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# GUETTARDITE FROM TUSCANY, ITALY: A SECOND OCCURRENCE

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## Abstract

Acicular black crystals of guettardite occur in small cavities at the Pitone marble quarry near Seravezza (Apuan Alps, Tuscany, Italy). The mineral is monoclinic *a* 20.05(5), *b* 7.95(2), *c* 8.44(2) Å, $\beta$ 102°46' ± 10', space group $P2_1/a$. Reflectance values have been determined in air and in oil at various wavelengths. $VHN_{20}$ = 189. The proposed ideal formula is $Pb(Sb,As)_2S_4$, *i.e.*, a ratio $PbS:(Sb,As)_2S_3$ = 1.

*Keywords*: guettardite, Tuscany, Italy, sulfosalt, sartorite, $Pb(Sb,As)_2S_4$.

## Sommaire

La guettardite se présente en cristaux aciculaires noir opaque dans de petites cavités du marbre de Pitone, exploité près de Seravezza (alpes Apouennes, Toscane, Italie). La maille a pour dimensions: *a* 20.05(5), *b* 7.95(2), *c* 8.44(2) Å, $\beta$ 102°46' ± 10', groupe spatial $P2_1/a$. Les valeurs du pouvoir réflecteur ont été mesurées dans l'air et dans l'huile pour diverses longueurs d'onde. $VHN_{20}$ = 189. On propose, comme formule idéale, $Pb(Sb,As)_2S_4$, c'est-à-dire un rapport $PbS:(Sb,As)_2S_3$ = 1.

(Traduit par la Rédaction)

*Mots-clés*: guettardite, Toscane, Italie, sulfosel, sartorite, $Pb(Sb,As)_2S_4$.

## Introduction

In our systematic study of the minerals of the marble formation in the Apuan Alps, we included the quarries close to Seravezza; we studied with particular interest the Pitone quarry, located on the right slope of the Serra brook (Giglia 1967), because of the presence of numerous sulfosalts.

In several samples from this and other quarries, we identified (by X-ray-diffraction patterns obtained with a Gandolfi camera) guettardite as well as the following mineral species: calcite, dolomite, fluorite, celestine, gypsum, quartz, albite, adularia, pyrite, sphalerite, wurtzite, galena, stibnite, orpiment, realgar, energite, tetrahedrite, zinckenite, jordanite, bournonite, boulangerite, jamesonite and sartorite, all located in small cavities along shear surfaces in the marble.

The aim of this short paper is to characterize the guettardite from the new locality and to compare its properties with those reported by Jambor (1967b) for the type locality of guettardite from Madoc, Ontario.

## Physical Properties

Guettardite occurs as small acicular crystals (2x0.4x0.4 mm) irregularly interlaced, with the

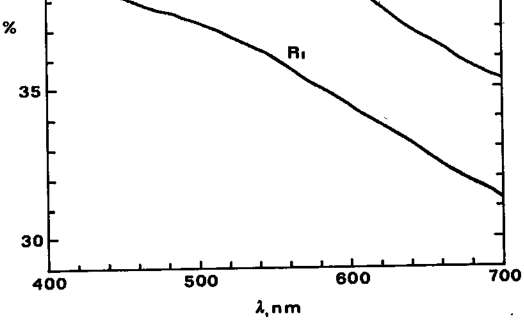


FIG. 1. Reflectance in air at various wavelengths.

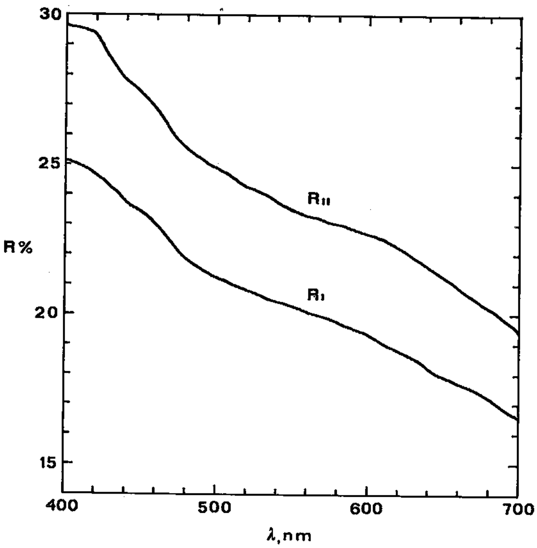


FIG. 2. Reflectance in oil at various wavelengths.

faces strongly streaked parallel to the elongation of the crystals, thus not permitting a morphological study. The crystals are black with metallic lustre. No cleavage was observed. Because of the very small quantity of material the specific gravity was not determined.

