VISÉITE, A ZEOLITE WITH THE ANALCIME STRUCTURE AND CONTAINING LINKED SiO_4, PO_4 AND H_xO_4 GROUPS

DUNCAN MCCONNELL, *National Bureau of Standards, Washington, D. C., and The Ohio State University, Columbus, Ohio.*

ABSTRACT

By combining the chemical data given by Mélon with information obtained by powder diffraction methods, a structural analogy between viséite and analcime is established. The cubic or pseudocubic unit cell is 13.65 Å and probably contains: $(Na_2Ca_{10})[(AlO_2)_{20}(SiO_2)_6(PO_2)_{10}(H_3O_2)_{12}]\cdot 16H_2O$. It is concluded, therefore, that a significant number of tetrahedral hydroxyls (H_xO_4) groups) occur in the framework of this tectosilicate-phosphate.

INTRODUCTION

Recent concepts on the isomorphic relationships amongst silicates and phosphates make possible certain mineral correlations which are not consistent with the more restricted classification according to anionic groups. Of particular importance is the possible substitution of $(OH)_4$ groups for both SiO_4 and PO_4 groups. Substitutions of the type $SiO_4 \rightarrow (OH)_4$ have been adequately demonstrated in nesosilicates for plazolite (Pabst, 1937) and grossularoid (Hutton, 1943) and in a nesophosphate, griphite (McConnell, 1942). Complete replacement of SiO_4 by $(OH)_4$ in the garnet structure yields $Ca_3Al_2(OH)_{12}$ and similar isostructural compounds (Flint, McMurdie, and Wells, 1941). These concepts need no further discussion.

More recently, substitution of $(OH)_4$ statistically for SiO_4 has been proposed to account for certain properties of a phyllosilicate, montmorillonite (McConnell, 1950). The present results will indicate the applicability of these concepts to a tectosilicate-phosphate.

Viséite was assigned the composition of $5CaO\cdot 5Al_2O_3\cdot 3SiO_2\cdot 3P_2O_5\cdot nH_2O$ (where $30>n>25$) by Mélon (1942) on the basis of four partial analyses by himself and by A. Jorissen. With the exception of the water content, which appears to be excessive, Mélon's determinations are quite in accord with theoretical requirements. Nevertheless, no relationship to any other known mineral was suggested by Mélon and it has only been possible to establish such a relationship after obtaining further experimental data and after re-examining these data in light of the theoretical concepts already mentioned.

The writer is indebted to Professor H. Brasseur of the University of Liège, Belgium, for an adequate sample of this rare mineral,* which per-

---

* The residue of the sample of viséite has been presented to the U. S. National Museum and entered under catalogue No. 106,364.

mitted certain additional measurements. It must be admitted that a study of this type would be quite impossible were it not for the prior existence of structural analyses on analcime by Gruner (1928), Taylor (1930), and Hartwig (1931), and on pollucite by Strunz (1936), Náray-Szabó (1938), and Taylor (1938). My colleagues have furnished constructive criticism, particularly P. M. Harris and W. J. McCaughey in Columbus and Herbert Insley and H. F. McMurdie in Washington. Michael Fleischer of the Geological Survey read the manuscript and made several helpful suggestions.

CHEMICAL CONSIDERATIONS

The chemical composition found by Mélon can be accepted without question in all respects except the water content. At 110° C. Mélon re-

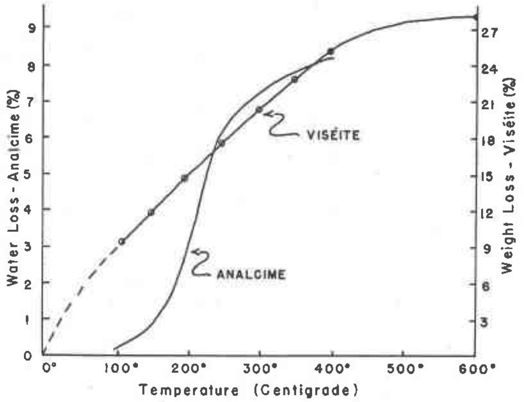

FIG. 1. Weight-loss data for viséite (Mélon) and selected, isobaric, water-loss data for analcime (Milligan and Weiser).

ports liberation of 9.02 per cent of H_2O after 2 hours of heating, but when his dehydration data are plotted (Fig. 1), it becomes immediately noticeable that a downward extension of the dehydration curve indicates loss of water at 0° C. unless the curve increases in slope at lower temperatures. This condition of greatest slope at temperatures below 110° C. is likely to occur only if free moisture is present, so it is deduced that all three of the water determinations are too high and that the average is too high by several per cent when compared with proposed theoretical composition.

