

## Downeyite, the first verified natural occurrence of $\text{SeO}_2$

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### Abstract

Downeyite, naturally occurring  $\text{SeO}_2$ , forms as acicular crystals from gases escaping through vents on culm banks in the anthracite region of Pennsylvania. This exceedingly hygroscopic mineral forms at temperatures of about  $200^\circ\text{C}$  in the vicinity of the vents; it is associated with elemental selenium, monoclinic sulfur, manganite, and anhydrous ammonium aluminum sulfate.

Generally, crystals of downeyite are colorless, transparent, and have adamantine luster. Downeyite is uniaxial positive, shows parallel extinction, and has moderate birefringence. Indices of refraction are  $>1.80$ . Downeyite crystallizes in the tetragonal system, with  $a = 8.36 \pm 0.01$  and  $c = 5.07 \pm 0.01 \text{ \AA}$ ; the cell parameters as well as the X-ray powder diffraction data are in good agreement with those published for synthetic  $\text{SeO}_2$ . Only semiquantitative microprobe analyses could be made because of insufficient material and the hygroscopic character of this mineral; these data confirmed that the only major detectable element in downeyite is selenium.

The name selenolite has been used for minerals assumed to be  $\text{SeO}_2$ . The descriptions of these minerals indicate that none could have had this composition. Therefore, the name selenolite has been rejected in favor of the name downeyite for this new mineral. The name is for Wayne F. Downey, Jr., whose ingenuity in collecting this unstable mineral permitted its identification.

### Introduction

During the past several years the U.S. Geological Survey and the Pennsylvania Geological Survey have been conducting a joint investigation on the minerals forming around vents created by escaping gases from burning coal seams and culm banks in the anthracite region of Pennsylvania (Finkelman *et al.*, 1974). Included among these minerals were clear, colorless, strongly hygroscopic crystals collected in 1972 by Wayne F. Downey, Jr. Downey, then a high school student in Harrisburg, Pennsylvania, first noticed these crystals on actively burning culm banks. His initial attempts to collect the crystals for study were unsuccessful because the mineral "disappeared" almost immediately upon removal from the culm bank. Downey correctly assumed that the crystals were hygroscopic; with an improvised desiccator he was able to collect and preserve sufficient material for subsequent characterization. Laboratory studies show that these crystals constitute the first verified natural occurrence of  $\text{SeO}_2$ .

This mineral is named downeyite (pronounced dōw'-nē-īt) for Wayne F. Downey, Jr., whose per-

severance and ingenuity in collecting this ephemeral mineral permitted its study. The mineral and name have been approved in advance of publication by the Commission on New Minerals and Mineral Names, IMA. Type material is on deposit at the National Museum of Natural History, Smithsonian Institution, Washington, D.C.

### Occurrence

Downeyite, a sublimation product of escaping gases from vents in actively burning culm banks in the anthracite region of eastern Pennsylvania, occurs as rare, transparent, acicular to prismatic crystals (Fig. 1) dispersed on a matrix of spent shale, locally referred to as "red dog." Less commonly, the needle-like crystals cluster to form radiating sprays (Fig. 2).

Crystals of downeyite were first observed on actively burning anthracite culm banks near Forestville (bank no. 55; numbers are keyed to map on p. 40 of McNay, 1971), and subsequently observed near Glen Lyon (bank no. 61, no longer actively burning), near Williamstown (bank no. 49, also extinguished) and near Shamokin (bank no. 50, still actively burning).

Downeyite was found neither in Shenandoah, Pennsylvania (bank no. 58), a thoroughly studied inactive culm bank, nor at several less intensively studied bituminous and anthracite culm banks and burning coal seams. Downeyite crystals are extremely hygroscopic and unstable under normal atmospheric conditions; therefore, their presence and preservation on the culm banks is restricted to areas within the hot dry environment immediately surrounding active vents. Temperature measurements made by Downey in the zones in which downeyite was forming were generally in the range of 190° to 230°C. Crystals of downeyite appear to have formed in association with elemental selenium, monoclinic sulfur, mascagnite,  $(\text{NH}_4)_2\text{SO}_4$ , and an unnamed anhydrous ammonium aluminum sulfate,  $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$ .

#### Physical and optical properties

Crystals of downeyite are generally transparent, colorless, and have adamantine luster. Some crystals, however, appear red from bright red inclusions of amorphous selenium; others have a yellowish tint at their base from a dusting of sulfur. Downeyite commonly occurs in the form of fine acute needles elongated along the *c* axis. Individual crystals range from 0.1 mm to 2 cm in length. Some specimens contained a few long prismatic crystals with very steep pyramidal terminations; it was not possible to make goniometric measurements for identification of the prism and pyramidal faces because of the extremely hygroscopic nature of the crystals.

