THE CRYSTALLOGRAPHY OF MCGOVERNITE, A COMPLEX ARSENOSILICATE

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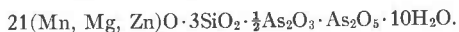
ABSTRACT

Mcgovernite has been found to have the largest unit cell yet discovered for an inorganic material which is not a stacking polytype. The mineral has probable space group $R\bar{3}2/c$ and unit cell dimensions $a = 8.22$ Å, $c = 205.5$ Å, as determined from oscillation photographs and confirmed by precession photographs. The primitive rhombohedral cell contains $6 \ Mn_9Mg_4Zn_2As_2Si_2O_{17}(OH)_{14}$. The cell dimensions indicate a close relationship to dixenite, another complex arsenosilicate.

INTRODUCTION

Mcgovernite is a complex arsenosilicate occurring in the zinc deposits at Sterling Hill, New Jersey. Well crystallized material occurs in slightly deformed, mica-like "books" and in coarse granular masses. The mineral is brittle with a very perfect micaceous cleavage. Nearly perfect crystals have a deep red-brown, somewhat bronzy color, while masses have a pearly appearance and a light brown color. The specimens examined were uniaxial positive with a barely detectable birefringence, and had $n_o = 1.761 \pm .002$.

The mineral was first reported by Palache and Bauer (1927) who were not able to determine a simple and satisfactory formula. The simplest empirical expression representing the results of their analysis was

$$21(Mn, Mg, Zn)O \cdot 3SiO_2 \cdot \tfrac{1}{2}As_2O_3 \cdot As_2O_5 \cdot 10H_2O.$$

This formula and the physical properties of the material indicated that it might be related to dixenite, $21(Mn, Ca, Fe)O \cdot 4SiO_2 \cdot 4As_2O_3 \cdot 5H_2O$ (Flink, 1920), and also more remotely related to the friedelite-schallerite group (Bauer and Berman, 1928).

PREPARATION OF CRYSTALS

Cleavage plates taken from well crystallized specimens appeared to be single crystals and, because of the brittle nature of the flakes, were easily broken into fragments of size suitable for x-ray analysis. Diffraction patterns subsequently showed, however, that these plates were not single crystals. Upon examination with an optical goniometer, it was observed that each cleavage surface gave rise to a series of reflections originating from different layers within the volume of the crystal, indicating that the cause of this trouble was partial cleavages in the plate induced by the breaking, rather than twinning or plastic deformation. In some cases, interference fringes were visible along the partially cleaved surfaces.

After considerable difficulty, single-crystal fragments were obtained from extremely thin cleavage plates which could be broken to appropriate size with application of only very slight pressure.

X-Ray Examination

Since the basal cleavage plane was the only morphological feature of aid in orienting the crystals, a c-axis rotation photograph was first obtained. This pattern indicated a (001) spacing which was so enormous that it would prove impossible to resolve the various l levels with the layer-line screens required in any moving-film method. The unit cell and space group were consequently determined with the oscillation method. Although this technique is not as powerful as the moving-film methods (Buerger, 1942a), it was nevertheless possible to unambiguously index all reflections and to determine the unit cell and space group of the crystal.

Five 20° oscillation photographs were obtained at 20° intervals to determine the symmetry along the c axis. MoKα radiation was used in order to obtain a large number of values of h and k. These photographs indicated diffraction symmetry $\bar{3}m$ and exhibited rhombohedral and c-glide space-group extinctions. Different photographs are obtained when the oscillation range is centered about each of two neighboring symmetry planes in a rhombohedral lattice. By comparing the observed l values with those predicted for each of these cases, it was possible to identify the oscillation range. This permitted indexing of all reflections on the films exhibiting the plane of symmetry of the Laue group. Within certain narrow limits, this indexing fixed the orientation of the crystal about c with respect to the x-ray beam, so that the remaining films in the set of oscillation photographs could be indexed.

