

# AN X-RAY STUDY OF THE SYSTEM K<sub>2</sub>SO<sub>4</sub>-MgSO<sub>4</sub>-CaSO<sub>4</sub>

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## ABSTRACT

X-ray examination of fused mixtures of K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub> and CaSO<sub>4</sub> revealed a continuous isomorphous series with K<sub>2</sub>Mg<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as end-members. No other compounds were found. The members of this series are simple cubic, with four molecules in the unit cell, and the length of the cube edge varies from 9.96Å for the Mg to 10.37Å for the Ca end-member. The data from this system suggest an explanation concerning the extraction of K<sub>2</sub>SO<sub>4</sub> from calcined polyhalite.

For several years the Nonmetallic Minerals Experiment Station of the U. S. Bureau of Mines, at New Brunswick, N. J., has been working on the extraction of potash from the mineral polyhalite, 2CaSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>·2H<sub>2</sub>O. During the course of this investigation the writer has assisted by making x-ray examinations of various samples which have been submitted to him. Certain of these x-ray photographs, together with additional ones from samples prepared in our own laboratory, furnish considerable information concerning the system K<sub>2</sub>SO<sub>4</sub>-MgSO<sub>4</sub>-CaSO<sub>4</sub>. The compositions of the samples for which x-ray data were obtained are indicated in the diagram of figure 1. These samples were prepared either by fusion of the appropriate minerals, or by the fusion of molecular proportions of the individual sulfates. Since no single crystals were available, the powder method alone was used.

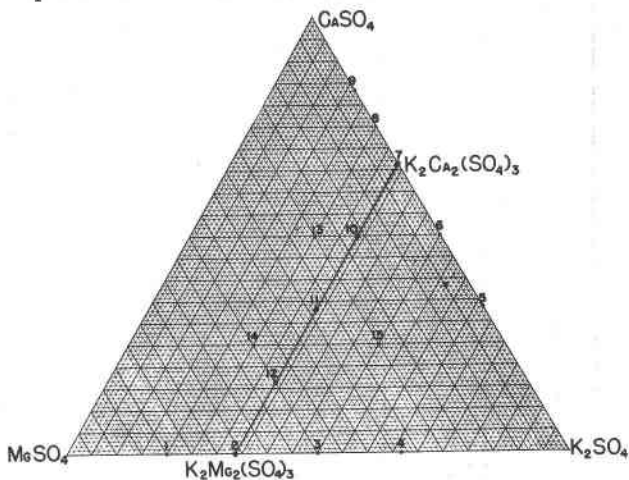


FIG. 1. Molecular compositions of samples studied.

In the system  $K_2SO_4$ - $MgSO_4$  samples ranging in composition from 20 per cent to 66 per cent of  $K_2SO_4$  were prepared (numbers 1-4). The only compound formed was  $K_2Mg_2(SO_4)_3$ . This corresponds in composition to the mineral langbeinite, and agrees with it in both optical<sup>1</sup> and  $x$ -ray data. As the composition shifts in either direction toward  $K_2SO_4$  or  $MgSO_4$ , the lines of the  $K_2Mg_2(SO_4)_3$  pattern remain unchanged, and additional lines of the corresponding simple sulfate appear.

The powder photographs of  $K_2Mg_2(SO_4)_3$  indicate a cubic unit

TABLE 1  
POWDER PHOTOGRAPH DATA FROM SYNTHETIC LANGBEINITE

| Spacing<br>in Å | <i>hkl</i> | Observed<br>intensity |  |
|-----------------|------------|-----------------------|--|
| 4.07            | 112        | m                     |  |
| 3.15            | 130        | vs                    |  |
| 3.00            | 113        | m                     |  |
| 2.77            | 230        | m                     | $d_{100} = 9.96 \text{ \AA}$ .                 |
| 2.66            | 123        | s                     | Four molecules $K_2Mg_2(SO_4)_3$ in unit cube. |
| 2.40            | {140}      | m                     | Calculated density 2.77.                       |
|                 | {223}      |                       | Natural langbeinite 2.83.                      |
| 2.28            | 133        | w                     |  |
| 2.16            | 124        | w                     |  |
| 2.12            | 233        | w                     |  |
| 2.03            | 224        | w                     |  |
| 1.95            | {134}      | m                     |  |
|                 | {150}      |                       | vs = very strong                               |
| 1.85            | {234}      | m                     | s = strong                                     |
|                 | {250}      |                       | m = medium                                     |
| 1.73            | {144}      | m                     | w = weak                                       |
|                 | {225}      |                       |  |
| 1.61            | {116}      | ms                    |  |
|                 | {235}      |                       |  |
|                 | {126}      |                       |  |
| 1.55            | {344}      | w                     |  |
|                 | {450}      |                       |  |
| 1.48            | {245}      |                       |  |
|                 | {360}      | m                     |  |
| 1.42            | {236}      | w                     |  |
|                 | {127}      |                       |  |
| 1.35            | {255}      | mw                    |  |
|                 | {336}      |                       |  |

