

*A new locality for Voelckerite and the validity of  
Voelckerite as a mineral species.<sup>1</sup>*

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IN 1912 the writer<sup>2</sup> proposed the name voelckerite (in honour of Dr. John Augustus Voelcker, the well-known English agricultural chemist, who made important contributions to our knowledge of the chemistry of apatite) for the basic calcium phosphate,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$ , related to apatite. The fact that apatite is often deficient in fluorine and chlorine was proved by Voelcker<sup>3</sup> and by Hoskyns-Abrahall,<sup>4</sup> both of whom gave as the general formula of apatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{F}_2, \text{Cl}_2, \text{O})$  or its equivalent  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_2, \text{Cl}_2, \text{O})$ . Carnot<sup>5</sup> also noted the deficiency of chlorine and fluorine in apatite from Tyrol, but he offered no explanation. Rammelsberg,<sup>6</sup> in a paper published shortly before his death, assumed the existence of the compound  $\text{Ca}_{10}\text{P}_6\text{O}_{25}$  (equivalent to  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$ ) to explain the chemical composition of various apatites, though he thought the presence of this molecule was due to alteration. This explanation is very improbable, for these minerals are perfectly fresh and homogeneous.

<sup>1</sup> With the addition of some new observations, this paper presents in an amplified form a portion of the material of the author's earlier (1912) paper on the minerals of the apatite group.—Ed.

<sup>2</sup> A. F. Rogers, 'Dahllite (podolite) from Tonopah, Nevada; voelckerite, a new basic calcium phosphate; remarks on the chemical composition of apatite and phosphate rock.' Amer. Journ. Sci., 1912, ser. 4, vol. xxxiii, pp. 475-482; translation in Zeits. Kryst. Min., 1913, vol. lii, pp. 209-217.

<sup>3</sup> J. A. Voelcker, Ber. Deutsch. Chem. Gesell., 1883, vol. xvi, p. 2460.

<sup>4</sup> J. L. Hoskyns-Abrahall, Inaug.-Diss., Munich, 1889. Abstract in Zeits. Kryst. Min., vol. xxi, p. 389.

<sup>5</sup> A. Carnot, Bull. Soc. franç. Min., 1896, vol. xix, p. 135.

<sup>6</sup> C. F. Rammelsberg, Neues Jahrb. Min., 1897, vol. ii, p. 37.

Groth<sup>1</sup> substitutes hydroxyl for oxygen and gives the formula  $(\text{PO}_4)_3(\text{Cl}, \text{F}, \text{OH})\text{Ca}_6$ . He has been followed by Lacroix, Naumann-Zirkel, and others.

Since the brilliant work of Penfield<sup>2</sup> on the isomorphous replacement of fluorine by hydroxyl in triploidite, amblygonite, topaz, herderite, and other minerals one would expect *a priori* that the deficiency in the fluorine and chlorine content of apatite might be explained by the presence of hydroxyl. The published analyses do not bear this out, for the water content of the hypothetical hydroxy-apatite (1.80 per cent.) is greatly in excess of that found in the minerals in question. The highest percentage of water ever recorded in apatite is only 0.48 per cent. In this apatite from Ceylon, which was described from Jannasch and Locke,<sup>3</sup> there is still a deficiency in the combined ratios of fluorine, chlorine, and hydroxyl. The ratios of  $\text{P}_2\text{O}_5 : \text{R}''_2\text{O} : (\text{F}, \text{Cl}, \text{OH})$  are 3 : 10.8 : 1.68, as against the theoretical ratios 3 : 10 : 2 required by the formula  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{F}_2, \text{Cl}_2, [\text{OH}]_2)$ . This is apparently a very accurate analysis. If the water is constitutional it may prove that hydroxyl replaces fluorine and chlorine, but it equally proves that oxygen replaces fluorine. As the water content of these apatites is usually very low (the average of four analyses of Zillerthal specimens made by Hoskyns-Abrahall is only 0.20 per cent.) the water may be hygroscopic or dissolved water instead of water of constitution. The water content of these minerals needs close inspection for two reasons. (1) It is a well-known fact that water of constitution is not given off until very high temperatures are reached. (2) Penfield and Minor<sup>4</sup> have proved that in the presence of fluorine, hydroxyl may be given off as hydrofluoric acid or hydrofluosilicic acid instead of as water. These two points have been borne in mind in the preparation of this paper and will be taken up later.

