# *On Zunyite and Guitermanite, two new Minerals from Colorado,* BY W. F. HILLEBRAND.

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## ZUNYITE.

The Zuñi mine on Anvil mountain, near Silverton, San Juan county, Colo., has furnished to science two new minerals, one of them being of a remarkably interesting nature.

A portion of the ore from this mine, as represented by two specimens for the use of which I am indebted to Mr. Franklin Guiterman, consists when unaltered of an uncrystallized sulphide of lead and arsenic, upon broken surfaces of which appear numberless projecting, glassy faces of tetrahedra of the regular system. On destroying the sulphide by nitric or nitro-hydrochloric acid, washing thoroughly by decantation, and finally employing a solution of high specific gravity to effect separation from a very small amount of barite and whatever other lighter or heavier impurities may be present, a product is obtained consisting of fine crystals on which the predominant form is $\frac{O}{2}$, generally modified by $-\frac{O}{2}$, and frequently also by $\infty O \infty$ and either $\infty O$ or $\frac{mO}{2}$, which of the two being as yet undetermined. While goniometric measurements of the tetrahedral angles by Mr. Whitman Cross varied frequently within a degree from the normal, this must have been owing to surface irregularities, since the crystals are entirely without action on polarized light and can therefore belong to none but the regular system.

Their size varies from that of extreme minuteness to a diameter, in rare instances, of five millimeters. The smallest of the crystals are generally quite clear and transparent, but the vast majority carrry more or less uncrystallized, unmagnetic, black inclusions, the nature of which the microscope does not reveal. Repeated preliminary tests showed that these were in no respect similar to the sulphide in which the crystals had been imbedded, being practically insoluble in the strongest acids with the exception of hydrofluoric acid. The tetrahedra themselves, even in fine powder, are also unaffected by any acids other than hydrofluoric, and even with this acid the action is very slow. Fusion with potassium hydrosulphate effects decomposition in time, and with alkaline carbonates quite readily.

The luster is glassy, cleavage octahedral, hardness about 7, and the specific gravity in the case of two different lots carrying, in so far as could be judged, the same amount of inclusions, was 2.906 and 2.894 at 18½°C. and 20°C. respectively. By diluting a portion of "Thoulet" solution until a few minute crystals free from black specks remained suspended in the liquid, and then taking the density of the latter by a Mohr balance, the specific gravity of the pure mineral was found to be 2.875 at 15°C.

The influence of the inclusions upon the specific gravity was not sufficient to allow of effecting anything like a complete separation, by the employment of a solution of high density, of pure matter from that carrying inclusions, even when finely powdered. For although the portions first falling consisted of the largest and blackest crystals or fragments, and each succeeding precipitate was of a slightly lighter shade, the last was still noticeably dark and by no means pure. The difficulty of separation in this manner was further enhanced by the fact that much of the material from which the portions taken for final analyses were obtained was more or less altered, and consequently of lower specific gravity, the result being that pure crystals and slightly altered ones containing many inclusions fell together. After very great labor, however, enough material for final tests was obtained by hand picking under the loupe. This showed no signs of alteration and but here and there a minute black speck.

Qualitative analysis of less pure material showed the presence of silica, titanic oxide, alumina, ferric oxide, soda potassa, lithia, fluorine, chlorine, phosphorus pentoxide and water. When heated in a tube acid water which attacked glass was given off. Whole crystals when heated sometimes decrepitated and always became opaque and porcelain-like, but showed no sign of fusion in the hottest blowpipe flame.

On account of the hardness, which rendered grinding in an agate mortar inadvisable, the sample was crushed in a steel mortar, the metal from the latter extracted by hydrochloric acid, and, after washing thoroughly by filtration, the finest portions were separated from the coarse by levigating with water. The most impalpable powder was reserved for alkali tests.

In these, decomposition was effected by igniting with three parts of bismuth oxide for half an hour at a dull red heat. Treatment with hydrofluoric acid would have required several days for the decomposition alone, and it is improbable that the Lawrence Smith method would have suceeeded well. Lithia could not be quantitively estimated, although the spectroscopic evidence of its presence was strong.

Silica, alumina, ferric oxide, titanic oxide and fluorine were generally estimated in the same portion, and in one instance also chlorine and phosphorus pentoxide. Fusion was made with potassium carbonate. After separation of silica, alumina etc., in the usual manner, the phosphoric acid remaining in solution was removed by silver nitrate. The fluorine was not calculated from the weight of calcium fluoride obtained, but from the difference between this weight and that after conversion into sulphate. In one instance (Anal. III, below), a considerable amount of pure silica was added before fusion with alkaline carbonate, and here somewhat more fluorine was found than when no silica was added. Silica was always examined for phosphoric as well as for titanic acid, when the latter was known to be present.

