COMPOSITION, SPACE GROUP AND UNIT CELL OF HANKSITE

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ABSTRACT

The composition of $9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$ for hanksite is verified. There are 2 formula weights in the hexagonal unit cell, which has $a = 10.46$Å and $c = 21.18$Å; $c/a = 2.02$. The space group is either $C_6^6-(C6_3)$ or $C_{6h}^2-(C6_3/m)$, with the morphological evidence indicating the latter. It is suggested that hanksite may have a superstructure, based on 12 unit cells of Na_2SO_4 I.

The composition of hanksite was originally reported[1] as $4Na_2SO_4 \cdot Na_2CO_3$, with KCl (or NaCl) present as an impurity. It was later shown[2] that an error had been made in the original calculation, and that the ratio of sulfate to carbonate was 9:2. Moreover, the constant percentage of KCl present indicated that this constituent was an essential part of the composition. The resulting formula, $9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$ is in general use, and the only reason for again raising the question as to the composition of hanksite is that Schulten[3] described microscopic crystals of artificial hanksite, which he obtained from a solution containing Na_2SO_4 and Na_2CO_3, with no KCl present. It is obvious that if hanksite can be prepared from a KCl-free solution, KCl cannot be an essential constituent.

Schulten's method is based on the reduced solubility of Na_2SO_4 and Na_2CO_3 in water when NaOH is added. The author has followed the detailed instructions given by Schulten, and has secured material which agrees perfectly with that described by him. Schulten's identification of the material as hanksite was based upon a chemical analysis, and upon approximate measurements of interfacial angles with the microscope. His crystals were about 0.05 by 0.03 mm. in size.

The compound $2Na_2SO_4 \cdot Na_2CO_3$, corresponding to the mineral burkeite, can be easily prepared by the slow evaporation of hot solutions of Na_2SO_4 and Na_2CO_3 in water.[4] It has been shown[5] that there is extensive solid solution of both Na_2SO_4 and Na_2CO_3 in $2Na_2SO_4 \cdot Na_2CO_3$. The range of compositions is reported as varying from $3Na_2SO_4 \cdot Na_2CO_3$ to $Na_2SO_4 \cdot Na_2CO_3$. It would seem evident that Schulten's material be-

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[1] Hidden, W. E., *Am. Jour. Sci.*, **30**, 133–5, 1885; Dana, E. S., and Penfield, S. L., *ibid.*, 136–7.

[2] Pratt, J. H., *Am. Jour. Sci.*, **152**, 133–5, 1896.

[3] Schulten, M. A. de, *Compt. Rend.*, **123**, 1325–7, 1896.

[4] Ramsdell, L. S., *Am. Mineral.*, **22**, 213, 1937.

[5] Schroeder, W. C., Berk, A. A., Partridge, E. P., and Gabriel, A., *Jour. Am. Chem. Soc.*, **58**, 846, 1936.

longs in this solid solution series, with an even higher ratio of sulfate to carbonate, namely, 4:1. The solution which Schulten used had a ratio of sulfate to carbonate of about 8:1, and the crystals precipitated from this solution happened to have approximately a 4:1 ratio, thus seeming to agree with the supposed composition of hanksite.

Schulten described his crystals as hexagonal, with the basal section usually showing a division into six sectors. This agrees with the pseudohexagonal penetration twins observed on synthetic burkeite.[4]

A conclusive proof as to the identity of Schulten's material can be obtained by *x*-ray methods. A powder photograph of crystals prepared according to his instructions, and agreeing with his description, shows that they are not hanksite, but rather material belonging to the Na_2SO_4-Na_2CO_3 solid solution series. They differ from burkeite in having a higher percentage of Na_2SO_4. It thus seems apparent that Schulten did not obtain hanksite crystals from a KCl-free solution.