An approximate value of a was graphically determined in the normal fashion (Buerger, 1942b) from ξ values measured with the aid of a Bernal chart; c was computed from measurements made on a c-axis rotation photograph which was taken with FeKα radiation to increase the separation of the closely spaced l levels. The unit-cell dimensions, as improved from measurements on precession photographs, were:

Referred to hexagonal axes	*Referred to rhombohedral axes*
$a = 8.22 \pm 0.02$ Å	$a = 68.7 \pm 0.3$ Å
$c = 205.5 \pm 1$	$\alpha = 6°52'$

Space group $R3c$ or $R\bar{3}2/c$

The two possibilities for the space group differ only by a center of symmetry and therefore cannot be distinguished by x-ray measurements. A test for piezoelectricity was made with an apparatus similar to that described by Stokes (1947) and yielded negative results. This test does not

entirely eliminate the acentric possibility, but does lend support to $R\bar{3}2/c$ as the most probable space group.

Within the limits imposed by the extreme size of the cell, it was desired to obtain a direct record of the reciprocal lattice. Reflections recorded in this fashion are more readily examined for possibilities of twinning and evidences of substructures. Figure 1 gives a c-axis MoKα precession photograph adjusted for zero-level geometry. The hexagonal nature of the lattice is clear in this photograph, but, since the separation of neighboring levels is very small, the upper levels could not be eliminated by the layer-line screen. These levels were also recorded along with the zero level. This record is therefore a projection of a small slice of the reciprocal lattice onto the zero level and thus has a falsely high symmetry. The various levels were also not resolved on c cone-axis photographs, but appeared as nearly continuous smears of coherent radiation.

Figure 2 shows a zero-level MoKα precession photograph taken about $[11\cdot0]$. The reflections on this photograph have indices of the form $h\bar{h}\cdot l$; the space group allows such reflections to be present only if l is even. It is interesting to note that reflections up to $l=246$ are observable on this film. Figure 3 shows an upper-level precession photograph taken about $[11\cdot0]$ giving general reflections having extinctions due only to the rhombohedral lattice.

TWINNING AND POLYTYPISM

Large cells are suspect since they may have been determined from twinned crystals of material having a smaller cell (Buerger, 1954). No "strange" extinctions were observed in the present study, however. No twinning model based on a smaller cell could be devised to give the observed patterns.

For materials exhibiting a basal cleavage, cells with large spacings are also good candidates for stacking polytypes. Although there is no evidence for a substructure in the photographs of Figs. 2 and 3, several samples from all specimens of mcgovernite available from the Harvard collection* were examined for polytypism. Cleavage flakes, usually imperfect, were optically aligned with their c axes parallel to the spindle of a precession apparatus, and a precession photograph of each was taken about a random direction in the $(00\cdot1)$ plane. By this procedure only $00\cdot l$ reflections were recorded, but these were a sufficient check on the length of c. This method eliminated the time-consuming necessity of orienting the flakes and a search for highly perfect cleavage flakes.

Although the specimens differed widely in physical appearance and

* Harvard Catalog Numbers 90380, 104668, 104674, 105531 (used for the unit cell and space group determination), 105532, 105533 and 105534.
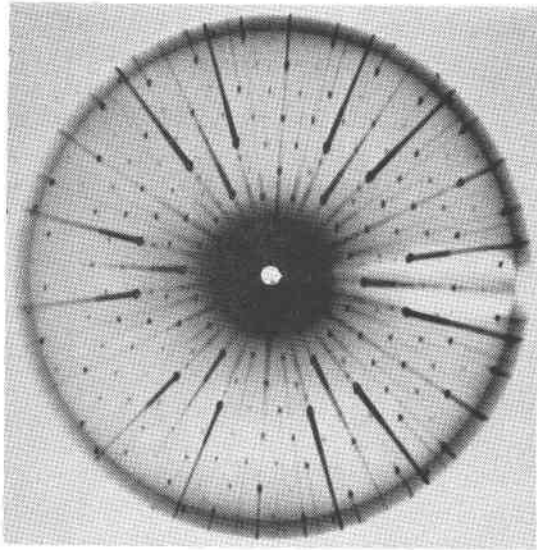
FIG. 1. Precession photograph of mcgovernite, c-axis, with settings for zero-level geometry. MoKα, 35 kv, 15 ma, 68 hours, $\bar{\mu} = 25°$. It was not possible to eliminate all neighboring levels with the layer-line screen. The record is therefore essentially a thin slice of the reciprocal lattice projected parallel to c^*.
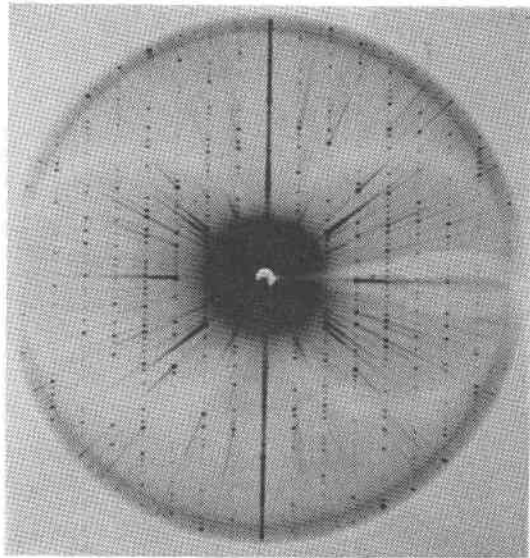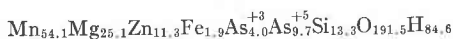

