THE MINERALOGICAL MAGAZINE

AND

JOURNAL

OF THE

MINERALOGICAL SOCIETY.

No. 49. APRIL, 1895. Vol XI.

A Chemical Study of Some Native Arsenates and Phosphates.

1. Euchroite. 2. Liroconite. 3. Clinoclase. 4. Tyrolite.
5. Pharmacolite. 6. Cacoxenite. 7. Kühnite.

By A. H. Church, M.A., F.R.S.

[Read June 19th, 1894.]

THE present series of notes is mainly based upon analyses executed during the years 1867-1877, but these have been supplemented in a few instances by recent work. The series may be regarded as a continuation of several papers published from time to time in the *Journal of the Chemical Society*, in the *Chemical News*, and in the *Proceedings of the Royal Irish Academy*. Throughout these inquiries particular attention has been paid to the degree of tenacity with which the water present in the hydrous species is held.

1. Euchroite.

A fine specimen of this mineral from Libethen, Hungary, was submitted to analysis in the year 1874. As the results simply confirmed the accepted composition of the species, they remained unpublished. But, on looking lately into the record of my analysis, I noted the hitherto unrecorded presence of phosphoric acid in this mineral. As the observation is of interest in connection with other native arsenates, and offers a parallel to the partial replacement of phosphorus by arsenic in some mineral phosphates, a brief note on the subject may be not unacceptable to mineralogists.

The specific gravity of the specimen was 3·42 at $\frac{16^\circ\cdot5}{15^\circ\cdot5}$C. This determination was made in alcohol of sp. gr. ·8892 at 16°·5. The balance used was an assay balance by the late L. Oertling, and was specially arranged for the purpose of taking specific gravities. The crystal of euchroite employed weighed ·4639 gram.

The following figures represent the analytical results with the corresponding percentages :—

Euchroite taken	·7365 gram		
Water lost *in vacuo*	·009 ,,	= 1·22 per cent.	
Water lost at 100° C.	·014 ,,	= 1·90 ,,	
Water lost at low redness	·119 ,,	=16·16 ,,	
Water, total	·142 ,,	=19·28 ,,	
Cupric oxide	·3481 ,,	=47·26 ,,	
2 $MgNH_4AsO_4, H_2O$	·376 ,,	=30·90 ,,	As_2O_5
$Mg_2P_2O_7$	·017 ,,	= 1·48 ,,	P_2O_5
Undetermined		1·08 ,,	

The formula of euchroite, 4 CuO. As_2O_5. $7H_2O$, as deduced from the analysis of Kühn and Wöhler, is in accord with the percentages given in the present note. For the purpose of comparison, I have converted the percentage of P_2O_5 into its equivalent of As_2O_5 :—

	Theory	Experiment
4CuO	47·12 per cent.	47·26 per cent.
As_2O_5	34·16 ,,	33·29 ,,
$7H_2O$	18·72 ,,	19·28 ,,

It might be argued that the loss of water *in vacuo* and at 100° indicates the existence in this mineral of one molecule of cupric hydrate. This loss does indeed correspond pretty nearly to that demanded by such a formula as

$$3CuO.\ As_2O_5.\ 6H_2O + CuO.\ H_2O,$$

if we deduct a small quantity—something less than 0·5 per cent.—of accidental or hygroscopic moisture. But if one-fourth of the copper present in euchroite exist in the form of cupric hydrate, it is hardly likely that the mineral would become yellowish-green and not blacken on being strongly heated. One may, however, affirm that one of the seven molecules of water in this mineral is less firmly retained than the remaining six. It is worth while comparing the theoretical and experimental percentages of water corresponding to 1 and to 6 molecules :—

	Theory	Experiment
H_2O	2·67	3·12
$6H_2O$	16·05	16·16

2. Liroconite.

A fine specimen of Cornish liroconite was analysed in 1874. Its specific gravity, determined with the same precautions as those observed in the case of euchroite, proved to be 2·97 at $\frac{16^\circ{\cdot}5}{15^\circ{\cdot}5}$ The analysis, though incomplete, shows that the water in this mineral is not all retained with equal tenacity :—

