

THE CRYSTAL CHEMISTRY OF SCAWTITE

DUNCAN McCONNELL,* *Ohio State University, Columbus, Ohio*

AND

JOSEPH MURDOCH, *University of California at Los Angeles, California.*

ABSTRACT

The crystal chemistry of scawtite is interpreted on the basis of a new chemical analysis, together with crystallographic and physical measurements on material from Crestmore, California.

Although no clue to the probable structure is obtained, it is evident that the principal cation (calcium) is not stoichiometrically related to either anion (silicate or carbonate) but rather to their sum. Water (as hydroxyl ions) is an additional complication of minor significance.

It is deduced that the smallest symmetrical unit contains 48 oxygen atoms and that carbon displaces silicon in this structure in the same general manner as has been postulated for the displacement of phosphorus by carbon in carbonate apatites.

INTRODUCTION

Any attempt to resolve the question of the crystal chemistry of a mineral as complex as scawtite must judiciously employ the meager data available and simultaneously consider all reasonable theories that may be applicable. At the outset, the difficulties should not be minimized. Considering the grosser aspects of the chemical data, it becomes apparent that certain cations are essential to this structure: calcium, silicon, carbon, and possibly hydrogen. More careful scrutiny of the analyses leads to the conclusion that no reasonably close approximation to a constant ratio obtains for any two of these cations. Obviously a determination of the structural equivalence of certain cations might contribute significantly to an understanding of the crystal chemistry of this substance.

ANALYTICAL DATA

Two chemical analyses of scawtite have been recorded previously, one by Hey (Tilley, 1930) and another by Scoon (J. D. C. McConnell, 1955). A third analysis is reported here; it is by Goldich and Ingamells. The difficulties of isolating an adequate quantity of pure material have necessitated semimicro methods for certain constituents in several instances. Although it must be admitted that the precision of the analyses may be somewhat less than might be desired, nevertheless, the work has been diligently performed by persons of recognized ability. Therefore significant differences, such as the following, cannot be dismissed because of lack of mutual agreement. Particular attention is directed to the silica

* Special Research Fellow, National Institute of Dental Research, U. S. Public Health Service.

and carbon dioxide of Table 1. It is noticeable that there must exist some type of inverse relationship between the amounts of these constituents. (We cannot suppose that a result for silica would contain an error as great as 20 per cent of the amount present and simultaneously contain an error for volatile constituents as great as 200 per cent of the amount present.) It is essential, therefore, that the chemical data be accepted at face value. That is, any acceptable interpretation must be generally consistent with all of the chemical data.

TABLE 1. ANALYSES OF SCAWTITE

	Scawt Hill (Hey)	Ballycraigy (Scoon)	Crestmore (Goldich-Ingamells)
CaO	46.4	46.1	46.93
SiO ₂	34.2	43.5	41.95
CO ₂	18.0	4.4	5.6
H ₂ O*	—	4.4	4.96
Others*	—	1.2	0.39
	98.6	99.6	99.83

* For Scoon's analysis: R₂O₃=1.2; of total water 0.1 was below 105° C. For the analysis by Goldich and Ingamells: MgO=0.16, Al₂O₃=0.14, total iron as Fe₂O₃=0.07, MnO=0.01, TiO₂=0.01, of total water 0.06 was below 105° C. Further tests indicated: P₂O₅ absent or small, Na₂O and K₂O each less than 0.1 per cent.

INTERPRETATION OF ANALYTICAL DATA

As an initial premise, we are concerned with the question of the substitution of CO₃ groups for SiO₄ groups, as has already been postulated as the probable mechanism for the occurrence of carbon dioxide in carbonate apatites (McConnell, 1952). As previously supposed, the number of oxygen atoms of the entire structure remains fixed, and the symmetrical arrangement is essentially preserved despite very small displacements necessary to form 4 CO₃ groups from oxygens that would otherwise comprise 3 SiO₄ groups. In the case of apatite, the general structure of which is well known, it has been feasible to assume specific loci for the substitution of carbon that are consistent with these general symmetry requirements. In the case of scawtite this is impeded by a lack of knowledge of the structure.

Inasmuch as the crystalline symmetry of silicate structures is determined essentially by the arrangement (or packing) of the oxygen atoms, it is permissible to assume that the number and arrangement of oxygen atoms is the same for all three samples of scawtite that have been analyzed.

The number of oxygen atoms per structural unit can be resolved by a method previously indicated (McConnell, 1954a) provided accurate measurements of the lattice and the specific gravity are available in addition to the chemical data. Although these calculations cannot be accomplished, in the absence of *x*-ray diffraction data for the original material (Tilley, 1930), nevertheless, such calculations can now be made for the material from Crestmore (Murdoch, 1955) and, with slightly less certainty, for the material from Ballycraigy (J. D. C. McConnell, 1955). The uncertainty in the latter case depends upon whether the reported specific gravity is merely a quotation of the determination by Tilley (1930) or represents a new determination.

Calculation of the number of oxygen atoms gives the following results:

<i>Crystallographic data by</i>	<i>Sp. gr.</i>	<i>Oxygens</i>
J. D. C. McConnell	2.77	46.0
J. Murdoch	2.71	47.1

Specific gravity determinations by one of us (J.M.) gave 2.707 (with the Berman balance) and 2.714 (with a pycnometer) at room temperatures.

A prime number as large as 47 is highly improbable. We conclude that the scawtite structure contains 48 oxygens rather than 46, which contains merely a factor of two and another moderately large prime number. This number (48) is the total number of oxygens, including any that occur with hydrogen bonding. Furthermore, it is assumed, in view of energy considerations, that all spaces large enough to be occupied by oxygen atoms are filled; that is, there are no large "holes" in the structure.

