

THE STRUCTURE OF LEACHED GILLESPIITE, A SHEET SILICATE

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ABSTRACT

Gillespite, a tetragonal sheet silicate, $\text{BaFeSi}_4\text{O}_{10}$, can be leached by hydrochloric acid leaving flakes of hydrated silica. By means of x -ray precession patterns it is shown that these flakes retain the chief features of the sheet structure. Gradual destruction of this structure which attends dehydration by heating and final recrystallization to an unoriented aggregate of crystalbite has been followed by x -ray diffraction observations.

INTRODUCTION

A number of natural silicates yield a residue of hydrated silica when acted on by acid (Murata, 1943). Some zeolites and phyllosilicates may be completely stripped of cations leaving a remnant of hydrated silica that retains the crystal shape and often has optical properties similar to those of the parent material. Rinne (1911) concluded the hydrated silica residue constituted a "well ordered remnant of the biotite structure" and suggested the name baueritization for the natural leaching of biotite. Soon thereafter (Rinne, 1913) he described experiments on the leaching of heulandite, brewsterite and stilbite. A few years later (Rinne, 1924, p. 152) he reported that " X -ray diagrams are no longer obtainable for the residual silica of the zeolites and mica."

The observations on leached zeolites were extended by Wyart (1933). He examined leached single crystals of heulandite by the rotating crystal x -ray method and obtained only diffraction rings characteristic of amorphous silica. Mehmel (1937) made an extensive study of the leaching of biotite by acids. In those cases in which he studied the product by x -ray diffraction by the powder method only amorphous silica was indicated. Bailey (1941) described "skeletonized apophyllite" whose retention of some optical and physical properties of the original mineral suggested "a selective leaching process in which calcium, fluorine and potassium have been removed without destroying the silica framework of the crystals." "A preliminary x -ray examination, using the powder method, failed to give any definite lines."

Gillespite, $\text{BaFeSi}_4\text{O}_{10}$, can be leached so that only "glistening silica scales" with a composition $8\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ remain (Schaller, 1929). At the time that the tetragonal sheet structure of gillespite was established (Pabst, 1943) the leaching experiments were repeated and earlier results confirmed. "Attempts to observe x -ray diffraction in the leached material by powder and rotation methods led to negative results, but a long exposure Laue pattern made with the aid of an intensifying screen, with

beam normal to the base of a well leached flake still shows a very faint tetragonal design" (Pabst, 1943, p. 388 and Fig. 5).

Improved techniques now available permit the study of *x*-ray diffraction effects that formerly escaped notice or remained uninterpretable. A study of leached gillespite by means of precession patterns has shown the extent to which the original structure is retained in the leached product.¹

MATERIAL

The new observations were carried out entirely on gillespite from California (Rogers, 1932). It occurs as small anhedral crystals with sanbornite, quartz, celsian, witherite and minor accessories in several compact lenses a few feet wide and some yards in extent in quartzite a few miles from the western contact of the Sierra Nevada batholith and the large barite-witherite deposits near El Portal. The locality is at an elevation of about 4,300 feet near the top of the eastern slope of Ned Gulch and a quarter of a mile north of the summit of Trumbull Peak in the NE $\frac{1}{4}$, Sec. 9, R. 19 E.; T. 3 S., El Portal Quadrangle, Mariposa County, California.

A pure concentrate of this gillespite was prepared by Dr. R. M. Douglass by repeated passing through the Frantz Isodynamic Separator and centrifuging in heavy liquids. The concentrate consisted of clean cleavage fragments, half a millimeter or less in maximum dimensions and 0.1 mm. or so in thickness, well suited for leaching experiments and *x*-ray study. An analysis of this purified material was made by Dr. R. Klemen of Vienna and is shown in Table 1. Spectrographic examination by Dr. T. G. Kennard showed also traces of Na, Mg, Sr, Cr, Mn and V.

The cell content calculated from the new analysis and the cell dimensions and measured density in Table 2 agrees well with the ideal cell content. The count of oxygen atoms shown in column 3 of Table 1 is not adjusted; it happens to come out just at the ideal value. It seems probable that there may be some substitution of Al for Si and a little shortage of Fe compensated for by other ions. The material prepared for analysis yielded an *x*-ray powder pattern free of extraneous lines. Still it may be that the impurities shown by the analysis, or some of them, are due to minute bits of contaminants that escaped detection.