FIG. 2. Precession photograph of mcgovernite, [11.0] axis, zero level. MoKα, 35 kv, 15 ma, 59 hours, $\bar{\mu} = 25°$. Reflections are all of special type $h\bar{h}\cdot l$ and exhibit both rhombohedral and c-glide extinctions.

grain size, no polytypes or further evidences for twinning were discovered.

CHEMICAL FORMULA

Because of the large variety of atomic species present, including the unusual occurrence of arsenic in two oxidation states, Palache and Bauer could assign no satisfactory formula to the mineral. Knowledge of the unit-cell dimensions now permits computation of the numbers of each type of atom in the unit cell, but because of the large cell volume the numbers tend to be large and subject to considerable uncertainty. The determination of a formula is therefore still somewhat arbitrary.

The triple hexagonal unit cell has a volume of 12,000 Å³, which, when combined with an experimental density of 3.719 gr./cm.³, results in a molecular weight per cell of 26,900. In Table 1 this is divided among the various atoms on the basis of Palache and Bauer's analysis. This leads to an empirical content for the primitive rhombohedral cell of

$$\text{Mn}_{54.1}\text{Mg}_{25.1}\text{Zn}_{11.3}\text{Fe}_{1.9}\text{As}^{+3}_{4.0}\text{As}^{+5}_{9.7}\text{Si}_{13.3}\text{O}_{191.5}\text{H}_{84.6}$$

Space group $R\bar{3}2/c$, when referred to rhombohedral axes, has 12-, 6-, and 4-fold equipoints with at least one variable parameter, one symmetry-fixed 6-fold, and two symmetry-fixed 2-fold equipoints. Space group $R3c$ has only 6-fold and 2-fold equipoints with variable parameters. After possibilities for substitution have been taken into account, the number of atoms contained in the cell must correspond to multiples of the multi-

