

# THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY

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No. 152

March, 1936

Vol. XXIV

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*Studies on the zeolites. Part IX. Scolecite and  
metascolecite.<sup>1</sup>*

(With Plates VIII and IX.)

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[Read January 24, 1935.]

SCOLECITE was recognized as an independent species by A. F. Gehlen and J. N. Fuchs<sup>2</sup> (1813), being one of the species into which they divided, on chemical grounds, the mesotype of R. J. Haüy (1801). Its individuality has rarely been doubted, though occasionally the union of natrolite, mesolite, and scolecite into one isomorphous group has been proposed.

<sup>1</sup> Parts I–VIII, *Min. Mag.*, 1930–5, vols. 22–24.

<sup>2</sup> These authors spelt the name ‘Scolezit’; the spelling ‘scolecite’ appears to be due to J. D. Dana (*Syst. Min.*, 1st edit., 1837, p. 271). The spelling ‘Skolezit’ appears to have originated with K. C. von Leonhard (*Handb. Orykt.*, Heidelberg, 1821, p. 454). G. Delafosse (*Cours de Min.*, Paris, 1862, vol. 3, p. 334) and A. Des Cloizeaux (1862) spell the name ‘scolésite’. C. Hintze (*Handb. Min.*, Leipzig, 1889–97, vol. 2, p. 1698) uses the spelling ‘Skolecit’. A. Dufrenoy (*Traité de Min.*, Paris, 1847, vol. 3, p. 428) incorrectly derives the name from ‘σχολῆς, cheveux’; Gehlen and Fuchs definitely state that the name was given ‘weil sich die nadelformigen Krystalle dieses Fossils wurmformig krümmen’ when heated, so that the derivation must be either from σκώληξ, a worm (as is usually stated), or, as suggested by W. X. F. von Kobell (*Mineral-Namen*, München, 1853, p. 87), from σκολιάζω, to be crooked.

Three varieties of scolecite have been described, but all have proved to be other minerals. Thus poonahlite (H. J. Brooke, 1831; = mesolite) was long included with scolecite. Lehuntite (T. Thomson, 1836; = natrolite) was classed as a soda-scolecite by A. Kenngott (1850) solely on account of its high water content. And a mineral from Pargas, Finland, was described by N. Nordenskiöld (1821) as anhydrous scolecite (wasserfreies Scolezit); this was copied by W. Phillips (1823) as 'scolecite', and this incorrect copy appears to be the authority for the citation of Pargas as a scolecite locality by Dana and others. There is no evidence that scolecite occurs at Pargas, and, according to M. L. Frankenheim (1842) and F. J. Wiik (1871), the material examined by Nordenskiöld was really a plagioclase. It may be noted that the locality 'Auvergne' cited by Dana and others for scolecite is also incorrect and is due to an error in a paper on an Auvergne natrolite by J. Guillemin (1826).

*Chemical composition, unit-cell formula, and specific gravity.*

Scolecite usually occurs fairly well crystallized, and free from admixture with other zeolites, hence most of the analyses in the literature<sup>1</sup> agree in suggesting the formula  $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$ , although only fourteen have been made on material for which there is any optical evidence of purity.

Two new analyses have been made on material the purity of which was optically checked, and are given in table I. The atomic ratios

TABLE I. New chemical analyses of scolecite. (Localities, see table II.)

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	SrO.	BaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
1.	45.16	25.90	14.86	nil	nil	0.16	0.06	13.66	99.80
2.	45.36	26.49	15.01	nil	nil	0.06	0.03	13.40	100.35

per 80 oxygen atoms, the oxygen atoms per unit cell, specific gravities, and some other physical data are given in table II for the two new analyses and for the fourteen from the literature for which there is some definite evidence of purity. The oxygen content, in atoms per unit cell, was calculated as usual from the analyses, specific

<sup>1</sup> In all, 56 analyses were collected, of which 27 were accounted first class, 12 second class, 12 third class, and 5 rejected as useless. The total alkalis were determined and reported as Na<sub>2</sub>O in 16 of the first-class analyses, while soda and potash were separated in only 8; for the second-class analyses the corresponding figures are 6 and 1, and for the third-class 8 and 2.

gravities, and the cell size, and shown to be 80 within the limits of probable error.

TABLE II. New analyses of scolecite and analyses from the literature of material of tested purity. Expressed as atomic ratios per 80 oxygen.

		1.	2.	3.	4.	5.	6.	7.	8.
Atoms per 80 oxygen.	Si ...	23.73	23.63	24.32	24.02	23.98	24.23	23.94	24.29
	Al ...	16.04	16.23	15.73	16.34	16.06	15.52	16.11	15.86
	Ca ...	8.36*	8.36*	7.22	8.14	7.94	7.98†	7.91	7.63
	Na ...	0.16	0.06	1.06	0.15	—	0.00	0.12	—
	K ...	0.03	0.02	0.09	—	—	0.02	—	—
	H <sub>2</sub> O ...	23.94	23.23	28.88‡	22.80	24.39	24.40	23.55	23.65
	Si + Al ...	39.77	39.86	40.05	40.36	40.04	39.75	40.05	40.15
Class of analysis	A	A	A	B	B	B	A	A	
Oxygen atoms per unit cell	80.20	80.43	—	81.52	—	—	81.19	—	
Oxygen %	40.62	40.79	40.35	41.06	40.38	40.69	40.89	41.18	
Sp. gr.	2.276§	2.273§	—	2.289	—	—	2.289	—	
		9.	10.	11.	12.	13.	14.	15.	16.
Atoms per 80 oxygen.	Si ...	23.89	24.04	24.03	23.86	23.55	23.25	23.92	24.15
	Al ...	16.14	16.09	16.09	16.09	16.51	16.38	15.90	15.84
	Ca ...	7.63	7.78	7.78	8.14	8.13	7.61	8.00	7.58
	Na <sub>2</sub> O ...	0.36	—	—	—	—	0.66	0.51	0.64
	K <sub>2</sub> O ...	0.04	—	—	—	—	0.12	0.07	0.09
	H <sub>2</sub> O ...	23.39	25.30	24.36	23.87	23.86	23.44	25.27	24.04
	Si + Al ...	40.03	40.13	40.12	39.95	40.06	39.63	39.82	39.99
Class of analysis	A	A	A	A	A	C	A	A	
Oxygen atoms per unit cell	78.75	79.56	79.42	—	—	—	80.58	79.56	
Oxygen %	40.31	40.55	40.33	40.80	40.73	40.96	40.92	40.76	
Sp. gr.	2.252	2.262	2.270	—	—	—	2.27	2.25	

\* Ba and Sr tested for and found absent.

† Also 0.25 atom Mg.

‡ By difference; probably high.

§ Probable error  $\pm 0.005$ ;  $D_4^{20^\circ}$  corrected to vacuum.

1. B.M. 33887, Syhadree Mts., Bombay, India.

2. B.M. 95304, Berufjord, Iceland.

3. W. F. Hillebrand, 1885. Table Mtn., Golden, Colorado, U.S.A.

4. G. Tschermak, 1905. Poonah, Bombay, India.

5. O. B. Bøggild (N. V. Ussing, analyst), 1905. Karsuanguitkakait, Greenland.

6. W. F. P. M'Lintock (E. G. Radley, analyst), 1915. An Gearna, Ben More, Mull, Scotland.

7. G. Tschermak, 1917. Poonah, Bombay, India.

8. G. Stoklossa, 1918. Iceland. (Mean of two analyses.)

9. T. L. Walker and A. L. Parsons (E. W. Todd, analyst), 1922. Digby Gut, Annapolis Co., Nova Scotia.

10 and 11. A. Bianchi and A. Cavinato, 1925. Miage, Mt. Blanc, Piedmont, Italy.

12. A. Cavinato, 1927. Teigarhorn, Berufjord, Iceland.
13. A. Cavinato, 1927. Maderanerthal, Switzerland.
- 14 and 15. V. Gennaro, 1929. Valle di Viù, Valle di Lanzo, Piedmont, Italy.
16. V. Gennaro, 1929. Bettolina, Valle di Ayas, Mt. Rosa, Piedmont, Italy.

Optical data are given in the literature for the material of analyses 5, 11, 12, and 15, crystallographic data for nos. 11 and 15, and dehydration data for nos. 8, 9, 11, 12, and 13. Correlated data are also available for several of the less reliable analyses.