NEW OBSERVATIONS

Leaching of the gillespite was carried out in 5N hydrochloric acid at room temperature. It is rapid enough to permit its recognition under

¹ A preliminary report on this work was presented at the Pasadena meeting of the American Crystallographic Association in June, 1955.

TABLE 1. ANALYSIS AND CELL CONTENT OF GILLESPIE FROM MARIPOSA COUNTY, CALIFORNIA

| | I | II | III | IV |
|--------------------------------|--------|-------|-------------------|-------|
| SiO ₂ | 49.98% | 51.62 | Si | 15.44 |
| TiO ₂ | 0.29 | | Ti | 0.07 |
| Al ₂ O ₃ | 1.51 | | Al | 0.55 |
| Fe ₂ O ₃ | 0.22 | | Fe ^{'''} | 0.05 |
| FeO | 14.61 | 15.43 | Fe ^{''} | 3.78 |
| CaO | 0.60 | | Ca | 0.20 |
| BaO | 32.38 | 32.95 | Ba | 3.92 |
| H ₂ O ⁻ | 0.22 | | | |
| H ₂ O ⁺ | 0.17 | | H | 0.37 |
| | 99.98 | | O | 40.00 |
| | | | | 40 |

I. Analysis by Dr. R. Klemen.

II. Ideal composition corresponding to BaFeSi₄O₁₀.

III. Cell content calculated from analysis in column I and data in Table 2.

IV. Ideal cell content.

the microscope by progressive bleaching and slight exfoliation of the deep red flakes treated individually on spot plates. X-ray examination of numerous flakes showed that the leaching is complete after half an hour or more and that continued acid treatment up to several months produces no further change.

Figures 1 and 2 show $hk0$ precession patterns of gillespite and of leached gillespite. It is clear that the flakes remain tetragonal and the dimensions in the $xy0$ plane are not greatly changed. The pattern of the leached material is very diffuse and the intensity relations entirely al-

TABLE 2. PROPERTIES OF GILLESPIE AND LEACHED GILLESPIE

| | Gillespite | Leached Gillespite |
|--------------------------|---|--|
| a_0 | 7.51 Å | 7.64 |
| c_0 | 16.08 | 15.10 |
| Cell Content | 4(BaFeSi ₄ O ₁₀) | 4(H ₄ Si ₄ O ₁₀)+2H ₂ O |
| Density _{obs.} | 3.40 | 2.05 |
| Density _{calc.} | 3.41 | 2.15 |
| Space Group | $P4/ncc$ | * |
| N_0 | 1.621 | 1.449 to 1.465 |
| N_e | 1.619 | 1.441 to 1.455 |
| Color O | pale pink | colorless |
| E | deep rose red | colorless |

* See text.



FIG. 1. Gillespite: $hk0$ precession pattern. Unfiltered Cu radiation. Exposure 4 hours.

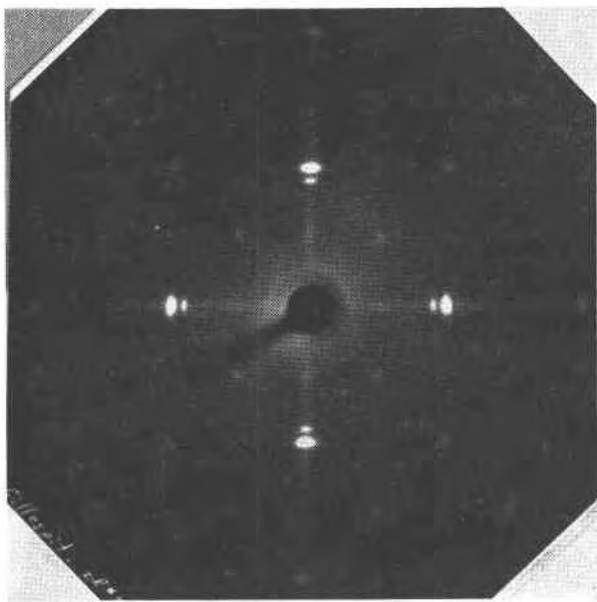


FIG. 2. Gillespite: leached for 45 minutes with 5N HCl: $hk0$ precession pattern. Unfiltered Cu radiation. Exposure 12 hours.

