

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 25

APRIL, 1940

No. 4

## GRATONITE—A NEW MINERAL FROM CERRO DE PASCO, PERU\*

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The mineral here named was sent to the Harvard Mineralogical Laboratory for identification by Mr. Vance of Ward's Natural Science Establishment in October 1938. The same month specimens sent by Dr. Rust of the Geological Staff at Cerro de Pasco were received at Chicago. The name *Gratonite* is in honor of L. C. Graton, Professor of Mining Geology at Harvard University and Consulting Geologist of the Cerro de Pasco Copper Corporation. The occurrence and paragenesis of the new mineral are discussed in the following paper by Dr. Rust.

*Crystallography.* All the specimens of gratonite seen show the new mineral in crystals only. They vary in size from slender needles 0.1 mm. in diameter and  $\frac{1}{2}$  mm. in length to stout prisms 1 cm. across and 1.5 cm. in length. They are generally in radiated groups implanted on a gray siliceous matrix; in some cases they encrust a considerable surface in nonparallel aggregate crystallization. The vast majority of the crystals are very simple, like Fig. 1, with a hexagonal prism and a trigonal pyramid the only forms. Such crystals when short are easily mistaken for slightly distorted rhombic dodecahedrons. Large crystals are clearly subparallel aggregates and their faces are faceted and poor. This is true to a considerable extent of most of the crystals, as the reflections are unexpectedly poor for crystals which look brilliant. Crystals about 1 mm. through give relatively good reflections and were used chiefly for both morphologic and *x*-ray study. Many of them show narrow and always brilliant truncation of the edges of the principal trigonal pyramid by *r* and minute brilliant facets of what proved to be a steeper pyramid *M* (Fig. 2). On one Harvard specimen every crystal showed the flat trigonal pyramid *e* near the summit of the crystal; this form was observed on a number of Chicago samples (Fig. 3) from both the 300- and 1400-foot levels. The ditrigonal pyramid  $\mu$  is present as a "line" face truncating the edge *a/s* (Fig. 3) on a number of tiny crystals in the Chicago collec-

\* A preliminary description of this mineral appeared in this journal, 24, no. 2, 136 (1939).

tion, and five of the six faces of the upper hexagonal pyramid ( $2\bar{2}\bar{4}1$ ) were seen as tiny "line" faces truncating the  $s/m$  edge on one Chicago individual on which the  $m$  faces were relatively large. The pedion  $c$  was

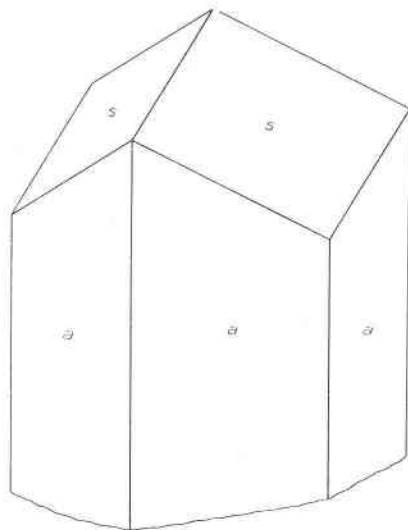


FIG. 1. Gratonite. Commonest type of crystal.

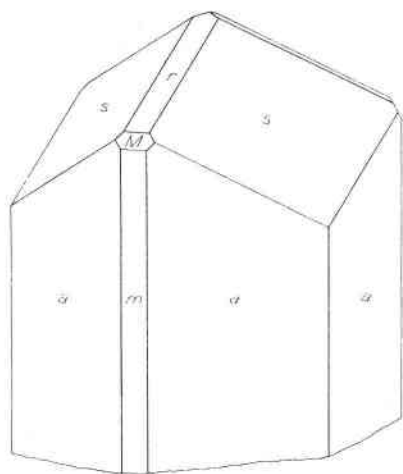


FIG. 2. Gratonite. Crystal showing trigonal prism and pyramids.

seen on large crystals of one Harvard specimen with large rough faces truncating the whole polar region of the crystal; it gave the impression of a face formed by solution.