cell, containing four molecules, and having  $d_{100} = 9.96\text{\AA}$ . (Table I). Since the reflections 112, 130, 230, 123, 140, 223, 124, and 233 are impossible for a face-centered cube, and 113, 230, 140, 223, 133, 124, 234 and 250 for a body-centered cube, the space lattice must be simple cubic. Powder photograph data alone are incapable of solving a structure as complex as this one. However, single crystals of the isomorphous  $(\text{NH}_4)_2\text{Ca}_2(\text{SO}_4)_3$  have been obtained, and a determination of its structure is in progress. According to Dana, langbeinite is isometric-tetartohedral. This is confirmed by the crystals of  $(\text{NH}_4)_2\text{Ca}_2(\text{SO}_4)_3$ , which consist of the pyritohedron (210) in combination with a tetrahedron.

The system  $\text{K}_2\text{SO}_4\text{-CaSO}_4$  is similar to the  $\text{K}_2\text{SO}_4\text{-MgSO}_4$  (numbers 5-9). The only compound found was  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ . Although this compound shows low double refraction,<sup>1</sup> the diffraction pattern is quite similar to that of  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ , and agrees with a unit cube having  $d_{100} = 10.37\text{\AA}$ .

No compounds could be found in the system  $\text{CaSO}_4\text{-MgSO}_4$ , nor are there any known hydrated double salts of these two sulfates.

A series of samples in the ternary system  $\text{CaSO}_4\text{-MgSO}_4\text{-K}_2\text{SO}_4$  revealed that the two compounds  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  are the end members of an isomorphous series, in which the  $\text{Mg}_2$  is apparently replaceable in all proportions by  $\text{Ca}_2$  (numbers 10-12). The size of the unit cube increases with increasing Ca content, as is shown in table 2. The  $x$ -ray patterns show a continuous series, with no evidence of a definite compound  $\text{K}_2\text{MgCa}(\text{SO}_4)_3$ , such as dolomite in the  $\text{CaCO}_3\text{-MgCO}_3$  system. Complete replacement of magnesium by calcium, such as is here found, is very unusual.

TABLE 2

| INCREASE IN SIZE OF UNIT CELL WITH INCREASING CALCIUM       |                              |
|---|------------------------------|
| $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$                      | $d_{100} = 9.96\text{\AA}$ . |
| $\text{K}_2(\text{Mg}_{3/2}\text{Ca}_{1/2})(\text{SO}_4)_3$ | 10.05                        |
| $\text{K}_2\text{MgCa}(\text{SO}_4)_3$                      | 10.15                        |
| $\text{K}_2(\text{Ca}_{3/2}\text{Mg}_{1/2})(\text{SO}_4)_3$ | 10.24                        |
| $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$                      | 10.37                        |

The  $x$ -ray patterns obtained from the calcium end of this series are of poorer quality than those from samples higher in magnesium. The lines are more diffuse, and not as many are present on the films. This fact, together with the double refraction, may indicate

that through the introduction of the larger calcium atoms, the structure is in a strained condition. That this structure is a reasonably stable one, however, is shown by the fact that this compound can be formed by the dehydration of syngenite,  $K_2SO_4 \cdot CaSO_4 \cdot H_2O$  at  $400^\circ C$ . The pattern of this dehydrated material is identical with that of fused syngenite (number 6), both consisting of the lines of  $K_2Ca_2(SO_4)_3$  and  $CaSO_4$ .

Sample number 13 represents the composition of dehydrated polyhalite. The pattern in this case consists of the lines of  $K_2CaMg(SO_4)_3$  and  $CaSO_4$ . This is no confirmation of the existence of a definite compound with Ca and Mg in equal proportions. Since  $CaSO_4$  is present in excess in the polyhalite, it crystallizes out as anhydrite, and the composition of the remainder drops until it intersects the line of the isomorphous series (figure 1). Likewise for samples 14 and 15, the patterns consist of the lines of  $K_2CaMg(SO_4)_3$  with those of  $K_2SO_4$  and  $MgSO_4$ , respectively. Thus all stable compounds in the range studied lie on the line joining the two compounds.