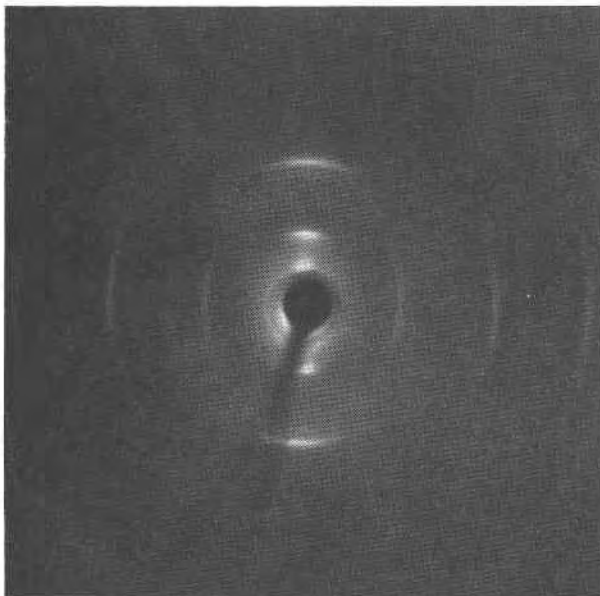


FIG. 3. Leached gillespite. Same flake as used for Fig. 2. hhl precession pattern. Unfiltered Cu radiation. Exposure 12 hours.

tered. The strongest spots seen on Fig. 2 are 200 "reflections." Weak 100 and 210 spots are also present. These are absent in the pattern for gillespite, being "prohibited" by the space group criteria. The cell dimensions of gillespite and leached gillespite are shown in Table 2 together with a few other data. There is a slight expansion of the Si_4O_{10} sheets which parallel (001). The basal spacing is reduced. The c_0 value for leached gillespite is one that would correspond to a 2-sheet structure. The diffuse reflections seen on such patterns as Fig. 3 require no more than a 7.55 \AA c axis.

In gillespite the two sheets within one cell height are fixed with respect to each other by the n glide parallel to (001). The loss of this relation shown by the $hk0$ pattern as well as the appearance of $h0l$ and hhl patterns suggests that there is little, if any, order in the stacking of the sheets in leached gillespite. It is, thus, impossible to assign a space group to it in the usual manner.² The arcuate appearance of the spots in Fig. 3 is due largely to the macroscopic bending of the sheets that attends the leaching and exfoliation. That this exfoliation leaves few closed voids is shown by the fact that the observed density of fully

² No way has been found of adapting the new concept of "space groupoids" (Dornberger-Schiff, 1957, p. 273) to this case.

leached flakes was found by suspension in a bromoform-alcohol mixture to be only a few per cent below the calculated value based on cell dimensions determined from such patterns as shown in Figs. 2 and 3 and a cell content corresponding to the composition reported by Schaller.

In a powder pattern of ground, leached gillespite taken with Ni filtered Cu radiation in a camera of 360 mm. circumference with collimator and beam catcher designed to confine scattering of x-rays by air as much

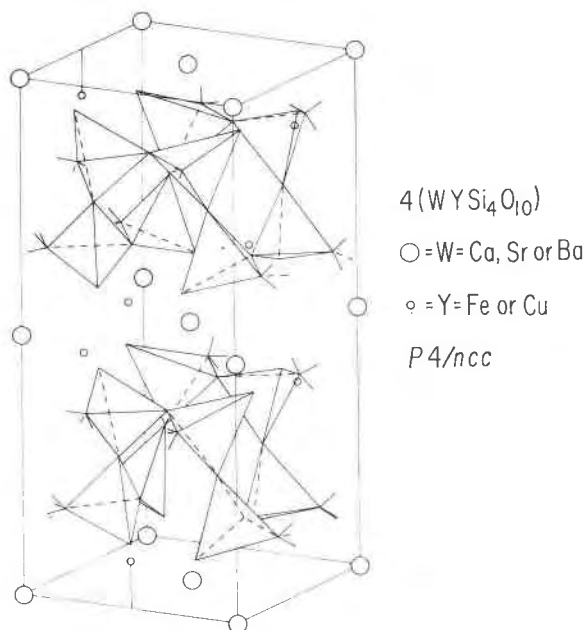


FIG. 4. Clinographic projection of the structure of gillespite and its isotypes. Two Si_4O_{10} sheets are shown within the height of one cell. The unshared corners of SiO_4 tetrahedra lie on both sides of each sheet. The Fe (or Cu) ions are at the level of these unshared corners and hence within the sheets, while the Ba (or Sr or Ca) ions are in the n glide planes between the sheets.

