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*Afwillite, a new hydrous calcium silicate, from  
Dutoitspan mine, Kimberley, South Africa.*

By JOHN PARRY (chemical study) and F. E. WRIGHT (optical and  
crystallographical study).

[Read January 20, 1925.]

MR. ALPHEUS F. WILLIAMS, General Manager of the De Beers Consolidated Mines, discovered in December, 1923, in the Dutoitspan mine, at Kimberley, crystals of a colourless mineral so different in appearance from other minerals observed in the Kimberley mines that it appeared to him to be new and worth detailed study. The mineral was found between the 500 and 750 ft. levels in a large dolerite inclusion in the kimberlite, and is associated with apophyllite, calcite, and natrolite. Up to the present time, less than a pound of the mineral has been found, and by far the larger part of this amount is represented by a few crystals of large size ( $11 \times 4 \times 1\frac{1}{2}$  cm.). On closer examination, these crystals are seen to be not a single crystal, but a group of sub-parallel individuals, a type of development that is often observed on the larger crystals of many minerals. The material is clear and colourless, and of excellent quality for chemical and optical investigations.

At the request of Mr. Williams, the senior author of this paper made a chemical analysis of one of the crystals and found its chemical composition to be unlike that of any mineral on record, thus confirming

Mr. Williams's anticipation. Its chemical behaviour proved, moreover, to be so interesting that it led to the performance of much more varied experimental work than is usually undertaken in a busy technical laboratory. The crystal first submitted was glassy and colourless, but its surface was somewhat dull and etched. This slight dullness was due to a fine film of calcium carbonate resulting from the corrosion of the crystal. Specimens that had not been so corroded were uniformly bright and clear. The material used for the final chemical analysis was clear and free from impurities. Standard methods for the quantitative analysis of silicates were followed in the analytical work.

TABLE I. *Chemical Analyses of Afwillite.*

	1.	2.	3.	4.	5.
SiO <sub>2</sub> ... ..	33.96	35.10	34.97	33.84	35.13
Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> ...	0.60	0.05*	0.06*	(2.27)†	—
MgO ... ..	—	0.02	(0.02)	(0.02)	—
CaO ... ..	49.28	49.00	49.13	48.62	49.09
BaO ... ..	—	nil	—	—	—
H <sub>2</sub> O (+110°) ...	15.89	15.81	(15.81)	(15.81)	15.78
H <sub>2</sub> O (-110°) ...	0.12	0.01	0.04	(0.01)	—
	<u>99.85</u>	<u>99.99</u>	<u>100.03</u>	<u>100.57</u>	<u>100.00</u>

\* Mostly Fe<sub>2</sub>O<sub>3</sub>.

† Residue from silica separation.

1. Afwillite from Dutoitspan mine, Kimberley, South Africa.

J. Parry, analyst.

2-4. Ditto. H. S. Washington, analyst.

5. Weight percentage composition represented by the formula  
3CaO. 2SiO<sub>2</sub>. 3H<sub>2</sub>O.

A comparison of the analyses with the theoretical composition shows that this mineral is unusually pure and is represented by the formula 3CaO. 2SiO<sub>2</sub>. 3H<sub>2</sub>O. Analyses 2, 3, and 4 were made for us by Dr. H. S. Washington of the Geophysical Laboratory on the same sample of material that served for the optical and crystallographical determinations. It is a pleasure to express to him our appreciation of his courtesy in this matter. His analyses 2 and 3 were made by the sodium carbonate fusion method and agree remarkably well with the formula. He found that, if the mineral was dissolved first in hydrochloric acid and then analysed by the usual methods, the values listed under 4 were obtained, which are similar to those under 1. This indicates that possibly complete solution was not effected by the hydrochloric acid, especially if the material was not very finely ground. The sodium carbonate fusion insures complete solution and is the method commonly followed in the analysis of silicates.

When the powdered substance is heated in a dry test-tube, a copious evolution of water occurs. In order to make certain that the 16 per cent. of volatile matter which escapes at 900° C. is entirely water, an accurately weighed quantity of the mineral powder was strongly heated in a combustion-tube with the usual precautions; the expelled water was collected in a weighed U-tube containing pumice saturated with strong sulphuric acid. By this method 15.9 per cent. of water was obtained; this is satisfactory agreement with the ignition loss.

