On Langbeinite from the Punjab Salt Range.

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IN the eleventh volume of the *Mineralogical Magazine*, p. 317, in connection with the occurrence of blödite at the Mayo mines, in the Salt Range, allusion is incidentally made to a potassio-magnesian deposit, which was discovered there by Dr. H. Warth in 1873. It occurred as a lenticular stratum in the 'kallar' (impure rock salt) band separating the Sujewal and Purwálla salt beds. The material was more or less mixed up with the 'kallar' itself, and the deposit appeared to be of very limited extent.[1] I am informed by Dr. Warth that no further deposit of the kind has been discovered, so far as he knows; but this does not prove very much, for, since his retirement from the management of the mines, no search for potassium salts seems to have been made.

Specimens sent to the Geological Survey Laboratory, in Calcutta, were examined by Mr. A. Tween, whose analyses, given below, were published in the Catalogue to the Collection of Indian Geological Specimens sent to the Vienna Exhibition of 1873.[2]

	No. 1. Colourless salt.	No. 2. Pink-coloured salt.
KCl	3·80	61·43
$NaCl$	—	29·32
K_2SO_4	38·00	—
$MgSO_4$	58·02	7·78
H_2O	·62	2·10
	100·44	100·63

Specimens in the Vienna collection similar to No. 2 were examined by Professor Tschermak, who described them as "a white or reddish

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[1] *Mem. Geol. Surv. India*, 1878, XIV. 80.

[2] Reprinted in Mr. A. B. Wynne's memoir on the geology of the Salt Range, *Mem. Geol. Surv. India*, 1878, XIV. 80.

granular mixture of sylvite, rock salt, and kieserite. The sylvite and rock salt can be at once recognised by the cleavage and flame reaction. The kieserite, which occurs in grains having a maximum diameter of 12 millimetres, is colourless, and shows the hardness and cleavage that I have given for the Hallstadt mineral.[1] In places, also, the kieserite is compact. An estimation of the water gave 12·99 per cent., which agrees with the theoretical amount, 13·04. From the kieserite changing, in a moist atmosphere, into epsomite, the pieces formed of that substance become quite disintegrated at the surface, and exhibit a constantly deciduous coating. In some pieces sylvite greatly predominates. Whether some kieserite also occurs in these, as might be conjectured in such association, has not yet been determined, for I have only been able to submit small pieces to examination."[2]

The colourless salt does not seem to have come under Professor Tschermak's observation. In Part IV. of *A Manual of the Geology of India*, published in 1887 (p. 142), I included it amongst the minerals of India, as a doubtful sulphate of magnesium and potassium, and remarked that, neglecting the KCl (doubtless intermixed sylvite) and H_2O, the percentages of $MgSO_4$ and K_2SO_4, amounting respectively to 60·43 and 39·57, when calculated to 100, although not corresponding accurately to any simple ratio between the bases, are fairly near 58·00 and 42·00, those required for the formula $(\frac{2}{3}Mg+\frac{1}{3}K_2)SO_4$, which is equivalent to $2MgSO_4.K_2SO_4$. I did not, however, consider that it would be justifiable to assume that the substance was a true double salt (and hence a simple mineral) without further examination, which circumstances did not allow of my making at that time.

Since then the existence of the compound just mentioned has been placed beyond doubt. In 1884 potassium salts were struck by a boring at the future mine of Wilhelmshall, north of Halberstadt, in Prussian Saxony. The result of Dr. S. Zuckschwerdt's examination of the fragments brought up led him, in 1891, to announce the discovery of "Langbeinite, a new potassium-magnesium sulphate," which his analyses, after he had freed the mineral from accompanying rock-salt, showed to agree very closely in composition with that required by the formula $K_2SO_4.2MgSO_4$.[3] Observations made by Director Steckert, after the

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[1] *Sitzungsber. Wien. Akad.* LXIII. 1871, 305.

[2] *Tscherm. Min. Mitth.* 1873, 135; *Jahrb. d. k. k. geol. Reichsanst. Wien*, 1873, XXIII.; *Rec. Geol. Surv. India*, VII. 1874, 64.

[3] *Zeits. f. angewandte Chemie*, 1891, 356.

