On Chlormanganokalite, a new Vesuvian mineral; with notes on some of the associated minerals.

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OCCURRENCE AND CHEMICAL COMPOSITION.

(By H. J. Johnston-Lavis.)

In 'Nature' of May 31, 1906, the senior author[1] gave a preliminary account of a new Vesuvian mineral, which he had found amongst the products of the eruption of April 1906, and for which he proposed the name chlormanganokalite. It was described as a hydrous chloride of manganese and potassium, occurring as deliquescent crystals apparently rhombohedral in form. A few days later, on June 5, 1906, Professor A. Lacroix[2] described, before the French Academy of Sciences, a Vesuvian mineral which he thought must be identical with chlormanganokalite: he stated it to be an anhydrous chloride of manganese, potassium, and sodium, and he determined the deliquescent crystals to be monoclinic and pseudo-rhombohedral. In a later paper, Professor Lacroix[3] rightly insists upon this identity.

A new analysis has now been made on better selected material, and the new mineral has been submitted to a detailed crystallographic examination. The specimens at our disposal are better than those exhibited in the Muséum d'Histoire Naturelle in Paris.

Towards the latter part of the eruption of April 1906, vast quantities of fragmentary material were shot out from Vesuvius. The earlier ejecta were chiefly 'essential',[4] and date from about half-past twelve (midnight) on April 7–8. These constitute the main portion of the two

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[1] H. J. Johnston-Lavis, 'A new Vesuvian mineral.' Nature, 1906, vol. lxxiv, pp. 103–104.

[2] A. Lacroix, 'Les cristaux de sylvite des blocs rejetés par la récente éruption du Vésuve.' Comptes Rendus Acad. Sci. Paris, 1906, vol. cxlii, pp. 1249–1252.

[3] A. Lacroix, 'Les minéraux des fumerolles de l'éruption du Vésuve en avril 1906.' Bull. Soc. franç. Min., 1907, vol. xxx, pp. 219–266.

[4] H. J. Johnston-Lavis, 'On the fragmentary ejectamenta of volcanoes.' Proc. Geol. Assoc., 1886, vol. ix, pp. 421–432, with plate.

strata, 0·20 metre in thickness, at the bottom of the 0·73 metre deposit that partially buried Ottajano. Practically all the rest of that deposit was made up of 'accessory' lapilli. As the axis of the eruption is approached, these materials, and especially the 'accessory', naturally increase in thickness and in the size of their constituents. At Ottajano the blocks rarely attain the size of one's fist, whereas at the foot of the great cone many masses were met with of a cubic metre or more in volume. One large block, on the plain of the Pedimentina almost south of the great cone and over a kilometre from the eruptive axis, I measured and found to be about 27 cubic metres, which would give a weight of over 70 tons.

Two blocks in this direction, each considerably over a cubic metre in volume, yielded the new mineral in association with sylvite. These blocks were seen on examination to be made up of masses of more or less porous scoria, so soldered together that they could be broken up only with difficulty. On breaking up these blocks with dynamite, the cavities between the component masses of scoria were found to be beautifully lined with fine crystals of potassium and sodium chlorides, or the interspaces were completely filled with crystallized chlorides. In certain places, implanted on these crystals, were crystals of chlormanganokalite; and at times the infilling mineral consisted almost entirely of chlormanganokalite.

When fresh, chlormanganokalite consists of splendent, well-shaped crystals with the form of flat rhombohedra, of a lemon- or canary-yellow colour. Exposure to moist air soon impairs their brilliancy, and in a short time they deliquesce to a yellow liquid. Unfortunately the weather was very damp at the time the mineral was discovered, and this, together with an accident to a case full of material, has made the supply available for investigation very limited.