Optically downeyite is uniaxial positive (+), has parallel extinction and moderate birefringence. Indices of refraction are  $>1.80$ ; attempts to determine omega ( $\omega$ ) and epsilon ( $\epsilon$ ) were unsuccessful because the crystals reacted with the high-index liquids. These data agree with observations reported by Brownmiller (1927) for synthetic crystals of  $\text{SeO}_2$ . Twinning was not observed by us; however, Downey (personal communication, 1976) reported that he had observed contact twins in samples that he had examined.

Downeyite crystals are readily soluble in cold water, mineral acids, and acetone. They do not fluoresce in either long- or short-wave ultraviolet radiation. Hardness, cleavage, and specific gravity could not be determined because of the hygroscopic nature of the mineral. The density of downeyite calculated from our X-ray data is  $4.146 \text{ g cm}^{-3}$ , in close agreement with the calculated density ( $4.161 \text{ g cm}^{-3}$ , at 25° C) reported for  $\text{SeO}_2$  by Swanson *et al.* (1969).

The most striking feature of downeyite is its extremely hygroscopic character. Removed from the

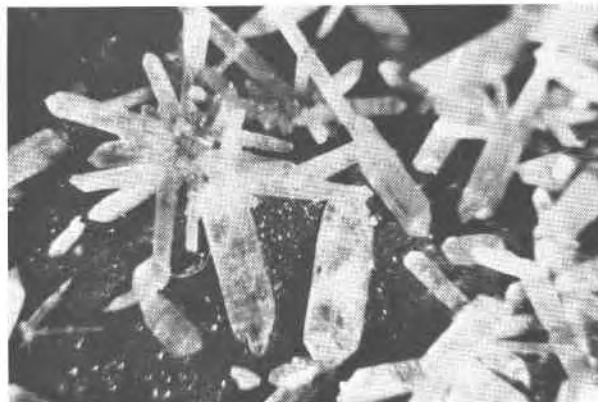


FIG. 1. Prismatic crystals of downeyite (1 mm to 2 mm in length).

hot dry environment in which they form, downeyite crystals quickly absorb water from the atmosphere and deliquesce in a few minutes, forming droplets of a clear liquid which the substratum absorbs, or which evaporates, leaving an unidentified colorless transparent film. Blocky crystals of synthetic  $\text{SeO}_2$  and needles of downeyite deliquesce and sublime at approximately the same rate; however, downeyite reacted slightly faster than the synthetic  $\text{SeO}_2$ , probably because of the difference in crystal size and shape.

The hygroscopic nature of downeyite necessitated rapid handling throughout the course of this investigation. Specimens encrusted with downeyite crystals were kept over a desiccant ( $\text{CaSO}_4$ ) in a sealed desiccator to retard deliquescence and decomposition. Downeyite samples were quickly removed from the desiccator and handled with instruments and glassware preheated to  $\sim 200^\circ\text{C}$ . Nevertheless

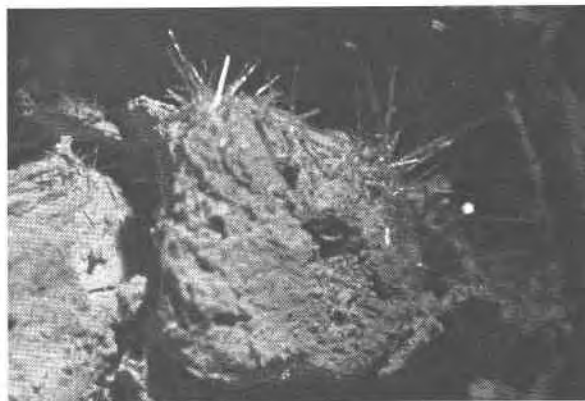


FIG. 2. Radiating sprays of acicular downeyite (as much as 2 cm in length).

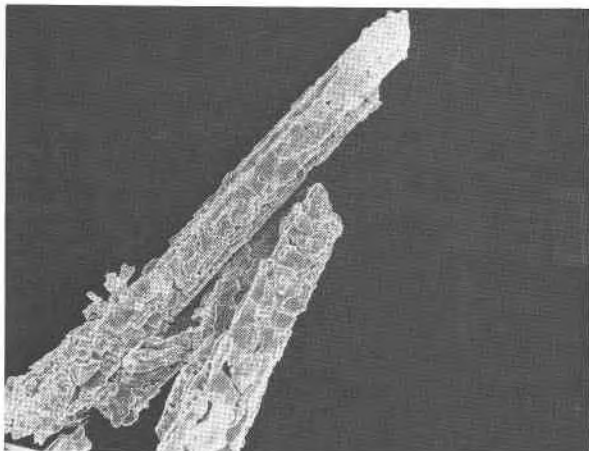


FIG. 3. Scanning electron photomicrograph of decomposing downeyite (81X).

some decomposition of downeyite crystals took place (Fig. 3).