The solution containing ferric, (titanic), and phosphoric oxides and alumina, was divided into two parts, in the one of which the phosphorus was determined, in the other the weight of the combined oxides. The latter were brought into solution by fusion with potassium hydrosulphate, the titanic oxide, if present, was then thrown down by boiling in presence of sulphurous acid, and the iron precipitated as sulphide from a tartaric acid solution and subsequently weighed as oxide. The alumina was found by difference.

Beryllia was carefully tested for by digesting the alumina and ferric oxide (introduced as chlorides) for several days with ammonium carbonate in excess. The very slight amount of matter found then in solution proved to be alumina.

Chlorine was estimated in a separate portion by precipitating as silver chloride in a platinum dish, after leaching the alkaline carbonate fusion and acidifying the filtrate with nitric acid. As a precautionary measure the chloride was then dissolved on the filter with ammonia and reprecipitated by nitric acid, after which it was collected and weighed in a Gooch crucible. In one instance the silver chloride thrown down before precipitating the fluorine as calcium fluoride was weighed and found to tally very closely with the results obtained on separate portions.

Water was estimated by heating the mineral with dry sodium carbonate in a glass tube and collecting in a weighed calcium chloride tube.

The results upon the purest material were as follows:

I. 0.9055 grm. gave 0.2200 $SiO_2$, 0.0018 $Fe_2O_3$, 0.5230 $Al_2O_3$ and 0.0466 F.

II. 1.1568 grm. gave 0.2817 $SiO_2$, 0.0022 $Fe_2O_3$, 0.6710 $Al_2O_3$ and 0.0613 F.

III. 0.8436 grm. gave 0.4882 $Al_2O_3$, 0.0018 $Fe_2O_3$ 0.0054 $P_2O_5$, 0.0244Cl and 0.0473 F.

IV. 0.6512 grm. gave 0.0058 $Mg_2P_2O_7$ hence 0.0037 $P_2O_5$

V. 1.0039 grm. gave 0.0060KCl, NaCl and trace LiCl, 0.0052 $K_2PtCl_6$, whence 0.0016 KCl and 0.0044 NaCl, LiCl, or 0.0010 $K_2O$ and 0.0023 $Na_2O$, $Li_2O$.

VI. 1.0042 grm, gave 0.0064 KCl, NaCl, LiCl, 0.0052 $K_2PtCl_6$, whence 0.0016 KCl and 0.0048 NaCl, LiCl, or 0.0010 $K_2O$ and 0.0025 $Na_2O$, $Li_2O$.

VII. 0.7022 grm. gave 0.0824 AgCl, whence 0.0204 Cl.

VIII. 0.7505 grm. gave 0.0891 AgCl, whence 0.0220 Cl.

IX. 0.5073 grm. gave 0.0552 $H_2O$.

X. 0.4021 grm. gave 0.0439 $H_2O$.

XI. 0.3502 grm. gave 0.0381 $H_2O$.

|  | I. | II. | III. | IV. | V. | VI. | VII. | VIII | IX. | X. | XI. | Mean |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 24.30 | 24.36 |  |  |  |  |  |  |  |  |  | 24.33 |
| $Fe_2O$ | 0.20 | 0.20 | 0.21 |  |  |  |  |  |  |  |  | 0.20 |
| $Al_2O_3$ | 57.76 | 58.00 | 57.87 |  |  |  |  |  |  |  |  | 57.88 |
| $K_2O$ |  |  |  |  | 0.10 | 0.10 |  |  |  |  |  | 0.10 |
| $Na_2O$ |  |  |  |  | 0.23 | 0.25 |  |  |  |  |  | 0.24 |
| $Li_2O$ |  |  |  |  | tr. | tr. |  |  |  |  |  | tr. |
| $H_2O$ |  |  |  |  |  |  |  |  | 10.88 | 10.92 | 10.88 | 10.89 |
| $P_2O_5$ |  |  | 0.64 | 0.57 |  |  |  |  |  |  |  | 0.60 |
| F | 5.15 | 5.30 | 5.61 |  |  |  |  |  |  |  |  | 5.61* |
| Cl |  |  | 2.89 |  |  |  | 2.90 | 2.93 |  |  |  | 2.91 |
|  |  |  |  |  |  |  |  |  |  |  |  | 102.76 |
| Less O for F and Cl. |  |  |  |  |  |  |  |  |  |  |  | 3.02 |
|  |  |  |  |  |  |  |  |  |  |  |  | 99.74 |

