## On Blödite from the Punjab Salt Range.

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THE Salt Range of the Northern Punjab derives its name from the numerous beds of rock salt which are there included amidst the pre-Cambrian strata. Some of these salt beds are of great purity and immense thickness, and have been utilised as a source of the mincral from a remote period, while extensive mines have been opened out by Government since the annexation of the province. The blödite referred to below was discovered in these workings by Dr. H. Warth, lately Deputy Superintendent of the Geological Survey of India, but who, at the time alluded to, held charge of the mines in question.

It appears, from information for which I am indebted to Dr. Warth, that the blödite was first discovered about the year 1875, in the Mayo mines at Khewra, a few miles north of Pind Dádun Khán. It occurred in crystals about half-an-inch long, which, together with colourless and transparent cubic crystals of salt, formed a drusy coating on the sides of a narrow fissure in the rock salt. It was not accompanied by any other mineral of secondary origin; except the salt crystals just mentioned. Although glauberite and selenite have been found under similar circumstances in the same mines, they were not in association with the About 1887, bigger crystals of the latter, some of which were as blödite. much as 3 or 4 inches long and nearly as broad, were discovered in the Varcha mine, which is situated 65 miles W.S.W. from those mentioned The mineral from both localities was in very perfect crystals, above. the majority of them possessing smooth, or even lustrous faces, and sharply-cut edges and angles.

Some of the crystals from the Mayo mines were given by Dr. Warth to Professor Quenstedt, who described their crystallographic character in his *Handbuch der Mineralogie.*<sup>1</sup> The similarity of the crystals to those of the same mineral from Stassfurt is pointed out; but the complication is introduced of choosing axes different from those previously adopted by Brezina, Groth and Hintze, and vom Rath, for the Hallstadt and

<sup>&</sup>lt;sup>1</sup> 3rd edition (1877), p. 645,

Stassfurt blödite, and of orientating the crystal in a different way. What these writers regard as the front of the crystal, in the normal position, Quenstedt places behind. The symbols for 11 or 12 forms are given, all of which are amongst those previously observed on the Stassfurt mineral.

About the same time the blödite from the Mayo mines was examined in respect to its crystallography by Professor Schimper.<sup>1</sup> Adopting the same axes as Groth<sup>2</sup> and vom Rath<sup>3</sup>, Schimper observed 13 forms which are common to the Stassfurt crystals, and which include all those recorded by Quenstedt. He likewise determined two new forms, not hitherto noticed on the Stassfurt blödite; and pointed out the similarity in habit of the mineral from the two localities, as well as the agreement in value of corresponding angles, Schimper's measurements generally differing from Groth and Hintze's by not more than one minute.

Dr. Warth has recently given me the opportunity of examining 11 specimens from Varcha, and I have also received some out of the same mine from Mr. Holland, of the Indian Geological Survey. Besides most of those mentioned by Schimper, I noticed three forms on one or other of the crystals, which are new in respect to the Salt Range mineral, but have been described by the authors quoted as occurring on the Stassfurt blödite; this makes a total of 18 forms as given below.

$$\begin{array}{l} c &= (001) = 0P \\ d &= (011) = P\infty \\ p &= (111) = -P \\ m &= (110) = \infty P \\ n &= (210) = \infty P2 \\ a &= (100) = \infty P\infty \\ b &= (010) = \infty P\infty \\ b &= (010) = \infty P3 \\ v &= (120) = \infty P3 \\ v &= (120) = \infty P2 \\ q &= (201) = +2P2 \\ u^4 &= (\bar{1}11) = +P \\ s &= (\bar{2}11) = +2P2 \\ o &= (121) = -2P2 \end{array}$$

- <sup>1</sup> Zeitsch. f. Kryst. u. Min., I. (1877), 70.
- <sup>2</sup> Zeitsch, d. deuts. geol. Gesell., XXIII. (1871), 670,
- <sup>3</sup> Pogg. Annalen, CXLIV. (1872), 586,
- $^{4}$  y in original,

x	=(121)=+2P2	Common to Stassfurt and
y	$=(\bar{2}21) = +2P$	Salt Range.
e	$=(021)=2$ P $\infty$	F. R. MALLET.
μ	$=(130)=\infty$ $\mathbb{P}3$	Salt Range only.
f	$=(\bar{1}44)=+\mathbb{P}4$	W. Schimper.