The obvious form to choose as the unit is the dominant terminal one. The *x*-ray study, however, gave a unit cell based unequivocally on the truncating form shown in Fig. 2 as *r*. The four trigonal pyramids found (*e*, *r*, *s*, and *M* of Fig. 3) are in the simplest possible relations, two posi-

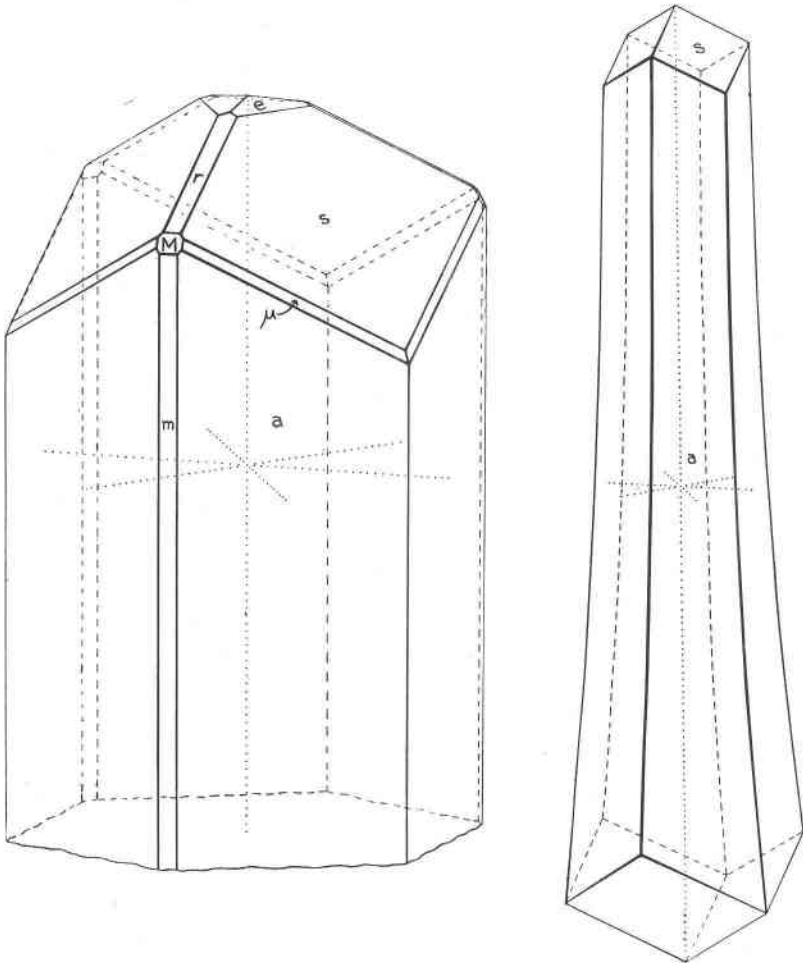


FIG. 3. Gratonite. The most complex combination of forms seen.

FIG. 4. Gratonite. Doubly terminated crystal with swollen basal portion.

tive and two negative, and each flatter one truncating in turn the edges of a steeper one. Many crystals show unmistakable truncations of three of the hexagonal prism edges in the positive sectants by the trigonal prism *m*, establishing the trigonal character of the vertical axis. But the crystals are almost invariably implanted so as to conceal the lower end;

in the two doubly terminated crystals found by the senior author the lower end showed the same dominance of *s* as did the positive end. The junior author had ten minute doubly terminated crystals which showed distinct differences in the two groups of terminal forms, and several of these were loaned to the senior author for confirmation; this observation points to the polar character of the vertical axis:

TABLE 1. GRATONITE: MEASURED ANGLES ON FIVE CRYSTALS

			Range	No. of faces	Calculated
<i>e</i>	01 $\bar{1}$ 2	$\phi$ -30°00'	$\rho$ 14°28'	$\phi$ $\rho$ 04' 30'	5 14°20½'
<i>r</i>	10 $\bar{1}$ 1	+30 00	27 10	32 49	17 27 04½
<i>s</i>	02 $\bar{2}$ 1	-30 00	45 36	26 48	17 45 38
<i>M</i>	40 $\bar{4}$ 1	+30 00	63 39½	— 40	7 63 56½