The unit-cell formula is therefore  $\text{Ca}_8\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\cdot 24\text{H}_2\text{O}$ . The Si : Al ratio is very constant, there being no evidence of any replacement of Si by Al or vice versa. But there is a certain degree of replacement of Ca by the alkalis (Na and K), though it is much less than the replacement of  $\text{Na}_2$  by Ca in natrolite; as may be seen from table II, this can reach to about 1 atom Na and 0.1 atom K per unit cell, though, of course, these figures cannot be regarded as a definite maximum. Higher alkali contents have been recorded (T. Thomson, 1840; P. Collier, 1868; J. Lemberg, 1877; L. Darapsky, 1888), but there is no proof of the purity of the material analysed.

There is no adequate evidence as to whether or no scolecites ever carry appreciable amounts of Ba or Sr. They were tested for and found absent in the two new analyses, but there is no evidence that they have ever been looked for before. Figures for the water content range from 21.6 to 25.3 mols.  $\text{H}_2\text{O}$  per unit cell, but some of the lower ones were probably obtained with material dried at  $100^\circ\text{C}$ .; taken in conjunction with the vapour pressure data, the evidence is fairly conclusive that the water content is 24 mols. per unit cell at saturation.

Data for the specific gravity of scolecite show a considerable range, both in the specific gravity found and in the probable accuracy of the result. The mean of seventeen of the most reliable determinations from the literature (eight were rejected), ranging from 2.246 to 2.31, is 2.272, while the two new determinations on the analysed specimens gave 2.273 and 2.276. The influence of the small amount of alkali often present must be negligible, and the most probable value for the specific gravity of fully hydrated scolecite is  $D_4^{20} = 2.274$ , corrected to vacuum.

#### *Crystallography, pyroelectricity, and X-ray measurements.*

The monoclinic symmetry of scolecite and its invariable twinning on  $a(100)$  were first observed by Sir David Brewster (quoted by W. Haidinger, 1825). True untwinned scolecite crystals probably

do not exist, but it is not uncommon for large crystals to have both  $o(111)$  and  $e(\bar{1}11)$  well developed on both individuals of the twin; in such cases there is frequently a deep notch between the two individuals, and it is not difficult to break off the upper ends to give apparently single crystals.

Ten crystals were examined goniometrically, with the results shown in table III. Each face  $o(111)$  or  $e(\bar{1}11)$  was found to be replaced

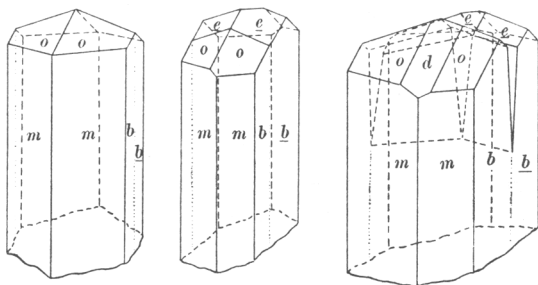


FIG. 1. Twinned crystals of scolecite.

by a vicinal pyramid; usually this is three faced, but occasionally one face may be suppressed, and often only one face is accurately measurable. The face  $d(101)$  sometimes gives good reflections, but is often slightly curved in the zone  $ad[010]$  over a range of  $10'$  to  $30'$ . The face  $R(\bar{1}01)$  was observed, very small, on two crystals from Berufjord, Iceland (B.M. 1914, 1195 b and c); this appears to be a new form for scolecite. The prism  $m(110)$  is often present almost exactly in true position, but may be replaced by a four-faced vicinal pyramid, of which one face (which may be on either side of the true position, but is generally truly in the zone  $[001]$ ) is generally much larger than the others. On one crystal (B.M. 1914, 1195 b) asymmetrical etch-pits were observed on  $m(110)$ , bounded by planes inclined at  $0^\circ 10'$  to  $0^\circ 40'$  to  $[001]$  and  $1^\circ$  to  $5^\circ$  to  $m(110)$ . On several crystals narrow facets of  $k(120)$ ,  $l(210)$ ,  $H(340)$ ,  $K(530)$ , and  $L(520)$  were observed; the last three appear to be new forms, but only the first of them was of any appreciable size, the other two being extremely narrow.

The goniometric data gave the elements  $a:b:c = 0.9759:1:0.3432$ ,  $\beta = 89^\circ 15'$ , in excellent agreement with the values deduced from the X-ray work,  $0.975:1:0.345$ ,  $\beta = 89^\circ 21'$ , and with the literature values. Probably the elements deduced by G. Flink (1888),

$a : b : c = 0.9764 : 1 : 0.3434$ ,  $\beta = 89^\circ 18'$ , are the most accurate; these differ only very slightly from the values obtained by V. von Zepharovich (1884) and by G. Kalb (1932), but the X-ray results suggest that they are nearest the truth.

TABLE III. Goniometric data for scolecite.  $a : b : c = 0.9759 : 1 : 0.3432$ ,  
 $\beta = 89^\circ 15'.$ \*

Interfacial angles  $b(010) : F(hkl)$ :—

Form.										
$m(110)$ .	$k(120)$ .	$H(340)$ .	$l(210)$ .	$K(530)$ .	$L(520)$ .	$d(101)$ .	$R(\bar{1}01)$ .	$o(111)$ .	$e(\bar{1}11)$ .	
Obs.†										
44° 18'	62° 49'	52° 35'	25° 40'	30½°	22°	90° 7'	89° 57'	72° 9'	71° 57'	
		52 23	26 10				90			
Calc.										
44 18†	62 53	52 27	26 1	30° 21'	21° 19'	90 0	90 0	72 8	72 0	

Interzonal angles  $ab[001] : bF[\bar{1}0h]$ :—

Form	...	...	$d(101)$ .	$R(\bar{1}01)$ .	$o(111)$ .	$e(\bar{1}11)$ .
Obs.†	...	...	69° 56'	71° 42'	69° 58'	71° 20'
				71 3		
Calc.	...	...	69 58	71 18	69 58	71 18

\* These elements are calculated from the observations cited by the method of weighted means; but it is probable that the elements found by G. Flink (1888) are more accurate.

† These values are means except for  $H$ ,  $l$ ,  $K$ ,  $L$ , and  $R$ , for which all the measured values are given.

‡ Half the measured cleavage angle; this was used as a fundamental value in the calculation of the elements.

Parallel growths and intimate intergrowths of scolecite with natrolite and with mesolite have already been described in connexion with the latter minerals (Min. Mag., 23-254, 429).

The piezoelectricity of scolecite has been in some doubt, contradictory reports being given by S. B. Elings and P. Terpstra (1928), M. von Laue (1926), and G. Greenwood and D. Tombouljian (1932). Prof. Terpstra kindly undertook a re-examination of the matter, using crystals from the analysed specimen no. 1 (B.M. 33887), and states that there can be no doubt that scolecite is piezoelectric, though occasionally crystal aggregates will fail to show any effect in the piezoelectric oscillator; he hopes to report more fully on these anomalies shortly.

J. N. Fuchs (1816) observed that scolecite is very strongly pyroelectric, and this observation has been repeatedly confirmed. The analysed specimens showed the property very well, and the crystals were attached by the analogous pole, as appears to be invariably the

case. The distribution of the pyroelectric charge indicates that scolecite belongs to the planosymmetric class  $S$ , a conclusion which is supported by the artificial etch-figures observed by F. Rinne (1894) and the natural etch-figures described above. Several crystals which had been etched with dilute nitric acid, as described by Rinne,<sup>1</sup> are included in the Trechmann collection, presented to the British Museum by Dr. C. T. Trechmann in 1926, and the figures correspond exactly to Rinne's description and drawings.

The X-ray study fully confirmed these conclusions as to the symmetry of scolecite, the space-group being clearly shown by the halvings to be  $S^4$ . There is, however, a very close approximation to the orthorhombic  $C_{2h}^{19}$ , and most of the diffractions which should be halved for that space-group are very weak, and some not detectable. Rotation photographs of scolecite (pl. IX, fig. 3) are very similar to those of natrolite (pl. IX, fig. 4), and there can be no doubt that these zeolites are isostructural, but the scolecite photographs show a number of extra lines, partly owing to the appreciable departure of  $\beta$  from  $90^\circ$ . Lauegrams (pl. VIII, fig. 1) confirmed the monoclinic symmetry. By taking a Lauegram of a very thin twinned needle along the  $b$ -axis and measuring the separation of several pairs of spots produced by the two members of the twin,  $\beta$  was estimated as  $89^\circ 23\frac{1}{2}'$  (this procedure, which does not seem to have been described before, allows of a very accurate estimation of  $\beta$  when suitably twinned crystals are available). By a comparison of the spacings of the  $(18.2.2)$  and  $(18.2.\bar{2})$  planes and of the  $(12.2.2)$  and  $(12.2.\bar{2})$  planes, using oscillation photographs, another determination of  $\beta$  was made, and the value  $89^\circ 18'$  obtained. Mean  $\beta = 89^\circ 21' \pm 5'$ . The other dimensions of the unit cell were found to be:  $a 18.48 \pm 0.04$ ,  $b 18.95 \pm 0.04$ ,  $c 6.54 \pm 0.02 \text{ \AA}$ .