Wilhelmshall deposit had been opened out by mining, showed that the langbeinite always occurs in the older rock-salt beds, and is a mineral of primary formation, taking the place of polyhalite in those parts of the potassium-salt deposits where the quantity of calcium sulphate is insufficient for the formation of the latter mineral.[1] Comparatively recently langbeinite has been discovered in large quantity near Wolfenbüttel in Brunswick, where it occurs in the same way as at Wilhelmshall; and it has been found likewise in Westerregeln, and in Neu-Stassfurt, but under different circumstances, being in association with sylvite as well as rock salt, and partly of secondary formation.[2] Near Bernburg, again, the mineral occurs abundantly, overlying the carnallite stratum and beneath beds of rock-salt.[3] The first crystals of the mineral discovered were obtained at the last-mentioned locality, by Dr. Siebert, in 1897, and submitted to an elaborate optical and crystallographic examination by Otto Luedecke, who showed that the very complex crystals belong to the tetartohedral group of the isometric system.[4]

In the light of the above researches on the langbeinite of Germany, there seemed little room for doubting that the Punjab salt was of the same nature; but, in order that the question might be placed beyond the region of supposition, all the available material in the Museum was, at my request, lately sent to me for examination by the Director of the Indian Geological Survey, Mr. C. L. Griesbach, C.I.E.

Of the two specimens received, one (*Mineral Register, No. G 861*) is labelled as from the Mayo Mines, and presented by Dr. Warth, with the date of analysis added in Mr. Tween's handwriting, and is noted in the laboratory book as "colourless salt from the Salt Range." It is beyond question that to which Mr. Tween's analysis No. 1 refers. The other specimen will be referred to later on.

The colourless salt (*G 861*), of which there is about 4 ozs., is in irregular pieces, the largest about 3½ centimetres long; and, but for a few scattered inclusions of reddish salt (NaCl, coloured by Fe_2O_3), mostly not larger than a pin's head, though two or three are some millimetres in diameter, there is no macroscopic foreign matter. Only one piece (on which two adjacent faces are visible) shows any outward sign of crystallisation, and no cleavage is apparent. The fracture is uneven, or some-

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[1] H. Precht, *Zeits. f. angewandte Chemie*, 1897, 68.

[2] H. Precht, *ibid.* 1897, 68.

[3] *Ibid.* 1897, 68; and O. Luedecke, *Zeits. Kryst. Min.* XXIX. (1898), 255.

[4] *Loc. cit.*

times conchoidal, and the hardness about 4. A determination of the specific gravity, by means of turpentine, in which the mineral is insoluble, gave 2·84 at 60° F., the pieces used being free from the NaCl mentioned above, and having surfaces composed of newly-made fractures. Portions of the mineral are whitish and translucent, owing to inclusions, but where it is free from such, or nearly so, it is colourless and transparent. In polarised light the mineral itself is isotropic. Luedecke, by the examination of slices (from near Bernburg) in sodium light between crossed nicols, was unable to detect any circular polarisation; but, as the material he employed was not fully transparent, he remarked that it was desirable that the experiment should be repeated on more perfect sections. I may add, therefore, that I obtained a similar negative result with the Punjab mineral, the plates used being perfectly transparent, and one of them about 4 millimetres thick.

The inclusions alluded to above, which, although nearly absent in some parts of the mineral, are abundant in others, range in size to over half a millimetre in length, though the great majority are much smaller. They are mostly of very irregular outline, but a few of them are lath-shaped, sometimes terminated by one or two pairs of parallel lines. In ordinary light the inclusions are as transparent and colourless as their host, and while the dark border to them is narrow, even where most pronounced, in some it is scarcely apparent. Hence they are not strongly differentiated from the enclosing mineral, and some are scarcely visible with the light mentioned, although very marked between crossed nicols. A good many of them contain bubble-like inclusions, with a dark border so broad that there is a comparatively small spot of light in the centre. These are presumably gas cavities. In no instance was any movement detected, or any indication of the presence of liquid.[1] Similar gas cavities, sometimes of larger size and more irregular outline, also occur in the langbeinite itself.

The transparent (solid) inclusions may be divided into a minority, which are isotropic, and the remainder, which are birefringent. Of the latter, those with irregular outlines either extinguish uniformly over the whole area, or else the area is divided into a few subordinate ones, often not more than two or three, in each of which uniform extinction takes place. There are but few lath-shaped inclusions, the extinction in most of them being oblique, and in the remainder straight, suggesting monoclinic crystallisation.

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[1] For reasons given below, water could scarcely exist, as such, in the inclusions.

