (Flink, 86° 24'); M'k 31° 13' (Flink, 31° 13½'). Franklin Furnace material gave bM 40° 2', bm 45° 14', ba 94° 43'; or after adjustment by the cotangent formula, bM 40° 2', bm 44° 45', ba 95° 11', while Flink gives for Harstig rhodonite bM 41° 38', bm 45° 53', ba 94° 26'. E. S. Larsen and E. V. Shannon found for a Franklin Furnace bustamite of very nearly the same composition as the present material: bM 40° 7', bm 44° 58', ba 94° 33'; or after adjustment by the cotangent formula, bM 40° 21', bm 44° 44', ba 94° 47'.



FIG. I. Stereographic projection showing the principal optical directions of bustamite (I and II) and rhodonite (III), for red and for green light.

Correlation of data with those of other observers.

A certain number of data on the physical constants of rhodonite and bustamite and allied species have been obtained by previous workers, and it appeared of interest to see how far the extended data will enable us to trace any regularities in the variation of the optical and other physical properties with the chemical composition. On the whole, an excellent agreement with the present results is obtained, and several of the physical properties appear to vary with the calcium content according to a simple linear relation.

In only one case are data for the complete location of the optical ellipsoid available. G. Flink (loc. cit.) determined the position of the optical ellipsoid for unanalysed rhodonite from the Harstig mine, Pajsberg, by a method of trial and error. The material was from the same locality as the analysed specimen III above, so it may probably be taken that it was about of the same composition. Unfortunately, Flink's extinction-angles disagree considerably with the position he assigns to the optical ellipsoid, and probably both his extinctionangles and ellipsoid orientation must be taken as approximate only. They agree roughly with the present values, within about the same degree of accuracy as that with which they agree among themselves. His extinction-angles are :

> On M, 17° 6' to [Ma] in the acute angle [Mc]: [Ma]. On a, 32° 26' to [ab] in the acute angle [ab]: [ac]. On b, 10° 48' to [ab] in the obtuse angle [ab]: [bc]. On c, 54° 26' to [cm] in the obtuse angle [cm]: [cM].

The axial angle he found to be $75^{\circ} 57'$ for red (Li) light, $76^{\circ} 12'$ for yellow (Na) light, and $76^{\circ} 22'$ for green (Tl) light, and the optical sign negative. The optical sign is almost certainly incorrect, as stated above.

For the orientation of the optical ellipsoid, Flink gave the following angles:

These values are incompatible, and a little study shows that the supplementary value should be substituted for those marked with an asterisk, when the position, projected on b as above, becomes :

		Bx ".	β.	Bx ₀ .	
ø		343°	251°	74°	
ρ	•••	89°	39°	52°	

No other investigator appears to have attempted the complete location of the optical ellipsoid, but a number of partial data are available, most of which support the present results.

A. Des Cloizeaux (loc. cit.) studied a rhodonite from Pajsberg, of optic axial angle (2V) 75° 4', positive, and found the obtuse bisectrix nearly perpendicular to a (100), the axial plane being inclined about 10° to 12° to the normal in a direction towards m (110), and cutting the edge [a: M] at about 39°, and [a:k] at $5\frac{1}{2}$ °, agreeing within 1° with the present results for the Harstig material which has the same sign and about the same axial angle. There was appreciable crossed dispersion about a. He also studied a bustamite from Långban, and found the acute bisectrix nearly perpendicular to a(100), the axial plane cutting the edge [a: M] at 31° ; the axial angle was 68° for red light and 72° for green, and the sign negative. There was strong crossed dispersion of the acute bisectrix. This, again, agrees well with the results for the present Långban material of somewhat higher axial angle. As will be seen below, this material was probably richer in lime than that analysed by Lindström (analysis IX).

Artificial manganese silicate, pure MnSiO_3 , has been prepared and studied by C. S. Kallenberg¹ and L. Bourgeois.² The former found an extinction-angle of 31° on *a* (100), agreeing closely with the present value for a rhodonite containing 8% of lime (analysis III); and the latter's extinction-angle of 18° on $M(1\overline{10})$ also agrees well, but his statement that the axial plane is nearly perpendicular to $M(1\overline{10})$ is probably an error.

E. S. Larsen and E. V. Shannon (loc. cit.) gave fragmentary data for bustamite with 25% lime, from Franklin Furnace (complete analysis X below), comparable with the present specimen I in composition. They found α nearly perpendicular to a(100), β nearly perpendicular to b(010), and γ inclined 36° to the zone of cleavage [001], a clearly incompatible set of results. There was strong crossed dispersion of the negative acute bisectrix.

Thus the scanty data available on the optical orientation of rhodonites and bustamites support the present results, as far as they go. Unfortunately, there is no additional evidence to check the peculiar migration curve (fig. 1), but the marked dispersion of the bisectrices found in the Franklin Furnace material (I) is amply confirmed. This dispersion, which approximates to a crossed dispersion about a, is slight in the manganese-rich rhodonites, and increases with the calcium content, becoming very strong in the calcium-rich bustamites.

¹ C. S. Kallenberg, Centr. Min., 1914, p. 388.