Calculation of  $p_0$ 

	$\rho$		$p_0$	
01 $\bar{1}$ 2	14°28'	$\frac{1}{2}p_0=0.25800$	.5160	weighted mean 0.5113
10 $\bar{1}$ 1	27 10	$p_0=0.51318$	.5132	
02 $\bar{2}$ 1	45 36	$2p_0=1.02117$	.5106	
40 $\bar{4}$ 1	63 39½	$4p_0=2.01965$	.5039	

## Elements

$p_0=.5113$	$\lambda=46^\circ26\frac{1}{2}'$
$c=.4428$	$\alpha=114^\circ04\frac{1}{2}'$

TABLE 2. GRATONITE: ANGLE TABLE

Hexagonal—R; ditrigonal pyramidal— $3m$ 

		$a:c=1:0.4428$			$\alpha=114^\circ04\frac{1}{2}'$
		$p_0:r_0=0.5113:1$			$\lambda=46^\circ26\frac{1}{2}'$
Bottom	Top	$\phi$	$\rho$	$A_1$	$A_2$
	<i>c</i>	0001	—	0°00'	90°00'
	<i>m</i>	10 $\bar{1}$ 0	+30°00'	90 00	30 00
	<i>a</i>	11 $\bar{2}$ 0	0 00	90 00	60 00
	<i>e</i>	01 $\bar{1}$ 2	-30 00	14 20½	90 00
$\bar{r}$	<i>r</i>	10 $\bar{1}$ 1	30 00	27 04½	66 47
<i>s</i>	<i>s</i>	02 $\bar{2}$ 1	-30 00	45 38	90 00
$\bar{M}?$	<i>M</i>	40 $\bar{4}$ 1	30 00	63 56½	38 55½
		2 $\bar{2}$ 41	0 00	60 33	64 11½
	$\mu$	24 $\bar{6}$ 1	-10 53½	69 43	52 07

The forms listed in Table 2 may be characterized as follows:

- c* (0001) Seen on one group of crystals as large rough faces, but not characteristic.
- m* (10 $\bar{1}$ 0) Confined to narrow faces on alternate edges only of *a* in the positive sectors. Generally not visible.
- a* (11 $\bar{2}$ 0) The dominant form on all crystals.
- e* (01 $\bar{1}$ 2) Seen not infrequently as a group of tiny faces at the summit of the crystal. Not observed on the lower termination.

- r* (10 $\bar{1}$ 1) Present on about half the crystals, generally as narrow but brilliant truncations of the dominant trigonal pyramid. Seen on two crystals by the junior author on a lower termination.
- s* (0221) The dominant form on all crystals. Generally brilliant but often unevenly faceted, especially on the larger crystals. Always found on the lower termination as well.
- M* (40 $\bar{4}$ 1) Infrequent, small and very brilliant. In many cases where the faces of *a* are of unequal size, *M* forms a line truncation of the edge between *a* and *s*. Seen once as but a single face very doubtfully by the junior author on a lower end.
- ? (22 $\bar{4}$ 1) Seen by the junior author as line faces between *s* and *m* on the upper end of a single individual on which *m* is exceptionally large.\*
- ? $\mu$  (24 $\bar{6}$ 1) A negative ditrigonal pyramid is present occasionally with line faces between *s* and *a*. Not seen on lower terminations. That it probably has the symbol assigned is indicated by zonal relationship and by the one approximate measurement obtained, as follows:

	$\phi$	$\rho$
Measured	$-10^{\circ}00'$	$68^{\circ}09'$
Calculated	$-10^{\circ}53\frac{1}{2}'$	$69^{\circ}43'$

*Aggregate forms.* Reference has already been made to the dodecahedral habit of the stouter crystals of gratonite. In one specimen of this habit each crystal is surrounded by a wreath of slender needles constituting a subparallel aggregate which sheaths all but the end of the crystal; there the plane-faced trigonal pyramid may still be seen in a hollow. Generally the larger crystals are entirely so sheathed and constitute a slightly curving prism: the terminal faces are also faceted or curved. Only the slenderest needles are entirely free from this effect. It appears to be due to an aggregate growth of fairly regular character. While many of the Harvard specimens have their swollen ends free, the smaller needles observed by the junior author were "bustled" at the lower termination. Figure 4 gives an idea of an exceptionally regular specimen of this habit which is  $\frac{1}{2}$  mm. in length. It quite resembles one shown in the right center of Rust's Fig. 4. The  $\rho$  angles of the lower  $\bar{s}$  faces were about  $2^{\circ}$  too low for the theoretical value ( $134^{\circ}22'$ ), which corresponds quite well with the angular change on a prism face ( $\rho = 90^{\circ}$  at the top and  $= 88\frac{1}{4}^{\circ}$  at the base).