A new analysis, made in May 1907 on nearly a gram of material, gave the following results:—

K	36·34	or	KCl	69·42
Mn	11·52		$MnCl_2$	26·45
Cl	48·13		$MgCl_2$	0·16
Mg	0·04		Na_2SO_4	1·19
Na	0·38		H_2O	1·52
SO_4	0·81		Insoluble	0·71
H_2O	1·52			
Insoluble	0·71			
	99·45			99·45

After deducting magnesium chloride, the atomic ratios are

$$\mathrm{K : Mn : Cl} = 0{\cdot}9282 : 0{\cdot}2096 : 1{\cdot}3560 = 4{\cdot}43 : 1 : 6{\cdot}47,$$

corresponding with a formula $4\frac{1}{2}\mathrm{KCl.MnCl_2}$. A more probable formula is, however, $\mathrm{4KCl.MnCl_2}$, and the slight excess of potassium chloride may be ascribed to the presence of admixed sylvite. The calculated percentage composition corresponding with this formula, $\mathrm{4KCl.MnCl_2}$, is:—

K	36·91	or	KCl	70·33
Mn	12·96		$\mathrm{MnCl_2}$	29·67
Cl	50·13			100·00
	100·00			

Calculating the potassium chlorides and manganese chlorides to 100 per cent., the amounts found in the analysis are KCl 72·41, $\mathrm{MnCl_2}$ 27·59 per cent.

In October 1906, I found on the northern slopes of the great cone, not far from the edge of the crater, another block, which on being broken open exhibited within its cavities a number of large rhombohedral crystals of a darker yellow (orange) tint. These crystals had obviously been contaminated with some dissolved erythrosiderite, kremersite, &c. The block had, of course, been exposed to fumarolic vapours from the ground on which it lay and to atmospheric weathering for about six months. These crystals showed no polished faces, but were roughened like ground-glass, and they seemed to be made up of minute granular crystals, consisting in fact of pseudomorphs after crystals of chlormanganokalite. On breaking these pseudomorphs open, they were seen to possess a zoned or crusted structure, and to be opaque right to their centre. An analysis of such material would give only uncertain results. Some of these pseudomorphous crystals attain a diameter of a centimetre, and it is unfortunate that they were not found before they had become altered. Even amongst the original specimens, found in April 1906, some of the crystals of chlormanganokalite implanted on the crystals of alkali chlorides have become granular and opaque.

The pseudomorphous crystals in the block found in October 1906 are also, as on the original specimens, associated with sylvite and halite; but in addition there are black, spear-like crystals of haematite, together with pseudomorphous crystals with the form of long, slender square prisms, and possibly some other soluble species. The genesis of the haematite was coincident with that of the other minerals, since it occurs both buried in crusts of them, and projecting from and implanted on their surfaces. Portions of these crusts were lixiviated in water, dried, and sifted, and the residue treated with a heavy solution of cadmium borotungstate. The heavy particles were collected one by one under the microscope, and analysed with the following results:—

Fe_2O_3	94·79
S	0·43
As	trace
Insoluble in aqua regia	4·78
	100·00

The insoluble residue represents rock-fragments adherent to the crystals, as was discernible under the microscope. The traces of arsenic are no doubt due to the presence of realgar and orpiment, and the sulphur to those minerals or to native sulphur, all of which occur in the neighbourhood. The crystals of haematite rarely attain a length of 2 mm. A few of the most perfectly developed crystals were selected under the microscope for crystallographic determination (p. 60).

There is little doubt but that chlormanganokalite and its associates are the result of sublimations deposited in the interstices of the fragmentary materials of the cone not far from the chimney of the volcano. By sublimates I do not mean the direct vaporizing of such from the volcanic paste or magma, but rather the production of the minerals by the interaction of different vapours when the latter reach a space where the temperature is sufficiently low to suit the formation of the particular compound. In other words, the minerals have been formed by so-called pneumatolytic action. I was able in 1880 to watch the deposition of well-formed crystals of sylvite and tenorite in such scoria overlying a radial dyke at less than 100 metres from the main chimney of Vesuvius.

No doubt the deposition of such material is constantly going on around the main chimney of the volcano. But it is only by the help of a violent eruption, like that of April 1906, that such deposits are broken up and ejected, and then they are liable to destruction by weathering before being found. An opportunity of examining minerals of this kind therefore but rarely occurs.