A series of experiments was conducted to ascertain the amount of water liberated at different temperatures. The experiments were carried on both in the De Beers Laboratory at Kimberley (K) and in the Geophysical Laboratory at Washington (W). The results are listed in Table II.

TABLE II. *Dehydration of Afwillite.*

Temperature in degrees C.	Time of total exposure at the given temperature.	Cumulative total loss in weight.	Laboratory.
80°	... 6 Hours ...	nil ...	K
105	... 3 ...	0.12 Per cent.	K
115	... 1 ...	0.04 ...	W
200	... - ...	0.20 ...	K
225	... 1.5 ...	0.20 ...	W
225	... 18 ...	0.34 ...	W
295-300	... 5.2 ...	3.35 ...	W
295-300	... 23 ...	11.88 ...	W
295-300	... 29.5 ...	12.67 ...	W
295-300	... 46.2 ...	12.75 ...	W
295-300	... 69.8 ...	12.90 ...	W
295-300	... 73.4 ...	12.93 ...	W
330	... 7 ...	14.40 ...	K
430	... 2 ...	14.35 ...	W
460	... 5.2 ...	14.93 ...	W
480	... 18.3 ...	15.03 ...	W
535	... 4 ...	15.10 ...	W
630	... 17 ...	15.32 ...	W
735	... 3 ...	15.78 ...	W
875	... 3 ...	15.85 ...	W
900	... 1 ...	16.01 ...	K
Blast-lamp	... 1 ...	15.85 ...	W

These results are in close agreement and show clearly that the amount of water given off above 115° C., namely 15.81 per cent., is all of the same kind and is water of constitution; evidently being bound to the other elements as an integral part of the combination, and not as water of crystallization as in the zeolites. The material that served for the experiments at the Geophysical Laboratory was water-clear and homo-

geneous. Examination under the microscope showed that the material after the final blast-lamp ignition was turbid and evidently decomposed.

The following chemical tests are characteristic of the mineral:

1. When a crystal is moistened with water and a drop of a solution of phenolphthalein is added, it assumes a beautiful magenta tint—a result typical of an alkaline base. Red litmus-paper placed on the wet crystal becomes blue.

2. The powdered material, both before and after intense ignition, produces a very deep and permanent magenta colour when moistened with a solution of phenolphthalein.

3. When the powdered material is shaken with water for a few minutes and filtered, the clear filtrate turns red litmus-paper blue; and becomes deeply coloured with a solution of phenolphthalein, thus showing the presence of an alkali soluble in water. On testing the water the alkali proved to be calcium oxide.

4. Both sulphuric acid and hydrochloric acid produce great heat when either is dropped on to the powder—a further indication of the presence of an alkaline base.

5. When weighed quantities of the material finely ground in an agate mortar were shaken with distilled water during 30 minutes and then titrated, unfiltered, with N/10 hydrochloric acid, and with phenolphthalein as indicator, there was found in solution calcium oxide equivalent to 23.68 per cent. of calcium hydroxide. When this titrated solution was allowed to stand, the pink colour of the phenolphthalein returned, showing the dissociation of more calcium base. This was again titrated till colourless, and again left to stand, when there was a further recurrence of alkalinity. The titrations were repeated until there was finally no return of the pink colour on standing 12 hours. In all, eleven such operations were required, occupying 35 hours, each increment of calcium hydroxide gradually lessening in quantity from 1 to 0.3 per cent. The total amount of calcium hydroxide taken into solution by this method was 59.57 per cent. out of a possible 64.99 per cent.

6. A weighed quantity of the fine powder was shaken with 250 c.c. of N/50 hydrochloric acid. After 60 minutes it was titrated with N/10 NaOH; the unused acid was deducted from the total 250 c.c.; and from the remainder the equivalent of the CaO dissolved was calculated out as  $\text{Ca}(\text{OH})_2$ ; it amounted to 63.82 per cent. When a 9-hour contact was permitted with N/50 acid, there was dissolved 64.75 per cent. out of a possible total of 64.99 per cent.