A further complication which causes uncertainty in regard to Mélon's water determinations is the fact that the sample of viséite examined by the writer was found to contain organic matter, the presence of which was indicated in two ways: (i) the pale yellowish-green powder turns brown on heating for several hours at 200° to 250° C. and (ii) when boiled in a solution of $AgNO_3$, small fragments of viséite turn black. Inasmuch as Mélon's water determinations appear to have been made solely by measuring loss in weight on heating, it seems highly probable that an unknown, though possibly significant, error may have resulted if organic material was present in his samples. The ability of analcime to occlude organic matter has been investigated by Barrer and Ibbitson (1944). Thus the occlusion of organic matter by viséite is not surprising, although it apparently escaped detection previously.

It should be emphasized, however, that the dehydration data obtained by Mélon (Fig. 1) probably do not represent equilibrium conditions because the isobaric dehydration data for viséite should not give a simple curve. If as postulated here, viséite is a definite hydrate, it should produce a dehydration curve of the type obtained for natrolite or for scolecite by Milligan and Weiser (1937). These authors were able to show that the erroneous, smooth curve which Kelley, Jenny, and Brown (1936) obtained for scolecite can be attributed to failure to maintain a constant aqueous vapor pressure or to allowance of insufficient time to permit establishment of equilibrium. For some points as many as 1200 hours were required, according to Milligan and Weiser. In the present instance, the quality and quantity of the viséite sample preclude precision measurement of isobaric dehydration.

Analyses for the non-volatile constituents indicated the approximate oxide ratios: 5CaO, $5Al_2O_3$, $3SiO_2$ and $3P_2O_5$. In addition 1.77 per cent of Na_2O and 0.67 per cent of fluorine were obtained. The latter constituent can substitute for hydroxyl ions in the structure but, since the amount present is not particularly significant, fluorine will be disregarded in all further considerations. The soda, however, will be taken into account.

If a perfect analogy with analcime is assumed, it is possible to formulate the chemical relationships in a series of simple steps, as follows:

The structural unit of analcime is:

$$Na_{16}[(Al_{16}Si_{32})O_{96}]\cdot 16H_2O.$$

This can be written in general form as:

$$X_{16}[(Y_{16}Z_{32})O_{96}]\cdot 16H_2O.$$

Examining the analytical data, one finds for viséite:

$$16X \rightleftharpoons 2Na + 10Ca + 4\text{ vacant positions}$$

$$16Y + 32Z \rightleftharpoons 20Al + 6Si + 10P + 12(H_3).$$

Thus viséite becomes:

$$(Na_2Ca_{10})[(Al_{20}Si_6P_{10}H_{36})O_{96}]\cdot 16H_2O$$

or

$$(Na_2Ca_{10})\left[(AlO_2)_{20}(SiO_2)_6(PO_2)_{10}(H_3O_2)_{12}\right]\cdot 16H_2O$$

where the brackets enclose the constituents of the structural framework.

The weight per cents required by this theoretical formula are compared with the average results given by Mélon in Table 1. The ratios of the non-volatile oxides indicate good agreement, particularly if an error in the water determination is assumed and other constituents are recalculated on this basis (Column 6). Thus, it can be concluded that in spite of the complex isomorphic substitutions encountered, the ratios suggested by Mélon are approximately correct, but they are somewhat improved if the sodium is considered. In light of the isomorphic relation $AlO_4 \rightarrow SiO_4 \rightarrow PO_4$, the slight excesses of SiO_2 and P_2O_5 and the slight deficiency of Al_2O_3 are quite understandable.

