

From the group-theory viewpoint,⁴ a twin is a *representation* of an abstract *factor group* (C_2 , $S_{2 \times 2}$, $S_{2 \times 2 \times 2}$ in twinning by hemihedry, tetartohedry, ogdohedry, respectively). In the above example the 48 symmetry operations of the holohedral point group $m\bar{3}m$ are divided into one subgroup and three cosets; the operations of the *subgroup* describe the crystal symmetry $2\bar{3}$, those in each *coset* are all the possible twin operations for one of the three twin laws. The factor group is a four-color group that differs in structure from the four-color space groups described by Belov and Tarkhova (1956). In our example all the elements of the factor group that correspond to changes of color are of order 2 ("element" being given its group-theory meaning, corresponding to "operation" in crystallographic groups); in the four-color space groups studied by Belov and Tarkhova, the factor group is the cyclic group C_4 .

We wish to thank Professor J. Wyart and Dr. Gabrielle Donnay for a critical reading of the manuscript.

REFERENCES

- BELOV, N. V. AND TARKHOVA, T. N. (1956), Chromatic symmetry groups: *Kristallografiya*, **1**, 615.
 BUERGER, M. J. (1954), The diffraction symmetry of twins: *Anais da Acad. Brasileira de Ciências*, **26**, 111-121.
 CURIEN, H. AND LE CORRE, Y. (1958), Notations des macles à l'aide du symbolisme des groupes de couleurs de Choubnikov: *Bull. Soc. fr. Minér. Crist.*, **81**, 126-132.
 FRIEDEL, G. (1904), Etude sur les groupements cristallins: *Bull. Soc. Ind. minérale, Saint-Etienne*, (4) **3** and **4**. Also reprinted in book form, Saint-Etienne.
 FRIEDEL, G. (1926), *Leçons de Cristallographie*—Paris, Berger-Levrault.

⁴ To readers unfamiliar with the subject of groups, we take pleasure in recommending Bryan Higman's "Applied group-theoretic and matrix methods" (Oxford, 1955). We have found this book illuminating, although we must say that not all its statements about crystals can be taken at face value. Mineralogists and crystallographers will not agree that the study of the external forms of crystals is "metaphorically, as well as literally, superficial" (p. 90); they will not be easily persuaded that the five trigonal point groups are possible only with a rhombohedral lattice (p. 110), nor will they see why the space groups of $\bar{4}2m$ are distributed among *four* lattice modes (p. 132) when only *two* are possible (p. 121)!

THE AMERICAN MINERALOGIST, VOL. 44, SEPTEMBER-OCTOBER, 1959

NOTE ON "REVOREDITE" AND RELATED LEAD-SULFUR-ARSENIC GLASSES*

CHARLES MILTON AND BLANCHE INGRAM
U. S. Geological Survey, Washington 25, D. C.

Recently Amstutz, Ramdohr, and de las Casas (1957) have described as a new mineral, "revoredite," from Cerro de Pasco, Peru, which is

* Publication authorized by the Director, U. S. Geological Survey.

"amorphous to x -rays" and consists essentially of lead, arsenic, and sulfur. We have studied another material "amorphous to x -rays," from Quiruvilca, Peru, also consisting essentially of lead, arsenic, and sulfur, in different proportions, however. We find that a probably continuous series of amorphous phases can be made in the compositional range from As_2S_3 to $2\text{As}_2\text{S}_3 \cdot \text{PbS}$ and probably in still more lead-rich parts of the join $\text{PbS}-\text{As}_2\text{S}_3$. "Revoredite" falls within this range; the Quiruvilca material ($\text{As}_2\text{S}_3 \cdot 2\text{PbS}$) is beyond it, but its properties are so similar to those of the synthetic glasses that no break in the series between As_2S_3 and $\text{As}_2\text{S}_3 \cdot 2\text{PbS}$ seems likely. The question is raised whether any particular composition in such a series of uncrystallized solids, virtually lead-arsenic-sulfur glasses, should be recognized as a mineral species or given a name, such as "revoredite." Certainly, we are not proposing a name for the Quiruvilca material; but will refer to it here as "the Quiruvilca lead-arsenic-sulfur glass," or briefly, the Quiruvilca material.