Liroconite taken	·812 gram		
Water lost *in vacuo*	·052 ,,	= 6·40 per cent.	
Water lost at 100° C. ...	·080 ,,	= 9·85 ,,	
Cupric oxide	·2983 ,,	=36·73 ,,	
$2\ MgNH_4AsO_4,\ H_2O$	·320 ,,	=23·85 ,,	As_2O_5
$Mg_2P_2O_7$	·013 ,,	= 1·02 ,,	P_2O_5

These results, so far as they go, are not inconsistent with the percentages demanded by the expression $4CuO.\ Al_2O_3.\ As_2O_5.\ 13H_2O$. In this formula $3H_2O$ correspond to 6·12 per cent. water, which may be represented by the loss suffered by liroconite *in vacuo*. Similarly, the further loss of 9·85 per cent. sustained at 100° may indicate the separation of $5H_2O$, which theoretically demands 10·19 per cent. The formula above given requires the following percentages :—

$4CuO$ =317·2=35·92 per cent.
Al_2O_3 =102·0=11·35 ,,
As_2O_5 =230·0=26·04 ,,
$13H_2O$ =234·0=26·49 ,,

Although these theoretical numbers agree fairly with the analytical results hitherto published, the empirical formula which they suggest

$$\left.\begin{array}{l} 3CuO.\ As_2O_5 \\ CuO.\ H_2O \\ Al_2O_3.\ 3H_2O \end{array}\right\}9\ aq$$

is not in precise accord with the losses of water which this mineral suffers *in vacuo* and at 100°. As I have pointed out elsewhere,[1] the native normal aluminium hydrate, gibbsite, loses no water *in vacuo* or even at 100° : this observation does not lend support to the view that $Al_2O_3 . 3H_2O$ exists as such in liroconite. Reasoning from the analogy of variscite, a normal native aluminium phosphate, which loses all its water at 100°, it might be concluded that a corresponding aluminium arsenate exists in liroconite : if this be the case, the formula for this species might be written :—

$$\left.\begin{array}{c} Al_2O_3 . As_2O_5 . 4H_2O \\ 4(CuO . H_2O) \end{array}\right\} 5H_2O$$

Unfortunately it is not possible to bring the loss of $3H_2O$ *in vacuo*, and of $5H_2O$ at 100°, into harmony with this expression. So, for the present and until further experimental evidence has been accumulated, we must be content with such a formula as this[2] :—

$$4CuO . Al_2O_3 . As_2O_5 . 5H_2O + 5H_2O + 3H_2O$$

3. Clinoclase.

The mineral clinoclase had been analysed with concordant results by Rammelsberg and by Damour when, in the year 1867, I came into possession of a particularly fine specimen. In studying the group of arsenates and phosphates to which this species belongs, I was anxious to ascertain the degree of tenacity with which the water present in the mineral was retained. I found that *in vacuo* and at 100° C. the finely powdered substance lost no more than ·08 per cent. of moisture. This having been deducted, the percentages of constitutional water, of arsenic pentoxide, and of cupric oxide were determined to be :—

	Experiment.		*Theory.* $3CuO . As_2O_5 . 3(CuO, H_2O)$
Water (by difference)	... 7·20	...	7·11
Arsenic pentoxide	... 30·08	...	30·27
Cupric oxide ...	... 62·72	...	62·62

The arsenic was weighed as $2MgNH_4AsO_4 . H_2O$. On further examination of this salt it was found to contain a minute trace of the corresponding phosphate.

---

[1] "On the Constitution of the Native Phosphates of Aluminium." *Proc. R. Irish Academy*. Ser. II., Vol. III., pp. 551-562 (1882).

[2] It would be convenient if different founts of type (black letter italic, for example) could be employed to discriminate molecules of H_2O held with different degrees of tenacity.