As with mesolite, it was desirable to be able to use the X-ray photographs as a means of deciding whether a given base-exchange product is, or is not, a scolecite. A list of the diffractions which may be observed near the centre of a rotation photograph of mesolite about the axis of elongation, in addition to the natrolite diffractions, has already been given (Min. Mag., 23-430); with scolecite the differences from the natrolite photograph are much fewer. Using Fe-K radiation<sup>2</sup> there is an additional diffraction due to  $(042)$  at

<sup>1</sup> These crystals (B.M. 1926,1835) were etched by the late Dr. C. O. Trechmann in 1894, a few months after Rinne's results were published.

<sup>2</sup> The data previously given for mesolite refer to Cu-K radiation.

$\xi$  0.41 on the second layer-line, while the diffraction at  $\xi$  0.29 is doubled, (222) and ( $\bar{2}22$ ), and on the first layer-line a triple spot at  $\xi$  0.73 replaces the double spot in natrolite. These are the only differences of diagnostic value for base-exchange products, for which mere intensity differences are in general valueless. The most noticeable intensity difference is much stronger (331) at  $\xi$  0.43.

### Optics.

A detailed optical study has been made of one of the analysed specimens (no. 1, B.M. 33887), while many other specimens have

TABLE IV. Refractive indices of scolecite (B.M. 33887) for various wavelengths. Observed values only, probable accuracy varies from  $\pm 0.0007$  to  $\pm 0.0022$ . For dispersion equations, giving refractive indices with an estimated accuracy of  $\pm 0.0001$ , see text.

$\lambda$ , Å.	$\alpha$ .	$\beta$ .	$\gamma$ .	$\lambda$ , Å.	$\alpha$ .	$\beta$ .	$\gamma$ .	
7200 ...	1.5087	—	1.5167	5350 ...	{ 1.5162	1.5233	1.5227	
6910 ...	1.5082	—	1.5164		{ 1.5150			1.5237
6708 ...	{ 1.5096	1.5162	1.5175		{ 1.5150			
	{ 1.5095			5250 ...	1.5159	—	1.5238	
6563 ...	{ 1.5096	1.5173	1.5171	5000 ...	{ 1.5187	1.5256	1.5246	
	{ 1.5108				{ 1.5167			
6500 ...	1.5106	—	1.5191	4930 ...	1.5186	—	1.5251	
6250 ...	{ 1.5113	1.5179	1.5193	4916 ...	1.5191	1.5262	—	
	{ 1.5114			4861 ...	1.5180	—	1.5255	
6070 ...	1.5129	—	1.5204	4830 ...	1.5188	—	1.5266	
5893 ...	{ 1.5125	1.5200	1.5205	4590 ...	1.5214	—	1.5291	
	{ 1.5133			4550 ...	{ 1.5205	1.5295	1.5284	
5850 ...	1.5118	—	1.5202		4358 ...			1.5230
5708 ...	1.5137	1.5208	—	4200 ...	1.5242	—	1.5326	
5690 ...	1.5125	—	1.5209	4100 ...	1.5263	—	1.5338	
5550 ...	1.5146	—	1.5230					
5461 ...	{ 1.5156	1.5224	1.5217					
	{ 1.5138							

been examined shortly. No appreciable variation in the optical properties has ever been recorded, so that it did not appear worth while repeating the detailed examination on several specimens. The measurements were made on cut plates and prisms, corrections being made where necessary for mal-orientation of the sections, and all the results were checked against one another to assist in determining their probable accuracy. Direct measurements were made of  $\alpha$ ,  $\beta$ , and  $\gamma$ ,  $\gamma - \beta$ ,  $2V$ , and the angle  $\alpha : c$  [001], and are given in tables IV to VII and fig. 2.

From these measurements dispersion equations were calculated, and it was found that the following expressions give values agreeing



with the measurements within the estimated probable accuracy of the latter; the estimated probable accuracy of the values computed from the equations is given in each case ( $\lambda$  in Å.).

$$\begin{aligned} \gamma - \beta &= 0.000701 - 3.3 \times 10^3/\lambda^2 + 1.2 \times 10^{11}/\lambda^4 \pm 0.000005, \\ \gamma - \alpha &= 0.01039 - 1.64 \times 10^5/\lambda^2 + 2.4 \times 10^{12}/\lambda^4 \pm 0.00010, \\ \gamma &= 1.5105 + 2.8 \times 10^5/\lambda^2 + 2.0 \times 10^{12}/\lambda^4 \pm 0.0001. \end{aligned}$$

From these equations  $2V$  can be calculated with a probable accuracy of  $\pm 5'$ , and a calculated curve is included in fig. 2 (p. 237).

TABLE V. Optic axial angles of scolecite (B.M. 33887) for several wave lengths. Estimated probable accuracy of these observed values,  $\pm 10$  to  $20'$ , of the calculated values,  $\pm 5'$ .

$\lambda$ , Å	...	6708.	6150.	5893.	5630.	5260.	5170.	4861.	4780.	4502.
$2V$	{ Calc.	$34^\circ 6'$	$34^\circ 51'$	$35^\circ 16'$	$35^\circ 38'$	$36^\circ 11'$	$36^\circ 20'$	$36^\circ 46'$	$36^\circ 54'$	$37^\circ 5'$
	{ Obs.	34 21	34 37	35 20	35 28	36 8	36 13	36 41	36 53	37 10
			35 12	35 18						

TABLE VI. Extinction-angle on  $b(010)$ ,  $a:[ab]$ , for scolecite (B.M. 33887);  $a$  lies in the obtuse angle  $\beta$ . 'Calculated' values from the smoothed curve, fig. 2. Estimated probable accuracy of the absolute values of the extinction-angle  $\pm 20'$ , of the horizontal dispersion,  $\pm 5'$ .

$\lambda$ , Å	...	7000.	6708.	6250.	5893.	5461.	5350.	5000.	4861.
$a:[ab]$	{ Calc.	$16^\circ 10'$	$16^\circ 13'$	$16^\circ 18'$	$16^\circ 22'$	$16^\circ 28'$	$16^\circ 30'$	$16^\circ 36'$	$16^\circ 39'$
	{ Obs.	16 10	16 8	16 18	16 22	16 29	16 30	16 37	16 35

O. Luedecke (1881), C. Schmidt (1886), G. Flink (1888), and A. Bianchi and A. Cavinato (1925) have observed some interesting optical anomalies in crystals of scolecite. Plates cut parallel to  $a(100)$  are said to give sometimes distinctly oblique extinction, and plates cut parallel to  $b(010)$  may give different extinction-angles in the two halves of the twin. Plates parallel to  $c(001)$  show varying phenomena, from simple non-parallel extinction in the two halves of the twin to a division into four, or even eight, fields with different extinction-angles. Several explanations have been suggested for these observations, but it seems probable that the true explanation must be strain, as suggested by G. Flink (1888); the anomalies are too irregular and too variable to indicate anorthic symmetry (O. Luedecke, 1881). Plates cut approximately parallel to  $c(001)$  were prepared from seven crystals from different localities.<sup>1</sup> None

<sup>1</sup> B.M. 43581, 47672, 47674, and 48234 from Syhadree Mts., Bombay; B.M. 55325 from Fellithal, Uri, and B.M. 60084 and 95305 from Berufjord, Iceland.

of these showed the major anomalies described, though one showed a slight difference in extinction-angle between the two halves of the twin ( $1-2^\circ$ ), which may be due to sub-parallel growth. Some tendency was noted for apparent field divisions to appear owing to light reflected from cleavage cracks, but in no case could the above anomalies be confirmed.

TABLE VII. Birefringence,  $\gamma-\beta$ , of scolecite (B.M. 33887), measured as extinctions in several orders on four different plates. Estimated probable accuracy  $\pm 0.000015$  to  $0.000040$ . For dispersion equation, giving the birefringence with an estimated accuracy of  $\pm 0.000005$ , see text.