TABLE 1. CHEMICAL COMPOSITION OF MCGOVERNITE

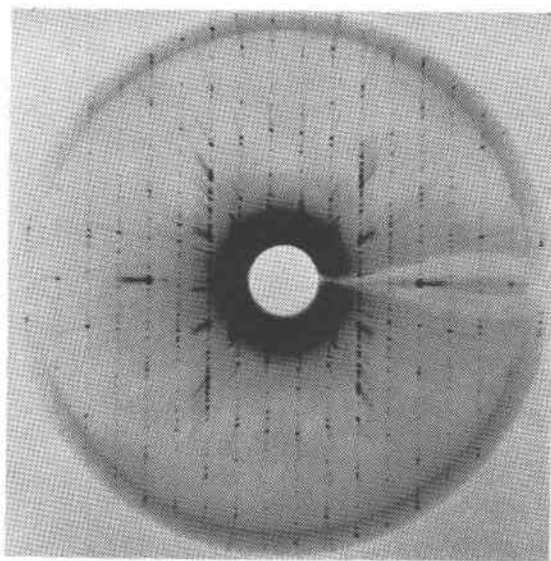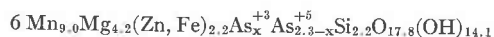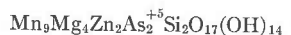| Component	Mol. wt.	Weight fraction (after Palache and Bauer, 1927)	Wt. fract. / mol. wt.	Molecules per hexagonal cell. (Equals $\frac{\text{wt. fract.}}{\text{mol. wt.}}$ × mol. wt./cell)	Metal	Oxygen
SiO_2	60.09	.00892	$14.8(10)^{-4}$	39.9	39.9	79.8
MnO	70.94	.4272	60.2	162.2	162.2	162.2
FeO	71.85	.0153	2.1	5.7	5.7	5.7
MgO	40.32	.1127	28.0	75.4	75.4	75.4
ZnO	81.38	.1022	12.6	34.0	34.0	34.0
As_2O_3	197.82	.0445	2.2	5.9	11.9	17.8
As_2O_5	229.82	.1248	5.4	14.6	29.1	72.8
H_2O	18.016	.0849	47.1	126.9	253.8	126.9
		$\sum = 1.0008$				$\sum = 574.6$

FIG. 3. Precession photograph of mcgovernite, [11·0] axis, first level. MoKα, 35 kv, 15 ma, 64 hours, $\bar{\mu}=20°$. Reflections are general and exhibit only extinctions due to the rhombohedral lattice.

plicities of the available equipoints. Although the correct space group is not definitely established, the number of atoms must still be multiples only of 6 and 2.

No further analyses of mcgovernite are available, so it is not known to what extent there is substitution present among the metal atoms. It may be noted, however, that, with the exception of the small amount of iron, all metals are present in near-multiples of 6. Hydrogen is arbitrarily assigned to hydroxyl radicals. Hey (1956) has shown that, in the chemically similar friedelite family, As does not substitute for Si and that As radicals do not substitute for OH. Accordingly, it is assumed that the As present is not in substitution with another species. With these assumptions, the rhombohedral cell contents may be written as

$$6\ Mn_{9.0}Mg_{4.2}(Zn, Fe)_{2.2}As_x^{+3}As_{2.3-x}^{+5}Si_{2.2}O_{17.8}(OH)_{14.1}$$

with $x = .66$. This suggests as an ideal formula for the As^{+5} end member of the series:

$$Mn_9Mg_4Zn_2As_2^{+5}Si_2O_{17}(OH)_{14}$$

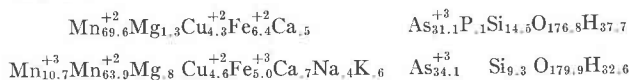More analyses are necessary before the exact nature of the substitutions and formula are established.

RELATION TO DIXENITE

The unit cell dimensions determined for mcgovernite show a remarkable relation to those reported by Wickman (1950) for dixenite.[†]

Dixenite (Långban, Sweden)	8.22 Å	37.44 = 2×18.72 Å
Mcgovernite (Sterling Hill, New Jersey)	8.22	205.5 = 11×18.68

The empirical rhombohedral unit-cell contents for dixenite, scaled by a factor of 11/2 to permit direct comparison with those of mcgovernite, are as follows:
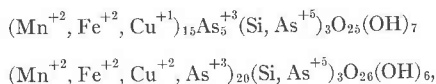
Dixenite (×11/2):

$$Mn_{69.6}^{+2}Mg_{1.3}Cu_{4.3}^{+2}Fe_{6.4}^{+2}Ca_{.5} \qquad As_{31.1}^{+3}P_{.1}Si_{14.5}O_{176.8}H_{37.7}$$

$$Mn_{10.7}^{+3}Mn_{63.9}^{+2}Mg_{.8}Cu_{4.6}^{+2}Fe_{5.0}^{+3}Ca_{.7}Na_{.4}K_{.6} \quad As_{34.1}^{+3} \quad Si_{9.3}\,O_{179.9}H_{32.6}$$

Mcgovernite:

$$Mn_{54.1}^{+2}Mg_{25.1}Zn_{11.3}Fe_{1.9}^{+2} \qquad As_{4.0}^{+3}As_{9.7}^{+5}Si_{13.3}O_{191.5}H_{84.6}$$

The cell contents for dixenite are based on analyses given by Mauzelius (Wickman, 1950) and Johansson (Wickman, 1951), respectively. The latter analysis is the more reliable and, furthermore, was determined from the material used for the measurement of the lattice constants given above.