### Chemistry

The extremely small amount of downeyite available, only a few milligrams, precluded a wet chemical analysis. The hygroscopic nature of the mineral did not permit the preparation of polished and coated samples for quantitative electron microprobe analysis. However, semiquantitative microprobe analyses were obtained from unpolished crystals mounted on a polished beryllium substrate. Intensities for selenium in downeyite and in a synthetic  $\text{SeO}_2$  standard were comparable. Qualitative energy-dispersive analyses of downeyite crystals and residue, after allowing the crystals to deliquesce and the resultant liquid to evaporate in air, showed only major selenium. Because downeyite must be maintained at  $\sim 200^\circ\text{C}$  in air to prevent deliquescence, it follows that the composition of the mineral must be  $\text{SeO}_2$ ; all other selenium oxide compounds melt or decompose above  $118^\circ\text{C}$  (Weast, 1971–1972, p. B-131, B-132).

### X-ray study

Special techniques were devised for obtaining X-ray single-crystal and powder diffraction data because of the rapid deliquescence of downeyite. For single-crystal study, an isolated crystal of downeyite was placed in a preheated capillary tube and the open end quickly sealed. For the powder diffraction pattern, several crystals first were crushed on a heated porcelain block and the powder thus obtained was sealed in a preheated capillary tube.

Precession photographs taken in zirconium-filtered

molybdenum radiation ( $\lambda = 0.71069\text{\AA}$ ) indicated tetragonal symmetry, with  $a = 8.36 \pm 0.01$  and  $c = 5.07 \pm 0.01\text{\AA}$ . These parameters, close to those reported for synthetic  $\text{SeO}_2$  by Swanson *et al.* (1969) ( $a = 8.3635 \pm 0.0001$ ,  $c = 5.0635 \pm 0.0002\text{\AA}$ ), further confirmed the composition and formula of downeyite. The space group for downeyite was not determined in this study; it was assumed to be  $P4/mbc$ , that established by McCullough (1937) in his crystal-structure determination of selenium dioxide.

An X-ray powder diffraction pattern of downeyite taken in a Debye-Scherrer camera (114.59 mm diameter), using nickel-filtered copper radiation ( $\lambda = 1.5418\text{\AA}$ ), contained more than 60 "slightly grainy" lines; no internal standard was used. The  $d$  values obtained by measuring this pattern are in good agreement with those cited by Swanson *et al.* (1969) for synthetic  $\text{SeO}_2$ .

### Historical review: status of the name selenolite

The name selenolite and the formula  $\text{SeO}_2$  were first assigned by Dana (1892, p. 201) to minute white acicular crystals from Cacheuta, Argentina, that had been incompletely described, but unnamed, by Bertrand (1882). Bertrand had characterized these crystals as a product of the oxidation of a lead selenide at Cacheuta. He referred to them as *l'acide selenieux* (Bertrand's italics), and stated that they were completely volatile. Investigators subsequently applied the name selenolite to synthetic  $\text{SeO}_2$  and to inadequately described selenium-bearing minerals from several localities. Zambonini and Coniglio (1925) used the name for an unobserved selenium phase within the yellow encrustation around a volcanic vent in the lava at Vesuvius, Italy. Herzenberg and Ahlfeld (1935) applied the name to a secondary white acicular mineral found as an oxidation product of penroseite,  $(\text{Ni},\text{Co},\text{Cu})\text{Se}_2$ , occurring in association with ahlfeldite,  $(\text{Ni},\text{Co})\text{SeO}_3 \cdot 2\text{H}_2\text{O}$ , at the Pacajake mine, Colquechaca, Bolivia. Babkin (1958) provisionally assigned the name selenolite to a product of the disintegration of platynite,  $\text{PbBi}_2(\text{Se},\text{S})_3$ , and guanajuatite,  $\text{Bi}_2\text{Se}_3$ , occurring as colorless needles associated with molybdomenite,  $\text{PbSeO}_3$ , on a specimen from a tin ore deposit in the Magadan district in northeast USSR. None of these minerals referred to as selenolite could have had the composition  $\text{SeO}_2$  for several specific reasons.