The Zillerthal apatite may be taken as the type of voelckerite. This mineral occurs in large euhedral crystals of thick tabular habit which often attain a diameter of six or eight centimetres. On the specimens, from this locality, which were examined for the present investigation, the only associated mineral noted is a thin film of chlorite. Koenigs-

<sup>1</sup> P. Groth, 'Tab. Uebersicht der Mineralien,' 4th edit., 1898, p. 87. Note also Groth's remark (speaking of apatite), 'Die Existenz freien CaO ist theoretisch höchst unwahrscheinlich, dagegen wäre eine Ersetzung von F1 durch HO wahrscheinlich.' (Zeits. Kryst. Min., 1886, vol. xi, p. 107.)

<sup>2</sup> S. L. Penfield, Amer. Journ. Sci., 1878, ser. 3, vol. xvi, p. 45; 1879, vol. xviii, p. 295; 1886, vol. xxxii, p. 107; 1894, vol. xlvii, p. 387.

<sup>3</sup> P. Jannasch and J. Locke, Zeits. Anorg. Chem., 1894, vol. vii, p. 154.

<sup>4</sup> S. L. Penfield and J. C. Minor, Amer. Journ. Sci., 1894, vol. xlvii, p. 388.

berger<sup>1</sup> in similar occurrences in Tyrol mentions adularia, albite, quartz, epidote, fluorite, calcite, and zeolites. The crystal forms present on the large voelckerite crystals are: *c* (0001), *m* (10 $\bar{1}$ 0), *x* (10 $\bar{1}$ 1), *s* (11 $\bar{2}$ 1), and *r* (10 $\bar{1}$ 2). On a smaller crystal minute faces of the forms  $\mu$  (21 $\bar{3}$ 1), *n* (31 $\bar{4}$ 1), *v* (11 $\bar{2}$ 2), and  $\alpha$  {11 $\bar{2}$ 0} were identified by the reflection goniometer. The symmetry, then, is hexagonal equatorial (A<sub>6</sub>P = hexagonal bipyramidal class) like fluor-apatite, for (31 $\bar{2}$ 1) and (41 $\bar{3}$ 1) are absent. The mineral is white, subtranslucent, with an imperfect basal (0001) and prismatic (10 $\bar{1}$ 0) cleavage. The specific gravity is 3.10 and the hardness about 5. The index of refraction determined by the Becke method is 1.634 ± 0.005. The double refraction, determined by grinding down a prismatic section alongside a basal section of barite, is about 0.003.

A number of analyses of the Zillerthal apatite made by Hoskyns-Abrahall<sup>2</sup> are on record, but carbon dioxide is not included. In view of the fact that Carnot<sup>3</sup> had found that the carbonate radical replaces fluorine in a number of apatites, it was thought that perhaps the carbonate radical had been overlooked in the Zillerthal mineral. It was partly with this idea in view that Mr. G. E. Postma, then a chemistry student at Stanford University, made a careful analysis of the Zillerthal mineral with the following results:

*Analysis of Voelckerite from Zillerthal, Tyrol, by G. E. Postma.*<sup>4</sup>

				Molecular ratios.	
CaO	... 55.73	Ca	... 39.83	0.994	... 10
P <sub>2</sub> O <sub>5</sub>	... 42.65	PO <sub>4</sub>	... 57.07	0.601	... 6
CO <sub>2</sub>	... 0.16	CO <sub>3</sub>	... 0.23	...	...
F	... 1.20	F <sub>2</sub>	... 1.20	0.032	} 0.089 ... 1
H <sub>2</sub> O	... 0.30	(OH) <sub>2</sub>	... 0.56	0.016	
		O	... 0.65	0.041	
	<hr/> 100.04				
Less O for F <sub>2</sub>	0.50				
	<hr/> 99.54		<hr/> 99.54		

This analysis is given in both the form of ordinary oxides and metals and acid radicals. The oxygen which replaces the fluorine is obtained by

<sup>1</sup> J. Koenigsberger, Neues Jahrb. Min., 1901, Beil.-Bd. xiv, pp. 43-119.