In polished section guettardite is white, without pleochroism. Anisotropism is strong and no internal reflections were observed.

The crystal we examined is twinned, with the two individuals having nearly equal dimensions. Reflectances (Figs. 1, 2) were measured on the individual that showed the greater difference in values at various wavelengths; they were obtained by using wolfram–titancarbide no. 144 (Zeiss) as standard. Values at the four principal wavelengths are listed in Table 1. The micro-indentation hardness *VHN* is 189 using a 20 g load.

TABLE 1. REFLECTANCE MEASUREMENTS IN AIR AND IN OIL

| λ,nm | $R_1$(air) | $R_2$(air) | $R_1$(oil) | $R_2$(oil) |
|---|---|---|---|---|
| 470 | 37.6 | 42.6 | 22.3 | 26.1 |
| 546 | 36.1 | 41.2 | 20.4 | 23.6 |
| 589 | 34.8 | 39.3 | 19.5 | 22.9 |
| 650 | 32.8 | 36.7 | 17.9 | 21.2 |

## CRYSTALLOGRAPHY

Cell parameters of guettardite, obtained from precession photographs and refined using the X-ray powder-diffraction data, are *a* 20.05(5), *b* 7.95(2), *c* 8.44(2) Å, *β* 102°46(10)′, *V* 1312.1 Å$^3$. The systematic absences (*h*0*l* absent for $h = 2n + 1$ and 0*k*0 absent for $k = 2n + 1$) give $P2_1/a$ as a unique space-group. The choice of the cell orientation was made, as in the case of guettardite from Madoc (Jambor 1967b), to emphasize the close structural relationship between this mineral and sartorite. The crystal under study appears twinned according to (100).

X-ray powder-diffraction data, obtained with a 114.6 mm Gandolfi camera, are reported in Table 2 and compared with the X-ray powder data for guettardite from Madoc.

TABLE 3. CHEMICAL DATA

| | Wt.% | Atomic ratio | $PbSbAsS_4$ Wt.% |
|---|---|---|---|
| Pb | 38.50 | 0.1858 | 38.94 |
| Cu | 0.49 | 0.0077 | |
| Sb | 23.57 | 0.1936 | 22.88 |
| As | 13.61 | 0.1817 | 14.08 |
| S | 23.46 | 0.7316 | 24.10 |
| Total | 99.63 | | 100.00 |

Analytical conditions: 15 kV, 0.20 μA specimen current. The following standards were used: galena for Pb and S, chalcopyrite for Cu, and synthetic sulfides of Sb and As for these elements. Data were computed on-line using the program MAGIC 4 (Colby 1968).

## CHEMISTRY

The microprobe analytical data obtained for guettardite from the Pitone quarry are given in Table 3. The results correspond almost exactly to the ideal formula $PbSbAsS_4$. On the basis of this formula a density of 5.26 g/cm$^3$ can be calculated from the density determinative curves given by Jambor (1967a). This is in good agreement with the value 5.39 g/cm$^3$ computed by assuming that eight such formula units are contained in the unit cell.

## CONCLUSIONS

Guettardite from the Pitone quarry is very similar to guettardite from Madoc in its crystallographic and physical properties; however, its chemical composition seems somewhat different. On the basis of the data collected, we propose the ideal formula $Pb(Sb,As)_2S_4$ for guettardite, with ratio $PbS:(Sb,As)_2S_3=1$ rather than 9:8 as proposed by Jambor (1967b). The close crystallographic relationship between sartorite (which has a ratio $PbS:As_2S_3$ of 1) and guettardite strongly supports this proposal.