Its history is as follows. In 1952 Mr. Lawson P. Entwistle, Chief Geologist, Northern Peru Mining Corporation, Lima, Peru, called the attention of Mr. Frank S. Simons of the U. S. Geological Survey to an unusual ore specimen taken from the Sin Nombre vein of the Quiruvilca Mine, La Libertad Department, Peru. The specimen was essentially massive brown sphalerite with galena and pyrite, but had a dark-gray botryoidal coating whose appearance is shown in Figs. 1*a*, *b*. The underlying massive sulfide ore and structure of the amorphous material are shown in Figs. 2 and 3.

In a letter dated October 1, 1953, Mr. Simons gave further data concerning the specimens. "The mineral is very scarce in the mine . . . The specimens come from the 50 level of the Sin Nombre vein, about 250 meters below the surface, from a large vug about 5 meters long in a vein slightly less than one meter wide. The vein consists of approximately 70% pyrite, 22% wurtzite (?), 6% galena, 2% tetrahedrite, and a little chalcopyrite. Gangue is quartz and is not abundant. Sulfide sequence of deposition is galena (oldest), wurtzite, pyrite, tetrahedrite and chalcopyrite; wurtzite veins pyrite; pyrite does not seem to replace anything; tetrahedrite replaces galena and wurtzite; tetrahedrite is associated with chalcopyrite and the two are probably essentially simultaneous. This section of the vein lies in the transition zone between enargite-pyrite veins in the center and lead zinc veins outside . . ." Later work in Washington indicated that the wurtzite (?) is mostly or all sphalerite.

An x -ray diffraction study by Joseph M. Axelrod of carefully separated material from the coating showed it to be "amorphous to x -rays." Chemical tests showed much lead and arsenic.

A chemical analysis is given in Table 1, analysis (*a*) and, for comparison, two published analyses of "revoredite," and one of "natural sulfide

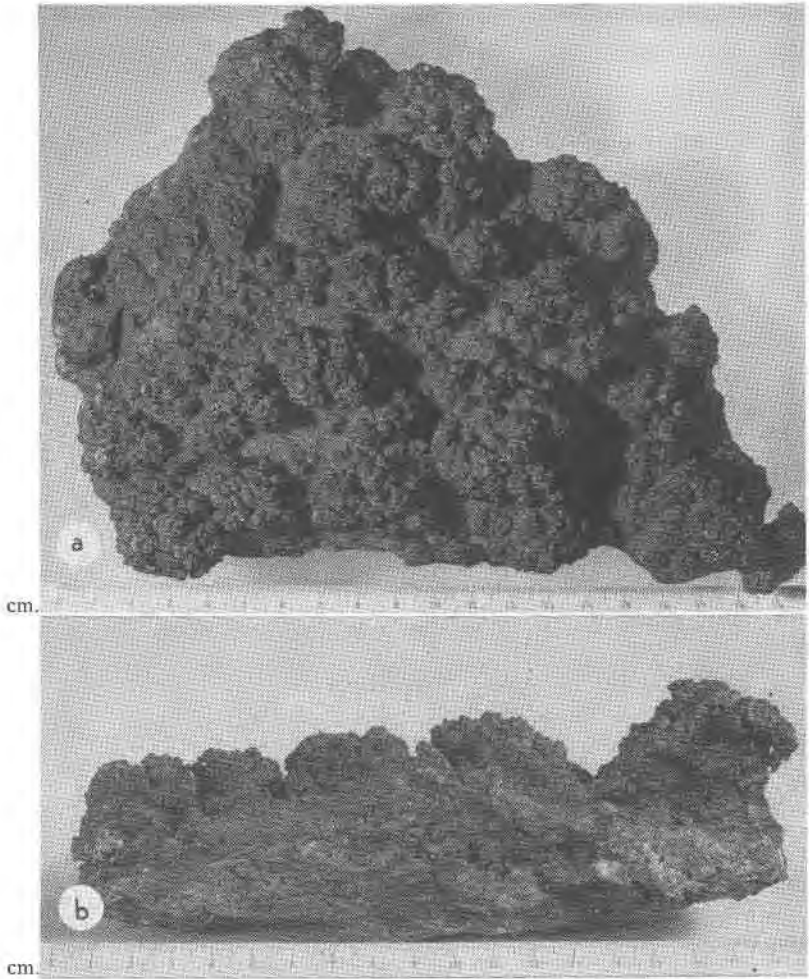


FIG. 1. Massive sphalerite-galena ore coated with botryoidal lead sulfarsenide glass, from Quiruvilca, Peru.