The fragments of mineral selected for quantitative analysis were free from macroscopic impurity, and the surfaces were all freshly made fractures. Water dissolved the sample rather slowly, but completely, without a trace of residue. The result obtained was :—

				Calculated to 100.		Theory.[1]
K_2O	...	22·23	...	22·55	...	22·70
MgO	...	19·08	...	19·36	.	19·41
SO_3	...	57·27	...	58·09	...	57·89
NaCl	...	·41	...	—	...	—
H_2O	...	·84	...	—	...	—
		99·83		100·00		100·00

The sodium is evidently combined with the chlorine,[2] and the isotropic inclusions mentioned above should doubtless be referred to the resulting salt. The analysis just given shows that the birefringent inclusions must consist of potassium sulphate or magnesium sulphate, or both, in some form or other, and the close approximation of the analysis to the theoretical composition of langbeinite, suggests that the two sulphates are present in the inclusions in something like the same ratio as in the langbeinite itself. This condition would be satisfied if the inclusions consisted of kieserite or epsomite, and picromerite, in the proportion of one molecule of each, and such a mixture would be in accordance with the presence of water as shown by the analysis, and with the birefringence of the inclusions.

The langbeinite, when exposed, in powder, to the air, absorbs water rather quickly, an increase in weight of nearly 5 per cent. in 24 hours having been noticed. On the exposure being continued until the mineral ceases to gain in weight, the total increase is found to be rather less than 57 per cent., the precise amount depending on the temperature and humidity of the air at the time. Thus ten weighings of the same sample at different times gave results varying between 56·36 and 57·01 per cent.[3] As an absorption of 13 molecules of water equals 56·44 per

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[1] K_2SO_4, 42·00 per cent.; $MgSO_4$, 58·00 per cent.

[2] The quantities found were Na ·15, Cl ·26, while theoretically the proportion is ·17 to ·26.

[3] Allowing for the water already present in the langbeinite (and the NaCl), this is equal to an absorption of about 58 to 58½ per cent., the excess over the theoretical amount being no doubt due to hygroscopic moisture. The latter cannot be extracted by H_2SO_4, as efflorescence takes place under such circumstances.

cent., it is clear that the decomposition of the langbeinite takes place in accordance with the following equation:—

Langbeinite. Water. Picromerite. Epsomite.

$$K_2SO_4.2MgSO_4+13H_2O = K_2SO_4.MgSO_4.6H_2O+MgSO_4.7H_2O.$$

The second specimen received from Calcutta (*Mineral Register, No. G 860*) is likewise from the Mayo Mines, and aggregates about half a pound, in pieces up to 5 or 6 centimetres long. The substance is grayish-white in some parts, pale reddish in others, and shows a rather coarse granular structure. I have, as yet, examined it qualitatively only, but it appears beyond doubt to be the material to which Mr. Tween's second analysis and Professor Tschermak's observations refer. It may, however, contain a larger proportion of kieserite than the portion examined by Mr. Tween, and I likewise picked some langbeinite out of it, the largest piece being about 2 centimetres long.

It is clear, therefore, that the saline deposit in question was composed of at least four minerals, their relative proportions varying considerably, perhaps greatly, in different parts of the stratum.[1]

The langbeinite melts at a red heat, and, on cooling, solidifies to a white, more or less distinctly crystallised, mass. This observation naturally suggested an easy method for its artificial production, and the inference was confirmed by experiment. When powdered K_2SO_4 and $MgSO_4.7H_2O$ are mixed (more conveniently after dehydration of the latter) in the molecular proportion of 1 to 2, and ignited, the mixture fuses at a full red heat to a clear transparent liquid. During cooling and solidification there is a considerable amount of crepitation. The resulting white mass generally has one or more drusy cavities in the interior, the crystals on the walls of which are (geometrically) octahedra, with faces some of which are smooth and others somewhat cavernous. A few crystals show faces of the rhombic dodecahedron, replacing octahedral edges. The crystals tend to arrange themselves with similar orientation, and sometimes form columns composed of octahedra with their respective axes parallel. The artificial mineral is isotropic, like the natural one. During fusion SO_3 is slowly given off, and eventually the melt becomes pasty from admixed magnesia, while it no longer dissolves completely in water.

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[1] Since the above was written Dr. Warth has informed me that the salts in question were found at two spots, about 300 feet apart. At one of these magnesium salts predominate; at the other, potassium salts; the latter may perhaps have been a little higher up (on a higher horizon) in the Kallar bed than the other, but this is uncertain.