\* The crystal in question is .15 $\times$ .61 mm.; thus the line face (22 $\bar{4}$ 1) is too small to reflect enough light for a goniometer signal. Its presence was first suspected from zonal relationships when studying the crystal under a binocular at  $\times 56$ . When mounted on a two-circle goniometer, in which the regular telescope was replaced with a polarizing microscope tube using a  $5\times$  ocular and a  $20\times$  objective (Leitz UM3 of long working distance), the crystal was oriented by using the Bertrand lens to give a minimized image of the signal from *a*. This orientation was checked by readings from *m*, *e*, and *s*. When the readings on the circles were then set to pick up the signals from the (22 $\bar{4}$ 1) faces, these appeared (without the Bertrand lens) as brilliantly illuminated line faces which disappeared (i.e., no longer reflected light into the microscope tube) when either circle was rotated slightly out of the positions computed for (22 $\bar{4}$ 1).

In short, the mechanism of crystal growth was such that  $\bar{s}\wedge a$  appears to remain fairly constant at the expense of  $\bar{s}\wedge\bar{s}'$ .

The subparallel aggregate crystals are often grouped in spheroids as is very well shown in Rust's photographs. No definite relation between the units constituting these spheroids was apparent to the senior author.

The junior author found one isolated pair of crystals springing symmetrically from a common base. After measuring and plotting these on the stereographic projection he saw that the two individuals were related as a simple type of complex twin involving the simultaneous operation of two mutually perpendicular twinning axes. As shown in the gnomonic projection of Fig. 5, these involve rotations of  $60^\circ$  anti-clockwise around the  $c$ -axis and  $30^\circ$  about the  $a_3$ -axis (anti-clockwise viewed from the positive end of the  $a_3$ -axis marked by the pole of  $a^{iv}$ ). Measured and calculated angles for two faces of each individual (where  $a^{iv}$  has  $\phi=0$ ) follow:

Face	Measured		Calculated	
	$\phi$	$\rho$	$\phi$	$\rho$
$a'''$	$299^\circ 30'$	$90^\circ 30'$	$300^\circ 00'$	$90^\circ 00'$
$s$	$149^\circ 50'$	$44^\circ 52'$	$150^\circ 00'$	$45^\circ 38'$
$\bar{a}'''$	$234^\circ 30'$	$64^\circ 00'$	$236^\circ 20'$	$64^\circ 20'$
$\bar{s}$	$90^\circ 20'$	$76^\circ 00'$	$90^\circ 00'$	$75^\circ 38'$

The lower ends of the  $c$ -axes of the two individuals start from a common point (Fig. 5); thus the two individuals have a common termination which resembles an orthorhombic pyramid of four faces, a pair from each of the lower trigonal pyramids  $\bar{s}$  belonging to each individual. The individuals are like those of Fig. 4 and joined at the swollen ends, which also mark the point of support during growth. Were more examples of this type of intergrowth available, it would certainly be classified as a twin. It cannot be designated a reflection twin over the contact plane (shaded in Fig. 5; indicated by  $p$  in the gnomonic projection) since the latter does not have simple indices (they are approximately  $73.\bar{7}\bar{3}.0.10$ ).