$\lambda$ , Å.	$\gamma-\beta$ .		Order of interference.	Effective thickness of plate, mm.
	Obs.	Calc.		
6980	...	0.000590?	2nd	2.37
6770	...	0.000693	3rd	2.93
6600	...	0.000673	3rd	2.94
6440	...	0.000680	4th	3.79
5630	...	0.000713	3rd	2.37
5510	...	0.000727	5th	3.79
5440	...	0.000724	4th	2.94
5150	...	0.000703	4th	2.93
4910	...	0.000777	6th	3.79
4770	...	0.000814	5th	2.93
4680	...	0.000796	5th	2.94
4670	...	0.000788	4th	2.37
4470	...	0.000826	7th	3.79
4300	...	0.000881	6th	2.93

#### *Base-exchange.*

Coarsely powdered scolecite was treated with fusions of sodium chlorate, potassium thiocyanate, and of lithium, ammonium, silver, and thallos nitrates; the products were examined chemically and optically, and such as remained sufficiently coarsely crystalline were examined by X-ray methods. As explained above, it was readily possible to characterize the products as natrolites, mesolites, or scolecites by the presence or absence of certain diffractions on X-ray rotation photographs about the axis of elongation.

Lithium nitrate gave a product which was identified from its X-ray photograph as lithium-natrolite; its chemical composition and optical properties agree with this, and it appears to be essentially identical with the products obtained by the action of lithium nitrate on natrolite and mesolite, only differing in its small residual lime content.

Potassium thiocyanate gave a product in which some of the crystals, which had a very low birefringence, were zoned, many of them having a core which gave oblique extinction and had an optically negative elongation and an outer zone which gave straight

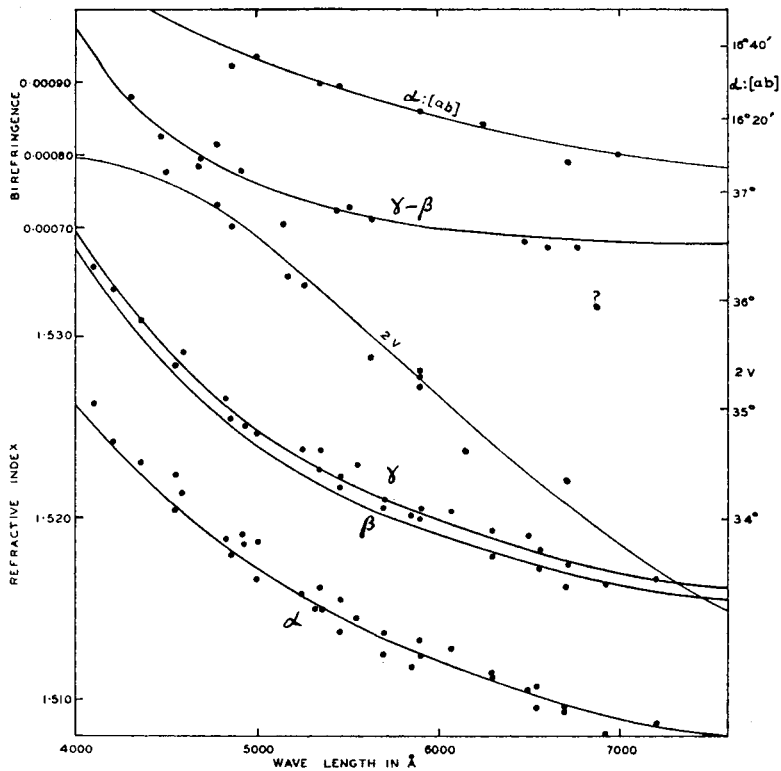


FIG. 2. The variation of the optical constants of scolecite with the wave-length of the light.

extinction and positive elongation, as did the bulk of the smaller-grained material. There was no definite intermediate zone. The crystals were unfortunately not suitable for X-ray study. Their chemical composition and optical properties indicate that the inner zone is probably a potassiferous scolecite, while the outer zone is either a potassium-mesolite or, more probably, a potassium-natrolite.

It was hoped that sodium chlorate would give rise to mesolite, but although the fusion did not last long, the product was found by optical and X-ray methods to be a natrolite; chemical analysis

showed it to contain a considerable proportion of lime, but not more than in some calciferous natrolites already known.

With the ammonium nitrate, base-exchange did not progress far,

TABLE VIII. Base-exchange data for scolecite.

	Un- treated.	270° C. 70 hrs. NaClO <sub>3</sub> .	200° C. 48 hrs. KCNS.	270° C. 70 hrs. LiNO <sub>3</sub> .	180° C. 48 hrs. NH <sub>4</sub> NO <sub>3</sub> .	270° C. 96 hrs. AgNO <sub>3</sub> .	220° C. 48 hrs. TiNO <sub>3</sub> .
		*	*	*			
Percentage composition.							
SiO <sub>2</sub> ...	45.16	45.31	43.33	49.77	44.30	39.74	31.80
Al <sub>2</sub> O <sub>3</sub> ...	25.90	28.71	26.94	31.97	28.60	26.58	20.16
CaO ...	14.86	5.38	5.84	0.64	14.30	9.89	6.89
R <sub>2</sub> O† ...	—	11.44	14.07	7.96	1.45‡	14.14	32.60
H <sub>2</sub> O ...	13.66	9.78	9.97	10.47	12.04‡	10.23	8.46
Total ...	99.80§	100.62	100.15	100.81	100.69	100.58	99.91
Oxygen % ...	40.62	41.88	39.76	45.64	41.30	37.26	29.65
Oxygen atoms per unit cell } ...	80.20	80.29	—	79.60	78.94	79.1	—
Atoms per 80 oxygen.							
Si ...	23.73	22.9	23.2	23.2	22.9	22.6	22.9
Al ...	16.04	17.1	17.0	17.5	17.3	17.8	17.1
Ca ...	8.36¶	2.9	3.3	0.3	7.8	6.0	5.3
R† ...	—	11.2	9.6	15.0	0.5	4.2	6.6
H <sub>2</sub> O ...	23.94	16.5	17.8	16.3	20.6	19.4	20.3
Sp. gr. ...	2.276	2.253	2.223	2.171	2.209	2.43 to 2.63	3.6
							Mixture
Mean refractive index } ...	1.517	1.484	1.500 ± ††	1.500	1.517	1.525 ± to 1.54 ±	1.544 1.53 ††
Birefringence ...	0.008	0.01	0.005 ± ††	0.01	0.01	0.01	small
Optical sign of elongation } ...	neg.	pos.	**	pos.	neg.	neg.	** neg.
Extinction-angle on cleavage faces to elongation } ...	—	0°	**	0°	{ 12 to 13°	{ 1 to 5°	0° 12°
Cell-sides in A. } ...	a ... 18.48	18.36	—	17.53	18.51	18.54	— —
b ... 18.95	18.71	—	18.70	18.90	18.99	— —	— —
c ... 6.54	6.54	—	6.47	6.53	6.55	— —	— —
Interaxial angle β } ...	89° 21'	90° 0'	—	90° 0'	89° 20'	≠ 90°	— —

\* These products are natrolites.

† R indicates the cation of the salt used in the base-exchange.

‡ The method used for the determination of NH<sub>3</sub> and H<sub>2</sub>O was that described in part III of this series (Min. Mag., vol. 23, p. 278).

§ Includes 0.16% Na<sub>2</sub>O and 0.06% K<sub>2</sub>O.

|| Taking the sp. gr. as 2.43.

¶ Also 0.16 atom Na and 0.03 atom K.

‡‡ Outer zone.

†† This product is either a mesolite or a natrolite.

\*\* Zoned; see text.

and the oblique extinction, optically negative elongation, and high water content indicated scolecite with a slight substitution of calcium by ammonium; this the X-ray evidence confirmed.

Silver nitrate gave rise to an argentiferous scolecite, as evidenced by oblique extinction, negative elongation, and X-ray data. The proportion of silver ions which can replace calcium is remarkable considering that two silver atoms must replace one calcium, and is perhaps evidence of the correctness of W. H. Taylor's view (1933) that the extra eight water molecules of scolecite do not occupy the eight cavities left vacant when the sixteen sodium ions of natrolite are replaced by eight calcium ions. A vapour pressure study of an argentiferous scolecite would be particularly interesting, but neither time nor material permitted of it.

The product obtained with thallos nitrate was a mixture of two derivatives; one is clearly a thallos-scolecite, having a relatively low refractive index and oblique extinction, while the other, with straight extinction and a much higher refractive index, is probably a thallos-natrolite, but may be a thallos-mesolite. The latter crystals were zoned, the interior having an optically positive, the exterior an optically negative, elongation. This material was not suitable for X-ray study.

These base-exchange experiments clearly show that scolecite is isostructural with natrolite, and hence with mesolite also; the method used precluded any possibility of solution and recrystallization, and optical and X-ray evidence show that identical products can be prepared from scolecite and natrolite.