<sup>2</sup> J. L. Hoskyns-Abrahall, loc. cit.

<sup>3</sup> A. Carnot, loc. cit.

<sup>4</sup> In A. F. Rogers, Amer. Journ. Sci., 1912, vol. xxxiii, p. 479.

subtracting the percentages of calcium and acid radicals from the percentages of the ordinary oxides. The small amounts of carbon dioxide and water are probably due to liquid inclusions with gas bubbles which are observable in thin sections with a high power objective.

In the analysis given above no special precaution was taken to avoid water being given off as hydrofluoric acid. Supplementary water determinations of the same lot of specimens have recently been made by the writer. The Penfield method<sup>1</sup> for water determination was used. The powdered mineral was placed in the end of a Jena glass tube wrapped with platinum foil. At a convenient distance from the end ignited lead oxide (PbO) enclosed by glass-wool was heated by means of an auxiliary burner. The mineral was heated at the highest heat of a blast-lamp for about an hour. The water collected at the cool end of the tube (a moistened cloth served to condense it). The tube was melted off and the water determined directly by weighing the tube plus water, then drying and weighing again. The water content was 0.113 per cent. With ignited lime (CaO)<sup>2</sup> instead of lead oxide, the water content was 0.109 per cent.

This is pretty good proof that the Zillertal mineral has the composition  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{O},\text{F})_2$  with oxygen predominating over fluorine. An analysis of the Zillertal mineral given by Hoskyns-Abrahall is even closer to the theoretical for voelckerite, as the fluorine content is only 0.62 per cent. and the water content 0.15 per cent. The excess oxygen content is correspondingly higher.

Most of the chlorine-bearing apatites from Norway show a deficiency in chlorine, while fluorine is absent and water (or hydroxyl) is present in very small amounts. The theoretical quantity of chlorine in chlor-apatite being 6.80 per cent., Voelcker's analyses prove that many of the Norwegian apatites are really voelckerite, as excess of oxygen predominates over chlorine. Other analyses of Norwegian apatites made by Voelcker and Waage gave respectively 5.06 per cent. and 5.8 per cent. of chlorine. It is remarkable that pure chlor-apatite has never been found.

If hydroxyl and fluorine, or hydroxyl and chlorine, were isomorphous in the above apatites, the hydroxyl would decrease as fluorine or chlorine increased, but no such relation is apparent. For this reason the existence of the compound  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ , even as a replacing molecule, is

<sup>1</sup> S. L. Penfield, Amer. Journ. Sci., 1894, vol. xlviii, pp. 30-37.

<sup>2</sup> The lead oxide and lime are probably superfluous, for the water content is no greater with them than without.

very doubtful. The water may be in solid solution, as in tremolite and other minerals.<sup>1</sup>

The writer has recently discovered voelckerite in Calaveras valley, a small valley north-west of Mt. Hamilton and east of Milpitas, Santa Clara county, California. It occurs in vein-like patches of coarse anhedral in a massive metamorphic rock composed of glaucophane, omphacite, chlorite, garnet, and titanite. If the garnet were more prominent the rock would be called an eclogite. The rock in which the voelckerite occurs is one of patchy outcrops of glaucophane-bearing rocks of the Franciscan series of the Coast Ranges of California. These and similar rocks have been described by J. P. Smith.<sup>2</sup>

The voelckerite is a white, subtranslucent mineral with imperfect cleavage and faint lustre. The specific gravity is 3.06, and the hardness about 5. In a thin basal section a negative uniaxial interference-figure was obtained. A roughly rectangular section with maximum interference colour for the slide has elongation parallel to the slower ray, which indicates that the mineral occurs in subhedral crystals of tabular habit. The index of refraction determined by means of the Becke test with respect to liquids of known indices of refraction is  $1.634 \pm 0.005$ . The double refraction is about 0.005, using glaucophane to determine the thickness of the slide.