² L. Bourgeois, Bull. Soc. Min. France, 1883, vol. 6, p. 64.

Turning to the refractive index and density data, these are by no means as numerous as could be desired, but are nevertheless sufficient to enable us to establish a straight line relation between these constants and the calcium or manganese ratio. For comparative purposes it is convenient to recalculate the analyses in molecular proportions, so that the sum of the monoxides (CaO, MgO, MnO, ZnO, FeO) is 100. Here we are only considering those members in which the total proportion of 'impurities' (MgO, ZnO, FeO) is low, not over about 10% expressed as above, for the aim is to trace the effect of the replacement of manganese by calcium. Besides the results given above in the experimental part, the following data are available:

	IV.	v.	VI.	VII.	VIII.	IX.	х.
SiO,	 93.54	96 ·18	100-8	89.92	100.75	98 •29	95.01
MnÕ	 87.14	73.42	80.34	69.46	59.05	$55 \cdot 28$	43.27
FeO	 2.65	5.75	0.62	1.66	1.65	0.83	0.46
ZnO	 		_	4.83	_	<u> </u>	0.79
BaO	 _		_	_	—	0.15	
CaO	 10.21	18.03	18.09	21.78	31.72	40.12	53.50
MgO	 	2.80	0.95	2.27	7.58	3.62	1.98
Sp. gr	 3.65	3.63	3.416	_	3.387	3.40	_
a a	 _	_	1.721	1.716			1.662
ŝ	 _			1.720	_		1.674
r v	 _		1.730	1.732	_	·	1.676
2V	 _	_	—	Med. large	—	_	$44^{\circ}\pm3^{\circ}$
Sign	 	—		Positive		—	Negative

IV. Viu, Turin, Italy. V. Fino, Atti Accad. Torino, 1883, vol. 18, p. 39.

V. Pajsberg, Sweden. L. J. Igelström, Öfv. Akad. Stockholm, 1851, p. 143; Journ. Prakt. Chem., 1851, vol. 54, p. 190.

- VI. Val d'Err, Grisons, Switzerland. J. Jakob, Schweiz. Min. Petr. Mitt., 1923, vol. 3, p. 236.
- VII. Franklin Furnace, New Jersey, U.S.A. E. S. Larsen and E. V. Shannon, Amer. Min., 1922, vol. 7, p. 149.
- Radauthal, Harz, Germany. J. Fromme, Tschermak's Min. Petr. Mitt., VIII. 1909, vol. 25, p. 308.
 - IX. Långban, Sweden. G. Lindström, Öfv. Akad. Stockholm, 1880, vol. 37, no. 6, p. 57.
 - X. Franklin Furnace, New Jersey, U.S.A. E. S. Larsen and E. V. Shannon, Amer. Min., 1922, vol. 7, p. 95.

Pure manganese silicate (MnSiO₃) has been studied by several workers. C. S. Kallenberg (loc. cit.) found n 1.714 and sp. gr. 3.63; while A. Gorgeu¹ found sp. gr. 3.68; and A. S. Ginsberg² found *n* 1.74. The former pair of values give (n-1)/d = 0.197, the latter, C. S. Kallenberg also studied artificial preparations of 0.201.¹ A. Gorgeu, Bull. Soc. Min. France, 1887, vol. 10, p. 264.

² A. S. Ginsberg, Zeits. Anorg. Chem., 1908, vol. 59, p. 346.

200

various Ca/Mn ratios, but it is very doubtful how far his preparations were homogeneous, which would affect his refractive index determinations to some extent. He found :

CaO/(Ca,Mn)	0	0	30	40	50	60	70	80
<i>n</i>		1.714	1.698	1.687	1.678	1.666	1.658	1.648

E. S. Larsen and E. V. Shannon examined several bustamites from Franklin Furnace, but unfortunately no one was completely studied.



FIG. 2. Plot of the refractive index (β) against chemical composition in the rhodonite-bustamite series. (XI and XII, for artificial MnSiO₃, A. S. Ginsberg, 1908, and C. S. Kallenberg, 1914.)

One is set out above (analysis X); a second was only studied optically —it was optically negative, 2V medium, $\alpha 1.667$, $\beta 1.678$, $\gamma 1.680$. The third was a zoned material, the manganese-rich core of which gave results set out above (analysis VII), while the outer zone, which was not analysed, was found to have $\alpha 1.687$, $\beta 1.692$, $\gamma 1.709$, 2V medium, positive, strong crossed dispersion. Another specimen of similar material gave for the inner zone $\alpha 1.708$, $\beta 1.716$, $\gamma 1.724$, 2V large, positive.

These refractive index and specific gravity data are shown in figs. 2 and 3 respectively. It will be seen that they are represented quite well by straight lines; the limit of probable error may be taken as about 0.003 for refractive indices; for specific gravities a limit is much more difficult to fix without knowledge of the method used. As mentioned above, some of C. S. Kallenberg's refractive indices are probably unreliable, and J. Jakob's low value for the specific gravity of rhodonite from Val d'Err (VI) is probably an error. In plotting



FIG. 3. Plot of the specific gravity against chemical composition in the rhodonite-bustamite series. (XII and XIII, for artificial MnSiO₃, C. S. Kallenberg, 1914, and A. Gorgeu, 1887.)

the specific gravities, the sum of the CaO and MgO has been taken as abscissae (the sum of the whole of the monoxides, in molecular parts, being taken as 100), for it seems preferable to include the magnesia with the lime rather than with the heavier oxides, MnO, FeO, and ZnO. If this is not done, analysis VIII falls right off the line, while the other points are not much affected, as they have but little magnesia.