(a) View of top showing continuous coating.

(b) Side view of broken specimen, showing massive ore with top coating of glass.

glass," also from Cerro de Pasco. Both "revoredite" and the "glass" have been recently described, by Amstutz, Ramdohr, and de las Casas (1957), and Amstutz (1958), respectively. Presumably "revoredite" and the "glass" are the same, the difference in analyses notwithstanding; and it may be noted that the name "revoredite" is not used by Amstutz in his later paper.*

* In a letter to C. M. (of date May 3, 1959) Amstutz states that the "Revoredite"

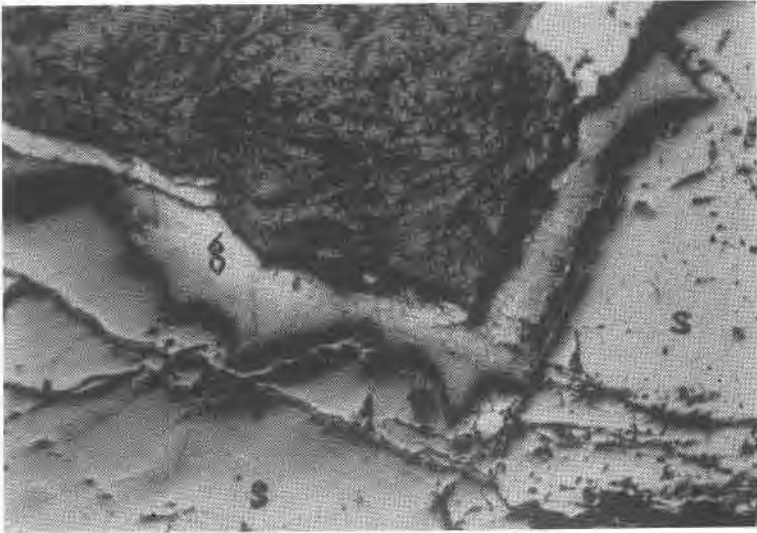


FIG. 2. Polished section ($\times 110$) of sphalerite (s) with continuous rim (g) of lead sulfarsenide glass.

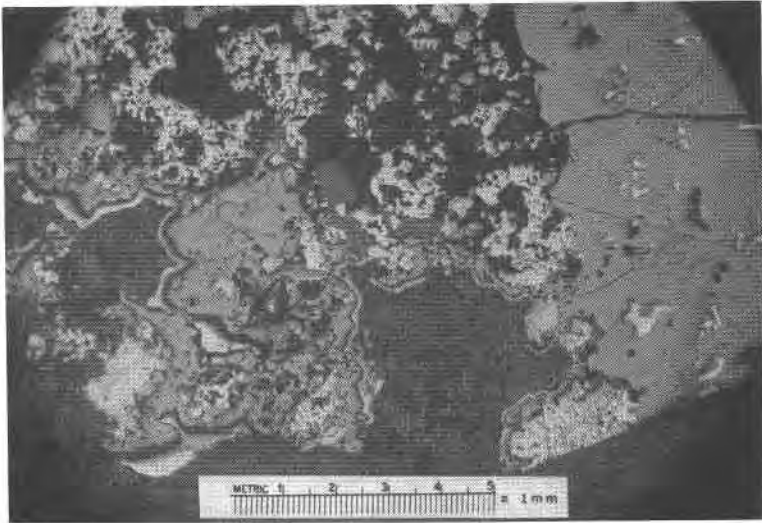


FIG. 3. Polished section of sphalerite (gray), galena (white) and lead sulfarsenide glass (continuous rim, light gray).

analyses "were made by a commercial lab . . . which was unfortunately not able and equipped for such . . . work. The natural sulfide glass analyses however are in 3 analyses of 3 samples from different places of one stope . . . all extremely close (only about .1 difference)."