The following chemical analysis of the Calaveras valley voelckerite was made by Mr. G. W. Jordan under the writer's direction. Each result (except  $\text{Al}_2\text{O}_3$ ) is the mean of two closely agreeing values.

*Analysis of Voelckerite from Santa Clara County, California.*

		Molecular ratios.	
CaO	... 54.46	Ca	... 38.42 ... 0.983
Al <sub>2</sub> O <sub>3</sub>	... 1.35	Al	... 0.71 ... 0.039
FeO	... 0.24	Fe''	... 0.19 ... 0.003
P <sub>2</sub> O <sub>5</sub>	... 41.47	PO <sub>4</sub>	... 55.47 ... 0.584
H <sub>2</sub> O	... 0.22	CO <sub>3</sub>	... 0.35 ... 0.006
CO <sub>2</sub>	... 1.03	OH	... 0.41 ... 0.012
Insol.	... 0.53	O	... 1.49 ... 0.093
		Insol.	... 0.53 ... —
99.30		97.57	

As in the Zillerthal analysis, the excess oxygen is determined by difference. The microscopic examination proves that the carbonate radical

<sup>1</sup> See E. T. Allen and J. K. Clement, *Amer. Journ. Sci.*, 1908, vol. xxvi, p. 101.

<sup>2</sup> J. P. Smith, *Proc. Amer. Phil. Soc.*, 1907, vol. xlv, pp. 183-242.

is due in whole or in part to admixed calcite. An attempt was made to determine the carbonate present as calcite by dissolving the powdered mineral in warm (about 70° C.) very dilute (1 : 8) hydrochloric acid. A little of the voelckerite was also dissolved<sup>1</sup> by the dilute acid, but as a separate sample was used this could not seriously affect the result. The analysis indicates that 1.04 per cent. of the carbonate radical belongs to calcite, and the remainder perhaps to voelckerite. If we subtract 1.04 per cent. of CO<sub>2</sub> and an equivalent amount of Ca (0.69) we have the figures given in the second column. The molecular ratios are very closely (Ca + Al<sub>2/3</sub> + Fe'') : PO<sub>4</sub> : (O + CO<sub>2</sub>) = 10 : 6 : 1. As the molecule 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.CaO predominates, the mineral must be called voelckerite.

As there was a chance that the mineral had not been heated sufficiently to drive off all the water, careful water determinations at high temperatures were carried out by the writer. As an extra precaution<sup>2</sup> lead oxide was used, as in the determination of water in the Zillertal mineral. Two determinations, made with hard glass heated for an hour with a blast-lamp, gave 0.197 and 0.214 per cent. of water, which agree very well with Mr. Jordan's determination of 0.22 per cent. (average of 0.17 and 0.26).

There are hints that voelckerite may frequently occur in metamorphic rocks. Turner,<sup>3</sup> for example, states that apatite occurring in a biotite-gneiss from the North Fork of the Mokelumne River, California, tested by Hillebrand, showed the absence of both fluorine and hydroxyl and very little chlorine. A thin section of this gneiss contains an accessory mineral which would ordinarily be called apatite.

The evidence of a number of apatite analyses, including several in which special care was taken in the water determinations, proves that the compound 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.CaO is the predominant molecule in many minerals of the apatite group. There is no proof that the compound 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.Ca<sub>2</sub>(OH) exists as the predominant molecule in any apatite, and it is also doubtful whether it exists as a replacing molecule.

The discovery that in many minerals fluorine and hydroxyl are isomorphous, instead of fluorine and oxygen as held by Rammelsberg, was one of the brilliant achievements of Penfield.<sup>4</sup> Rammelsberg, up to the very last, maintained that oxygen and fluorine were isomorphous. It

<sup>1</sup> The voelckerite is also slightly soluble in hot water.

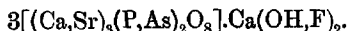
<sup>2</sup> The results prove this precaution was unnecessary.

<sup>3</sup> H. W. Turner, *Amer. Journ. Sci.*, 1902, vol. xiii, p. 348.