as possible, one observes a halo in the region corresponding to spacings 3.5 to 5.0 Å and superposed on this a diffuse line at the 3.8 Å position. This would correspond to (200), 3.82, and (004), 3.78, of the cell assigned to leached gillespite, but the absence of a line corresponding to (002), 7.55, which may be seen on precession patterns, suggests that the 3.8 line is largely due to (200) whose intensity is many times that of (004) as seen on $h0l$ precession patterns not reproduced.

The structure of gillespite is shown in Fig. 4. The structure of leached

gillespite may be derived from this by removal of all Ba and Fe and the balancing of charges by H, which requires 4/5ths of the water content reported in the leached material by Schaller (1929), giving a cell content of $H_{16}(Si_4O_{10})_4$ or $Si_{16}(OH)_{16}O_{24}$, the number of oxygens in the cell remaining unchanged. The n glide planes in the structure lie in $xy0$ and $xy\frac{1}{2}$. The sheets by themselves have the symmetry $P42_12$.

TABLE 3. OBSERVED AND CALCULATED F_{hk0} 's FOR GILLESPIITE AND LEACHED GILLESPIITE

| Gillespite | | | Leached Gillespite | | | | | | |
|------------|--------|-------|--------------------|-----|-----|-----|-----|------|------|
| | F Obs. | Calc. | Calc. | | | | | | Obs. |
| $hk0$ | I | II | III | IV | V | VI | VII | VIII | IX |
| 100 | — | — | — | 7 | — | — | 7 | — | 8 |
| 110 | 33 | 26 | 11 | 4 | 19 | 11 | 4 | 19 | 25 |
| 200 | 18 | 15 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 210 | — | — | 41 | 44 | 39 | — | 5 | — | 16 |
| 220 | 92 | 90 | 21 | 24 | 24 | 21 | 24 | 24 | 35 |
| 300 | — | — | — | 4 | — | — | 4 | — | 0 |
| 310 | 53 | 39 | 16 | 18 | 11 | 16 | 18 | 11 | 18 |
| 320 | — | — | 2 | 6 | 2 | — | 4 | — | 5 |
| 400 | 100 | 100 | 43 | 44 | 44 | 43 | 44 | 44 | 39 |
| 410 | — | — | 13 | 16 | 13 | — | 3 | — | 3 |
| 330 | 0 | 12 | 22 | 24 | 17 | 22 | 24 | 17 | 35 |
| 420 | 65 | 64 | 8 | 11 | 11 | 8 | 11 | 11 | 10 |

All values arbitrarily adjusted to make highest F in each column 100.

Dashes indicate extinction required by symmetry.

Basis for calculated F's as follows:

- Gillespite, II. Corresponding to structure given by Pabst, 1943.
 Leached Gillespite, III. Uncoupled sheets only.
 IV. Uncoupled sheets plus H_2O in $00z$.
 V. Uncoupled sheets plus H_2O in $0\frac{1}{2}z$ (and $\frac{1}{2}0z$).
 VI. Coupled sheets only.
 VII. Coupled sheets plus H_2O in $00z$.
 VIII. Coupled sheets plus H_2O in $0\frac{1}{2}z$ (and $\frac{1}{2}0z$).