TABLE 1. ANALYSES OF THE QUIRUVILCA MATERIAL, OF "REVOREDITE," AND OF "NATURAL SULFIDE GLASS"

| | Quiruvilca material ¹ (Analyst, Blanche Ingram) (a) | 2PbS·As ₂ S ₃ (Theoretical) (b) | "Revoredite" Cerro de Pasco (Amstutz, Ramdohr, and de las Casas, 1957) (c) (d) | | "Natural sulfide glass" Cerro de Pasco (Amstutz, 1958) (e) |
|----|--|---|---|---------|---|
| As | 18.4 | 20.7 | 52.1 | 51.9 | 23.10 ± .70 |
| Sb | 1.7 | — | — | — | — |
| Pb | 55.6 | 57.2 | 8.7 | 2.7 | 20.55 ± .45 |
| Cd | 0.7 | — | — | — | — |
| Zn | 1.1 | — | — | — | — |
| S | 22.4 | 22.1 | 34.9 | 34.9 | 56.35 ± .25 |
| Tl | — | — | 0.5-1.0 | 0.5-1.0 | .04 |
| | 99.9 | 100.0 | | | |

¹ Semiquantitative spectrographic analysis by Katherine V. Hazel, U. S. Geological Survey, showed the following trace elements: Sb 1.0, Cd 1.0, Zn 0.3, Ca 0.01, Cu 0.01, In 0.03, Fe 0.003, Mg 0.003, Al <0.001, Ag 0.0003, Ba 0.0003, Bi 0.003, Si 0.0003. Figures are reported to the nearest number in the series 1.0, 0.3, 0.1, 0.03, 0.01, 0.003, etc., in per cent. These numbers represent midpoints of group data on a geometric scale. Comparisons of this type of semiquantitative results with data obtained by quantitative methods, either chemical or spectrographic, show that the assigned group includes the quantitative value about 80 per cent of the time. Thallium, if present at all, is less than 0.01 per cent in the Quiruvilca material.

For the analysis of the Quiruvilca lead-arsenic-sulfur glass, 175 milligrams of carefully hand picked (under the microscope) material was used. Any particle showing galena or sphalerite was rejected.

For the arsenic determination, about 50 milligrams of sample was decomposed with HNO₃. Lead sulfate and elemental sulfur precipitated on decomposition. The sulfur was brought into solution by prolonged digestion with HNO₃. The HNO₃ was evaporated and arsenic was separated from the other constituents of the sample by distillation from a hydrochloric acid medium at 110° C. The acidity of the distillate was adjusted to 9 N and the distillate was treated with H₂S. Arsenic was precipitated and weighed as As₂S₃.

Antimony was determined colorimetrically as iodoantimonous acid. A 50-mg sample was decomposed with HNO₃. Tartaric acid was added to lessen chances of coprecipitation of Sb with PbSO₄. The nitric acid was evaporated with PbSO₄ filtered off. The filtrate was used for color development. The other elements, in amounts present, do not interfere in the colorimetric method.

Lead was determined gravimetrically as PbSO₄. Sample size was approximately 50 mg.

An aliquot of the filtrate from the lead determination was used for the cadmium determination. Cadmium was precipitated and weighed as cadmium thiourea reineckate. A separation of Cd and Zn is not necessary in this procedure.

Zinc was determined colorimetrically with zincon reagent on an aliquot of the filtrate

from the lead determination. Zn was separated from Cd by use of ion exchange resin Dowex—1×8. Cadmium and zinc were absorbed from a 2 M HCl solution. Zinc was eluted with 0.01 M HCl.

Sulfur was determined gravimetrically as BaSO₄. A 25-mg. sample was fused with Na₂CO₃-KNO₃. The fusion mixture was leached with H₂O. The water solution was used for the analysis.

Our colleague, Priestley Toulmin, III, prepared for us lead-arsenic-sulfur glasses of molar compositions 3.95As₂S₃·PbS and 2.00As₂S₃·PbS by fusing at 1100° ± 10° C., a mixture of synthetic As₂S₃ glass and crystalline PbS in sealed evacuated silica glass tubes, and quenching in water.

As to the genesis of the natural glasses, the microscopic evidence indicates that a sphalerite with galena inclusions (this relation points to earlier events in the history of the ore with which we are not now concerned) came in contact with vapors or solutions with varying lead content and rich in arsenic trisulfide, whereby stalactitic crusts such as "revoredite," or a glass of the Quiruvilca type with composition close to dufrenoyite were formed. The possibility of a mine fire being involved in the formation of these substances has been considered; but there is no record of any fire in these workings.