The deposition of chlormanganokalite and of the alkali chlorides was contemporaneous, though the new mineral seems to have terminated its deposition later, for it is sometimes superposed on the other minerals.

The formation of these chlorides I infer to have taken place during the state of chronic activity of the volcano, for hydrochloric acid is the dominant emanation in the vapour from the main chimney, and it is only during eruptive paroxysms that sulphurous acid becomes very evident.

CRYSTALLOGRAPHIC AND OPTICAL CHARACTERS.

(By L. J. Spencer.)

Chlormanganokalite.—The material which I have examined consists of specimens sent by Dr. Johnston-Lavis for the British Museum collection and also of some of the crystals taken from the specimen used by him for analysis. Owing to the rapidity with which the mineral deliquesces in moist air, and especially when exposed to the breath, the specimens had to be examined from behind a glass screen; and when a crystal was placed on the goniometer it was surrounded by a glass tube.

The crystals have the form of simple obtuse rhombohedra, *r* {100}, sometimes truncated on their median edges by narrow faces of the prism *a* $\{10\bar{1}\}$. The faces of the crystals, though at first bright and smooth, soon become moist and dull on exposure to the air, and only approximate measurements could be obtained. On one crystal the angle over the rhombohedral edge was measured in three different zones as 57° 40′, 122° 23′, and 122° 23′; and on another crystal, also in three zones, as 57°, 122° 43′, and 122° 37′. The mean value for the rhombohedral angle rr' is 57° 36′; hence $cr = 33° 48'$, and the axial ratio $a : c = 0{\cdot}5801$.

The crystals measure 2–3 mm. along a rhombohedral edge, and they are sometimes arranged in parallel groups a centimetre across. They are pale wine-yellow in colour, and are transparent with a vitreous lustre. The material is brittle, and shows no cleavage; it breaks with a bright, glassy, conchoidal fracture, which soon becomes dull on exposure to the air. The specific gravity was determined, by floating in methylene iodide, to be 2·31. The hardness is 2½.

An approximate determination of the refractive index was obtained by the method of minimum deviation through a prism formed by the natural faces of the rhombohedron; only a blurred image was seen, and there was no separation into two images; the value in white light was 1·59. The crystals extinguish uniformly when the vibration-directions of the nicols bisect the angles on the rhombohedral faces. By scraping off with a knife the obtuse, polar corners of the rhombohedron, a plate perpendicular to the optic axis was obtained: this showed a good uniaxial cross with no separation of the arms into a hyperbola. The optic sign is positive. Although the section was rather over a millimetre in thickness, the interference-figure showed no rings, only the black cross; so that the double refraction is very low.

From the measurements of the angles and the optical determinations given above there can be no doubt but that chlormanganokalite is rhombohedral, and not monoclinic (pseudo-rhombohedral) as stated by Lacroix.

Fragments of the crystals when examined in oil under the microscope were seen to contain minute cavities with more or less regular crystal-outlines. These cavities enclose a liquid and a bubble of gas; and in the liquid were seen two kinds of crystals, one kind having the form of cubes. The mineral readily dissolves in a drop of water on a microscope-slide, and while it is being dissolved there is an abundant evolution of minute bubbles of gas. On evaporating the drop of solution, the potassium chloride separates out as skeletal cubes, which are optically isotropic; and on gently warming the slide, the manganese chloride separates as numerous minute birefringent spherulites, which quickly disappear again as the slide cools in moist air.

A fragment of a crystal when heated to 195° C. in an air-oven for half an hour still remained transparent and birefringent. A fragment heated in a bulb-tube gave off a little water, and readily fused to a clear, mobile, yellow liquid; on consolidation the mass is at first white, and when cool reddish in colour, changing again after some time to white.