In 1880 Dr. H. Precht described the artificial production of a salt to which he assigned the formula $K_2SO_4.2MgSO_4.H_2O$, but which, after the publication of Dr. Zuckschwerdt's results in 1891, he regarded as $K_2SO_4.2MgSO_4$. It is precipitated at a boiling heat, preferably at a steam pressure of 2 or even 4 atmospheres, from a concentrated solution of magnesium chloride, with potassium sulphate and excess of magnesium sulphate.[1] This latter method will, perhaps, be regarded as not without interest in connection with the views expressed by Messrs. Middlemiss and Holland as to the origin of the salt marl and gypsum of the Salt Range.[2]

In conclusion, I may add that the known minerals associated with the rock salt of the Salt Range include the following[3] : –

1ST. OF PRIMARY FORMATION.

Rock-salt (stratified; in beds of immense thickness and extent). A. B. Wynne, *Mem. Geol. Surv. India*, 1878, XIV. 76, 213, 231, 284.

Sylvite[4] (stratified; the mineral has been found in one or two spots only, mixed with rock-salt, kieserite, and langbeinite). G. Tschermak, *Min. Mitth.* 1873, 135, and *Rec. Geol. Surv. India*, 1874, VII. 64.

Anhydrite (stratified; more or less mixed with gypsum; *cf.* secondary gypsum). A. B. Wynne, *loc. cit.* 74; T. H. Holland, *Rec. Geol. Surv. India*, XXIV. 1891, 235.

Gypsum? (stratified; in extensive beds, as a rule overlying the rock-salt; *cf.* secondary gypsum). A. B. Wynne, *loc. cit.* 73, 300.

Kieserite (stratified; *cf.* sylvite). G. Tschermak, *loc. cit.*; F. R. Mallet, *Min. Mag.* XI. 1897, 317.

Langbeinite (stratified; *cf.* sylvite). F. R. Mallet, *Min. Mag.* Vol. XII, 1899, 159.

Dolomite (stratified). A. B. Wynne, *loc. cit.* 74, 134, 231, 267; C. S. Middlemiss, *Rec. Geol. Surv. India*, XXIV, 1891, 26; H. Warth, *ibid.* XXIV. 69.

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[1] *Chemische Industrie*, III. (1880), 418, and *Zeits. f. angewandte Chemie*, 1897, 68.

[2] *Records, Geol. Surv. India*, XXIV. 26 and 235.

[3] The references are far from complete, only some of the more important being given. For the literature of the subject, *Mem. Geol. Surv. India*, Vol. XIV.; *A Manual of the Geology of India*, Parts II. III. and IV., and *Rec. Geol. Surv. India*, XXIV, 19 and 230, may be consulted.

[4] The primary nature of the sylvite and kieserite, and secondary character of the selenite, glauberite, and blödite, was pointed out by Dr. Warth in a letter respecting blödite that I received from him in 1897.

Quartz (as crystals in the anhydrite and gypsum). H. Warth, *Inland Customs Administration Report,* 1870-71 ; A. B. Wynne, *loc. cit.* 268 ; T. H. Holland, *Rec. Geol. Surv. India,* XXIV, 1891, 231.

2ND. OF SECONDARY FORMATION.

Halite (crystals in fissures of the rock salt, and fibrous). H. Warth, *Inland Customs Admin. Report,* 1869-70, Appendix H ; *Manual Geol. Ind.,* IV. 34.

Gypsum (altered anhydrite). A. B. Wynne, *loc. cit.* 74 ; T. H. Holland (who holds that much of, possibly all, the gypsum of the Salt Range is altered anhydrite), *Rec. Geol. Surv. India,* XXIV. 1891, 235 (altered dolomite ?) ; C. S. Middlemiss, *ibid.* 26.

Selenite (crystals in fissures of the rock salt). H. Warth, *Mem. Geol. Surv. India,* XIV. 1878, 80 ; *Min. Mag.* XI. 1897, 311.

Glauberite (crystals in fissures of the rock salt). H. Warth, *cf.* selenite ; W. Schimper, *Zeits. f. Kryst.* I. 1877, 70.

Blödite (crystals in fissures of the rock salt). H. Warth, *Min. Mag.* XI. 1897, 311 ; W. Schimper, *loc. cit.* ; F. R. Mallet, *Min. Mag.* XI. 1897, 311.

Picromerite ? (probably exists in small quantity, owing to the hydration of langbeinite). *Cf.* p. 163.

Epsomite (as an efflorescence, due, in part at least, to hydration of kieserite). H. Warth, *Inland Customs Admin. Report,* 1869-70, Appendix H ; G. Tschermak, *loc. cit.* ; A. B. Wynne, *loc. cit.* 79 (probably also in small quantity, owing to hydration of langbeinite). *Cf.* p. 163.