#### *Vapour pressure.*

New vapour pressure data obtained for scolecite (B.M. 33887) by the isohydric method have yielded results of considerable interest. Sixteen isohydric curves were worked out (table IX and fig. 3), and interpreted in the light of the kinetic theory of zeolitic vapour pressure equilibrium. The first five curves gave results in good agreement<sup>1</sup> with the equation:

$$\log p = S_0 + \frac{1}{2} \log T - \log x_s / (1 - x_s) - 2 \log \{1 + \phi(x_s)\} - E/RT \cdot \log_e 10$$

(where  $p$  is the vapour pressure in mm.Hg,  $T$  the absolute temperature, and  $x_s$  the fraction of the more volatile group of sixteen water

<sup>1</sup> Good agreement could also be obtained with another interpretation, as far as these five curves are concerned, but it would then be impossible to explain the next three adequately.

molecules which have been removed), if the constants and unknown function  $\phi(x_s)$  are taken as:  $S_0$  9.28,  $E$   $2.21 \times 10^4$  cal. per gram-mol.  $H_2O$ , and  $\phi(x_s) = -0.9x_s$ . With these constants the equation gives an excellent representation of series 4 and 5, as will be seen by comparison of the observed and computed values of  $\log p$  in table IX. For series 2 and 3 the agreement is not so good, but in these series the degree of dehydration was very small, and a slight error in the weighing of the vapour pressure apparatus would have a very serious effect on the computed pressure; if it is supposed that an error of 1.8 mg. was made in determining the water loss in series 3, and 0.8 mg. in series 2, good agreement results. In series 1 the degree of dehydration was so small that it is no longer possible to compare observed and computed pressures, and observed and computed degrees of dehydration are therefore shown in table IX instead; the observed values are calculated from the temperature, pressure, and known dead-space volume, assuming negligible dehydration at room-temperature; they are very approximate, but will be seen to be of the right order; the agreement would certainly be improved could allowance be made for the adsorption of water vapour by the glass walls of the bulb.

With series 6 a new phenomenon is observed; it is no longer possible to lay a single straight line through the experimental data when plotted in the form  $\log p$  against  $1/T$ . And series 7 and 8 give decidedly less steep lines when so plotted than do series 2 to 5, and do not agree with the above equation even approximately. The interpretation of this result is definite and simple; scolecite undergoes a transition into a high-temperature form, presumably the metascolecite of F. Rinne (1890). While series 1 to 5 are due to scolecite, series 7 and 8 represent vapour pressures of metascolecite, and in series 6 the transition occurs within the range of the experimental data,<sup>1</sup> so that this series plots as two intersecting straight lines (fig. 3).

Before considering further the data obtained for metascolecite (which, as a distinct crystal phase, must rank as a definite species), it will be convenient to consider further the significance of the scolecite results. The heat of combination of the group of sixteen more volatile water molecules in scolecite,  $Q = E + \frac{1}{2}RT$ , is  $2.24 \times 10^4$  cal.

<sup>1</sup> It will be shown below that the transition temperature is actually within the temperature range of series 4, 5, 7, and 8 as well as series 6, but owing to the unavoidable experimental errors only the last shows the break clearly.



The interpretation has required an assumption that sixteen of the water molecules in scolecite are more volatile than the other eight. While it would be possible to interpret series 2 to 5 on the assumption that the more volatile group is one of eight molecules, such an interpretation would lead to the conclusion that scolecite should be stable over a large part of the range, over which metascolecite is in fact observed; in other words, no reasonable interpretation of series 6, 7, and 8 could then be found.

TABLE IX. The water vapour pressure of scolecite and metascolecite at various temperatures and degrees of hydration, and the transition temperatures and three-phase equilibrium pressures at various degrees of hydration.  $c$  = water content in mols. per unit cell =  $24 - 16x$ , or  $24 - 8x_m - 16x'_m$ .  $\delta c$  = dead-space loss, to be subtracted from  $c$ .

Series 1. Scolecite.				Series 1 (continued).				
$c$ 24.0 mols.				$\log x_2$				
$t^\circ \text{C.}$	$\log p.$	$\log x_2$		$t^\circ \text{C.}$	$\log p.$	$\log x_2$		
		obs.	calc.			obs.	calc.	
48	0.81	5.7	6.7	59	1.76	5.5	6.4	
55	1.00	5.9	6.9	81	2.00	4.7	5.2	
60	1.05	4.0	5.1	132	2.41	3.3	4.3	
70	1.32	4.2	5.2	164	2.59	3.4	3.0	
74	1.53	4.4	5.2	<i>Transition temperature:</i>				
90	1.75	4.7	5.6	240° C. (calc.)				
96	1.88	4.8	5.7	<i>Series 2. Scolecite. <math>c</math> 23.906 mols.</i>				
102	2.00	4.9	5.8	(obs.) decreasing to 23.836, but better				
71	1.76	5.7	6.7	agreement is obtained by taking $c$				
91	1.91	4.8	5.4	23.975 mols., decreasing to 23.904.				
107	2.05	4.9	5.9	With this assumption $x_2 = 0.0016$ , in-				
116	2.14	3.0	4.1	creasing to 0.0060.				
124	2.22	3.0	4.3	$\log p^*$				
135	2.33	3.1	4.5	$t^\circ \text{C.}$	$\log p^*$			
144	2.42	3.2	4.7		obs.	calc. 1.	calc. 2.	$\delta c.$
159	2.56	3.4	3.0	90	0.08	1.51	0.08	0.000
168	2.65	3.4	3.1	102	0.53	1.91	0.48	0.000
177	2.70	3.5	3.2	113	0.98	0.28	0.85	0.001
188	2.82	3.5	3.4	140	1.71	1.11	1.72	0.006
193	2.87	3.6	3.5	110	0.59	0.20	0.77	0.000
194	2.88	3.6	3.5	125	1.32	0.67	1.22	0.002
72	1.89	5.7	6.7	138	1.63	1.07	1.59	0.005
87	2.00	5.8	5.3	146	1.79	1.25	1.75	0.007
87	2.02	5.9	5.3	157	2.08	1.57	2.03	0.012
118	2.19	5.9	4.2	171	2.32	1.88	2.28	0.021
131	2.24	4.0	4.5	184	2.50	2.13	2.48	0.032
41	1.49	5.0	7.7	198	2.66	2.45	2.75	0.045

\*  $\log p$  (calc. 1) is derived by taking the observed value of  $c$ ,  $\log p$  (calc. 2) by using the above assumed value.



TABLE IX (continued).

*Series 2 (continued).*

$t^{\circ}\text{C.}$	$\log p^*$			$\delta c.$
	obs.	calc. 1.	calc. 2.	
203	2.73	2.52	2.80	0.051
214	2.88	2.70	2.94	0.071
209	2.81	2.63	2.88	0.062
203	2.72	2.47	2.76	0.050
194	2.59	2.41	2.73	0.038

*Transition temperature :*  
240° C. (calc.)

*Series 3.* Scolecite.  $c$  23.77 mols. (obs.), decreasing to 23.72, but better agreement is obtained by taking  $c$  23.86, decreasing to 23.81. With this assumption  $x_s = 0.009$ , increasing to 0.012.

$t^{\circ}\text{C.}$	$\log p^*$			$\delta c.$
	obs.	calc. 1.	calc. 2.	
120	0.23	0.17	0.42	0.000
124	0.42	0.31	0.57	0.000
137	0.97	0.65	0.91	0.001
148	1.28	0.99	1.26	0.002
155	1.52	1.14	1.39	0.003
170	1.89	1.52	1.77	0.008
178	2.05	1.70	1.95	0.012
182	2.15	1.80	2.04	0.014
196	2.41	2.09	2.31	0.029
206	2.58	2.32	2.54	0.036
212	2.68	2.44	2.66	0.045
217	2.76	2.53	2.75	0.054

*Transition temperature :*  
240° C. (calc.)

*Series 4.* Scolecite and metascolecite.  $c$  23.36 mols., decreasing to 23.29,  $x_s$  0.040, increasing to 0.045,  $x_m$  0.090,  $x'_m < 3 \times 10^{-5}$ .

$t^{\circ}\text{C.}$	$\log p$		$\delta c.$
	obs.	calc.	
<i>Scolecite :</i>			
126	1.85	1.88	0.00
144	0.46	0.46	0.00

*Series 4 (continued).*

$t^{\circ}\text{C.}$	$\log p$		$\delta c.$
	obs.	calc.	
160	0.99	0.85	0.00
174	1.32	1.19	0.00
190	1.67	1.63	0.00
207	2.00	1.93	0.01
218	2.26	2.18	0.02
228	2.43	2.38	0.03
238	2.60	2.57	0.04

*Transition conditions (calc. for  $x_s$  0.040):*

243	—	2.68	—
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*Metascolecite :*

244	2.72	2.71	0.05
249	2.82	2.79	0.06
253	2.88	2.82	0.07

*Series 5.* Scolecite and metascolecite.  $c$  21.73 mols.,  $x_s$  0.142,  $x_m$  0.284,  $x'_m < 0.0002$ .