4. TYROLITE.

In a paper published in 1873 (*Chem. Soc. J.* XXVII., 108) I gave the results of some analyses of tyrolite. The specimen examined was conjectured to have come from Libethen, but recent study of its matrix leads me to assign it to Falkenstein. In the above paper tyrolite was stated to contain "calcium carbonate as an essential ingredient not as an accidental impurity." This position, confirmed as it is by the results of three analysts working independently, is not accepted by Professor E. S. Dana (*Mineralogy*, 6th ed., p. 839), whose opinion is obviously influenced by the results of several recent analyses of a mineral from the Mammoth Mine in the Tintic District of Utah. After a careful comparison of the Utah and Falkenstein minerals, I am bound to confess that they appear to belong to the same species. About the same proportion of lime occurs in both. May not the absence of carbon dioxide from the former be explicable by means of the theory that it is represented by some other acid constituent? Anyhow, I am now in a position to offer fresh evidence in favour of my original view. Fortunately, I had preserved several grams of the tyrolite with which I had worked in 1872-3.

The following experiment seems to be decisive. A portion of the mineral, carefully selected, was ground to an impalpable powder and suspended in distilled water. A current of carbon dioxide was then passed through the mixture for some hours. The liquid was filtered, then the clear filtrate was tested for calcium with a positive result. But as copper and arsenic pentoxide were also found in the liquid it became necessary to ascertain the *proportion* of calcium to copper present therein. These metals occurred in the ratio of 1 : 5, the precise ratio in which they exist in the original mineral. As it is inconceivable that calcium carbonate and pentabasic cupric arsenate should possess identical solubilities in carbonated water, it is evident that the mineral tyrolite dissolves *as a whole* in that solvent. This conclusion is greatly strengthened by a further observation accidentally made during the course of the above described experiment. About 100 cc. of the clear filtrate, prepared as just mentioned, were left in a beaker for 48 hours. At the end of that time it was noticed that the liquid was no longer clear. There was a film on its surface and numerous shining particles were floating in it. Both film and particles presented the precise greenish-blue colour and satiny aspect of the original tyrolite; neither could be mistaken for the calcium carbonate which would have been precipitated had the carbonated water simply withdrawn that compound from a mineral in which it existed in admixture. That no carbon dioxide can be found in the Utah mineral, if it be a different species, would have no bearing on these facts. But if the American and the European minerals be really identical the absence from the former of carbon dioxide may be explicable on the theory of substitution. In further confirmation of the view that calcium carbonate does not exist as an intruding substance in tyrolite, I may state that when the coarsely powdered mineral is dissolving in acid it continues to evolve minute bubbles of carbon dioxide so long as a particle remains.

But if the view I formerly propounded as to the relation subsisting between the calcium carbonate in tyrolite and its other constituents has now been confirmed, yet the formula which I proposed in 1873 for this species needs modification in one particular. For I certainly misinterpreted the meaning of the phenomena which I had then observed as to the loss of water sustained by tyrolite when kept *in vacuo*, or heated to 100 C. Such loss, amounting to 7 or 8 per cent., does *not* represent accidental or hygroscopic water, but corresponds to a definite number of molecules of H_2O. An appearance, which I had observed and had attributed to the presence of interstitial water between the laminæ of the crystals in their central portions, is due to an optical illusion arising from the perfect contact of these portions. So many cases are now known where essential water is lost by minerals, and especially by arsenates and phosphates, when subjected to the influence of dry air or of lowered barometric pressure, that one need feel no surprise at the discovery of another instance of this phenomenon.