In Table 3 are given the observed and calculated structure factors for the first 12 $hk0$ planes for gillespite and leached gillespite, F's being adjusted for ease of comparison so that the highest value in each column is 100. The structure factors for leached gillespite have been calculated on several different assumptions. If the $H_{16}(Si_4O_{10})_4$ sheets retain gillespite parameters, but are not coupled to each other in any fixed manner except in orientation, the structure factors of column III result, with

(100) and (300) prohibited by the $P4_212$ symmetry of the sheets. If the sheets remain coupled as in gillespite, the criteria for $P4/ncc$ require additionally the extinction of (210), (320) and (410), column VI. As seen in column IX and Fig. 2, all of these spots are observed, though (210) and (410) with intensities much lower than those corresponding to the F's in column III. Possibly this could be accounted for by a structure in which some of the sheets remain coupled to adjacent sheets by the n glide in $xy0$ while many are uncoupled.

This still leaves unexplained the observation of a certain intensity of the (100) spots which can be seen in Fig. 2 superposed on the continuum streaks between the center and the very strong (200) spots. As shown in columns IV and VII of Table 2 a weak (100) reflection would arise if the remaining fifth of the water content, which is not required in the sheet structure so far described, were situated at $00z$, a likely position so far as space is concerned. The observed value of F_{320} is also in accord with this. On the other hand, water situated only in $0\frac{1}{2}z$ (and $\frac{1}{2}0z$) would not give rise to these features (columns V and VIII). Summarizing one may say that evaluation of the somewhat diffuse $hk0$ diffraction effects, for which good estimation of intensities is difficult, indicates that the silicate sheet structure of gillespite persists in the leached product but that the hydrated sheets are in part uncoupled and that there is a suggestion that the small amount of excess water is preferentially held in $00z$ locations (see Fig. 5).

The dehydration of leached gillespite was studied with care by Fairchild (Schaller, 1929). Upon heating water is lost gradually, about one third being driven off at 90° C. and some water being retained even at 400° . An attempt has been made to follow the changes attending gradual loss of water by repeated x -ray examination of the same flake of leached gillespite after heating to successively higher temperatures. Figs. 6, 7 and 9 show x -ray patterns made from the same flake that was used for the patterns of Figs. 2 and 3. They show three stages in the process. After heating to 115° and the loss of about $2/5$ ths of the water the dimensions of the lattice remain unchanged and the few spots still discernible are, if anything, less diffuse but only the strong (200) spots can be seen in the reproduction. The $hk0$ patterns of the same flake after heating to 185° and 405° (not reproduced) show further weakening of the pattern and after heating to 520° , at which temperature little, if any, water is still held, the " $hk0$ " precession pattern is blank.

Figure 7 shows a diffraction pattern made from this flake after heating to 520° with beam normal to what had been (001), and the flake stationary at 3 cm. from the plane film. Just outside the diffuse ring suggesting "amorphous" silica one can discern four small spots conforming

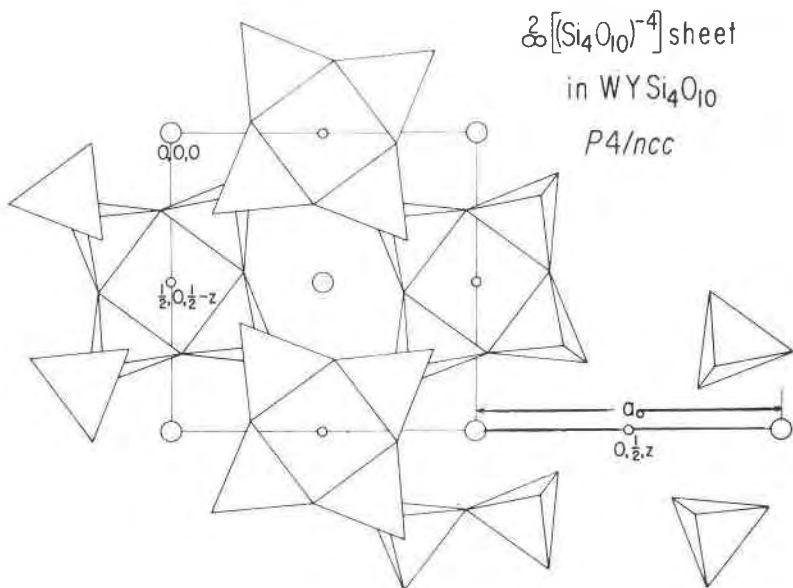


FIG. 5. Structure of a single tetragonal Si_4O_{10} sheet orthographically projected onto (001). Such sheets persist in leached gillespite.