In deducing a formula from these data the $Fe_2O_3$ and $P_2O_5$ may for reasons subsequently mentioned be neglected. Since none of the water escapes at 270°C., it may be assumed that it exists as water of constitution, or basic water, and it is perhaps to be reckoned with the small quantities of alkalies. The atomic ratio is then found to be

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*The highest figure for fluorine is here taken as probably nearer correct than the others, because of a possible analytical error in the latter having in this case been lessened by the addition of silica before making the alkaline fusion.

$(H,K,Na) : Si : (Al_2) : (O,F_2,Cl_2)$
1.2208 : 0.4055 : 0.5674 : 3.1232
or
18.06 : 6.00 : 8.39 : 46,21
which is not far from
9 : 6 : 8 : 45
giving the formula

$R_{18}Si_6 (Al_2)_8 (O,F_2,Cl_2)_{45}$ or
$9 R_2O. 6 SiO_2, 8 Al_2O_3$. with part of the oxygen replaced by fluorine and chlorine.

The $Fe_2O_3$ of the above analyses came undoubtedly from a thin film of ferric oxide on the tetrahedral crystals which had not been entirely removed by the various treatments with acids to which they had been subjected.

The $P_2O_5$ cannot well be a constituent of the tetrahedra, and is probably derived from a small proportion of an admixed aluminium phosphate. The excess of alumina constantly found over that required for the above formula renders this the more likely. Evidence of the presence of an admixed phosphate was also obtained by direct experiment. In material not specially purified there were observed a few irregular and generally dull grains which at first were supposed to be fragments of tetrahedra, perhaps slightly altered. Half a dozen of these, weighing in all less than one milligram, were picked out, crushed, fused with sodium carbonate, the fusion dissolved in nitric acid, and a few drops of molybdate solution added. A distinct yellow precipitate formed in a short time. Yet while the presence of an aluminium phosphate would, by lowering the aluminium of the above analyses, make the ratio $Si : Al_2$ nearer 6 : 8 than it has been shown to be, I am not at all certain that the discrepancy is hereby entirely to be explained. For the given amount of $SiO_2$ only 55.19 per cent. of $Al_2O_3$ is required, leaving 2.69 per cent. for combintion with only 0.60 per cent. of $P_2O_5$. Moreover the above given ratio between $SiO_2$ and $Al_2O_3$ has been found by repeated careful analyses, not included in the above, made on entirely different samples, to be practically constant. It is therefore possible that the true formula is more complex than that given above, or that some source of contamination exists which I have not as yet been able to discover.

As a name for the mineral I propose *Zunyite*, after the mine from which it was obtained.

The black inclusions in the zunyite were shown to consist of titanic oxide by the following partial analyses of dark crystals:

| | | |
|---|---|---|
| $SiO_2$ | 23.93 | 23.86 |
| $TiO_2$ | 0.75 | 0.84 |
| $Al_2O_3$ | 58.30* | 58.45* |

By far the greater part of the zunyite-bearing ore seems to be in an advanced stage of decomposition. Through the kindness of Mr. J. A. Porter, of Durango, Colo., the Society is the possessor of about fifty ponnds of this altered ore completely filled with zunyite. The original double sulphide has almost disappeared, being changed into lead sulphate and other less well defined compounds. While the zunyite is here in great measure still perfectly fresh, a considerable portion has been more or less altered, incipient change being indicated by a faint cloudiness throughout the crystals, which, beginning apparently at the center, spreads outward and increases in degree until as a final product there ensues a dull white, opaque substance retaining in a measure the outlines of the original crystal and showing here and there a black grain of titainic oxide.

It was from this partially altered ore that the material for the final analyses above given was obtained, as the specimens of unaltered sulphide were too small to afford sufficient material by hand picking

## GUITERMANITE.

The metallic sulphide forming the matrix of the zunyite, of which in a fresh state, as before observed, I have been able to handle but two specimens, is of a bluish-gray color, possesses slight metallic luster and a hardness of about 3, on places free from the included zunyite. A small amount of pyrite is visible in spots.

Heated in the closed tube, it fuses readily and there appears a slight sublimate of sulphur, followed by a heavy one of arsenic sulphide, while on charcoal the usual reactions for lead, arsenic and sulphur may be observed.

