

*Anomalies in the analytical determination of water
in epidote.*

By THE REV. A. F. SMETHURST, B.Sc., A.R.C.S., F.G.S., F.C.S.
Geological Department, Imperial College of
Science and Technology, London.

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NUMEROUS veins and veinlets of epidosite traverse the crystalline schists and associated igneous rocks of the Malvern complex. They are fine-grained, compact rocks, of uniform texture and pale greenish-yellow colour, and vary in composition from almost pure epidote to mixtures of epidote with small quantities of quartz, sphene, sericitic mica, apatite, and, in almost insignificant amount, albite.

Analytical investigation of these rocks revealed the fact that the epidote they contain holds its water more tenaciously than has hitherto been suspected: the determination of water-content by the methods usually applied to the analysis of rocks and minerals gave results which were so seriously low as to suggest that the mineral was essentially anhydrous. Though more drastic methods increased the yield considerably, they failed to liberate more than about 75 % of the amount of water which, theoretically, should be present.

The anomaly was first observed in an analysis (made by the author) of almost pure epidote-rock (specimen A) taken from a vein in the lower level of the most westerly quarry at the north end of the Malvern Hills—one of the Pyx quarries. The figure obtained for the sum of all the constituents of the rock was only 98.46 %; the total water-content was only 0.06 %, one-third of which was given up at temperatures below 110° C. The determination of water was carried out by the ordinary method, viz., by the use of an absorption apparatus, in contact with which the sample, placed in a silica boat, was heated in a silica tube in a furnace for one hour, the temperature rising to approximately 1000° C., and a current of dry air passed through the tube.

To check this disturbing result, the determination of water was

repeated three times; but the four sets of figures, as shown below, were essentially the same :

Total water-content	0.06 ; 0.05 ; 0.05 ; 0.06 %.
Combined water (above 110° C.)	0.04 ; 0.03 ; 0.03 ; 0.04 %.
Theoretical percentage	1.80–2.00.

In the last two determinations, heating was continued for about 2½ hours, instead of the customary 1 hour; and the furnace was heated as intensely as possible.

A sample of another epidosite (specimen B, from the eastern Pyx quarry in the same hill) was then analysed by Dr. A. W. Groves, who also obtained a low total for the rock (98.52 %), and a low figure for the total water-content (0.35 %, being 0.28 % combined water and 0.07 % free water).

Dr. Groves next repeated the water determination on specimen A, and succeeded in raising the figure for total water-content to 0.15 % (0.12 % combined water, 0.03 % free water). He also analysed a duplicate of this specimen A, obtaining 0.14 % total water-content, only half of which was in the combined state; while on analysing a less pure epidosite from a vein in contact with granite on the eastern slope of the same hill he returned a figure of 0.56 % combined water and 0.10 % free water.

The persistence of this anomaly raised the question whether the mineral under consideration was a true epidote, or some other species having essentially the same physical and optical properties, in which the water had been replaced by some other constituent of rare occurrence. To decide this question, Dr. R. W. B. Pearse, of the Physics Department, Imperial College of Science and Technology, kindly carried out a spectroscopic investigation of specimen A, with a view to discovering whether any unusual element was present which might have passed through the analysis undetected; but he failed to identify any such element, or to discover any substance not already determined in the course of the chemical analysis. Mr. F. A. Bannister, of the Mineral Department, British Museum, then very kindly took X-ray powder photographs of the epidosite A and the pure mineral (specimen C), which the author had separated from specimen A by elutriation, fractional gravity separation in Clerici solution, and electro-magnetic methods; on comparing these with similar photographs of pure epidote from a well-known locality, it was seen that the two sets of photographs were so exactly similar as to prove that the mineral C was a true epidote.

Since tests showed that sulphur or chlorine, released only by fusion, were not present in greater amount than would be accurately indicated by the figures obtained by acid attack, and that carbon was absent, while fluorine had already been determined and was not present in such quantities as to suggest that it had replaced water, it became clear that the shortage in the totals for specimens A and B could only be accounted for by incomplete expulsion of the water.

Fusion methods were then employed for the determination of the water in specimens A, B, and C, a platinum boat and combustion-glass tube being used. First the powdered epidosite was mixed with sodium carbonate: this failed to give a complete melt at 800° C., and 'fritting' produced no higher figure for water, as the rock was unattacked. Carefully dried sodium tungstate was then used instead, and the full temperature of 1000° C. was maintained for a prolonged period. A much higher figure was thus obtained, but the decomposition was not complete in any one case, and the largest figure for water was reached where decomposition had proceeded farthest. The figures for water obtained by the sodium tungstate fusion method, as compared with those resulting from the normal method, were as follows:

	Specimen		
	A.	B.	C (pure mineral).
Water expelled below 110° C.	0.03	0.07	0.03 %
„ „ above 110° C.	0.12	0.28	0.12
„ „ on heating with sodium tungstate	1.15	0.41	1.17
Total water	1.30	0.76	1.32

In the case of specimen B, heating with sodium tungstate was less prolonged than in the other two cases; whereas the residue of specimen C from the first fusion with sodium tungstate was recovered, washed, dried at red-heat, and then subjected to a second fusion with sodium tungstate. A figure of 0.73 % was obtained from the first fusion, and a further 0.44 % of water was expelled on re-fusing; but the indications were that the mineral still retained some water (0.2 %-0.3 %) which was even now unexpelled.