Of these forms, p, c, d, m, n are predominant (as they are in the Stassfurt crystals also). None of them are absent, or even subordinate, in any fairly perfect crystals that I have examined. o and q are sometimes of fair size, while the rest are generally small and often quite minute. Some are of very rare occurrence; although a and b are mentioned by both Quenstedt and Schimper, I have never noticed the latter, and the former only once. f was also absent on the Varcha crystals, and  $\lambda$  appeared on but one.

The authors quoted observed 21 forms on the Stassfurt crystals, of which five have not been noticed on those from India. But probably this number would be reduced if still further specimens were submitted to examination.

The mineral is colourless, and to a large extent transparent; but there are few crystals in which the limpidity is not here and there imperfect. The examination of sections under the microscope shows that this cloudiness is due to multitudinous cavities, which generally vary in size from 0.1 or 0.2 millimetres downwards. Some are very irregular in outline, but the larger proportion are less markedly so, and often rudely elliptical. Many look more or less like negative crystal cavities, and some with distinct polyhedral boundaries undoubtedly are such. In rare cases one or two of the predominant forms like (001), OP and (111), -P can be With few exceptions the cavities are nearly filled by a recognised. colourless liquid, the accompanying bubbles being comparatively minute; but in a small minority no bubble is apparent, or again, there is no liquid. In some exceptionally large cavities, about a millimetre long, the movement of the bubbles can easily be seen when the specimen is turned. A few cavities were noticed containing colourless crystals in the liquid : the outline of the only one with very determinate form was rectangular, and nearly square, suggestive of sodium chloride.

An optical examination of the mineral gave results in fairly close agreement with those obtained by Groth and Hintze in respect to that from Stassfurt.<sup>1</sup> The crystals are negative, with the optic axes in the plane of symmetry, the bisectrix a nearly bisecting the acute angle between the vertical and clino-diagonal crystallographic axes. With sections parallel to the plane of symmetry, and bounded on one side by the trace of the basal plane, the mean of numerous determinations of the angle  $\mathfrak{A} \wedge c$  (= angle  $\beta$ -angle between trace of basal plane and  $\mathfrak{A}$ ) was:--

For red light <sup>1</sup>	•••	$42^{\circ}9'$
For blue light <sup>2</sup>	•••	41 5

The values obtained by the authors quoted, using similar light, were  $44^{\circ}48'$  and  $43^{\circ}21'$ .

With sections perpendicular to the bisectrices, the following mean results were obtained :---

		$2 H_{a}$ .	$2H_{o}$ .
For red light		$71^{\circ}22'$	$111^{\circ}51'$
For blue light	•••	$73 \ 26$	109 0

The value of  $2V_a$  derived from these is 70°18' for red, and 72°36' for blue; Groth and Hintze's angles are 70°5' and 72°34'. When a section perpendicular to a is examined by white light, the inclined dispersion is very clearly displayed in the colouration of the rings and brushes.

The sections employed not having been cut, nor the observations made, with the precision now attainable by means of the instruments devised by Mr. A. E. Tutton, the above results cannot be regarded as more than fairly good approximations. In the one or two cases where my results differ from Groth and Hintze's by only a few minutes, such close agreement is little more than fortuitous.

In some of the earlier accounts the blödite from more than one European locality is described as efflorescent,<sup>3</sup> while two or three writers allude to the substance attracting moisture.<sup>4</sup> The Indian crystals are, however, perfectly stable in the air (of London). Some which I have had in my possession for the last eight years, without protection from the atmosphere, show no sign of alteration; and further, a sample taken for

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<sup>&</sup>lt;sup>1</sup> Red glass.

<sup>&</sup>lt;sup>2</sup> Ammoniacal supric sulphate.