Positive evidence as to the essential character of the KCl content in hanksite is available from two sources. In the first place, the number of formula weights in the unit cell can be calculated, using the density, unit cell volume, and the weight of one molecule. The result is 2.1 formula weights per unit cell, if the composition is assumed to be $9Na_2SO_4 \cdot 2Na_2CO_3$, whereas the number is 2.002 when the composition of $9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$ is used. Since the number of formula weights should be an integer, the latter result is more plausible. This can be stated in another way. Assuming the number of formula weights per unit cell to be 2, the calculated density for the 9:2 formula is 2.45, and that for the 9:2:1 formula is 2.57. The latter agrees closely with the density of the natural crystals, which is 2.56.

Further evidence as to the essential role of the KCl is found in the behavior of hanksite when heated. If clear fragments of hanksite, appearing homogeneous under the microscope, are fused and cooled, the resulting material consists of a clear groundmass containing microscopic blebs and stringers. Actual fusion is not necessary. Heating to a temperature slightly below the melting point causes hanksite to separate into the two phases. The *x*-ray diffraction pattern of the main phase no longer corresponds to that of hanksite, but is identical to that obtained when Na_2SO_4 and Na_2CO_3 are fused together in the proportion of 9:2. No positive identification of the minor phase has been made, but it appears that upon heating above a certain temperature, hanksite is no longer stable, and decomposes, forming $9Na_2SO_4 \cdot 2Na_2CO_3 + KCl$. The KCl forms less than 5 per cent by weight of the total, and does not show in the powder photographs. The blebs and stringers have an index above that of the ground mass, which agrees with the respective indices for KCl and the Na_2SO_4–Na_2CO_3 fusion.

Comparable results are obtained from melts. If Na_2SO_4 and Na_2CO_3 in the 9:2 ratio are fused together, the product is homogeneous. If KCl be added, corresponding to the 9:2:1 ratio, the blebs and stringers appear. Thus hanksite cannot be synthesized from a melt of the 9:2:1 composition, because it is unstable at the temperature of the melt. The $9Na_2SO_4 \cdot 2Na_2CO_3$ formed by the decomposition of hanksite does not represent a definite compound, but is a member of a solid solution series which will be described later in this paper.

X-RAY DATA

Unit cell. Accurate measurements from high order reflections on Weissenberg films, and from powder photographs standardized with KCl, give the values $a = 10.46$Å and $c = 21.18$Å. These agree closely with those reported by Gossner and Koch.[6] The axial ratio, $c/a = 2.02$, is almost exactly twice that given for the natural crystals, namely, 1.0056. From the cell volume and density, it is found that the unit cell contains $18Na_2SO_4 \cdot 4Na_2CO_3 \cdot 2KCl$.

Symmetry. Laue photographs taken with the *x*-ray beam parallel to the *c* axis show a 6-fold axis, with no vertical planes of symmetry. Photographs taken parallel to the *a* and the intermediate *b* axes likewise show no vertical planes, but a horizontal plane of symmetry is present. This corresponds to the symmetry of the hexagonal bipyramidal class, C_{6h}. However, since a Laue photograph indicates a center of symmetry, whether present or not, both the trigonal bipyramidal, C_{3h}, and the hexagonal pyramidal, C_6, classes are possibilities, for when a center of symmetry is added to either of these, C_{6h} is obtained.

Space group. In none of these three symmetry classes is a rhombohedral unit cell possible, so there is no choice to be made between rhombohedral and hexagonal units. In symmetry class C_{3h} there is only one space group, characterized by a normal rotation axis. C_6 has six space groups, as follows: one with a normal rotation axis; an enantiomorphous pair characterized by screw axes with translations of $\frac{1}{3}$ and $\frac{2}{3}$, respectively; a second enantiomorphous pair with translations of $\frac{1}{6}$ and $\frac{5}{6}$; and a final space group having a screw axis with a translation of $\frac{1}{2}$. The C_{6h} class has only two space groups, one with a normal rotation axis, and one with a screw axis with a translation of $\frac{1}{2}$.