In the original paper (*loc. cit.*) to which reference has been made, there occurred an error in the substitution of the symbol for phosphorus for that of arsenic. It may be well, therefore, to reproduce here the figures of the more complete of the two analyses previously published, and at the same time to set down the water found in the mineral in accordance with the view as to its function which must now be held. These are the figures of analysis ii. :—

Tyrolite taken	·4585 gram		
Water lost *in vacuo*	·024 ,,	= 5·23	per cent.
Water lost at 100° C. ...	·011 ,,	= 2·40	,,
Calcium carbonate	·0505 ,,	=11·01	,,
Cupric oxide	·212 ,,	=46·24	,,
2 $MgNH_4AsO_4$, H_2O	·205 ,,	=27·07	,, As_2O_5
Water retained at 100°, by difference		8·05	,,

Here is the comparison between these experimental percentages and those demanded by the expression—5 CuO. As_2O_5. $CaCO_3$. 8 H_2O

	Experiment	Theory
CuO	46·24	45·55
As_2O_5	27·07	26·42
$CaCO_3$	11·01	11·49
H_2O	15·68	16·54

As the loss of water suffered by tyrolite *in vacuo* and at 100° C. is half of its total content, the formula of the species may be written :—

$$\left.\begin{array}{l} Cu_3As_2O_8.\ 2H_2O \\ CaCO_3 \\ 2Cu(OH)_2 \end{array}\right\} 4H_2O$$

The slight deficiency in the experimental percentage of water which corresponds to the $4H_2O$ in the above formula is probably attributable to the imperfect methods of desiccation adopted; for in many similar cases it is observable that a really good vacuum and the actual temperature of 100° C. (and not the heat attained in the water-oven) are required in order to secure the complete expulsion of the loosely-attached molecules of water.

5. PHARMACOLITE.

An incomplete analysis of well-crystallised pharmacolite furnishes another example of a perfectly definite mineral species which loses much constitutional water at the ordinary temperature *in vacuo*. The following figures represent the analytical results with the corresponding percentages :—

Pharmacolite taken	·962 gram		
Water lost *in vacuo* at 16° C.	·1155 gram	= 12·37 per ct.	after deduction of silica, &c.
Water lost between 100° & 200°	·029 ,,	= 3·11 ,,	
Silica and insoluble matter	·028 ,,		

The composition of pharmacolite is usually represented by the formula 2CaO. H_2O. As_2O_5. 5aq. From the desiccation experiments above recorded it would seem that $3H_2O$ are lost *in vacuo*, and $1H_2O$ at temperatures up to 200°. For $3H_2O$ are equal to a percentage of 12·0, while $1H_2O$ corresponds to 4·0 per cent., while experiment gave, respectively, 12·37 and 3·11, or a total of 15·48 per cent. against the 16 per cent. required by theory for $4H_2O$. If these conclusions be correct we shall have these expressions for

Pharmacolite in normal state ... ... $2CaO. H_2O. As_2O_5. 5aq.$
Pharmacolite dried *in vacuo* at 16° ... ... $2CaO. H_2O. As_2O_5. 2aq.$
Pharmacolite dried at 200° ... ... $2CaO. H_2O. As_2O_5. 1aq.$

Rammelsberg[1] has pointed out that the second of these formulæ represents the species haidingerite, but his remark seems to be based on the observations of Petersen, who found that pharmacolite suffered a loss of 11 to 12 per cent. of water on being heated to 100° C. That such loss occurs by reduction of pressure only, without having recourse to increase of temperature, does not appear to have been hitherto recorded.

It should be noted that in the new (1892) edition of Dana's *Mineralogy* pharmacolite is assumed to contain one molecule less of water than is assigned to this species in the present note. All the results obtained in the analysis of the native compound confirm the view here adopted.

It may be mentioned here that a specimen of pharmacolite which presented the more transparent aspect of haidingerite furnished me with analytical results confirming those just given as regards the water in this species. In this case the lime and the arsenic pentoxide were also determined, the percentage of the former constituent being 25·04, of the latter 47·95. This latter percentage is indeed about 3 units lower than that demanded by theory, but it is still less in accord with the number (53·3) required by a formula having $5H_2O$ instead of $6H_2O$.