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Not freed from $Fe_2O_3$ and $P_2O_5$

The following analyses were made:

| | I. | | | II. | | |
|---|---|---|---|---|---|---|
| | a | b | Mean | a | b | Mean |
| Zunyite | 1.77 | | 1.77 | 3.81 | 3.82 | 3.82 |
| As | 13.50 | 13.30 | 13.40 | 13.00 | | 13.00 |
| Pb | 63.40 | 63.80 | 63.60 | 61.65 | 61.62 | 61.63 |
| Cu | 0.17 | 0.18 | 0.17 | 0.17 | 0.17 | 0.17 |
| Ag | 0.02 | | 0.02 | 0.02 | | 0.02 |
| Fe | 0.42 | 0.43 | 0.43 | 0.87 | 0.89 | 0.88 |
| S | 19.65 | 19.70 | 19.67 | 19.67 | 19.45 | 19.56 |
| O | | | | 0.55 | | 0.55 |
| | 98.93 | | 99.06 | 99.74 | | 99.63 |

Analyses I, a and b, were first made on material which had a specific gravity of 5.828 at 17½°C. Corrected for admixed zunyite of specific gravity 2.9, this becomes 5.94. As the total could hardly be brought above 99 per cent, in spite of great care in analyzing, the cause of this was sought for and found, as will be subsequently explained. In the experiments (not of a quantitative nature) having this end in view, the sample was exhausted, therefore fresh material was used for two subsequent analyses, II, a and b.

In both these and the previous ones the sulphur was found in excess of that required for the metals, on the assumption that all arsenic was present as trisulphide and the iron as disulphide. This was due to the presence of free sulphur, which was estimated quantitively by extracting with carbon disulphide and carefully evaporating the filtrate to dryness in a weighed crucible. After three extractions no more sulphur was dissolved. The amount thus obtained represented 0.59 per cent. of the material used for analyses II, a and b.

While accounting completely and satisfactorily for the excess of sulphur, this did not explain the low summation shown in the first analysis. It was found, however, that notwithstanding the apparent purity of the mineral, lead sulphate was present in some quantity. The sulphur trioxide of this was estimated by extracting the sulphate from the mineral by digestion with warm dilute hydrochloric acid in an atmosphere of carbonic acid—three or four digestions being sufficient for complete extraction—and, after partial neutralization of the filtrate, precipitating as barium sulphate.

The result was 0.69 per cent $SO_3$. The lead oxide of the sulphate could not be estimated in this extract, because even the dilute acid slightly decomposed the sulphide, taking lead, but no arsenic, into solution. Under the conditions of the experiment, practically no hydrogen sulphide could be oxidized in the short time required for making the extraction.

As a check, the lead oxide of the sulphate was estimated quantitively by extracting the sulphate with neutral ammonium acetate in a closed flask—three or four digestions with fresh solution being sufficient—throwing down the lead as sulphide and converting into sulphate before weighing. The percentage of lead oxide thus found was 2.70 instead of 2.61 required by the 0.69 of $SO_3$ found. 2.61 of $PbSO_4$ contains 1.78 of lead, 0.28 of sulphur and 0.55 of oxygen. Thus the sum total was brought much nearer to 100.

Excluding now the lead sulphate, free sulphur and pyrite, the following atomic values are obtained:

| | | | | |
|---|---|---|---|---|
| Pb | $59.85 \div 207 = 0.2891$ | 0.2904 | 3.35 | 10.15 |
| $Cu_2$ | $0.17 \div 126.8 = 0.0013$ | | | |
| $As_2$ | $13.00 \div 150 = 0.0866$ | | 1.00 | 3.00 |
| S | $17.68 \div 32 = 0.5525$ | | 6.38 | 19.14 |

which leads to the formula $10PbS, 3As_2S_3$. If a small quantity of galena was present, of which, however, there was no evidence other than that afforded by the decomposition of some lead sulphide by dilute hydrochloric acid without simultaneous solution of arsenic, the latter formula is probably the correct one. But this evidence is of little value, for any arsenic dissolved from the double sulphide would probably be immediately thrown down again by the hydrogen sulphide evolved. Whichever formula may be the true one, the mineral appears to be new to science, and, as a name, *Guitermanite* is proposed, in honor of Mr. Franklin Guiterman, by whom this mineral and its associate zunyite were first brought to my notice.

## [DISCUSSION.]

Mr. Guiterman, in reference to the occurrence of the zunyite in the Zuñi mine, mentioned that there seemed to be no indication of a fissure vein, but that the ore appeared