Comparison of 0-level and *n*-level Weissenberg photographs, taken with either the *a* or *b* axes as rotation axes, shows that the translations are doubled on the reciprocal lattice line through the origin and parallel to *c*. This indicates a screw axis with a translation of $\frac{1}{2}$. This immediately eliminates the one space group of C_{3h}, five of the space groups of C_6,

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[6] Gossner, B. and Koch, I. *Zeits. Krist.*, **80**, 461–4, 1931.

and one of C_{6h}, leaving only one space group in each of C_6 and C_{6h} as possibilities. These are C_6^6–($C6_3$) and C_{6h}^2–($C6_3/m$). *X*-ray methods can make no distinction between these two possibilities.

Attempts to obtain etch figures have been unsuccessful. Likewise, tests for pyro- and piezo-electricity have been negative. Therefore, the only remaining evidence lies in the morphology of the crystals. The lack of hemimorphic development suggests that the probable space group is C_{6h}^2($C6_3/m$), but this cannot be regarded as proved.

Possible structure. The unit cell of hanksite contains two molecules, which means that there are 44 Na, 18 SO_4, 4 CO_3 and 2 KCl to be located. The largest number of equivalent points in the space group C_{6h}^2 is 12. These positions are defined by three variable parameters. Special positions of six and four equivalent points have two and one variable parameters, respectively. It would be almost hopeless to attempt a direct determination of such a structure. However, there is some indirect evidence as to a possible structure.

In order to explain this possibility, it must be pointed out that Na_2SO_4 exists in three crystalline modifications: I, the high temperature form, stable only above 241°C.; III, the intermediate form obtained by the inversion of I, and which, although metastable, can be kept at ordinary temperatures for indefinite periods; and V, the low temperature stable form. The high temperature form, I, can be stabilized by the addition of Na_2CO_3.

It has been found[5] by optical methods that melts of Na_2SO_4 and Na_2CO_3 are miscible in all proportions from 0 to 0.75 mole fraction of Na_2CO_3. *X*-ray data confirm the existence of this solid solution series in the range from about 0.1 to 0.6 mole fraction of Na_2CO_3. In this range, diffraction photographs are almost indistinguishable, indicating that CO_3 replaces SO_4 with very little change, either in structure or dimensions. Moreover, except for a slight decrease in spacing, such photographs give data agreeing very closely with those reported for Na_2SO_4 I, taken above 241°C.[7] (Table 1). With less than 0.1 mole fraction of Na_2CO_3, powder photographs indicate that Na_2SO_4 I inverts to III on cooling, but with more than 0.1, the high temperature form persists. Both optical and *x*-ray data indicate that this solid solution series is hexagonal, and it is dimorphous with the low temperature series, which is orthorhombic, pseudo-hexagonal, and includes synthetic burkeite and possibly Na_2SO_4 III.

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[7] Kracek, F. C. and Ksanda, C. J., Polymorphism of sodium sulfate. IV. *X*-ray analysis. *Jour. Phys. Chem.*, **34**, 1741–4, 1930.

TABLE 1. DIFFRACTION DATA FOR Na_2SO_4 I ABOVE 241° AND FOR THE HEXAGONAL Na_2SO_4-Na_2CO_3 SOLID SOLUTION

Na_2SO_4 I (Kracek and Ksanda)[7]		Na_2SO_4-Na_2CO_3 2:1	
Spacing	Intensity	Spacing	Intensity
4.684A	3	4.60A	2
3.917	10	3.85	9
3.616	6	3.55	7
2.863	9	2.80	10
2.699	9	2.66	10
2.348	2	2.30	1
2.213	2	2.18	5
1.961	7	1.92	9
1.814	2	1.77	5
1.583	2	1.56	4
1.555	3	1.53	2
1.503	4	1.47	4
1.427	1	1.40	1
1.348	2	1.33	3
1.27	2	1.25	1
1.21	2	1.20	2
1.18	2	1.17	1