TABLE 1. CALCULATION OF THE CHEMICAL COMPOSITION OF VISÉITE ACCORDING TO THE ANALCIME STRUCTURE

(1) Oxides	(2) Theoretical oxide ratios	(3) Mol. wts.	(4) Weight percents (theoretical)	(5) Experimental results (average)	(6) Experimental results (re-calculated using theoretical water content)
Na_2O	1	62	1.87	1.77	1.97
CaO	10	561	16.88	14.79	16.50
Al_2O_3	10	1019	30.65	26.15	29.18
SiO_2	6	360	10.83	9.93	11.08
P_2O_5	5	710	21.36	20.49	22.86
H_2O	34	612	18.41	26.11	(18.41)
F	—	—	—	0.67	—
			100.00	99.91	100.00

Thus by assuming a structural analogy with analcime, it is possible to account for the chemical composition of viséite. It remains to examine the validity of this structural analogy.

PHYSICAL PROPERTIES

Before proceeding to a detailed consideration of the contents of the unit cell, discussion of the physical and optical properties of viséite and analcime might be advantageous. Comparative data follow.

	Analcime	*Viséite*
Optical character	isotropic or nearly so	isotropic
Refractive index	1.48–1.49	1.53
Specific gravity	2.22–2.29	2.2
Fusibility	2½	2½
Hardness	5–5½	3–4
Behavior with HCl	gelatinizes	gelatinizes

In comparing analcime and viséite it is noteworthy that the refractive index of the latter mineral is greater whereas the density is less. Unless the ionic refractivity of $(H_3O_2)^-$ is unexpectedly large, no explanation of this phenomenon is forthcoming. In part, the higher refractive index of viséite is probably explainable in view of the significantly greater ionic refractivity of Ca as compared with Na. The hardness would be expected to decline with the introduction of hydrogen in place of silicon.

The similarities of these physical properties deserve attention because they offer important clues to structural relationships. The ability to gelatinize with HCl is a property typical of tectosilicates in which Al substitutes for Si and $Al:Si>2:3$ (Murata, 1943). Evidently the phosphate ions do not significantly decrease the ability to gelatinize and there is no theoretical reason why they should, except insofar as they would affect the concentration relations.

STRUCTURAL DATA

Powder diffraction patterns of viséite were obtained in precision cameras with a diameter of 114.6 mm. using CuK_α and FeK_α radiation. The patterns were not as sharp and clear as might have been desired but, nevertheless, it soon became apparent that many of the diffraction lines of viséite were similar in both intensity and spacing to those of analcime (Table 2).

Because of the existence of abundant experimental data on analcime (Gruner, 1928; Taylor, 1930; Hartwig, 1931), the interpretation of the pattern of viséite was a simple matter, once these similarities had been discovered. Several important conclusions are permissible from these data:

(*a*) The structure of viséite is probably essentially similar to the open framework of linked AlO_4 and SiO_4 tetrahedra which constitutes analcime according to Taylor (1930) and later workers.

(*b*) The oxygen framework of viséite probably contains 96 oxygens (exclusive of water) and the unit cell probably contains 16 water molecules.

(*c*) Inasmuch as the silica content is completely inadequate to build such a framework with the alumina content, PO_4 and H_xO_4 tetrahedra

TABLE 2. COMPARISON OF POWDER DIFFRACTION DATA FOR ANALCIME AND VISÉITE (CU K_α RADIATION, $r=57.3$ mm.)