<sup>&</sup>lt;sup>8</sup> John: Chemische Schriften. VI. (1821), 240 (as quoted by Tschermak: I have been unable to refer to the original). Göbel; G. Rose, Reise nach dem Ural (1842), II. 270. Tschermak: Silzungsb. d. k. Akad. der Wiss. Wien, IX. 1 Abth. (1869), 722. Also v. Funllon; Jahrb. k. k. geol. Reichanst. Wien, XXXVIII. (1888), 3. Tschermak, however, found the Hallstadt mineral perfectly stable.

<sup>4</sup> liages; Proc. Nat. Hist. Soc. Boston, V. 391. Groth and Hintze; l.c.: v. Foullon; l.c.

analysis, after being finely powdered and placed in a desiccator with oil of vitriol till the weight remained constant, only lost .07 per cent., which was, no doubt, partly due to the liquid in the cavities. Another portion, again, exposed in fine powder to the air for a week during weather of medium humidity, only gained .08 per cent.

The mineral, freed from moisture as mentioned above, yielded on analysis-

		Ι.	11.	Mean.1	Theory.1
MgO	•••	11.96	11.97	11.97	12.04
$Na_2O$	•••	18.48	18.59	18.53	18.56
$SO_3$	•••	47.75	47.89	47 82	47.86
$H_2O$	•••	21.59	$21 \cdot 50$	21.54	21.54
NaCl	•••	•07	.07	•07	
		99.85	100.02	99.93	100.00

There was likewise an unweighable trace of material insoluble in water, and the same of lime. The chlorine is doubtless in combination with sodium. As previously mentioned, the blödite was found on rock salt, and crystals of salt are associated with it, and sometimes embedded in it; hence care is necessary in obtaining a sample as free from chlorine as the above. The minute quantity found is probably due, in part at least, to the saline matter dissolved in the liquid of the cavities.

Some of the earlier accounts differ as to the tenacity with which the water in blödite is retained on heating the mineral. According to John the massive blödite of Isehl loses the whole of its water when heated for two hours in a water bath.<sup>2</sup> Tschermak, on treating the Hallstadt mineral in the same way until the weight remained constant, found that three-eighths of the water was expelled, the remainder being given off on ignition; he consequently wrote the formula of the mineral (which he named simonyite)  $2MgSO_42Na_2SO_4.5H_2O.8aq.^3$  Groth and Hintze, on the other hand, found that Stassfurt blödite loses about 8.8 per cent. at 100° C. and 10.12 per cent. at 150°, the former figures being, as they point out, in excess of three-eighths (8.08 per cent.) of the total water.<sup>4</sup> These

<sup>&</sup>lt;sup>1</sup> The atomic weights used are those adopted by Prof. F. W. Clarke in his Recalculation of the Atomic Weights. New Edition, 1897.

<sup>2</sup> l. c.

<sup>&</sup>lt;sup>8</sup> l. c. and Jahrb. k. k. geol. Reichsanst. XXII. (1872), Min. Mitth. 58.

<sup>4</sup> loc. cit.

results are in agreement with those obtained by vom Rath<sup>1</sup> on heating the mineral from the same locality, which are as follows :----

Loss on heating	up to 130	ρ	•••		10·05 p	er cent.
Further loss on	heating up	to 30	00 <sup>c2</sup>	•••	10.09	,,
,,	,, til	l the s	salt mel	ted	1.16	,,
Total loss	•••	•••		•••	21.30	

The loss at 130°, as he remarked, is nearly half the total, and he consequently adopted the formula  $MgSO_4.Na_2SO_4.2H_2O + 2aq$ .