to tetragonal symmetry. From the conditions of the experiment these would be expected to be "Laue" spots. Measurement shows that they cannot be so interpreted. Rather they are 200 spots due to characteristic radiation and arise from the remnants of a single crystal because of the bending of the flake. This interpretation has been checked by a pattern taken of a stationary flake of unheated leached gillespite with beam normal to cleavage, and crystal to plane film distance 3 cm., reproduced in Fig. 8. This corresponds to an oscillation pattern for which oscillation is about axes in the plate in all azimuths and through angles of about 50° . The spots lie on hyperbolae corresponding to the higher layers of plane film rotation patterns and the entire pattern consists of spots on overlapping hyperbolae. A "Laue" pattern of leached gillespite could only be obtained by excluding characteristic radiation from the incident beam and such a pattern would be expected to consist of diffuse streaks.

Leached gillespite which has been mostly changed to "amorphous" material by heating to 520° is converted to an unoriented aggregate of cristobalite by further heating at higher temperature as shown in Fig. 9.

Attempts were made to reconstitute leached gillespite by treatment with a concentrated aqueous solution of barium and ferrous chlorides or to convert it to the isostructural barium copper silicate (Pabst, 1954).

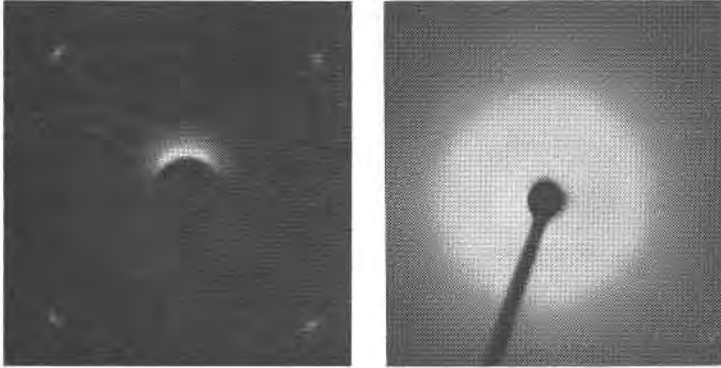


FIG. 6. (left) Leached gillespite after heating for 6 hours at 115°C .; $hk0$ precession pattern. Unfiltered Cu radiation. Exposure 12 hours. Natural size; only central part of film reproduced.

FIG. 7. (right) "Laue" pattern of leached gillespite after further heating for 14 hours at 520°C . Beam normal to cleavage, crystal to film distance 3 cm. Unfiltered Cu radiation. Exposure 12 hours. Natural size.

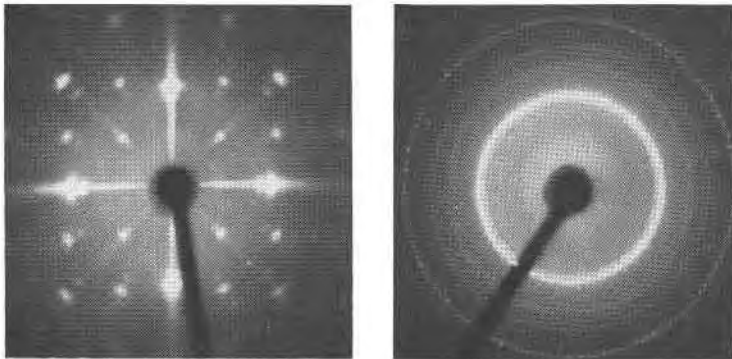


FIG. 8. (left) Pattern obtained from stationary flake of leached gillespite, beam normal to cleavage, crystal to plane film distance 3 centimeters, unfiltered Cu radiation, 35 KV, 18 MA, exposure 4 hours. Natural size. See text for explanation.

FIG. 9. (right) "Powder" pattern of leached gillespite flake after further heating for 18 hours at 780°C . Flake fixed, beam normal to cleavage, crystal to film distance 3 cm. Ni filtered Cu radiation. Exposure 4 hours. Natural size.

X-ray examination of flakes treated at room temperature for several months showed no indication of reconstitution or conversion. Treatment of fresh gillespite with concentrated solutions of copper, strontium or calcium salts produces no discernible change in color or cell dimensions that might be taken to indicate ion exchange.

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