Finally, in view of the almost complete absence of CO₂, and the extremely low percentage of FeO in the pure mineral, it seemed possible that the determination of loss on ignition would give a good approximation to the correct figure for total water. A temperature of 1300-1400° C. was employed, and the mineral blasted for half an

hour; the loss was equivalent to 2.52 %, but the mineral had sintered and fused on the bottom of the crucible, so that evidently some of it had volatilized at this temperature.

The complete analyses of the three specimens A, B, and C are given below :

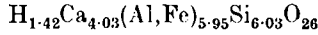
	Specimen A (A. F. Smethurst).	Specimen B (A. W. Groves).	Specimen C (pure mineral) (A. W. Groves).
SiO ₂	42.94	52.27	37.22
TiO ₂	0.41	0.91	0.33
Al ₂ O ₃	20.00	15.34	21.99
Fe ₂ O ₃	12.81	10.13	14.25
FeO	0.30	0.92	0.63
MnO	0.18	0.17	0.17
MgO	0.16	0.37	0.28
CaO	20.60	17.07	23.22
Na ₂ O	0.27	0.07	nil
K ₂ O	0.36	0.21	0.09
H ₂ O (Na ₂ WO ₄)	1.15	0.41	1.17
H ₂ O (>110° C.)	0.12	0.28	0.12
H ₂ O (<110° C.)	0.03	0.07	0.03
P ₂ O ₅	0.13	0.37	0.11
BaO	nil	0.10	nil
SrO	0.04	0.11	0.17
CO ₂	0.05	0.15	nil
F	0.03	0.08	0.03
Cl	0.03	0.04	0.08
SO ₃	nil	n.d.	n.d.
S	0.07	n.d.	n.d.
V ₂ O ₃	n.d.	n.d.	0.05
Li ₂ O	n.d.	nil	nil
CuO	0.01	n.d.	n.d.
Cr ₂ O ₃	0.002	n.d.	0.002
	<u>99.69</u>	<u>99.07</u>	<u>99.94</u>
O for F & Cl	0.02	0.04	0.03
	<u>99.67</u>	<u>99.03</u>	<u>99.91</u>

The molecular proportions for the pure mineral C calculated from the above figures are as follows :

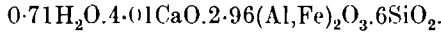
	Molec. Propns.	No. of (O, OH, F) atoms.	No. of metal atoms on basis of 26 O atoms.
SiO ₂	0.620	1.240	6.03
TiO ₂	0.004	0.008	0.04
Al ₂ O ₃	0.216	0.648	4.20
Fe ₂ O ₃	0.090	0.270	1.75
FeO	0.009	0.009	0.09
MnO	0.003	0.003	0.03
MgO	0.007	0.007	0.07
CaO	0.415	0.415	4.03
K ₂ O	0.001	0.001	0.02
H ₂ O	0.073	0.073	1.42
F ₂	negligible	—	—

2.674

Except in the deficiency of water, analysis C of the pure mineral corresponds closely with the empirical formula usually adopted for epidote, viz., $\text{HCa}_2\text{Al}_3\text{Si}_3\text{O}_{13}$ or $\text{H}_2\text{O}.4\text{CaO}.3\text{Al}_2\text{O}_3.6\text{SiO}_2$. On the basis of 26 oxygen atoms the analysis gives:



or from the molecular proportions with 6SiO_2 :



In either case, the figures suggest that the mineral C has the exact composition of a normal epidote, except that there is a striking deficiency of over 25 % in the water, i.e., in the hydrogen-content to which it is an index.

But the following unusual chemical behaviour was noticed when the chemical analysis was being carried out:

1. The mineral underwent no colour change after being heated to 1000°C ., and the residue could not be decomposed with concentrated HCl, even after repeated evaporations on the water-bath.
2. The mineral was not attacked by concentrated HCl, either before or after ignition.
3. The mineral was extraordinarily resistant to the attack of fused sodium carbonate.

It seemed possible that the anomaly in regard to tenacity of water and the above abnormalities in chemical reaction were both indicative of some unusual feature in the internal structure of the mineral.

To ascertain whether they were peculiar to this individual specimen of epidote, or common to all occurrences of the mineral, experiments were carried out on three typical examples of epidote most generously supplied from the mineral collection of the British Museum. The chemical behaviour was identical in every case with that observed in the Malvern epidote (specimen C), and the same difficulty was found in driving off the water, as will be seen from the following figures:

	I.	II.	III.
H_2O expelled below 110°C	0.14	0.08	0.01 %
H_2O ,, ,, 1000°C	0.29	0.37	0.24
H_2O ,, on heating with sod. tungstate ...	1.25	1.01	1.00
Total water	1.68	1.46	1.25

- I. Balmedie quarry, five miles north of Aberdeen.
- II. (Clinzoisite), Moneta mine, Timmins district, Ontario.
- III. Kammegg, Steinhaushorn, Haslithal, Canton Bern, Switzerland.