The hygroscopic nature of  $\text{SeO}_2$  would cause a mineral of this composition to deliquesce rapidly in air at temperatures much below  $200^\circ\text{C}$ . This fact, coupled with ready solubility of the mineral in cold

water, makes it impossible for such a mineral to form or persist for any length of time in the environments described by Bertrand (1882), Herzenberg and Ahlfeld (1935), and Babkin (1958), or in the laboratories where the investigations were carried out.

Although Bertrand (1882) alluded to the Cacheuta material as being "entirely volatile" and Herzenberg and Ahlfeld (1935) noted that the mineral from the Pacajake mine sublimed in a test tube, neither mentioned the hygroscopic property so characteristic of selenium dioxide; nor did Babkin (1958), in his description of the physical and optical properties of the Magadan "selenolite (?)," which he stated were comparable to those of an analogous mineral described from the Pacajake mine, Colquechaca, Bolivia. Furthermore, none remarked that any precautionary measures had to be taken in transferring their samples from the field to the laboratory, or during study of the mineral in the laboratory. Hence, the minerals they described almost certainly could not have had the composition  $\text{SeO}_2$ .

Ahlfeld and Muñoz Reyes (1938) cited a communication from Professor Palache of Harvard University which indicated that the optical properties of the Pacajake mineral did not agree with those for synthetic  $\text{SeO}_2$ . In that report and subsequent publications referring to the Pacajake mineral as selenolite, Ahlfeld drifted farther and farther from the notion that the composition of the Bolivian mineral was  $\text{SeO}_2$  (Ahlfeld and Angelelli, 1948; Ahlfeld and Muñoz Reyes, 1943, 1955). Ahlfeld and Muñoz Reyes (1955) concluded that the Pacajake and Cacheuta minerals are probably identical, but that they are a hydrated compound of selenium (*not*  $\text{SeO}_2$ ).

Zambonini and Coniglio (1925) noted the presence of a small amount of selenium, predominantly in the plus 4 oxidation state, in a yellow incrustation that they examined at Vesuvius. They tentatively suggested that selenolite might be present within this incrustation, acknowledging that the selenium could be in the form of selenious acid or some alkaline selenite.

Goñi and Guillemin (1953) examined specimens from Pacajake (specimen no. 630-53; Laboratoire de Mineralogie, Sorbonne) and Cacheuta (specimen no. 10-41214; Museum National d'Histoire Naturelle) during their study of natural selenites and selenates. Both specimens contained a mineral which they characterized as an unnamed lead selenate,  $\text{PbSeO}_4$ , on the basis of qualitative chemical tests; Goñi and Guillemin suggested that this lead selenate is "sans doute le mineral considéré comme selenolite par Ahl-

feld" (Goñi and Guillemin, 1953, p. 424). Physical, optical, and X-ray powder diffraction data cited by Goñi and Guillemin for their mineral from Pacajake are in excellent agreement with those reported for olsacherite,  $\text{Pb}_2(\text{SO}_4)(\text{SeO}_4)$ , named and described by Hurlbut and Aristarain (1969) as an alteration product of penroseite  $(\text{Ni}, \text{Co}, \text{Cu})\text{Se}_2$ , at the Pacajake mine. In their paper on olsacherite, Hurlbut and Aristarain made no reference to the possibility that their mineral is the selenolite of Herzenberg and Ahlfeld (1935). However, the olsacherite of Hurlbut and Aristarain (1969), the "lead selenate" of Goñi and Guillemin (1953), and the selenolite of Herzenberg and Ahlfeld (1935) appear to be the same mineral. This line of reasoning makes it apparent that the mineral from Cacheuta, originally described by Bertrand (1882), and possibly the mineral from Magadan, described by Babkin (1958), also are olsacherite.

The authors feel that they should not be bound to use the name selenolite for the mineral described in this paper because: (1) the name selenolite was never applied to minerals whose composition was determined to be  $\text{SeO}_2$ ; they were only shown to contain selenium; (2) minerals to which the name selenolite has been applied could not possibly have had the composition  $\text{SeO}_2$  for the reasons discussed above; and (3) the mineral from Pacajake designated as selenolite by Herzenberg and Ahlfeld (1935) is in all probability the olsacherite of Hurlbut and Aristarain (1969).

We have, therefore, rejected the name selenolite and proposed the name downeyite for this new mineral with proven composition  $\text{SeO}_2$ . The application of the name selenolite to inadequately described minerals is unfortunate; we have recommended that the name selenolite be relegated to synonymy to avoid further confusion. These proposals have been approved by the Commission on New Minerals and Mineral Names, IMA.

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*Manuscript received, May 28, 1976; accepted  
for publication, August 19, 1976.*