As previously stated, when hanksite is heated above a critical temperature, it decomposes to form $9Na_2SO_4 \cdot 2Na_2CO_3$ and KCl. The diffraction pattern of this material corresponds to that of the high temperature hexagonal Na_2SO_4-Na_2CO_3 series. However, the pattern has marked resemblances to the original hanksite pattern. Most of the lines of the fused hanksite are also found in the normal hanksite pattern, with a slight decrease in spacing. But the hanksite pattern has additional lines, not appearing in the pattern of the Na_2SO_4–Na_2CO_3 series, which cause it to correspond to a different hexagonal unit. The axial ratio for the hanksite unit is 2.02, whereas the value of c/a for the Na_2SO_4-Na_2CO_3 series is about 1.34. The indices $(hk\bar{i}l)$ of the reflecting planes of the normal and of fused hanksite have the relationship shown in Table 2. It will be noticed that for the lines common to both patterns, all values of h and k for fused hanksite are multiplied by 2, and those of l are multiplied by 3, to give the corresponding indices of normal hanksite. This indicates that the unit cell of hanksite has a c axis 3 times as long, and an a axis 2 times as long as those of the Na_2SO_4-Na_2CO_3 series, or of Na_2SO_4 I.

TABLE 2. PARTIAL POWDER PHOTOGRAPH DATA FOR HANKSITE AND THE HEXAGONAL Na_2SO_4-Na_2CO_3 SOLID SOLUTION

Hanksite 9:2:1		Na_2SO_4-Na_2CO_3 9:2	
Spacing	Indices	Spacing	Indices
5.24A	$11\bar{2}0$	—	—
4.58	$20\bar{2}0$	4.60A	$10\bar{1}0$
3.83	$20\bar{2}3$	3.85	$10\bar{1}1$
3.54	0006	3.55	0002
3.42	$21\bar{3}0$	—	—
2.78	$20\bar{2}6$	2.80	$10\bar{1}2$
2.63	$22\bar{4}0$	2.66	$11\bar{2}0$
2.52	$31\bar{4}0$	—	—
2.27	$40\bar{4}0$	2.30	$20\bar{2}0$
2.16	$40\bar{4}3$	2.18	$20\bar{2}1$
1.91	$40\bar{4}6$	1.92	$20\bar{2}2$
1.77	00012	1.78	0004

This relationship between the unit cells of hanksite, Na_2SO_4 I and the Na_2SO_4-Na_2CO_3 series, suggests that hanksite has a structure based upon $3\times2\times2=12$ smaller pseudo-cells, each corresponding to one unit cell of Na_2SO_4. This latter cell contains 2 molecules of Na_2SO_4, and 12 such cells would contain the equivalent of 24 molecules.

If the Na_2CO_3 and KCl content of hanksite were distributed statistically throughout the Na_2SO_4, the true unit would be the Na_2SO_4 unit cell. This would seem to be the situation where only CO_3 replaces the SO_4, as in the solid solution series. But if they occupy definite positions, the true unit must be larger. For example, there are only 2 molecules of KCl for every 18 of Na_2SO_4, so the unit of repetition must be at least 9 times as large. The unit as actually determined contains $18Na_2SO_4+4Na_2CO_3+2KCl$, which gives a total of $24(Na_2SO_4, Na_2CO_3, KCl)$, if the three different molecules are grouped together. Assuming that the Na_2SO_4 and Na_2CO_3 are mutually replaceable, then 2 out of every 24 molecules are KCl, and the unit of repetition must be 12 times as large as the simple Na_2SO_4 unit.

According to this interpretation, the hanksite structure would be described as a superstructure, based on 12 unit cells of Na_2SO_4 I, in which the KCl occupies a definite position. The conditions under which the KCl will assume this definite position are not known, but apparently the arrangement is not highly stable. Heating causes it to break down, and the structure degenerates into the simple Na_2SO_4 I type.

It should be pointed out that there is no proof as yet of the existence of this superstructure, but in the absence of any direct determination of the structure, this conjecture offers a plausible explanation of the observed relationships between hanksite, Na_2SO_4 I, and the Na_2SO_4-Na_2CO_3 series.