$t^{\circ}\text{C.}$	$\log p$	
	obs.	calc.
<i>Scolecite :</i>		
158	1.90	0.30
163	1.90	0.39
175	0.62	0.76
191	1.11	1.13
183	0.83	0.88
207	1.50	1.48
217	1.66	1.67
227	1.89	1.82

*Transition conditions (calc.):*

230	—	1.98
-----	---	------

*Metascolecite :*

237	2.13	2.09
242	2.20	2.18
252	2.34	2.33
260	2.48	2.41
267	2.65	2.53
277	2.74	2.64

\*  $\log p$  (calc. 1) is derived by taking the observed value of  $c$ ,  $\log p$  (calc. 2) by using the above assumed value.

TABLE IX (continued).

Series 6. Scolecite and metascolecite.  $c$  20.06 mols.,  $x_s$  0.246,  $x_m$  0.492,  $x'_m < 0.0005$ .

$t^\circ \text{C.}$	$\log p$	
	obs.	calc.
<i>Scolecite :</i>		
192	0.99	0.95
200	1.18	1.15
218	1.46	1.50
232	1.78	1.79
<i>Transition conditions (calc.) :</i>		
253	—	2.16
<i>Metascolecite :</i>		
261	2.15	2.24
268	2.30	2.36
276	2.42	2.48
280	2.48	2.52
290	2.67	2.65

Series 7. Scolecite and metascolecite.  $c$  17.50 mols.,  $x_s$  0.406,  $x_m$  0.812,  $x'_m < 0.0005$ .

$t^\circ \text{C.}$	$\log p$	
	obs.	calc.
<i>Scolecite :</i>		
196	1.23	0.93
182	0.95	0.58
208	1.23	1.17
220	1.43	1.41
228	1.56	1.55
<i>Transition conditions (calc. and obs.) :</i>		
243	1.70	1.74
<i>Metascolecite :</i>		
248	1.91	1.90
261	2.10	2.09
273	2.22	2.27
280	2.31	2.34
294	2.50	2.50
302	2.65	2.62

Series 8. Scolecite and metascolecite.  $c$  16.46 mols.,  $x_s$  0.467,  $x_m$  0.935 to 0.932,  $x'_m$  0.001 to 0.003;  $x'_m$  increases with rise of temperature.

$t^\circ \text{C.}$	$\log p$	
	obs.	calc.
<i>Scolecite :</i>		
183	0.53	0.51
190	0.85	0.75
<i>Transition conditions (calc.) :</i>		
197	—	0.86
<i>Metascolecite :</i>		
198	0.95	0.93
212	1.23	1.12
222	1.40	1.27
242	1.57	1.49
253	1.78	1.72
270	2.06	1.95
276	2.13	2.02
286	2.27	2.13
292	2.31	2.21
302	2.43	2.26
316	2.54	2.38
322	2.60	2.48
328	2.70	2.53
330	2.73	2.66

Series 9. Metascolecite.  $c$  16.08 mols.,  $x_m + 2x'_m$  0.990, increasing to 0.993.

$t^\circ \text{C.}$	$\log p$		$x_m$	$x'_m$
	obs.	calc.		
<i>Transition conditions (calc.) :</i>				
84	—	2.75	0.990	$3 \times 10^{-7}$
<i>Metascolecite :</i>				
186	0.0	0.04	0.990	0.0002
202	0.5	0.40	0.989	0.0003
222	0.70	0.77	0.989	0.0005
243	0.85	1.14	0.988	0.0010
264	1.34	1.44	0.987	0.0013
299	1.99	1.92	0.985	0.0025

TABLE IX (continued).

<i>Series 9 (continued).</i>					<i>Series 11.* Metascolecite. c 15-20</i>		
<i>t</i> ° C.	log <i>p</i>		<i>x<sub>m</sub></i>	<i>x<sub>m</sub>'</i>	<i>t</i> ° C.	log <i>p</i>	
	obs.	calc.				obs.	calc.
270	1.43	1.56	0.987	0.0016	336	0.3	1.31
298	1.99	1.92	0.985	0.0025	339	0.7	1.38
311	1.86	2.10	0.984	0.0030	358	0.97	1.78
245	1.08	1.10	0.988	0.0009	363	1.11	1.86
272	1.48	1.56	0.987	0.0016	369	1.20	1.99
297	1.74	1.92	0.985	0.0025	375	1.36	2.06
310	1.88	2.10	0.984	0.0030	390	1.59	2.31
332	2.10	2.30	0.983	0.0041	405	1.80	2.53
354	2.32	2.58	0.981	0.0055	415	2.02	2.72
373	2.42	2.82	0.978	0.007			
381	2.49	2.94	0.976	0.008			
391	2.58	3.04	0.974	0.009			
395	2.63	3.09	0.973	0.010			
415	2.72	3.29	0.971	0.011			

<i>Series 10. Metascolecite. c 15-54</i>					<i>Series 12.† Metascolecite. c 13-52</i>		
mols., $x_m + 2x_m'$ 1.0575, increasing to 1.0588.					<i>t</i> ° C.	log <i>p</i>	
<i>t</i> ° C.	log <i>p</i>		<i>x<sub>m</sub></i>	<i>x<sub>m</sub>'</i>		obs.	calc.
	obs.	calc.			obs.	calc.	
397	1.98	2.60	0.9948	0.0317	315	1.7	0.51
409	2.16	2.79	0.9940	0.0324	336	0.4	0.85
391	1.95	2.54	0.9950	0.0319	375	1.32	1.60
380	1.78	2.34	0.9952	0.0314	380	1.43	1.70
373	1.72	2.29	0.9956	0.0312	391	1.59	1.88
363	1.60	2.09	0.9960	0.0310	404	1.92	2.07
350	1.49	1.84	0.9968	0.0305	409	2.01	2.15
340	1.32	1.64	0.9975	0.0301	417	2.11	2.28
334	1.20	1.50	0.9978	0.0300			
281	0.47	0.59	0.9997	0.0289			
292	0.60	0.78	0.9991	0.0292			
301	0.72	0.99	0.9987	0.0295			
333	1.20	1.50	0.9978	0.0300			
369	1.63	2.23	0.9971	0.0304			

<i>Series 13. Metascolecite. c 11-84</i>		
mols., $x_m > 0.999$ , $x_m'$ 0.26.		
<i>t</i> ° C.	log <i>p</i>	
	obs.	calc.
297	1.7	1.89
316	0.0	0.29
340	0.57	0.77
356	0.84	1.03
362	1.00	1.17
367	1.15	1.28

\* It is clear that final equilibrium was not attained in this series. The time between dehydration and the commencement of pressure readings was probably insufficient for complete lattice shrinkage. An error in weighing the water pumped off would also account for the discrepancy, but the error would have to be large—10.5 mg.

† Final equilibrium was probably not attained in the earlier measurements of this series.

TABLE IX (continued).

Series 13 (continued).			Series 15.* Metascolecite. c 5-40 mols., $x_m > 0.999$ , $x'_m 0.663$ .		
$t^\circ\text{C.}$	$\log p$		$t^\circ\text{C.}$	$\log p$	
	obs.	calc.		obs.	calc.
371	1.32	1.38	336	1.23	0.58
380	1.42	1.48	362	1.54	1.12
391	1.73	1.63	375	1.78	1.33
397	1.85	1.72	387	2.00	1.55
402	2.04	1.82	395	2.26	1.67
409	2.22	1.93	402	2.32	1.80
			411	2.41	1.94
Series 14. Metascolecite. c 11-35 mols., $x_m > 0.999$ , $x'_m 0.29$ .			Series 16. Metascolecite. c 5-17 mols., $x_m > 0.999$ , $x'_m 0.677$ .		
$t^\circ\text{C.}$	$\log p$		$t^\circ\text{C.}$	$\log p$	
	obs.	calc.		obs.	calc.
268	1.8	1.29	336	0.83	0.47
290	0.15	1.75	365	1.15	1.20
315	0.53	0.23	388	1.45	1.44
365	1.46	1.26	403	1.81	1.69
373	1.55	1.38	412	2.19	1.83
391	1.83	1.63			
407	2.18	1.93			
380	1.85	1.48			
364	1.56	1.17			
358	1.48	1.03			

\* The cause of the anomalously high pressures observed in this series remains uncertain.