<sup>4</sup> S. L. Penfield, *Amer. Journ. Sci.*, 1878, vol. xvi, p. 45.

looks as though he may have been correct in a single instance. It is probable, in the light of recent work in chemical mineralogy, that in ordinary compounds hydroxyl and fluorine are isomorphous. Apatite, however, is complex in composition, and it is probable that the compound  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$  is isomorphous with  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ , because of the mass-effect of  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}$  with a formula weight of 971. This is a reasonable explanation, for it does no violence to the isomorphism of hydroxyl and fluorine in ordinary compounds. The idea of mass-effect isomorphism we owe also to Penfield.<sup>1</sup>

There is no reason why hydroxyl should not occur in apatite. There is simply lack of evidence that it occurs, except in trifling amounts. In the mineral svabite,  $3\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{CaF}_2$ , the arsenate analogue of fluor-apatite, the water percentages are only 0.25 and 0.33, yet there is a great deficiency in the fluorine and chlorine content. In the mineral ferromite, a strontium-bearing arsenical apatite, described by Smith and Prior,<sup>2</sup> only a trace of water is given in the analysis, yet the fluorine (F = 0.83 per cent.) is deficient, and the formula is written



If the compound  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$  exists it deserves a distinctive name. Voelckerite is preferable to the name oxy-apatite suggested by analogy with fluor-apatite. The name voelckerite is similar to voelknerite, but the latter is a synonym of hydrotalcite, so no longer needs to be used except as a synonym. The question arises as to what names shall be used for other members of the apatite group. The name apatite may be reserved for fluor-apatite or applied as a group name for calcium phosphate minerals of the type  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaX}_2$ . The latter is perhaps preferable to the former on account of the difficulty of distinguishing the individual minerals without an accurate chemical analysis. The general tendency with increase of knowledge is to divide minerals into species. Formerly mica, feldspar, mesotype, uranite, were considered individual minerals; they are now group names.

If apatite is the group name, we have the names fluor-apatite, chlor-apatite, dahllite (podolite), and voelckerite. Dahllite, or podolite, was previously called carb-apatite, but the name was withdrawn. As I have suggested elsewhere,<sup>3</sup> it is advisable to restrict combined chemical and arbitrary names such as soda-orthoclase, silver-analcite, carb-apatite, &c.,

<sup>1</sup> S. L. Penfield, Amer. Journ. Sci., 1899, vol. vii, p. 118.

<sup>2</sup> G. F. H. Smith and G. T. Prior, Mineralogical Magazine, 1911, vol. xvi, p. 84.

<sup>3</sup> A. F. Rogers, Proc. Amer. Phil. Soc., 1913, vol. lii, pp. 610, 612.

to artificially-prepared compounds and hypothetical compounds or end-members of isomorphous series. In this case new names should be given to fluor-apatite and chlor-apatite. This has been done in many other cases. Barbierite was formerly soda-orthoclase, autunite was lime-uranite, genthite was nickel-gymnite, &c.

#### *Conclusions.*

Many minerals of the apatite group are deficient in combined fluorine and chlorine. This deficiency has generally been explained by assuming the compound  $3\text{Ca}_3(\text{PO}_4)_2\cdot\text{Ca}(\text{OH})_2$ . It is, however, more probable that the compound has the composition  $3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaO}$  for the following reasons :

(1) The water percentage in apatite is too small for the compound  $3\text{Ca}_3(\text{PO}_4)_2\cdot\text{Ca}(\text{OH})_2$ .

(2) In analogous minerals such as svabite and fermorite the water percentage is also very low.

(3) There is no correlation between the amounts of hydroxyl (or water) and combined fluorine and chlorine.

(4) The exception to the general rule of the isomorphism of fluorine and hydroxyl may be easily explained by mass-effect isomorphism.

For a mineral with the composition  $3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaO}$ , or one in which this molecule predominates, the name voelckerite may be used.

Apatite is a group name for four distinctive minerals, viz. :

Fluor-apatite	...	$3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaF}_2$
Chlor-apatite	...	$3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaCl}_2$
Dahllite (podolite)	...	$3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaCO}_3$
Voelckerite	...	$3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaO}$ .

The similarity in the properties of these minerals may be explained by mass-effect isomorphism.