## ACKNOWLEDGEMENTS

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TABLE 2. X-RAY POWDER-DIFFRACTION DATA

| 1 | 1 | 1 | 2 | 2 | 2 |
|---|---|---|---|---|---|
| $I_{est}$ | $d_{obs}$ | hkl | $I_{est}$ | $d_{obs}$ | hkl |
| 3 | 9.89 | 200 | w | 9.73 | 200 |
| 1/2 | 7.41 | 110 | | | |
| 1 | 6.20 | 210 | | | |
| 1 | 5.82 | $\bar{1}$11 | | | |
| 1 | 5.33 | $\bar{2}$11 | | | |
| 1 | 4.93 | 400 | | | |
| 1/2 | 4.68 | $\bar{3}$11 | | | |
| 5 | 4.19 | 410 | w | 4.17 | 410 |
| 1 | 3.97 | 020,401 | | | |
| 5 | 3.90 | 120 | w | 3.89 | 120 |
| 3 | 3.69 | 220 | vw | 3.67 | 220 |
| 2 | 3.60 | $\bar{4}$02,$\bar{1}$21 | | | |
| 10 | 3.52 | 510,411 | s | 3.51 | 510 |
| 1 | 3.40 | 320 | w | 3.40 | 320 |
| 1 | 3.27 | 221,600,$\bar{4}$12 | | | |
| 2 | 3.25 | $\bar{3}$21 | vw | 3.26 | 600,221,$\bar{3}$21 |
| 3 | 3.10 | 420,511 | m | 3.08 | 420 |
| 1/2 | 3.04 | - | m | 3.02 | 610,321 |
| 1 | 3.00 | $\bar{5}$12 | m | 2.97 | $\bar{5}$12 |
| 3 | 2.97 | 402 | m | 2.95 | 312 |
| 1 | 2.912 | 022,$\bar{6}$02 | | | |
| 9 | 2.795 | $\bar{3}$22,520,421 | m | 2.805 | $\bar{2}$03 |
| | | | w | 2.767 | 421 |
| 5 | 2.670 | $\bar{4}$22 | m | 2.687 | 412 |
| 5 | 2.653 | 710 | m | 2.637 | 710,222 |
| 1/2 | 2.561 | | vw | 2.557 | 230 |
| 1 | 2.531 | | | | |
| 1 | 2.475 | | vw | 2.471 | $\bar{7}$12 |
| 1/2 | 2.456 | | | | |
| 1/2 | 2.405 | | | | |
| 3 | 2.357 | | w | 2.347 | $\bar{8}$02 |
| 4 | 2.334 | | m | 2.327 | 430 |
| 1 | 2.318 | | | | |
| 2 | 2.238 | | w | 2.234 | $\bar{2}$32 |
| 1/2 | 2.195 | | | | |
| 4 | 2.136 | | w | 2.100 | 910 |
| 2 | 2.063 | | w | 2.061 | $\bar{6}$31,004,$\bar{9}$12 |

| 1 | 1 | 2 | 2 | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $I_{est}$ | $d_{obs}$ | $I_{est}$ | $d_{obs}$ | $I_{est}$ | $d_{obs}$ | $I_{est}$ | $d_{obs}$ | $I_{est}$ | $d_{obs}$ | $I_{est}$ | $d_{obs}$ |
| 1/2 | 2.050 | | | 1 | 1.832 | | | 1 | 1.637 | m | 1.634 |
| 1/2 | 2.013 | | | 1 | 1.816 | | | 1/2 | 1.603 | | |
| 1/2 | 1.979 | | | 1 | 1.798 | w | 1.794 | 1/2 | 1.571 | | |
| 1 | 1.961 | | | 1/2 | 1.776 | | | 1 | 1.544 | m | 1.548 |
| 2 | 1.950 | w | 1.951 | 1 | 1.761 | | | | | w | 1.482 |
| 1 | 1.928 | | | 1 | 1.751 | m | 1.746 | | | w | 1.433 |
| 1 | 1.911 | | | 1 | 1.737 | | | | | | 1.393 |
| 1 | 1.866 | | | 1 | 1.688 | m | 1.689 | | | w | 1.365 |
| 1 | 1.851 | | | 1 | 1.669 | | | | | w | 1.330 |
| 1 | 1.844 | | | 1 | 1.654 | | | | | | |

1) Guettardite from Madoc (Jambor 1967b)
2) Guettardite from Seravezza

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