' In order to deduce an ideal formula for dixenite, it was necessary for Wickman to assume different valence states for some of the metal atoms. The two results for dixenite may then be expressed:

$$(Mn^{+2}, Fe^{+2}, Cu^{+1})_{15}As_5^{+3}(Si, As^{+5})_3O_{25}(OH)_7$$

$$(Mn^{+2}, Fe^{+2}, Cu^{+2}, As^{+3})_{20}(Si, As^{+5})_3O_{26}(OH)_6,$$

respectively. Mcgovernite may be written:

$$(Mn^{+2}, Mg, Zn)_{15}As_2^{+5}Si_2O_{17}(OH)_{14}.$$

It may be seen that there is a strong similarity between the unit cell contents of the two minerals, although the numbers of atoms contained in the cells are not quite in the same ratio as the lengths of their *c* axes. Assumptions slightly different from those made in this paper had to be made by Wickman in deducing the ideal formulae for dixenite. Since the space group of dixenite has not been reported, and in view of the fact that only three chemical analyses exist for two minerals of such variable composition, there is as yet no real basis for establishing the true relation between the formulae.

[†] The cell dimensions for dixenite, reported in kX units, have been converted to Å.

Discussion

Referred to hexagonal axes, mcgovernite has the largest cell edge yet discovered as a basic translation in an inorganic material. It is true that a few larger cells have been reported, but only as members of a set of polytypes of certain crystals. In such instances the large period is due to a curious compounding of a simpler period and is not a fundamental characteristic of the structure. For example, Honjo *et al.* (1950) have discovered a SiC modification, type $594R$, with c approximately equal to 1500 Å.

The formula determined above suggests that, in spite of its perfect basal cleavage, mcgovernite is not a phyllosilicate. The lack of evidence in the diffraction patterns for a substructure equal to a submultiple of c, the brittle nature of the cleavage flakes, the negligible birefringence (indicating the absence of more loosely bound electrons perpendicular to the sheets), and the absence of polytypes despite the large cell size, all confirm the unlikelihood of a mica-like sheet structure.

Despite the difficulties encountered when a unit cell contains a large number of atoms, some progress has been made in a crystal-structure analysis of the two minerals.

Acknowledgments

References

BAUER, L. H. AND BERMAN, HARRY (1928), Friedelite, schallerite and related minerals. *Am. Mineral.* **13**, 341–348.

BUERGER, M. J. (1942*a*), *X*-ray Crystallography. John Wiley and Sons, New York, p. 162–165, 214.

BUERGER, M. J. (1942*b*), op. cit., p. 160.

BUERGER, M. J. (1954), The diffraction symmetries of twins. *Anais. Acad. Brazil. Cienc.*, **26**, 111–121.

FLINK, G. (1920), Trigonit och dixenit. *Geol. Fören. Förhandl.*, **42**, 436–452.

HEY, MAX H. (1956), The empirical unit cell contents of the friedelite family. *Am. Mineral.*, **41**, 134–138.

HONJO, GORO; MIYAKE, SHIZUO; AND TOMITA, TAKANORI (1950), Silicon carbide of 594 layers. *Acta Cryst.*, **3**, 396–397.

PALACHE, C. AND BAUER, L. H. (1927), Mcgovernite, a new mineral from Sterling Hill, New Jersey. *Am. Mineral.*, **12**, 373–374.

STOKES, RALPH G. (1947), An improved apparatus for detecting piezoelectricity. *Am. Mineral.*, **32**, 670–677.

WICKMAN, FRANS E. (1950), From the notes of the late K. Johansson. IV. Dixenite. *Geol. Fören. Förhandl.*, **72**, 64–65.

WICKMAN, FRANS E. (1951), From the notes of the late K. Johansson. VII. A revised chemical analysis of dixenite from Långban. *Geol. Fören. Förhandl.*, **73**, 637–638.