6. CACOXENITE.

Having sacrificed a very fine specimen of this mineral, from Hrbek, near St. Benigna, in Bohemia, I obtained sufficient material for analysis. The deep gold-coloured acicular crystals were separated as far as possible by mechanical means from the traces of impurities which had been detached from the matrix. In dissolving the selected material in dilute hydrochloric acid, the process of solution was not urged forward to its extreme limit. In calculating the percentages given below, the matter which was not dissolved by the acid, and the trace of silica subsequently separated, together amounting to 6·15 per cent., were previously deducted. Much water was lost by the mineral *in vacuo* over oil of vitriol, but none in the air-bath at 100° C.

---

[1] *Mineral-Chemie.* 2te Auflage, p. 339.

	Experiment	Theory
Water lost *in vacuo* over H_2SO_4	18·69	18·45
Water (with trace of F) lost on ignition	13·11	12·92
Ferric oxide	48·57	49·22
Phosphorus pentoxide	19·76	19·41

These figures correspond with the formula

$$9Fe_2O_3.\ 4P_2O_5.\ 51H_2O,$$

which demands the percentages placed by the side of the experimental numbers. In these theoretical percentages I have divided the 51 molecules of water into two groups, one consisting of 30 molecules and the other of 21; it will be observed that the percentage of water lost *in vacuo* corresponds very closely with that demanded by the escape of $30H_2O$. This observation is consistent with such a formula as the following:—

$$\left.\begin{array}{l} 4\ (Fe_2O_3.\ P_2O_5.\ 4H_2O) \\ 5\ (Fe_2O_3.\ H_2O) \end{array}\right\} 30H_2O$$

This expression is doubtless somewhat complex, and I am not prepared to maintain that the substance analysed was perfectly homogeneous. The results of the analysis might be said to represent a mixture of about one molecule of limnite ($Fe_2O_3.\ 3H_2O$) or of xanthosiderite ($Fe_2O_3.\ 2H_2O$) with four molecules of a basic ferric phosphate having the comparatively simple formula:—

$$\left.\begin{array}{l} Fe_2O_3.\ P_2O_5.\ 3H_2O \\ Fe_2O_3.\ 2H_2O \end{array}\right\} 7H_2O$$

It will, however, be seen on comparing the percentages demanded by this last formula with those obtained in the analysis of cacoxenite, that they agree fairly well even if we make no allowance for the supposed presence of an excess of some ferric hydrate such as xanthosiderite. Here are the percentages in question:—

		Theory $\left.\begin{array}{l} Fe_2O_3.\ P_2O_5.\ 3H_2O \\ Fe_2O_3.\ 2H_2O \end{array}\right\} 7H_2O$	Experiment
$2Fe_2O_3$	320	47·20	48·57
P_2O_5	142	20·94	19·76
$5H_2O$	90	13·28	13·11[1]
$7H_2O$	126	18·58	18·69[2]
		100·00	

---

[1] lost *in vacuo*. [2] lost on ignition.

I am inclined to think that the above formula may be accepted as that of cacoxenite. It is in fair agreement with the analytical results obtained by v. Hauer in one of his analyses of the Hrbek mineral: a higher percentage of P_2O_5 and less Fe_2O_3 are shown in the two other analyses cited by Dana. But to whatever conclusions further work on cacoxenite may lead, the experiments now placed on record prove, for the first time, that $\frac{7}{12}$ths of the water present in this mineral are retained with far less tenacity than the remaining $\frac{5}{12}$ths.