7. Some of the material was heated very strongly over a petrol blast-

lamp to a temperature of about 1300° C. When a weighed quantity of this was shaken for 72 hours with 500 c.c. of distilled water in a mechanical shaker, and the solution filtered and titrated, the liquid was found to have dissolved lime equivalent to 23.1 per cent. as calcium hydroxide (=17.5 CaO). Further prolonged contact with water failed to dissolve any more. It seems probable that the intensive ignition produced a firmer combination of the silica with the lime, thus rendering it less susceptible to dissociation, and therefore insoluble in the N/50 acid. The significance of this result is seen when this 17.5 CaO is deducted from the total lime in the mineral (49.28); there is left 31.78. If this exists as calcium metasilicate ( $\text{CaSiO}_3$ ), it will be found that it requires 34.05 of silica; and the silica actually found is practically that amount (33.96): the small difference, 0.09, may be ignored here. It seems a sound inference that the whole of the silica is chemically combined with 31.78, or about two-thirds, of the lime. This inference receives further support from another curious feature. If the whole of the silica be assumed to be hydrated, it will be found that 10.19 of the water will be required for the 33.96 of the silica. If this 10.19 be deducted from the total water of constitution there will be left 5.62, the exact molecular equivalent of the 17.5 per cent., or about one-third uncombined CaO; which corresponds to 23.1  $\text{Ca}(\text{OH})_2$ . This may be taken to indicate that the mineral consists of 75.84 per cent. hydrated calcium silicate ( $\text{H}_2\text{CaSiO}_4$ ) and 23.10 per cent. calcium hydroxide in chemical combination; but that the bond is feeble and may be disturbed by mere contact with water.

The empirical formula  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  may accordingly be written  $2\text{H}_2\text{CaSiO}_4 \cdot \text{Ca}(\text{OH})_2$  to represent the combination of calcium acid silicate with calcium hydroxide. The fact that the bulk of the water escapes at about 300° C. with no evidence of different dissociation-points is interesting. The vapour-pressures of calcium hydroxide were found by J. Johnston<sup>1</sup> to be, in millimetres of mercury: at 389°, 17.4 mm.; at 428°, 32.5 mm.; at 468°, 149 mm.; at 507°, 355 mm.; at 547°, 760 mm. From his data, the vapour-pressures at 300°, 325°, and 350° were found by computation to be 0.9 mm., 2.1 mm., 5.2 mm. of mercury respectively. The pressure of saturated water-vapour at 20° C. is 17.5 mm. of mercury; at 25°, 23.7 mm. On a dry day the aqueous vapour-pressure in the atmosphere may be only a small fraction of these amounts. At 325° the water vapour-pressure of  $\text{Ca}(\text{OH})_2$  exceeds 2 mm. of mercury, and if the pressure of the water in the atmosphere does not exceed this amount, the water will escape slowly at this temperature. These relations may

<sup>1</sup> Journ. Amer. Chem. Soc., 1908, vol. 30, pp. 1357-1365.

be sufficient to veil any dissociation temperature of the mineral. The experiments show only the rates of evaporation at the different temperatures, but not the equilibrium relations at any given temperature. The fact that almost exactly one-third of the lime is leached out of the strongly ignited material is significant, but not necessarily conclusive evidence of the presence of that part of the lime in the form of the hydroxide. It is probably best in the light of present knowledge to use only the empirical formula  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  to express the composition of the mineral.

8. After the mineral powder had been heated to  $735^\circ \text{C}$ . and had lost 15.78 per cent. in water, it was placed for 17 hours over water in a closed vessel and gained thereby in weight an amount equivalent to 0.75 per cent. of water. The porous nature of the material, developed on heating to  $735^\circ$ , increases the surface area and with it the ability to take up water.

9. A crystal heated in a bulb-tube gives off water freely and turns dull white. It decrepitates strongly if heated in a flame, shows a strong calcium flame-reaction, and is fused only with difficulty.

For the crystallographical and optical measurements a specimen that appeared to consist essentially of a single prismatic crystal  $3\frac{1}{2}$  cm. long, 2 cm. wide, and  $1\frac{1}{2}$  cm. thick was used. Careful examination showed, however, that it is an aggregate of prismatic individuals arranged in sub-parallel grouping such that the greatest angle included between the prism-axes does not exceed  $3^\circ$ . The exposed faces are more or less etched. The crystallographical measurements were made on small selected prisms broken out from the aggregate. These are water-clear, homogeneous crystals on which measurements of a fair degree of accuracy could be made. In the prism (ortho-) zone the larger faces are ribbed or striated parallel with the elongation, as a result of the development of a relatively large number of small crystal-faces. Reflection signals obtained from these faces with the aid of a Goldschmidt two-circle goniometer were poor and in many cases multiple; as a result many of the forms given below are considered uncertain. The measurements were obtained in large part with the aid of the reducing attachment on the goniometer and are not of a high degree of accuracy. Seven crystals were measured with the following results:

Crystal-system: Monoclinic.