#### THE DEHYDRATION OF POLYHALITE

Many experiments have been carried on to determine the optimum conditions for the extraction of potash from polyhalite.<sup>2,3,4,5</sup> Polyhalite loses its water of crystallization rather suddenly at a temperature above  $300^\circ C$ . It has been found that when it is calcined at a temperature of about  $475^\circ C$ . for a short time, a product of low density is formed, from which almost complete extraction of  $K_2SO_4$  and  $MgSO_4$  is obtained with hot water. The  $CaSO_4$  residue is peculiar in that it is rapidly converted to gypsum when treated with cold water. This latter phenomena suggested the possibility of the residue being "soluble" anhydrite, but x-ray photographs show it to be normal anhydrite.

If the polyhalite is calcined at a higher temperature, or for a longer time, the product is more dense, and the percentage of extraction is lower. A still higher density and a lower yield is obtained from fused polyhalite. As stated previously, the fused product consists of isotropic  $K_2CaMg(SO_4)_3$  and  $CaSO_4$ .

The initial problem in this study was to determine what differences exist between the properly calcined, over-calcined, and the fused polyhalite. Powder photographs of all three are practically

identical. Slightly sharper patterns are obtained from the fused material, and some of these films showed a few weak lines which were either not present or rather doubtful in the films of the calcined samples. This indicates a difference in the perfection of crystallization rather than a variation in structure or composition.

When polyhalite is dehydrated, there is a loss of water and a consequent decrease in density. At some stage, whether at complete dehydration or not is not known, the structure becomes unstable, and breaks down into  $K_2CaMg(SO_4)_3$  and  $CaSO_4$ . At the initial stage the material consists of porous dehydrated grains, composed of an intimate mixture of sub-microscopic crystallites of the two decomposition products. When this is treated with hot water, the  $K_2CaMg(SO_4)_3$  dissolves, leaving a skeleton of  $CaSO_4$ , on which is redeposited the  $CaSO_4$  which went into solution as part of the  $K_2CaMg(SO_4)_3$ .

The formation of two distinct compounds from the polyhalite when dehydrated, implies an actual migration of atoms and a recrystallization. The velocity of such a reaction should increase with temperature. With increased temperature (or time) the larger crystallites will grow at the expense of the smaller, forming a more coarsely crystallized and a more dense material. Such changes might reasonably be expected to cause poorer yields on extraction with hot water. Actual fusion, resulting in well-formed crystals of anhydrite in a dense groundmass of  $K_2CaMg(SO_4)_3$ , gives a product with a still lower yield.

It might be possible to carry out this process so slowly that the intermediate stages of dehydration, decomposition and recrystallization could be separated. But under ordinary conditions the exteriors of the grains probably have decomposed and possibly recrystallized before the interiors are completely dehydrated. Accordingly the optimum conditions for calcination are those that give most decomposition with least recrystallization. These same conditions would likewise give the most porous and minutely crystalline residue of  $CaSO_4$ , and therefore most easily converted into gypsum by cold water.

This interpretation is in harmony with such observations as are obtainable by microscopic study, and also agree with the increase in sharpness of the diffraction patterns from the fused samples over those from the low temperature calcines.

## REFERENCES

- (1) Private communication from Dr. A. Gabriel, petrographer at Nonmetallic Minerals Experiment Station, New Brunswick, N. J.
- (2) A study of the properties of polyhalite pertaining to the extraction of potash. III—Calcination of polyhalite in a laboratory-sized rotary kiln, L. Clarke, J. M. Davidson and H. H. Storch: *Bur. Mines, Reports of Investigations*, **3061**, 1931.
- (3) A study of the properties of Texas polyhalite pertaining to the extraction of potash. VI—A study of the calcination of polyhalite in a 6 by 132 inch rotary kiln. Density measurements as control tests for efficiency of calcination, J. E. Conley, F. Fraas and J. M. Davidson: *Ibid.*, **3167**, 1932.
- (4) A study of the properties of Texas-New Mexico polyhalite pertaining to the extraction of potash. VII—Effect of particle size, sodium chloride concentration and temperature upon hot extraction by a multistage process, J. E. Conley and F. Fraas: *Ibid.*, **3210**, 1933.
- (5) Extraction of potash from polyhalite, J. E. Conley and F. Fraas: *Ind. Eng. Chem.*, vol. **25**, pp. 1002-9, 1933.