A detailed scrutiny of all the recorded analyses of epidote shows that there are a considerable number of instances in which the figure

for water is low. E. Ludwig (1872) quotes 89 analyses, in which the percentage of water ranges from 1.78 % to 2.46 %, but in only one case is it abnormally low, viz., 0.63 %. W. Eitel (1919) cites 120 analyses of common epidote, of which 32 contain figures below 1.60 % for the water-content: but many of these also are old analyses, in which the loss on ignition was taken as the percentage of water present, a method which, as Eitel remarks, 'leaves very much to be desired'. C. Doelter, in his 'Handbuch der Mineralchemie' (1915) gives over 100 analyses of epidote, and in 10 of these the water-content is low. A search, by the present author, of the literature on epidote has revealed 16 analyses published since the year 1900 in which the percentage of water is less than 1.30 %, and in some cases it falls as low as 0.10–0.30 %. In 6 of the 16 analyses the total for the sum of all the constituents is low by something like 0.5 %, which suggests that in these cases, as in the case of the Malvern epidote, it was impossible to drive off all the water by the methods usually available.

There appears to be no relation between low water-content and the amount of any other constituent present; it does not vary, for example, with the ratio of Fe_2O_3 to Al_2O_3 . The anomalous behaviour of water is evidently not found in all epidotes; but clearly it does exist in some cases.

Now in all ordinary circumstances the water of a rock or mineral, present in the 'combined' as well as in the 'free' state, is completely and easily driven off when the sample under investigation is heated alone for one hour in a silica tube at a temperature of 1000°C . It is very unusual to find any difficulty in obtaining correct figures for water by this method; but W. F. Hillebrand (Bull. U. S. Geol. Surv., 1919, no. 700, p. 78) states that certain minerals, such as talc, topaz, chondrodite, and staurolite, do not give up their water wholly, even over the blast. H. S. Washington mentions the same four minerals as being particularly tenacious of their water. Dr. H. F. Harwood informs me that he personally has only known this method to fail in the case of talc; and Mr. E. G. Radley tells me that he has only known one mineral in addition to those given above which offers special difficulty, namely phlogopite, and even this yields up its water by the silica tube method, if the heating is prolonged for about three hours. It would thus appear that certain types of common epidote must be included in the list of the very few minerals which are extremely retentive of their water. This in itself

is an interesting fact; but its interpretation raises points which may turn out to be of deep significance.

W. F. Hillebrand (*loc. cit.*, p. 65) attempts a classification of the various combinations of hydrogen found in minerals, in accordance with the difficulty of expelling their hydrogen atoms in the form of water. In this scheme he notes that it is most difficult to drive off the water in cases where what he calls the 'acidic' linkage (H) is present, whereas when the 'basic' group (OH) occurs the expulsion of water is much easier. In accordance with this principle, it would appear probable that in those cases where the water of epidote is very firmly held, the hydrogen is present in the 'acidic' rather than the 'basic' state.

Various modifications of the empirical formula of epidote given above have been suggested¹ in which an (OH) group is included, e.g., $(\text{SiO}_4)_3\text{Al}_2(\text{AlOH})\text{Ca}$. But recent X-ray work has revealed the existence of an (OHO) group; and where such a group is present, there is a marked increase in stability. It is conceivable that some such structure as this might occur in certain forms of epidote, and might result in the observed anomaly, viz., the extreme stability of their hydrogen atoms as manifested by their marked tenacity of water. However, until the structure of epidote has been fully worked out by modern X-ray methods, the problem cannot be solved: it is hoped that the pointing out of this curious feature of the mineral may induce some physicist to undertake the task.²

In conclusion the author wishes to thank Dr. A. W. Groves for carrying out two complete analyses and several water determinations, for much helpful discussion of the problem, and for the interest he has displayed in the chemical aspect of the matter; Mr. F. A. Bannister for most generously taking X-ray photographs of the mineral, and for valuable suggestions and advice; Dr. R. W. B. Pearse for carrying out a spectroscopic investigation; Dr. L. J. Spencer for supplying the specimens of normal epidote; Dr. H. F. Harwood and Mr. E. G. Radley for information with regard to their own experiences in the analysis of epidote; and above all to Dr. A. Brammall for constant help and advice.

¹ P. Groth, *Tab. Übers. Min.*, 1889, p. 109; B. Gossner and F. Mussgnug, *Centr. Min., Abt. A*, 1930, p. 369 [*M.A.* 5-324]; D. J. Bujor, *Zeits. Krist.*, 1931, vol. 78, p. 386 [*M.A.* 5-29].

² I am informed by Prof. W. L. Bragg that work is already being carried out on the subject in his laboratory.