Axial ratios:  $a:b:c = 2.097:1:2.381$ ;  $\beta = 98^\circ 26'$ .

[Goldschmidt:  $\rho_0 = 1.135$ ;  $\rho_0 = 2.355$ ;  $\mu = 81^\circ 34'$ .]

In Table III are listed the different forms observed, the averages (in which there may be an error of  $10'$  or more) of the observed angles, the computed angles, and the crystals on which the different forms occurred.

Many of these forms are listed as uncertain and need confirmation before they can be accepted.

TABLE III. *Crystal angles of Afwillite.*

Letter.	Form.	Observed.		Computed.		Observed on crystals:
		$\phi$	$\rho$	$\phi$	$\rho$	
<i>c</i>	(001)	90° 00'	8° 26'	90° 00'	8° 26'	1, 2, 3, 4, 5, 6, 7
<i>a</i>	(100)	90 00	90 00	90 00	90 00	1, 2, 3, 5, 7
<i>m</i>	(110)	25 38	90 00	25 44	90 00	1, 2, 7
<i>l</i>	(310)	55 41	90 00	55 20	90 00	1, 3, 5, 7
	(106)?	90 00	17 39	90 00	18 45	1
	(104)?	„	24 34	„	23 22	2, 3
	(308)?	„	30 29	„	30 03	2, 7
<i>k</i>	(102)	„	35 25	„	35 49	5, 6
	(203)?	„	42 17	„	42 24	3
<i>d</i>	(101)	„	52 42	„	52 20	1, 5, 7
	(504)?	„	57 45	„	57 28	1
	(302)?	„	62 00	„	61 51	4, 6
	(301)?	„	74 38	„	74 26	5
	( $\bar{3}$ 08)?	-90 00	16 22	-90 00	15 45	5, 6
<i>f</i>	( $\bar{1}$ 02)	„	23 15	„	23 04	3
	(304)?	„	35 02	„	35 01	6
<i>e</i>	( $\bar{1}$ 01)	„	44 58	„	44 58	1, 2, 3, 4, 5, 7
	(504)?	„	51 43	„	51 48	3, 6
<i>g</i>	( $\bar{2}$ 01)	„	65 26	„	65 01	1
	(301)?	„	72 59	„	73 07	4, 6
<i>o</i>	(011)	3 34	67 16	3 34	67 15	1, 2, 6, 7

Calculated values for the more important interfacial angles are the following:

$$\begin{aligned}
 ac &= (100):(001) = 81^\circ 34' & cd &= (001):(101) = 43^\circ 54' \\
 al &= (100):(310) = 34 40 & ce &= (001):(\bar{1}01) = 53 24 \\
 am &= (100):(110) = 64 16 & co &= (001):(011) = 66 59
 \end{aligned}$$

The crystals are prismatic in habit and are elongated parallel with the *b*-axis. The basal pinakoid is easily recognized by its highly perfect cleavage. The chief development of crystal-forms is in the ortho-zone; end-terminations and forms in the crystallographic prism-zone are poorly developed. The general shape of the crystals is illustrated in fig. 1.

Etch-figures on the cleavage-plane (001) are easily obtained by immersing a crystal or cleavage-flake in dilute (1:50 or 1:100) cold hydrochloric acid for 10 seconds. The etch-figures on (001) have the form indicated in fig. 2 and range from 0.02 to 0.08 millimetres in length. If the crystal is left too long in the acid, etch-hills elongated in the plane of symmetry are developed. The etch-figures show clearly the monoclinic symmetry of the mineral. No satisfactory etch-figures were obtained on the other crystal-faces.