No.	Indices	Analcime		Viséite		
		d	I	I	d	a_0
1	211	5.57	9	4	5.68	13.91
2	220	4.87	4	1	4.98	14.08
3	321	3.66	2			
4	400	3.42	10	5	3.46	13.84
5	332	2.915	7	10	2.92	13.70
6	422	2.800	2			
7	510, 431	2.690	3			
8	521	2.505	3			
9	440	2.430	2			
10	611, 532	2.222	3	2	2.20	13.56
11	620	2.171	1			
12	541	2.122	1	<1	2.11	13.67
13	631	2.023	1	<1	2.014	13.66
14	640	1.903	4	3	1.886	13.60
15	721, 633, 552	1.870	3			
16	732, 651	1.746	5	6	1.740	13.70
17	800	1.719	2			
18	811, 741, 554	1.692	3			
19	820, 644	1.668	1			
20	822, 660	1.622	1			
21	831, 750, 743	1.598	3			
22	842	1.501	2	Diffuse band		
23	921, 761, 655	1.482	2			
24	664	1.465	1			
25	930, 851, 754	1.449	1			
26	932, 736	1.417	3			
27	941, 853, 770	1.389	<1	1	1.380	13.66
28	10.00, 860	1.376	1			
29	10.11, 772	1.361	4			
30	950, 943	—	—	1	1.323	13.62
31	10.31, 952, 765	1.307	2			
32	871, 855, 774	1.287	3	1	1.282	13.69
33	10.33, 961	1.264	2			
34*	11.30, 970	—	—	2	1.196	13.64
35*	10.62	—	—	2	1.155	13.67
36*	12.00, 884	—	—	1	1.138	13.66
37*	12.40, 10.64	—	—	1	1.105	13.62

* For lines with $2\theta > 75°$ similarities between the patterns of viséite and analcime apparently do not exist, and lines for analcime with $d < 1.264$ consequently are not tabulated here.

must occur in this framework with essentially the same linkages as the AlO_4 and SiO_4 tetrahedra.

If these premises are acceptable, it becomes possible to reconstruct the atomic constituents of the unit cell from a knowledge of the analysis, as follows:

96 O	20 Al	10 Ca	2 Na	6 Si	10 P	36 H	16 H_2O
1536	540	400	46	168	310	36	288/3324

A further test of these premises can be applied. If 13.65 Å is taken as the edge of the unit cube, then

$$\rho = \frac{1.66 \times 3324}{(13.65)^3} = 2.17$$

and this calculated density shows good agreement with the specific gravity determination of 2.2, which Mélon made with a pycnometer.

The structure of viséite is highly defective, as indicated by the broad diffuse nature of the low-order diffraction lines as well as the disappearance of many of the low intensity reflections. Therefore, although there are marked similarities between the structures of viséite and analcime, one can not conclude that viséite is truly cubic. However, it seems reasonable to conclude that the framework structure of tetrahedral groups obtains in both instances, and the disorder of viséite arises largely from non-systematic substitution of phosphorus and hydrogen for silicon, as well as vacancies in the sodium positions.

In all of the above considerations the structure of analcime has been assumed to be in accord with the proposal of Taylor (1930) rather than the proposal of Náray-Szabó (1938*a*). Taylor (1938) has presented certain objections to the structure described by Náray-Szabó (1938*a*), which seem to be valid. Admitting that such a highly defective structure as viséite cannot furnish critical evidence concerning the relative merits of these structures for analcime, nevertheless, it is interesting to assume the structure of Náray-Szabó in order to make certain comparisons, as follows:

	Structure of Taylor	*Structure of Naray-Szabo*
Theoretical Na positions (analcime)	24	16
Number occupied in viséite	12	12
Number occupied in analcime	16	16
Number of H_2O positions (analcime)	16	24
Number of H_2O positions (viséite)	16	24
Calculated density (viséite)	2.17	2.26
Weight per cent of H_2O (viséite)	18.41	21.80

Although the experimental data for viséite, show better agreement with the water content of 24 molecules, the agreement is still far from satisfactory.

Still another possible structure for viséite can be obtained by assuming that half of Taylor's 24 positions for large cations are occupied by Ca and Na while the other half are occupied by water molecules. Under these circumstances the calculated density becomes 2.31 and the calculated water content 23.39 per cent, the oxide ratios then being: Na_2O, $10CaO$, $10Al_2O_3$, $6SiO_2$, $5P_2O_5$ and $46H_2O$. Still another possibility would be the placement of water molecules in the vacant positions for large cations in the structure of Náray-Szabó, in which case the number of water molecules would be the same, i.e. 46. The analytical data will not permit selection of one probable structure amongst the several possibilities.