Were it possible to discover an analogous structure having similar periodicities, optical properties, etc., a fairly straightforward approach to the crystal chemistry of scawtite would be possible. However, scawtite does not appear to resemble any known structure closely. It shows no resemblance to xonotlite, as suggested by J. D. C. McConnell (1955), for example, either in lattice dimensions or optical properties.

The refractive indices are similar to those of tremolite, and it is possible that the structure of scawtite is composed of double chains of silicate tetrahedra, but neither the orientation nor the periodicities of such chains are suggested by the lattice dimensions obtained by Murdoch (1955) or J. D. C. McConnell (1955).

Allocating the charges of the cations to the 48 oxygen atoms in the proportions indicated by the chemical analyses gives the following results

	<i>Crestmore</i>	<i>Ballycraigy</i>	<i>Scawt Hill</i>
Ca	14.58	14.54	14.26
Si	12.10	12.80	9.82
C	2.22	1.76	7.04
H	9.54	8.64	—

Except for the material from Scawt Hill, it is noticeable that the sums of the silicon and carbon atoms are approximately the same as the numbers of calcium atoms, but the number of hydrogen atoms is about 9.5 for the Crestmore sample, but merely 8.6 for that from Ballycraigy. Unfortunately very little can be concluded concerning the material from Scawt Hill except that it must be considerably lower in water. If then, the tremolite formula is taken as a guide and is written in its most general form $X_7(OH)_2Si_8O_{22}$, and the substitution of carbonate groups $3SiO_4 \rightarrow 4CO_3$ is considered, this formula can be rewritten in doubled form as $Ca_{14}(OH)_4(Si_{16-x}C_{4x/3})O_{44}$, in which case it has 48 oxygen atoms (the probable number in scawtite). In case hydrogens occur in excess of those

TABLE 2. CATION CONTENTS CALCULATED FOR 48 OXYGEN ATOMS

	Crestmore	Ballycraigy	Scawt Hill
Ca	14.58	14.54	14.26
H ₄ (of (OH) ₄)	1.00	1.00	—

Si	12.10	12.80	9.82
C _{4/3}	1.66	1.32	5.28
H ₄ (tetrahedral)	1.38	1.16	—
Σ (tetrahedra)	15.14	15.28	15.10

necessary for the four hydroxyl groups, a concomitant diminution of silicon atoms is taken as evidence of the occurrence of tetrahedral hydroxyls (McConnell, 1954b and 1956) and requires further modification of the formula, thus $Ca_{14}(OH)_4(Si_{16-x-y}C_{4x/3}H_{4y})O_{44}$. The next question is how this general formula fits the chemical analyses of scawtite. In Table 2, then, the subscripts for the derived tremolite formula are given for the scawtite analyses.

Although it cannot be asserted that the Ca to Si ratio is 7:8 (as in tremolite), fairly good results are obtained if the carbonate, silicate and excess hydroxyl hydrogens are summed according to the methods outlined. Particularly, this is true for three samples that gave 18 and 4.4 per cent as their maximum and minimum carbon dioxide contents. This can hardly be a fortuitous relationship despite the fact that it was obtained by indirect methods.

CONCLUSIONS

Thus, although the ratio of Ca to anionic groups in scawtite cannot be decided—there being two possible choices, 7:8 or 1:1—there can be little doubt that the carbon dioxide enters the structure as triangular groups in such a manner that the amount is variable and that silicon

atoms are eliminated as a consequence. Two of the existing analyses strongly imply that the structure may contain hydroxyl ions at particular sites in the structure. Nevertheless, it seems highly probable that groups of tetrahedral hydroxyls occur also, because of the inadequacies in silicon and carbon when compared with the material from Scawt Hill.

ACKNOWLEDGMENTS

The chemical analysis of scawtite was made at the Rock Analysis Laboratory of the University of Minnesota through financial arrangement with the Graduate School of the Ohio State University. This research was supported (with respect to D. McC.) by the National Institutes of Health of the U. S. Public Health Service, and is related indirectly to fundamental studies on the structure and crystal chemistry of teeth and bones.

Added in press. The very recent work of R. E. Moore and Wilhelm Eitel (*Naturwiss.* **44**, 259 (1957)) discusses a borosilicate of the apatite group and raises the question of the coordination number of the boron, i.e. whether the structure contains (BO₃) or (BO₄) or both. Although Gruner and McConnell (*Zeits. Krist.* **97A**, 208–215 (1937)) considered the occurrence of (CO₄) in francolite, the slight displacement of the three oxygens necessary to produce 4(CO₃) rather than 3(CO₄) seems more probable and more closely fits the chemical calculations.

REFERENCES

- McCONNELL, D. (1952), the problem of the carbonate apatites. IV. Structural substitutions involving CO₃ and OH: *Bull. Soc. Franç. Min., Crist.*, **75**, 428–445. (See also: *Jour. Dental Research* **31**, 53–63).
- (1954a), Crystal chemistry of schallerite: *Am. Mineral.*, **39**, 929–936.
- (1954b), Ortho-antigorite and the tetrahedral configuration of hydroxyl ions: *Am. Mineral.*, **39**, 830–831.
- (1956), Comments on tetrahedral hydroxyls: *Am. Mineral.*, **41**, 661.
- McCONNELL, J. D. C. (1955), A chemical, optical and X-ray study of scawtite from Ballycraigy, Larne, N. Ireland: *Am. Mineral.*, **40**, 510–514.
- MURDOCH, J. (1955), Scawtite from Crestmore, California: *Am. Mineral.*, **40**, 505–509.
- TILLEY, C. E. (1930), Scawtite, a new mineral from Scawt Hill, Antrim: *Mineral. Mag.*, **22**, 222–224.

Manuscript received August 19, 1957