The cleavage parallel to the basal pinakoid (001) is perfect; parting or imperfect cleavage parallel to the orthopinakoid (100) is noticeable. The fracture is conchoidal. The material is brittle with hardness = 4. The specific gravity was measured both in water and in pure benzene ( $C_6H_6$ ); the latter has no solvent action on the mineral. The specific gravity of the benzene was found by the Westphal balance and also by the bottle methods to be 0.878. With water as the immersion fluid the specific gravity was found to be 2.619; with benzene a somewhat higher value 2.630 at 18° C. was obtained. Because of the solvent action of the water, the value obtained with the use of benzene is preferable.

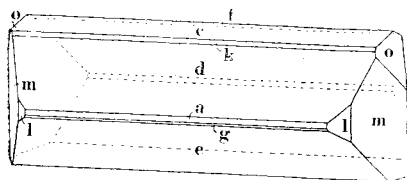


FIG. 1.

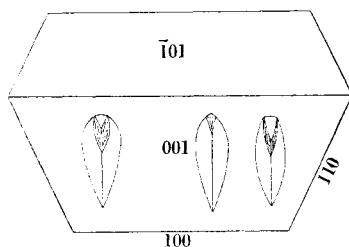


FIG. 2.

FIG. 1.—Crystal of awillite showing the more common forms.

FIG. 2.—Etch-figures on the cleavage-plane (001) of awillite, obtained by immersing a crystal-flake in dilute (1:100) cold hydrochloric acid for 10 seconds.

The lustre is vitreous; colour, white or colourless. The crystals are water-clear; if corroded on the surface they appear to be translucent. The streak is white.

The optical orientation is  $b = \beta$ ,  $c : a_{Na} = +30.6^\circ$  (red  $31.2$ , blue  $29.9^\circ$ ). The plane of the optic axes is normal to the elongation of the crystals. The acute bisectrix,  $\gamma$ , includes an angle of  $-22.2^\circ$  with the basal pinakoid; in other words the extinction-angle on (010) with reference to the basal cleavage lines is  $a : \gamma_{Na} = -22.2^\circ$ . The optical sign is positive. The optic axial angle was measured on a plate cut normal to the acute bisectrix; for different spectral lines the following values were obtained :

Line	...	Li(671).	Na(589).	Hg(578).	Hg(546).	Hg(436 $\mu\mu$ ).
2E	...	94° 08'	96° 05'	96° 18'	97° 13'	100° 28'
2V	...	—	54 40	—	55 00	—

The dispersion of the optic axis  $A$  for the different wave-lengths was found to be about twice the dispersion for the optic axis  $B$ ; thus on a section normal to the acute bisectrix  $\gamma$ , the angles included between the optic



axis *A* for lithium-light and the same axis *A* for sodium-light and the mercury lines 546 and 436  $\mu\mu$  were  $1^\circ 23'$ ,  $1^\circ 32'$ ,  $2^\circ 12'$ , and  $4^\circ 23'$ , respectively; whilst for the optic axis *B* the corresponding values were  $34'$ ,  $38'$ ,  $53'$ , and  $2^\circ 10'$ . The optic axis *A* for sodium-light includes an angle of  $-32.1^\circ$  with the *c* axis, and the *B* axis includes an angle of  $-86.7$  with the same crystallographic axis. These data prove the inclined dispersion of the optic axes characteristic of a monoclinic crystal for which the plane of symmetry is the plane of the optic axes.

The refractive indices were measured on polished plates on a crystal refractometer with reducing attachment; the probable error of the values obtained is about  $\pm 0.0005$ , but may be more in certain cases. The principal refractive indices are:

Light (and wave-length).		<i>a.</i>	<i><math>\beta</math>.</i>	<i><math>\gamma</math>.</i>
Helium red line (668 $\mu\mu$ ) ...	...	1.6148	1.6179	1.6312
Sodium-light (589) ...	...	1.6169	1.6204	1.6336
Mercury green line (546) ...	...	1.6201	1.6236	1.6366

Polished sections of this mineral are easy to obtain if, after fine grinding, the plates are polished with rouge on a flat base of bees-wax to which a little rosin has been added. This is softer than ordinary polishing pitch and is preferable for use with soft mineral surfaces.

A number of other hydrous silicates of calcium have been described, but most of them are fibrous or lamellar-radiate in structure and do not show the perfect crystal development of afwillite. These are listed in Table IV (p. 286) for comparison with afwillite.