This conclusion that the water in scolecite consists of a more volatile group of sixteen and a less volatile group of eight molecules tends to support W. H. Taylor's suggestion as to the probable crystal-structure of scolecite (1933) as against L. Pauling's (1930). In both structures sixteen water molecules occupy the same positions as in natrolite, which agrees with the fact that the heats of hydration of natrolite and of the sixteen-molecule group in scolecite are very similar. But in Pauling's structure the other eight water molecules occupy the positions of eight of the sodium atoms of natrolite, and are each surrounded by four oxygen atoms and two water molecules, all at 2.5 Å. distance, the nearest calcium atom being 3.6 Å. away; in such a position the eight water molecules should be much more loosely attached than the sixteen, which are only 2.5 Å. from the calcium atoms. In Taylor's structure, on the other hand, the eight water molecules are if anything rather nearer the calcium atoms (2.3 Å.) than are the sixteen, which would agree with their rather

lower volatility. Moreover, it will be shown below that in metascolecite the relative volatilities of the two groups are reversed, and it seems more probable that such a reversal could be effected by small adjustments of the atomic positions in Taylor's structure than in Pauling's.

The lattice-shrinkage factor,  $\phi(x_s)$ , in the vapour-pressure equation, has a very high value for scolecite, indicating considerable lattice shrinkage. In agreement with this is the fact that scolecite, dehydrated to a loss of 1.43%  $H_2O$  (2.5 mols.), had a specific gravity  $D_4^{20}$  of 2.260, whereas the value calculated from the specific gravity of fully hydrated scolecite, assuming no lattice shrinkage, is 2.243, a shrinkage of nearly 0.8%.

#### *Metascolecite.*

It has been shown above that the consideration of the vapour-pressure data leads to the conclusion that there exists a high-temperature dimorphous form of scolecite, and optical evidence shows that this must be identical with the metascolecite of F. Rinne (1890). The higher-temperature results of series 4 to 8 and the whole of series 9 to 16 represent the vapour-pressure relations of this species. On examination, it appears that there is a more volatile group of eight water molecules and a less volatile group of sixteen. The vapour pressures are well represented by the equations:

$$\begin{aligned} \log p &= M_o + \frac{1}{2} \log T - \log x_m / (1 - x_m) - 2 \log \{1 + \psi(x_m)\} - E/RT. \log_e 10 \\ &= M'_o + \frac{1}{2} \log T - \log x'_m / (1 - x'_m) - 2 \log \{1 + \Phi(x'_m)\} - E'/RT. \log_e 10 \end{aligned}$$

(where  $x_m$ ,  $E$ , and  $M_o$  refer to the more volatile group of eight water molecules, and  $x'_m$ ,  $E'$ , and  $M'_o$  to the less volatile group of sixteen). The values of the constants are:  $E$   $1.75 \times 10^4$  cal. per gram-mol.  $H_2O$ ,  $M_o$  7.62,  $\psi(x_m) = -0.8 x_m$ ,  $E'$   $3.03 \times 10^4$  cal.,  $M'_o$  9.52, and  $\Phi(x'_m) = -0.9 x'_m$ .

The transition equation for the scolecite  $\rightleftharpoons$  metascolecite equilibrium may therefore be written:

$$1000/T = 1.65 - \log (1 - x_m) (1 - 0.45 x_m)^2 / (2 - x_m) (1 - 0.8 x_m)^2.$$

This gives a transition curve which varies only between 230° and 255° C. over the hydration range 24 to 17 mols.  $H_2O$  per unit cell, and then drops sharply, reaching room-temperature for a composition very near 16.00 mols. (see figs. 3 and 4); this circumstance explains the fact that the maximum water content of metascolecite has

generally been supposed to be 16 mols. per unit cell. This supposition is quite untrue, for from the above transition equation, scolecite should transform into metascolecite if the temperature exceeds  $255^{\circ}\text{C}.$ , whatever its water content; and when scolecite is heated in contact with liquid water, the transformation should take place at  $240^{\circ}\text{C}.$ , under 25,000 mm. Hg (33 atmos.), to give a metascolecite containing 23.990 mols.  $\text{H}_2\text{O}$  per unit cell.

Owing to the difficulty in establishing the vapour-pressure constants with any accuracy, especially the functions  $\phi(x_s)$  and  $\psi(x_m)$ , the above transition curve cannot be regarded as of any great accuracy, but it is believed to be substantially correct.

The above equations reproduce series 7 and 8, the high-temperature part of series 5 and 6, and series 12, 13, 14, and 16 very well. Series 11 and 15 are not satisfactory, the former probably owing to insufficient time being given for equilibrium to be established. Series 9 and 10 show fair agreement considering that a small error in the observed degree of hydration would have a very marked effect on the calculated vapour pressure in these series. Series 9, with a composition very near 16 mols. water per unit cell, shows clearly the tendency for the water to become more equally distributed over the different sets of lattice positions as the temperature rises.

The optical properties found for the high-temperature form agree almost completely<sup>1</sup> with those found for metascolecite by F. Rinne (1890, 1894) and A. Cavinato (1927, 1928), but no evidence could be found to confirm the latter's view that there are three phases involved, with different maximum water contents (3, 2, and 0  $\text{H}_2\text{O}$  to  $\text{CaAl}_2\text{Si}_3\text{O}_{10}$ ). All the evidence seems rather to indicate that the maximum water content for both scolecite and metascolecite is 24 mols. per unit cell, and that there is no third polymorph. The difference between the X-ray powder photographs of metascolecite-I ( $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ ) and metascolecite-II (anhydrous) found by Cavinato (1927) is probably due to lattice shrinkage, which would also account for the loss of reversibility when the dehydration is carried nearly to completion.

A pair of Lauegrams taken by Mr. Bannister agree with those of F. Rinne (1923) and A. Cavinato (1927) in showing the monoclinic

<sup>1</sup> The author finds for a metascolecite with about 5 mols.  $\text{H}_2\text{O}$  per unit cell,  $\beta:c = 5^{\circ} \pm$ , birefringence very weak,  $n1.523$ ; and for a metascolecite with 16 mols.  $\text{H}_2\text{O}$  per unit cell,  $\beta:c = 18^{\circ} \pm$ , birefringence  $0.01 \pm$ ,  $n1.505$ . These refractive indices are markedly lower than Cavinato's values.

symmetry of metascolecite and confirming the position of the symmetry plane relative to its position in scolecite, found optically by F. Rinne (1890). Rotation photographs indicate considerable lattice shrinkage, but cannot be indexed. Density determinations show clearly a marked shrinkage in metascolecite with 16.03 mols.  $H_2O$  per unit cell, as compared with scolecite with 21.5 mols., and it

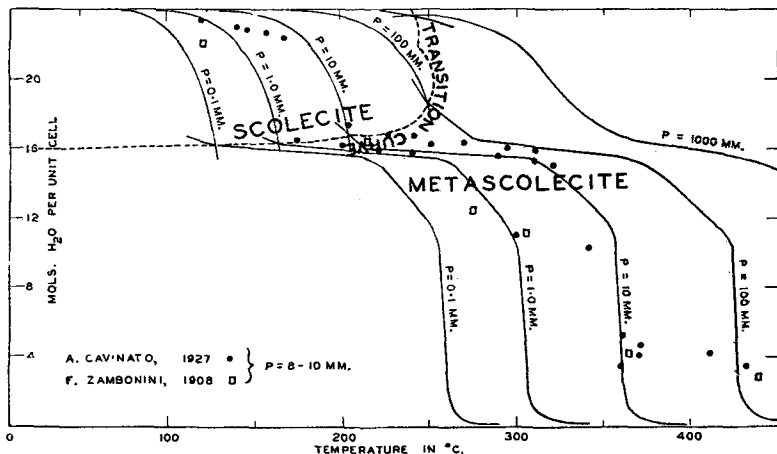


FIG. 4. Isobaric dehydration curves of scolecite and metascolecite.

seems probable that much of this shrinkage takes place during the transition. For metascolecite with 16.03  $H_2O$ ,  $D_4^{19} = 2.441$ ; calculated without allowing for lattice shrinkage, 2.172, or allowing for shrinkage at the rate found for scolecite, 2.225.

Metascolecite is strongly pyroelectric (Sir David Brewster, 1821, 1822; F. Rinne, 1894), and X-ray photographs, though poor, confirm the evidence of the distribution of the pyroelectric charge that the symmetry is still planosymmetric; it was not possible to establish the space-group. Owing to the low conductivity of dehydrated metascolecite and its great power of keeping its own surface truly dry by absorbing any moisture film, the pyroelectric charge is very persistent, dehydrated metascolecite powder balling into lumps as if moist weeks after the charge was first developed if it is kept in a sealed tube.