In respect to the Salt Range mineral, it was found that decomposition by loss of water commenced at about  $85^{\circ}$  C.; but, at even considerably higher temperatures, very protracted heating was necessary before the weight remained constant :—

Duration of heating.		Temp.	Los	s per cent.	Total loss per cent.	
<b>39</b> hours			100° C.	9.44 (weight constant)		9.44
<b>62</b>	,,	more	$110^{\circ}$	·37	(ditto)	9.81
114	,,	,,	$120^{\circ}$	$\cdot 95$	(ditto)	10.76

Thus at  $120^{\circ}$  exactly two molecules of water were driven off, and no further loss of weight took place on continued heating at the same temperature. But a very slight increase of temperature was sufficient to induce still further loss. After 16 hours at  $125^{\circ}$  this amounted to  $\cdot07$  per cent., and after 27 hours longer at increasing temperatures up to  $150^{\circ}$ , to  $1\cdot05$  per cent. more (total  $11\cdot88$ ), these experiments not being continued till the weight was constant. When the mineral was heated at once to  $150^{\circ}$   $10\cdot92$  per cent. was expelled in 4 hours, but 12 hours more were required to raise the loss to  $10\cdot78$ , and the substance continued to lose water slowly when the heating was carried on still longer.

The Salt Range blödite, therefore, like the Stassfurt, loses two molecules of water more easily than the other two. The first were expelled between  $85^{\circ}$  and  $120^{\circ}$ , while the remainder began to go off at about  $125^{\circ}$ .

As long ago as 1842, Rose expressed the opinion that the blödite of certain salt lakes near Astrakhan was formed through the mutual decomposition of Epsom salt and common salt, whereby sodium sulphate and magnesium chloride result, the former uniting with the undecomposed Epsom salt.<sup>3</sup> Tschermak originally thought that the Hallstadt blödite

<sup>8</sup> l. c

<sup>&</sup>lt;sup>1</sup> loc. cit.

<sup>&</sup>lt;sup>2</sup> Or 200? The original is not clear.

was due to the alteration of polyhalite; but later on he suggested that it was derived from kieserite.<sup>1</sup> Comparatively recently van't Hoff and van Deventer, incidentally to a research on transformation temperature in relation to chemical change, refer to two methods by which blödite may be formed artificially: firstly, by the combination of sodium sulphate with magnesium sulphate. and secondly, which is of more interest at present, by the double decomposition of magnesium sulphate and sodium chloride, according to the following equation:—

 $2SO_4Mg.7H_2O + 2NaCl = (SO_4)_2MgNa_2.4H_2O + MgCl_2.6H_2O + 4H_2O.$ 

The transformation temperature with the salts in the above proportions is  $31^{\circ}$ C. Below this point the reaction from right to left occurs, but above it the reverse chemical change takes place, and blödite is formed together with magnesium chloride. The transformation temperature may, however, apparently be greatly lowered by the presence of common salt in excess, with which is probably connected "the technical prescription which forbids the transgression of a temperature of 5°, during the working of brine containing common salt and magnesium sulphate for glauber salt; as above that temperature, according to the preceding experience, astrakanite (blödite) instead of glauber salt might separate out."<sup>2</sup>

In 1873, a lenticular band of mixed sylvine and kieserite was discovered by Dr. Warth in one of the beds of "kallar," or impure rock salt, of the Mayo mines. In a moist atmosphere the kieserite becomes disintegrated on the surface, and exhibits a constantly deciduous coating owing to its changing into epsomite.<sup>3</sup> As the latter mineral "impregnates the kallar and thin layers between the salt beds, and also effloresces from the surfaces of the red marl in old workings,"<sup>4</sup> it may perhaps be inferred that, although but one actual band of kieserite has been discovered, the mineral is still somewhat widely, if sparingly, distributed, in a scattered way, through the saline strata; and there scarcely seems much room for doubting that the blödite has been formed by the solution and interaction of rock salt and the magnesian minerals just alluded to.

<sup>&</sup>lt;sup>1</sup> l. c. & Sitzungsb. d. k. Akad. Wiss. Wien. LXIII. 1 Abth. (1871), 321.

<sup>&</sup>lt;sup>2</sup> Zeit. f. physikalische Chemie, I. (1887), 176.

<sup>&</sup>lt;sup>3</sup> Jahrb. d. k. k. geol. Reichanst, XXIII, 2 Abth., 136; and Records, Geol. Surv. India, VII, 64; Memoirs, Geol. Surv. India, XIV, 80.

<sup>\*</sup> Wynne, Memoirs, l. c. 79.