Sylvite and Halite.—The large and well-developed crystals of sylvite and halite which occur in association with chlormanganokalite have already been described at some length by Professor Lacroix.[1] Shortly afterwards Dr. Johnston-Lavis[2] published an analysis of these cubic crystals, which led to the formula 6KCl.NaCl, and in the belief that this represented a double salt he proposed the name 'chlornatrokalite'. In his later paper Professor Lacroix[3] expresses the opinion that this is evidently a mixture of the two salts.

Specimens labelled 'chlornatrokalite', sent by Dr. Johnston-Lavis for the British Museum collection, were seen on careful inspection to consist of cubes of two kinds, namely, cubes of sylvite (KCl) and cubes of halite (NaCl). The former show a bluish opalescence by reflected light, but are yellowish by transmitted light; under the microscope the yellow colour is seen to be arranged in bands parallel to the faces of the cube. Cavities containing a liquid and a bubble are also arranged in lines parallel to the edges of the cube. The specific gravity was found, by floating a crystal in methylene iodine, to be exactly the same as that

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[1] Loc. cit., 1906.

[2] H. J. Johnston-Lavis, 'Another new Vesuvian mineral.' **Nature**, June 21, 1906, vol. lxxiv, p. 174.

[3] Loc. cit., 1907, p. 242.

(1·99) of sylvite from Galicia, Austria; and a prism bounded by a cleavage-surface and an artificially ground face gave for sodium-light the refractive index 1·491. Finally, the material gave a good violet coloration to the Bunsen-flame. On the other hand, the cubes of halite are colourless and perfectly transparent; they have a specific gravity of 2·15, and a refractive index of 1·547, and they give an intense yellow coloration to the Bunsen-flame.

The crystals of sylvite and halite are intimately and confusedly grouped together, and they appear to have grown simultaneously. On the specimens which I examined the crystals of both salts average $\frac{1}{2}$ cm. along their cubic edges; larger crystals were found, and, according to Lacroix, exceeding 2 cm. across.

The association together of cubes of sylvite and of halite has also been recently described by Dr. F. Zambonini[1] on material from the 1861 eruption of Vesuvius. It may be here remarked that sylvite and halite are only very rarely found at Vesuvius as distinct crystals, saline encrustations of the mixed salts, such as those analysed by A. Scacchi (1875), being much more frequent. As recently pointed out in this magazine,[2] sodium chloride and potassium chloride do not form mixed crystals.

Haematite.—The crystals isolated by Dr. Johnston-Lavis are about 1 mm. in length, and they have the form of acute scalenohedra.[3] The faces are bright, though not perfectly smooth. The following measurements over the three sets of edges prove the form to be $\beta\,\{31\bar{3}\} = \{24\bar{6}1\}$.

	Measured.		Calculated.
Obtuse polar edge	... 37° 57′	...	37° 56′
Acute polar edge	... 81 5	...	81 6
Median edge ...	... 25 28	...	25 33

At the ends of the crystals there are minute faces of the basal pinacoid c {111} and the rhombohedron r {100}. A rhombohedral plane lies in a zone over the median edge of the scalenohedron at 77° 11′ (calculated

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[1] F. Zambonini, 'Notizie mineralogiche sull' eruzione Vesuviana dell' Aprile 1906.' Atti R. Accad. Sci. Napoli, 1906, Mem. vol. xiii, pp. 1–40.

[2] T. V. Barker, Min. Mag., 1907, vol. xiv, p. 247; this vol., p. 43.

[3] Crystals of haematite of a scalenohedral habit appear to be of rare occurrence. In the British Museum collection there are two such crystals 'from an island in the Red Sea'; the larger crystal is nearly 3 cm. in length, and the predominating form is $\xi\,\{13\bar{2}\} = \{2352\}$.

77° 13′) from two scalenohedral planes; the rhombohedron is therefore direct and the scalenohedron inverse.

With these spear-shaped crystals there are a few others of quite a different habit and of rather smaller size ($\frac{1}{2}$ mm. long). They have the form of slender hexagonal prisms, *a* {10$\bar{1}$}, terminated by the basal pinacoid *c* {111} ; very small faces of the rhombohedron *r* {100} are sometimes also present.