H. Michel (1920) described material from Hegeberg, Eulau, Bodenbach, Bohemia, which he had formerly (1911) described as okenite, and regarded it as natural metascolecite. The chemical composition

was that of a fully hydrated scolecite, but it differed optically. The optics were not, however, those of metascolecite, and the identification must be incorrect; it is not possible to identify the material from the data given, and further investigation is very desirable.

It is possible that some of the base-exchange products above described may be really metascolecites; it would be interesting to test the matter, but very difficult.

#### *Summary.*

Two new chemical analyses, combined with optical data, confirm the conclusion of J. Wyart (1933) that the unit-cell formula of scolecite is  $\text{Ca}_8\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\cdot 24\text{H}_2\text{O}$ . The limit of natural substitution of Ca by  $\text{Na}_2$  appears to be about 1 atom Na per unit cell, and by  $\text{K}_2$  about 0.1 atom. The crystal elements as deduced from X-ray and goniometric measurements agree excellently. The cell size is  $a$  18.48,  $b$  18.95,  $c$  6.54 Å.,  $\beta$  89° 21', and the space-group  $S^4$ . A detailed optical study of one of the analysed specimens was made. Base-exchange experiments were made, introducing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$  in place of  $\text{Ca}^{++}$ , and the effect on the optical properties studied; in several cases the products were natrolites, confirming the view that natrolite and scolecite are isostructural. Vapour-pressure study showed that on partial dehydration a transition to metascolecite occurs at a degree of hydration dependent on the temperature of the experiment; except at low temperatures, the transition occurs considerably before the composition  $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ , commonly attributed to metascolecite, is reached. In both scolecite and metascolecite the water consists of two distinct groups, in scolecite a more volatile one of sixteen and a less volatile one of eight mols. per unit cell; in metascolecite the group of eight is the more volatile. The vapour-pressure constants of both groups have been ascertained for metascolecite, and of the first for scolecite. There is no evidence that anhydrous metascolecite constitutes a third crystal phase. The vapour-pressure data tend to support the crystal-structure suggested for scolecite by W. H. Taylor, C. A. Meek, and W. W. Jackson, rather than that proposed by L. Pauling. The material described by H. Michel as natural metascolecite was incorrectly identified.

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## EXPLANATION OF PLATES VIII AND IX.

X-ray photographs of scolecite and metascolecite (and natrolite).

- PLATE VIII. FIG. 1. Laue photograph of scolecite (single crystal) along the axis  $b[010]$ .
- „ FIG. 2. Laue photograph of metascolecite twin along the axis  $a[100]$ , which corresponds to  $b[010]$  of scolecite. The same crystal was used as for fig. 1, and the photograph taken in the same direction. (Intensifying screen used.)
- PLATE IX. FIG. 3. Rotation photograph of scolecite about the axis  $c[001]$ . ( $Cu-K_{\alpha}$  radiation,  $\lambda 1.539 \text{ \AA}$ .)
- „ FIG. 4. Rotation photograph of natrolite about the axis  $c[001]$  for comparison with fig. 3. ( $Cu-K_{\alpha}$  radiation,  $\lambda 1.539 \text{ \AA}$ .)

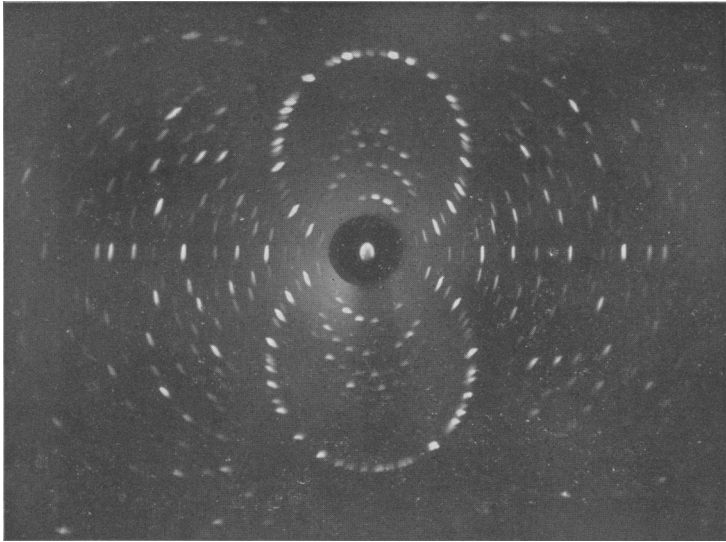


FIG. 1

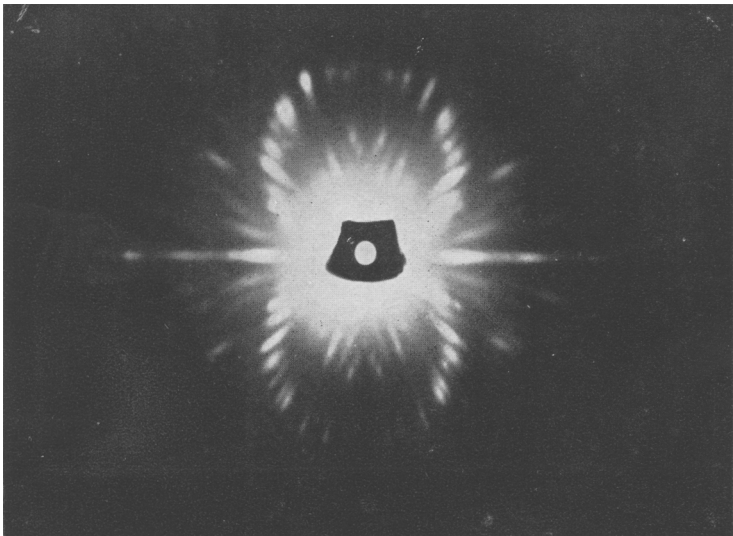


FIG 2

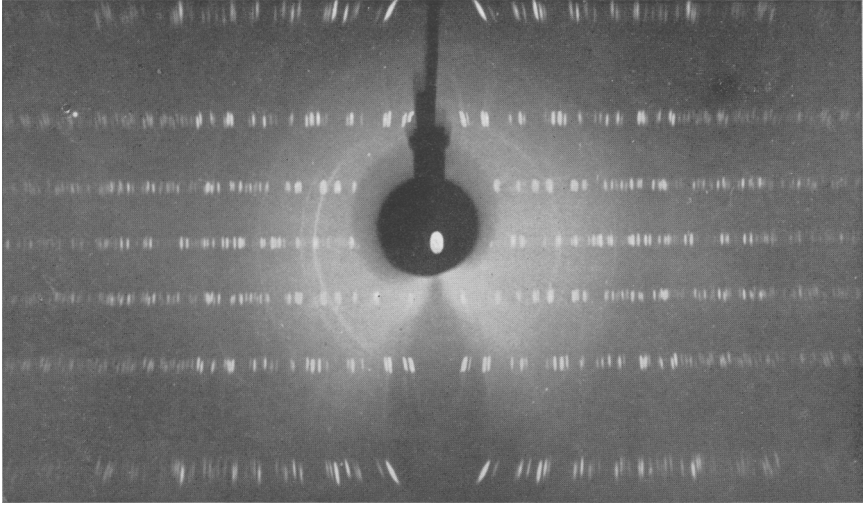


FIG. 3

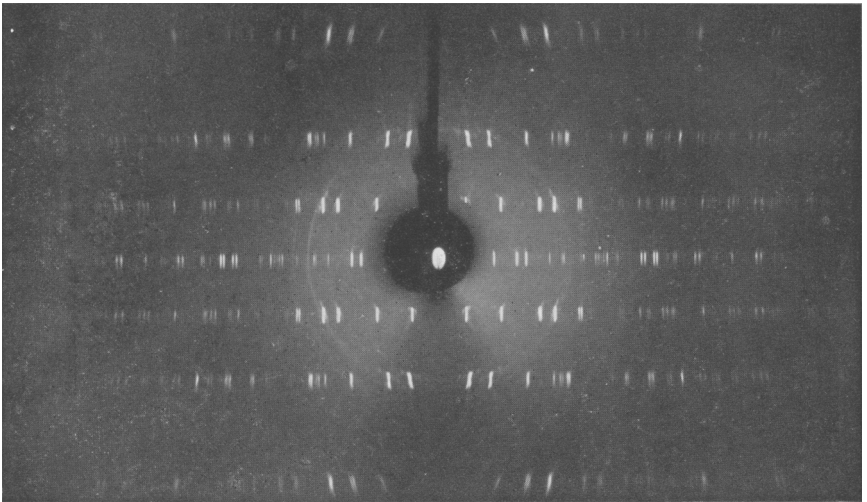


FIG. 4

M. H. HEY: SCOLECITE AND NATROLITE