Amstutz, Ramdohr, and de las Casas (1957, p. 30) observe that amorphous lead sulfarsenides similar to "revoredite" have been found in Wiesloch, Baden, Germany. Ramdohr's (1955) description of jordanite from that locality is of interest, ". . . concentric spheroidal to botryoidal masses, often forming crusts on sphalerite, with clearly marked former gel-structure, now coarsely crystallized in roughly parallel crystals." Presumably the crystallized and the amorphous lead sulfarsenide have a similar origin. The "colloidal" character of synthetic arsenic trisulfide is familiar to all analytical chemists. That a lead sulfarsenide composition such as dufrenoyite may have a colloidal or glassy state is not so well known. Concerning these substances, Pascal (1933) observes, "The physical chemistry of these substances does not appear to have been studied. Other than purely mineralogical studies on this group, there is only the work of Sommerlad who attempted the synthesis of some of these minerals." Sommerlad (1898) melted together PbS and As₂S₃ and obtained a lustrous black, brittle mass of specific gravity 4.585, which was shown by analysis to have the composition PbS·As₂S₃ (sartorite). The specific gravity of the natural mineral is considerably higher (5.05) and Sommerlad may have had a glass. On moderately heating this material in a current of hydrogen sulfide, As₂S₃ was formed, and the dark gray residue had the composition and specific gravity of dufrenoyite, 2PbS·As₂S₃. Further heating until no more As₂S₃ formed, left a dark-gray substance with the composition of jordanite, 4PbS·As₂S₃. Dufrenoyite, or a crys-

talline mass of that composition and specific gravity, was also made by fusing 2PbS and As₂S₃ at a moderate temperature.

The name "revoredite" proposed by Amstutz, Ramdohr, and de las Casas appears untenable for the very reason that these authors propose for its acceptance. "The name Revoredite . . . was proposed . . . in case that a crystalline sample should be found, or that by some method, it might be possible to attribute a crystalline structure to this so far amorphous mineral." If crystalline phases do appear, they will simply be orpiment or one or more of the series of sartorite-dufrenoy-site-jordanite.

REFERENCES

- AMSTUTZ, G. C. (1958), Some properties of natural sulfide glasses (Abstract), *1958 Milwaukee meeting A.C.A.*
- AMSTUTZ, G. C., RAMDOHR, P., AND DE LAS CASAS, F. (1957), A new low temperature mineral of hydrothermal origin from Cerro de Pasco, *Sociedad Geologica del Peru, Annals Pt. II*, 25-53.
- PASCAL, P. (1933), *Traite de Chimie Minerale IX*, Paris, Masson, p. 282.
- RAMDOHR, P. (1955), *Die Erzminerale und ihre Verwachsungen*, Berlin, Akademie Verlag, pp. 579-580.
- SOMMERLAD, HERMANN (1898), Über Versuche zur Darstellung von Sulfantimoniten und Sulfarseniten des Silbers, Kupfers und Bleis auf trockenem Wege: *Z. anorg. Chem.*, **18**, 442.

THE AMERICAN MINERALOGIST, VOL. 44, SEPTEMBER-OCTOBER, 1959

MINERAL SEPARATION WITH ASYMMETRIC VIBRATORS

HENRY FAUL, *U. S. Geological Survey, Washington 25, D. C.*

AND

GORDON L. DAVIS, *Geophysical Laboratory, Carnegie Institution of Washington, Washington 8, D. C.*

INTRODUCTION

Geochemical studies often require the separation of gram amounts of pure minerals from rocks. Hand picking is usually out of the question and one resorts to such well-known techniques as heavy liquid separation with bromoform, tetrabromoethane, or methylene iodide (Fairbairn, this journal, 1955), magnetic separation, (*ibid.* and Gaudin and Spedden, 1943; McAndrew, 1957; Rosenblum, 1958; Rubinstein *et al.*, 1958) or to laboratory adaptation of industrial beneficiation processes like flotation or the Wilfley table. Many other techniques are used for particular problems: sieving, panning, various arrangements for elutriation with air or