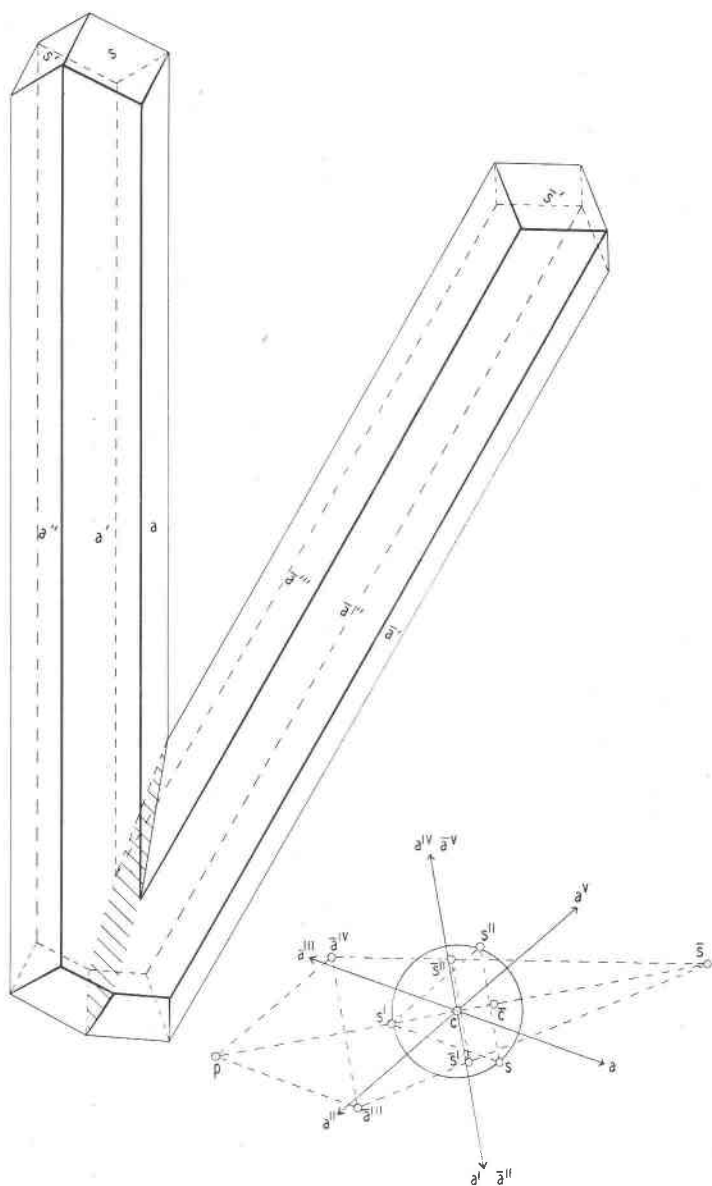


FIG. 5. Gratonite. Intergrown crystal and explanatory gnomonic projection.

*X-ray crystallography.* Space group  $C_{3v}^5$  ( $R\ 3\ m$ ).  $a_0 = 17.69\ \text{\AA}$ ,  $c_0 = 7.83\ \text{\AA}$ ;  $a_0:c_0 = 1:0.4426$ ;  $a_{rh} = 10.54\ \text{\AA}$ ,  $\alpha = 114^\circ 05'$ .  $V_0$  for hexagonal unit =  $2122\ \text{\AA}^3$ , triple that of the rhombohedral unit.

The data given are derived from a rotation picture about [0001] and Weissenberg pictures about [0001] and [11 $\bar{2}$ 0], with zero, first, and second layers of the former. The following omission criteria led to the space group:

$$\begin{aligned} (hk\bar{l}) & \text{ present when } h-k+l=3n \\ (h.h.2h.l) & \text{ with } l=3n \\ (hh0l) & \text{ with } 2h+l=3n \end{aligned}$$

*Chemistry.* Analyses have been made as shown in Table 3.

TABLE 3. ANALYSES OF GRATONITE

	1	2	3	4	5	6	7
Pb	71.12	.343	27.5	70.79	70.49	71.36	71.78
As	10.82	.144	11.6	10.60	11.33	11.47	10.92
Sb	0.21	.002	0.1	0.08			0.21
Fe	0.39	.007	0.6				
S	17.38	.542	43.4	18.01	18.18	17.17	17.09
Total	99.92			99.48	100.00	100.00	100.00
G	6.22 ± .02			6.1	6.17	6.09	

1. Gratonite. Analysis, F. A. Conyer.
2. Molecular proportions.
3. Atoms per unit hexagonal cell with  $M_0=8000$ , derived from x-ray data.
4. Gratonite. Analysis, Oroya Research Laboratory of the Cerro de Pasco Copper Corporation.
5. Calculated composition for  $Pb_{27}As_{12}S_{45}$ .
6. Calculated composition for  $Pb_{27}As_{12}S_{42}$ .
7. Gonyer's analysis recalculated to 100% after removing 0.39 Fe and 0.45 S.