Previous studies of structures related to nesosilicates and nesophosphates have indicated the existence of separated H_4O_4 groups. The present calculations are consistent with the postulate of adjacent H_3O_4 groups in which the tetrahedrally arranged oxygen atoms are shared between neighboring similar groups, thus giving an over-all composition for this part of the structure of $(H_3O_2)^-$. Because of uncertainty arising from the non-critical nature of the analytical data for viséite, it seems best to regard these tetrahedral groups merely as H_xO_4 and thus avoid a premature conclusion concerning the number of hydrogens associated with 4 oxygens. Certainly the geometrical concept of H_4O_4 is not as disturbing as H_3O_4, unless it is assumed that the tetrahedra are significantly distorted.

SUMMARY

Viséite has a highly defective structure which is essentially pseudocubic. The chemical, physical, optical, and x-ray diffraction data indicate analogies between the structures of analcime and viséite. Inasmuch as the Si, P and Al contents of viséite are completely inadequate to build a structural framework similar to that of analcime, oxygen tetrahedra containing hydrogen ions are called upon to complete the framework. The tetrahedral group, H_xO_4, is tetrahedrally linked and x appears to be 3, giving rise to $(H_3O_2)^-$. The structural formula suggested for the average unit cell of viséite is: $(Na_2Ca_{10})[(AlO_2)_{20}(SiO_2)_6(PO_2)_{10}(H_3O_2)_{12}]\cdot 16H_2O$. Half of Taylor's 24 positions for sodium appear to be vacant in viséite. The edge of the unit cell is 13.65 Å which permits calculation of the density as 2.17. By pycnometer measurement Mélon obtained 2.2.

REFERENCES

BARRER, R. M., AND IBBITSON, D. A. (1944), Occlusion of hydrocarbons by chabazite and analcime: *Trans. Faraday Soc.*, **40**, 195–206.

FLINT, E. P., McMURDIE, H. F., AND WELLS, L. S. (1941), Hydrothermal and x-ray studies of the garnet-hydrogarnet series and the relationship of the series to hydration products of portland cement: *Nat. Bur. Standards, Jour. Research*, **26,** 13–33.

Gruner, J. W. (1928), Die Struktur des Analcims. I. Die Raumgruppe: *Zeits. Krist.*, **68,** 363–378.

Hartwig, W. (1931), Strukturbestimmung des Analcims: *Zeits. Krist.*, **78,** 173–207.

Hutton, C. O. (1943), Hydrogrossular, a new mineral of the garnet-hydrogarnet series: *Trans. Royal Soc. New Zealand*, **73,** 174–183.

Kelley, W. P., Jenny, H., and Brown, S. M. (1936), Hydration of minerals and soil colloids in relation to crystal structure: *Soil Sci.*, **41,** 259–274.

McConnell, Duncan (1942), Griphite, a hydrophosphate garnetoid: *Am. Mineral.*, **27,** 452–461.

——— (1950), The crystal chemistry of montmorillonite: *Am. Mineral.*, **35,** 166–172.

Mélon, J. (1942), La Viséite, nouvelle espèce minérale: *Ann. Soc. Géol. Belg.*, **66,** *B*53–*B*56.

Milligan, W. O., and Weiser, H. B. (1937), The mechanism of the dehydration of zeolites: *Jour. Phys. Chem.*, **41,** 1029–1040.

Murata, K. J. (1943), Internal structure of silicate minerals that gelatinize with acid: *Am. Mineral.*, **28,** 545–562. (Also: *U. S. Geol. Survey, Bull.*, **950,** 25–33 (1946).

Náray-Szabó, St. v. (1938*a*), Die Struktur des Pollucits Cs $AlSi_2O_6 \cdot xH_2O$: *Zeits. Krist.*, **99,** 277–282.

——— (1938*b*), Note on the structure of analcime: *Zeits. Krist.* **99,** 291.

Pabst, Adolf (1937), The crystal structure of plazolite: *Am. Mineral.*, **22,** 861–868.

Strunz, H. (1936), Die chemische Zusammensetzung von Pollucit: *Zeits. Krist.*, **95,** 1–8.

Taylor, W. H. (1930), The structure of analcime ($NaAlSi_2O_6 \cdot H_2O$): *Zeits. Krist.*, **74,** 1–19.

——— (1938), Note on the structures of analcime and pollucite: *Zeits. Krist.*, **99,** 283–290.

Manuscript received Oct. 20, 1951