The specific refractivities, $(\beta - 1)/d$, agree well with the values calculated, using E. S. Larsen's data¹ for CaO, MnO, and SiO₂, with

¹ E. S. Larsen, The microscopic determination of the nonopaque minerals. Bull. U.S. Geol. Survey, 1921, no. 679, p. 31. the exception of the rhodonite from Val d'Err, for which Jakob's density is probably incorrect. The difference between $(\beta - 1)/d$ and



FIG. 4. Plot of the double refractions against chemical composition in the rhodonite-bustamite series. (XIV and XV, bustamite studied optically only by E. S. Larsen and E. V. Shannon, 1922. The chemical composition deduced from the refractive index (β) by the aid of fig. 2.)

 $(a+\beta+\gamma-3)/3d$, the more correct form of the specific refractivity, is well within the limit of experimental error.

The discovery of the exact relations between the chemical composition and the optic axial angle and double refractions $\gamma - a$ and $\beta - a$ is not so easy. A priori, we should expect a straight line relationship for the double refractions, and if this is so, the optic axial angles cannot follow the same law. Unfortunately, the available data do not cover quite a large enough range to check this, but the assumption of a straight line law for the double refractions fits the experimental results well within the limit of error. The data for the double refractions are quite erratic, for the probable error of the refractive index determinations is large in comparison with the double refractions. On the whole, $\gamma - \alpha$ appears to remain nearly constant at about 0.014, while $\beta - \alpha$ ranges from about 0.005 for the Harstig



FIG. 5. Plot of the optic axial angle against chemical composition in the rhodonite-bustamite series.

rhodonite (III) to about 0.012 for Franklin Furnace bustamite (X). If we take $\gamma - a$ as constant at 0.014, and plot $\beta - a$ as a straight line function, using values calculated from $\gamma - a$ and the measured values of 2V for the materials III and X (75° and 44°), and then take $\gamma - \beta$ by difference, we obtain the lines plotted in fig. 4, which will be seen to lie fairly well among their respective points. Then calculating 2V for other compositions from these lines for the double refractions, we obtain the curve shown in fig. 5, which agrees very well with the value experimentally found for the Långban bustamite (II) and gives the correct sign and rough magnitude for 2V in other instances, showing that our method is at least approximately right. One interesting point emerges from these comparisons: the curves for $\gamma - a$ and for $\beta - a$ cross at about 70 mols. % of lime in the monoxides. Accordingly, bustamite of about this composition should exhibit crossed axial plane dispersion, becoming uniaxial for one wave-length, and the axes opening out in another plane with a further increase in the lime. This conclusion cannot be checked experimentally for lack of material, since the bustamite richest in lime (analysis X) had only 56 mols. % of lime and magnesia together.

We also see that the reasons raised by A. N. Winchell¹ for regarding artificial manganous silicate, rhodonite, and bustamite as separate species all disappear; the most important, viz. that the optic axial angles cannot be made into a continuous series, being based on an erroneous determination of the optical sign of rhodonite.

In a number of instances where an isomorphous series capable of all gradations covers a number of species, conventional limits have been set to the several species, defined, for example, by chemical composition, as in the albite-anorthite series. In the particular case of rhodonite and bustamite, a very convenient and natural division appears to be available in the optical sign, and it is suggested that all optically positive material should be called rhodonite, and all negative, bustamite. This will make bustamite cover all material containing 30 mols. % or more of lime in the monoxides, which corresponds roughly with the division at present made. In practice, the density or refractive index would of course be a more convenient criterion, and we see from graphs 3 and 2 that the division falls at a density of 3.47 or a refractive index (β) of 1.709.

In conclusion, I wish to acknowledge my indebtedness to Dr. L. J. Spencer for the introduction to a most interesting problem, and for his continual assistance and encouragement throughout the work, and to Mr. W. Campbell Smith, for instruction and assistance in the use of the Fedorov universal stage.

¹ A. N. Winchell, Amer. Min., 1927, vol. 12, p. 10 [Min. Abstr., 3-373].

Note added during proof correction :---

F. M. Jager and H. S. van Klooster, Proc. Sect. Sci. K. Akad. Wet. Amsterdam, vol. 18, pt. 2, p. 908, have studied artificial manganous silicate (MnSiO₃). The sp. gr. of 3.716 agrees well with the present results, but the optical data are not easily interpreted; the 107° rhombs with 14° extinction were probably tables parallel to b (010), giving a 1.733, and γ' 1.739 about midway between β and γ . Material prepared by Georgeu's method, and possibly less pure, was probably needles lying on a (100) and giving β 1.728 and γ 1.741. These optical constants agree fairly with the present results.