The formula  $Pb_{27}As_{12}S_{45}$  (or  $Pb_9As_4S_{15}$  for the rhombohedral unit) seems best to fit the observed cell volume and density, and is preferred by the senior author. However, theoretical considerations suggest to the junior author that  $Pb_{27}As_{12}S_{42}$  is a more probable alternative. These considerations are that from column 3 of Table 3 it is clear that the value for Pb is too high (not too low, since the value obtained must be exactly divisible by 3) and that for S is almost exactly midway between its two possible values of 42 and 45. Now since the numbers of this column are dependent on  $M_0$ , they are all probably proportionately high or low, the former in this case. Further theoretical considerations regarding atom sizes may also tend to favor the 42 S formula, but too little is known as regards the structure of the sulpho-salts to generalize safely in this respect.\*

\* *Note by junior author:* At the request of the junior author, Mr. A. C. Lundahl (graduate student in the Department of Geology) tested a carefully selected crystal of gratonite in the arc spectrograph (ultra-violet) in the laboratory of Professor W. C. Pierce (Department of Chemistry) and found absence of Bi, Ir, Co, and Ni, Ag less than 0.001%, Cu just over



Tests: Decrepitates violently and melts very easily. Closed tube gives a slight sublimate of arsenic trisulphide ( $\text{As}_2\text{S}_3$ ). On charcoal gives a coating of lead oxide and arsenic fumes.

*Physical properties.* Cleavage none. Fracture slightly uneven to smooth conchoidal. Brittle;  $H = 2\frac{1}{2}$ ,  $G = 6.22 \pm .02$  (average of 6 determinations). Color dark lead-gray; streak black. Luster metallic. Opaque; anisotropic in polished section. Weaker anisotropism than any other lead sulph-arsenide. Etch reactions:  $\text{HNO}_3$ —stains iridescent to black; effervesces abundantly after short wait with liberation of free sulphur.  $\text{HCl}$ ,  $\text{KCN}$ ,  $\text{FeCl}_3$ ,  $\text{KOH}$ , negative.

#### RELATION TO OTHER MINERALS

*Chemical relations.* Table 4 lists the significant variations in the minerals most similar in composition to gratonite.

TABLE 4. RELATION TO OTHER MINERALS

	Guitermanite	Jordanite	Gratonite	Geocronite
Formula	$\text{Pb}_{10}\text{As}_6\text{S}_{13}$	$\text{Pb}_{14}\text{As}_7\text{S}_{24}\dagger$	$\text{Pb}_9\text{As}_4\text{S}_{15}$	$\text{Pb}_5(\text{Sb}, \text{As})_2\text{S}_8$
Ratio Pb:As+Sb:S	20:12:38	24:12:41	27:12:45	30:12:48
Crystal system	orthorhombic?	monoclinic	rhombohedral	orthorhombic? pseudo-hexagonal
Cleavage	none?	(010) perfect	none	(001)
Hardness			same	
Anisotropism	medium	medium	weak	medium
Etch reactions			same	
Specific gravity	$5.9 \pm$	6.39	$6.22 \pm .02$	6.3–6.45

† The junior author prefers  $\text{Pb}_{14}\text{As}_7\text{S}_{23}$ ; see p. 297.

In terms of percentage composition the relations are as shown in Table 5.

0.02%, Fe less than 0.01%, Mg, Mn, and Sn each less than 0.1%, and Sb about 0.1%. In short, it seems certain that the 0.39% Fe found by Gonyer is due to impurity in sampling. If it be assumed that this is present as pyrite (a common associated mineral) and an equivalent amount of S be removed from Gonyer's analysis and the whole recalculated to 100%, the results are as shown in column 7 of Table 3. It is clear that these results are much closer to the 42 S than to the 45 S formula for Pb and for S; as regards As there is (speaking practically) no choice between the two suggested formulae. The density given in column 6 is based on  $a_{7h} = 10.54$ . If the latter figure were 10.48 the density would compute to 6.20. Both of these figures are within probable observational limits of error. While one might expect the observed value of  $a_{7h}$  to be low rather than high, nevertheless for a calculated density of 6.20 for the 45 S formula this value must be 10.52. Unfortunately Fe was not determined in the Oroya analysis; so it cannot satisfactorily be treated in a similar fashion.