8. KÜHNITE.

In the year 1876 I acquired a specimen of a honey-yellow mineral labelled "Chondrarsenite, Långban, Sweden." Quantitative analysis showed that the substance differed from chondrarsenite in containing far less manganese but much more lime and magnesia than that species, and that its blow-pipe reactions were not the same. In fact it bore a very close resemblance to another arsenate of lime, magnesia, and manganese, which was analysed by Kühn (*Liebig Annal.*, XXXIV., 211, 1840), and named by him *Berzeliite*. It occurred in irregular crystalline masses imbedded in a granular limestone and accompanied by hausmannite. It lost nothing *in vacuo* or at 100° (in one experiment the loss on 1·0928 gram was ·0004 gram), but gave a small amount of residue insoluble in acid (·0025 gram from ·3874 gram of mineral; ·002 from ·294; ·001 from ·226; and ·002 from ·3245). The following figures represent the analytical results with the corresponding percentages, the insoluble matter having been in all cases deducted :—

I.	Mineral taken ...	·3849 gram				
	2 $MgNH_4AsO_4, H_2O$	·358	,,	=56·29	per cent.	As_2O_5
II.	Mineral taken ...	·292	,,			
	2 $MgNH_4AsO_4, H_2O$	·2758	,,	=56·21	,,	As_2O_5
	$CaCO_3$	·1115	,,	=21·38	,,	CaO
III.	Mineral taken ...	·225	,,			
	Mn_3O_4	·008	,,	= 3·52	,,	MnO
	$CaCO_3$	·0905	,,	=22·52	,,	CaO
	$Mg_2P_2O_7$	·079	,,	=12·65	,,	MgO
IV.	Mineral taken ...	·3225	,,			
	Mn_3O_4	·0105	,,	= 3·04	,,	MnO
	$CaCO_3$	·1205	,,	=20·92	,,	CaO
	$Mg_2P_2O_7$	·1195	,,	=13·35	,,	MgO

The mean percentages are :—

CaO	21·61
MgO	13·00
MnO	3·28
As_2O_5	56·25
Deficiency ...	5·86
	100·00

The questions naturally arise " what constituent of the mineral has been missed ? " and " was water present ? " Kühn had indeed noticed a loss on ignition of his mineral, equal in one case to 0·3 per cent. ; in another to 2·95 per cent. ; but he did not prove such loss to arise from the escape of water. In order to determine the point I heated to very low redness a most carefully selected sample of the mineral, and found that the loss on 1·539 gram amounted to 0·004 gram only, or 0·26 per cent. —a negligible quantity. The species is obviously anhydrous. But an explanation of the analytical deficit was soon discovered. On dissolving the finely powdered mineral in dilute hydrochloric acid a brisk evolution of a gas which proved to be carbon dioxide was observed. No selection, however careful, of the fragments of the crushed mineral could eliminate the substance giving rise to this effervescence, and I am forced to conclude that the embedded nodules of Kühnite are interpenetrated with the calcareous matrix in which they occur. If this conclusion be just, we may look upon the substance analysed as an intimate mixture of true kühnite with about 7 per cent. of calcite, kühnite itself being represented by the formula $(CaMgMn)_3As_2O_8$. The analytical results correspond fairly well with the expanded formula—$4{\cdot}5CaO.\ 4MgO.\ 0{\cdot}5MnO.\ 3As_2O_5$, although nearly 2 per cent. of the constituents of the mineral remain still unaccounted for.

Thus far had I written, in recording the results obtained by me in 1876, when I observed, on referring to the 1892 edition of Dana's *Mineralogy*, that some work has been done during recent years towards clearing away the obscurity in which the constitution of kühnite was involved. In the variety known as pyrrhoarsenite carbon dioxide has been found to the extent of between 1 and 2 per cent. This result confirms the observation already recorded in the present note, and is probably to be explained in the same way. As ordinary kühnite is isometric, I asked Mr.

Miers to examine optically some fragments of the specimen which I had analysed. He tells me that the appearance of the mineral in polarised light is in accord with my view that it consists of an isometric compound interpenetrated with small particles of calcite. It seems, however, that a doubly-refracting arsenate, having the same composition as kühnite, also exists. It is the pseudoberzeliite of W. Lindgren, and also the similar mineral from the Moss Mine, Nordmark, described by Igelström (Dana, *Min.*, 6th ed., p. 753).