TABLE 5. COMPARATIVE ANALYSES

	1 Güitermanite	2 Jordanite	3 Gratonite	4 Geocronite
Pb	65.99	68.72	70.96	69.27
As	14.33	12.39	10.71	4.52
Sb			0.15	8.56
S	19.49	18.31	17.70	17.32
Total	99.81	99.42	99.52	99.67

1. Güitermanite. Zuni mine. Hillebrand (*Colorado Sci. Soc., Proc.*, **1**, 129, 1884), recalculated after deducting impurities.

2. Jordanite, Binnenthal. Jackson anal. in Solly (*Min. Mag.*, **12**, 282, 1900). Average of 2 analyses.

3. Gratonite. Average of 2 analyses, by Gonyer and by Cerro de Pasco Co. chemists.

4. Geocronite. Average of 5 closely agreeing analyses, by three chemists.

On the basis of composition alone, the analyses indicate that *gratonite* is certainly different from *güitermanite*, and from *geocronite*, which is essentially an antimony-arsenic sulpho-salt with the Sb:As near 1:1. Considering the probable high quality of the jordanite analyses and the special care exercised in the gratonite analyses, the differences between the two, though small, are significant. The chemical composition is therefore adequate to make a distinction among these minerals.

*Physical relations.* *Gratonite* has no distinct cleavage, and only in polished section is there any indication of a weak separation surface parallel to one of the rhombohedral planes. On the other hand, *jordanite* has a very perfect cleavage  $b(010)$ , and *geocronite* is said to have a fair cleavage in one plane. The hardness values of all the minerals discussed here are of the same order (.4 on the Talmadge machine, or "B", i.e. between galena and chalcopyrite). The etch reactions for the lead arsenic sulpho-salts are, in general, the same and are of little diagnostic value. However, *gratonite* shows a weaker anisotropic effect (in an oriented section) than any of the other minerals examined in this study, and this property is therefore of diagnostic value for the determination of *gratonite* in polished section. In the hand specimen, *gratonite* shows little color difference as compared with *geocronite*, but is darker (perhaps by tarnish) than the light steel-gray of *jordanite*. The density of *gratonite* is certainly lower ( $6.22 \pm .02$ ) than that of *jordanite* (6.39) and of *geocronite* (6.3–6.45) and probably higher than that of *güitermanite* ( $5.9 \pm$ ).

*Crystallographic relations.* *Gratonite* is definitely rhombohedral, as proved by the morphological and *x*-ray studies. *Jordanite* is, with equal

certainly, monoclinic, without any simple relation to the crystal elements of *gratonite*. For *guitermanite* we have no crystallographic data, but the  $x$ -ray picture of material from the type locality is different from the powder picture of *gratonite*, and it has been elsewhere proposed that *guitermanite* has the same spacings as *jordanite*. The powder picture of *geocronite* (from Sala) is likewise different from that of *gratonite*.

The junior author notes the close homeomorphism between *gratonite* and tourmaline.

	$c$	$a_0$	$c_0$
Gratonite	.4428	17.69	7.83
Tourmaline*	.4490	15.93	7.15

The habit of certain simple tourmalines on which  $a$  and  $o$  (equivalent of  $s$  on *gratonite*) predominate, closely resembles that of *gratonite*. See Figs. 30, 90, 81, 301, 365 and 369 of Goldschmidt's *Atlas der Krystallformen* 9, plates, 1923.

The authors desire to express their indebtedness to Dr. Harry Berman, who determined the density of *gratonite* and made the  $x$ -ray study, as well as the interpretation of the analyses in terms of these data. He also prepared the tables showing the relations of *gratonite* to other similar minerals.

\* Buerger and Parrish, *Am. Mineral.*, **22**, 1139 (1937).